A Study of Leaching Tests for Cement Stabilised Waste

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STATEMENT

This thesis is original work. It contains no material previously submitted for a degree or diploma in any university and, to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference is made in the text.

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ABSTRACT

A cement-stabilised waste was subjected to batch, column, and dynamic leaching tests, and the leaching behaviour of arsenic, copper, lead, selenium, and zinc was investigated. Batch tests included the Australian Bottle Leaching Procedure (ABLP, *AS 4493.3-1997*), Toxicity Characteristic Leaching Procedure (TCLP, *USEPA Method 1310*); column testing included small columns (internal diameter = 24mm) and a large column (internal diameter = 500mm); and dynamic leaching tests were run with both short (1 hour) and long (4 hour) leachant renewal frequencies. A maximum availability test was used to indicate maximum leaching potential for the metals under investigation.

The results show that it is extremely difficult to find any obvious, simple correlations between short-term (batch and sequential batch tests) and long-term (column and dynamic) leaching tests. However, evaluation of the experimental data has demonstrated that minor changes in test methodology and/or the design, and construction of test vessels led to significant differences in both the mass of metal species released, and the patterns of release from the waste. The major differences identified between the tests, leading to variations in leaching behaviour, were the method of leachant contact and the liquid to solid (L/S) ratio. The possibility of using L/S ratio for predictive purposes was suggested and trialed with the data produced from these experiments. It was shown that arsenic leaching generally correlated well with changes in L/S ratio for the batch and column tests. However, once the mass of waste, rather than the liquid volume, was altered in the small column tests, the correlation did not follow suit.

Finally, the question of what the ABLP or TCLP results really indicates remains a matter of conjecture. While no correlations were found between the batch and column tests, this work further questions the applicability of single-point leaching data as a basis for decisions on disposal. Data from the more benign column tests based on rainfall observations have shown that lead, copper, and zinc leach in greater amounts than those observed in the ABLP and TCLP, while selenium leached less from the columns and arsenic remained unchanged. This strongly suggests that the waste may present a more significant hazard when disposed to landfill than would have been otherwise suspected based solely upon the results of regulatory testing, and calls into question both TCLP and ABLP testing as sole bases for disposal decisions.

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1. Introduction

1.1 Foreword

For the better part of the 20th century, unwanted domestic and industrial wastes have been traditionally disposed of by either incineration or burial in landfill. Prior to the last thirty years, a landfill site was essentially nothing more than a hole in the ground, occasionally fitted with a membrane or clay liner system. In addition, minimal thought was given to the types of wastes disposed of into the landfill, nor their medium to long-term effects on the immediate environment or nearby population.

No attempts were made to segregate hazardous from non-hazardous, flammable from non-flammable, biodegradable from non-biodegradable, nor pathological from non-pathological wastes. Further to this, and of utmost importance, no consideration was given to leachate control. Once the material became sufficiently dehydrated, the volume was reduced by controlled burning (McGahan 1978).

These waste disposal practices have left a legacy of serious health impacts and environmental contamination levels that are essentially irretrievable because of the extreme technical requirements and the cost of remediating them (Martin 1990). It was not until these environmental insults became more prevalent, and the populace became more aware, that governments around the world began to regulate landfills (McGahan 1978).

For approximately the last thirty years landfills, in the developed world, have been designed and built according to strict guidelines governing, among other things, liner protection, leachate collection systems, groundwater monitoring and possible fugitive odours and emissions. Added to this, a 'cradle to grave' or 'product stewardship' approach is now advocated for wastes whereby the manufacturer of a product is responsible for that product during its entire life cycle (Victorian EPA 1999). These changes, albeit forced through generations of neglect, now mean that all waste producers (and receivers) have the facilities and the regulatory impetus to ensure previous environmental mistakes are never repeated.

More recently, in Australia, the Victorian EPA has taken waste management a step further, introducing and policing their '4 R's' policy: Reduce, Re-use, Recycle, and Recovery (of energy). Only as a last resort are we to dispose (Victorian EPA 1999). The impetus for this push is not a concern that the landfills are not sufficiently safe to accept Victoria's wastes but, rather, that it costs around $700 million per annum to collect, transport, and dispose of the 4 million tonnes of waste produced (Victorian EPA 1999). There is also the more important fact that, although Victoria has the room for a prescribed waste landfill, any municipalities containing suitable sites, along with their residents, vehemently oppose the construction of such a facility. This last point was emphasised recently when the council and residents of Werribee, a suburb between the cities of Melbourne and Geelong in Victoria, succeeded in their fight to prevent the conversion of a quarry into a prescribed waste facility.

For many wastes, applying the '4 R's' approach need not be a problem. For years, many different types of wastes have been re-used in other applications. For example the well-documented pozzolanic properties of heavy metal laden fly-ash allow its use in construction, while, more recently, chromium contaminated tannery sludge is being fired into safe bricks used for building houses (Knott 1996). Nonetheless, no matter how much industry reduces, re-uses, recycles, and recovers waste products, there will always be something left over. As unfortunate as it is, most alternatives leave a hazardous residue that must be managed (Pojasek 1978).

Landfilling will probably remain the most widely used method for the disposal of solid industrial wastes for the foreseeable future. For contaminants and wastes that cannot be disposed of in any other way using currently available disposal facilities, the challenge is to find the safest practicable repository while alternative technologies are being developed (N.S.W. EPA 1993).

Unfortunately, landfills, even today's, are not the perfect solution. Liners will crack, leachate collection systems can fail, and contaminants will leach from the entombed wastes. This can lead to contamination of groundwater that may affect flora, fauna, and people within the immediate vicinity and also remote from the site due to the flow of the groundwater. These problems are minimised by good landfill practice and design, by segregating wastes within a landfill, and by ensuring that the wastes buried do not 'have the propensity to generate toxic levels of contaminants in a leachate' (Koo 1989). A waste's potential to generate toxic levels of contaminants in a leachate is measured by subjecting it to a leaching test, with the leachate being analysed for contaminants of concern, such as heavy metals and persistent organic pollutants.

Regulatory leaching tests vary from one country to another and can even differ between provinces and states. However, one feature common to most is that they are generally pass/fail tests. Crushing a waste to a small particle size, mixing it with a certain volume of liquid for a specified time period, and then assessing the levels of chemicals in the leached material against statutory criteria is the essence of a regulatory test.

If a waste passes some particular regulatory test and, consequently, is deemed fit for re-use or landfill disposal, the subsequent leaching of any toxic constituents is assumed to be minimal no matter how bad the disposal conditions. If a waste fails the test, it is usually treated by a stabilisation or encapsulation process designed to retard the leaching of the problem contaminants. Such treated waste would then, once again, be subjected to leach testing to assess its suitability for re-use or landfilling.

For the last thirteen years, the US EPA Toxicity Characteristic Leaching Procedure (TCLP) (*Federal Register, vol. 261*, 29 Mar. 1990) has been the world's most recognised and frequently employed leaching test. It is a rapid, 18 hour, single result, pass/fail test that caters for most organic and inorganic contaminants. As the test uses an acetic acid leachant (based on modelling an environment conducive to the production of organic acids in a landfill containing putrescible material) many industry and regulatory bodies consider it has limited applicability when used with wastes traditionally disposed of in a monofill type environment (American Mining Congress 1986).

More recently, Standards Australia has adapted the basic TCLP to produce the new regulatory leaching test, Australian Bottle Leaching Procedure (ABLP) (Standards

Australia 1997). This procedure is more flexible than the TCLP, as it takes into account both the destination of the waste, and its properties, in determining the type of leaching fluid employed during the test.

Aside from the obvious improvements of the ABLP over the TCLP, there remains some doubt as to the relevance of a single pass/fail test for predicting long term leachability in a landfill. Questions have been posed concerning both the breadth of applicability and the relevance to particular disposal sites of these tests.

Alternative tests, such as column leaching, diffusion-based tank leaching tests, and sequential ABLP-type tests, can provide more information about leachability. This is because they are time dependent tests and are generally regarded as being more representative of actual field leaching. However, column and tank tests can take periods ranging from weeks to months to complete, while sequential tests are labour intensive. Thus, there is limited interest in their application for regulating disposal to landfill.

Many of the reasons for dissatisfaction with current tests could be obviated if there were adequately characterised correlations between longer term testing and ABLP/TCLP tests. Economically viable and rapid short-term tests could then be used with the single point results given more meaning through comparison with the more realistic, time dependent, long-term leaching tests. It would also lead to a better understanding of the leaching mechanisms that occur for particular contaminants in specific wastes, and for specific disposal scenarios.

This thesis describes such a methodology where a series of leaching tests are run on a particular waste, and the data obtained is analysed and compared between tests.

The thesis is organised as follows:

The first half of Chapter one provides a detailed explanation of the stabilisation and solidification of hazardous wastes. This includes types and methods of containment as well as the effects of various contaminants and wastes on the success of the stabilisation/solidification. The second half of this chapter features the various methods and techniques employed to evaluate the suitability of these wastes for re-use or disposal. This includes brief descriptions of physical and micromorphological testing, and a more extensive review of leaching tests. The methodologies and applications of past and present leaching tests are reviewed in this section, with a greater emphasis on the modern, and more commonly used, column, tank, and regulatory batch procedures. This is followed by a brief evaluation of the selection of leaching tests, and the interpretation of test data in order to obtain as much relevant information as possible. The final part of Chapter one outlines the aims of the thesis.

Chapter two details all experimental methods used during the course of the research. The characterisation of the raw waste, cement, and final solidified waste are covered, as are the steps involved in stabilising/solidifying the raw waste for use in the leaching tests. All leaching test methodologies are then detailed, followed by a thorough description the methods of analysis employed to test the leachates.

Chapters three through seven present and discuss the experimental results for zinc, copper, lead, arsenic, and selenium respectively. Batch, column, and tank leaching data are thoroughly investigated and possible mechanisms of leaching proposed for each metal. Similarly, potential correlations for release of each metal between the various tests are also explored. A brief summary of leaching for each metal is also included at the end of each chapter, recapping the major aspects of leaching discussed.

Chapter eight initially provides an overall summary of the leaching data before continuing on to more thoroughly discuss the inter-test leaching comparisons/correlations observed and raised in chapters three through seven. The tests compared include: ABLP/TCLP, ABLP/Sequential ABLP, Sequential ABLP/ABLC100, ABLC100/ABLC180, Large Column/LCC100, and MAT/DLT. The chapter concludes by presenting the conclusions to the work and discussing the possibilities for future work.

1.2 Stabilisation/Solidification of Hazardous Wastes

1.2.1 Preamble

The methods by which hazardous wastes are treated can have a significant impact on leaching test results. A thorough understanding of any applied waste treatment processes is, therefore, an important part of the waste characterisation process, and fundamental to the ultimate interpretation of any investigative or regulatory leaching test.

Consequently, a discussion of leaching methodologies would be incomplete without first reviewing the many types of treatment technologies available for a waste, prior to its re-use or disposal.

1.2.2 Definitions

There are many wastes that, provided they pass the appropriate regulatory tests, go straight to landfill. However, in almost every waste producing process there will be something, a dust, ash, or sludge for example, which cannot be re-used in its existing form. More often than not, these wastes will have been derived from some sort of mass or volume reduction step, which essentially concentrates any hazardous constituents into a minimal, and sometimes highly toxic, volume of waste. For these wastes, the safest and most economically viable alternative is to treat the waste in a way that addresses the needs of ultimate (long-term) disposal (Kyle 1991). Once treated, again assuming they pass the regulatory tests, they too can be landfilled.

The most commonly employed practice for long-term disposal of hazardous wastes over the past thirty years has been stabilisation/solidification, and the terminology used to define this practice varies, depending upon the source (Wiles 1987). Almost every paper contains its own individual interpretation of what a stabilised, solidified, or (as a combination of the two) fixed waste entails.

The use of the words *stabilisation*, *solidification*, and *fixation* interchangeably is lamented by Conner (1990) since the terms do have distinctly different meanings.

In this study, the definitions by Kyle (1991) are used:

> **Solidification:** The process of mixing materials with the waste to produce a solid. It may or may not include chemical interaction between the additive and the toxic component.
>
> **Stabilisation:** The process of converting the waste to a more chemically stable and less toxic form. It includes solidification and, usually, also chemical fixation.
>
> **Chemical Fixation:** The conversion of a toxic contaminant to a new non-toxic form, either by a chemical reaction or by chemical bonding of the contaminant to a binder.
>
> **Encapsulation:** The process of completely coating toxic particles (microencapsulation) or agglomerates of particles (macroencapsulation) with a new substance in order to limit the solubility or mobility of the toxic substance in the environment.
>
> **Fixation:** A term used loosely to cover any or all of the above terms.

There has been a variety of opinion on the broad classification of stabilisation/solidification (S/S) processes. For example, the definitions above are similar to those of Wiles (1987). Whereas Kyle's (1991) and Wiles' (1987) definitions state that stabilisation **does** include solidification, the USEPA defines stabilisation as a process which does not necessarily change the physical nature of the waste (Cullinane & Jones 1986). That is, solidification does not always take part in stabilisation processes. Further to this, the USEPA claims that solidification refers to those techniques that encapsulate the waste in a monolithic solid of high structural integrity. More often than not, however, the EPA (both US and Victorian) requirement of waste solidification is that it leads to a 'spadeable' solid (Good, J. 1996, pers. comm).

Indeed, Jones (1990) points out that most hazardous wastes to be stabilised/solidified are liquid slurries with relatively low solids content (10%-40% w/w). As a consequence, the mixture of a solidification agent, such as Portland cement, with a slurried waste, more often than not, closely resembles a hydrated cement paste rather than typical concrete.

Support for Kyle (1991) and Wiles (1987) is provided by Pojasek (1978), who suggests that in most cases stabilisation and solidification **do** go together, and that this is probably the safest mechanism of all. While the solidification, itself, encapsulates the waste and prevents the release of toxic components to the disposal site, the stabilisation provides a fail-safe mechanism against the remote possibility of the physical or chemical breakdown of the solid agent over time. If the collapse of the solid matrix were to occur, the waste would be in its most stable form, thus limiting the rate of release of any toxic constituents to the surrounding areas.

1.2.3 Types of S/S Processes

The objective of waste stabilization is to contain the waste and prevent its hazardous constituents from re-entering the environment at rates that would cause a danger to public health and the environment. This is achieved by producing a solid with improved handling characteristics and decreased surface area, to limit the leachability of the waste. The contaminants should also be converted to a form with limited solubility in the leaching fluids (Kyle 1991).

The most commonly employed ways in which the objectives can be achieved are cement-based S/S, pozzolan-based S/S, and organic-based S/S.

As much of the S/S that now occurs around the world is based on the chemistry of cement, this will be discussed in detail after a very brief overview of the other processes.

1.2.3.1 Organic Stabilisation/Solidification

The main solidifying agents are either thermoplastic resins (e.g. bitumen, polyethylene, paraffins and waxes) or cross-linked polymers (e.g. urea-formaldehyde) (Kyle 1991).

With organic S/S the waste materials do not react with the solidifying material to stabilise the contaminants. It is merely a microencapsulation process (Conner 1986; USEPA 1989). That is, the solidifying agent acts by immobilising the constituents of concern and trapping them in a polymer matrix. This technology has been used mainly for the stabilisation/solidification of radioactive wastes and, on a limited basis, for non-radioactive hazardous wastes (USEPA 1989).

The main problems with organic systems are that most are expensive, solvent-based and hydrophobic. Consequently, for use on water-based wastes, the system must usually be formulated as an emulsion – which is not always easy to accomplish. In addition to these problems, the presence of water and other ingredients can interfere with the polymerisation reaction (Conner 1986).

1.2.3.2 Pozzolan-Based Stabilisation/Solidification

Pozzolanic stabilisation/solidification involves the use of siliceous and aluminosilicate materials that display limited, if any, cementing properties when used alone. However, when combined with cement or lime and water, they form cementitious substances of low solubility at ambient temperatures (Côté 1986, USEPA 1989). The primary containment mechanism is the physical entrapment of the contaminant in the pozzolan matrix. Although pozzolanic reactions are not identical to Portland cement reactions, they are thought to resemble them (Côté 1986) (Refer to section *1.2.3.3.2* on cement reactions).

Probably the best known and most frequently used pozzolan is fly ash, an industrial by-product which is the finely divided residue resulting from the combustion of coal (Côté 1986). One significant advantage of using coal fly ash in pozzolanic solidification is that fly ash is a hazardous waste product itself. A number of researchers have investigated the potentially hazardous nature of fly ash leaching in both laboratory experiments, and in the actual ash ponds themselves (Mudd *et al* [1998a, 1998b]; Förstner *et al* 1990; Villaume *et al* 1981; Dodd *et al* 1981; Murarka 1988; Sack *et al* 1981; Vela *et al* 1994; de Groot *et al* 1989; van der Sloot *et al* 1989; Bridle *et al* 1987; Bishop *et al* 1992).

An example of the applicability of fly ash in S/S procedures is the combination of the pozzolanic fly ash with some cement, and chromium contaminated tannery waste. Here, a number of problems can be solved. Firstly, the chromium waste can be stabilised through the higher and more strongly buffered pH environment provided by the cement. Secondly, the fly ash combined with the cement physically traps the chromium within the matrix. Finally, the fly ash itself has been incorporated into a high pH cement-based matrix, and effectively stabilised and solidified, thus reducing the mobility of any hazardous metals that may have been present. Thus this process can treat two problem wastes at the same time without significantly compromising the integrity of the final mix, a problem often encountered when fixing two different waste types together.

The other common industrial pozzolans are blast furnace slags and kiln dusts. Blast furnace slag is a glassy product consisting of calcium silicates and aluminosilicates that is developed simultaneously with iron in a blast furnace, while kiln dust is a by-product in the production of cement (Conner 1990, Côté 1986). Although generating cementing reactions that are generally much slower than cement only S/S, pozzolanic S/S has been used in many waste reuse situations such as road bases and construction. Less frequently, it has also been used as a cheaper method, compared with cement, for safely disposing of hazardous wastes to landfill (USEPA 1989; Gourmans *et al* 1991; Gourmans *et al* 1994).

In volume of waste treated, the lime/fly ash process has probably been the most used in the United States, although generally more narrowly applied to specific types of sludges. On the other hand, the Portland cement/fly ash process has been used in Canada and Europe but has not been applied very broadly in the United States (Conner 1990).

There are, of course, multitudes of pozzolanic processes, both commercial and experimental. Those not of a proprietary nature that have been used, or proposed for use, are generally variants of the types above. The specific methods are widely available and provide detailed information on the individual pozzolanic processes (Côté & Hamilton 1984; Pojasek 1979; van der Hoek & Comans 1996; Weng & Huang 1994; Landreth 1980; Kovacik 1988; NTIS 1979; Roy *et al* 1991).

1.2.3.3 Portland Cement-Based Stabilisation/Solidification

Since its initial use in the 1950s for the containment of nuclear wastes, Portland cement has been the most widely applied ingredient in S/S systems. 'Portland Cement', so called due its similarities with stone of that area in England, is the most commonly utilised cement in Australia, not just for waste fixation but also for the majority of general engineering applications. In 1997, production of Portland cement worldwide exceeded 10^9 tonnes per year (Glasser 1997). As a result of this popularity any use of the word 'cement', unless otherwise stated, should be taken to mean 'Portland cement'.

As with other S/S systems, the premise behind using cement is to chemically and physically immobilise any contaminants, while, at the same time, improving the handling characteristics of the waste. The advantage cement has over other options is that it can perform these functions equally well on a large number of wastes, as opposed to other processes, which may only cater for one or two requirements and be applicable to relatively few contaminants.

1.2.3.3.1 Portland Cement Constituents

In order to better understand cement-based S/S processes, the chemistry and mineralogy of Portland cement are outlined below. Portland cement is a mixture of calcium silicate and calcium aluminate minerals, produced by the calcination of limestone and clay, at about 1500°C, to form a clinker (Conner 1990, Popovics 1979). The four main compounds that make up the clinker are indicated in Table 1.1.

Table 1.1: Mineralogical Composition of Type I Portland Cement (Conner 1990)

Mineral Name	**Chemical Name**	**Chemical Formula**	**Symbol**	**Percentage**
Alite	Tricalcium Silicate	$3CaO.SiO_2$	C_3S	45
Belite	Dicalcium Silicate	$2CaO.SiO_2$	C_2S	27
Aluminate	Tricalcium Aluminate	$3CaO.Al_2O_3$	C_3A	11
Ferrite	Tetracalcium Alumino Ferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	8
Others				9 (<1 each)

Note that this mineralogical composition is based on normal Portland cement, also known as Type I Portland cement. This is a general-purpose cement and usually the least expensive. All in all there are five types of Portland cement that, depending on the additives, perform a number of specialised functions. These types are detailed in Table 1.2. Type II, for example, protects against moderate sulphate attack, while Type IV has a low heat of hydration and is used in structures where temperature rise must be controlled (Conner 1990).

Other cement types such as high alumina cement, Sorel cement, and even the pozzolans mentioned in section *1.2.3.2* also have different functions, once again depending upon their respective mineralogies. Côté (1986), Conner (1990), and Glasser (1997), among others, use ternary diagrams to provide an indication of differences in oxide type and content between various cementing materials. Figure 1.1, adapted from Glasser *et al* (1987), details those differences. Class C and F are two obsolete but persistent classifications of fly ash.

Table 1.2: Typical Compositions of Portland Cements (Conner 1990)

Type	**Designation Characteristic**	**% C_3S**	**% C_2S**	**% C_3A**	**% C_4AF**	**% Others**
I	General Purpose	45	27	11	8	9
II	Moderate Heat Evolution/ Sulphate Resistance	44	27	11	8	10
III	High Early Strength	53	19	11	9	8
IV	Low Heat Evolution	28	49	4	12	7
V	Sulphate Resistance	38	43	4	9	6
	Rapid Hardening					
	Super Rapid Hardening	66	11	8	9	6
	Jet Cement	68	5	9	8	10
		52	0	22	5	21

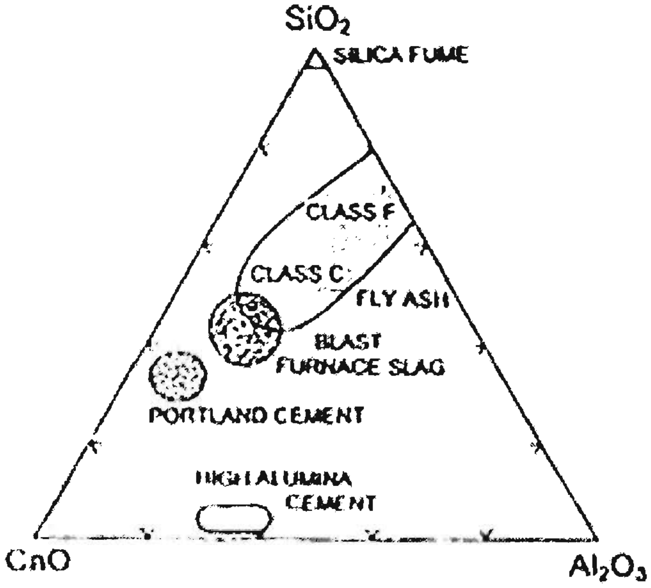


Figure 1.1: Cement/Pozzolan Compositions (Glasser *et al* 1987)

1.2.3.3.2 Portland Cement Hydration

Despite the long history of use of cement, the literature has a surprising amount of conjecture on the detailed mechanism of cement hydration. However, although the specifics of reaction and interaction have not been completely elucidated, the basic reactions of the setting of cement are well documented.

Aluminate is the first mineral to undergo hydration following the addition of water. Formation of Aluminate hydrates causes a relatively rapid setting that produces a rigid structure while evolving a moderate amount of heat (Table 1.3, Reaction 1). To ensure the mixture does not set too quickly, a certain amount of calcium sulphate (Gypsum) is present in the original cement. The Gypsum, upon reacting with the Aluminate, forms Ettringite (Table 1.3, Reaction 2) as very small particles on the surface of the cement grains (Côté 1986). These particles retard the hydration of the Aluminate, ensuring that flash setting does not occur.

As expected from their percentage contribution, the calcium silicates (Alite and Belite) contribute most to the binding power and strength of the set cement. In spite of this, however, the silicates effect two vastly different contributions to the final product.

Alite hydration begins very early and continues for approximately 28 days by which time the cement is essentially two-thirds set (Table 1.3, Reaction 3). Virtually no Alite hydration occurs later than one year. As such, its principal contribution is to the strength development of cement. Belite, on the other hand, hydrates much more slowly (Table 1.3, Reaction 4). The greater part of its hydration does not take place until after 28 days, but continues beyond one year. Its contribution is, therefore, at later ages. As can be seen from reactions 3 and 4, the overall hydration reaction of both silicates leads to the formation of a gel of calcium silicate hydrates (CSH), the main binding agent in cement pastes, and crystalline calcium hydroxide, the compound most readily leached from Portland cement concrete (when exposed to soft or acid waters) (Eglinton 1987).

Table 1.3: Portland Cement Hydration Reactions (Côté 1986)

1) $3CaO.Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO.Al_2O_3.Ca(OH)_2 + 12H_2O$
(Aluminate) (Tricalcium aluminate hydrate)

2) $3CaO.Al_2O_3 + 30H_2O + 3CaSO_4.2H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$
(Aluminate) (Calcium trisulphate aluminate)
(Ettringite)

3) $2(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$
(Alite) (Calcium silicate hydrate gel [CSH])
(Tobermorite gel)

4) $2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$
(Belite) (Calcium silicate hydrate gel [CSH])
(Tobermorite gel)

$Ca(OH)_2$, one of two main crystalline phases (20-30%), appears as plates or columnar crystals, and the other, Ettringite (<10%), as rods and needles. The CSH gel phase is typically massive and rather featureless at the micrometer scale. Nevertheless, it is the principal constituent of Portland cement and controls many of the properties associated with hydrated cements (Glasser 1997).

1.2.3.4 Application of Portland Cement-Based Stabilisation/Solidification to Metal-Contaminated Waste Immobilisation

The popularity of cement for waste S/S stems not only from an economic or convenience perspective, but predominantly from the way in which the fixation of the waste is effected: stabilisation and solidification in essentially the one step.

The alkalinity of the cement-waste matrix is advantageous because most metal ions have poor solubility at high pHs, while the physical integrity of the waste compensates for any amphoteric species which are not as easily stabilised at pHs greater than 7. Added to this, is the advantage that the fixation of aqueous wastes is not a problem as cement needs water to hydrate and form a solid matrix.

Of course, the use of cement, no matter how strong the final product may look, is not suitable for all wastes. The most popular application of cement S/S is for heavy metal contaminated sludges and soils, and it is this application and resultant assessment which will be covered in the remainder of this chapter. Although some cement-based systems have been shown to cope with a reasonable quantity of organic materials, more often than not they are not well retained within the matrix and can have deleterious effects on the cementation reactions (Conner 1990). These effects are discussed in Section *1.2.3.4.3.3*.

Cement-based S/S aims to provide a strong, durable matrix of low permeability while at the same time rendering any contaminant insoluble. Thus, the contaminants are immobilised through both physical and chemical mechanisms, and must, therefore, be able to adequately resist any chemical or physical changes in a specific disposal environment (Stegemann & Côté 1996).

1.2.3.4.1 Physical Containment

The physical properties of a cement-based solidified waste revolve around durability and strength in a number of environmental conditions. Conner (1990) points out that waste forms derived from S/S processes can vary markedly in their physical natures, depending on the disposal requirements. Monolithic blocks, soil-like granular materials, soft clay-like solids, and even powders, are some of the physical forms that can result from these processes.

The long-term containment of a waste depends on the ability of the matrix to maintain its integrity in a number of conditions (Côté 1986). The matrix must be able to resist both physical wear and chemical attack. Physical mechanisms of degradation include wind and water erosion, pressure from earth moving equipment, freeze/thaw effects, and any excessive wet/dry cycling that may occur over the life of a landfill or intended disposal situation (Environment Canada 1991a). This physical resistance ensures any contaminants that are only physically retained in the matrix, remain so.

1.2.3.4.2 Chemical Containment

According to Côté (1986), the main objective of cement S/S is to immobilise contaminants by preventing their leaching into surrounding liquid. This can often prove difficult, as during cement hydration any excess aqueous phase becomes pore water. As the matrix hardens, the mix water gradually diminishes and any remaining aqueous phase becomes trapped in the pores (Glasser 1997). The alkali content of the cement and waste concentrates in the pore water, providing a pH anywhere in the range of 12-14 (Glasser 1997). It is in this high pH environment, in the pores, that the majority of metallic species are converted to their insoluble hydroxide forms, while any soluble species remain there available for leaching. It is also possible that some of the metals may be physically bound to the paste lattice of the cement (Côté 1986, Bishop 1988).

The removal of contaminants from these pores or the paste is, therefore, only restricted by the physical constraints of any matrix breakdown or weakening through leaching that may occur. In this way, both physical and chemical mechanisms of containment are connected. In fact Calleja (1980) defines physical durability as 'the resistance of the matrix to chemical interactions in an aqueous environment'. Glasser (1997) goes one step further, by stating that 'the distinction between the purely chemical and purely physical mechanisms (of immobilisation) is not always clear-cut'. In many situations both physical and chemical mechanisms operate in unison and it is often impractical to make a distinction between the two.

So it is with the removal of contaminants from a cement-based waste by water permeability. Water is probably the most wearing of all substances on a cement S/S waste, and, although it may appear to affect the waste form physically, its effects can be readily observed and accounted for on a chemical level.

In neutral water, calcium hydroxide (lime) is the only soluble product of cement hydration, while at the same time providing nearly all of the alkalinity. It has been shown that lime will leach easily from cement until 10-15% of the original wet weight has dissolved (Côté 1986). This corresponds, roughly, to the amount of lime produced from the hydration of the tricalcium and dicalcium silicates as shown in Table 2 (Côté 1986).

Even though this leaching occurs without significant reduction of cement strength, it is the increase in the porosity of the waste form that could become a problem, since the higher porosity allows any metals to more easily leach out into solution. Added to this, is the gradual reduction in alkalinity, which lowers pore water pH, thus further solubilising metallic species. Although this simplistic example of metallic leaching may adequately describe some cement S/S wastes, the greater percentage are complex mixtures of metals and minerals, in which interactions between contaminants and cement can differ markedly in containment mechanisms.

1.2.3.4.2.1 Metal/Cement S/S Waste Interactions

In the basic environment present during cement hydration, the surfaces of cement particles are negatively charged. While uncharged (and to a lesser extent positively charged) surfaces can also adsorb cationic metals, it is the negatively charged surfaces that are expected to adsorb the majority of metal cations. The most readily available cations in solution are Ca^{2+}, and these are believed to coat the silicate surfaces forming a high charge density Ca^{2+} layer. Metal anions in solution will then compete for adsorption sites, forming a further layer (Asavapisit *et al* 1997).

Asavapisit *et al* (1997) investigated this competition for adsorption sites by studying the effects of 10% additions of lead (Pb), zinc (Zn), and cadmium (Cd) hydroxide synthetic wastes on Ca^{2+} during hydration of ordinary Portland cement.

They found that, during early Alite hydration, Pb was resolubilised from the waste at high concentrations, probably forming $Pb(OH)_3^-$ species. It is believed that this species is responsible for retarding $Ca(OH)_2$ formation throughout the first week of Alite hydration, by competing for the Ca^{2+} adsorption sites and forming a low permeability layer. They also found that, as new silicate hydration products were formed, the soluble lead concentration fell from 1000mg/L to 20mg/L , indicating the $Pb(OH)_3^-$ is being rapidly absorbed onto the newly created silicate surfaces.

The researchers found Zn exhibited similar behaviour causing severe inhibition of hydration, while Cd appeared to behave quite differently by promoting rapid formation of $Ca(OH)_2$. Poon *et al* (1985a & 1985b) also demonstrated, via porosity and leaching experiments, that zinc is well retained in a cementitious matrix. In fact, because the observed leachability was not consistent with the measured porosity of the matrix, they stated that chemical stabilisation was more important than physical retention in confining metal mobility.

As Asavapisit *et al* (1997) point out, a number of recent studies have demonstrated the adverse effects of heavy metals on cement hydration (Hills *et al* 1992; Hills *et al* 1993; Hills 1993; Tashiro *et al* 1977; Hanna *et al* 1995a; Hanna *et al* 1995b). More specifically, the containment mechanisms and effects of lead have been covered.

Indeed, Asavapisit's work has backed up previous research that hypothesized the formation of a colloidal membrane by lead precipitates around the cement grains, thus retarding cement hydration (Conner 1990; Thomas *et al* 1981; Alford *et al* 1981).

Bishop (1988) demonstrated that cadmium, being adsorbed onto pore surfaces, was released as the alkalinity, or $Ca(OH)_2$, was released from the matrix. This was however not the case for lead and chromium, which are believed to be bound into the silica matrix itself, and, therefore, will not leach to any great extent until the silica matrix itself break down. Further proof of this action comes from the lead and chromium leach rates which were well below their respective hydroxide solubilities, indicating strong complexation with silicon in the matrix.

Arsenic is also difficult to fix, while at the same time having deleterious effects on cementation. Arsenic does not form insoluble hydroxides so the mechanism of stabilisation that operates during the S/S of many heavy metal cations does not apply here. The most common arsenic oxides (III & V) are also water soluble (Cartledge 1993). Hence, many previous attempts at fixation have not worked well as the arsenic leaches readily. Conner (1990) has summarised leaching results from a number of arsenic contaminated cement-waste composites.

Thomas (1987) has shown arsenate to be a moderate retarder of cement and tricalcium silicate hydration reactions. Similarly, Cartledge (1993) has investigated the effects of arsenate and arsenite on hydration, showing that arsenate prolonged the retardation. Of more interest, the silicate phase appeared to undergo depolymerisation over a period of time. Arsenate samples had increased leachability after one year of cure, as opposed to the samples cured for 28 days. This long-term effect of arsenic on the cement matrix could have serious implications for cement stabilised arsenic wastes disposed to landfill.

1.2.3.4.3 Factors Affecting Cement S/S

Aside from these variations in metal containment and leaching, and the effects of $Ca(OH)_2$ discussed earlier, the leaching of metals and changes in cement hydration can be further affected by other factors.

1.2.3.4.3.1 Accelerators/Retarders

Whether they are intentional additives or constituents of the waste itself, many materials exist which either retard or accelerate the setting of cement.

Inhibition, or retardation, results from interactions, between the waste constituents (or additives) and the cement, having a deleterious effect on cement hydration. In a common heavy metal sludge/cement mix, the different heavy metals themselves can have varying effects. Roy and Cartledge (1997) observed increases in the crystallinity and porosity of a cement matrix through additions of copper nitrate. Akhter *et al* (1997), through spectroscopic and thermal analysis, have shown both arsenate and arsenite to significantly reduce the amount of calcium hydroxide in the cement. Similarly, as mentioned in Section *2.3.4.2.1*, Cartledge (1993) demonstrated the effects of arsenic on the long-term stability of cement matrices. Hills and Pollard (1997) demonstrated a reduction in strength of approximately 99%, compared to the cement control, by adding a 3% (w/w) addition of zinc-containing metal plating sludge. Lead salts were found to cause extreme retardation of the hydration reactions that applied to the aluminate and silicate phases. This is consistent with Asavapisit *et al* (1997). There was, however, no effect on the long-term strength of the cement (Soroka (1979).

Although the effects and interactions in delaying cement hydration and decreasing strength will always occur, one way to reduce or eliminate their time-related constraints is to add an accelerator or anti-inhibitor to the mix. Calcium chloride is the most popular and common accelerator (Soroka 1979). Although the way in which it works is not fully understood, it is clear the mechanism involves acceleration of Alite and Belite hydration (Rixom & Mailvaganam 1986). Ramachandran (1984) concluded that no single mechanism could explain the effects of $CaCl_2$ on the kinetics of hydration of the silicate phases. Nor could the pore volume, surface area changes and strength development be singularly explained. He suggests that a combination of mechanisms may be operating, depending on the experimental conditions and the period of hydration.

1.2.3.4.3.2 Liquid to Solid Ratio

Côté (1986) has stated that a number of researchers regard the water to cement ratio as the single most important factor influencing the morphology of the matrix and its physical and engineering properties.

For obvious economic reasons, a minimum amount of cement is added to waste to obtain solidification. This can, however, cause a problem when determining the amount of water to add. Some wastes may already contain water while others may absorb large amounts themselves. Therefore, it can be difficult finding a compromise between economics, workability (mixability) of the waste, and the strength and setting time of the final product.

Too little water may create a waste mix which is difficult to homogenise and only partially hydrated, while too much may result in a layer of freestanding water on the surface of the solidified product, as well as low resistance to weathering, reduction in strength due to an increase in pore water, and an increase in porosity, permeability and leachability of the final product (Conner 1990, Côté 1986).

1.2.3.4.3.3 Organic Compounds

The majority of research conducted on cement-based organic waste stabilisation, over the last two decades, has demonstrated that organic compounds affect both the strength and setting time of cement (Wiles 1987).

Some organic materials appear amenable to cement based S/S. Wastes such as rolling mill sludges, electroplating residues or oily sludges from petroleum refineries have been successfully treated. However, wastes containing hydroxyl or carboxylic acid groups can be expected to delay or completely inhibit cement hydration (Wiles 1987).

Leaching tests (Kolvites and Bishop 1989) have shown phenol to be poorly retained by a three day old cement paste (93% leached), with improved results from a 28 day old paste (58% leached). This decrease in leaching was ascribed to decreases in total pore volume and mean pore diameter of the cement paste with increasing cure time.

Jones (1990) has proposed conceptual models of possible interference mechanisms of organic materials on cement/waste mixes. Adsorption of added waste molecules on the surface of the cement particles is thought to block the normal hydration reactions. Similarly, organic retarders can be adsorbed onto the calcium hydroxide nuclei and effectively cover crystal growth surfaces. Any organic based aluminate, ferrite, or silicate complexation may also be responsible for delaying the formation of hydration products.

1.2.3.4.3.4 Carbonation

The hydration of cement is affected by the presence of carbon dioxide which, in turn, may lead to deleterious effects in containment of the waste over time (Lange *et al* 1997). This process, known as carbonation, occurs when Portlandite and other calcium-bearing phases in the wasteforms react with CO_2 to form Calcite ($CaCO_3$) (Walton *et al* 1997).

The two primary effects of carbonation are a reduction in porosity of the matrix and pH reduction. The porosity drops as the previously open, large pores fill with calcite, while progressive carbonation drops the pH of the system from around 13 to as low as 8. These effects can result in reduction in leaching, due to the decrease in matrix porosity and, conversely, an increase in metal leaching due to the decrease in matrix pH (Walton *et al* 1997, Dayal & Reardon 1992). Walton et al (1997) and Bin Shafique *et al* (1998) have supported these ideas. Static and dynamic leach tests showed that carbonation was not a uniformly favorable process, and that its influence on waste form release was both complex and variable.

1.3 Evaluation of Stabilised/Solidified Wastes

1.3.1 Preamble

Responsible hazardous waste management involves much more than just the fixation process. The effectiveness of containment depends on the waste, S/S process used, and the conditions at the disposal site. As a generalisation, the following parameters could be expected to be important:

1. Contaminant solubility
2. Diffusive and advective transports through the treated waste interstices
3. Ability to maintain physical integrity (Hannak *et al* 1988)

For the greater part of the last thirty years, hazardous wastes have been evaluated and characterised using leaching tests. In addition, but more specifically for wastes that are, at least in part, solidified by cement or pozzolan, wastes are characterised via physical and micromorphological testing.

This section of the review deals extensively with the methods used to evaluate potential toxicity of wastes and the effectiveness of specific stabilisation/solidification technologies. Physical and micromorphological methods of waste characterisation are discussed briefly before detailed exploration of the many types of leaching tests used.

1.3.2 Physical Testing of Stabilised/Solidified Wastes

Physical testing of S/S wasteforms is conducted to characterise waste before and after the fixation process. Physical property characterisation of unstabilised/unsolidified wastes focuses on treatability, excavation, transport, storage, and mixing considerations while similar testing of a fixed waste helps (in conjunction with leaching tests) to ascertain the relative success or failure of a stabilisation/solidification process (USEPA 1989).

Some of the more common physical tests used include bulk density, specific gravity and moisture content, which are used to determine the volume change factor for a solidification process, which is an important cost consideration (Environment Canada 1991b). Hydraulic conductivity, unconfined compressive strength, and freeze thaw and wet/dry weathering resistance relate to the physical integrity and ruggedness of the waste (Environment Canada 1991b).

1.3.2.1 Bulk Density, Specific Gravity, and Moisture Content

These are basic physical characteristics of a S/S waste, which can also be used in calculations for other parameters. Bulk density is the ratio of the total mass to the total volume, specific gravity is the mass of the dry solid portion of the waste per mass of an equivalent volume of water, while moisture content includes all surface water, pore water, and waters of hydration contained within the waste (USEPA 1989, Environment Canada 1991b).

Hannak *et al* (1988) point out that, of itself, bulk density has no bearing on containment efficiency. However, when combined with specific gravity and moisture content, it could be used to calculate porosity, which is related to permeability and, hence, potential release of contaminants by advective transport of liquid through the waste form.

1.3.2.2 Hydraulic Conductivity

Hydraulic conductivity, measured in metres per second, is the permeability to water of a stabilised/solidified waste and is usually determined in a triaxial cell using a falling head method (Environment Canada 1991a).

In a landfill, any liquid will flow via the path of least resistance. If the surrounding landfill media are more permeable than the S/S waste, water will be channelled around the bulk of the waste form. Conversely, if the waste is more permeable, water will preferentially flow through it. In the first case, the leaching of contaminants will be less severe, with slow diffusion being the controlling mechanism. The alternative case presents a situation where the water flow will more rapidly wash contaminants out of the waste. Thus, the hydraulic conductivity of a solidified waste, relative to that of its surroundings, has an important impact on the rate of leaching (Stegemann & Côté 1990).

1.3.2.3 Unconfined Compressive Strength

This is a measure of a solidified product's ability to withstand mechanical stresses such as might be imposed in a landfill by overburden or heavy moving equipment (Environment Canada 1991b). If a S/S waste were to succumb to external pressures, the formation of cracks and subsequent generation of particulates could result. This would, in turn, increase permeability, liquid to solid ratio and, therefore, lead to greater leaching of contaminants (Hannak *et al* 1988; Environment Canada 1991b).

The test itself is adapted from the ASTM Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (C 109-80) where a 5.08cm (2 inch) cube of S/S waste is compressed vertically until failure. The stress at failure is deemed the waste's unconfined compressive strength (Environment Canada 1991b).

Even though the USEPA considers 50psi (345kPa) to be a satisfactory unconfined compressive strength (UCS) for S/S wastes disposed of to a segregated or controlled landfill, a study by Steggemann *et al* (1988) reported UCS values for 69 S/S wastes ranging from 10 to 2900 psi (USEPA 1989, Environment Canada 1991a)

1.3.2.4 Freeze/Thaw and Wet/Dry Weathering

In a similar vein to the UCS, both types of weathering tests are aimed at measuring or evaluating durability of a S/S waste. In the case of weathering however, the aim is to look at effects of varying climatic regimes on landfilled S/S wastes.

In colder climates, repeated seasonal cycles of freezing and thawing can cause physical deterioration of a S/S product, leading to cracking and a subsequent increase in leachability. The method for measuring this physical characteristic of a waste (ASTM D4843) involves subjecting a small cylindrical S/S specimen to twelve cycles of freezing at –20°C for 24 hours, followed by thawing in water at room temperature for 24 hours. The weight loss of the specimen after each cycle is determined and compared with that of a control (Environment Canada 1991b).

Similarly, wetting and drying may also cause deterioration of a S/S waste. Here (ASTM Method D4842) a small cylindrical specimen is subjected to twelve cycles of drying at 60°C in a vacuum oven for 23 hours followed by soaking in distilled water at room temperature for 23 hours. Again, the weight loss of the specimen is determined after each cycle and compared with a control (Environment Canada 1991b).

Steggemann and Côté (1990) showed the wet/dry procedure to be more reproducible. They tested some 75 S/S wastes and found that most products survived more than seven freeze/thaw and wet/dry cycles with minimum weight loss. The weight loss from twelve freeze/thaw cycles was also found to be negligible. However, twelve cycles of wet/dry weathering resulted in weight losses of up to 30%. They concluded that the wet/dry weathering method was more sensitive to differences between the different solidified products.

It is worth noting, however, that there are no currently established standards for determining whether S/S material has passed weathering testing (USEPA 1989). The tests, therefore, are merely a guide (as with the USEPA *recommendation* of 50 psi as a minimum UCS) and should not be taken to mean a S/S waste is unsuitable or otherwise for landfilling.

1.3.3 Micromorphological Testing of Stabilised/solidified Wastes

Methods used for micromorphological characterisation include X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDXRA), Scanning Electron Microscopy (SEM), and Optical Microscopy (OM).

XRD is an excellent tool used for studying changes in crystallinity, and appearance or disappearance of phases in a S/S waste form. Any physical or chemical changes in cement caused by the addition of a particular contaminant or waste can be characterised by comparing the XRD composite patterns (Poon *et al* 1985b). One problem, however, is that in most cases with cement stabilised/solidified products, any new crystalline salts formed are present in such low concentrations that they are not evident in the already complex diffraction pattern of cement (Hills & Pollard 1997).

EDXRA allows examination of the chemical distribution across the S/S waste matrix. However, it must be pointed out that no conclusion regarding the environmental stability of the contaminant immobilisation mechanism can be reached using this method alone (Environment Canada 1991b).

Any alteration of the cement matrix through the addition of contaminants can also produce a visible variation in the matrix structure. Therefore, through microscopic observation of the matrix by SEM and even OM, useful information can be obtained on structural alterations that may have occurred (Poon *et al* 1985b). Klich *et al* (1999) investigated mineralogical alterations affecting the durability and metals containment of aged S/S wastes. Their results led them to suggest that models used to evaluate the durability and permanence of solidified and stabilised wastes should involve the use of microscopic analysis as well as leaching and chemistry analyses. They point out that microscopic and mineralogical analyses show specifically what is being altered, the mode of alteration, alteration pathways, and secondary products of alteration, all without destroying the character of the sample being analysed (unlike leaching tests).

As a final point, Steggemann and Côté (1990) make it clear that solidified products tend to be heterogeneous at a microscopic level, so that obtaining a representative sample for those tests requiring a small mass, is difficult. Consequently, these methods find greater application as research tools, for examining a few samples for well-defined features, rather than as general methods for the overall investigation of large numbers of solidified products.

1.3.4 Leach Testing of Stabilised/Solidified Wastes

Leaching tests have been studied extensively for approximately the last 25-30 years. Consequently, interpretation is varied as to what constitutes a leaching test, and, more importantly, what information can be obtained and how it should be interpreted.

No matter how well a waste is fixed with cement, there will always be some matrix dissolution. In a landfill this will arise though contact with liquid from rainfall or other wastes within the fill. Therefore, when a waste, treated or not, is exposed to liquid, a rate of dissolution can be measured. This process is called *leaching*, the extracting liquid the *leachant*, and the resultant contaminated liquid that has passed through or around the waste the *leachate*. The capacity of the waste material to leach is termed its *leachability* (Conner 1990).

Lewin (1996) provides a simple, yet excellent, definition covering all tests: '*In its simplest form a leaching test involves bringing a test material into contact with a liquid under reference test conditions followed by the analysis of the resultant liquor (leachate). Data from these tests can be used to classify materials or waste products by reference to relevant control criteria*'.

Data is usually presented as concentration of the constituent in the leachate, and, especially with regulatory tests, referenced to drinking water standards, thus providing (in theory) an indication of its potential toxicity or potential for landfilling. Further, the leaching result is usually compared to the original contaminant levels in the waste, thus providing a proportion of contaminant that leached out during the test and a measure of the leachability of the material (Conner 1990).

The leachability of a waste is measured by conducting leaching tests of which there are three basic categories: batch, column, and static/dynamic tests. Basically, a batch test involves agitation of a waste with a leachant, a column test has the leachant pumped in an up or downflow manner through a column packed with waste, while a static or dynamic test evaluates diffusion and uses no agitation or movement of leachant or waste. Most regulatory tests are batch tests (USEPA 1989).

1.3.4.1 Leaching Processes

1.3.4.1.1 Contaminant Containment/Entrapment

As explained briefly in Section *1.2.3.4*, the containment of contaminants in a solidified waste matrix is a function of both physical and chemical mechanisms. According to Côté (1986), the main objective of cement S/S is to immobilise contaminants by preventing their leaching into surrounding liquid. This can often prove difficult, as during cement hydration any excess aqueous phase becomes pore water. As the matrix hardens, the mix water gradually diminishes and any remaining aqueous phase becomes trapped in the pores (Glasser 1997). The alkali content of the cement and waste concentrates in the pore water, providing a pH anywhere in the range of 12-14 (Glasser 1997). It is in this high pH environment, in the pores, that the majority of metallic species are rendered immobile, while any soluble species remain there available for leaching. The immobilisation of metallic species can occur due to any number of processes, with the most common being their conversion to insoluble hydroxides, precipitation with other ligands, or adsorption. Cheng *et al* (1991) support this information by pointing out that most of the polyvalent metal ions, which are capable of forming insoluble hydroxides in alkaline aqueous solution, tend to be chemically stabilised in insoluble forms in the cement paste matrix. For some amphoteric metals and anions, physical encapsulation could be the major immobilising mechanism at the high pore water pH generally present. It is also possible that some of the metals may be physically bound to the paste lattice of the cement (Côté 1986, Bishop 1988).

In non-porous waste forms such as glasses and ceramics, where there are no voids within the waste, leaching is a result of interfacial exchanges at the outer surface by dissolution. In porous wastes, which includes all cement-based S/S wastes, leaching is initiated at the pore scale, or the particle interface. These wastes consist of individual particles, which may or may not be consolidated, with voids between the particles (Environment Canada 1991a).

Côté (1986) has shown porosity to be typically distributed among three different pore sizes. Pores larger than 100µm are voids between clumps of waste and/or additive particles. Pores approximately 1µm are inter-particle spaces within the clumps, while those smaller than 0.1µm include the voids inside solid particles (e.g. hydrated cement). Similarly, in their work on the effects of leaching on pore size, Bishop *et al* (1992) point out that pores in the solid matrix are dominated by capillary pores and gel pores. The capillary pores are the remnants of water-filled space that exist between the partially hydrated grains, and have a pore size range of 10nm (0.01µm) to 10µm. The gel pores, on the other hand, are included in the volume occupied by calcium silicate hydrate compounds, which have a range of pore sizes of 10nm or less.

Regardless of the size of the pore distribution, Côté (1986) showed that only a fraction of the pores are linked to each other and to the exterior of the waste form. This fraction constitutes the connected porosity of the S/S waste. The pores that are not linked to this network constitute the closed porosity. Further to this it is stated that the total amount of a contaminant in a cement waste may be associated with one of two fractions: 1) the fraction present in or adjacent to the connected porosity; and 2) the fraction present in or adjacent to the closed porosity. Contaminants can also be classified by their chemical partitioning in the matrix in that the total amount of a contaminant can be associated with either the pore solution or a component of the solid phase (Environment Canada 1991a). This is supported by Côté (1986) and Bishop (1988) who suggest that, as well as those metals trapped in and around the pores, some of the metals may also be physically bound to the paste lattice of the cement.

1.3.4.1.2 Mechanisms of Leaching

Leaching encompasses the physical and chemical reactions that mobilise a contaminant, as well as the mechanisms of transport that carry the contaminant away from the waste (Environment Canada 1990). According to de Groot and van der Sloot (1992) there are three basic types of release mechanisms: surface wash-off, matrix dissolution, and diffusion. These are illustrated in Figure 1.2.

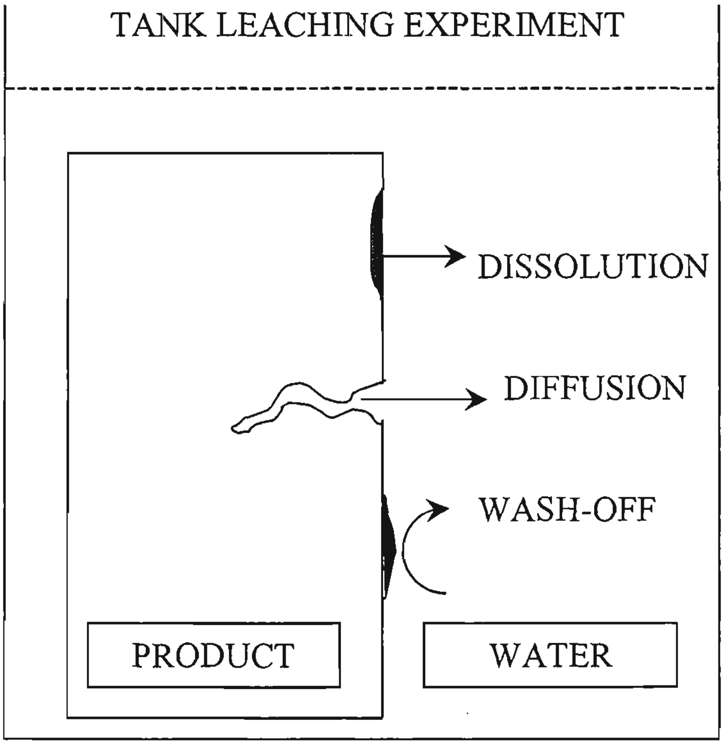


Figure 1.2: Mechanisms of Leaching (de Groot & van der Sloot 1992)

Surface wash-off occurs when a soluble coating on the surface of the waste mass is dissolved in the initial phase of the leaching experiment. In a plot of mass leached versus time, this behaviour can be clearly seen as a rapid increase in leaching at the beginning of the test. Diffusion Control is the most common, long-term form of release in cement-based wastes. Here, leaching is initiated at the pore scale where, the more porous the matrix, the greater the degree of diffusion. As diffusion control is considered to be the primary mechanism of contaminant release from cement S/S wastes, it is therefore discussed in greater detail in Section *1.3.4.1.2.1.* Matrix Dissolution generally occurs when the dissolution of the material occurs faster than diffusion through the pores of the matrix. As the matrix further breaks down, this of course leads to a greater surface area available for leaching. One additional mechanism, known as advection, involves the flow of water through the waste at various velocities. Since most waste forms have relatively low permeability, this type of transport is generally not important in either a leaching test or actual field conditions.

Depending upon the rapidity of transport of contaminant away from the waste, leaching from a waste can be described as 'equilibrium' or 'kinetic'. When the flow of fluid through (or around) the waste is low, there is time for many of the contaminants in the waste to reach an equilibrium with the fluid, and the concentration of a contaminant in the leachant reflects its solubility at equilibrium. Conversely, when the fluid flow is high, the concentration of contaminants in the leachant is controlled by the rate at which they can dissolve or otherwise be transformed. There are often situations between these two extremes, in which the concentration of a contaminant is a function of both equilibrium processes and kinetics (Batchelor 1999). Further, the leachant in a test does not need to be flowing to accord it a title of a 'kinetic leaching test'. In the Dynamic Leach Test (DLT, see Section *1.3.4.5*) a solid block (or sphere or cylinder) is leached with stagnant liquid. However, the fact that the liquid is renewed periodically to ensure the continual diffusion of species, makes it a kinetic leaching test.

1.3.4.1.2.1 Diffusive Release

Cement-based wastes are porous solids, at least partially saturated with water. They consist of one or more solid phases, entrapped air in the form of air voids, and a liquid phase called the pore-solution – all in chemical equilibrium (or close to it). However, when the solid is exposed to leaching conditions, this equilibrium is disturbed. The resulting difference in chemical potential between the solid and the leaching solution causes a mass flux between the solid surface and the leachant which, in turn, leads to concentration gradients. It is these concentration gradients that induce bulk diffusion in the solid (Conner 1990).

For most cement-based wastes in contact with neutral water, the leaching rate is controlled by molecular diffusion of the solubilised species. Of course, there are many other reactions and processes which can assist the diffusion of contaminants, or retard their transport from the waste. These include, but are not exclusive to:

- leachant and waste pH
- redox conditions
- particle size of the waste
- presence of ligands in the leachant and the waste
- presence of other metals
- formation and dissolution of precipitates
- sorption and desorption
- contaminant transport from the closed pores to the connected porosity (Batchelor 1999, Environment Canada 1991a)

For any constituent to leach, it must first dissolve in the pore water of the solid matrix or in the leachant permeating the solid. Some species dissolve more slowly than others, with the rate of solubilisation being controlled both by basic solubility considerations and by the concentration in the solution near the surface. It should also be pointed out that diffusion through the solid matrix (solid-state diffusion) is slow compared to diffusion through the solution in the connected pores (Conner 1990). This does not mean that solid-state diffusion cannot occur, just that the levels leached are generally much lower than from pore-based diffusion.

Probably the most well known explanations for diffusive leaching are the bulk diffusion model, and shrinking unreacted core (SUC) model. Both of these are based on an acidic leachant in a DLT-like scenario, where a solid sample of solidified waste is immersed in stagnant leachant, which is periodically renewed.

According to Baker and Bishop (1997), the basic premise of the bulk diffusion model is that contaminant release is a result of the concentration gradient between the leachant and the bulk concentration within the monolith. The rationale behind this model is that, in a disposal environment, diffusion through a solid represents a maximum contaminant loss rate when the waste permeability is less than 10^{-3} times that of the surrounding geologic media. Because the main driving force in bulk diffusion models is the bulk contaminant concentration, it is expected that a proportional increase in contaminant concentration would theoretically yield a proportional increase in leaching rates. As noted by Baker and Bishop (1997), this is not often the case. They go on to point out that the bulk diffusion model does not recognise the acidity dependence of contaminant leaching. In fact, under this model, increasing the acidity of the leachant would have no impact on the observed leaching rate, which has been demonstrated to be false.

The shrinking unreacted core (SUC) model was developed to describe leaching mechanisms from S/S specimens. While the bulk diffusion model considers contaminant leaching to be a result of diffusion from the monolith into the leachant, in the SUC model, contaminant leaching results from acidic species diffusing into the solid matrix. As acid penetrates into the monolith, a leached 'shell', depleted of free calcium and contaminants, is formed. Solubilised species are subsequently released into the leachant, or diffuse inward, where they are reprecipitated at the higher pH conditions of the unreacted matrix (Baker & Bishop 1997). Baker and Bishop (1997) evaluated three possible limitations in kinetics during the development of the SUC model, and determined hydrogen ion diffusion into the leached shell to be the limiting leaching mechanism.

Cheng *et al* (1991) idealise the acid penetrating process as three sequential steps. In the first step, acids diffuse from the leachant to the solid surface. The second involves acid diffusion through the leached layer to the leaching boundary, and, in the third, acids diffuse into the unleached kernel and react with alkaline materials in the pore water.

At the leaching boundary, acids diffuse through the pore structure and dissolve metals. The leaching rates of metals are, therefore, controlled by the diffusion rates of the acids into the unleached kernel. The dissolved metal ions form a concentration peak at the leaching boundary, which can diffuse either outwardly to the bulk solution or inwardly to the centre of the sample. The ions that diffuse inward could be supersaturated in the pore water, and reprecipitate when they encounter the increasing pH of the unleached cement-based material. It is believed calcium is the dominant species in this reprecipitation zone due to the fact that type I Portland Cement contains about 65% CaO (Cheng & Bishop 1992, Cheng *et al* 1991). It must, however, be noted that, although cement chemists report the content of calcium as CaO, very little of the calcium is actually present as CaO.

In their work on metals distribution in S/S wastes, Cheng and Bishop (1992) suggest that the reprecipitation of calcium hydroxide in the pores could create a resistant barrier to slow down acid attack. They also found that the acid chemically altered the surface layer, and that, while most of the calcium was removed, some silicon, iron, and aluminium remained. As silica gel, iron oxides, and aluminium hydroxides have been commonly used as sorption materials, the remaining silicon, iron, and aluminium in the leached layer are very likely to absorb/adsorb dissolved free metal ions leaching through this surface layer. In other words, the metals leaching rate could be hindered by the presence of the leached surface layer.

Cheng *et al* (1991) provide an excellent diagram, reproduced in Figure 1.3, which illustrates the various regions of an acid-leached cement-based waste form.

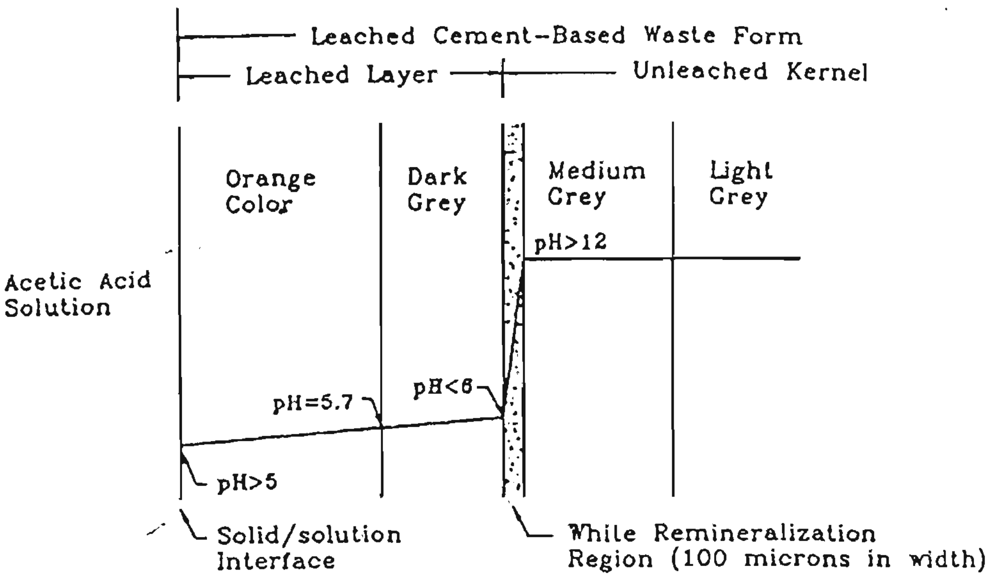


Figure 1.3: Schematic Profile of an Acid-Leached Sample (Cheng *et al* 1991)

1.3.4.1.2.2 Determination of Controlling Leaching Mechanisms

Unless mathematical models are designed and formulated to assess contaminant release from hazardous wastes, evaluating the types of release that may have occurred can prove difficult.

Although surface wash-off is generally quite easy to detect in a plot of mass leached versus time, it can be a lot more difficult establishing when dissolution or diffusion processes are also taking place. Andrés *et al* suggest that, for a tank leaching- type of test, a linear relationship between the cumulative fraction leached and time is indicative of matrix dissolution (1995). For the same types of test, Côté has identified four categories of leaching mechanisms, illustrated in Section *1.3.4.4* (Environment Canada 1991b). Of these, diffusion control is identified when a linear relationship exists between the cumulative fraction leached and the square root of time. Other methods of tank test data interpretation are provided later in Section *3.4.1.1*.

Assessment of mechanisms from tank tests is a lot easier due to the lack of leachant and solid movement. This is different for column and sequential batch tests where other processes can affect the mechanisms that occur. Consequently, distinguishing between diffusion and dissolution can be a great deal more difficult. Brown *et al*

(1986) and Bishop (1988) do however claim that metals that are trapped in the pores of a cement-based waste will be released as alkalinity is released from the pores. In their research on cement-based solidified soils contaminated with lead, Sanchez *et al* (1999) performed a number of physical and chemical leaching tests and found that TDS was 'probably dominated' by the release of calcium and its anions. Therefore, any correlation between conductivity and metal release in cement-based wastes can be a good indicator of diffusive processes.

1.3.4.2 A Brief History of Leaching Tests up to the Extraction Procedure

Perket and Webster (1981) report that the initial investigative leaching tests were based on column rather than batch methods. In the early 1970s, Hespe (1971) proposed a column method aimed at determining the leaching rate from immobilised radioactive solids, while Conner (1971) referenced a Japanese government batch test in his work on developing a column test.

The Japanese method involves mixing a 10g sample of waste with a pH 5.8-6.3 leachant in a 10:1 liquid to solid ratio for six hours. The pH of the leaching solution is maintained at 5.8-6.3 via the addition of HCl, NaOH, or CO_2, and the resulting leachate separated by filtration or centrifugation prior to analysis. The parameters of the test, for which no boundaries or specifications are set, included the method of sample preparation, type of leaching vessel, and method of sample mixing (ARC & EEM 1984).

In 1973, the U.S. Army Corps of Engineers, in conjunction with the USEPA, developed a similar batch procedure, which was used in the evaluation of contaminants released from dredge material. This method uses a sample aliquot of 200ml which, after determining solids content of the sample, is diluted to a liquid to solid ratio of 10:1, with water from the intended disposal site used as the leachant. An Erlenmeyer flask is used as the leaching vessel in an unspecified mechanical mixing method of 30 minutes duration. Following 60 minutes of settling, the leachant is decanted and subsequently vacuum filtered through a 0.45μm filter. This test has no specific method of sample preparation, nor does it facilitate pH control (Perket & Webster 1981; ARC & EEM 1984).

Other early significant work in a similar procedural vein included tests conducted by the American Foundrymen's Society, the Minnesota Pollution Control Agency, the Illinois EPA, the Federal Republic of Germany, and IU Conversion Systems, Inc. (ARC & EEM 1984).

As can be seen, the majority of the early work concentrated on batch type leaching procedures. Inevitably, all of the early leaching work contributed important parcels of information that influenced the development of the forthcoming standard methods. The first attempt at developing a standard leaching test for wastes was undertaken in 1977, by researchers at the University of Wisconsin for the USEPA. This test was known as the Standard Leach Test (SLT) (ARC & EEM 1984).

The SLT, a batch method, uses either water or a buffered mixture comprising acetic acid, glycine, pyrogallol, and ferrous sulphate as the leaching solution in a 10:1 liquid to solid ratio. In the SLT, multiple elutions are run with both leaching solutions at room temperature, with the elution itself involving agitation by physical rotation of bottles for 24 hours (Perket & Webster 1981; ARC & EEM 1984).

The SLT, however, was claimed (Perket & Webster 1981) not to have met the USEPA's regulatory needs for a single test allowing classification of a waste as hazardous or non-hazardous to the environment or human health, based on its potential to leach selected metals or organic compounds. Consequently, the USEPA proposed a regulatory method, then known as the Toxicant Extraction Procedure (TEP), a method very similar to that originally designed by the Illinois EPA. Concurrently, ASTM were working on their own methods, both batch leaching procedures, with one utilising a neutral water leachant and the other an acidic leachant (Perket & Webster 1981; ARC & EEM 1984).

The proposal of the TEP, however, was an historically important step, since it changed the emphasis of the hazardous waste industry and technical community alike regarding leach test development. Whereas previous methodologies had seen an emphasis placed on prediction of potential contamination from hazardous wastes under conditions of mono or codisposal, the TEP proposed a method development based on classification of wastes as hazardous or non-hazardous by testing their leaching potentials under standard conditions. At this point, regulatory testing started being less about the prediction of potential leaching rates, and more about a 'black & white' classification of a waste as hazardous or non-hazardous. As a consequence, subsequent efforts by the USEPA, and also ASTM, in test method development were directed toward classification procedures rather than predictive methods (ARC & EEM 1984).

Following input from various sources, the TEP was modified several times until, in the final regulations, the method adopted by the USEPA in 1980 was designated as the Extraction Procedure (EP) (ARC & EEM 1984).

1.3.4.3 Batch Leaching Tests

A leaching test can be used for either waste classification or leachate quality prediction. In the former case, a standardised methodology is appropriate, since it allows comparison between laboratories and ensures better reproducibility of the results (Côté & Constable 1982). For regulatory purposes, batch leaching tests are most often used as this standard methodology.

Commonly, a batch test involves agitating a waste sample with a predefined quantity of liquid, for a specified time. The EP was the first batch method in the U.S. to be used in a regulatory capacity on a wide scale.

1.3.4.3.1 Extraction Procedure (EP)

1.3.4.3.1.1 EP Method

A flow chart of the EP can be seen in Appendix A. Once a representative sample (at least 100g of waste) is obtained, one of three paths can be chosen depending on solid content. If the sample contains free liquid, the solids are separated by filtration and the liquid portion withheld from the actual extraction. Subsequently, the solid portion may undergo size reduction, to reduce the particles to the specified size for the extraction (Perket & Webster 1981).

A volume of de-ionised water, equal to sixteen times the sample mass, is mixed with the solid sample, in a glass or plastic bottle. The bottle is then placed in a rotating shaker/mixer and agitated for 24 hours. During the extraction, the pH is adjusted and held between 4.8 and 5.2 by addition of 0.5M acetic acid, or until a maximum of 4ml per gram of sample has been added. After 24 hours, the liquid volume is adjusted to equal 20 times the mass of the sample. Filtration is performed and the liquid is combined with the liquid, if any, from the first filtration to form the extract (Perket & Webster 1981). The extract is analysed for the presence of the prescribed constituents, detailed in Table 1.4.

The maximum allowable concentrations in Table 1.4 were derived by multiplying the US National Interim Primary Drinking Water Standards of these 14 toxic constituents by a dilution and attenuation factor of 100 to account for groundwater dilution prior to reaching a receptor. This was not derived from any model or empirical data, but rather was an estimated factor that the EPA believed would indicate 'substantial hazard'. If any one of the maximum allowable concentrations were exceeded, the waste was considered hazardous and treatment deemed necessary. Further EP testing was then performed to assess the treated waste's suitability for landfilling (TCLP Information [Online], accessed 1998, http://earth1.epa.gov/OSWRCRA/other/mining/minedock/tclp.htm 1998).

Table 1.4: EP Contaminants and Maximum Extract Levels (Millipore Corporation 1988)

Contaminant	**Maximum Allowable Concentration (mg/L)**
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
2,4-D	10.0
2,4,5-TP Silvex	1.0

1.3.4.3.1.2 Problems with the EP

Through the use of an acetic acid leachant and relatively harsh extraction conditions, the EP predisposes itself to being a worst case scenario test for the mismanagement of wastes, via the simulation of leaching in a sanitary (municipal) or codisposal environment. Martin (1990) and Larson *et al* (1981) both comment that the EP approaches the acid conditions associated with landfill leachate from codisposal operation, where microbial activity is prominent, in that the pH is mildly acidic, and the major aggressive component is acetic acid, one of the more dominant carboxylic acids present in municipal waste leachate.

The stated objective of the EP is that the test should 'simulate (the) leaching a waste will undergo if disposed of in a sanitary landfill' (Perket & Webster 1981). Additional interpretation states that 'the test was designed to simulate leaching of hazardous wastes disposed to a municipal solid waste landfill that overlies a ground-water aquifer: in other words, the EP represented a worst-case scenario for the mismanagement of hazardous wastes'(The Hazardous Waste Consultant 1994). Hence, although designed to provide an acidic environment, the EP was often maligned for the narrow view it presented when dealing with a number of disposal scenarios and waste types.

The most common difficulty with the EP was its ambiguity with respect to the test parameters. These problems (Perket & Webster 1981) included:

- No set method of agitation is required
- A 20°C range in temperature is permissible throughout the duration of the test.
- The focus of the test is a co-disposal scenario that does not take into account the segregated disposal of wastes.
- Only 14 toxicants are covered in the test.

Without a doubt, the biggest concerns revolved around the inherent lack of reproducibility and repeatability of the test.

A review of batch extraction procedures, by Perket and Webster (1981), demonstrates that the EP had poor inter- and intra-laboratory reproducibility. In fact, it was suggested that the major source of error with the EP was interlaboratory analysis, rather than the method itself. This was contradicted by a Department of Energy (1980) study, that found the main source of variability was attributable to the leaching process itself.

Mason and Carlile (1986) tested a number of utility wastes and found that extract reproducibility of the EP differed for each chemical tested and for each waste sampled. They found that the variability among EP extracts was mainly caused by the amount of material extracted at different laboratories. Similarly, Dietrich *et al* (1993) found the EP gave highly variable results for municipal wastewater sludges.

1.3.4.3.2 Toxicity Characteristic Leaching Procedure (TCLP)

To combat the deficiencies of the EP, the USEPA proposed significant changes, involving the addition of more compounds to the test and the redesign of the leaching procedure. The new procedure was fully implemented in 1990 in the United States, and later in most Australian states, and is known as the Toxicity Characteristic Leaching Procedure or TCLP (Kastner 1990).

1.3.4.3.2.1 TCLP Method

A flow chart of the TCLP method is shown in Appendix B. Initially a sample of the waste in question is collected. For liquid wastes (those containing less than 0.5% solids) the waste, after filtration, is defined as the TCLP extract. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis (*Federal Register, vol. 261*, 29 Mar. 1990).

The particle size of the solid sample is then reduced to <9.5mm and a 100g subsample of this size-reduced waste is extracted with a volume of fluid equal to 20 times its weight (ie. 2000ml). Two leachants are specified in the procedure and the leachant employed is a function of the pH of the solid being tested. For moderate to highly alkaline wastes a pH 2.88 (0.1M) acetic acid solution is used, while other wastes are leached with a pH 4.93 (0.1M) buffered acetic acid solution (*The Hazardous Waste Consultant* 1994; *Federal Register vol. 261*, 29 Mar. 1990).

These concentrations derive from a USEPA study into acid production by decomposing municipal waste. They found, over a seven year period, that one gram of industrial waste could potentially be acted upon by two milliequivalents (meq) of acid, in a hypothetical co-disposal environment. For a 100g sample, this translates to 200 meq, and is employed for wastes of moderate to high alkalinity. For less alkaline wastes, the 70 meq buffer is employed (USEPA 1986c).

The extraction procedure lasts 18 hours and is carried out by tumbling a zero-headspace bottle containing the solid and liquid in an end over end fashion at 30±2 rpm (see Figure 1.4). Following the extraction, the liquid extract is separated from the solid phase by pressure filtration through a 0.6 – 0.8μm glass fibre filter (*The Hazardous Waste Consultant* 1994; *Federal Register vol. 261*, 29 Mar. 1990). The extract is analysed for the presence of the prescribed constituents detailed in Table 1.5.

The TCLP method, when used in conjunction with a zero-headspace apparatus, can also be used to test for the volatile contaminants listed in Table 1.5 (*Federal Register, vol. 261*, 29 Mar. 1990). This application will not be further examined.

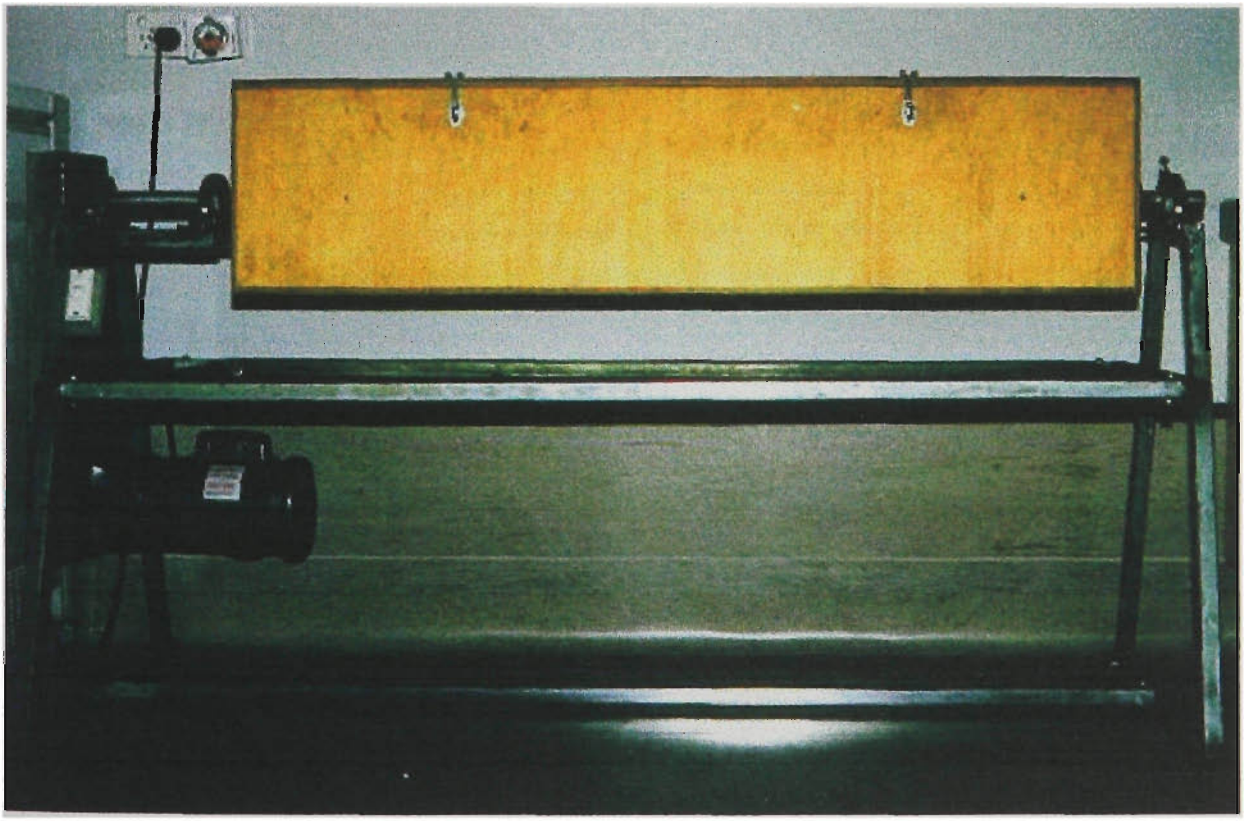


Figure 1.4: End-Over-End TCLP Rotary Agitator

Table 1.5: Prescribed TCLP Constituents

(Federal Register vol. 55, pp. 11804 & 11815-11816)

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its hydroxide)	0.008
Hexachlorobenzene	0.13
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl Chloride	0.2

1.3.4.3.2.2 Problems with the TCLP

The TCLP is based on essentially the same worst-case hazardous waste mismanagement scenario as the EP. However, it differs significantly from the EP in several experimental respects. These are contrasted in Table 1.6.

Table 1.6: Comparison Between TCLP and EP
(Martin 1990; Millipore Corporation Technical Brief *TB024*)

Parameter	**Extraction Procedure (EP)**	**Toxicity Characteristic Leaching Procedure (TCLP)**
Contaminants Covered	Metals, Pesticides, Herbicides	Metals, Pesticides, Herbicides, Semi-volatiles, Volatile organics
Extraction Fluid	16 x weight of solids with distilled water; 0.5M acetic acid added to maintain pH of 5	20 x weight of solids with 0.1M pH 2.9 acetic acid solution for moderate to high alkaline wastes and 0.1M pH 4.9 acetate buffer for other wastes
Method of Agitation	No specific form of agitation recommended	Rotary agitation only in an end over end fashion at 30 ± 2 RPM
Extraction Time	24 hours	18 hours
Temperature	20° – 40°C	22 ± 3°C
Filtration Pressures	Filtration to 75psi in 10psi increments	Filtration to 50psi in 10psi increments
Filter Material	0.45μm cellulose membrane with prefilter	0.6-0.8μm binderless glass fibre filter

Although a number of changes were made from the original EP to the new TCLP, the responses from industry and regulators were equally harsh. It was considered unfair that, although designed specifically as a conservative, worst case scenario test, the TCLP was being used to characterise wastes that would only ever be disposed to a non-acidic environment. This was one aspect of the TCLP that had not changed from the original EP (American Mining Congress 1986).

According to Martin (1990), the municipal codisposal scenario is a reasonable mismanagement scenario for many industrial wastes. Although not as common in recent times, codisposal does still occur, and, even though it may not be the most likely scenario, it still represents a reasonable worst case scenario.

Many others disagree with this viewpoint, however. The American Mining Congress (AMC) believed the TCLP was inappropriate for use in the nonferrous metals industry for several reasons. They point out that mining wastes are typically land disposed in a monofill manner. The TCLP makes no attempt to simulate the actual chemical environment that is anticipated to occur in a mine waste disposal unit and assumes that acidic conditions will prevail. Further, when one considers that different metal species are mobilised at different pH values, the extraction test may be rated as too conservative or not conservative enough. The AMC also had a major concern with the precision and repeatability of the TCLP, and these parameters were seen to be very sensitive to sample preservation, size distribution, and the detailed step by step procedures during the performance of the test (American Mining Congress 1986). Cioffi and Santoro (2000) examined the effect of an acetate buffer leachant on ettringite-based stabilising matrices, and discovered that such liquids can have significant effects on stabilised systems which may not occur in an actual disposal site.

There has been extensive research performed on the TCLP, investigating the various parameters of the test. Newcomer *et al* (1986) found that the TCLP gave higher concentrations of metals than did the EP, and this was supported by Shively and Crawford (undated) and Murarka (1988). A round robin study of leaching methods applied to solid wastes from coal-fired power plants, reported by Murarka (1988), also found that the reproducibility of the TCLP differed by waste type and constituent, as opposed to the method itself. He also found that the TCLP had reproducibility equal to or better than the EP for most metals. Mason and Carlile (1986) supported this finding in an interlaboratory comparison between the two methods.

In later work, Newcomer *et al* (1990) measured the robustness of the TCLP by varying a number of the test conditions, including liquid/solid ratio, extraction time and acidity. They concluded that the acidity of the extraction solution had the greatest impact on results. This work also cites other studies that showed concentrations of leached metals were affected by the type of filter used in the final filtration.

In other ruggedness testing, Prange and Garvey (1990) concentrated on the influence of waste particle size on the TCLP results. They investigated cement-stabilised metallic wastes and found that an increase in particle size resulted in an increase in leaching. This was thought to be because, during the early stages of the extraction, the smaller particle sizes have a greater capacity to quickly neutralise the acidic leachant by virtue of the large amount of calcium hydroxide in the cement and the large surface area available for leaching. By the end of the tests, the pH is not low enough to extract the metals in significant amounts, thus effectively voiding the nature of a worst case codisposal scenario for these waste types. Conversely, large particle sizes take the full 18 hours to reach a high pH, so more metals can leach out in the time the fluid remains acidic.

This problem, of cement stabilised wastes establishing their own chemical environment, is in stark contrast to the philosophy of the TCLP, which was designed to prevent just that from happening. A CRC report from 1993 (Extract from CRC Report *CRC-7-1* 1993) takes this point further, by warning that the ability of the waste to neutralise the acid in the leachant is a key factor in determining the fixation of metals, as measured by the TCLP. A major point of concern is the ability to manipulate favourable TCLP results simply by adding alkali to the waste in order to neutralise the TCLP leachant and retain the metal hydroxides in a high pH environment. The concern arises when the waste is deposited into an environment (eg acid rain or acid leachant) where the buffering capacity is sufficient to eventually neutralise the high pH of the waste, resulting in the ready solubilisation of metals.

Bisson *et al* (1991) echo this point by confirming the limited applicability of the TCLP to assessing metal-containing cementitious samples.

Further criticisms of the TCLP were also based around the size reduction step of the test, especially with respect to solidified wastes. The size reduction aspect of the test is designed to simulate the weight of trucks and other heavy machinery that may compress the waste, as well as freeze-thaw cycles and wet-dry cycles (*The Hazardous Waste Consultant* 1994). However, in many cases, solidified wastes are disposed of as large blocks of relatively high strength, and such a size reduction is manifestly excessive, regardless of the worst case premise of the test (Activon Document *3AD 2A*).

An alternate view is that the size used in the TCLP hinders reproducibility. For a sample size of 100g at 9.5mm, a sampling error of 44% is possible. By reducing the sample particle size to 2.4mm the possible error is reduced to 5% and any subsequent repeatability issues can also be accounted for (Correspondence between BHP & Victorian EPA 1992).

1.3.4.3.3 Australian Bottle Leaching Procedure (ABLP)

In the early to mid 1990s, members of the Standards Australia Committee CH/35 - Examination of Wastes, focused attention on producing an improved leaching procedure for use within Australia. For reasons previously cited, the TCLP was considered to provide an inadequate assessment of the toxicity or hazardous nature for different types of wastes. In 1997, Standards Australia issued the leaching methods as AS4439.33-1997: *Wastes, sediments and contaminated soils – Preparation of leachates – Bottle leaching procedures* (referred to as the Australian Bottle Leaching Procedure or ABLP). The methods covered wastes contaminated by non-volatile and volatile constituents, and, as such, also included directions on waste assessment via the use of a zero-headspace apparatus. This discussion will focus specifically on the non-volatile method.

Currently in Australia, depending on specific local requirements, hazardous wastes could be characterised by either the TCLP or ABLP. The ABLP is, in fact, quite similar to the original TCLP. During its conception, a number of the useful technical features of the TCLP were incorporated into the ABLP, the final method taking advantage of Australian familiarity with the TCLP and the availability of suitable test equipment. At the same time, however, the Committee sought to provide a test that is not only more precise than the TCLP, but one that is also better suited to the particular waste disposal practices and regulatory requirements that exist in Australia (Standards Australia 1997).

1.3.4.3.3.1 Differences Between the ABLP and TCLP

The Committee noted the widespread criticism of the TCLP for its sole specification of an acidic leach fluid (pH 4.93 acetate for other than highly alkaline wastes) to represent all waste disposal scenarios. As many different types of wastes are disposed of in Australia, this fluid was seen to be either more or less protective than necessary. Consequently, the ABLP contains a number of leach fluids from which a choice may be made, according to the intended disposal situation (Standards Australia 1997). These differences, along with others, are summarised in Table 1.7.

The Committee agreed that the specification of a pH 2.88 acetate fluid for highly alkaline wastes was a reasonable precaution for a worst case scenario and, as such, incorporated the feature into the ABLP. Apart from the two acidic fluids, a pH 9.2 borate buffer and deionised water are also permissible leachants (Standards Australia 1997).

The problem of lack of reproducibility has been addressed by reducing the maximum particle size of the waste to be tested from 9.5mm in the original TCLP to 2.36mm. This is expected to lead to more representative samples, which will, in turn, translate to better method reproducibility (Standards Australia 1997).

Table 1.7: Differences Between ABLP & TCLP

Parameter	ABLP	TCLP

Allowable Leaching Fluids	pH = 2.88 & 5.0 acetate leachant;
	pH = 9.2 borate leachant;
	de-ionised water
		pH=2.88 & 5.0 acetate leachant

Waste Particle Size	<2.36mm diameter	<9.5mm diameter
Method of Filtration	Positive Pressure Only	No specific method
Analysis of Leachate	Non-Combination of Liquids for Analysis	Combination Permitted

In a similar vein, the Committee focused on methods of filtration used in the test as another source of variability. It was considered that, for some wastes, the amount of sample liquid removed by vacuum filtration may be considerably lower than that using pressure. Therefore, while the TCLP requires no specific method of filtration, the ABLP requires use of pressure filtration. This includes the 'percentage solids' determination of a sample prior to leaching and the filtration step following the leaching (Standards Australia 1997).

The final significant difference between the two tests involves the non-combination of liquids for analysis in the ABLP. In other words, the ABLP requires that if two liquids are derived from a waste (the waste liquid and the leachate from the waste solids), they must be analysed separately. The TCLP, on the other hand, permits combination of these liquids, provided they are miscible. The Committee believes that, for some wastes, the nature of the sample liquid and the solids leachate may be significantly different, both in their toxicant concentrations and the rates of toxicant release that each represents. Combination of these liquids could result in a loss of information that could be valuable in judging the level of hazard posed by the waste (Standards Australia 1997).

As a final point, there is no regulatory test that directly takes account of oxidation-reduction (redox) potential, or E_h of wastes, when establishing a degree of potential toxicity. In this respect the ABLP is no different. However, the method does recommend the E_h of the extracted sample liquid and the solids leachate be measured and reported, acknowledging that E_h is known to affect the leaching of metals and possibly some organic species (Standards Australia 1997).

1.3.4.4 Column Leaching Tests

Column leaching tests involve placing a material in a suitable column and eluting it with an appropriate leachant, under specific conditions designed to model a particular disposal scenario. Flexibility allows the investigator to design and adopt appropriate conditions. For example, the column itself may be constructed to certain dimensions in order to model those of a landfill field cell, or, the design may be such that the investigator wishes to eliminate any leachate/column wall effects by using a wider column than normal.

Another variable involves the leachant which, among other choices, can be sprayed onto a large column to simulate rainfall, or be pumped up through a smaller column to provide completely saturated conditions. Further, the leachant, as in the many and varied regulatory batch tests, could simulate groundwater from a specific site or be merely deionised water. Added to this, while a batch test generally takes less than a day, a column test can take hours, weeks, or months to complete. Examples of column leaching setups can be seen in Figures 1.5a and 1.5b.

In essence, column tests are carried out to obtain more information about the leaching properties of a waste than can be provided from a single point batch test. Also, because they can provide rate release and time dependent data on contaminants of interest, they allow evaluation of, not only how much contaminant will leach out over time, but how that contaminant responds to the changing as the surrounding matrix is leached.

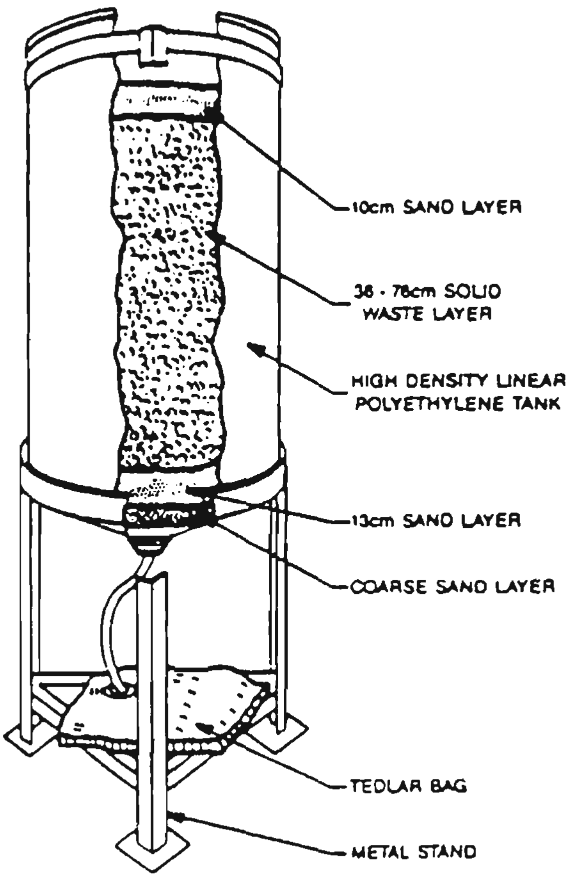


Figure 1.5a: Example of a Large Column Setup (Jackson & Bisson 1990)

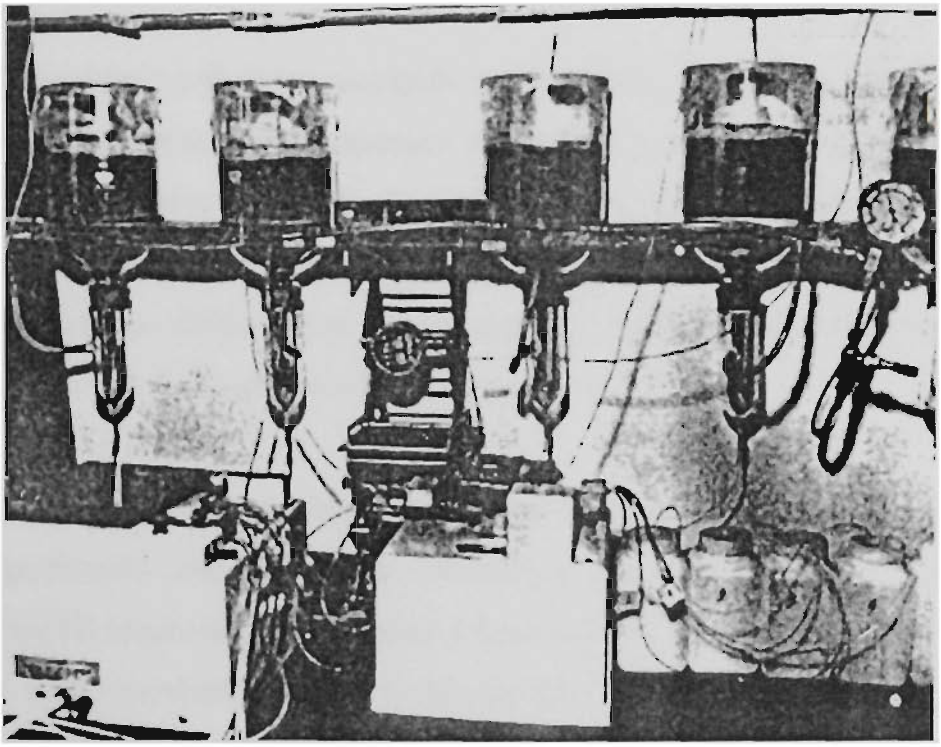


Figure 1.5b: Example of a Small Column Setup

(Jackson, Benedik & Jackson 1981)

1.3.4.4.1 Advantages and Disadvantages of Column Leaching Tests

Probably the major deterrent from using column tests is the time needed to obtain the results. Although generally up to the discretion of the analyst, most work in this area has involved tests taking many days, weeks, or months to complete rather than, for example, the 18 hours of the TCLP. This is because the majority of tests look at simulating natural infiltration rates which, of course, are very small (Cheremisinoff 1990). Kolvites and Bishop (1989) used a continuous-flow small column setup to model the leaching of phenol and trichloroethylene stabilised with Portland cement. The experiments were devised to simulate the flow of groundwater through a landfill containing stabilised waste. In this case vapor samples were taken every 48 hours for an eight-day period.

Although this sort of experiment can provide a great deal of time dependent information, it is not as attractive for regulatory work or commercial laboratories due to the costs in design, equipment, and time to carry out the investigation. In these respects, a quick 18 hour, worst-case scenario test will always be the most attractive option.

Of course, the work by Kolvites and Bishop (1989) also supports the notion that using a rainfall or groundwater based leachant to simulate natural conditions provides far more information than a batch test. An endless range of possible field conditions can be simulated by varying parameters such as leachant flow rate, pH, and E_h, conditions that would prove too difficult and time consuming to effect on a constantly changing basis in a batch test (Cheremisinoff 1990; Miner *et al* 1986).

However, care is needed in selecting these parameters, as leaching results can be altered significantly and may prove misleading. For example, if the test method employs rainfall simulation via spraying a leachant onto a large column, there can be a problem with reproducibility due to channelling and wall effects. Other problems include non-uniform packing of the wastes, biological growth and clogging of the column (USEPA 1989). These are common problems in column tests and have been highlighted by a number of authors (Dodd *et al* 1981; Cheremisinoff 1990; Miner *et al* 1986; Jackson *et al* 1984; Förstner *et al* 1991; Wahlström 1996).

To minimise channeling, Fällman and Aurell (1996) followed the Dutch Nordtest recommendations of a height to diameter relationship of no less than 4 (i.e. h>4d) for a leaching column. Also, the largest waste grain size allowed in the column was less than 1/10 of the column diameter.

Alternatively, the leachant can be pumped in an upflow manner to alleviate this problem. There still may be some problems due to wall effects, but they will not be as great as for downflow. The shortcoming of this method is that this type of constant saturated leaching is rarely seen in the field and can lead to an overestimation of species concentrations in the leachate (Cheremisinoff 1990).

Column leaching methods have also been used to simulate existing batch methods. Darcel (1983) employed a column flow rate (400ml/100g/day) which closely corresponds to the liquid to solid (L/S) ratio in the EP and many other batch tests of its time.

Similarly, Jackson *et al* (1981) investigated correlations between batch and column leaching of fly ash using a number of L/S ratios for both tests. They found that selenium leached similar amounts in both methods while arsenic leached three times as much from the column as from the batch test. It was thought that this effect on arsenic was probably due to a solubility limiting factor.

Of course, this not only demonstrates that vastly different results can be obtained from different tests, but also that the results are metal, waste, and test dependent. This emphasises the fact that test parameters can have very different effects on different wastes due to the chemical form of any particular metal, even if the metal within each waste is similar in concentration. Jackson and Bisson (1990) used five batch procedures and a number of large columns (see Figure 1.5a) to characterise five different solid wastes. Among other things, their results show that nickel leached from mine tailings in twice the amount from the large column as it did in the Monofill Waste Extraction Procedure (MWEP), a USEPA multiple extraction batch test designed with monofill disposal facilities in mind (USEPA 1989). Conversely, when electric arc furnace dust was tested the opposite effect was observed.

1.3.4.5 Tank Leaching Tests

Tank or diffusion type leaching tests have been extensively used in recent times to establish, not only the extent of contaminant leaching from solidified wastes, but also the type of leaching process(es) that have occurred.

Their main function is to provide an environment of static leaching, so that the main driving force for leaching is diffusion. Added to this, these tests are predominantly used on solidified wastes in specific geometric forms, which, therefore, allows accurate measure of the surface area available for leaching. The idea is that the diffusion can be quantified and, thus, provide a measure of leachability for a specific contaminant.

The first real test of this kind was the American Nuclear Society Leach Test (ANS-16.1). The method was published in 1986 and applied to stabilised/solidified low level radioactive wastes. A monolithic cylinder (length: diameter of 0.2 up to 5.0) is placed in a container of demineralised water at a volume to sample surface area ratio of 10. At the start of the experiment, the sample is rinsed to obtain zero contaminant concentration at the surface of the sample. Afterwards, the water is replaced at specific intervals up to a period of 90 days, with leachate samples being taken at each interval. Neither the sample nor leachant is agitated throughout the test and the results are recorded as a cumulative fraction leached over the total mass of contaminant in the waste form. An effective diffusion co-efficient, De (cm^2/s), can then be calculated, and, from this, a leachability index (LX = -log De). The LX values range from 5 to 15 and signify rapid diffusion and very slow diffusion respectively (USEPA 1989).

Although this test was a standard in the radioactive waste field, it was being used more and more in the area of hazardous waste assessment (Environment Canada 1991a). Soon after the ANS-16.1 was proposed, Côté (1986) developed an alternative test, the Dynamic Leach Test (DLT), which he characterised and employed in his extensive work on solidified hazardous wastes (Côté 1986; Environment Canada 1991b; Stegemann & Côté 1990; Côté & Isabel 1984; Côté *et al* 1987).

The DLT is only slightly different from the ANS-16.1, in that the test time is shorter and the schedule for changing the leachant is chosen so that the amount leached in each interval is equal. Two leaching schedules are available, depending on contaminant mobility. The test may be performed for seven or nine leaching intervals, for total times of five or nine days respectively (Environment Canada 1991b).

Along with ANS-16.1, the DLT is based on the solution of a semi-empirical diffusion model (Equation 1.1), with the aid of a number of assumptions from Godbee and Joy (Environment Canada 1991b; Côté & Isabel 1984):

1) The mobility of a contaminant is limited by diffusion
2) The specimen has a uniform initial contaminant concentration
3) The specimen behaves as a semi-infinite medium, provided that the cumulative fraction leached does not exceed 20%
4) The concentration of a contaminant at the specimen surface is approximately zero.

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e'}{\pi}\right)^{1/2} t_n^{1/2}$$

Where a_n = contaminant loss during leaching interval n (mg)
A_0 = initial amount of contaminant in the specimen (mg)
V = specimen volume (cm^3)
S = specimen surface area (cm^2)
t_n = time at the end of leaching period n
D_e' = apparent diffusion coefficient (cm^2/s)

Equation 1.1 (Environment Canada 1991b)

A linear relationship exists between the cumulative fraction leached and the square root of time in Equation 1.1. This is a consequence of diffusion control. Therefore, Assumption 1 above can be verified by plotting these two parameters (Environment Canada 1991b).

Assumption 2 can be assured by carefully preparing the specimens in the laboratory. Assumption 3 is satisfied by selecting a specimen size or test duration so that a negligible fraction of the initial amount (A_0) will be leached during the test. The final assumption of a zero surface concentration can be fulfilled by selecting a combination of sample size and shape, ratio of leachant volume to sample surface area, and a leachant renewal frequency that minimises the concentration leached during each leaching interval, yet allows analytical detection (Côté & Isabel 1984).

Côté (Environment Canada 1991b) has identified four general categories of leaching mechanisms, illustrations of which can be found in Figures 1.6a to 1.6c.

For DLTs conducted on cement containing metals with different initial concentrations and under different renewal schedules, Côté has shown that calculated values of De varied within one order of magnitude. He also demonstrated that the method had excellent reproducibility, within and between laboratories (USEPA 1989; Environment Canada 1991b; Côté & Isabel 1984).

There has also been considerable work in this area, by other researchers, looking at the leaching characteristics of metals from stabilised wastes (van der Sloot *et al* 1989; Cheng *et al* 1992; Cheng & Bishop 1990, 1992; Barna *et al* 1994; Pera *et al* 1997; de Groot & van der Sloot 1992; Andrés *et al* 1995). Many of the experiments are either slight variations of the DLT or utilise the actual method itself. All of them, however, are after the same types of information: a better understanding of the rates and mechanisms for metals leaching from these types of wastes. Once again, this is information that cannot be garnered from a simple, regulatory batch type test.

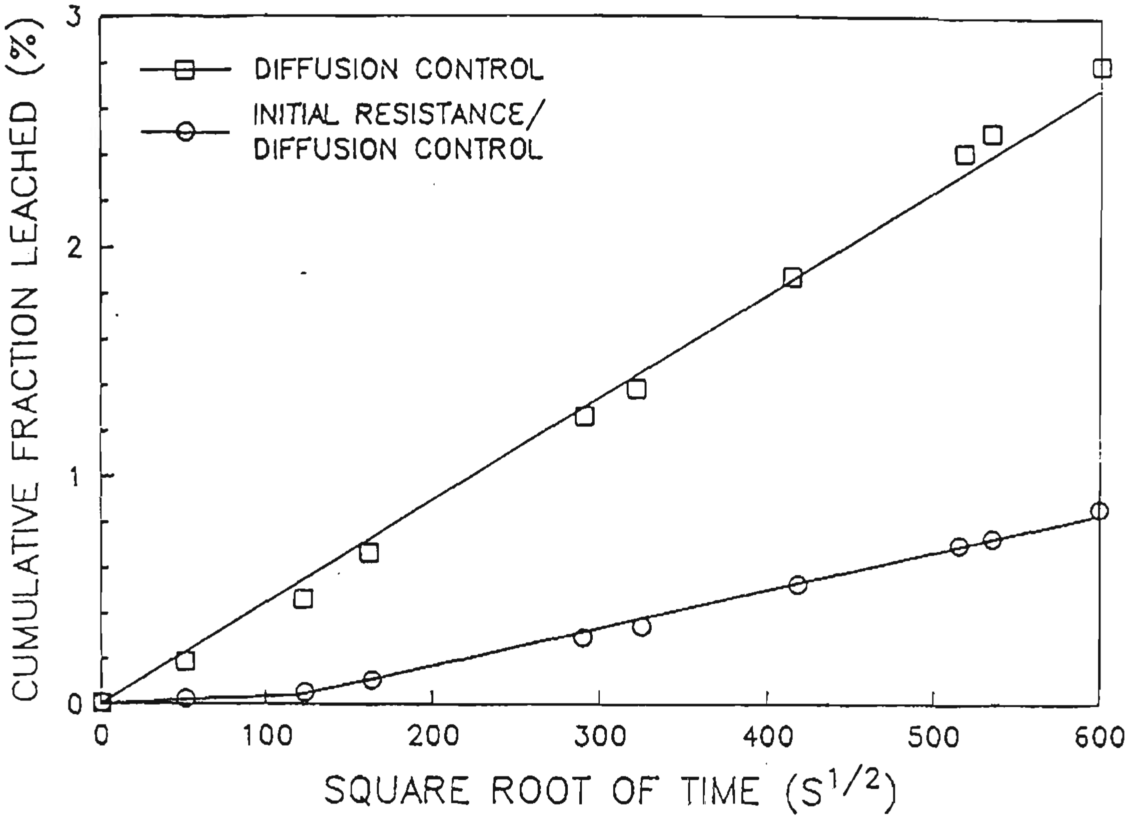


Figure 1.6a: Diffusion Controlled Release and Diffusion Control Following Initial Resistance to Leaching (Environment Canada 1991b)

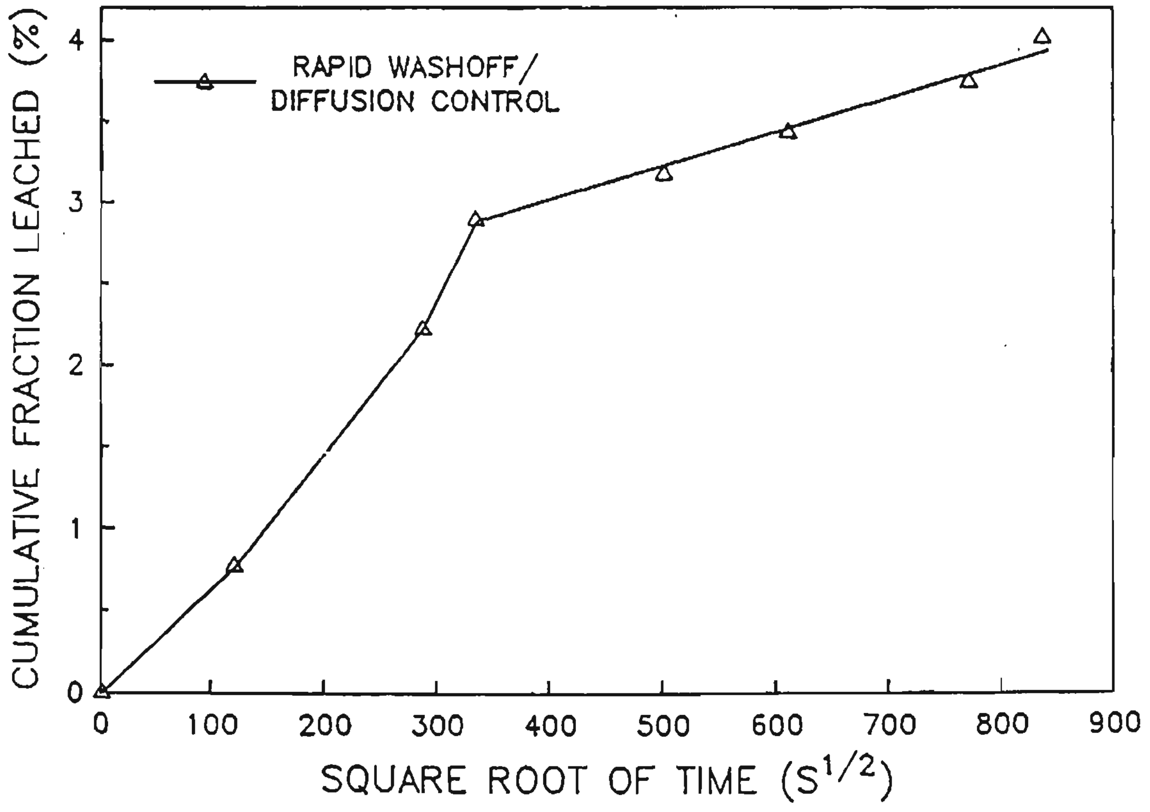


Figure 1.6b: Diffusion Controlled Release Following Initial Rapid Wash-off (Environment Canada 1991b)

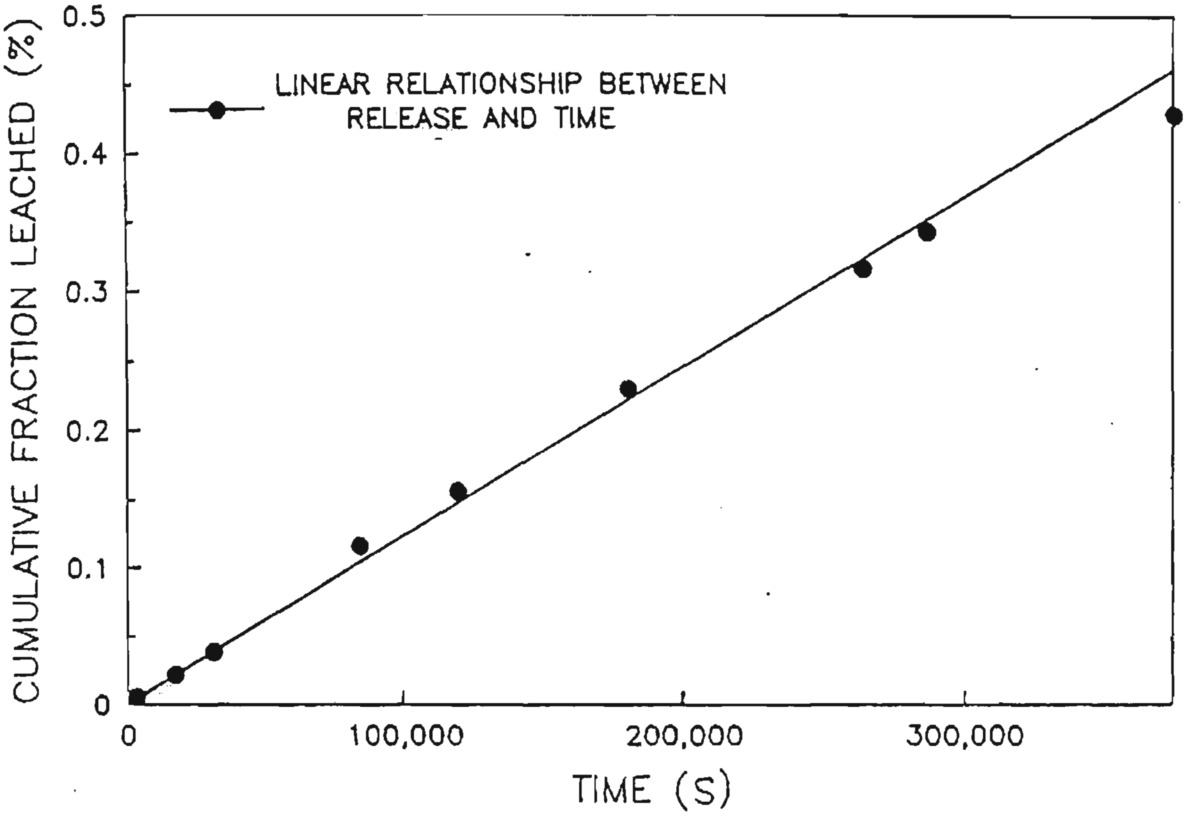


Figure 1.6c: Linear Relationship Between Release and Time (Environment Canada 1991b)

1.3.4.6 Other Leaching Tests

The preceding sections have detailed the main leaching tests used to study and characterise hazardous wastes. There are, however, a number of other tests which can be used to gain more information on a contaminant or waste type, information that cannot be provided by single batch, column, or tank tests.

1.3.4.6.1 Sequential Batch Testing

Sequential batch tests follow the methodology of a batch test, the basic difference being that the same initial sample of waste is leached a number of times with fresh leachant. For example, after the final filtration in a TCLP, the same 100g of waste would be placed back in the extraction vessel, a fresh two litres of leachant added, and the 18 hour leaching cycle started again. These steps can be repeated a number of times, in order to get some time dependent data from what was, previously, a single point test.

The advantage of this leaching method is that no extra equipment or design is required. Any laboratory that has equipment for a batch test can run it in a sequential fashion. The drawbacks, of course, are the labour and cost. Once set up, a column test only requires the analyst to collect samples whereas a sequential batch test can occupy half a working day depending on the number of replicates required.

Sequential batch tests are considered well suited to the assessment of metal-contaminated cement-stabilised wastes, since any buffering effect the waste may have is eroded over a number of extractions. This, therefore, provides a better understanding of how metals' will leach in the longer term, when natural erosion has eliminated any acid neutralising capacity the waste may have once had (Extract from CRC Report *CRC-7-1* 1993; Bisson *et al* 1991).

Although there appear to be no regulatory sequential batch tests, the Multiple Extraction Procedure (MEP) (USEPA 1986a) and the Monofill Waste Extraction Procedure (MWEP) (USEPA 1986b) are two U.S. EPA methods that can be used for alkaline and/or monolithic waste types. The MWEP can be used to derive reasonable leachate compositions in monofilled disposal facilities, and this information can be used to assess waste-liner compatibility under mild leaching conditions. It can also be used with the TCLP to determine delays in the release of hazardous constituents. The MEP is used to determine maximum leachate concentrations occurring under acidic conditions and can be used with the EP or MWEP to compare leachability of hazardous constituents under mild and acidic conditions (USEPA 1989).

1.3.4.6.2 Acid Neutralisation Capacity

An acid neutralisation test is used to determine the buffering capacity of a solidified/stabilised waste form. The higher the buffering capacity of the waste, the greater the possibility of maintaining alkaline conditions and minimising the amount of metals leached. Acid neutralisation capacity, therefore, is very important in field evaluation of the amount and rate of metals leached from stabilised wastes (USEPA 1989; Stegemann & Côté 1990).

The Acid Neutralisation Capacity (ANC), a method devised by Environment Canada and the Alberta Environmental Centre, involves eleven separate extractions of several pre-dried, crushed, waste sub-samples with increasing amounts of mineral acid for 24 or 48 hours, before measuring a final pH. Particle size of the waste is less than 150μm (100 mesh), and the liquid to solid ratio of the extraction is 3:1 (USEPA 1989; Environment Canada 1991a; Stegemann & Côté 1990). A similar test, the Generalised Acid Neutralisation Procedure (GANC) (Isenburg & Moore 1992), uses a larger particle size (425μm) and 21 extractions, increasing in acidity from zero acid equivalents to 0.04 acid equivalents (Cheng *et al* 1992). With these tests, the pH measurements of the extracts are plotted on a titration curve, which is used to evaluate the capacity of the solidified waste to neutralise acid (Stegemann *et al* 1997).

Stegemann and Côté (1990) studied a number of solidified wastes and found them capable of neutralising large quantities of acidic groundwater before reaching a pH where metal hydroxides would be dissolved. For example, 1kg of waste with an acid neutralisation capacity of 2 meq/g can neutralise 20,000L of pH4 groundwater.

1.3.4.6.3 Maximum Availability Test

A maximum or total availability test is designed to reflect the quantity of a metal that can eventually be leached, in the very long-term, after the complete disintegration of the waste material. Like the TCLP and ABLP it is a worst-case scenario test, albeit on the excessive side of this interpretation (Stegemann *et al* 1988; de Groot & van der Sloot 1992).

The most commonly used availability test is the second part of a Dutch procedure (NVN 5432), known as the Maximum Availability Test (Netherlands Normalisation Institute 1989). Here, two sequential 3 hour extractions are carried out on three replicate samples of finely ground material (<125μm) at a solid-to-liquid ratio of 1:50.

1M nitric acid is added continuously to maintain a pH of 7 during the first extraction, and a pH of 4 during the second extraction. The leachates from both extractions are filtered and combined prior to analysis (Stegemann *et al* 1988).

Similarly, de Groot and van der Sloot (1992) extracted a finely crushed sample (<125μm) at a liquid-to-solid ratio of 100 and a pH of 4. Steggemann *et al* (1997), on the other hand, used a pH 5 acetate buffer to extract a finely ground sample, in an end-over-end fashion, for 24 hours.

It is thought this type of test has some practical significance, not as a regulatory test in its own right, but as a screening tool for assessing the ultimate release of contaminants from solidified wastes over the very long term (de Groot & van der Sloot 1992).

1.3.4.6.4 Sequential Chemical Extraction

In 1979, Tessier and co-workers designed a chemical extraction that aims to differentiate between the exchangeable, carbonatic, reducible, oxidisable, and residual fractions of solid wastes (Förstner 1992).

The original extraction, which has been modified by various authors to meet their own specific requirements, consists of five steps as detailed in Table 1.8 (Förstner 1992). Basically, a sample of ground waste is treated with a series of five chemical extractions of increasing aggressiveness ranging from ion exchange with ammonium acetate to total digestion with hot nitric acid. The components measured in each successive fraction are increasingly refractory, which relates to their availability for leaching (Stegemann & Côté 1990).

Through this test, an understanding of metal speciation in solidified wastes and the determination of contaminants available for leaching in different chemical environments can be obtained (Environment Canada 1991b).

Table 1.8: Sequential Extraction Method (Förstner 1992)

Fraction	Extractant	Extracted Component
Exchangeable	1M NH_4CH_3COO, pH 7	Exchangeable ions
Carbonatic	1M NaOAc, pH 5 w/ HOAc	Carbonates
Easily Reducible	0.01M NH_2OH HCl w/ 0.01M HNO_3	Mn-Oxides
Moderately Reducible	0.1M oxalate buffer pH 3	Amorphous Fe-oxides
Sulphidic/Organic	30% H_2O_2 pH 2 w/ 0.02M HNO_3 extr. w/ 1M NH_4OAc-6% HNO_3	Sulphides together with organic matter
Residual	Hot HNO_3 conc.	Lithogenic material

Despite the advantages of this type of differential analysis over a standard batch test, there still appear to be a number of questions and uncertainties associated with these procedures. For example, the reactions are not selective and may be influenced by variations in method parameters, and labile phases could be transformed during sample preparation (Förstner 1992).

1.3.4.7 The Future of Leaching Test Selection and Interpretation

Regardless of the many types of tests available, there are very few researchers that advocate the use of just one test for the characterisation of stabilised wastes. The reasons for this are many and relate to a number of the test types previously explained (Environment Canada 1991b):

1) It is difficult to simulate field conditions with laboratory-scale tests.
2) One test (or a small number of tests) cannot be applicable to many site disposal situations.

3) It is impossible to simulate the effects of long periods of time using only a short-term test.
4) No information concerning stabilisation mechanisms is gained.

Work by Steggemann and Cote (1990, 1996) and Environment Canada (1991b) has looked at using a number of physical and chemical tests to characterise the properties of solidified wastes and evaluate potential leachability. By employing many of the physical and chemical tests previously discussed, it is possible to establish the degree of chemical immobilisation of the contaminants and the potential for contact of groundwater with the waste. This approach of utilising a number of solidified waste properties to evaluate its potential toxicity has advantages corresponding to the disadvantages of a single test (Environment Canada 1991b):

1) Solidified wastes with particular characteristics can be matched to the disposal scenarios for which they are most suited.
2) The characteristics may be used as source terms in mathematical models for estimating the effects of long periods of time.
3) A better understanding of stabilisation mechanisms can be gained.

The USEPA has also contributed to this work, leading to a number of important publications (USEPA 1989; Environment Canada 1990, 1991a, 1991b). It has also led to the proposal of a three level testing protocol for stabilised/solidified wastes by the Wastewater Technology Centre in Canada. The three levels include physical and chemical tests and, depending on the results, the waste is considered for four utilisation and disposal scenarios. The protocol was one of the first attempts to develop a management tool for solidified wastes that accounts for their physical and leaching characteristics, in the context of different disposal scenarios (Stegemann & Côté 1996; Environment Canada 1991a). Further to this, a database of waste leachability has been suggested (Côté & Constable 1983; de Groot & van der Sloot 1992) which would allow all waste producers and analysts access to much information on the characteristics of solidified wastes. The Netherlands Energy

Research Foundation (ECN) is also a world leader in developing leachability databases, focusing especially on construction materials (van der Sloot 1996).

Work by van der Sloot (1996) at the ECN has also focussed on the need for a number of different tests to be harmonised in order to deal with the complexity of contaminant release through leaching. Lewin (1996) adds to these ideas by proposing an international standardised reference leaching test material for regular incorporation in batches of materials for leaching tests. In this way it is hoped that any interlaboratory inconsistencies can be accounted for.

More recent work by van der Sloot has led to the development of the International Network Harmonization of Leaching/Extraction Tests (van der Sloot 1999b). This group has several goals including:

- Identification of needs in relation to leaching test use and interpretation.
- Comparison of different leaching test methods currently used or proposed in one specific field.
- Horizontal comparison of leaching test methods between different fields.
- Evaluation of leaching test data, interpretation, and modeling for environmental assessment.
- Development of cost-efficient quality control systems through a hierarchy in testing. (van der Sloot 1999a)

As a result of this effort, a leaching test hierarchy has been adopted by the European Community under Standard TC 292 consisting of a characterisation test, compliance test, and an on-site verification test. A Characterisation test is aimed at understanding the leaching behaviour of metals under a variety of exposure conditions, and typically runs from a few days to weeks or even a month. Following the leach testing, the leaching behaviour is then modeled. The Compliance test does not necessarily have to be a leaching test, but does need to provide data that can be compared to the Characterisation test data. Compliance tests are generally of a much shorter duration

(1-2 days), and used to determine if a waste is behaving as predicted by the Characterisation test. The On-site Verification tests are rapid tests (<1 hour) typically used to verify or refute that a waste is behaving as predicted from the Characterisation and Compliance testing. As a result of this work, characterisation data from static pH leaching tests, column leaching tests, and tank leaching tests are available for an extensive list of materials (van der Sloot 1998, 1999a).

van der Sloot (1999a) also points out that, while comparison and evaluation of such test data provide are extremely important for the harmonisation of wastes and tests, 'modeling forms the basis for long-term predictions' for environmental assessment. Consequently, the characterisation tests can provide the input parameters for such geochemical and transport modeling. This would then lead to the introduction of scenario-specific and site-specific parameters to account for different applications or disposal environments for the same materials. Therefore, based on this understanding of leaching behaviour, integrated and concise testing protocols can be drafted for quality control and regulatory purposes.

Most recently, Kim and Batchelor (2001) have proposed taking the modeling of leaching data for predictive purposes one step further. While the data from longer term tests were modeled in the harmonisation work of van der Sloot (1999), Kim and Batchelor have been developing an empirical leach model capable of being calibrated from shorter-term batch tests. Their model, the Empirical Partitioning Leach Model (EPLEM), has been shown to be capable of accurately predicting the dynamic leaching behaviour of selected metal contaminants. It is able to use short-term laboratory experiments (e.g. Acid Neutralising Capacity, Maximum Availability, Equilibrium Extraction) to predict dynamic leaching and, because it describes the fundamental processes involved in dynamic leaching, it has the potential for greater accuracy in predicting leaching under different conditions than other purely empirical models. Kim and Batchelor do, however, note that the EPLEM is a simple model with some limitations. For example, it does not take into account potential changes in effective diffusivity as the porosity of the material being leached changes over time, and it assumes that only one factor (pH) affects how contaminants are partitioned between mobile and immobile forms.

What makes these new areas of research being conducted by the likes of Batchelor and van der Sloot so valuable is that common regulatory batch tests are now being utilised to a much greater extent. While these tests will continue to be used based predominantly on economics and convenience, it is becoming increasingly likely that the data produced will soon be used as more than just a pass/fail number. On the one hand, the work by van der Sloot (1998, 1999a, 1999b) has led to the introduction of a three tiered process which has already characterised massive amounts of wastes. Once characterised, the data on such wastes can be accessed at will and similar wastes effectively compared to this data via the use of a rapid leaching test. Similarly, Batchelor has spent many years developing and utilising leaching models to predict the dynamic leaching of contaminants in wastes (1992, 1998). The latest work by Kim and Batchelor (1999) suggests that it is possible to combine the data from a batch test with a model (EPLEM) to do exactly that.

Such research is at the forefront of waste management as it potentially allows the continual use of short- term tests while, at the same time, supplying a great deal more information than a single-point regulatory batch test carried out alone could possibly provide.

1.3.4.8 Aims of the Thesis

The ideal leaching test is one that is cheap, rapid, and provides the greatest amount of data that can be used to predict future leaching behaviour for any contaminant, from any waste, in any environment. While this may never be achieved, any information that contributes to that goal will be extremely useful.

With that in mind, the premise behind this work was to investigate the leaching behaviours of a number of metals in a cement-stabilized waste using long-term, short-term, and single-point regulatory leaching tests. By comparing and contrasting the patterns and amounts of metal released from these different leaching methodologies, a greater understanding of metal leaching under diverse conditions could be obtained. Further, the evaluation of the data produced from these tests allows suggestion of possible mechanisms of release, based upon the wealth of information available in the literature.

The work also aimed to examine the effects of different leaching test parameters, and their influences on interpretation of the regulatory tests. More specifically, correlations between the tests will be examined closely, and the information used to try to ascribe a greater value to the single-point regulatory data.

It should be emphasised that the interpretations of leaching behaviour and how they relate to regulatory tests are based on comparisons between experimental data and those presented in the literature. Therefore, it is the release behaviour of the specific metals themselves, rather than their complex interaction with their environments, which are of most interest in this study. Consequently, while it is acknowledged that mineralogical and geomorphological studies are important with respect to the understanding of metal, waste, and cement solution chemistries, any major experimentation of that kind was beyond the scope of this work.

2. Experimental

Unless otherwise stated, all chemicals used in this research were of analytical purity and all water was deionised. Similarly, all glassware used was 'A class' and prepared for use by rinsing three times with deionised water, followed by soaking in a 10% nitric acid bath for 7 days, and finishing with further rinsing in deionised water.

All columns, plasticware, and glassware used in the leaching processes were first washed with 10% nitric acid and then rinsed with de-ionised water.

A listing of the suppliers of all chemicals used can be found in Appendix D.

2.1 Characteristics of the Raw Waste

The waste used in this study was sourced from a former industrial site. The waste, green in colour and with the consistency of moist clay, arrived in polyethylene bags, placed in sealed metal tins. The sample weights in the five tins ranged from 14kg to 28kg. All waste was from the same site. The method of sampling employed by the waste supplier could not be ascertained.

2.1.1 Analysis of the Raw Waste

2.1.1.1 Moisture Content

The moisture content of the waste was 58.9%, determined according to ASTM method D-2216-92 (1992), and is summarised as follows.

A single core sample was taken from the centre of one of the drums. Five subsamples of waste were then taken from different depths of the core sample.

The subsamples were placed in pre-weighed crucibles and the total mass measured and recorded. The crucibles were then placed in a drying oven set to 110 ± 5°C.

Once the samples had dried to constant mass the crucibles were removed from the oven, cooled and weighed. The mass lost was attributed to water.

2.1.1.2 Metals Content

Metals contents for both the waste and cement used for its fixation were determined as described below.

2.1.1.2.1 Digestion Method

After milling and homogenising, a 10g sample of the dried, raw waste (see Section *2.3.1)* was crushed to a fine powder using a mortar and pestle. Triplicate 1g subsamples of crushed waste were then measured into Teflon® beakers. The samples were moistened with a few drops of de-ionised water to ensure no dust was lost due to the evolution of any gases during subsequent reaction with acid (Bock, 1979). The digestion reaction was performed as follows.

15ml of 40% hydrofluoric acid was added followed by 4ml of concentrated sulphuric acid. The acid mixture was then evaporated to fumes of sulphuric acid on a sand bath. Removal of final traces of fluoride was achieved by rinsing down the side of the whole beaker with de-ionised water and heating again to H_2SO_4 fumes. This process was repeated twice more for each sample. The remaining fluids were then quantitatively transferred to 100ml standard flasks and made up to the mark with de-ionised water. Blank samples were also prepared using the same protocol.

2.1.1.2.2 Analysis

The digests, prepared in Section *2.1.1.2.1*, were analysed for metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results obtained were used to determine the metal content of the dried, raw waste, and are detailed in Table 2.1.

Table 2.1: Raw Waste and Cement Metal Content

Analyte	**Dried Waste (g/kg)**	**Cement (g/kg)**
Aluminium	2.055	59.6
Arsenic	15.8	0.035
Cadmium	5.89	0.003
Calcium	5.755	409.7
Chromium	0.086	0.06
Copper	67.9	0.02
Iron	45.67	31.53
Lead	288.3	0.037
Magnesium	9.31	8.013
Manganese	0.088	1.32
Mercury	<0.04	<0.04
Nickel	0.835	0.265
Selenium	0.923	<0.019
Silver	0.014	<0.002
Tin	0.685	<0.08
Zinc	78.33	0.434

2.2 Characteristics of the Cement

The cement used in this study was a Type I Portland Cement obtained from Blue Circle Cement in Geelong, Australia.

2.2.1 Analysis of the Cement

The cement was digested in triplicate using the method described in Section *2.1.1.2.1*, and the digests analysed for their metal content by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results obtained were used to determine the metal content of the cement, and are detailed in Table 2.1.

2.3 Stabilisation/Solidification of the Raw Waste

2.3.1 Preparation of the Raw Waste for Stabilisation/Solidification

The raw waste was air-dried by spreading it in a thin layer on sheet polyethylene inside a standard laboratory fume hood. Any large clumps of the waste were reduced by breaking them up to a diameter of no greater than 10mm using a plastic spatula. The raw waste was then left to dry for approximately 72 hours, by which time it was dry and crumbly.

The dried waste was then crushed in a ring-mill, in 400g lots, for five minutes and sieved by hand to a particle size of less than 200μm. Remaining material over 200μm in size was re-milled for five minutes and re-sieved. Any material over 200μm was discarded.

The sieved waste was placed in a large polyethylene vessel that was then sealed and subsequently tumbled for five minutes to adequately mix the waste. The resultant mixed powder was then placed in polyethylene bags, which were stored in sealed containers until ready for solidification/stabilisation.

2.3.2 Preparation of Solidified Waste Spheres for the Investigation of a Suitable Solidification Recipe

Preparation of the spheres was achieved as described by Cheng and Bishop (1992), by injecting the mixed cement/waste slurry into a table tennis ball (diameter 36mm). The ball had a small hole cut in it with a razor blade and injection was done using a 50ml plastic syringe. This hole was then sealed with Teflon® tape and the ball placed in a beaker which was itself placed sideways in a rotary tumbler (see Figure 1.4). This allowed the mould to be rotated and tumbled on more than one axis for 24 hours. After this, the mould was placed in a ziplock-type polyethylene bag with a 100ml beaker full of water, and then stored in a cupboard. This provided an environment of 100% humidity. After 27 days the ball was taken out of the bag, the mould removed, and the solidified product evaluated.

It was found that mixtures consisting of cement, waste, and water alone produced spheres soft enough to be scored with a thumbnail. The adverse effects of heavy metals on cement hydration are discussed in Section 1.2.3.4.2.1. In order to produce a harder product within the 27-day setting period, accelerators (as discussed in Section 1.2.3.4.3.1) including flyash, carbon and $CaCl_2$ were trialed. The various mixtures are described below in Sections 2.3.2.1 - 2.3.2.4. The best results were achieved with a blend consisting of cement, waste, $CaCl_2$ solution (300g/L) and water in the ratio of 6.43kg : 3.215kg : 2.68L : 1L. This blend was also used to prepare S/S waste for all other leaching tests.

2.3.2.1 Cement/Waste Mixtures

The cement/waste slurry was prepared by combining the dried raw waste with the cement powder in a polyethylene mixing bowl using a Teflon® spatula. Then, de-ionised water was added, followed by further mixing to a consistent paste. Mass ratios of cement to waste ranging from 1:1 up to 50:1 and solid to liquid ratios from 1:1 up to 8:1 were investigated.

2.3.2.2 Cement/Waste/Fly-Ash Mixtures

The fly ash used was obtained from Victoria's Loy Yang Power Station via the Department of Civil and Building Engineering at Victoria University of Technology.

These mixtures, prepared in a fashion similar to that detailed in Section *2.3.2.1*, consisted of fly ash, cement, and water in the total mass ratio of 1:5:2.4 respectively, and also fly ash: cement: waste: water in mass ratios from 1:5:0.1:2.4 to 1:5:1.5:2.4.

2.3.2.3 Cement/Waste/Activated Carbon Mixtures

Mass ratios of cement: waste: activated carbon: water from 0:5:0.2:2.5 up to 1.5:5:0.3:3 were mixed according to the method detailed in Section *2.3.2.1*.

2.3.2.4 Cement/Waste/Calcium Chloride Mixtures

In this method, the cement and waste were mixed first, followed by the addition of a 2%w/v solution of calcium chloride ($CaCl_2$). Following the addition of $CaCl_2$ solution, de-ionised water was added to the mix until it was homogeneous and injectable as detailed in Section *2.3.2.1*. Mass ratios of cement: waste: $CaCl_2$: water (including that used to dissolve the $CaCl_2$) ranged from 5:1:0.1:1 to 2:1:0.25:1.

2.3.3 Preparation of Fixed Waste For Use in Leaching Tests

2.3.3.1 Preparation of Fixed Waste for use in Batch and Column Leaching Tests

The dried, milled, raw waste, as prepared in Section *2.3.1*, was added to the cement in a 20L-polyethylene vessel using the amounts in Table 2.2. The vessel was sealed and tumbled by hand until its contents were thoroughly mixed.

The masses and volumes detailed in Table 2.2 were employed after preliminary studies (Section *2.3.2.4*) showed these ratios provided the most suitable final product. The ratio of cement to waste is 2:1, and that for cement to solid $CaCl_2$ is 8:1.

The unusual mass and volume sizes were due to fact that only 2765g of the dried, milled, raw waste was available for the first batch of fixed waste. To minimise changes to the preparation of the fixed waste, these masses and volumes were therefore kept the same for the remainder of the project.

Table 2.2: Ingredient Composition of Fixed Waste

Cement (g)	**Waste (g)**	**$CaCl_2$(ml)**	**H_2O(ml)**
5530	2765	2305	860

A 2.305L solution of $CaCl_2$ was prepared by adding 691.25g of granular $CaCl_2$ and making up to volume with de-ionised water.

This solution was poured into a rotating Hobart-type cement mixer and the cement/waste mixture added slowly. As the mixture gradually absorbed the liquid and appeared to dry out, more de-ionised water was added up to a total volume of 860ml.

The mixer was run until the mixture bore the consistency of a slightly pasty slurry, at which point it was poured into a 12L circular polyethylene mould, 30cm in diameter by 15cm in height.

The container was placed in a polyethylene bag together with a beaker containing water, sealed, and placed in a cupboard. This ensured an environment of 100% humidity for the sample.

After 28 days, the sample was removed from its mould and broken up with a plastic mallet to pieces no greater than 10mm in diameter. Further size reduction was achieved using a 'Pro-Lab' jaw crusher set to an outlet width of approximately 2.4mm. The jaw-crushed sample was then sieved to a particle size of less than 2.36mm. Throughout this process sample particles were exposed to atmospheric carbon dioxide.

2.3.3.2 Preparation of Fixed Waste Spheres for use in Tank Leaching Tests

Dry, milled, raw waste (see Section *2.3.1*) and cement were mixed together, in the proportions indicated in Table 2.3, in a 2L-polyethylene vessel with a Teflon® spatula until homogeneous.

Table 2.3: Ingredient Composition of Spherical Fixed Waste

Cement (g)	**Waste (g)**	**$CaCl_2$(ml)**	**H_2O(ml)**
40	20	20	2

A 200ml solution of $CaCl_2$ was also prepared by adding 50g of granular $CaCl_2$, and making up to volume with de-ionised water. 20ml of this solution was placed in another 2L-polyethylene vessel and the cement/waste mix added slowly while constantly stirring. An extra 2ml of de-ionised water was also added to obtain the desired consistency. The preparation of the spheres was achieved with the use of ping-pong balls, as detailed in Section *2.3.2.*

2.3.4 Characterisation of Fixed Waste

The spherical and crushed fixed wastes were analysed for As, Cu, Pb, Se, and Zn using the methods detailed in Section *2.4.* The metal content of the fixed wastes can be seen in Table 2.4

Table 2.4: Fixed Wastes Metal Content

Metal	Crushed Fixed Waste (g/kg)	Spherical Fixed Waste (g/kg)
Arsenic	4.325	4.361
Selenium	0.264	0.267
Copper	18.542	18.70
Lead	86.821	87.713
Zinc	22.59	22.68

Digests for analysis were prepared using a fusion method (Rio Tinto, 1996). This method employed a peroxide/carbonate fusion and is described below.

2.3.4.1 Fusion Method

2.3.4.1.1 Fixed Waste Spheres

A sphere was first crushed to a powder using a mortar & pestle. A 0.25g subsample of the crushed sphere was then weighed into a zirconium crucible. To this, 2.0g of sodium peroxide was added using a plastic spatula. Finally, 1.0g of sodium carbonate was added to the crucible and the three components mixed gently. The mixture was then fused over a Bunsen burner (bright yellow flame) with a gentle swirling action until no evidence of a solid was seen. At this point, the reaction mixture was cooled for approximately two minutes, after which the crucible was placed on its side in a plastic beaker containing 100ml of de-ionised water. The beaker was then covered with a watchglass and, after all visible reactions had ceased, 15ml of concentrated HNO_3 was slowly added to the beaker. Once the mixture had cooled, the watchglass was removed and washed using de-ionised water, and the washings added to the reaction mixture. To the reaction mixture were added 2ml of 15% hydrogen peroxide solution followed by 25ml of 5%w/v ammonium fluoride solution. Using plastic tweezers, the crucible was then removed from the beaker and rinsed with deionised water and the washings added to the beaker. The contents of the beaker were then quantitatively transferred to a 250ml plastic volumetric flask, before being made up to the mark with de-ionised water. This process was carried out for three spheres and one method blank.

2.3.4.1.2 Crushed Fixed Waste

A 100g subsample of the crushed fixed waste was further size-reduced to a powder using a mortar and pestle. From this powder, 3 X 0.25g samples were taken and digests prepared as described in Section *2.3.4.1.1*. Metal analyses are shown in Table 2.4.

2.4 Leaching Methodologies

2.4.1 Large Column

2.4.1.1 Construction and Preparation

The large column (see Figure 2.1) was adapted from one described by Jackson and Bisson (1990) and constructed out of polyethylene by Fordaire Australia (see Figure 2.2).

Two layers of different sized glass beads were laid at the base of the column to assist filtration, and these were placed on top of a small circle of Geofabric. The Geofabric is a felt filter, supplied by Colloid Australia Pty. Ltd., that is used on the top of the leachate drainage layer of a landfill to prevent sedimentation occurring in the drainage layer. The use of the beads was not only to ensure minimal fines were lost from the column, but also to ensure that those ending up at the base did not obviate flow of leachant through clogging of the Geofabric.

The beads were first cleaned by thoroughly rinsing in tap water, followed by de-ionised water, before immersing in a polyethylene bath containing 10% HNO_3 for seven days. Following the acid washing they were once more rinsed in de-ionised water, until the pH of the washings was neutral.

The lower layer consisted of 8mm diameter glass beads filled to a height of approximately 10cm, while the upper layer consisted of 3mm diameter glass beads filled to the top of the cone.

38.1kg of the prepared solidified/stabilised waste (see Section *2.2.3.1*) was then filled into the column in 5kg lots. After the addition of each 5kg lot of waste, the waste was evenly spread over the base and lightly tamped to allow settling to occur. After filling, the waste layer was approximately 14cm high.

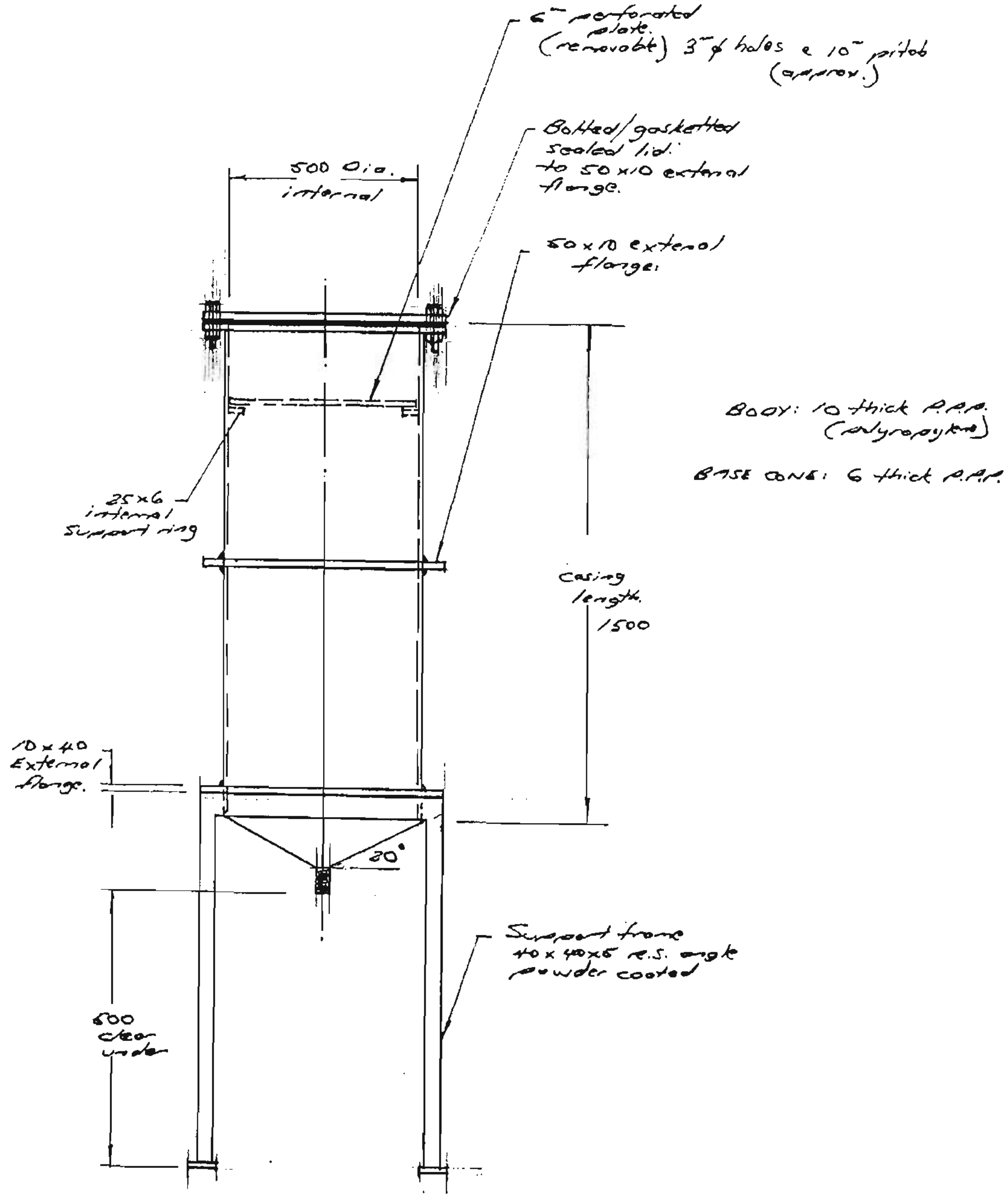


Figure 2.1: Large Column Schematic

Figure 2.2: Large Column Construct

2.4.1.2 Leaching Protocol for the Large Column

A 5L plastic, manual-pump pressure sprayer was used to spray deionised water into the column for the duration of the test. An initial volume of 14L of deionised water was sprayed into the top of the column at a rate of approximately 500ml/min as a surface wash-off step. Thereafter, 2L of deionised water per day for one year was sprayed into the top of the column at the aforementioned rate. The reasons behind the employment of a 2L/day volume are explained below. Following each day's leachant addition, a loose fitting lid (see Figure *2.2*) was placed on top of the column to prevent excessive evaporation while at the same time allowing gravity feed of leachant through the waste. The leachate was collected in a twenty-litre polyethylene container.

This method employed as its flow rate the average rainfall for the lower East Coast of Australia adapted to a worst-case landfill scenario. The method used rainfall data from Laverton in Victoria, Australia, a suburb in a non-rain belt and 15km from a proposed hazardous waste facility at Werribee.

The wettest year on record from nearby Laverton was 713.3mm of rain. Conservatively rounding up, the amount of rainfall on which the flow rate was modelled was 750mm/year.

For a column with a radius of 25cm, this works out to be:

$$\pi * (25\text{cm})^2 * 75\text{cm}$$

$$= 147.26\ \text{dm}^3/\text{year}$$

$$= 403.46\ \text{cm}^3/\text{day}$$

To facilitate a worst case rainfall scenario, and allow the data to be applied to wetter areas, an amount five times that of the rainfall for that area was used as the model. Therefore, 2017.30ml was the calculated amount to be sprayed. Rounding off, 2000ml per day was sprayed into the column.

2.4.1.3 Sampling and Analysis Protocols for the Large Column Leachates

Leachate was allowed to accumulate for a week before being sampled. A weekly sample therefore consisted of 14L of leachate (7 X 2L). Pressure filtering of the 14 litres of collected leachate, through a 60μm - 80μm Millipore filter using a positive-pressure filtration apparatus, was followed by thorough mixing and sub-sampling.

Sub-samples of the filtrate were then analysed for pH, redox potential, and conductivity, before being acidified to 1% v/v HNO_3 for subsequent metal analysis. The initial surface wash-off leachate was collected and prepared in the same manner as that for the weekly samples.

2.4.2 Small Columns

2.4.2.1 Construction and Preparation

The small column was designed and constructed by Bartelt Instruments and Art Blowing (see Figure 2.3).

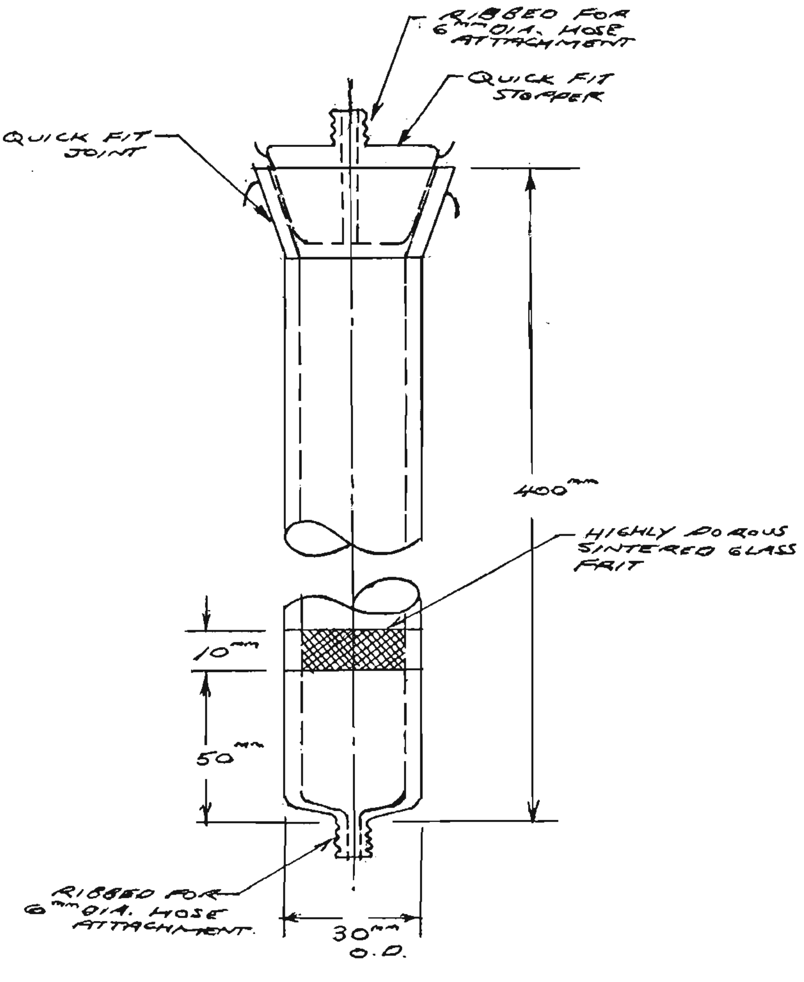


Figure 2.3: Small Column Schematic

Of the three columns prepared, two were filled with 100g of crushed fixed waste while another was filled to its top with approximately 180g. The waste was poured into each column in 2cm high lots followed by light tamping, and this continued until each column contained its appropriate mass. Each column had a small circle of

Geofabric placed at its base over the sintered glass frit as a means of preventing the loss of excessive amounts of fines.

2.4.2.2 Leaching Protocols for Small Columns

The flow rates and types of flow for each column are detailed in Table 2.5 and the experimental setup can be seen in Figure 2.4.

The pumps used were Alitea peristaltic pumps and they used Activon PVC flow-measured pump tubing. The tubing that ran from the pump to the columns was made of Tygon, with an O.D of 3.2mm and a wall thickness of 1.6mm.

Table 2.5: Small Column Flow Rates

Column	LCC100 Large Column Comparison (100g)	ABLC100 Australian Bottle Leaching Comparison (100g)	ABLC180 Australian Bottle Leaching Comparison (180g)
Fixed Waste Mass (g)	100.00	100.00	179.48
Flow Rate (L/Day)	4.65×10^{-3}	2.67	2.67
Direction of Flow Through Column	Down	Up	Up

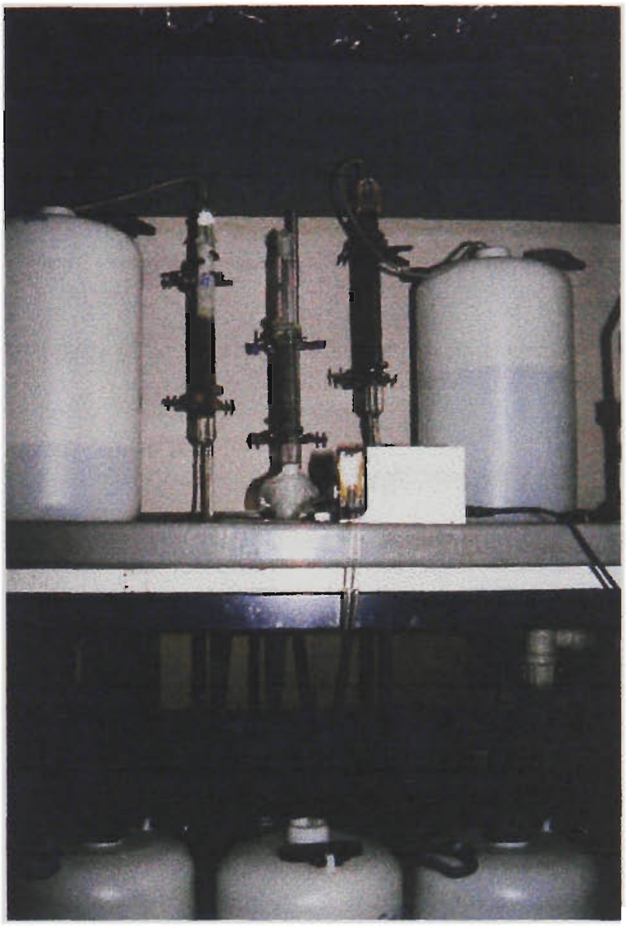


Figure 2.4: Small Column Experimental Set-up

Prior to any continuous leaching, the waste in all columns was surface washed by pumping deionised water through them in an upflow fashion at the rate of 1ml/min. Once the water began to rise above the surface of the waste, the pump was stopped and the leachate drained and collected.

Continuous leaching from one of the 100g columns (LCC100) was achieved by pipetting 4.65ml of deionised water onto the surface of the waste at the top of the column every day for one year. A Quick Fit stopper with a small hole was placed in the top of the column. The leachate was collected in a 50ml polyethylene container.

The 4.65ml volume was calculated using the same reasoning as for the large column (see Section *2.4.1.2*).

For a column radius of 12mm; $\text{flow rate} = \pi * (1.2\text{cm})^2 * (75\text{cm} * 5)$

$$= 1696.46\ \text{cm}^3/\text{year}$$

$$= 4.65\ \text{cm}^3/\text{day}$$

In the other 100g column (ABLC100) and the 180g column (ABLC180), a volume equivalent to 2L every 18 hours (the volume of liquid/time used in the ABLP & TCLP), or 2.67L per day was pumped up through the columns, by peristaltic pump, at a constant rate. The waste in these columns was also leached continuously for a one-year period. Leachates were collected in 20L acid-washed polyethylene containers.

The reason for using a larger waste mass with the same flow rate in the ABLC180 (compared to the ABLC100) was to observe any possible effects on total metal release, and rate of metal release this change may bring about.

2.4.2.3 Sampling and Analysis Protocols for the Small Column Leachates

Sampling of the LCC leachates took place weekly. Each sample, of approximately 32ml, was pressure filtered in the fashion described in Section *2.4.1.3* before being analysed for conductivity, redox potential, and pH. Each sample was then acidified to 1%v/v HNO_3 and stored, prior to subsequent analysis for metals of interest.

Sampling of the ABLC100 and ABLC180 leachates occurred daily, before gradually stretching out to weekly over the duration of the experiment. These samples were filtered and analysed as above.

The initial surface wash-off leachate, for each small column, was collected and prepared in the same manner as that for the weekly samples.

2.4.3 Dynamic Leaching Tests

2.4.3.1 Construction and Preparation

Dynamic Leaching Tests (DLTs) were carried out for one year on spherical samples of fixed waste, 36mm in diameter. These samples were prepared as described in Section *2.3.2*.

The tests were performed in 500ml acid-washed polyethylene bottles and conducted by immersing a sphere, held in a nylon cradle, in a volume of deionised water leachant, renewed at intervals defined in Section *2.4.3.2*. The experimental set-up is illustrated in Figure 2.5.

Figure 2.5: Dynamic Leaching Experimental Set-up

2.4.3.2 Leaching Protocol for Dynamic Leaching Tests

Leaching tests were performed in duplicate at two leachant renewal schedules and were run for a one-year period. These schedules are detailed in Appendix C.

The leachant renewal schedules were based on Equation 2.1 (below) that ensures equal amounts of contaminants are leached per leaching period (for diffusion controlled leaching).

$$t_n = n^2 t_1$$

Where: n = leaching period; 1, 2, 3, etc.
t_1 = time to end of the first leaching period
t_n= time to end of the *n*th leaching period

Equation 2.1 (Côté 1986)

Two different values of t_1 were used for contaminants of various mobilities, to ensure their concentrations in the leachate did not approach saturation and, thus, limit leaching. For very mobile contaminants, a value of t_1 = 1hr was selected, and for less mobile contaminants t_1 = 4hr.

A leachant volume of 407ml was added to the sample bottles according to these aforementioned schedules.

For the DLT, Côté *et al* (1987) recommend a specimen surface area to volume of leachant ratio of 0.10cm^{-1}. This ratio is generally used to ensure the sample is surrounded adequately on all sides by leachant, thus providing even diffusion around the sample. It is also used to ensure a detectable quantity of contaminant leaches out of the sample within a reasonable time frame.

For a spherical sample with an 18mm radius the surface area ($4\pi r^2$) is 40.7cm^2. Therefore, the volume used for each leaching interval in the tank leaching tests, was 10 x 40.7, or 407ml.

Blanks were also run for both schedules, using identical renewal schedules and 407ml of water, the exception, of course, being that they contained no spheres. After 1764 hours (74 days approx.) of leaching, samples were then taken weekly at 12pm until 4620 hours had passed, and then fortnightly until a total sampling time of 1 year had passed.

2.4.3.3 Sampling and Analysis Protocols for Dynamic Leaching Test Leachates

At the end of each leaching period, the leachates were pressure filtered, as described in Section *2.4.4*, before being analysed for conductivity, redox potential, and pH. Each sample was then acidified to 1%v/v HNO_3. A subsample was taken and stored in a 50ml polyethylene bottle, prior to subsequent analysis for metals of interest.

2.4.4 Australian Bottle Leaching Procedure (ABLP) and Sequential Australian Bottle Leaching Procedure

The exact procedure for the Australian Bottle Leaching Procedure (ABLP) can be found in the referenced standard (Standards Australia 1997). The method is detailed, briefly, as follows.

Four 100g samples of the fixed waste were placed into four 2L acid-washed polyethylene screw capped bottles, followed by 2L each of deionised water. A blank container was also prepared containing only water and no waste. The containers were tumbled end-over-end in a rotary agitator (see Figure 3.3) at 30±2 rpm for a period of 18 hours. Following this, all leachates were decanted and pressure filtered through

0.6-0.8μm Millipore filters. These filters had been acid-bathed in 1% v/v HNO_3 for 2 hours, prior to rinsing with deionised water until the washings were pH neutral (pH neutrality was determined using pH paper). A temperature range was also recorded on a Brannan Digital Thermometer probe for the duration of each leaching period. The subsequent leachates were analysed for conductivity, redox potential, and pH, prior to being acidified to 1% nitric acid and stored for metals analysis.

Sequential ABLPs were performed by retaining the filtered solids and, as quantitatively as possible, scraping them back into their respective containers. A further 2L of deionised water was added to each and a second period of leaching commenced. This process was repeated until a distinct pattern of leaching emerged.

2.4.5 Toxicity Characteristic Leaching Procedure (TCLP)

The method is described briefly here and more extensively in the referenced standard (Federal Register, *vol. 261*, 29 Mar. 1990).

The method follows the exact steps described in Section 2.4.4, the differences being the leachant used and the fact that this was a single extraction only.

Following determination of the pH of the waste, Extraction Fluid No.2 was chosen as the leachant. This fluid was made up in individual 2L lots, by adding 11.4ml of glacial acetic acid, purchased from Merck, to a 2L volumetric flask and making up to the mark with deionised water. A blank was also run, using only 2L of the extraction fluid and no waste.

As with all other samples, following filtration the leachates were analysed for conductivity, redox potential, and pH, before being acidified to 1% HNO_3 and stored ready for subsequent metals analysis.

2.4.6 Maximum Availability Test

This test was adapted from a method described by Lewin (1996) and involves two sequential three-hour extractions on replicate samples.

Three 16g fixed waste samples were finely ground with a mortar and pestle and sieved to a particle size of <125μm. Each 16g sample was then added to 800ml of deionised water in a 1L beaker containing a stirrer. A 0.5M HNO_3 solution was added dropwise, via burette, to each sample for the first 3 hours to maintain the solution at a pH of 7. Each sample was then filtered through a 0.60μm Millipore filter using a Millipore positive pressure filtration apparatus.

The solids were then, as quantitatively as possible, scraped back into their beakers and a further 800ml of de-ionised water added. The second extraction was the same as the first, except that the solution was maintained at a pH of 4. For both extractions, acid addition was manual via burette, with constant pH monitoring (refer to Section *2.5.3.3*).

Following filtration, the two extraction filtrates for each sample were combined and final conductivity, redox potential and pH measurements measured. The samples were then stored for subsequent metal analysis.

A fourth vessel, containing leachant only, was subjected to the same treatment as the test material and used as the test blank.

The 0.5M HNO_3 solution was prepared by adding 45ml of concentrated HNO_3 to 500ml of deionised water in a 1L volumetric flask, and then making up to the mark with deionised water.

2.5 Methods of Analysis

All leachates were analysed for arsenic and selenium by Hydride Generation Atomic Absorption Spectroscopy (HGAAS), and copper, lead, and zinc by Differential Pulse Anodic Stripping Voltammetry (DPASV).

2.5.1 Hydride Generation Atomic Absorption Spectroscopy (HGAAS) Method

The method used for the analysis of arsenic was taken from work by Leist (1997), and that for selenium from work by Zhu and Tabatabai (1995).

Analyses were performed on a Varian AA-1475 Series Atomic Absorption Spectrometer with a quartz cell and a Varian VGA-76 Vapour Generation Accessory as the gas-liquid separator. The working conditions for the analysis of each metal can be seen in Table 2.6. The reductant and carrier solutions were made up freshly prior to every analysis and their preparation is described below.

The sodium borohydride ($NaBH_4$) solution for the arsenic analyses consisted of 1g of $NaBH_4$ and 6.5ml of 0.5M sodium hydroxide made up to 250ml in a volumetric flask. For selenium analyses, 0.75g of AR $NaBH_4$ and 6.5ml of AR 0.5M sodium hydroxide were made up to 250ml in a volumetric flask.

The 10% by volume hydrochloric acid solution, used for the analysis of both metals, was prepared by diluting 100ml of concentrated HCl to 1L in a volumetric flask.
An instrument warm up time of one hour was allowed prior to every analysis. Following this, a warm-up procedure was carried out, where a mid-range standard was pumped through the system and into the cell until a stable reading was obtained. This usually took from 30 – 45 minutes and ensured the system was stable, preventing any major drift during the analysis. The same mid-range standard was checked after every five samples, to provide confirmation of instrument stability.

All readings were taken in 'running mean' mode, at 0.5-second intervals, with an average absorbance recorded after 20 seconds.

Table 2.6: HGAAS Working Conditions for Arsenic and Selenium Analysis

Element	**ARSENIC**	**SELENIUM**
Wavelength (nm)	193.7	196.0
Lamp Current (mA)	7	10
Slit Width (nm)	1.0	1.0
Background Correction	Off	Off
Flame Type	Air/Acetylene	Air/Acetylene
Air Flow Rate (L/min.)	19	19
Acetylene Flow Rate (L/min.)	6	6
Reductant	4g/L $NaBH_4$	3g/L $NaBH_4$
Carrier	100ml/L HCl	100ml/L HCl
Purge Gas	N_2	N_2
Reductant Flow Rate (ml/min.)	1	1
Carrier Flow Rate (ml/min.)	1	1
Sample Flow Rate (ml/min.)	6	6
Purge Gas Pressure (kPa)	300	300

2.5.1.1 Arsenic Analysis – Preparation of Solutions

2.5.1.1.1 Preparation of Calibration Standards

Standards were prepared freshly prior to each analysis starting with a 1000ppm arsenic stock solution.

From this stock, serial dilutions were made from 1000ppm down to 100ppb arsenic. From this 100ppb solution the working standards of 2.5ppb, 5ppb, 7.5ppb and 10ppb were made.

Each dilution in the series also contained a 10%v/v addition of a potassium iodide – ascorbic acid solution (KI-AA) which was added to ensure that there was no oxidation of the As (III) to the As (V) form throughout the course of the analysis.

This solution was prepared by making 50g of potassium iodide and 50g of ascorbic acid up to 1L with deionised water.

2.5.1.1.2 Preparation of Leachate Samples

Samples were prepared for analysis, in triplicate, by pipetting 10ml each of concentrated hydrochloric acid, KI-AA solution, and the leachate sample of interest into a 50ml beaker. The beaker was then covered with a watchglass and stirred for 45 minutes with a magnetic stirrer. This preparative step ensured all As(V) was converted to the As(III) form suitable for analysis.

Following the stirring, samples were made up to the mark in the appropriate volumetric flask ready for immediate analysis.

2.5.1.1.3 Standard Additions Analysis

The method of standard additions was investigated for the analysis of arsenic. Four 3ml aliquots were taken from a Dynamic Leaching Test leachate, prepared according to Section *2.5.1.1.2*, and pipetted into 25ml volumetric flasks. These were half filled with de-ionised water before additions of 0μ/L, 37.5μL, 75μL and 112.5μL of 10ppm arsenic standard was made to each. Each flask was then made up to the mark with de-ionised water.

A blank, containing a 3ml aliquot of deionised water, was also prepared, according to the method detailed in Section *2.5.1.1.2.* This too, was made up to the mark with deionised water.

All these samples were analysed using the conditions detailed in Section *2.5.1.*

2.5.1.1.4 Arsenic Recovery Analyses

Method validation was carried out via recovery analyses. A Dynamic Leaching Test leachate was prepared in replicates of eight, as described in Section *2.5.1.1.2.* To four of these, a 75μL aliquot of 10ppm As standard was added. Following dilution of all samples to 250ml in volumetric flasks, this constituted an addition of 3.75ppb As. A blank was also prepared using de-ionised water. All these samples were analysed using the conditions detailed in Section *2.5.1.*

2.5.1.2 Selenium Analysis – Preparation of Solutions

2.5.1.2.1 Preparation of Calibration Standards

Analysis was carried out using a standard calibration plot. Standards were prepared freshly prior to each analysis starting with a 1000ppm selenium stock solution.

From this stock, serial dilutions were made from 1000ppm down to 100ppb selenium. From this 100ppb solution, the working standards of 2.5ppb, 5ppb, 7.5ppb, 10ppb and 20ppb were made. All dilutions were made using de-ionised water.

The initial dilution of the 1000ppm to 100ppb also included a concentrated H_2SO_4 addition to give a final concentration of 1%v/v H_2SO_4. Similarly, all subsequent dilutions received a 10% by volume concentrated HCl addition. These standard preparations are a precaution against the oxidation of the desired species prior to analysis.

2.5.1.2.2 Preparation of Leachate Samples

The preparation of samples for selenium analysis involved heating in 6M HCl in order to reduce the oxidation state of the metal from +6 to +4.

A 20ml aliquot of sample was pipetted into a 100ml beaker followed by a 20ml aliquot of 6M HCl. After placing a watchglass on the beaker, the sample was heated to boiling on a hotplate for 30 minutes, or until the volume had reduced to 10ml.

After cooling, the sample beaker was emptied and washed into the appropriate volumetric flask with successive 5ml volumes of deionised water, ready for immediate analysis.

2.5.1.2.3 Standard Additions Analysis

The method of standard additions was investigated for the analysis of selenium. Four 20ml aliquots were taken from a Dynamic Leaching Test leachate and prepared according to Section *2.5.1.2.2*. A further de-ionised water sample was also prepared as a method blank.

The samples and blank were then rinsed into 50ml volumetric flasks. The sample flasks were half filled to the mark with de-ionised water before additions of 0μL, 100μL, 200μL, and 300μL of 500ppb selenium standard were made to each. Each flask was then made up to the mark with de-ionised water. All these samples were analysed using the conditions detailed in Section *2.5.1*.

2.5.1.2.4 Selenium Recovery Analyses

Method validation was carried out via recovery analyses. A Dynamic Leaching Test leachate was prepared, in replicates of eight, as described in Section *2.5.1.2.2*. To four of these, a 200μL aliquot of 500ppb Se standard was added. Following dilution of all samples to 25ml in volumetric flasks, this constituted an addition of 4ppb Se. A blank was also prepared using de-ionised water. All these samples were analysed, using the conditions detailed in Section *2.5.1*, and selenium recoveries determined.

2.5.2 Differential Pulse Anodic Stripping Voltammetry (DPASV) Method

Copper, lead, and zinc analyses were performed using a Metrohm Polarecord E-506 Control Unit with a Metrohm 663 VA Stand Series 5. The method used for these analyses was developed by adapting work described in the Polarecord Control Unit manual.

The 663 VA Stand contained a mercury working electrode, glassy carbon auxiliary electrode, and a Ag/AgCl reference electrode.

The working electrode is a glass capillary that dispenses small drops of mercury. For these analyses, it was used as a Hanging Mercury Drop Electrode.

The instrument parameters used are detailed in Table 2.7. The method of analysis used for all metals was that of a standard calibration.

Table 2.7: DPASV Working Conditions for Copper, Lead, and Zinc Analysis

U_{Start}	-1.2V
ΔU	+1.5V
Pulse Amplitude (U_{DP})	40mV
mm/t_{drop}	1
t_{drop} [s]	0.8
Scan Rate	7.5mV/sec
Stirrer Speed	1500 rpm
Mercury Drop Size	2
Nitrogen Pressure (psi)	50
Purge Gas	N_2

2.5.2.1 Copper, Lead, and Zinc Analysis – Preparation of Solutions

2.5.2.1.1 Buffer Solution Preparation

Blanks, standards, and samples analysed by DPASV were done with a final sample volume of 20ml. For the samples, this volume consisted of 17ml of acidified sample and 3ml of 3M sodium acetate. Similarly, for the blank and standards, the 20ml of buffer solution consisted of 17ml of 1% v/v HNO_3 and 3ml of 3M sodium acetate. In all cases an acetate buffer with a pH of approximately 4.76 was produced.

The 1% v/v HNO_3 solution was prepared prior to every analysis by adding 50ml of concentrated HNO_3 to 250ml of de-ionised water in a 500ml volumetric flask. This flask was then made up to the mark with de-ionised water.

The sodium acetate solution was also prepared prior to every analysis. 24.609g of sodium acetate was dissolved gradually in a beaker containing approximately 75ml of de-ionised water and a magnetic stirrer. The solid usually took between 30 to 60 minutes to go into solution after which it was transferred to a 100ml volumetric flask and made up to the mark with deionised water.

2.5.2.1.2 Standards Preparation

Standards were run by means of small additions of high metal concentrations to 20ml of the buffer solution. Due to potential intermetallic interferences between copper and zinc, these standards were made up in separate flasks (Wang 1985).

From 1000ppm standards of each metal, stock standards were prepared, one containing 10ppm of zinc, and the other 10ppm of both lead and copper. The final standards required for the analysis were 25ppb, 50ppb and 100ppb for all metals.

2.5.2.2 Analysis Procedure

2.5.2.2.1 Analysis Blank

Following an instrument warm-up period of approximately one hour, at the conditions detailed in Table 2.7, an analysis blank was prepared by pipetting 17ml of 1% v/v HNO_3 into a glass cell followed by 3ml of the 3M sodium acetate solution.

This cell was then placed in its holder and a number of drops of mercury released into the solution to ensure the correct drop size was being reproduced. The blank solution was then stirred for one minute, before being degassed for five minutes with nitrogen.

After turning off the gas, the stirrer was turned back on and an initial voltage of –1.2V applied to the hanging mercury droplet. After one minute, the stirrer was turned off, allowing the solution to settle, and to ensure solution movement did not influence the migration of metal ions. Following another 30 seconds of voltage application a run was started.

2.5.2.2.2 Metal Standards

Following analysis of the blank solution, the stirrer was turned back on and 50uL each of the 10ppm Zn and 10ppm Cu/Pb standards added through the port at the top of the cell. These additions gave final concentrations of 24.88ppb for each metal.

After stirring for one minute, the samples were degassed for a further minute and a run commenced in an identical fashion to that described in Section *2.5.2.2.1*. Further 50μL and 100μL additions of standards gave concentrations for each metal of 49.5ppb and 98ppb respectively.

After triplicate runs of all standards and blanks, the electrodes were rinsed with deionised water and immersed in dilute (1 drop concentrated HNO_3 per 100ml) nitric acid solution with stirring for ten minutes. A final rinse of the electrodes with deionised water was given and the instrument was ready for sample analysis.

The cell was cleaned by immersing it in a 5L polyethylene container filled with 10%v/v HNO_3 for 15 minutes. It was then removed and rinsed with deionised water until the washings were pH neutral.

2.5.2.2.3 Sample Analysis

The method used here was almost identical to that described in Section *2.5.2.2.1*. The exceptions were that 17ml of sample was pipetted into the cell, as opposed to 17ml of acidified water. Between each triplicate run of samples, the probes and cell were cleaned, as described in Section *2.5.2.2.2*.

Peak heights were used to calculate metal concentrations in the samples.

2.5.2.3 Method Validation

2.5.2.3.1 Standard Calibration versus Standard Additions

A 17ml aliquot was taken from a large column test leachate and prepared according to Section *2.5.2.2.3*.

Peak heights for Zn, Pb and Cu were first measured for the sample, before three successive additions of 20μL of a 10ppm Cu-Pb standard and 20μL of a Zn standard, prepared as in Section *2.5.2.1.2*, were made. Following each set of additions, peak heights were measured.

This process was carried out on two further 17ml samples of the same column test leachate, and on de-ionised water as a method blank.

Following these analyses, the same column test leachate was analysed according to the method described in Section *2.5.2.2*.

2.5.3 Wet Analysis Methods

2.5.3.1 Conductivity Testing

Sample conductivity was determined according to APHA Method 2510 (1995). A handheld TDScan 20 model conductivity meter with a range of 10μS to 19.9mS was used for all measurements.

Prior to its use the meter was zeroed with de-ionised water and then calibrated with 1412μs and 2760μS KCl standard solutions. These solutions were prepared on a weekly basis as described below.

For the 1410μS standard (0.01M KCl) 0.7455g of KCl was weighed into a 100ml volumetric flask and made up to the mark with de-ionised water. For the 2760μS standard (0.02M KCl) 1.491g of the KCl was weighed into a 100ml volumetric flask and made up to the mark with de-ionised water.

2.5.3.2 Redox Potential Testing

The redox potential of all samples was determined according to ASTM Method D 1498-93 (1993).

An Activon AEP122 Hi-Flow Ag/AgCl double-junction reference electrode was used in conjunction with an Activon AEP513 mono-glass platinum redox probe and a temperature sensor. These were connected to a Cyberscan 500 pH/Redox meter.

The method called for calibration solutions of known redox potential, and these solutions were prepared according to ASTM Method D 1498-93 (1993). The probes were calibrated, bi-weekly, using ferrous-ferric reference solutions and quinhydrone reference solutions.

The ferrous-ferric solution was prepared by dissolving 39.21g of ferrous ammonium sulphate, 48.22g of ferric ammonium sulphate, and 56.2ml of AR concentrated sulphuric acid in de-ionised water and diluting to the mark in a 1L volumetric flask.

The pH 4 quinhydrone solution was prepared by mixing 10g of quinhydrone with 1L of a pH4 phthalate reference buffer solution. The pH7 quinhydrone solution was prepared by mixing 10g of quinhydrone with 1L of a pH7 phosphate reference buffer solution.

The pH4 phthalate reference buffer solution was prepared by dissolving 10.12g of potassium hydrogen phthalate in de-ionised water and diluting to 1L in a volumetric flask.

The pH7 phosphate reference buffer solution was prepared by dissolving 3.39g of potassium dihydrogen phosphate and 3.53g of anhydrous disodium hydrogen phosphate in de-ionised water and diluting to 1L in a volumetric flask.

2.5.3.3 pH Testing

Sample pH was determined according to APHA Method 4500-H^+ (1995).

The probe used was an Activon AEP312 Ag/AgCl refillable combination glass pH electrode filled with 4M KCl saturated with AgCl. This probe, along with a temperature sensor, was connected to a Cyberscan 500 pH/redox meter.

The electrode was suitable for samples of low to high ionic strength and was used and maintained according to manufacturer's instructions.

The probes were calibrated regularly with commercially purchased pH 4.01, 7.01, and 10.01 buffers.

2.5.4 Proton-Induced X-Ray Emission (PIXE) Analysis

Trace elements in the cement spheres leached in the DLT experiments were measured using PIXE analysis, performed on the 3MV Van De Graaff Accelerator at the Australian Nuclear Science and Technology Organisation (ANSTO), Sydney, Australia. At the end of the leaching period the cement spheres were air-dried and stored in sealed plastic bags awaiting sample preparation for PIXE analysis.

2.5.4.1 Preparation of Spheres for Analysis

The cement-spheres were cut in half using a diamond saw with water-cooling. As the cutting process only lasted a matter of seconds it was considered that the cooling water had negligible effect on metals on or near the surface of the cross section of the resulting semi-spheres. Spheres 1A, 1B and 4A were cut along the seam indent produced from the moulds used to prepare the spheres. The cutting of these spheres successfully produced semi-spheres, with a smooth flat cross-section and with only minor crumbling. Sphere 4B, which had fractured, was cut along the fracture, but, in the process, the sphere broke into two irregularly shaped sections and major crumbling occurred. In order to produce two semi-spheres with a smooth flat cross section, a 3 mm thick cross section wafer was cut from each section. A photo of all semi-spheres is shown in Figures 3.47 to 3.50.

The semi-spheres were air-dried and placed in sealed plastic bags after which they were delivered to ANSTO. At ANSTO the semi-spheres were outgassed and carbon coated.

2.5.4.2 Analysis of Spheres

The samples were analysed using 2.5 MeV proton beam with a target current of 2-10nA and a total charge between 1-5mC, depending on the spot sizes. The spot sizes of the ion beam and thus the lateral resolution of the measurements were between 0.1-1mm. In front of the X-ray detector a 1.2 mm Perspex filter was used in order to suppress the high count-rate and thus pulse pile-up coming from the light matrix elements such as Si and Ca. The samples were carbon coated in order to suppress charging of the samples.

The data was recorded in spot-size increments of 0.100-1.000mm, with the left edge of the sample surface represented by 387mm and the right edge by 423mm. This covered the entire sample width of 36mm. The sample points at 424mm did not measure the sphere and, consequently, all metals provided readings at blank levels.

3. Results and Discussion: Zinc

3.1 Zinc Analysis: Method Validation

Method validation for zinc by DPASV was carried out according to Section *2.5.2.3.1* using a 17ml aliquot of a Large Column leachate of unknown concentration. Zinc concentration by standard calibration was 22.35ppb and by standard additions was 21.63ppb. This difference is not significant. Accordingly the method of standard calibrations was used throughout the leaching experiments for the analysis of zinc. Zinc recoveries were all between 96% and 110% Method validation also demonstrated that no matrix effects were present in the analysis by standard calibration.

3.2 Batch Tests

The batch tests investigated in this study were the Maximum Availability Test, ABLP, Sequential ABLP, and TCLP. Details of the fixed waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.4 – 2.4.6*.

3.2.1 Maximum Availability Test Results

The Maximum Availability Test was run in triplicate. An average of these results for mass and percentage of zinc leached, pH, redox potential, and conductivity are detailed in Table 3.1. Results for each replicate for mass of zinc leached, pH, redox, and conductivity, are shown in Appendix E (i).

An average 58.31ml (29.15 meq) of 0.5M HNO_3 in the first part of the extraction to keep the solution at pH 7, while 98.57ml (49.28 meq) of 0.5M HNO_3 was added in the second part to maintain a solution pH of 4.

Table 3.1: Zinc Maximum Availability Test Data

Mass of Zinc Leached (mg)	**Percentage of Total Mass of Zinc Leached (±1σ)**	**pH**	**Redox Potential (mV)**	**Conductivity (mScm^{-1})**
158.6	43.9% (±0.3%)	4.68	564.1	6.6

As explained in Section *1.3.4.5.3*, the Maximum Availability Test is designed to reflect the quantity of metal that can eventually be leached, in the very long term, after the complete disintegration of the waste material. This result, therefore, demonstrates that no greater than 43.9% of the zinc present in this solidified waste should leach out over time, with the remaining 56.1% staying bound within the cement matrix.

3.2.2 TCLP Results

The average concentration, mass and percentage of zinc leached, pH, redox potential, and conductivity in the TCLP are detailed in Table 3.2. Results for each of the four replicates for mass of zinc leached, pH, redox, and conductivity, are shown in Appendix E (ii). The temperature during the extraction ranged from 20°C to 22°C.

Table 3.2: Zinc TCLP Data

Concentration Leached (ppm)	Mass of Zinc Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Zinc Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.095	0.19	0.01% (±2.0 x 10^{-4}%)	12.11	232.1	12.8

Although not covered by the TCLP limits detailed in Table 1.5, some sources do provide more extensive lists of potential contaminants that include a number of less hazardous metals such as zinc. A Victorian EPA document (1993) lists the TCLP limit for zinc at 100ppm. As only 0.095ppm zinc present in the waste leached in the TCLP, it can be said that the zinc in the waste appears to have been successfully stabilised with respect to Victorian EPA regulations for disposal to a secure landfill.

The small amount of zinc leached is also significant when taking into account the pH results of the extraction and the concern with wastes establishing their own leaching environments in the TCLP (Section *1.3.4.2.2.2*). The average pH reading from the extractions was 12.11, obviously much higher than the starting pH 3.00 of TCLP Extraction Fluid No.2. This result demonstrates that the waste has indeed established its own high pH leaching environment.

The TCLP data for zinc is also in stark contrast to that from the Maximum Availability Test, where the pH was kept to less than or equal to 7, and 43.9% of the zinc leached from the waste.

3.2.3 ABLP Results

The average concentration, mass and percentage of zinc leached, pH, redox potential, and conductivity in the ABLP are detailed in Table 3.3. Results for each of the four replicates for mass of zinc leached, pH, redox, and conductivity, are shown in Appendix E (iii). The temperature during the extraction ranged from 27°C to 29°C.

Table 3.3: Zinc ABLP Data

Concentration Leached (ppm)	Mass of Zinc Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Zinc Leached ($\pm 1\sigma$)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.40	0.80	0.04% ($\pm 8.1 \times 10^{-4}$%)	11.60	210.3	8.20

This result shows that zinc leached approximately 4 times more in the ABLP using de-ionised water than it did in the TCLP, which employs an acetic acid leachant. Of further interest, the pH of the leachate had a final average value of 11.60 for the ABLP, 0.51 units lower than that for the TCLP.

There has been a great deal of research detailing the effects of acid on the leaching of cement-based wastes, and the subsequent pH of the leachates produced at the end of the tests (Shively *et al* 1986; Bridle *et al* 1987; Bishop 1988; Cheng *et al* 1991; Cheng & Bishop 1990, 1992; Baker & Bishop 1997). Bridle *et al* (1987) point out that, when a non-aggressive leachant (water) is used, the pH of the leachate is indicative of the pH of the waste. In this case, however, a higher pH was obtained from a much more acidic leachant as opposed to a non-aggressive one. An explanation for this could be that an acidic leachant speeds decomposition of $Ca(OH)_2$ in a cement-based waste, leading to a more rapid increase in solution pH than might be obtained with water only (Shively *et al* 1986; Cheng *et al* 1991).

Asavapisit *et al* (1997) studied the effects of 10% additions of Pb, Zn, and Cd hydroxide synthetic wastes on the early hydration of ordinary Portland cement. They found zinc caused severe inhibition of hydration forming a number of crystalline hydroxides. This apparent pH dependency of zinc solubility is supported by the data observed in the TCLP, ABLP, and Maximum Availability experiments where, regardless of the type of test, the lower the pH of the final leachate, the more zinc that was leached. This data also agrees with the research of de Groot *et al* (1989) who performed a shake experiment at a L/S ratio (L/kg) of 100 for 5 hours, with a pH 4 nitric acid leachant, on bag-house dusts and mine tailings. They found that zinc showed a minimum in solubility at high pH values, likely caused by the formation of low solubility hydroxide compounds. In their work on the effects of pH and redox potential on metal solubilities in solid waste incinerator residues, DiPietro *et al* (1989) also found zinc solubility decreased at low pH combined with a highly oxidising environment. Results from the single ABLP carried out in this work also shows that low levels of zinc leached from a system with a high pH and moderately oxidising redox levels.

Although working with dynamic leaching tests, Baker and Bishop (1997) intimate that the models of leaching from cement stabilised wastes can differ depending on whether the leachant is neutral or alkaline, where diffusion may play a greater role as opposed to dissolution of the matrix by an acid leachant.

In terms of observing the ABLP as a worst-case scenario test, the data illustrates that insignificant amounts of zinc leached in the ABLP, as compared to the initial amount of zinc in the fixed waste, and also the amount leached in the Maximum Availability Test.

3.2.4 Sequential ABLP Results

The average concentration, mass and percentage of zinc leached in the Sequential ABLP are detailed in Table 3.4. Results for each of the four replicates for mass of zinc leached, pH, redox, and conductivity, are shown in Appendix E (iv).

The data, in Table 3.4, shows that less than 0.17% of the zinc present in the waste was removed after ten successive leaches. This demonstrates that the metal is well retained in the fixed waste system. It also demonstrates that the first ABLP leach acted as a worst case scenario test, where the maximum amount of zinc leached in the first of the sequential extractions. Increases later in the testing indicate that the amount of zinc leached may increase again, in time, and this has been further investigated by looking at time-dependent column results in Section *3.3*.

Table 3.4: Zinc Sequential ABLP Data

Sequential Leach Number	Concentration leached (ppm)	Mass of Zinc Leached (mg)	Percentage of Total Mass of Zinc Leached ($\pm 1\sigma$)
1	0.40	0.80	0.036% (±8.1 x 10^{-4}%)
2	0.31	0.63	0.028% (±1.6 x 10^{-3}%)
3	0.26	0.52	0.023% (±1.7 x 10^{-3}%)
4	0.20	0.40	0.018% (±8.3 x 10^{-4}%)
5	0.18	0.37	0.016% (±3.5 x 10^{-4}%)
6	0.17	0.33	0.015% (±8.9 x 10^{-4}%)
7	0.12	0.24	0.011% (±1.7 x 10^{-4}%)
8	0.07	0.14	0.006% (±1.5 x 10^{-4}%)
9	0.07	0.14	0.006% (±5.1 x 10^{-4}%)
10	0.13	0.25	0.011% (±5.9 x 10^{-4}%)
Total	N/A*	**3.83**	**0.169%** (±7.6 x 10^{-3}%)

*N/A = Not Applicable

3.2.4.1 Leaching Behaviour of Zinc

Figure 3.1 (below) shows that the leachate pH steadily increases over the course of the 10 extractions, a reverse trend to that observed for zinc leaching. The increase in pH indicates an ongoing leaching of alkalinity ($Ca(OH)_2$) from the fixed waste mass (Baker & Bishop 1997; Cheng & Bishop 1990).The figure also illustrates that the first leaching interval provided the highest mass of zinc leached, after which the amount steadily decreases. Following the 8th leaching interval (144hrs), the amount of zinc leached began to increase. This increase in zinc leachability could be either a physical removal from the matrix (matrix dissolution), a pH dependent release due to the amphoteric behaviour of zinc, or a combination of the two. The Pourbaix diagram of zinc species in solution clearly shows the amphoteric nature of zinc, and supports the suggestion that higher leachate pH (>12) may lead to increased zinc leaching (Pourbaix 1974). Cheng *et al* (1991) point out that, for some amphoteric metals, physical encapsulation could be the major immobilising mechanism at the high pore-water pH generally present. At first glance this appears to be true for these results where the mass leached decreases until the leachant reaches a pH of 13, at which point it begins to increase once again. However, as detailed in Section *3.2.3*, a number of authors have indicated that zinc exists primarily as insoluble hydroxides at such high pH. Further leaches need to be conducted to establish whether this increase in zinc leachability continues.

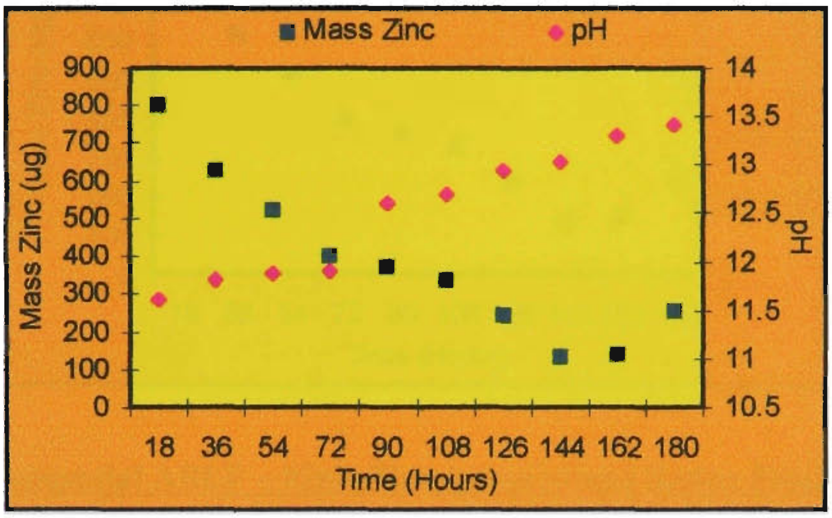


Figure 3.1: Sequential ABLP – Mass Zinc Leached and pH v's Time

3.2.4.1.1 Redox Potential and Conductivity Effects on Zinc Leachability

Figures 3.2 and 3.3 illustrate broad correlations between the leaching of zinc and the levels of conductivity and redox potential in the leachants.

As the Sequential ABLP is only a relatively short test with a non-aggressive leachant (in this case), the leachants end up showing only minor changes in redox potential and conductivity. Therefore, although the redox potential appears to show a reverse pattern to that of the leached zinc, no conclusions can be drawn, as the actual redox potential variation was little more than 50mV over the course of the extractions.

Dusing *et al* (1992) investigated the effects of ORP on metal leachability from various fixed wastes using the TCLP. They did this by manipulating the system ORP, extracting the wastes with neutral, oxidising, and reducing leachants. De-ionised water was used as the neutral leachant, providing a post-leaching Eh range of –50mV to +100mV. This neutral range is lower than the Eh levels observed in the present work for the Sequential ABLP.

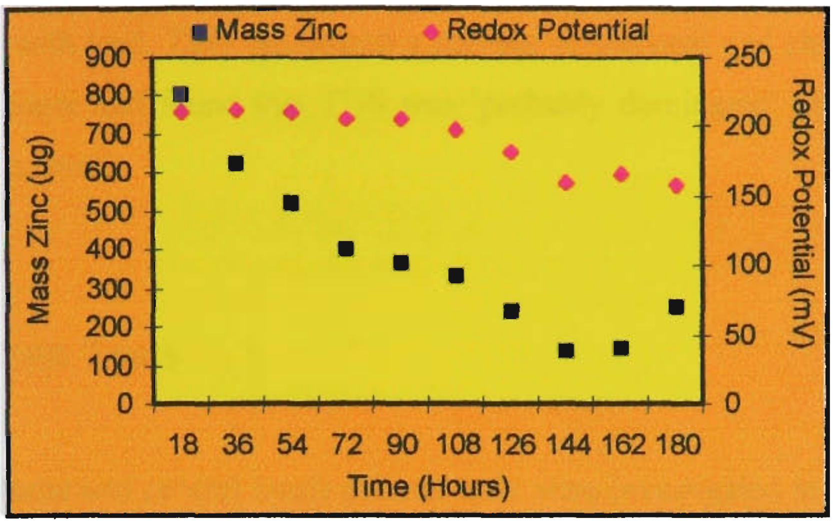


Figure 3.2: Sequential ABLP – Mass Zinc Leached and Redox Potential v's Time

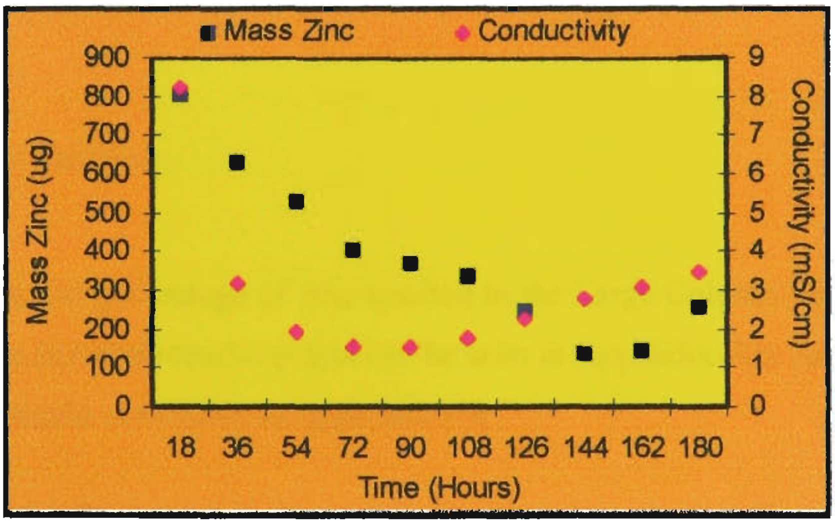


Figure 3.3: Sequential ABLP - Mass Zinc Leached and Conductivity v's Time

Also of interest, the conductivity levels increase following a sharp decrease from the high levels at the start of the test. This could indicate that the agitation of the system has begun to break up the matrix, subsequently freeing more alkalinity for leaching, as the sharp rise in pH also shows. The fact that this did not coincide with an increase in zinc leaching is not of great importance, as it is expected that the main contributor to conductivity levels will be Ca^{2+} and its associated anions (e.g. $Ca(OH)_2$), meaning that the small amounts of zinc leached will, therefore, have minimal influence on the overall leachate conductivity. This influence of calcium on conductivity was also presented by Sanchez *et al* (1999) in their research on cement-based solidified soils contaminated with lead. They performed a number of physical and chemical leaching tests on this waste and found that TDS was 'probably dominated' by the release of calcium and its anions.

3.3 Column Tests

One large column and several small column tests were investigated in this study. The small columns were the 100g Large Column Comparison (LCC100), 100g ABLP Comparison (ABLC100), and the 180g ABLP Comparison (ABLC180). Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.1 – 2.4.2*.

3.3.1 Large Column

The total mass and percentage of zinc leached in the Large Column test are detailed in Table 3.5. The complete leaching data can be seen in Appendix F(i). All pH, redox and conductivity results are shown in Appendix F(ii).

Table 3.5: Large Column Test Data

Mass of Zinc Leached (mg)	Percentage of Total Mass of Zinc Leached
796.2	0.09%

Although the actual mass of zinc leached from the large column was much higher than that leached from any of the batch tests, the percentage of zinc leached is still small. As shown in Table 3.6, the large column, TCLP, ABLP, and Sequential ABLP, all leached less than 0.2% of the zinc that was present in the waste. Only the Maximum Availability Test leached zinc to any appreciable extent.

Table 3.6: Percentages of Zinc Leached in Batch Tests and Large Column

Leaching Test	Percentage of Total Mass of Zinc Leached
Large Column	0.09%
TCLP	0.01%
ABLP	0.04%
Sequential ABLP	0.17%
Max. Avail. Test	43.9%

3.3.1.1 Leaching Behaviour of Zinc

There are a number of possible explanations why the Maximum Availability Test leached a great deal more zinc than the other tests investigated.

As the method of leachant delivery and system agitation were similar for all batch tests but different for the large column, this could not be the cause of the difference. Another parameter that should be examined is the solid to liquid ratio used in the leaching tests. The ABLP and TCLP employed liquid to solid ratios of 20:1, while, after one year of leaching, the large column had a final liquid to solid ratio of 19:1. For the maximum availability test and Sequential ABLP the ratios were much higher with final ratios of 110:1 and 200:1 respectively. The liquid to solid ratio, therefore, has not significantly influenced the leaching of zinc from the solidified waste product. Further to this, due to the different methods of leachant delivery in the tests, the contact times of liquid to solid for the column would actually be much less than for the batch tests.

The most probable explanation is that the much larger percentage of zinc leached in the Maximum Availability Test is due to the pH control in that method. It is worth repeating that Di Pietro *et al* (1989) reported that, for municipal solid waste residues, zinc solubility increased with decreasing pH combined with oxidising Eh conditions. These exact conditions were observed in the final Maximum Availability Test leachates where the average pH was 4.68, and the average Eh was 564.1mV.

It is also interesting to note the work of Lewin (1996) who suggested that, for zinc, surface wash-off is the dominant form of leaching. This correlates well with the large column results, illustrated in Figure 3.4.

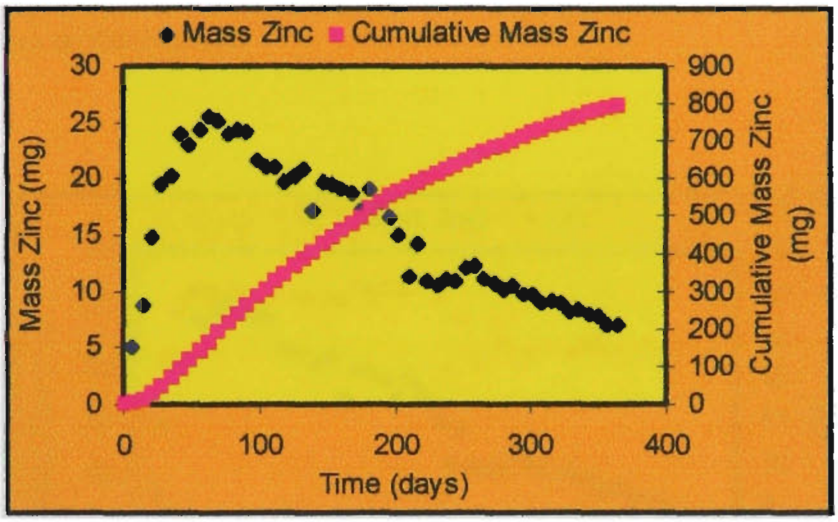


Figure 3.4: Large Column – Mass Zinc Leached v's Time

For the first ten weeks, zinc leached in rapidly increasing amounts. After this time, and within a period of two to four weeks, the rate of leaching immediately slowed and the mass of zinc released began gradually decreasing in the remaining months of the experiment. The effect is just as obvious in Figure 3.1 with the Sequential ABLP results, where there is no rapid increase at the beginning, but the mass leached merely begins high before decreasing. It appears then, for the tests investigated, that methods of leaching where the waste establishes its own environment provide similar results for zinc leachability.

Figure 3.5, below, shows some correlation between pH and mass of zinc leached from the Large Column. At the beginning of the experiment, this is more pronounced where, as the pH increases, so does the mass of zinc leached. After 42 days the pH levels off, before suddenly decreasing after 196 days of leaching. The leaching of zinc behaves differently, increasing until the 63rd day, before immediately decreasing. These results contrast to those of the Sequential ABLP that showed an immediate decrease in zinc leaching as pH increased from 12.5 to 13.5.

Consequently, rather than the leaching being pH dependent, it may be that zinc leaches immediately as surface wash-off, with the levels decreasing as it is washed away. The remaining zinc may be bound in the cement matrix, and only leached as the cement-based solid is slowly broken down over time (matrix dissolution), or by diffusion as zinc in the pores is solubilised.

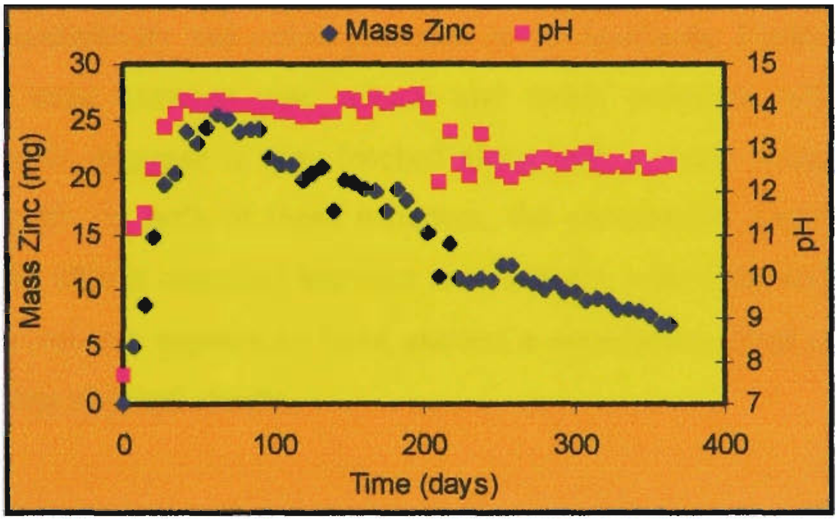


Figure 3.5: Large Column - Mass Zinc Leached and pH v's Time

This is supported by Cheng and Bishop (1990) who point out that the 'mixing of pozzolanic-based binders with wastes converts heavy metals in the waste to insoluble hydroxides and silicates, which are entrapped within the solid paste'. Therefore, if the remaining zinc in the waste in both tests *was* in the form of zinc hydroxide, then it would be expected to leach extremely slowly due to the poor solubility of this species (K_{sp} $Zn(OH)^2 = 3.3 \times 10^{-17}$) (Aylward & Findlay, 1994).

Another equally likely possibility involves zinc release complications arising from the residence time of the liquid in the column. Korfiatis *et al* (1984) extensively studied the physical processes governing moisture transport in large columns and solid waste landfills. They showed that (as soon as the waste is saturated) the addition of a certain volume of liquid to the top of a landfill (or column) would not necessarily produce an immediately equal volume of leachate discharge. Hence, any retention of leachant in the waste pores could also lead to a delay in zinc release, a delay more marked than the same effects on pH. Further, this retention would lead to rate-limiting conditions for leaching, where a build-up of zinc in the leachant reduces the driving force for leaching, and hence the final levels of zinc in the leachate.

3.3.1.1.1 Redox Potential and Conductivity Effects on Zinc Leachability

Figures 3.6 and 3.7 illustrate broad initial correlations between the leaching of zinc and the levels of conductivity and redox potential in the leachants. Figure 3.6 shows an initial reverse trend between zinc release and redox potential, while Figure 3.7 illustrates a steady decrease in zinc leached along with a much sharper drop in the conductivity levels. In both of these instances, the correlations demonstrate similar behaviour to the effects observed between zinc and pH, where the residence time of leachate in the column appears to have exerted a significant effect on zinc release compared to other physical results.

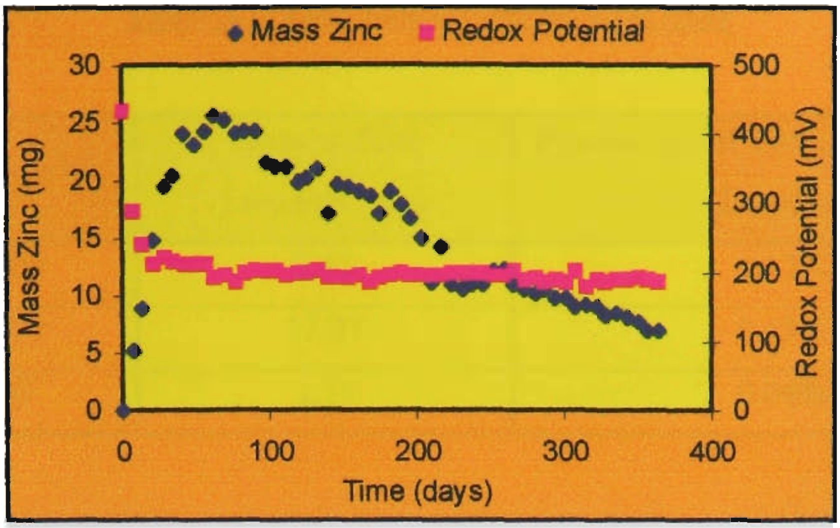


Figure 3.6: Large Column - Mass Zinc Leached and Redox Potential v's Time

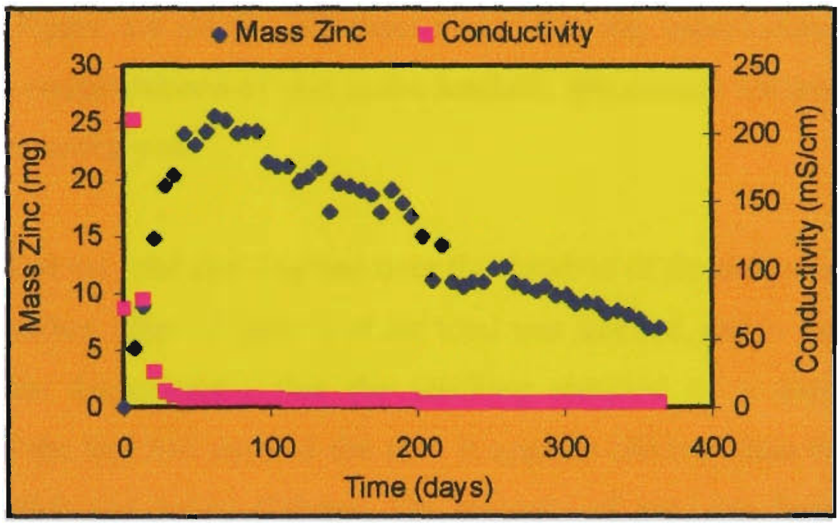


Figure 3.7: Large Column – Mass Zinc Leached and Conductivity v's Time

3.3.2 Small Columns

The total mass and percentage of zinc leached in the small columns ABLC100, ABLC180, and LCC100 are detailed in Table 3.7. The complete leaching data can be seen in Appendices G(i)-(iii) respectively, while all pH, redox and conductivity results are shown in Appendices G(iv)-(vi) respectively.

Table 3.7: Zinc Small Column Test Data

Small Column	Mass of Zinc Leached (mg)	Percentage of Total Mass of Zinc Leached
ABLC100	7.15	0.32%
ABLC180	17.27	0.43%
LCC100	1.75	0.08%

3.3.2.1 ABLC100; Leaching Behaviour of Zinc

Table 3.7 shows that ABLC100 leached a very small amount of zinc over the year the test was run. Figure 3.8 clearly illustrates that, following approximately a one week period of high concentrations of zinc in the leachate, the amount leached does not vary much in the following year.

In fact, over ¼ of the total zinc leached over the duration of the test, was leached in the first 4 days. Further, after 53 days ½ of the total was leached, and ¾ was leached after 200 days. This demonstrates that the leaching steadied to a constant level for approximately the last 310 days of the test. It appears obvious then that, as with the Sequential ABLP and Large Column, the majority of zinc has been leached in a surface wash-off at the beginning of the test. The lack of an obvious correlation between pH and zinc leachability for the other leaching tests is also evident for the small column ABLC100, as illustrated in Figure 3.9.

A continuing pH decrease can clearly be seen, as the amount of zinc released remains steady. This supports the data for the other leaching tests that suggest zinc levels in the leachate originate primarily from surface wash-off, with lesser contributions (in the medium term) from matrix dissolution and diffusion.

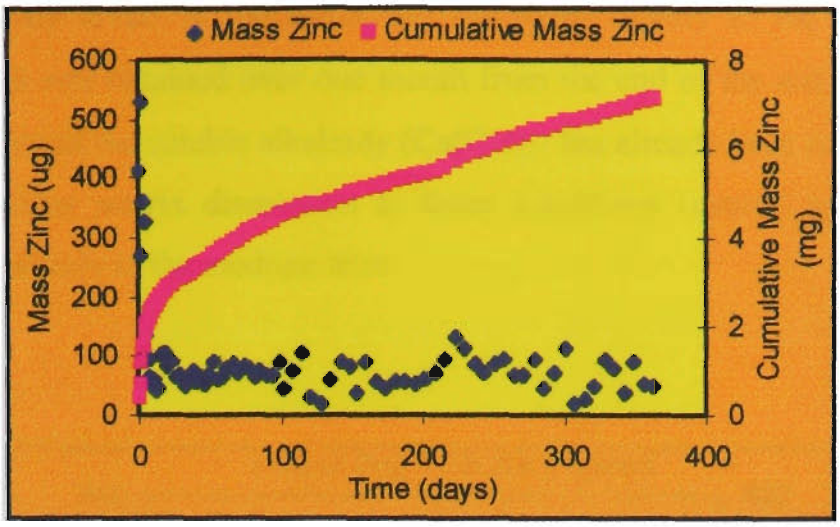


Figure 3.8: ABLC100 - Mass Zinc Leached v's Time

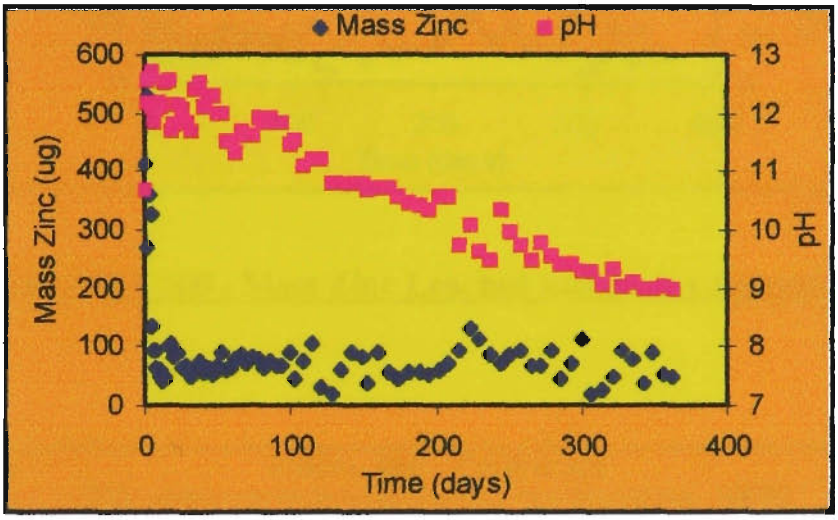


Figure 3.9: ABLC100 - Mass Zinc Leached and pH v's Time

3.3.2.1.1 Redox Potential and Conductivity Effects on Zinc Leachability

For the ABLC100, there appears to be no apparent correlation between redox potential or conductivity and zinc leachability (Figures 3.10 and 3.11). In fact, the only trend observed for redox potential in all leaching tests discussed thus far, is the expected reverse correlation between pH and redox potential.

The conductivity levels in the ABLC100 decreased rapidly to the point where a reading of 0μS was obtained over one month from the end of the test. This indicates that the majority of the soluble alkalinity ($Ca(OH)_2$) has already been leached from the waste and further matrix dissolution at those conditions (neutral leachant and no agitation) is unlikely in the medium term.

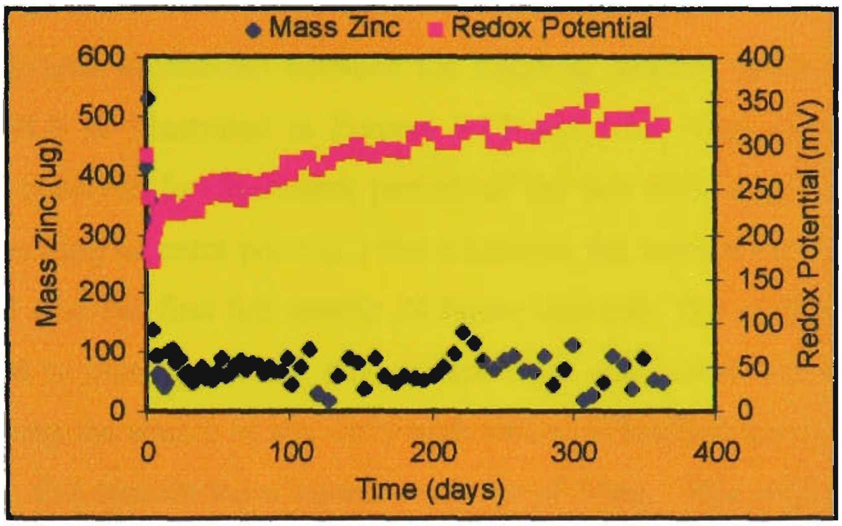


Figure 3.10: ABLC100 - Mass Zinc Leached and Redox Potential v's Time

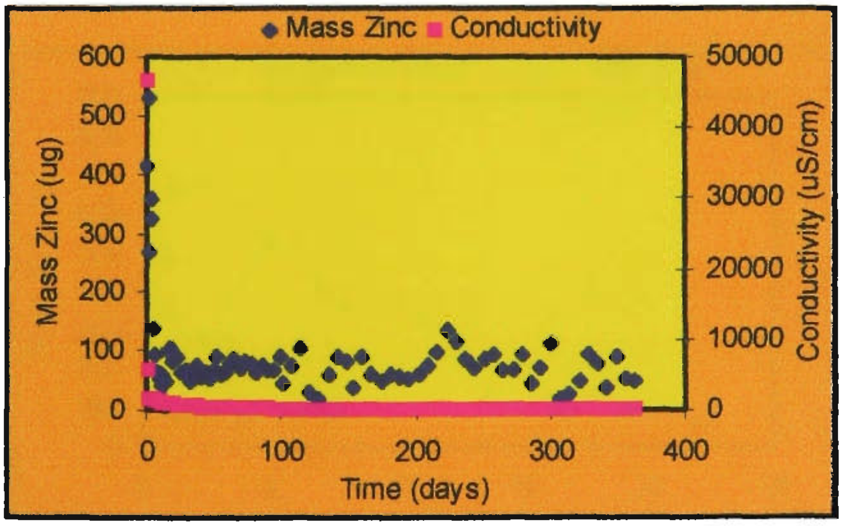


Figure 3.11: ABLC100 - Mass Zinc Leached and Conductivity v's Time

3.3.2.1.2 Comparison to Sequential ABLP

A comparison between the ABLC100 small column results and those of the Sequential ABLP can only be investigated over an identical time period or L/S ratio. Although each test leached 100g of waste, and employed an effective 'flow rate' of 2L of leachant every 18 hours, cross-test comparisons are simplified when using volume as a scale for test duration, as opposed to a specific unit of time.

There were obvious similarities between the leaching patterns of the ABLC100 and Sequential ABLP as illustrated in Figures 3.12 and 3.13. Very similar patterns of leaching were observed for equivalent periods of the two tests, with the dotted line in Figure 3.12 showing an extra point (C) that combines the surface wash-off step on the ABLC100 (A) with the first full sample 24 hours later (B). The surface wash-off step was performed to quickly remove any surface fines attached to the waste particles, thereby clarifying the source of any early high values of leached metals. In the case of the ABLC100, this constituted a leachant volume of 54ml. This step was not carried out for any of the batch tests, meaning that the first 2L of leachant included these surface fines. Therefore, to better compare the two tests, the surface wash-off data was combined with that of the first leach for the ABCL100.

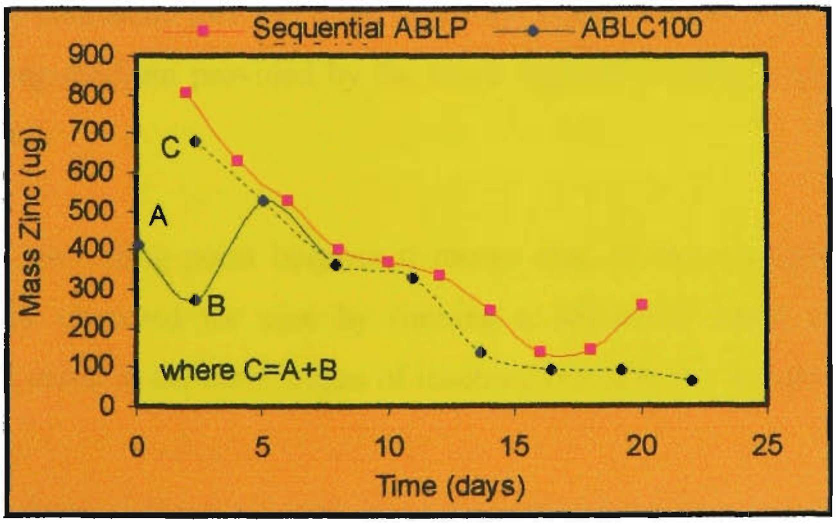


Figure 3.12: ABLC100 & Sequential ABLP – Mass Zinc Leached v's Time

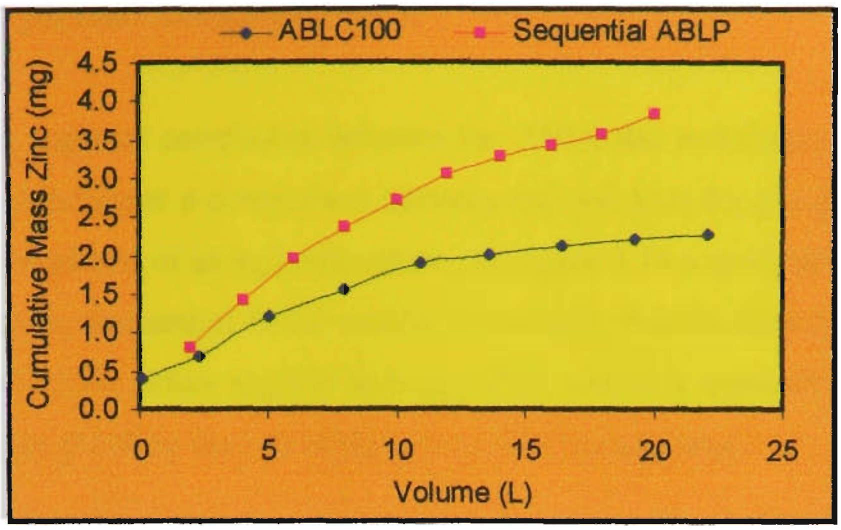


Figure 3.13: ABLC100 & Sequential ABLP - Cumulative Mass Zinc Leached v's Time

The only significant difference between the two tests is that almost twice the amount of zinc leached out in the Sequential ABLP, in an equivalent volume leached, compared with that in the ABLC100 (Figure 3.13). Early work by Jackson *et al* (1984) compared column leaching of polystill bottoms to an 18 hour batch test and used equivalent flow rates over four 18 hour time periods. They found that the pattern of zinc leaching from the waste was also very similar between the two tests, the difference, once again, being that much larger amounts of zinc were leached from the batch test. They concluded that this trend probably reflected better contact of the waste with the leaching medium provided by the more aggressive sample agitation used in the batch method.

This is a very interesting point because it means that, in this instance, a pattern of leaching can be observed for zinc by running a sequential batch test due to the correlation that exists in the early stages of leaching between the Sequential ABLP and the ABLC100.

3.3.2.1.2.1 *pH and Conductivity Effects*

There was no apparent correlation between the ABLC100 and Sequential ABLP for redox potential, however a comparison between the two tests for pH and conductivity demonstrate the effects of an agitated system. In Figure 3.14 a gradually increasing pH is observed for the Sequential ABLP results. In contrast, that for the ABLC100 reaches a maximum of 12.71, before slightly leveling off to relatively constant pH values (and then dropping to pH<9 by the end of the test some 50 weeks later).

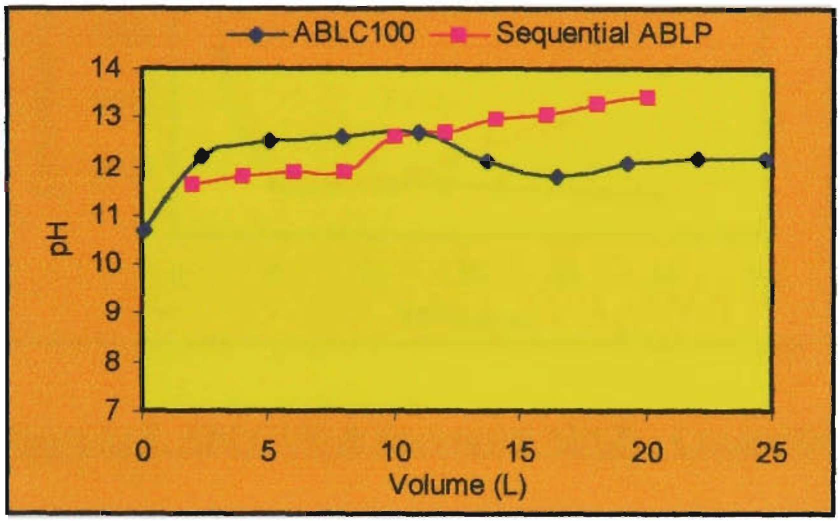


Figure 3.14: ABLC100 & Sequential ABLP – pH

The constant physical agitation of the system in the Sequential ABLP has resulted in a greater concentration of $Ca(OH)_2$ more rapidly leaching from the cement stabilised waste. This has, in turn, led to higher pH values. Not only does the agitation rapidly solubilise the surface available $Ca(OH)_2$ and zinc, it also, by way of particle abrasion or break-down, frees up more surface area for leaching. This effect, observed in batch tests, is obviously not apparent with column tests where the only movement is the leachant through the waste. A column test, therefore, will abrade the waste to a much lesser extent, and lead to lower pH levels in the leachant for cement-based wastes.

The same effect was observed in the conductivity results, illustrated in Figure 3.15. The first point in the ABLC100 conductivity results is not included as it was from the surface wash of 54ml and, consequently, was extremely concentrated in surface fines. Regardless, it can be seen that the conductivity levels in both tests start off extremely high before stabilising at around 1500μScm^{-1} after 8L of leaching. It is at this point that the Sequential ABLP shows a rapid rise in conductivity while the ABLC100 demonstrates a steady decrease.

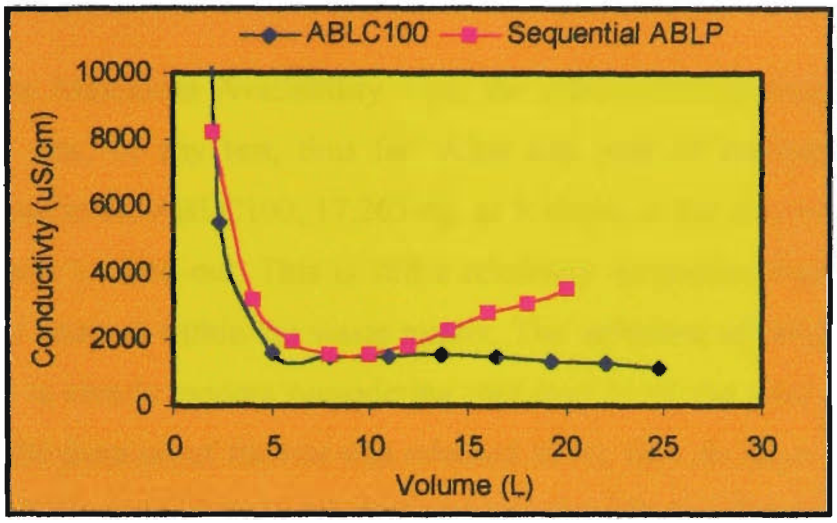


Figure 3.15: ABLC100 & Sequential ABLP – Conductivity

Although there is no distinct correlation between the leaching of zinc and the conductivity results for the Sequential tests, the results suggest that the leachant concentrations of both zinc and $Ca(OH)_2$ are heavily dependent upon the surface area of the waste that is available for leaching. Further, the fact that $Ca(OH)_2$ seemed more leachable as surface area increased (as compared to zinc) may only be due to the higher concentrations of calcium in the original waste. This increase in $Ca(OH)_2$ leaching with increase in leachable surface area has been detailed by many authors (Brown *et al* 1986, Shively *et al* 1986, Bishop 1988). The results do, however, contrast with similar work which suggests that an increase in porosity arising from the leaching of $Ca(OH)_2$ will lead to greater metal leachability (Brown *et al* 1986, Bishop 1988, Kolvites & Bishop 1989, Bishop *et al* 1992).

These are important results as they demonstrate the effects a single parameter can have in a leaching test. The situation could quite conceivably arise where a heavily contaminated zinc-containing waste fails a TCLP or ABLP in the laboratory due to a combination of the leachant agitation, sample abrasion and the crushing step required in both tests, yet never be a concern in a landfill situation where matrix breakdown would be gradual over a long period of time.

3.3.2.2 ABLC180; Leaching Behaviour of Zinc

Apart from the Maximum Availability Test, the ABLC180 has leached the largest percentage of zinc, of any test, thus far. After one year of leaching at flow rates identical to those in the ABLC100, 17.265mg, or 0.426%, of the zinc originally present in the waste was leached out. This is still a relatively insignificant amount, showing zinc to be well retained within the waste matrix. The influence of early zinc release in the ABLC180 is clearly evident considering that over ¼ of the total amount of zinc leached over the duration of the test was released in the first six days. Further, it took 51 days for half the amount to be leached and 151 days for ¾. Figure 3.16 illustrates the leaching behaviour of zinc for this column and depicts the influence of surface wash-off early in the test.

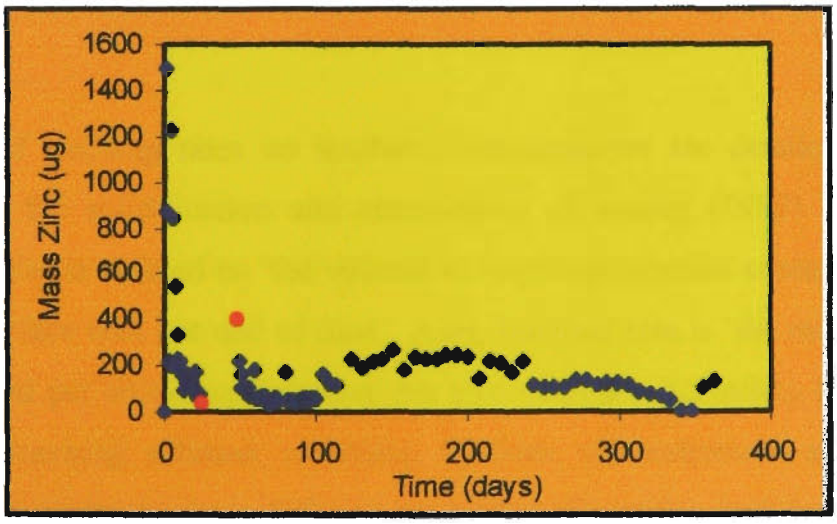


Figure 3.16: ABLC180 – Mass Zinc Leached v's Time

Notice the break in sampling between the two red points at 24 and 48 days. Unfortunately, the water de-ioniser and peristaltic pump broke down for 17 days meaning there was no flow of water through the column during that time. In a real landfill situation, it was essentially equivalent to a deluge followed by a drought. In order to try and still obtain some useful information from this 'hiccup', it was decided that the flow of water would remain off for a total period of four weeks.

Therefore, the experiment began with four weeks of flow where a steady pattern of leaching had begun to develop, followed by four weeks of stagnant or no flow. The effect this had on the mass of zinc leached can be clearly seen in Figure 3.16. After earlier steadily decreasing to just under 40μg leached, following the period of no flow, the mass of zinc in the leachate jumped back up to over 400μg. It was a further 21 days before the levels of zinc dropped back down to 40μg in the leachate.

All evidence in this research thus far has pointed to zinc leaching being dominated by surface wash-off in the early stages of leaching, followed by more gradual release thereafter where contributions from diffusion and dissolution become more dominant. If there was no flow, and the matrix would not be expected to break down as quickly in this sort of environment, then the fact that high concentrations of zinc accumulated in the leachate so rapidly suggests the possibility of another contributory leaching mechanism.

The effects of leaching rates on leachate concentrations are detailed in a USEPA document on the solidification and stabilisation of wastes (1989). In it, leaching solution velocity is defined as 'the volume of leaching solution contacted with waste per unit of surface area per unit of time'. Also, leaching rate is 'the mass of the waste species leached per unit of surface area per unit of time'. According to this research, under rapid leaching solution velocities, leachate concentrations are very low if leaching of the waste species is diffusion controlled. Therefore, high leaching rates and low leachate concentrations occur at the particle surface under rapid leaching velocities because non-equilibrium conditions at the particle surface are maintained.

At low leaching solution velocities (static hydraulic conditions), the amount of a species leached approaches the saturation limit. Low leaching solution velocities and maximum leachate concentrations will therefore occur when the leaching solution is not replenished, and the same leaching solution is allowed to equilibrate with the waste (USEPA 1989). Batchelor (1997) has also discussed these limiting cases of leaching.

In the case of ABCL180, both scenarios have been effected. For the first 24 days and the last 317days of the test, high leachant velocities were pumped through the column. After the leaching of some high concentrations of zinc in the beginning by surface wash-off, low concentrations were observed for most of the remainder of the test. According to the previous paragraphs, these low levels would suggest diffusion control as the main cause of leaching.

Closer inspection of the ABLC180 data illustrated in Figure 3.16 reveals a high value, as expected, for the first sample following the resumption of leachant flow. However, after this, a further 21 days elapsed before the mass of zinc dropped to the levels observed prior to the dry period. This suggests that the mechanism originally responsible for leaching zinc toward equilibrium with the leachant may have continued to affect the quantity of zinc available for leaching once the flow of water resumed. Note that this mechanism is, however, still influenced by an equilibrium condition. That is, during the dry period, zinc will gradually diffuse through the pores toward the leachate-particle boundary to maintain equilibrium. Consequently, when the leachant flow resumes, the distance for zinc to travel to the leachate boundary is reduced resulting in a greater rate of zinc release until the original concentration profile is re-established. In this case, 21 days had elapsed before this occurred.

One anomaly with this theory for the ABLC180 was also observed consistently in the ABLC100 and, to a lesser extent, in the large column. This was the periodic decreases and increases in the mass of zinc in the leachate. If zinc were leaching predominantly by equilibrium/diffusive processes, these positive and negative spikes would not be expected to occur as frequently as they did. In fact, these fluctuations are more likely to be the result of a gradual matrix breakdown freeing up more waste surface for leaching. Hence the sudden increases, followed by less rapid decreases.

It appears from these results that diffusion and matrix dissolution also affect zinc leaching, although those mechanisms do not seem to leach zinc as readily as surface wash-off. The idea that diffusion is a contributory mechanism certainly makes sense for the period of no-flow. Here, there was no movement of liquid or waste, so the only mechanism by which metals could leach would be diffusion. After the flow resumed, diffusion was still significant as the zinc took some time to return to 'pre-drought' levels, relative to the conductivity results. However, eventually the diffusive contribution decreased in comparison to that from matrix dissolution, hence the steady leaching and random release spikes as the experiment wore on.

Although the period of no flow was unintended in this case there has been other work where stop/start flow was investigated. Foster (1998) carried out a series of column experiments, using the same small columns and fixed waste as those used in this study, that focused primarily on the effect of a stop-start leachant flow regime on waste leaching. The only difference was that the waste was separated into two particle size ranges (0.6-2.36mm and 2.36-4.75mm), whereas the waste used in this work was all reduced to be less than 2.36mm.

He employed two irrigation scenarios nominated as 'wet then drain' and 'constant soak'. The 'wet then drain' scenario involved a surface wash of 100g of the fixed waste in the small column to initiate the irrigation. After one week, 2L of de-ionised water was passed through the column (downflow) and removed under suction leaving only a fine film of water on the waste particles. The 2L flushing was repeated the following week meaning that for a seven day period the waste was not immersed in leachant. The fixed waste in the 'constant soak' scenario was not surface washed, and was immersed in de-ionised water from the outset. Every seven days the leachate was removed under vacuum from the column while, at the same time, a fresh 2L of leachant was introduced. This 2L of fresh leachant was used to flush the old leachate out, and its introduction was halted when a small amount of liquid was visible at the head of the column. In this way the column was filled with fresh leachant every seven days, but was never exposed to air. These experiments were carried out for 18 weeks. The 'constant soak' scenario is effectively the same as occurred in the present work for the ABLC180 where the flow stopped for a period of four weeks before resuming.

Foster's results show that, for both large and small particles, the 'constant soak' scenario leached significantly higher amounts of zinc than did the 'wet then drain scenario'. Further, the levels for zinc increased sharply in the second week of leaching for the 'constant soak' with the small particles, before slowly decreasing in concentration over the following weeks. This agrees with the results in the ABLC180, which showed zinc levels increasing sharply following resumption of leachant flow after the dry period, and then taking a few weeks to return to their previous levels.

Another interesting result from Foster's work is that the small particles leached more zinc than the large particles for both scenarios. This disagrees with previous reports that larger cement-based waste particles will initially leach higher masses of metals than smaller ones due to the much higher pH in the leachate from the smaller particles (see Section *1.3.4.2.2.2*). His work was, however, conducted over a very short time frame, and the expected results may be borne out over a longer time period with such a low leachant velocity. Evidence for this was presented where the leaching of zinc from the large and small particles (for both scenarios) appeared to be drawing toward one another as the tests neared their conclusions.

3.3.2.2.1 pH, Redox Potential, and Conductivity Effects on Zinc Leachability

There appeared to be no obvious correlations between the mass of zinc leached in the ABLC180 and the pH, or redox potential of the leachates. Figures 3.17 and 3.18 also show pH and redox trends unaffected by the dry period during the second four weeks. Foster's research also demonstrated that zinc leaching within each column was not notably influenced by variations in pH and redox potential (1998).

Figure 3.19, however, shows a relatively strong correlation between the leaching behaviour of zinc from the 180g small column and the conductivity measurements. The conductivity of the leachant samples was seen to decrease in an almost identical fashion, at the start of the test, to the mass of zinc leached. Following the dry period, the conductivity also increased for the first sample collected. However it immediately decreased to original levels following this first sample, as opposed to the zinc levels which took three weeks to drop as far.

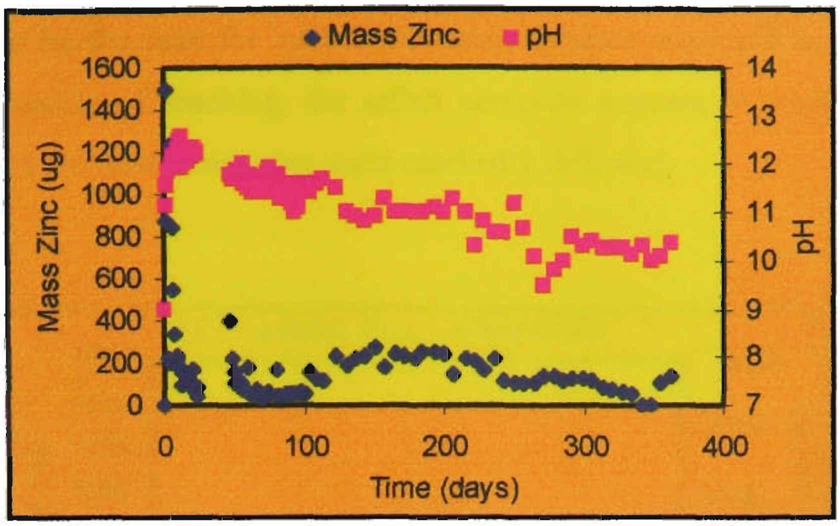


Figure 3.17: ABLC180 - Mass Zinc Leached and pH v's Time

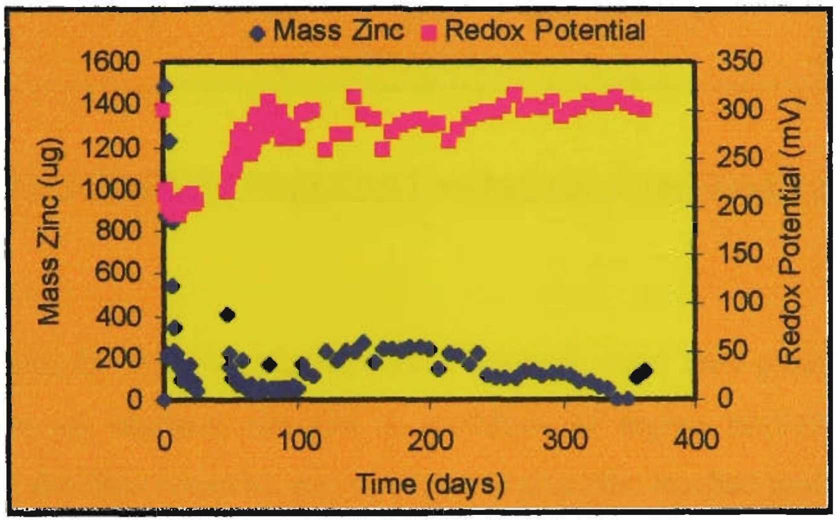


Figure 3.18: ABLC180 - Mass Zinc Leached and Redox Potential v's Time

It has already been intimated in Section *3.3.2.1.1* that the majority of the species released from this waste would be soluble calcium salts (specifically $Ca(OH)_2$). Consequently, conductivity is believed to be a good indicator of leached alkalinity. Therefore, this initial similarity between conductivity and metal release suggests pore-initiated diffusive leaching is a contributory mechanism of leaching during the period of no flow in the ABLC180 (Brown *et al*; 1986, Bishop; 1988).

It was mentioned in Section *3.3.2.1.2.1* that the effect the leaching of $Ca(OH)_2$ has on matrix porosity has been shown to result in greater metal leachability. Although this did not seem to be the case for ABLC100 where surface wash-off is the suspected dominant mechanism of leaching, the effect certainly appears be more obvious for ABLC180 where the flow conditions were markedly different.

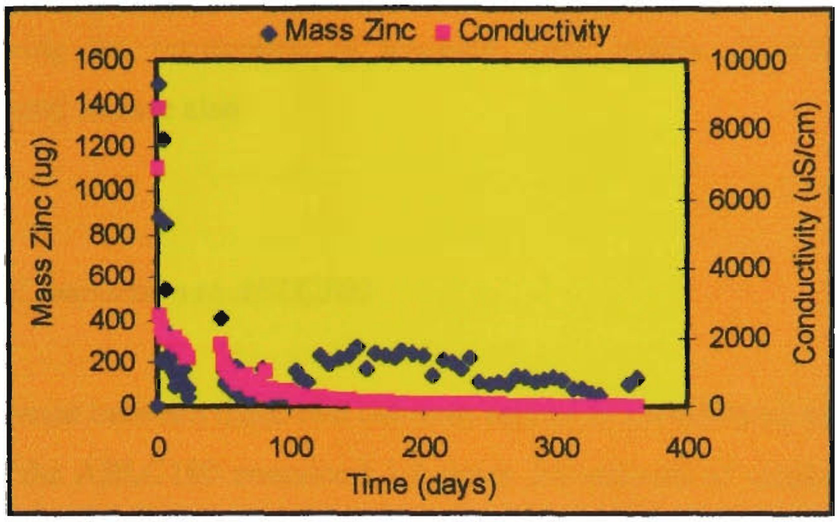


Figure 3.19: ABLC180 - Mass Zinc Leached and Conductivity v's Time

In this case, where the waste was immersed in stagnant water for a period of time, the inward diffusion of leachant has led to a matrix of higher porosity, and hence tortuosity. Once the flow resumed, any newly available zinc leached gradually over the following weeks, while $Ca(OH)_2$ release was elevated for only a short time.

It appears, therefore, that, the alkalinity (and some zinc) diffused purely from the pores and leached immediately once the flow resumed. The greater levels of zinc removed in the following weeks, however, suggest that other soluble zinc species trapped in the solid matrix were also made available during the period of no-flow. As the alkalinity leached from the pores, and the liquid leaching front diffused into the waste particles leading to a more tortuous waste, these zinc species were mobilised, and, subsequently, gradually leached over the following weeks when the leachant flow resumed. If zinc release occurred by a number of mechanisms as suggested, it is to be expected that the release pattern will not match that for alkalinity as measured by conductivity. Hence the lack of long-term correlation between alkalinity and metal release which, as suggested by Brown *et al* (1986) and Bishop (1988), is indicative of diffusion from the waste pores.

These assumptions are reasonable, since, with no movement of waste or liquid in the system, diffusion is the only mechanism by which species could be leached from the matrix. Following the resumption of leachant flow, matrix dissolution can then contribute to metal release also.

3.3.2.2.2 Comparison to ABLC100

The only difference between these two columns relates to the differing masses of waste in each. Since the ABLC180 contained 1.8 times the amount of waste but employed the same flow rate, it was expected that this difference would result in greater amounts of zinc being leached from the ABLC180 than from the ABLC100. Further, the leaching patterns for both tests were expected to be very similar, as were the percentages leached from each column. Figure 3.20 illustrates the actual differences in leaching patterns observed between the two tests.

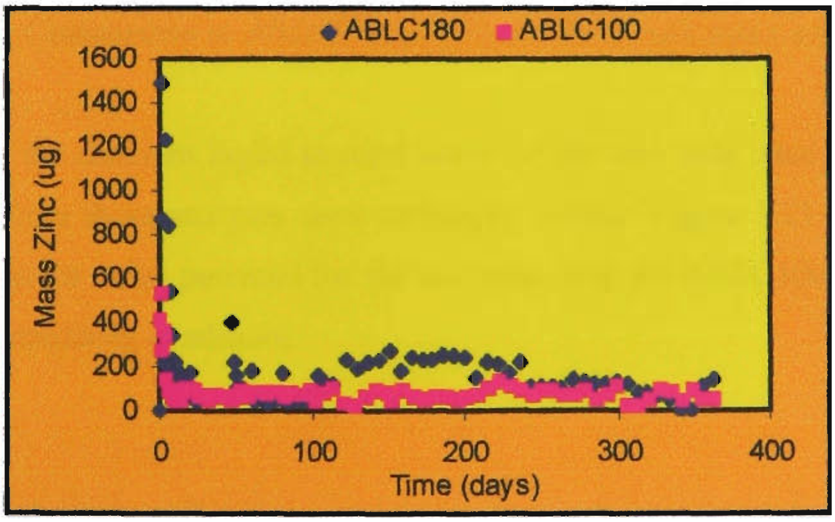


Figure 3.20: ABLC180 & ABLC100 – Mass Zinc Leached v's Time

The mass of zinc leached in the ABLC180 fluctuated significantly over the course of the experiment. There was a significant increase in zinc levels (>270μg) after 100days that wasn't observed with the ABLC100. The cause of this may be related to the dry period of four weeks in the ABLC180. The levels of zinc leached in the ABLC100 were essentially constant after 2 weeks of leaching, with minor spikes in either direction.

The percentage of zinc leached for each test also shows that the mass of waste (and contaminant) in the columns is not the only parameter that affects mass of contaminant leaching. While the ABLC180 leached 0.43% of zinc present in the waste, the ABLC100 leached only 0.32% of zinc. Obviously then, it cannot be assumed that twice the amount of waste present will lead to twice the amount of zinc leached. This difference in percentage leached could have resulted from any one of a number of factors (e.g. a sampling problem when filling the columns, leading to an uneven distribution of zinc in the waste), but most likely it was a combination of the dry period in the ABLC180, and the different L/S ratios in the two tests. Unfortunately, as the ABLC100 was operated uninterrupted, it is very difficult to compare these tests and provide a satisfactory answer.

3.3.2.2.2.1 Comparison to ABLC100; pH, Redox Potential, and Conductivity

The effects of the different liquid to solid ratios for the two tests were not significant. In fact, data from these analyses were strikingly similar. Figure 3.21 illustrates very similar patterns for redox potential for the two tests, with the ABLC100 recording only slightly more oxidising conditions.

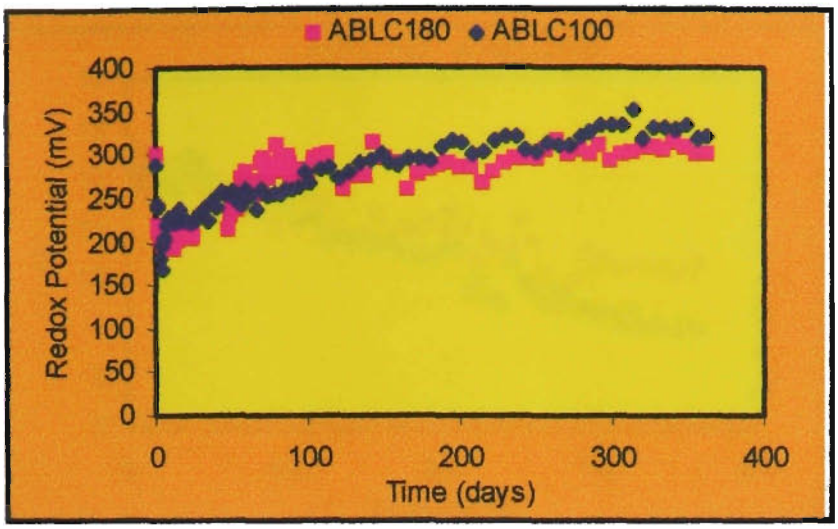


Figure 3.21: ABLC180 & ABLC100 – Redox Potential

The conductivity and pH results, as shown in Figures 3.22 and 3.23, are as expected. They show the ABLC180 to have leached higher amounts of alkalinity, although with the same pattern as that observed for the ABLC100. This has led to a higher final pH for the ABLC180, once again, with a pattern similar to the ABLC100. Townsend *et al* (1999) used lysimeters, both saturated and unsaturated with simulated rainfall, to investigate the leachate produced from a variety of mixed and unmixed construction and demolition wastes (C&D). Their research showed that, in contrast to the small column work presented here, a change in L/S ratio actually had a minimal effect on dissolved solids in some of the leachates. They found that 'the steady-state concentrations of dissolved solids in the mixed C&D waste unsaturated columns for both Experiment 1 and 2 were relatively the same despite a greater leaching volume addition during experiment 1'. Although the waste and methodology are different to those used in this work, the C&D research shows that variations in L/S ratio can also have different effects on other types of wastes.

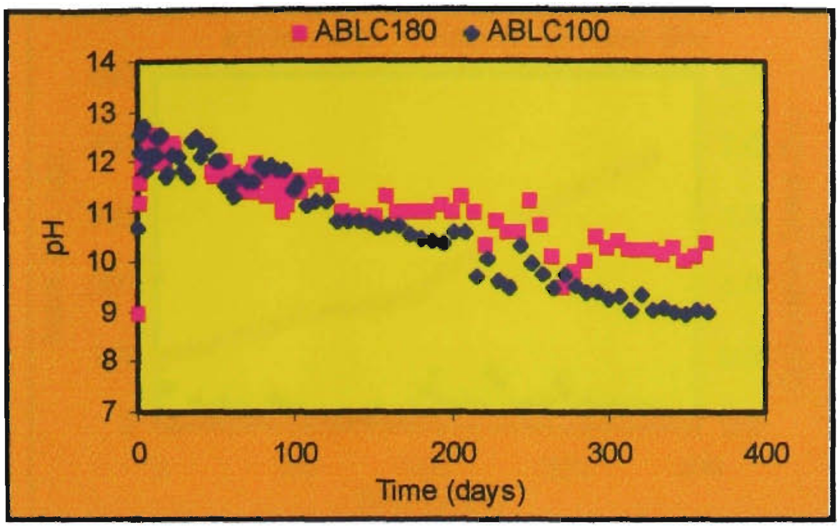


Figure 3.22: ABLC180 & ABLC100 – pH

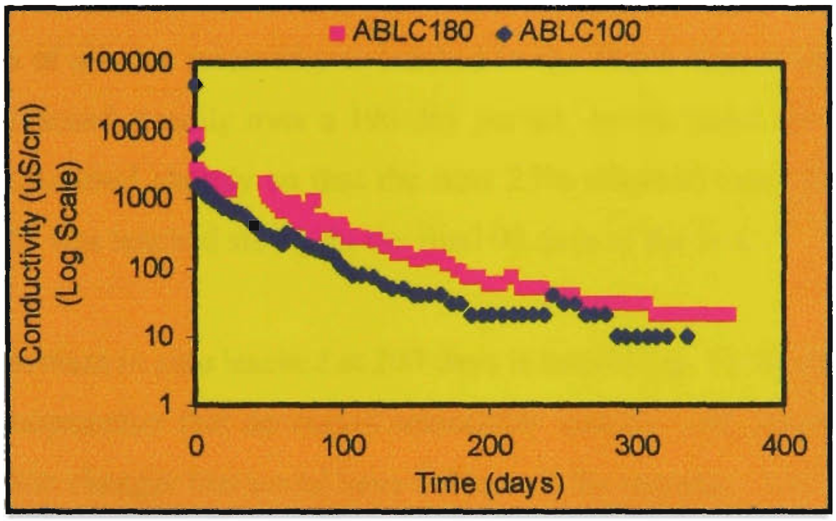


Figure 3.23: ABLC180 & ABLC100 – Conductivity

3.3.2.3 LCC100; Leaching Behaviour of Zinc

Tables 3.5 and 3.7 show that LCC100 leached the least of all the columns with only 0.084% of zinc present in the column being released to the leachate. As with all of the columns observed thus far, a substantial quantity of zinc was released in the first few days, as illustrated in Figure 3.24. Surface wash-off, therefore, appears to be a dominant mechanism of leaching once again in the early stages of the leaching test.

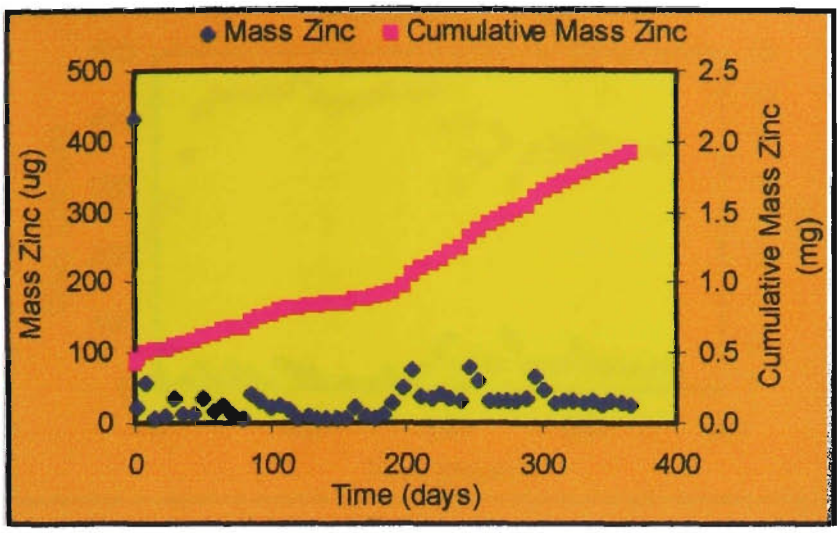


Figure 3.24: LCC100 - Cumulative Mass Zinc Leached v's Time

The first 25% of all zinc released was leached in the first 8 days of the test. The next 25% of zinc leached steadily over a 190-day period. At this point the mass of zinc in the leachate increased sharply so that the next 25% released took only 70 days. The remaining 25% was leached slowly in the final 90 days of the test.

The sudden increase in zinc leached at 200 days is interesting. Firstly because it wasn't a spike in concentration that decreased reasonably quickly, and, secondly, there were no test condition changes that could have influenced the increase. The steady pattern of leaching appears to correlate well with diffusive/dissolution type of leaching.

3.3.2.3.1 pH, Redox Potential, and Conductivity Effects on Zinc Leachability

Probably the most interesting feature of the pH chart in Figure 3.25, is that the pH levels sharply decrease around the time the zinc levels rise. The Pourbaix diagram for zinc shows it to be soluble above pH 12 and form an insoluble hydroxide ($Zn(OH)_2$) between pH 8-12 (Pourbaix 1974). It appears, then, that the decrease in pH may have led to an increase in zinc leachability. However, had the pH decreased much further, the hydroxide species would probably have been formed and the zinc levels in the leachates decreased markedly.

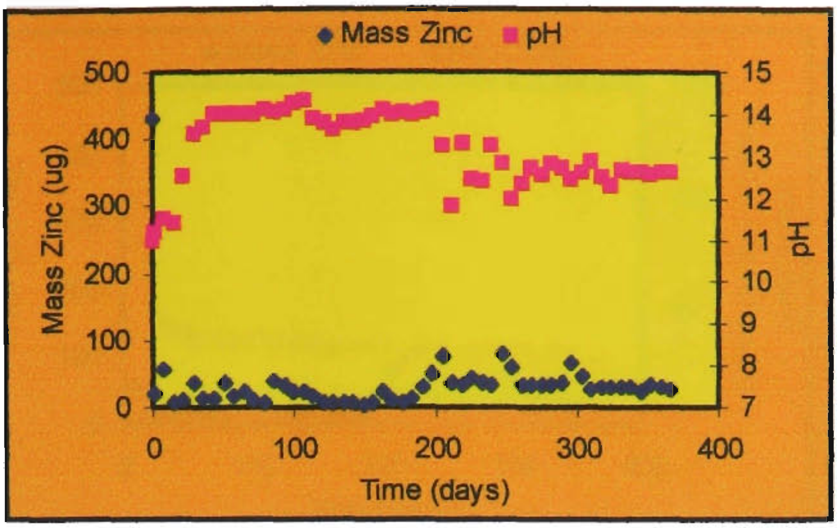


Figure 3.25: LCC100 - Mass Zinc Leached and pH v's Time

This sudden drop in pH also suggests a rapid drop in leachable $Ca(OH)_2$ levels within the waste matrix. This was observed to a minor extent where, as shown in Figure 3.26, the conductivity levels in the leachates decrease from 5000µS to 3500µS within a week at around the 200 day mark. Following this drop, the levels hovered around 3000-4000µS for the remaining 165 days of the test, and did not constitute a significant change.

The correlation, therefore, was not as strong as that for the Sequential ABLP (Section *3.3.2.1.2.1*) which showed higher pH levels coinciding with higher conductivity levels in those leachates. However, the data concurs quite well with the findings of a number of authors that suggest an increase in porosity arising from the leaching of $Ca(OH)_2$ will lead to greater metal leachability (Brown *et al* 1986, Bishop 1988, Kolvites & Bishop 1989, Bishop *et al* 1992).

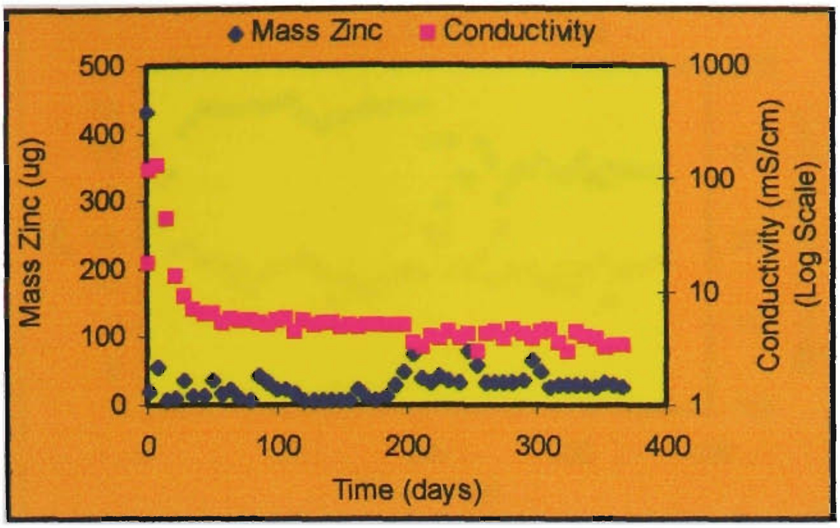


Figure 3.26: LCC100 - Mass Zinc Leached and Conductivity v's Time

More so than for any of the other leaching experiments investigated, the LCC100 showed a good correlation between mass of zinc leached and redox potential (Figure 3.28).

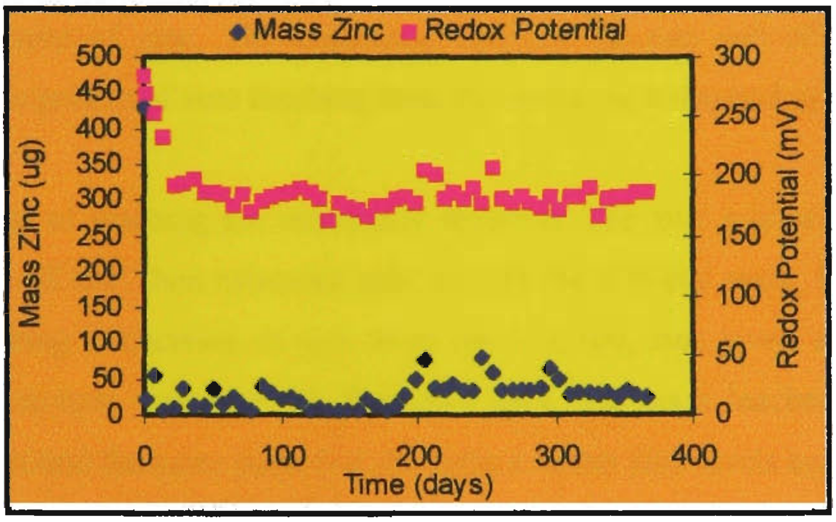


Figure 3.27: LCC100 - Mass Zinc Leached and Redox Potential v's Time

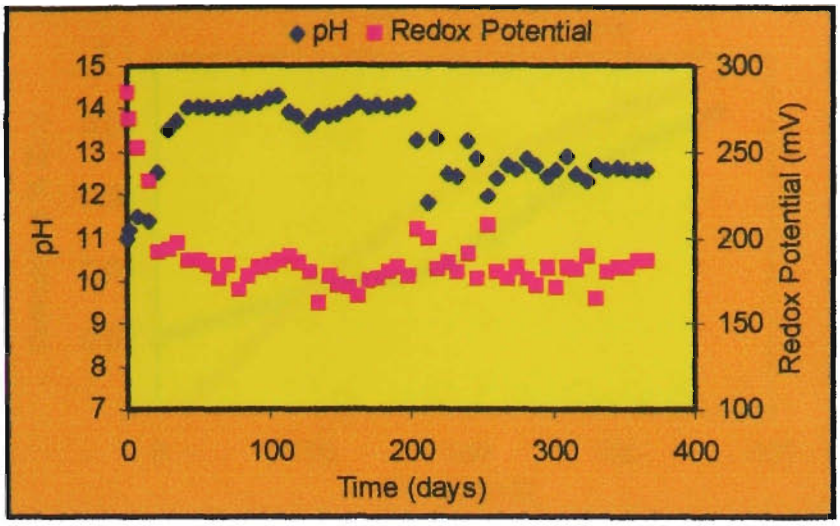


Figure 3.28: LCC100 - Redox Potential and pH v's Time

3.3.2.3.2 *Comparison to Large Column*

The LCC100 and Large Column leached very similar percentages of zinc from the waste, 0.085% and 0.093% respectively. What is important about these results is that two columns with identical liquid to solid ratios and leachant velocities leached almost identical fractions of zinc. The difference between the two sets of results can be observed in the pattern of zinc leaching from the waste, as illustrated in Figure 3.29.

The two trends of leaching are essentially reversed. The zinc release from the large column starts off low, then increases until around the 200-day mark, before levelling off and beginning to decrease in rate. With the LCC100, zinc levels are immediately high in the leachate, and, for the first 200 days, the mass leached is essentially constant. At around the same point that the large column zinc levels begin to decrease, those for the LCC100 increase sharply, before also beginning to decrease after around 300 days. By the end of both leaching tests, the zinc levels appear to be drawing toward one another.

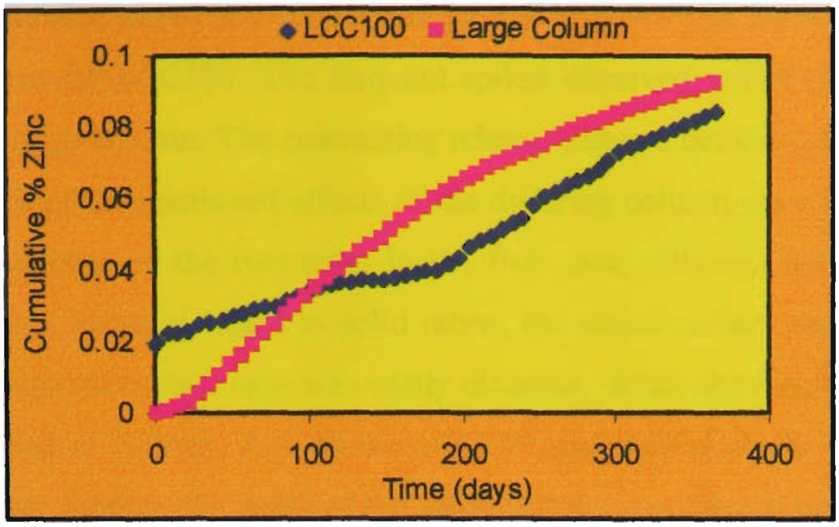


Figure 3.29: LCC100 & Large Column – Cumulative Percentage Zinc Leached v's Time

Therefore, aside from the early high zinc levels in the LCC100, the large column releases zinc at a much greater rate in the first half of both tests, with the LCC100 releasing zinc at a slightly greater rate for the remainder of the tests. This point is clarified by observing the data in Figure 3.30.

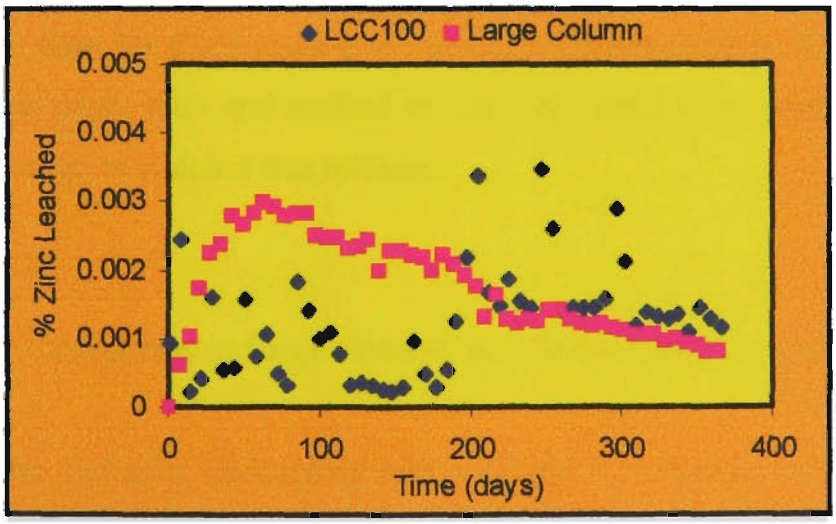


Figure 3.30: LCC100 & Large Column – Percentage Zinc Leached v's Time

What this figure also shows is that the trend for zinc release from the large column was far steadier than for LCC100. The frequent spikes observed with LCC100 were not seen with the large column. The contrasting release patterns between the two columns may be a result of the combined effects of the differing column sizes and methods of leachant introduction in the two tests. In the first case, although the columns were prepared to have identical liquid to solid ratios, the actual surface area to which the leachant was applied in each case was vastly different. While the large column had an internal diameter of 500mm, that for the LCC100, and indeed all the small columns, was only 25mm. Further, the depth of the waste in the large column was no more than 140mm, while the waste in the LCC100 was filled to a depth of approximately 230mm. Secondly, the leachant in the large column was sprayed onto the waste surface in the form of a fine mist, whereas, due to obvious size and volume limitations, the leachant for LCC100 was pipetted onto the surface of the waste.

The combination of these two factors would certainly have led to different types of channelling and wall surface effects in each column. Further, it has long been the contention of workers in this field that channelling, and surface effects, are two factors which can lead to significant uncertainty in the interpretation of column leaching results (Darcel 1983; Korfiatis *et al* 1984; Miner *et al* 1986; Förstner *et al* 1990; Förstner *et al* 1991; van der Sloot 1996). Therefore, while not affecting the overall release of zinc from the fixed waste over the one year period of the tests, the column diameter: waste depth ratio and method of leachant introduction may certainly have affected the manner in which it was released.

3.3.2.3.2.1 Comparison to Large Column; pH, Redox Potential, and Conductivity

In spite of the probable channeling and wall-effect variations between the two columns, the pH, redox potential, and conductivity results were almost identical. Of these, the pH results, illustrated in Figure 3.31, were the most striking in similarity. Not only is the overall trend for leachate pH the same, in many cases sudden positive or negative spikes are also the same between the two tests. As these column experiments were started one month apart, and hence the leachates were tested one month apart, the similarities could not be construed as laboratory error. That is, a faulty pH system did not contribute to the results. Further proof of this is the excellent correlation between the conductivity and redox potential results (Figures 3.32 and 3.33 respectively). Figure 3.33 shows slightly higher redox potential results for the large column, however the difference between the two is relatively insignificant when taking into consideration the overall trend correlation.

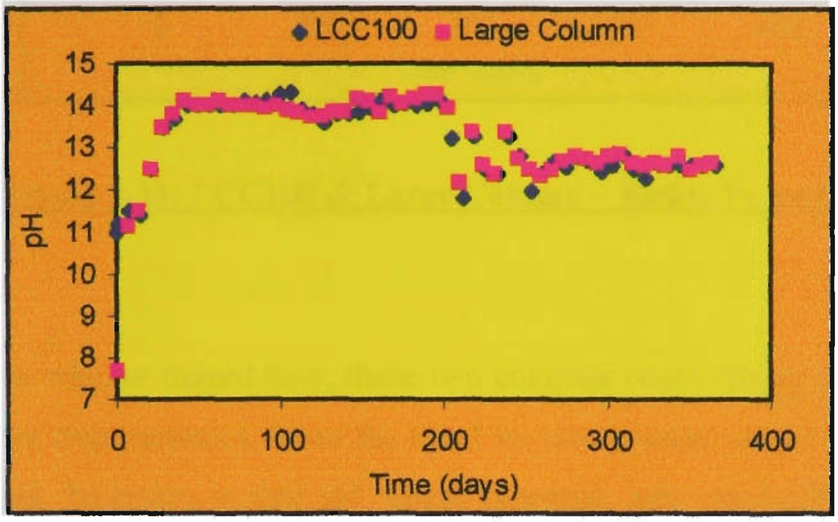


Figure 3.31: LCC100 & Large Column - pH

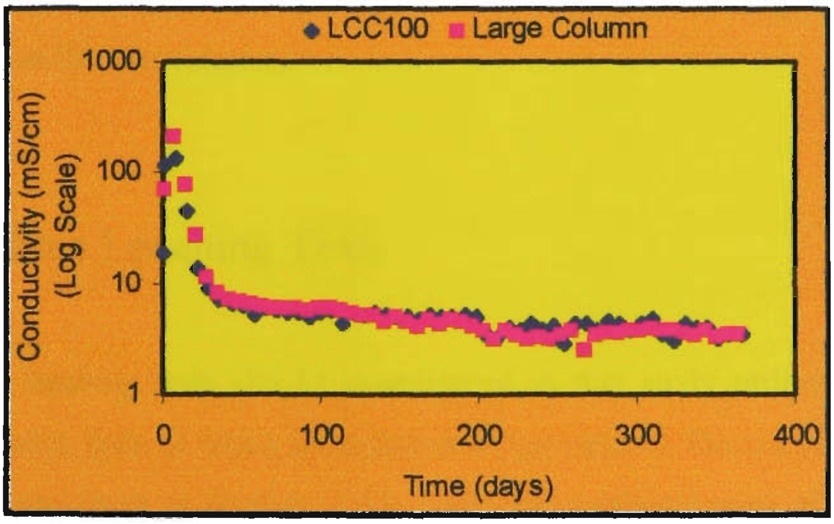


Figure 3.32: LCC100 & Large Column – Conductivity

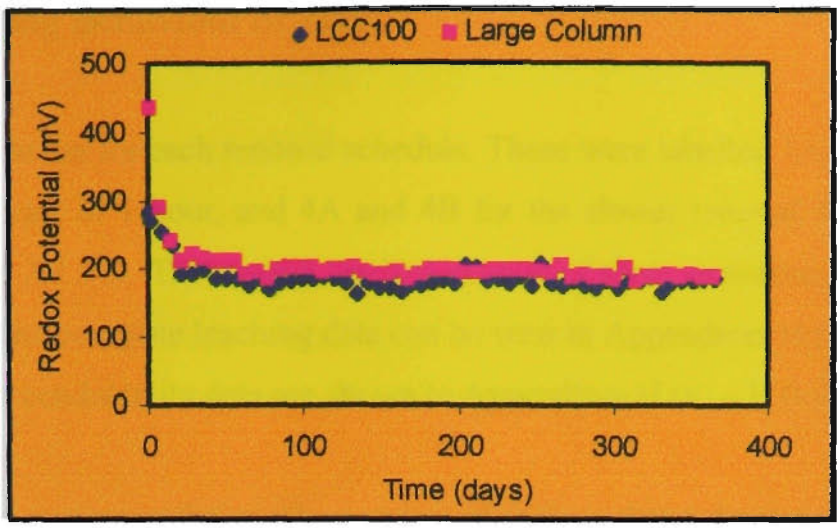


Figure 3.33: LCC100 & Large Column – Redox Potential

It is not known why, or indeed how, these two columns could supply almost identical results for these characteristics, when the trend for zinc release was so different. What this emphasises, however, is that pH, redox potential, and conductivity cannot, by themselves, provide a clear picture of how a metal will leach from a waste. As has been shown with this work, if that was attempted with the LCC100 and Large Column, the trend for either test would be incorrectly approximated in the short term. After one year of leaching, however, there was shown to be a correlation for percentage of zinc leached between the two columns.

3.4 Dynamic Leaching Tests

The dynamic leaching tests (DLT) investigated in this study utilised two leachant renewal schedules, both of which are detailed in Appendix C. Details of the waste used in these tests are given in Section *2.3.2*, while the methodologies of these tests are provided in Section *2.4.3*.

3.4.1 Leaching Behaviour of Zinc

Two DLTs were run for each renewal schedule. These were labelled 1A and 1B for the rapid renewal rate of 1 hour, and 4A and 4B for the slower renewal rate of 4 hours (Refer Section *2.4.3.2)*. The masses leached in each of these experiments are detailed in Table 3.8. The complete leaching data can be seen in Appendices H (i) – H (iv). All pH, redox, and conductivity data are shown in Appendices H (v) – H (viii).

It has been the recommendation of a number of authors that only one replicate of the DLT is performed due to the large number of samples taken in any one test (Environment Canada 1991b, Stegemann & Côté 1990). It was, however, deemed prudent that at least one more of each renewal schedule be run in case of any unexpected failures.

Table 3.8: Zinc DLT Test Data

Replicate	**t_n = 1A**	**t_n = 1B**	**t_n = 4A**	**t_n = 4B**
Mass Leached (mg)	0.71	0.74	0.60	0.90
% Leached	0.07	0.07	0.06	0.09

As it turned out this was a wise decision. Approximately 2 weeks after beginning the testing, a significant crack had appeared in sample 4B, almost completely bisecting the sphere. However, as the sphere was still in one piece the experiment was continued as normal. In fact, this provided an opportunity to observe the effects of increased surface area on the leachability of zinc in the DLT.

Table 3.8 shows the replicates for the 1-hour renewal schedule to be almost identical in terms of the percentages of zinc leached. Figure 3.34 further illustrates the similarity between the trends for the two replicates.

Spheres 4A and 4B, on the other hand, compare poorly. This may be ascribed to the aforementioned cracking of 4B. Figure 3.35 further illustrates the differences between the leaching of zinc from the two spheres.

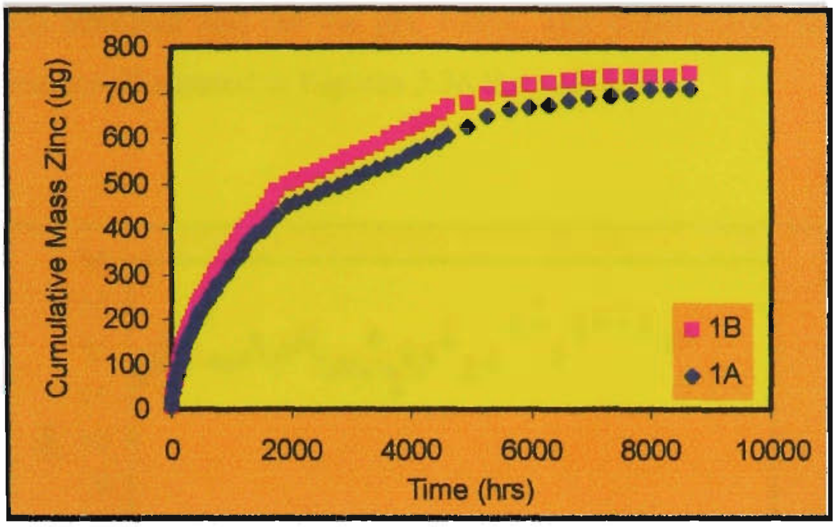


Figure 3.34: t_n = 1A & 1B – Cumulative Mass Zinc Leached v's Time

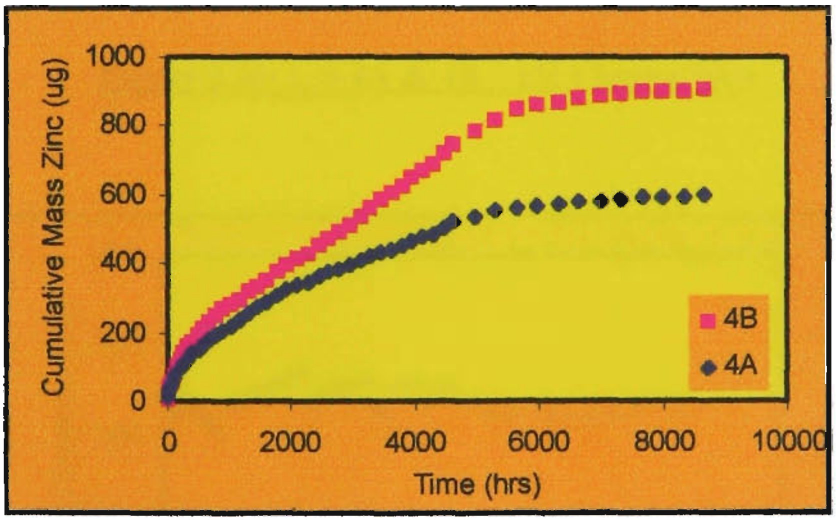


Figure 3.35: t_n = 4A & 4B – Cumulative Mass Zinc Leached v's Time

As the split was relatively symmetrical, an increase in surface area can be approximated. This increase would comprise an extra two available circular surfaces, lifting the available surface area from 40.7cm^2 to approximately 61cm^2, an increase of about 50%. As the results in Table 3.8 show, the percentage of zinc leached from sphere 4B was about 50% more than that from sphere 4A, and appears to show a direct relationship between surface area and the amount of zinc leached. This data supports earlier suggestions in Section *3.3.2.2* that zinc leaching may be a combination of wash-off from gradually increasing surface areas, followed by diffusion. The results are also similar to those from the comparison between LCC100 and the Large Column, where zinc release was different and yet the pH, redox, and conductivity results compared quite well. These are illustrated in Figures 3.36 through 3.38.

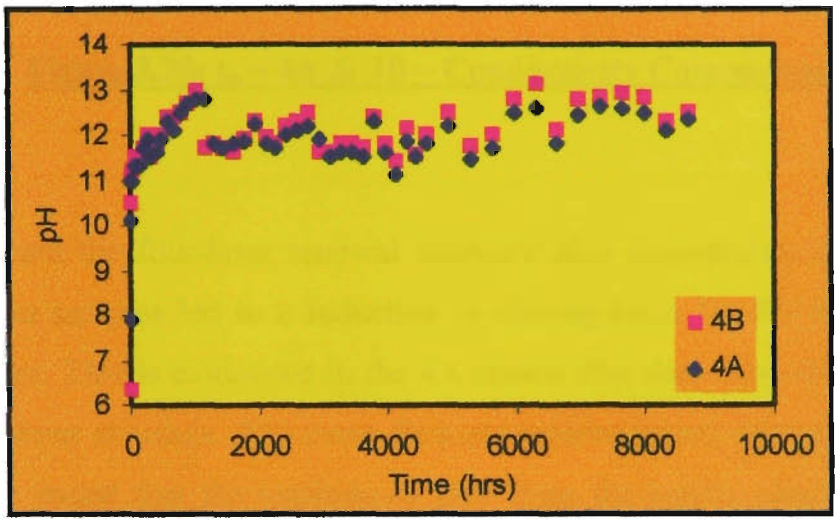


Figure 3.36: t_n = 4A & 4B – pH Comparison

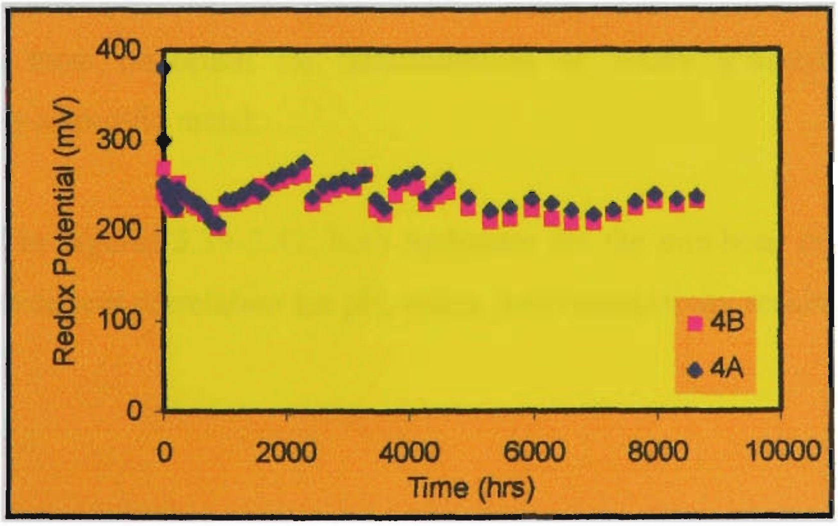


Figure 3.37: t_n = 4A & 4B – Redox Potential Comparison

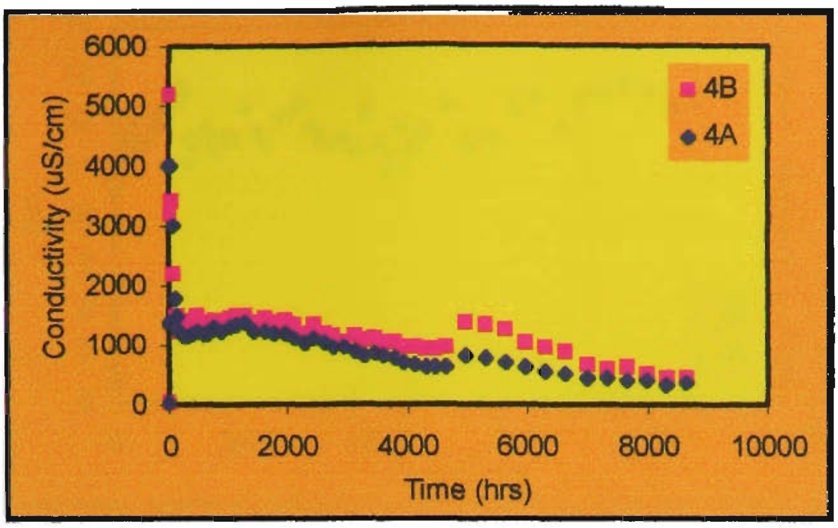


Figure 3.38: t_n = 4A & 4B – Conductivity Comparison

The results from the four-hour renewal schedule also demonstrate the longer time period between samples led to a reduction in driving-force for the leaching of zinc from the sphere. This is evidenced in the 4A results that show less zinc leached than from the one-hour schedule. The more frequent replenishment of leachant for the 1-hour schedule meant that the leaching of zinc from the matrix was essentially at a maximum. This differs from the 4-hour schedule where the zinc leaching was rate limited, decreasing significantly toward the end of each sampling period as the concentration of zinc in the leachant increased. Of course, as the renewal schedules were the same after 1764 hours of both tests had elapsed, the initial part of the leaching curve is the most important for determination of which schedule is the most appropriate for a specific metal.

As illustrated in Figures 3.39-3.41, both replicates for the one-hour renewal schedule also showed excellent correlation for pH, redox, and conductivity results.

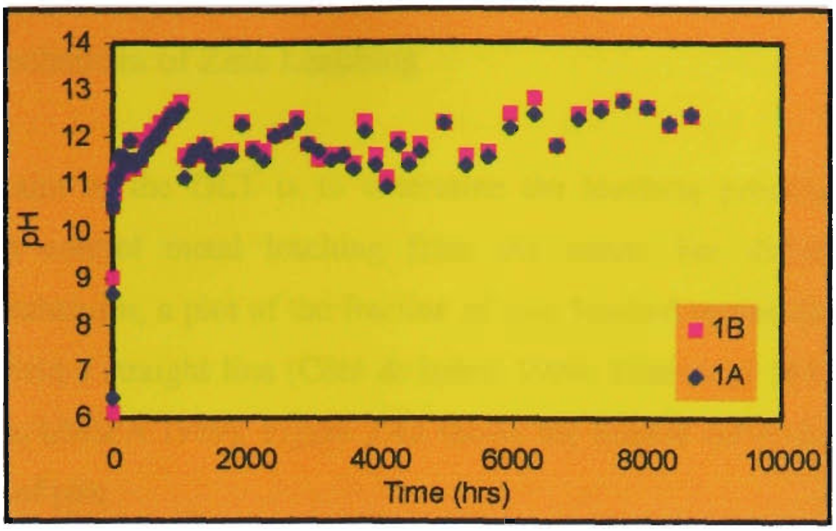


Figure 3.39: t_n = 1A & 1B – pH Comparison

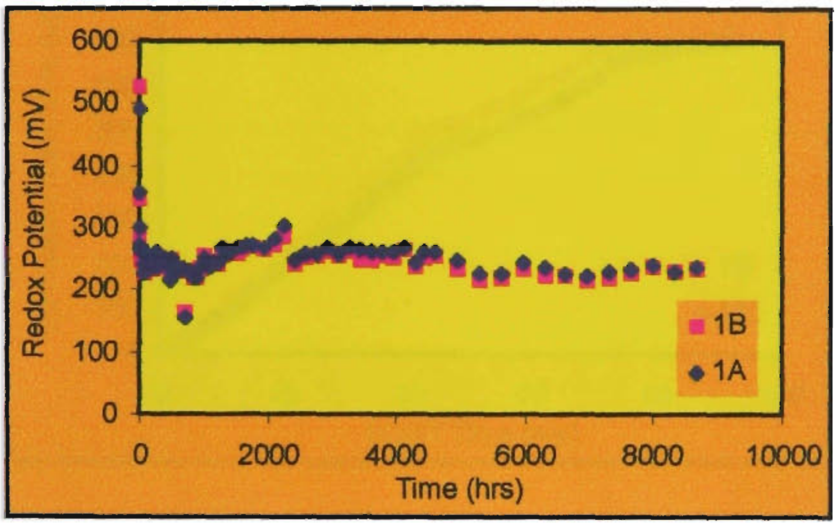


Figure 3.40: t_n = 1A & 1B – Redox Potential Comparison

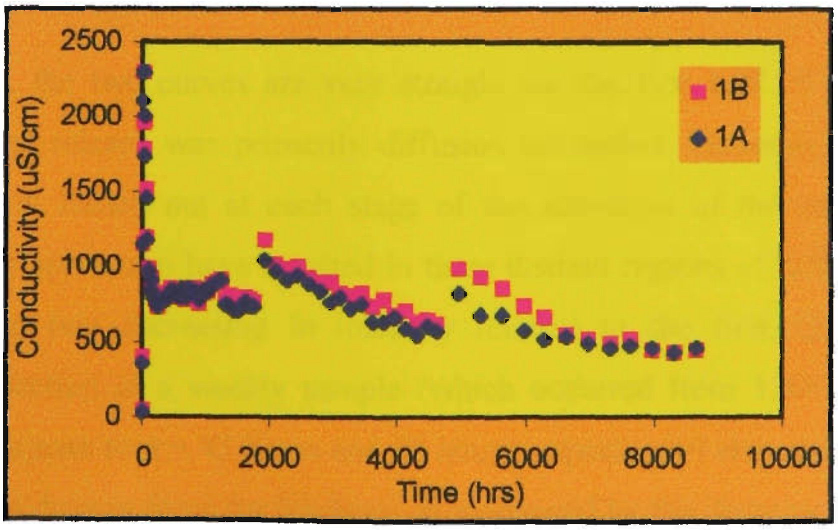


Figure 3.41: t_n = 1A & 1B – Conductivity Comparison

3.4.1.1 Mechanism of Zinc Leaching

The primary aim of the DLT is to determine the leaching processes, specifically diffusive, that control metal leaching from the waste. For diffusion to be the controlling mechanism, a plot of the fraction of zinc leached versus the square root of time should yield a straight line (Côté & Isabel 1984; Côté *et al* 1987; Environment Canada 1991b, USEPA 1989). Figure 3.42 shows the release curve for t_n = 1A & 1B with this type of plot.

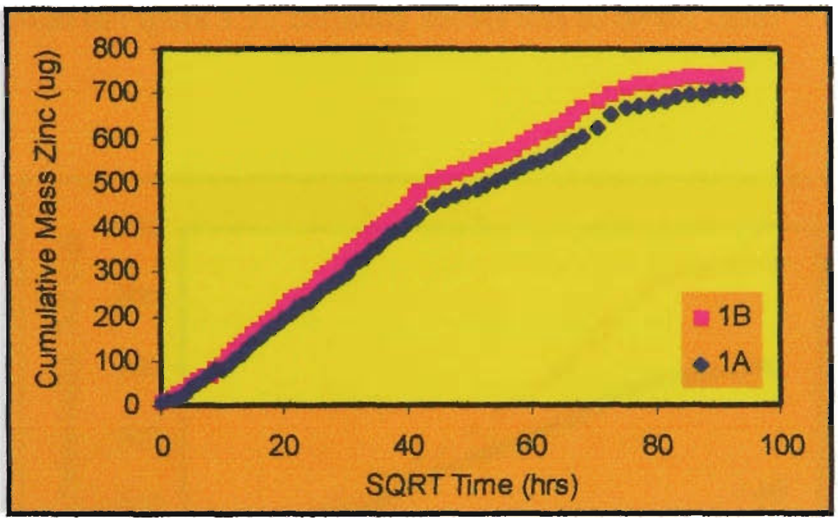


Figure 3.42: t_n = 1A & 1B – Cumulative Mass Zinc Leached v's Square Root of Time

As illustrated, the two curves are very straight for the first half of the experiment suggesting zinc release was primarily diffusion controlled. However, after this, the curves begin to flatten out at each stage of the alteration of the leachant renewal schedule. This appears to have resulted in three distinct regions of diffusive leaching, with the latter two decreasing in intensity relative to the first. Quite obviously, therefore, collection of a weekly sample (which occurred from 1764 hours to 3280 hours, where square root = 42 hours and 68 hours respectively) also resulted in a slight decrease in the driving force for leaching, as evidenced by the decrease in diffusion of zinc from the sphere.

While the overall amount of zinc released from sphere 4A was much less than from the 1 hour schedule, Figure 3.43 shows that, unlike spheres 1A & 1B, the change to a weekly renewal schedule had no obvious impact on the pattern of zinc diffusion from sphere 4A. Only when the renewal stretches out to fortnightly after 4620 hours does the pattern of leaching clearly alter. Sphere 4B shows yet another pattern of release altogether. Here, diffusive release is evident from the beginning of the test until around three months. At this point the plot of curves upward for some time until the renewal frequency becomes fortnightly. According to Andrés *et al* (1995) a linear relationship between cumulative release and time is indicative of matrix dissolution, and the upward curve observed in Figure 3.43 is the consequence of a linear plot. Comparison to the same period in Figure 3.35 certainly shows this to be the case.

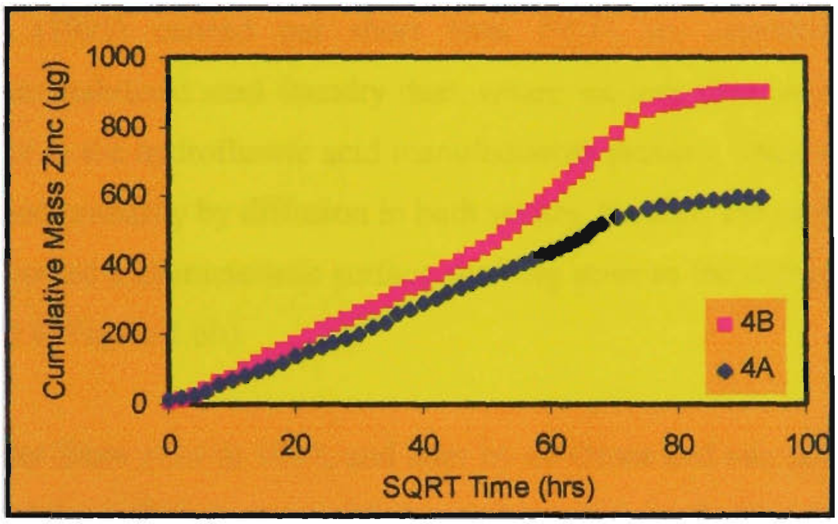


Figure 3.43: t_n = 4A & 4B – Cumulative Mass Zinc Leached v's Square Root of Time

The cracking of sphere 4B has, therefore, resulted in an increase in zinc leaching due to not only to an increase in diffusion of species from the sphere, but also matrix dissolution. This is important data as it demonstrates the significance of producing a strong solidified waste. If a waste such as that produced in this work was landfilled, and ended up cracking in situ, the result would be an increased release of zinc via processes other than purely diffusive release.

What all this data shows is that, regardless of the leaching schedule employed, diffusion is the dominant mechanism of zinc leaching in the DLT. Any extension of the schedule in terms of the time allowed between sampling resulted in a reduction in the amount of zinc released from the spheres, but did not alter the actual mechanism of zinc leaching. Further, the cracking of the sphere led to a greater release of zinc through matrix dissolution, rather than simply increasing the degree of diffusion that occurred.

Lewin (1996) investigated the leaching properties of cement-solidified incinerator ash using, among other tests, a 384 hour tank test very similar to the DLT. He found that zinc leached primarily via diffusion, and that leachate pH was unlikely to be a factor in influencing zinc release.

Andrés *et al* (1995) carried out short term DLTs on cement-stabilised and cement/anhydrite-stabilised steel foundry dust, where the anhydrite was obtained as a residual product in the hydrofluoric acid manufacturing process. They also found that zinc was released primarily by diffusion in both wastes. Further, the sample containing no anhydrite showed a characteristic surface washing prior to the diffusive release (as seen previously in Figure 1.6b).

Work by van der Sloot *et al* in 1989, and later by de Groot and van der Sloot (1992), provided a slightly different means of determining the mechanism of release. By plotting the cumulative release against the time on a log-log scale, and observing the basic slope of the resultant curve, the major contributing mechanism (or combination of mechanisms) can be determined. They ascertained that a slope of +1 is indicative of dissolution of the matrix, +0.5 points to diffusion control, while a slope of zero signifies surface wash-off. Anything in between the lines is a combination of those mechanisms. These release mechanisms are illustrated in Figure 3.44.

These plots are depicted in Figures 3.45 and 3.46 for both DLT schedules. According to these figures, the mechanism of zinc leaching from the spheres in both schedules was primarily diffusion with a small amount of surface wash-off in the first few hours of the test. This finding is also in agreement with earlier data assessment showing diffusion to be the dominant mechanism of leaching for zinc in this type of system.

Due to the compression of data in these plots it is difficult to see any evidence of the period of dissolution observed in Figure 3.43, however the overall influence of diffusive release is the important aspect of these plots.

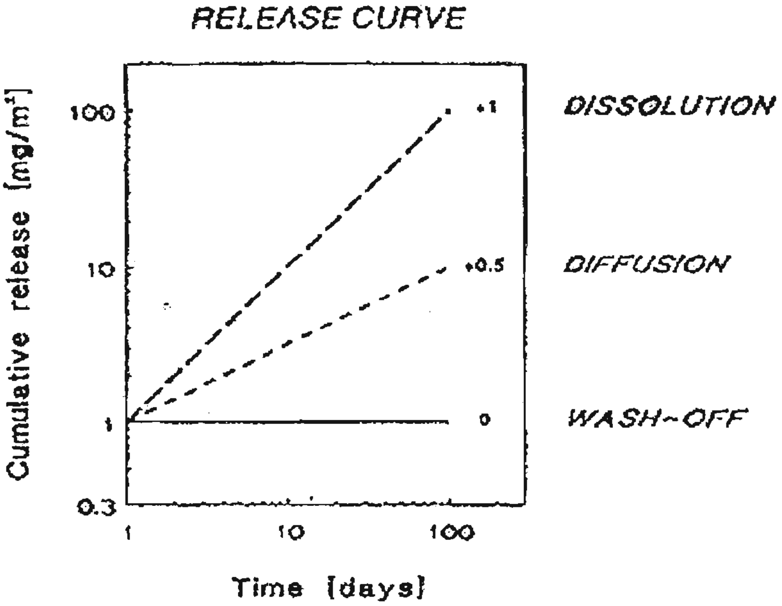


Figure 3.44: DLT Release Mechanisms (de Groot & van der Sloot 1992)

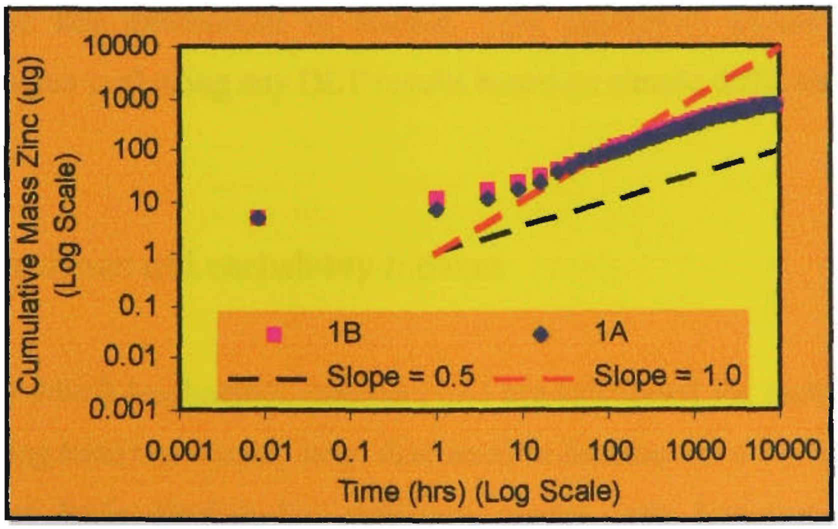


Figure 3.45: t_n = 1A & 1B –Cumulative Mass Zinc Leached v's Time

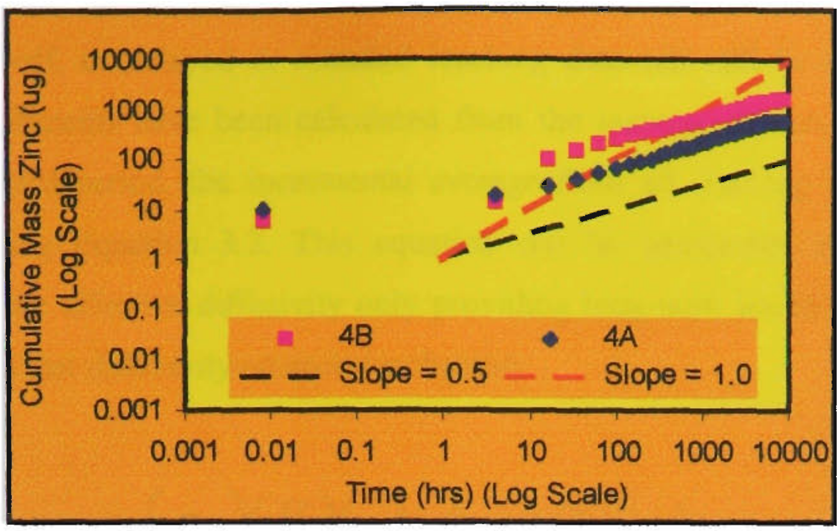


Figure 3.46: t_n = 4A & 4B –Cumulative Mass Zinc Leached v's Time

Although the DLT data for zinc suggests diffusion is the controlling leaching mechanism, it should also be noted that simple chemical equilibrium between a metal and the leachant can often be (at least partly) responsible for this correlation. That is, according to the sampling periods chosen using the formula detailed in Section *2.4.3.2*, when the leaching rate is sufficient to have a chemical equilibrium form between the contaminants in the leachate and those in the solid, constant concentrations of contaminants will be released in different leaching periods. Consequently, although equilibrium is a significant contributor to the leaching process, it will appear that diffusion is the key mechanism of release. This possibility should always be a consideration when evaluating any DLT results based on simple diffusion models.

3.4.1.2 Calculation of Leachability Indexes

The method by which leachability indexes (LX) are calculated for metal release from dynamic leaching tests has already been discussed in Section *1.3.4.5*. An alternative to the well-known basic Godbee-Joy diffusion model (see Equation *1.1*) for the calculation of diffusion coefficients was proposed by Côté and Isabel (1984) and is detailed in Equation 3.1. While Equation 1.1 allows diffusion coefficients to be calculated from only the straight part of the curve, Equation 3.1 allows the inclusion of all data. That is, although diffusion must still be the dominating mechanism of release, surface wash-off, or delayed or retarded leaching data can still be included. Once diffusion coefficients have been calculated from the incremental leach rate of each leachant renewal period, the incremental average from all leaching periods is then calculated using Equation 3.2. This equation can be interpreted as the negative logarithm of the effective diffusivity only providing long-term leaching data support the hypothesis that diffusivity controls leachability.

$$\left(\frac{a_n}{A_0}\right)\left(\frac{V}{S}\right)\left(\frac{1}{\Delta t_n}\right)=\left(\frac{D_e}{\pi}\right)^{\frac{1}{2}}\frac{1}{T_n^{\frac{1}{2}}}$$

where:

Δt_n = Duration of the leaching period (s)

T_n = Time (middle of the leaching period) (s)

a_n = contaminant loss during leaching period, n, (mg)

A_0 = initial amount of contaminant present in the specimen (mg)

V = specimen volume (cm^3)

S = specimen surface area (cm^2)

D_e = effective diffusion coefficient (cm^2/s)

Equation 3.1 (Côté and Isabel 1984)

$$LX=\frac{1}{m}\sum_{n=1}^{m}\log\left[\frac{\beta}{D_e}\right]_n$$

where:

LX = Leachability index

β = Constant, 1 cm^2/s

m = Number of leaching periods

D_e = effective diffusion coefficient (cm^2/s)

Equation 3.2 (Côté and Isabel 1984)

Although Côté and Isabel state that this approach is more generally applicable to shorter term leaching tests, it was chosen here to allow the inclusion of all leaching data, and not just that which is included in the straight part of the curve. In this way, even if diffusion is the dominant mechanism, any metals released due to other processes can be included in the calculations which will, hopefully, better represent the leachability of the species from the spheres.

3.4.1.2.1 Zinc LX Values

The LX values for zinc release from the DLT spheres are detailed in Table 3.9. The table shows the overall LX values for zinc release as well as the indexes for the first seven leachant renewal periods, which is the number employed in the ANS-16.1 protocol (USEPA 1989).

Table 3.9: Zinc LX Data

Sphere	**t_n = 1A**	**t_n = 1B**	**t_n = 4A**	**t_n = 4B(a)**	**t_n = 4B(b)**
LX - 1st 7 Periods	13.21	13.19	12.60	13.08	13.42
LX - Total	14.21	14.18	13.46	13.92	14.27

The values for sphere 4B are split into two columns. Column t_n = 4B(a) represents the calculation of the LX value based on the external surface area of the sphere, while column t_n = 4B(b) uses a total surface area which includes an approximation for the increase in surface area due to the cracking of the sphere.

As can be seen from this data, the diffusion of zinc from the spheres was quite minimal. A simplified interpretation of LX data represents values of between 5 and 10 as being indicative of higher leach rates, while 10 to 15 suggests slower leach rates (USEPA 1989). As the range of overall LX data was 13.46 to 14.27, this certainly shows zinc release from the spheres to be quite slow. The LX values for the first seven intervals are also lower than those for the entire experiment due to the greater influence of the surface wash-off in the early stages of the test.

Another interesting aspect to this data is the fact that sphere 4A released far less zinc than 4B, yet was shown to have a lower LX value. It is possible that this can be explained by looking at the model boundary condition of zero concentration in the leachate. Côté and Isabel (1984) point out that, for a given renewal frequency, a lower waste strength more closely approximates this boundary condition. That is, as the measured concentration in the leachate increases, the simple diffusion model assumption of zero surface concentration becomes less valid, and the diffusivities calculated are underestimated (and LX values become inflated). Therefore, as sphere 4B, by virtue of its cracking, had a far greater amount of zinc available than 4A over the course of the experiment, its LX values are higher due to a poorer approximation of that boundary condition. It is just as likely, however, that, when taking into account the cracking of sphere 4B, the surface area may have been over-approximated. This, in turn, would also have contributed to an under-approximation of leaching.

Due to the same violation of the model boundary condition explained above, LX values were expected to decrease with increasing renewal frequency (Côté & Isabel 1984). This was, however, not the case as the LX values from the 1-hour schedule were higher than for sphere 4A meaning that, in this case, the boundary condition was not violated. This suggests that, when the spheres remain intact, the simple diffusion model assumption of zero surface concentration remains valid for zinc in the 4-hour DLT.

It is also important to note that Côté and Isabel (1984) recommended that a pseudo-equilibrium test be performed on the spheres to ensure that saturation does not limit the leaching process. By this, it is meant that a sphere should be immersed in the leachant for thirty days without leachant renewal to provide a saturation limit for the species of interest. When calculating diffusion coefficients, it is recommended that any data utilised falls between the analytical detection limit of the method of analysis, and the saturation limit, to ensure that the calculations are derived from testing where saturation did not limit the leaching process. Unfortunately, these experiments were not performed. However, the fact that two leachant schedules were carried out for the

DLT experiments should provide a range of leachability for each metal which takes into account any variation in metal diffusion brought about by the possibility of in the longer-term renewal frequencies.

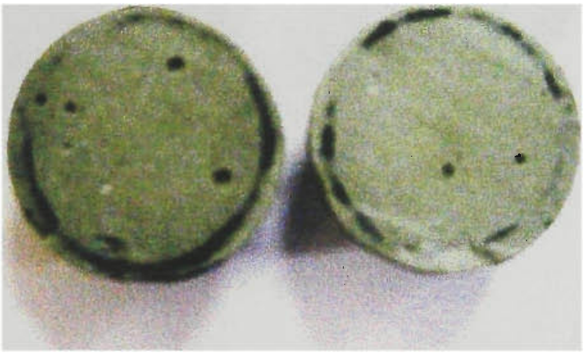
3.4.1.3 PIXE Analysis

PIXE analysis on the cement spheres was made possible via a grant from the Australian Institute of Nuclear Science and Engineering (grant number 00/176) and was conducted at the Australian Nuclear Science and Technology Organisation nuclear facility at Lucas Heights, Sydney, Australia. The grant allowed for three days of instrument time.

PIXE is a fast, simultaneous, multi-element, surface analysis technique. The PIXE work conducted allowed observation of the relative concentrations of metallic species within the leached spheres as a function of distance from the surface of the spheres. This information assisted in characterising the leaching behavior of metals as they escape the matrix. The spheres were cut in half using a water-cooled diamond saw and subjected to PIXE analysis along the diameter of the cross section of the semi-spheres. In initial trials on the semi-spheres, the concentration profiles for K, Ca, Ti, Mn, Fe, Cu, Zn, As and Pb were obtained. Interpretation of the data was difficult due to its erratic nature. This erratic behaviour of the data was an artifact of the small size of the proton beam spot (50 microns) and the heterogeneity of the cement. Further trials conducted on sphere 4B using larger spot sizes (100-1000 microns) produced much less erratic data since chemical heterogeneities between neighboring cement grains across the surface were averaged out. Due to restricted instrument availability, only one of the halves of sphere 4B was re-examined. PIXE experimental details are given in Section *2.5.4*.

As detailed above only one half of sphere 4B was re-examined by PIXE analysis. Sphere 4B was cut along the fracture to allow observation of its effect on leaching in the vicinity of the fracture compared to behaviour exhibited by the other spheres which had not fractured. However, the two halves of sphere 4B had a 4mm wafer of cross section removed and this may destroy any such effects (see Section 2.5.4). Figures 3.47 to 3.50 show the photographs of all semi-spheres and, as can be seen, their cross sections appear similar, with a dark concentric ring present near the outer edge. The dark streaks on the cross sections of the sphere 4B halves are believed to have been produced by the saw when the wafers were removed. Even though the two halves of sphere 4B had a 3mm wafer of cross section removed, the PIXE examination of this sphere still reveals information on the movement of metallic species as they are leached from the spheres.

Figures 3.47 to 3.50 also show small air bubbles to be present in all spheres, suggesting that, regardless of the time and effort spent to ensure minimal imperfections in the test samples, some degree of structural heterogeneity will always occur.



Sphere 1A

Figure 3.47: Sphere 1A

Sphere 1B

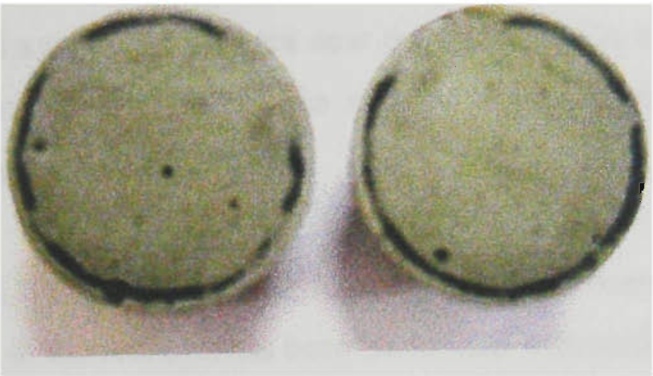


Figure 3.48: Sphere 1B

Sphere 4A

Figure 3.49: Sphere 4A

Sphere 4B

Figure 3.50: Sphere 4B

Similarly, each sphere displays evidence of a small 'crater' where the cement/waste mixture was injected into the mould. Cheng *et al* (1991) found that water segregation during casting created a more porous area near the crater which, in their case, led to greater acid penetration in that area of the sphere. They also mention that longer leaching periods can exaggerate this effect.

The effects of the DLT on cement-based waste spheres has been well documented, although the majority of the research has been performed with acidic leachants (Baker & Bishop 1997; Cheng & Bishop 1992; Cheng *et al* 1991). Baker and Bishop (1997) present an excellent diagram which summarises the principles of the shrinking unreacted core (SUC) model, and this is reproduced in Figure 3.51.

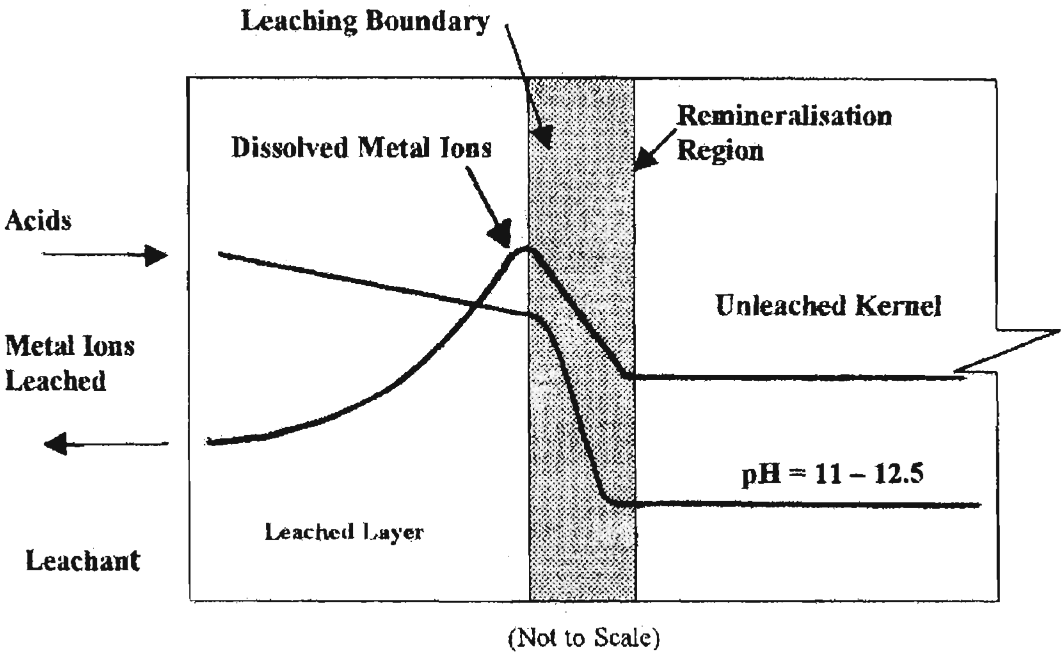


Figure 3.51: Principles of the Shrinking Unreacted Core (SUC) Model (Baker & Bishop 1997)

While it is essentially designed for acid leaching, the fundamental processes outlined in the model (and detailed in Section *1.3.4*) can still be applied to water leaching. As the leachant moves through the solid, a leached shell, depleted of free calcium and contaminants, will be formed. Lea and Desch (1970) found water to decompose cement pastes by dissolving lime and some alumina. Further, continued leaching left a residue of hydrated silica, iron oxide and alumina, which was a soft and mushy mass. Although these physical characteristics were not observed for any of the spheres leached in the DLT experiments, it is not known how long leaching must take place in water before these characteristics will present themselves. It was also suggested that this decomposition can be accelerated by acidifying the water. Similarly, Cheng and Bishop (1992) have presented research that shows that the metal leaching rate could be affected by the presence of this leached layer. They also found that the acid leaching of cement spheres removed the majority of species, while silicon and some iron and aluminium remained. It was suggested that, as these remaining species are likely to absorb/adsorb dissolved free metal ions leaching through this surface layer, the metals leaching rate could be hindered.

The movement of the leaching front through the solid will also lead to the dissolution of metals and the subsequent formation of a concentration peak at the leaching boundary. These dissolved metals can then diffuse either inwardly to the centre of the sample or outwardly to the bulk solution. The ions that diffuse inward could be supersaturated in the pore water and re-precipitate when they encounter the increasing pH of the unleached cement-based material. It is believed that calcium is the dominant species in this reprecipitation zone, and will show itself as a thin white line on the inside of the leaching front. Although this does not seem to be present in Figures 3.47 to 3.50, the fact that the line is generally only 100μm wide and the resolution of the photographs is poor may be why it is difficult to see.

As shown in Figures 3.47 – 3.50, all spheres have dark rings near the outer edges. Cheng *et al* (1991) investigated the leaching of cement/waste spheres via dynamic leaching tests. They found that the leaching boundary existed on the inner edge of a dark grey ring around the sphere, just before the remineralisation region. This was also supported by Baker and Bishop (1997), and is illustrated in Figure 3.51. According to this, and previous discussion, it is believed that the dark rings on the spheres investigated in this work represent the leaching boundary, and that the metal concentration peaks would be expected to be on the outer edge of the dark rings. Figure 3.52 illustrates the PIXE data for zinc and shows concentration peaks at 388mm and 421mm, approximately 1mm in from the left edge of the sphere and 2mm from the right. This supports earlier suggestions that metal concentration will be present in higher amounts at the leaching boundary. Further, the concentration of zinc drops sharply toward each edge of the sample, and to a much lesser extent toward the centre. In fact, the middle area of the plot demonstrates zinc levels to be quite homogeneous throughout the sphere. It appears, therefore, that, as the zinc at the leaching boundary has dissolved, the majority has diffused outward into the bulk solution with a much smaller amount reprecipitating further into the sphere.

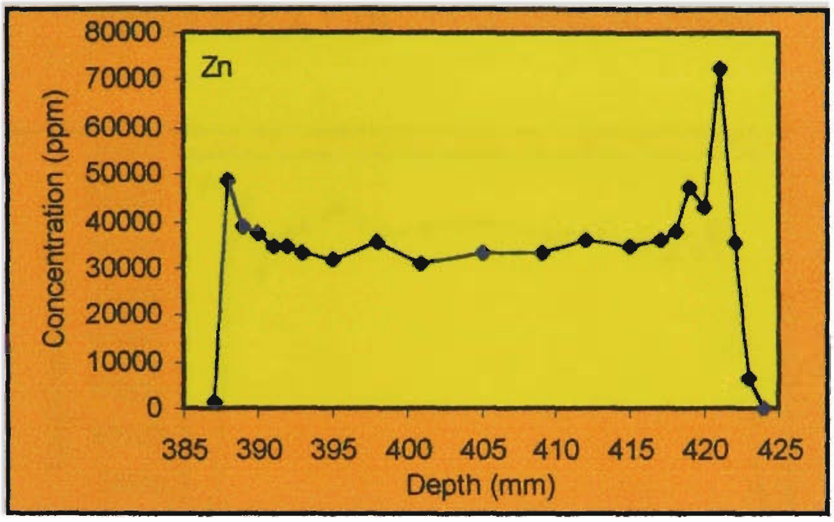


Figure 3.52: t_n = 4B – PIXE Data for Zinc

It is also interesting to note that the zinc levels on the left side of the plot form a lower concentration peak than those on the right by some 25,000ppm. It was thought that this may be due to an increased amount of silicon, iron, and aluminium in that part of the sphere, which would lead to greater retention of metallic species via adsorption. However, as Figures 3.53 – 3.55 illustrate, the iron, aluminium, and silicon levels show varying degrees of increased concentrations on the left side versus the right, suggesting if any retention of zinc did occur, it would be on the left side of the surface of the sphere that was analysed.

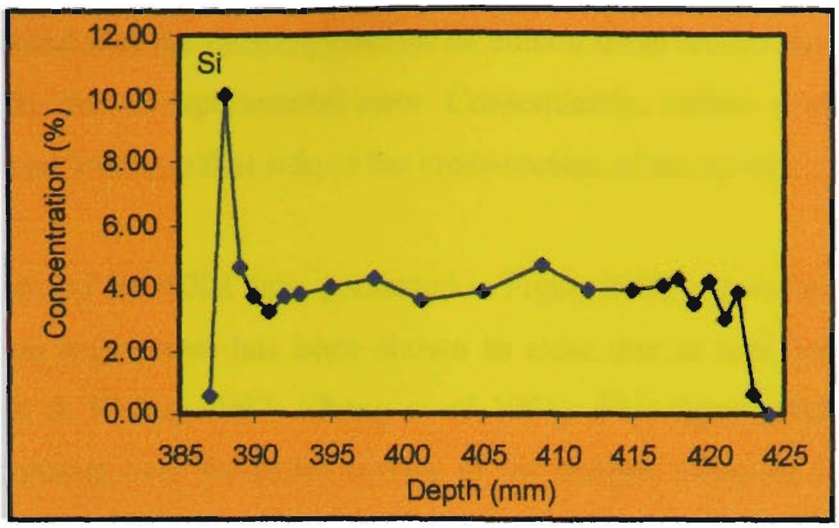


Figure 3.53: t_n = 4B – PIXE Data for Silicon

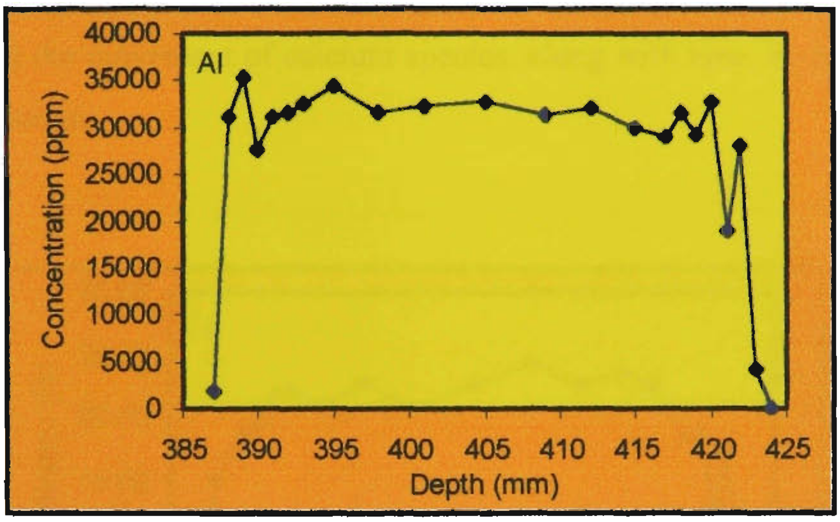


Figure 3.54: t_n = 4B – PIXE Data for Aluminium

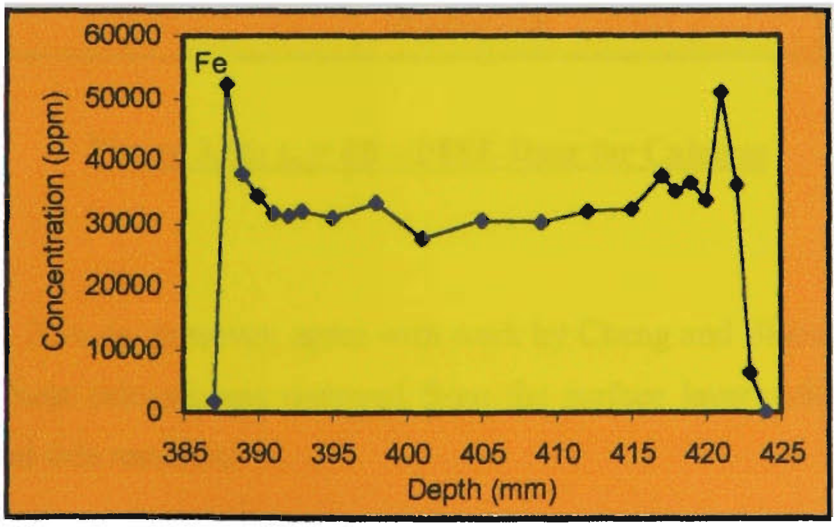


Figure 3.55: t_n = 4B – PIXE Data for Iron

It should be noted that the massive amount of silicon observed on the left side of the sphere might be due to experimental error. Consequently, further work is required to determine silicon levels on that side of the cross-section of the sphere.

The calcium plot of the PIXE data, presented in Figure 3.56, shows no evidence of the remineralisation region that has been shown to exist due to acid leaching by other authors (Baker & Bishop 1997; Cheng *et al* 1991). This figure shows the calcium levels to be constant over the entire surface of the sample, dropping away over a 5 – 6mm width at each edge of the sample surface. If the calcium was diffusing into the sphere, a concentration spike would be expected to be seen on the inside of the leaching front, and this would be at around 5mm in from the left and right sides. Since this is not the case, and calcium levels decrease toward the outer edges, it can be concluded that the movement of calcium species, along with zinc, is out of the sphere to the bulk solution.

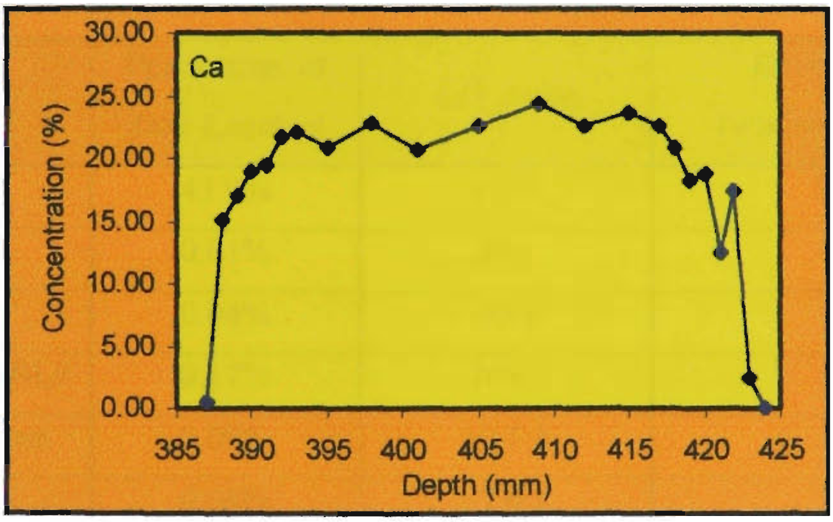


Figure 3.56: t_n = 4B – PIXE Data for Calcium

Figures 3.53 – 3.56 do, however, agree with work by Cheng and Bishop (1992) which showed that most calcium was removed from the surface layer, while some silica, aluminium, and iron remained.

While the PIXE work has proven valuable in describing the concentration gradients of the metals over the cross-section of sphere 4B, further work on other spheres will shed more light on the leaching behaviour of the metals as they leach from the spheres.

3.5 Summary of Zinc Leaching

A summary of zinc leaching from every leaching test conducted in this work is presented in Table 3.10. Not only does this table provide an absolute percentage of zinc leached from each test, and the final L/S ratio from each test, it also displays the amount of zinc leached as a ratio relative to the ABLP result, which has been given the arbitrary unit of 1. This allows for a better visual comparison between the results.

Table 3.10: Summary of Zinc Results From All Tests

Test	Percentage of Zinc Leached	L/S Ratio	Ratio Leached (where ABLP = 1)
MAT	43.9%	9.8:1	1097.5
TCLP	0.01%	20:1	0.25
ABLP	0.04%	20:1	1
Sequential ABLP	0.17%	200:1	4.25
Large Column	0.09%	19.1:1	2.25
LCC100	0.08%	17.6:1	2
ABLC100	0.32%	9571:1	8
ABLC180	0.43%	4873:1	10.75
DLT; T_n = 1A	0.07%	634.3:1	1.75
DLT; T_n = 1B	0.07%	626.2:1	1.75
DLT; T_n = 4A	0.06%	445.2:1	1.5
DLT; T_n = 4B	0.09%	447.5:1	2.25

Table 3.11 provides a breakdown of when the majority of the zinc was leached in the column and tank tests. That is, it shows how long was required for each 25% increment of the total amount of zinc to be leached from the waste.

Table 3.11: Leaching Breakdown of Zinc From Column and Tank Tests

Test	Time to Leach 1st 25% of Total Zinc (days)	Time to Leach 2nd 25% of Total Zinc (days)	Time to Leach 3rd 25% of Total Zinc (days)	Time to Leach 4th 25% of Total Zinc (days)
Large Column	77	63	84	140
LCC100	8	198	70	90
ABLC100	4	49	147	163
ABLC180	6	45	100	211
DLT; $T_n = 1A$	15	36	92.5	217
DLT; $T_n = 1B$	13.5	31.9	77.1	238
DLT; $T_n = 4A$	32.7	40.8	84	203
DLT; $T_n = 4B$	28.2	73.3	77	182

What the majority of the results demonstrate is that, regardless of the methodology, similar percentages of zinc are released from tests in which the waste is allowed to establish its own leaching environment (i.e. all tests except the MAT). Further, observations reveal that, in tests where the waste is agitated or leachant flow occurs, surface wash-off dominates zinc leaching early, with comparatively minor contributions from both diffusion and dissolution processes. It was noticed, however, that, as the surface area of the waste increased, the mass of zinc released also increased significantly. It is under these conditions that the diffusive and dissolution mechanisms of release can have a greater influence on the amount of zinc leached.

The DLT results showed that, when diffusion is the primary contributory leaching mechanism, minimal zinc is released. However, while the DLT did leach more zinc than the ABLP and TCLP, the time required was much greater, as was the L/S ratio over that time. Still, L/S ratio was considered to play a minor, if not insignificant part in zinc release, as any major changes in this parameter did not result in concordant changes in the total amount of zinc released from the waste.

It is also important to emphasise that, apart from the MAT, 8 different types of leaching tests were investigated, all under varying conditions of L/S ratio, solid structure, leachant flow, column dimensions, test duration, etc. With all these variations, the overall difference between the lowest amount leached (TCLP: 0.01%) and largest amount leached (ABLC180: 0.43%) was only *43 times*. That is, if a TCLP and any number of time-dependent tests (using de-ionised water) were run on this waste, the difference between the highest and lowest results would be *less than* two orders of magnitude. Considering the majority of zinc has been shown to leach early in the experiments, it is unlikely that, in tests of a longer duration, a great deal more would be released. Thus, presuming the leaching tests allow the waste to establish its own leaching environment, the proposition of a maximum 10^2 magnitude of difference between the highest and lowest results should hold no matter what type of column or batch tests are employed.

Based on the previous information, an effective landfill scenario for this waste, with respect to its zinc content, would be to dispose of the waste as a monolith in a monofill environment. This would minimise surface area, reducing the likelihood of increases in zinc leachability, as well as allowing the waste to control its own leaching environment, thus minimising the potential for greater leaching in the future.

4. Results and Discussion: Copper

4.1 Copper Analysis: Method Validation

Method validation for copper by DPASV was carried out according to the procedure described in Section *2.5.2.3.1* using a 17ml aliquot of a Large Column leachate of unknown concentration. Copper concentration by standard calibration was 5.63ppb and by standard additions was 5.49ppb. The difference is not significant. Accordingly, the method of standard calibrations was used throughout the leaching experiments for the analysis of copper. Copper recoveries were all between 92% and 105%. Method validation also demonstrated that no matrix effects were present in the analysis by standard calibration.

4.2 Batch Tests

The batch tests investigated in this study were the Maximum Availability Test, ABLP, Sequential ABLP, and TCLP. Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.4 – 2.4.6*.

4.2.1 Maximum Availability Test Results

The Maximum Availability Test was run in triplicate An average of these results for mass and percentage of copper leached, pH, redox potential, and conductivity are detailed in Table 4.1. Results for each replicate for mass of copper leached, pH, redox, and conductivity, are shown in Appendix E (i). Volumes of acid added during the test are detailed in Section *3.2.1*.

Table 4.1: Copper Maximum Availability Test Data

Mass of Copper Leached (mg)	Percentage of Total Mass of Copper Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
79.34	26.7% (±0.19%)	4.68	564.1	6.6

This result demonstrates that no greater than 26.7% of the copper present in this solidified waste should leach out over time, with 73.3% remaining bound within the cement matrix.

4.2.2 TCLP Results

The average concentration, mass and percentage of copper leached, pH, redox potential, and conductivity in the TCLP are detailed in Table 4.2. Results for each of the four replicates for mass of copper leached, pH, redox, and conductivity, are shown in Appendix E (ii). The temperature during the extraction ranged from 20°C to 22°C.

Table 4.2: Copper TCLP Data

Concentration Leached (ppm)	Mass of Copper Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Copper Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.025	0.050	0.003% (±3.1 x 10^{-5}%)	12.11	232.1	12.8

The TCLP limit for copper is 100ppm (Victorian EPA, 1993). As only 0.025ppm of the copper present in the waste leached out in the TCLP, it can be said that the zinc in the waste appears to have been successfully stabilised with respect to Victorian EPA regulations for disposal to a secure landfill.

This data also contrasts strongly to that observed in the Maximum Availability Test. In that test, the waste is not permitted to dictate system pH (average final pH = 4.68) and, consequently, 26.7% of the copper present leached out. In the TCLP tests, where the pH rose over 9 units from start to finish, only 0.003% leached. These results indicate that when this particular cement-stabilised waste is allowed to impose a high system pH, negligible levels of copper will leach from the waste.

Another quite minor possibility, not previously discussed, is that as the copper is leached from the waste it is immediately precipitated as an oxide or hydroxide at the high pH environment encountered in the leachant. The filtration step employed in the TCLP then filters out the precipitate. Although it is possible that such behaviour may have occurred to a small extent, any effects on the data are believed to be relatively minor. This is because the formation of insoluble copper oxides or hydroxides is more likely to occur in the high pH of the waste (thus preventing their release), rather than in the leachate (once it has also reached a pH at which these species can form).

4.2.3 ABLP Results

The average concentration, mass and percentage of copper leached, pH, redox potential, and conductivity in the ABLP are detailed in Table 4.3. Results for each of the four replicates for mass of copper leached, pH, redox, and conductivity, are shown in Appendix E (iii). The temperature during the extraction ranged from 27°C to 29°C.

What has not yet been covered in this work, is the possibility that the temperature during the extractions may have contributed to the differences observed in total copper release. Conner (1990) states that the 'solubility of constituents is a function of temperature, and leaching test results are, at least partially, functions of the solubility of the species being investigated'. The 5-9°C increase in experimental temperature for the ABLP compared to the TCLP cannot be discounted as a contributing factor. As the temperature was merely recorded, and not a parameter deliberately varied and studied in these experiments, no more can be drawn or implied from this data.

Table 4.3: Copper ABLP Data

Concentration Leached (ppm)	Mass of Copper Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Copper Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.076	0.153	0.008% (±2.5 x 10^{-4}%)	11.60	210.3	8.20

These leaching results show that three times as much copper leached from the ABLP compared to the TCLP. Explanations for the neutral leachant of the ABLP releasing higher amounts of metals (at a lower final pH) than the acidic TCLP revolve around acid-induced matrix attack and subsequent increased alkalinity release. This has already been discussed in Section *3.2.3*.

Further support for these explanations was provided by de Groot *et al* (1989), when they leached coal fly ash using leachants of different acidities at various liquid to solid ratios. Their work suggested that copper, like zinc, has a tendency to precipitate as low-solubility hydroxide compounds at the high pH present in the cement-waste matrix. Stegemann and Côté (1990) carried out equilibrium extractions on a multitude of wastes, their results also showing the tendency of copper to leach poorly at high pH. DiPietro *et al* (1989) evaluated the effect of pH and Eh on the leachability of municipal solid waste incinerator residues. Their research indicated that copper solubility in water was higher at low pH combined with high Eh. In their work on the effects of carbonation on the properties of cement/waste forms, Lange *et al* (1997) point out that the minimum solubility of $Cu(OH)_2$ is at pH 9. Therefore, on that basis, it would be expected that a higher amount of copper would leach as the pH drops below this. In fact, with their leaching work on fractured cement/waste cylinders, they found this to be the case. The Pourbaix diagram certainly shows this to be the case, with copper forming insoluble oxides and hydroxides at pH 9 under positive redox conditions (Pourbaix 1974).

As the pH in the ABLP did not drop below 11, the leaching of copper was therefore minimal. However, once the leachant neutralises the waste over time in a real landfill situation, the leaching of copper may become significant.

4.2.4 Sequential ABLP Results

The average concentration, mass and percentage of copper leached in the Sequential ABLP are detailed in Table 4.4. Results for each of the four replicates for mass of copper leached, pH, redox, and conductivity, are shown in Appendix E (iv).

The data, in Table 4.4, shows that approximately 0.05% of the copper present in the waste was removed after ten successive leaches.

Table 4.4: Copper Sequential ABLP Data

Sequential Leach Number	Copper Concentration Leached (ppm)	Mass of Copper Leached (mg)	Percentage of Total Mass of Copper Leached (±1σ)
1	0.08	0.15	0.008% (± 2.5 x 10^{-4}%)
2	0.05	0.10	0.005% (± 4.3 x 10^{-4}%)
3	0.04	0.08	0.004% (± 1.5 x 10^{-3}%)
4	0.03	0.06	0.003% (± 6.0 x 10^{-4}%)
5	0.03	0.06	0.003% (± 8.2 x 10^{-4}%)
6	0.04	0.08	0.004% (± 1.9 x 10^{-4}%)
7	0.04	0.08	0.004% (± 6.0 x 10^{-4}%)
8	0.03	0.06	0.003% (± 5.8 x 10^{-4}%)
9	0.06	0.12	0.007% (± 2.4 x 10^{-4}%)
10	0.09	0.18	0.009% (± 4.5 x 10^{-4}%)
Total	N/A*	**0.97**	**0.052%** (± 5.7 x 10^{-3}%)

*N/A = Not Applicable

This demonstrates that the metal is well retained in the waste system. It also demonstrates that the first ABLP leach did not act as a worst case scenario test, since the maximum amount of copper leached in the last of the sequential extractions, instead of the first. Further leaching would be required to ascertain whether the trend for copper release continues to increase.

4.2.4.1 Leaching Behaviour of Copper

An important piece of information illustrated in the comparison between copper release and pH in Figure 4.1 is that, as mentioned above, more copper leached during the final leaching interval than at any other time during the test. Further, there is a somewhat broad correlation between the two sets of results, where they generally both increase after about 90 hours of leaching. According to previous research, this trend for pH data is indicative of alkalinity ($Ca(OH)_2$) release from the fixed waste (Baker & Bishop 1997, Cheng & Bishop 1990).

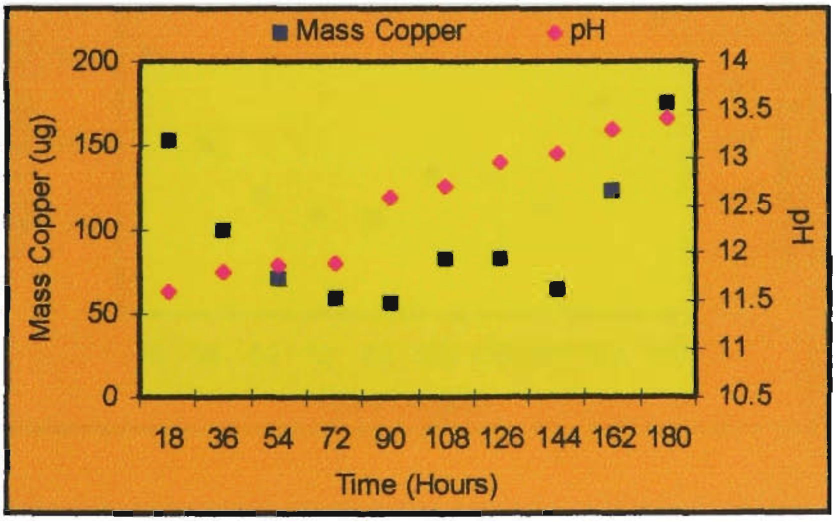


Figure 4.1: Sequential ABLP – Mass Copper Leached and pH v's Time

It is also important to note that the copper release data contrasts with the consensus that it leaches less at the higher pH environment found in cement-stabilised wastes due to the formation of low-solubility hydroxides (see Section *4.2.3*). According to

Pourbaix (1974), copper solubility at pH less than 7.5 or greater than 11.5 is supposed to be greatest under positive redox conditions. While Figure 4.1 certainly shows copper release to increase at higher pH, there is also a noticeable decrease in leaching until half way through the test when the pH is 11.5 – 12.5. Therefore, while pH has certainly affected copper release, its leaching behaviour appears to have been influenced more by the effects of surface wash-off, diffusion and matrix dissolution.

4.2.4.1.1 Redox Potential and Conductivity Effects on Copper Leachability

The data illustrated in Figure 4.2 indicates the relationship between the mass of copper leached and redox potential. The data suggests that copper may be capable of leaching from moderately oxidising to neutral environments, although the change in redox potential over the course of the experiment was little more than 50mV. The significance of this 50mV change is discussed in Section *3.2.4.2.1*.

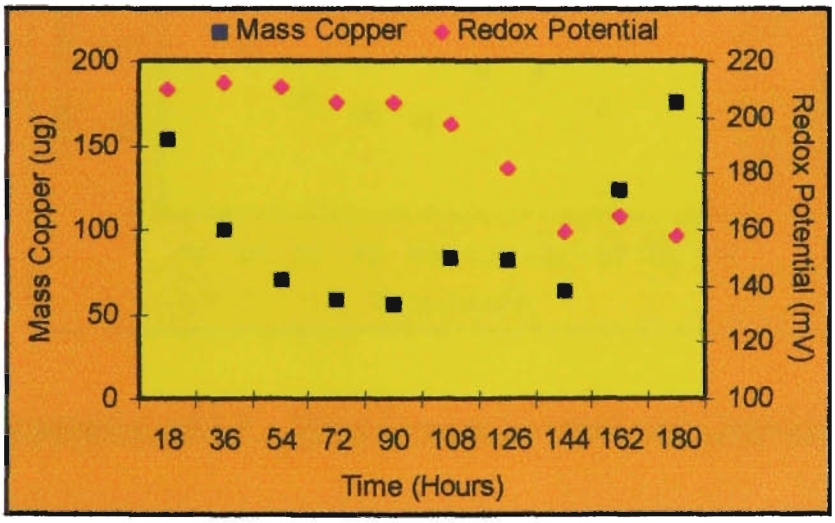


Figure 4.2: Sequential ABLP – Mass Copper Leached and Redox Potential v's Time

This type of behaviour may, however, be influenced by waste and environment specifics and this is evidenced when comparing some previous work from other authors. Hermann and Neumann-Mahlkau (1985) investigated the mobility of metals in ground water and found copper to be highly concentrated in environments of high Eh. Mention is made, however, that the low levels of copper in low Eh environments are most probably due to sulfide formation. They also point out that the solubility of copper in such environments depends largely on pH. In contrast, Calmano *et al* (1993) carried out sequential chemical extractions on river sediments and found that more copper was released under oxidising conditions than reducing, for the same pH in the range 3 – 6. This work, along with the pH and redox data from the Sequential ABLP, appears to suggest that copper release is not significantly affected at the high pH and slightly oxidising environment of this waste system.

The conductivity data in Figure 4.3 shows good correlation with the trend for copper release.

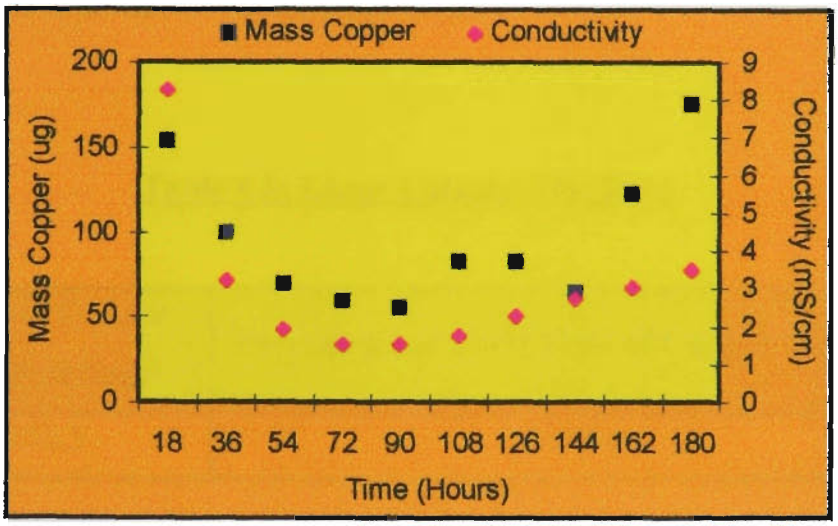


Figure 4.3: Sequential ABLP – Mass Copper Leached and Conductivity v's Time

The high conductivity levels for the first extraction are indicative of surface wash-off, and this is also the case for copper release. After this, the conductivity levels decrease as the surface-available calcium (and hence copper) salts wash away. In time the matrix begins to break up due to particle abrasion facilitating the steady release of alkalinity and copper from the fixed waste.

4.3 Column Tests

One large column and several small column tests were investigated in this study. The small columns were the 100g Large Column Comparison (LCC100), 100g ABLP Comparison (ABLC100), and the 180g ABLP Comparison (ABLC180). Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.1 – 2.4.2*.

4.3.1 Large Column

The total mass and percentage of copper leached in the Large Column test are detailed in Table 4.5. The complete leaching data can be seen in Appendix I. All pH, redox and conductivity results are shown in Appendix F(ii).

Table 4.5: Large Column Test Data

Mass of Copper Leached (mg)	Percentage of Total Mass of Copper Leached
250.5	0.04%

The data in Table 4.6 also clearly demonstrates, by comparison, that copper is not released from the fixed waste in large amounts, regardless of liquid to solid ratio or method of leachant application and contact. For all of the Large Column, TCLP, ABLP, and Sequential ABLP, no more than 0.06% of the copper originally present in the waste leached out. Only the pH-stable Maximum Availability Test leached copper to any appreciable extent.

It is also interesting to compare this data to the equivalent results for zinc (Table 3.6). The fixed waste in all tests contained approximately 20% more zinc than copper, and yet, in all but one of the tests detailed in Table 4.6, at least 250% more zinc than copper leached from the solid. Even the one test that didn't leach 250% more, the Maximum Availability Test, still released 165% more zinc than copper. The fact that the solubility product for $Cu(OH)_2$ is 4.5×10^{-21} mol L^{-1} as compared to 3.3×10^{-17} mol L^{-1} for $Zn(OH)_2$ (Aylward & Findlay 1994) may partly explain the differences in the results. Further, the amphoteric nature of zinc may also be a contributing factor.

Table 4.6: Percentages of Copper Leached in Batch Tests and Large Column

Leaching Test	Percentage of Total Mass of Copper Leached	Liquid to Solid Ratio	Method of Leachant Contact
Large Column	0.035%	19.1:1	Downflow Spraying
TCLP	0.003%	20:1	Rotary Agitation
ABLP	0.008%	20:1	Rotary Agitation
Sequential ABLP	0.052%	200:1	Rotary Agitation
Max. Avail. Test	26.7%	9.8:1	Stirring

4.3.1.1 Leaching Behaviour of Copper

Figure 4.4 details the leaching pattern of copper from the Large Column. Apart from a spike in release for the second data point, negligible amounts of copper were released from the waste over the first four weeks of the test. This appears to suggest that surface wash-is not the dominant release mechanism in this case, resulting in relatively low release of copper from the matrix. However, in the following few weeks up to 63 days, release increases markedly. This sudden increase in copper levels was most probably a consequence of surface washing. However, due to influences of leachant retention in the column (see Section *3.3.1.1*) the release of copper to the leachate may have been delayed. After 63 days the levels of copper detected in the leachates decline until, by the final sample, only 1.02mg of copper leached from more than 700g still available in the column. The only 'aberration' to this release pattern was the spike in release for the second data point, however this is no doubt a consequence of the initial saturation of the waste (see Section *2.4.1.2*). As the volume of the first sample taken following the saturation was only 165ml, any dissolved copper initially retained on the particle surfaces (and in the liquid between the particles) within the column would have been almost completely flushed out with the following 14L of leachant. Following this, the copper levels increased in concentration as anticipated for a system in which surface wash-off is the dominant release mechanism early in the test. It is, however, worth noting that this was not observed for zinc.

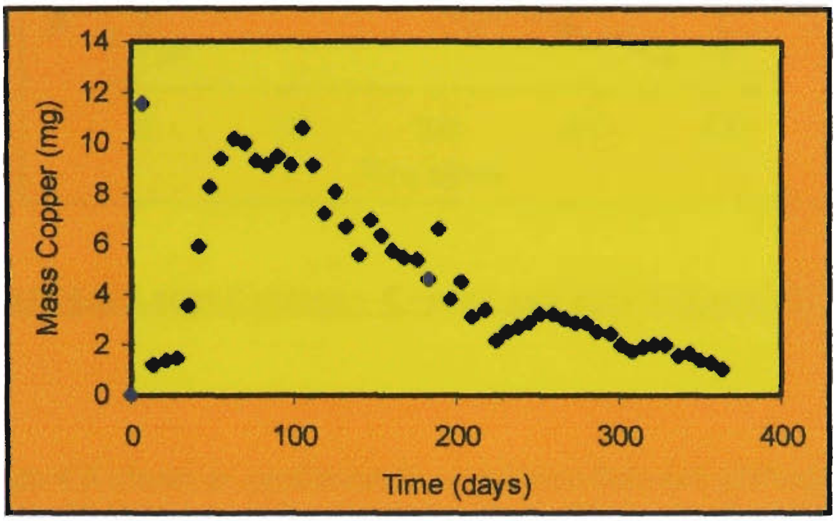


Figure 4.4: Large Column – Mass Copper Leached v's Time

4.3.1.1.1 pH, Redox Potential, and Conductivity Effects on Copper Leachability

Aside from the early, sharp spike mentioned previously, the pattern of copper release was almost identical to that of zinc from the Large Column (see Figure 4.5).

This striking similarity in release patterns between the two metals is most likely a consequence of the similarities in species produced in the test. As detailed earlier in Section *4.2.3*, copper, like zinc (and indeed most common transition metals), has a tendency to exist as insoluble oxides or hydroxides at elevated pH. Research by Golden *et al* (2000) on wastewater from chemical-mechanical polishing showed these species to be present, more specifically at elevated pH and under oxidising conditions.

The Pourbaix diagram for copper in water also provides another example of the (hydr)oxy species expected under those conditions (Pourbaix 1974).

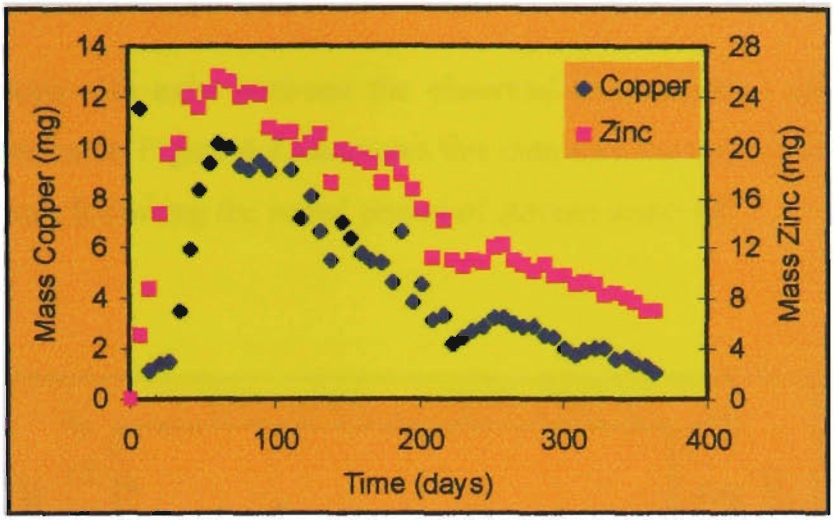


Figure 4.5: Large Column – Copper and Zinc Release v's Time

Although Figure 4.6 shows an approximate correlation between pH and copper release, the important point here is that the pH remains high for the duration of the experiment thus impeding copper leachability.

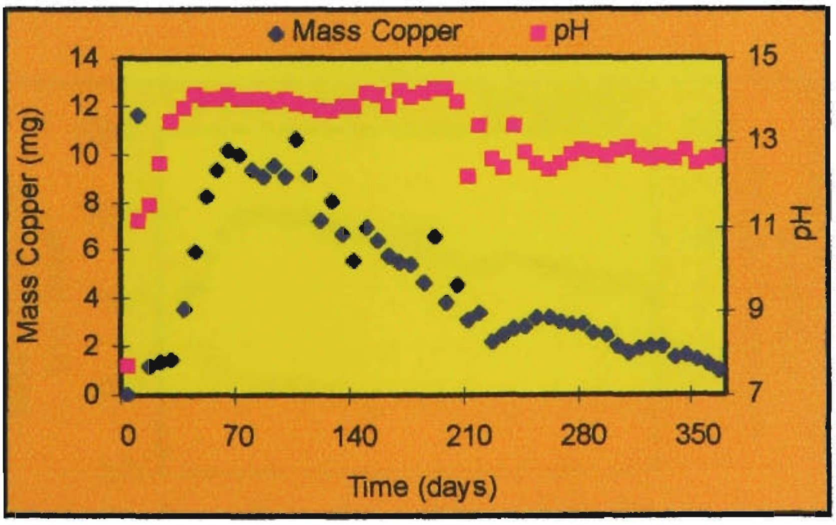


Figure 4.6: Large Column – Mass Copper Leached and pH v's Time

Figure 4.7 shows that Eh started off highly oxidising and then dropped rapidly to be only moderately oxidising for the remainder of the experiment. The redox conditions for the majority of the experiment do not appear to have had a significant effect on copper leachability.

Broad correlations also exist between the observed conductivities and the mass of copper in the leachates. Figure 4.8 illustrates this data on a log scale and shows both to gradually decrease following the initial period of surface wash-off.

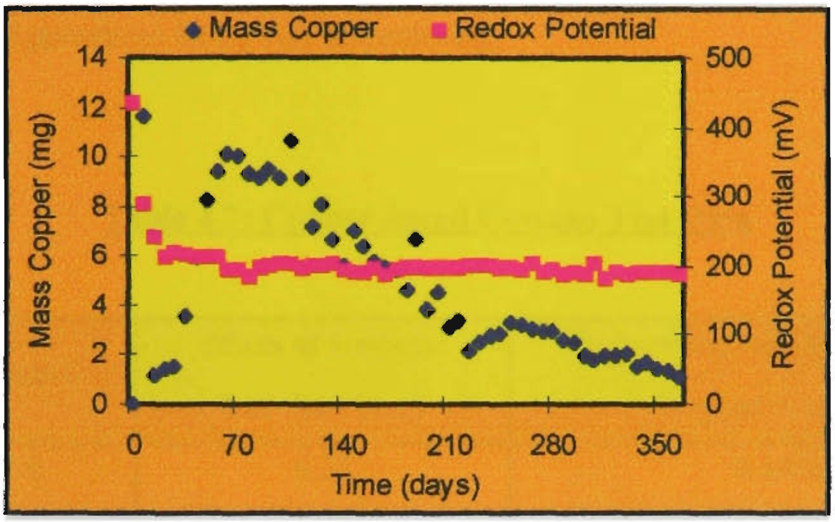


Figure 4.7: Large Column – Mass Copper Leached and Redox Potential v's Time

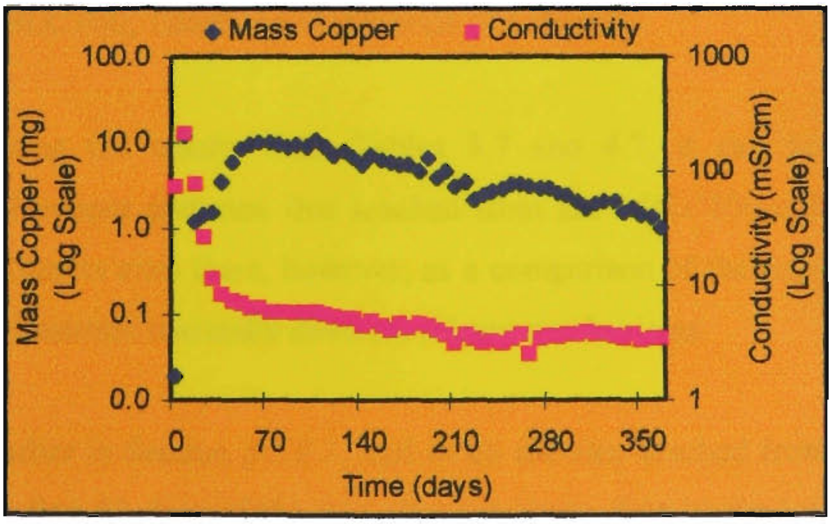


Figure 4.8: Large Column – Mass Copper Leached and Conductivity v's Time

As mentioned in Section *3.3.2.2.1*, this type of correlation is indicative of pore-based diffusive release, although the patterns are not so similar that this prediction can be made without reservations.

4.3.2 Small Columns

The total mass and percentage of copper leached in the small columns ABLC100, ABLC180, and LCC100 are detailed in Table 4.7. The complete leaching data can be seen in Appendices J(i)-(iii) respectively, while all pH, redox and conductivity results are shown in Appendices G(iv)-(vi) respectively.

Table 4.7: Copper Small Column Test Data

Small Column	Mass of Copper Leached (mg)	Percentage of Total Mass of Copper Leached
ABLC100	6.27	0.34%
ABLC180	4.59	0.14%
LCC100	0.69	0.04%

4.3.2.1 ABLC100; Leaching Behaviour of Copper

When comparing the results from Tables 3.7 and 4.7, it can be seen that the percentages of copper and zinc that leached from the ABLC100 column were very similar. The likeness ends there, however, as a comparison of the patterns of leaching (Figures 4.9) illustrates markedly different release mechanisms.

As covered earlier in Section *3.3.2.1*, half of all the zinc leached from the ABLC100 column in the first 53 days of the test. The remaining half leached steadily over the duration of the experiment. The contrast between those results and the release of copper is that copper leached steadily throughout the entire year of the experiment.

That is, the surface wash-off period was much less extreme than that for zinc. The differences between the release patterns of the two metals can be seen even more clearly in Figure 4.10.

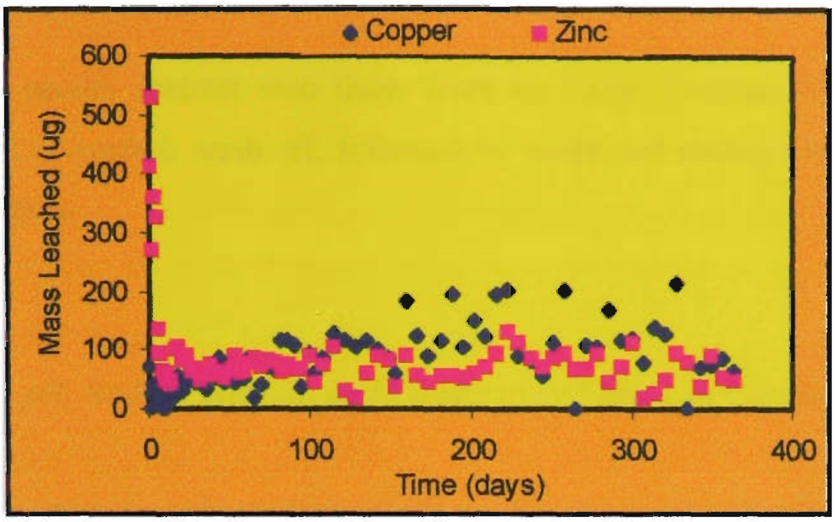


Figure 4.9: ABLC100 – Mass Copper and Zinc Leached v's Time

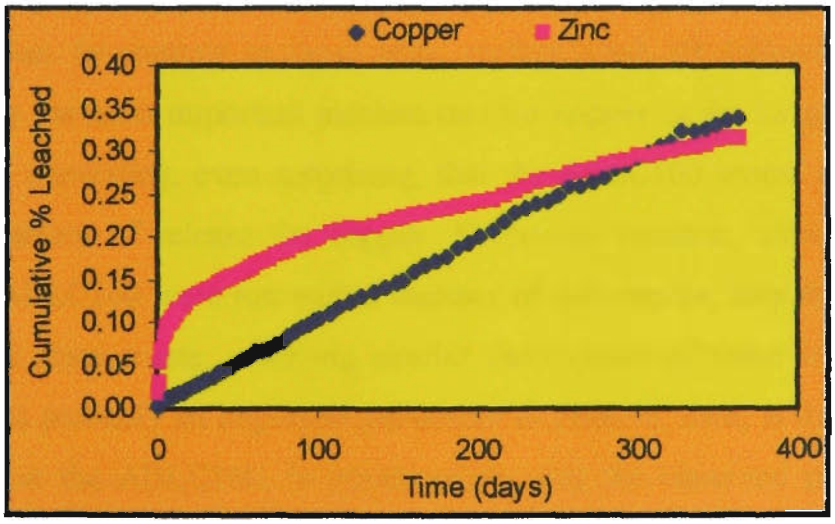


Figure 4.10: ABLC100 – Cumulative Percentage Copper and Zinc Leached v's Time

This data clearly suggests that, for the ABLC100, the surface wash-off period is very short. The regular release pattern is not only indicative of at least partial diffusive release, but also seems to suggest dissolution of the matrix might play an important part in the leaching of copper. Andrés' *et al* (1995) suggests that a linear relationship between cumulative mass (or fraction) leached and time is indicative of matrix dissolution. Although based on tank leaching tests, this suggestion also appears relevant for the ABLC100 copper results.

Further, these results contrast with those from the Large Column, which showed a distinct period of surface wash-off, followed by suspected release via diffusion and matrix dissolution.

4.3.2.1.1 pH, Redox Potential, and Conductivity Effects on Copper Leachability

All the leaching tests investigated thus far have shown copper to behave differently in different situations. The high surface area of the crushed waste, combined with the harsh agitation at a constant low pH and high L/S ratio, led to high levels of copper being leached in the Maximum Availability Test. The Sequential ABLP showed copper to be more prone to physical release from the waste matrix, mainly due to particle abrasion. In contrast to those tests, surface wash-off followed by diffusion appeared to be the most important mechanisms for copper in the Large Column. It is therefore very interesting, even surprising, that the ABLC100 seems to have yielded yet another pattern of release for copper. Surprising because, although the Large Column and ABLC100 were run with a number of differences, they still are columns filled with the same waste, receiving similar daily doses of water over a one year period. What is probably an important parameter to observe, then, is the way in which the L/S ratio in the ABLC100, in combination with the observed pH, Redox, and conductivity results, may have affected the rate of copper leaching.

The L/S ratios for the Large Column and ABLC100 tests are approximately 19:1 and 9571:1 respectively, obviously a significant difference. Another important difference is the method of leachant application. In the case of the Large Column this was achieved by spraying the liquid onto the column resulting in unforced downward flow. The ABLC100, on the other hand, utilised a forced (pumped) upward flow method of leachant application. The combination of these two differences result in conditions for the ABLC100 which appear more likely to lead to a greater rate of matrix dissolution than would be observed in the Large Column. In the Large Column, the constant stagnant saturation of the column that occurred between the collection of one days leachate, and the spraying of the following days leachant, would lead to diffusive leaching as the dominant release mechanism (during that particular time period). As mentioned in Section *3.3.1.1*, Korfiatis *et al* (1984) extensively studied the physical processes governing moisture transport in large columns and solid waste landfills. They showed that (as soon as the waste is saturated) the addition of a certain volume of liquid to the top of a landfill (or column) would not necessarily produce an equal volume of leachate discharge. This mechanism would further amplify any diffusive processes that may be occurring.

It was suggested earlier in Section *4.3.1.1.1* that the similarity between the leaching patterns of copper and zinc for the large column was most likely a consequence of the similarities in species produced in the test. Although this seems likely, what may be of greater importance is the way in which the experiment produced such similar species. That is, when comparing the Large Column results to the differences observed for the ABLC100, the experimental parameters themselves (specifically L/S ratio and leachant application) appear to have had a significant effect on pH/conductivity levels, and, in turn, the subsequent leachabilities of the metal species produced. While surface wash-off followed by diffusion are considered to have been the dominant release factors for the Large Column, the linearity of copper release in the ABLC100 suggests a combination of matrix dissolution followed by diffusion (as the waste becomes more porous).

The steadily decreasing pH observed in Figure 4.11 (and the consequent increase in Eh in Figure 4.12) combined with the constant decrease in conductivity (Figure 4.13) points to the gradual removal of alkalinity from the system. This was also discussed in Section *3.3.2.1.1*.

While this data helps explain any removal of copper via the mechanism of matrix dissolution, the pH levels during the test also seem to provide conditions for easier diffusion for the copper species. In the Large Column test, the pH did not fall far below 13, whereas for the ABLC100 it started at a value of less than 13 before 'steadily' decreasing to less than 9. Even though these condition changes did not greatly vary the pattern of zinc leaching between the two tests, it appears to have obviously had a much greater effect on copper.

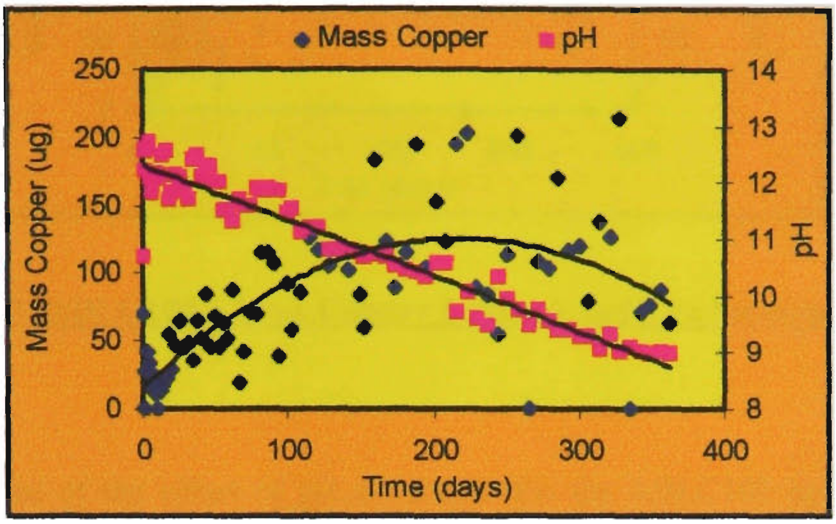


Figure 4.11: ABLC100 – Mass Copper Leached and pH v's Time

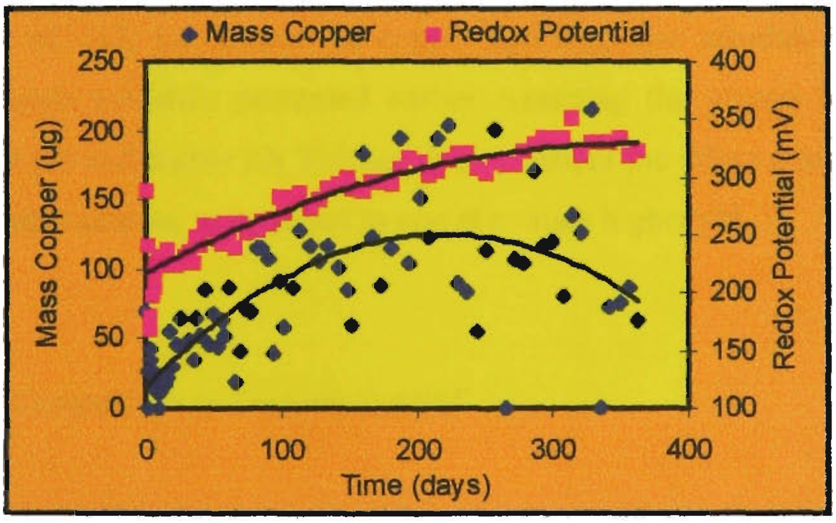


Figure 4.12: ABLC100 – Mass Copper Leached and Redox Potential v's Time

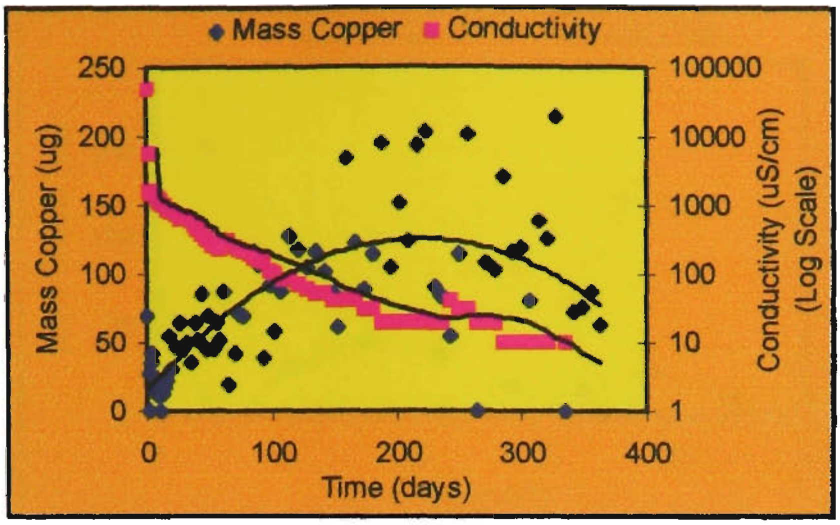


Figure 4.13: ABLC100 – Mass Copper Leached and Conductivity v's Time

Further evidence of the effect of pH on copper for the ABLC100 can be found by actually observing the pH v's copper leached data for the Large Column in Figure 4.6. Here, the surface washing of copper occurs at a pH well in excess of 13. Then, after around 100 days, the copper levels begin to drop even though the pH remains at >13. At around the 210-day mark, the pH then drops to below 13. Once the pH steadies to a constant value of <13, the pattern of copper leaching also steadies. This type of behaviour supports evidence presented earlier regarding the greater leachability of copper at lower pH and higher Eh. Further, it emphasises the effect a more neutral pH can have on copper release, as opposed to one at a much higher pH.

4.3.2.1.2 Comparison to Sequential ABLP

Figures 4.14 and 4.15 illustrate the leaching pattern of copper between the ABLC100 and the Sequential ABLP. The leaching patterns observed in Figure 4.14 are quite similar for the first ten litres of each extraction, the dashed line indicating the combination of the first and second data points for the ABLC100 (See Section *3.3.2.1.2*). This is also obvious in Figure 4.15 where both cumulative mass plots increase steadily, the significant difference between the two, of course, being the large variation in actual mass of copper leached.

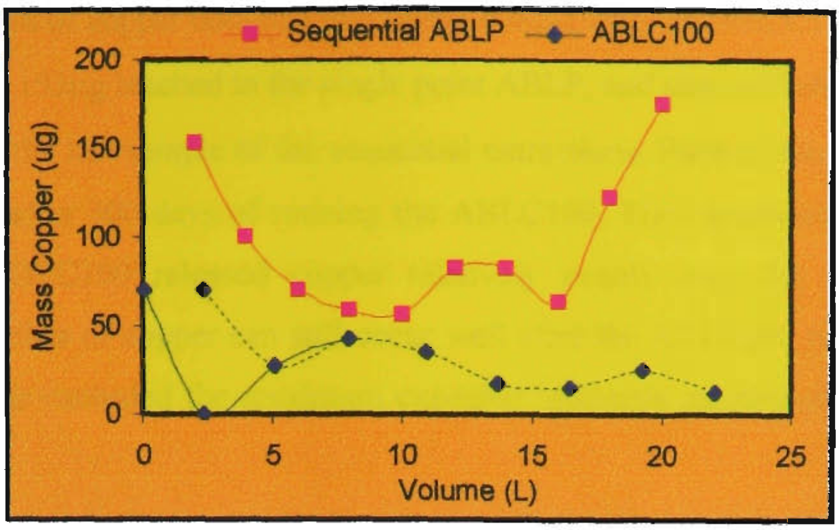


Figure 4.14: ABLC100 & Sequential ABLP – Mass Copper Leached v's Time

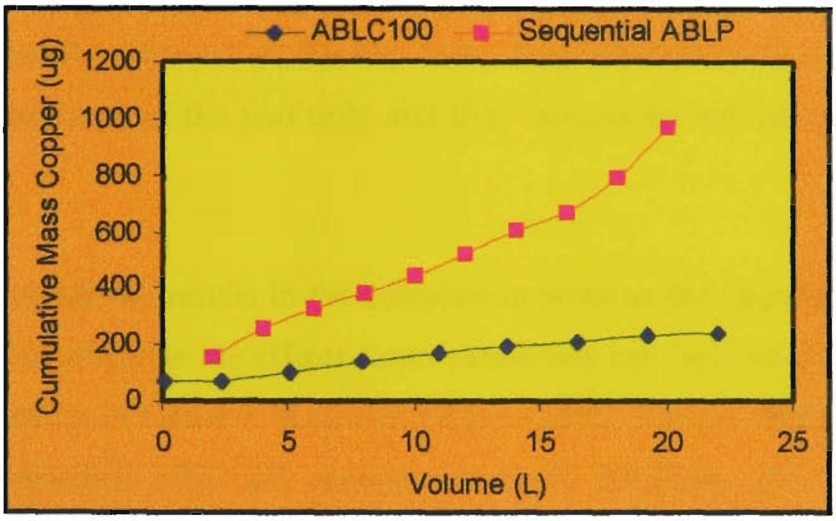


Figure 4.15: ABLC100 & Sequential ABLP – Cumulative Mass Copper Leached v's Time

Following the ten-litre point in Figure 4.14, the Sequential ABLP release increases significantly while that for the ABLC100 only slightly declines. In fact, approximately five times the amount of copper leached out in the Sequential ABLP, in an equivalent volume leached, compared with that in the ABLC100. In the same comparison for zinc, twice the amount leached out in the sequential tests as opposed to the small column (Section *3.3.2.1.2*).

The largest mass of copper obtained in a single sample from the ABLC100 was 215μg, well above the 153μg leached in the single point ABLP, and also well above the 175μg obtained from the last sample of the sequential extractions. Further, the 215μg sample was collected after 300 days of running the ABLC100. This demonstrates that, even though the ABLC100 released copper relatively evenly over the course of the experiment, spikes of copper can still occur well after the ABLC100 has started, and these spikes far exceeded the maximum expected leachable amount predicted by the ABLP.

4.3.2.1.2.1 pH, Redox Potential, and Conductivity Effects

As covered in Section *3.3.2.1.2.1*, there doesn't appear to be any correlation between the redox potentials observed in the two tests. Also detailed in that section is the relative aggressiveness of the two tests and their subsequent effects on conductivity and pH results.

The pH and conductivity results in the comparison between the Sequential ABLP and ABLC100 further illustrate the effects those parameters can have on copper leaching. The pH comparison in Figure 3.14 shows a dip in ABLC100 pH after the 10L mark, whereas the Sequential ABLP pH continues to climb. Similarly, after the 10L point, the conductivity for the Sequential ABLP climbs rapidly, in contrast to the very slightly decreasing ABLC100 values. This data corresponds well to the copper leaching data in Figures 4.14 and 4.15, which show the Sequential ABLP release to increase after the 10L point, while that for the ABLC100 remains much the same.

Here, an increase in $Ca(OH)_2$ leaching has feasibly led to greater matrix porosity, higher leachate pH, and increased copper diffusion for the Sequential ABLP. In contrast, the relatively constant pH/conductivity levels in the ABLC100 have resulted in a more steady release of copper species from the fixed waste. Obviously, therefore, the increase in copper release via the breaking up of the matrix in the Sequential ABLP far outweighs any decrease effected by the high pH in this experiment.

4.3.2.2 ABLC180; Leaching Behaviour of Copper

After one year of leaching, the ABLC180 released a little over 4.5mg of copper, or 0.138% of the original amount in the column. At such a high flow rate of leachant, this result demonstrates copper to be well retained within the matrix.

Figure 4.16 illustrates that the break in leachant flow and sampling (explained in Section *3.3.2.2*) appeared to have no significant effect on the pattern of copper leaching. Figure 4.17 further clarifies this point, and also shows the mass of copper released to have been relatively unaffected by the 'deluge-drought' conditions.

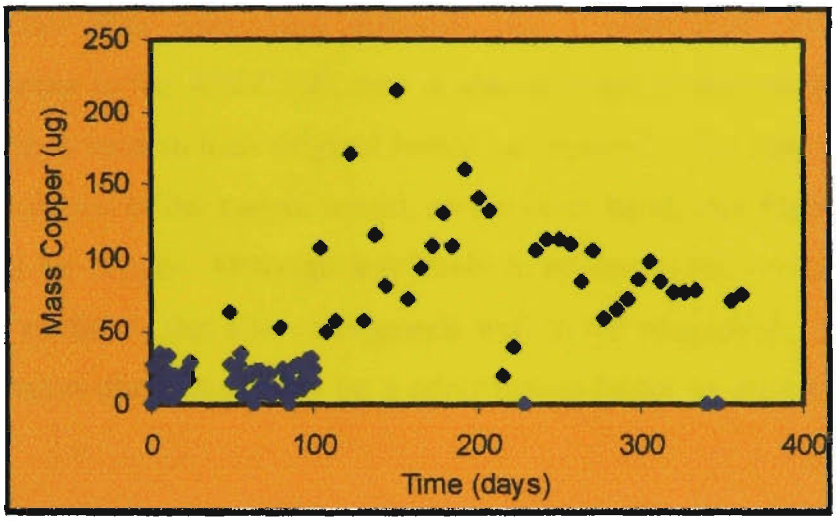
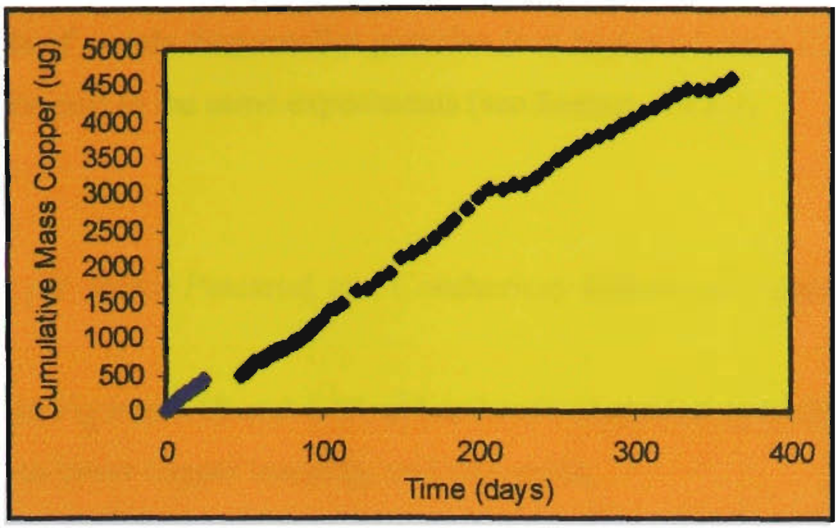


Figure 4.16: ABLC180 – Mass Copper Leached v's Time

The first sample following the resumption of leachant flow contained more than twice the amount of copper as the previous sample. After this, the levels immediately dropped back to the copper levels observed prior to the break in leachant flow. Under these stop-start conditions, this higher value due to the attainment of equilibrium with the waste, followed immediately by decreased copper masses, is exactly what was expected as per the explanations of Batchelor (1997) and the USEPA (1989) regarding limiting cases of leaching (see Section *3.3.2.2*).



<u>**Figure 4.17: ABLC180 – Cumulative Mass Copper Leached v's Time**</u>

If anything other than pore-based diffusion *was* a significant contributor to the leaching of copper in the ABLC180, then it was anticipated that the levels of copper would slowly drop back to their original levels, as opposed to the rapid drop observed. A gradual dissolution of the matrix would, on the other hand, also facilitate the release pattern viewed for copper. Although less likely to be due to the benign conditions of the period of 'no-flow', this also corresponds well to the suggestion, made in Section *4.3.2.1*, that matrix dissolution may be a contributing factor in copper release for the ABLC100.

Foster also demonstrated that this type of break in leachant flow had little effect on copper leachability (1998) (refer to Section 3.3.2.2 for a description of his experiments). He showed that the levels for copper increased sharply in the second week of leaching for the 'constant soak' leaching scenario on small waste particles, before immediately decreasing in concentration the following week, and remaining low for the rest of the experiment. His work also showed that leaching methodology and waste particle size had little effect on the pattern of leaching for copper, observations that differ from those for made for zinc. The only significant particle size related effect was that copper leached less from the large particles than the small particles at the beginning of the 'constant soak' scenario, and more at the end. This agrees with the general consensus that larger cement-based waste particles will leach higher amounts of metals than smaller particles (see Section *1.3.4.2.2.2*), but contrasts to his results for zinc in the same experiments (see Section *3.3.2.2*).

4.3.2.2.1 pH, Redox Potential, and Conductivity Effects on Copper Leachability

As illustrated in Figures 4.18 and 4.19, pH and redox potential appears to show that a high pH leads to lower copper leaching, and vice-versa.

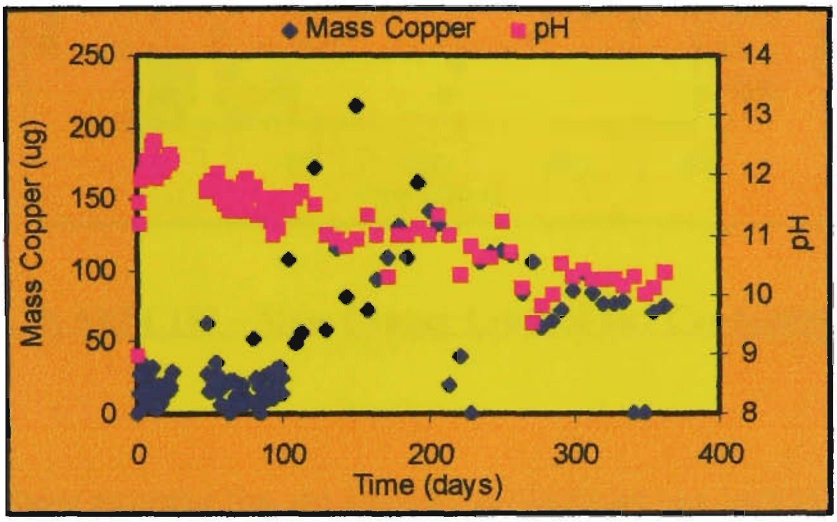


Figure 4.18: ABLC180 – Mass Copper Leached and pH v's Time

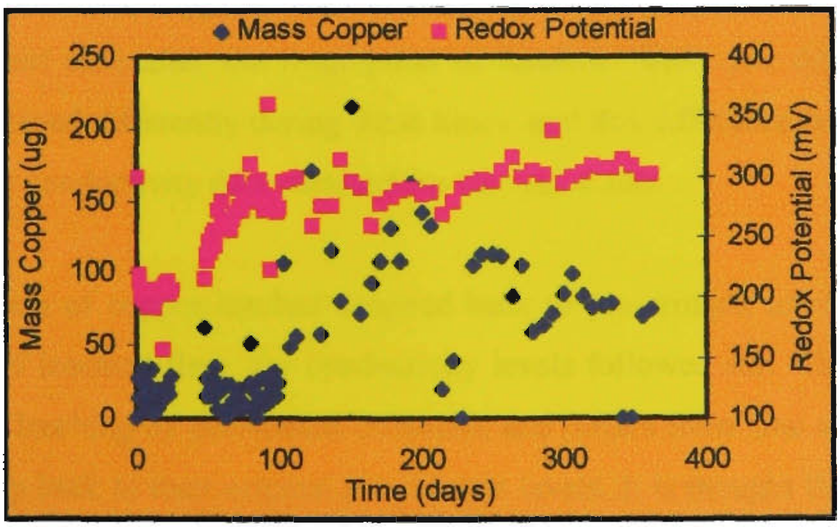


Figure 4.19: ABLC180 – Mass Copper Leached and Redox Potential v's Time

Although the comparison between copper leaching and conductivity was not much better, Figure 4.20 still provides considerable insight into the mechanistic possibilities for copper release.

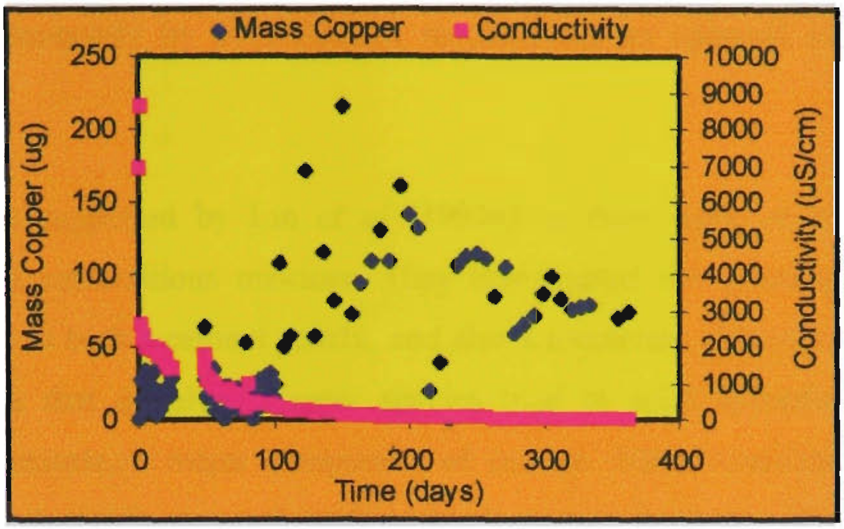


Figure 4.20: ABLC180 – Mass Copper Leached and Conductivity v's Time

While it has been accepted that the leaching of alkalinity can lead to increased metal leachability (see Section *3.3.2.1.2.1*), the effects this can have on different metals, waste types, and experiments can, of course, vary. Section *3.3.2.2.1* pondered the effects of the deluge-drought on zinc leachability in relation to conductivity data for the ABLC180. It was suggested that the dominant mechanism in the drought period, and for a short time after the resumption of leachant flow, was diffusion. Copper, however, behaved differently during these times, and this difference is amplified when observing the conductivity data obtained for the ABLC180.

When the mass of copper leached dropped back to pre-drought levels following the resumption of leachant flow, the conductivity levels followed suit. This correlation is indicative of leaching by pore-based diffusion, and differs from zinc which took three weeks to drop back to their original pre-drought levels. It is thought this behaviour (of zinc) is indicative of both diffusion from the pores, and the release of previously trapped species in the solid matrix (by diffusion/dissolution) following the resumption of leachant flow. The copper data, on the other hand, suggests only pore-based diffusion will take place during periods of no leachant flow, as there is a direct correlation between conductivity (Ca^{2+} release) and metal release. In fact, the deluge-drought data for copper supports the earlier suggestion that dissolution of the matrix may be the dominant mechanism for the leaching of copper in the ABLC180 when flow occurs. Therefore, it appears that copper retention within the cement matrix is effected predominantly by solidification mechanisms, as opposed to processes of stabilisation.

This theory is supported by Lin *et al* (1993b) in their work on mechanisms of stabilisation in cementitious matrices. They investigated the interaction of various copper species in both a cement matrix, and also a tricalcium aluminate matrix. Their work indicates that dissolved copper species bind in solid hydration products of tricalcium aluminate, a major component of cement. More specifically, CuO was found to be physically trapped within the hydration products of the tricalcium aluminate. Lin *et al* (1993a) also studied the leaching processes of the dicalcium silicate and copper oxide solidification/stabilisation system. Their results showed that the dissolution of $Ca(OH)_2$ is the primary mechanism for the destruction of the matrix, and the subsequent leaching of copper ion. Therefore, while stabilisation complexes may form between copper and the products of cement hydration, a great deal of research suggests that copper species are more likely to be physically entrapped within the cement solid.

4.3.2.2.2 Comparison to ABLC100

There were significant differences between these two tests with respect to percentage of copper leached. While the ABLC180 contained 1.8 times more copper than the ABLC100, it leached little more than 40% of what was released from the 100g column. The actual linearity of the patterns of release, though, were very similar, as evidenced in Figure 4.21.

Regardless of the actual mechanisms responsible for leaching more copper in the ABLC100, the only parameter that has changed between the two tests is the L/S ratio.

Therefore, a higher L/S ratio for the ABLC100 has led to increased levels of copper release.

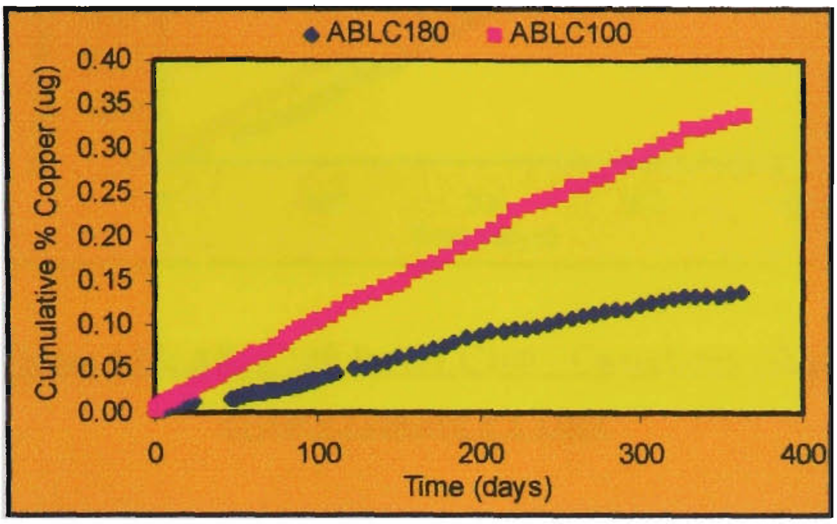


Figure 4.21: ABLC180 & ABLC100 – Cumulative Percentage Copper Leached v's Time

4.3.2.2.2.1 Comparison to ABLC100; pH and Conductivity

Although it cannot solely explain the difference in copper release between the two tests, the pH certainly had an effect on leaching from the ABLC180. Figure 3.22 in Section *3.3.2.2.2.1* illustrates a comparison between the pH data from the ABLC180 and the ABLC100. At around the 200 day mark, the pH in the ABLC180 began to level off between 10 and 11, while the ABLC100 pH continued to decrease until the end of the experiment, dropping to just above 9. The effects of this difference in pH can be seen in Figure 4.22, where, once again at the 200-day point, copper release in the ABLC180 slows while, at the same time, the ABLC100 release remains unchanged.

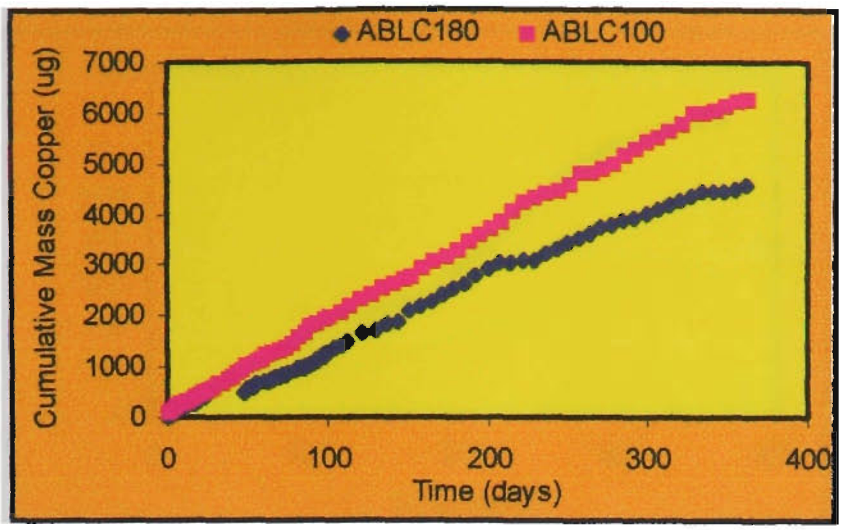


Figure 4.22: ABLC180 & ABLC100 – Cumulative Mass Copper Leached v's Time

This agrees well with previous research, mentioned earlier in this chapter, regarding the potential for increase in copper leachability at lower pH levels. Further, in Section *4.3.2.1.1* on pH and other effects on copper leachability in the ABLC100, it was also suggested that the lower pH provided conditions of easier diffusion for the copper species. It therefore seems that pH has, in some small way, affected copper release in the ABLC180 and the ABLC100. However, it must be pointed out that the lack of diffusive leaching of copper in the ABLC180 comprises only a fraction of the difference between that test and the ABLC100, no doubt a consequence of the poor diffusive capability of copper in these tests. The remainder, as mentioned previously, is an effect of the difference in L/S ratios between the two tests.

4.3.2.3 LCC100; Leaching Behaviour of Copper

Table 4.7 (Section *4.3.2*) shows that LCC100 leached the least of all the small columns with only 0.037% of copper present in the column being released to the leachate. Figure 4.23 reveals a complete lack of surface wash-off for the leaching of copper.

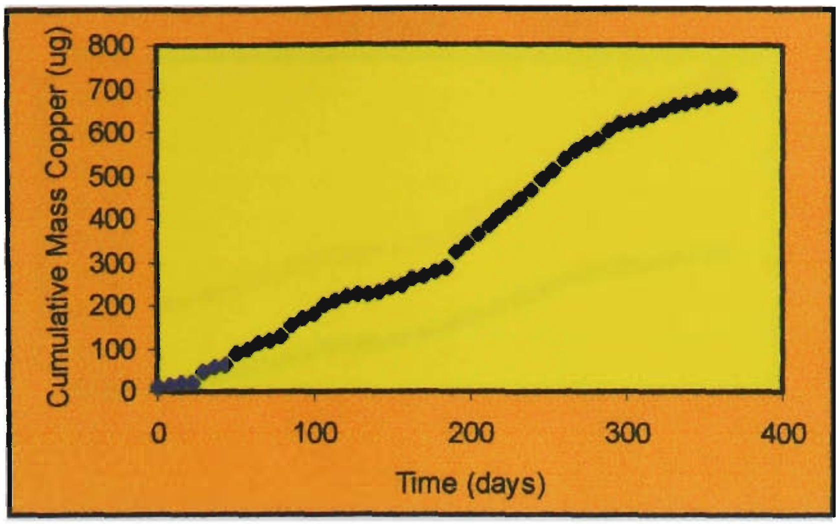


Figure 4.23: LCC100 – Cumulative Mass Copper Leached v's Time

The delay in leaching at the beginning of the test reveals that minimal initial surface washing took place. This corresponds well to the other small columns which also had insignificant levels of copper released via surface wash-off. It is also similar to the results from the Large Column where only a small amount of copper appeared to be released by surface washing very early in the test (See Section *4.3.2.3.2*).

The copper results for the LCC100 do, however, differ from those for zinc. As Figure 4.24 illustrates, there was a significant amount of surface washing for zinc. Following the reduction in zinc release due to surface washing, the zinc levels steadied into a diffusive/dissolution-leaching pattern, much like that observed for copper.

This point is highlighted when observing incremental copper and zinc release over the course of the experiment. Of the total amount of copper released in the LCC100, the first 25% were leached in 93 days, the second 25% in 91 days, the third in 70 days, and the last 25% in 112 days. This is relatively constant, with the quickest and slowest periods of release occurring in the third and fourth quarters respectively. For zinc (see Section *3.3.2.3*), the results were 8 days, 190 days, 70 days, and 100 days respectively. This comparison between the copper and zinc data is depicted in Figure 4.25. Obviously if it weren't for the initial wash-off, the zinc release would have been much the same as for copper.

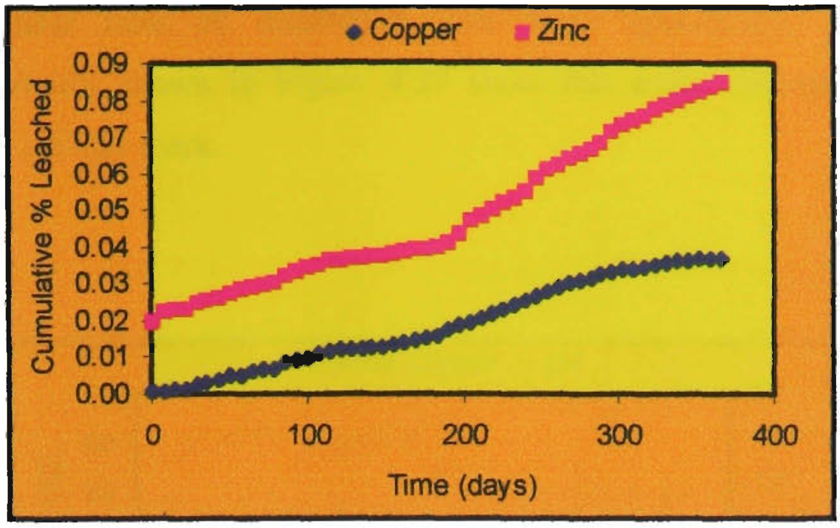


Figure 4.24: LCC100 – Cumulative Percentage Copper and Zinc Leached v's Time

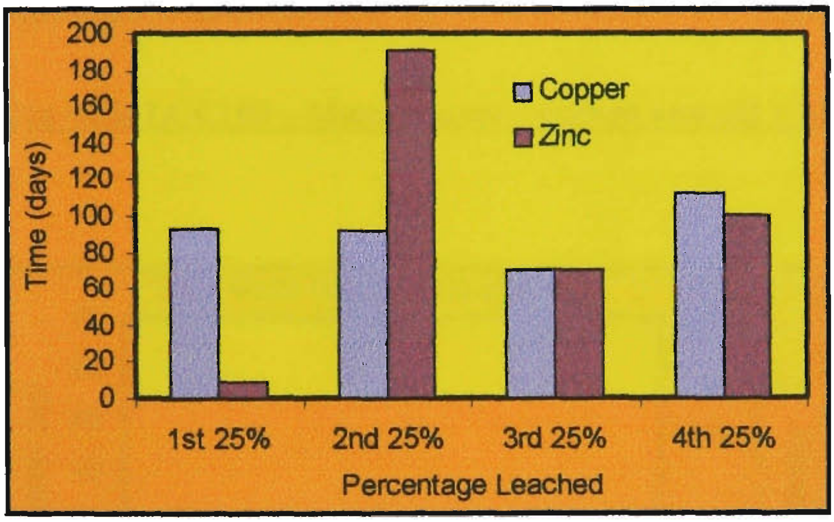


Figure 4.25: LCC100 - Incremental Copper and Zinc Release

4.3.2.3.1 pH, Redox Potential, and Conductivity Effects on Copper Leachability

As with the zinc results detailed in Section *3.3.2.3.1*, the levels of copper leached increased once the pH decreased at around the 200-day mark. This is illustrated in Figure 4.26. As stated in the aforementioned section, the decrease in pH suggests a similar decrease in $Ca(OH)_2$ available for leaching. If the majority of the $Ca(OH)_2$ has already been leached, the waste would be expected to have greater porosity, and, therefore, greater rates of dissolution and, more specifically, diffusion. The conductivity results shown in Figure 4.27 show this exact decrease in alkalinity leached at the 200-day mark.

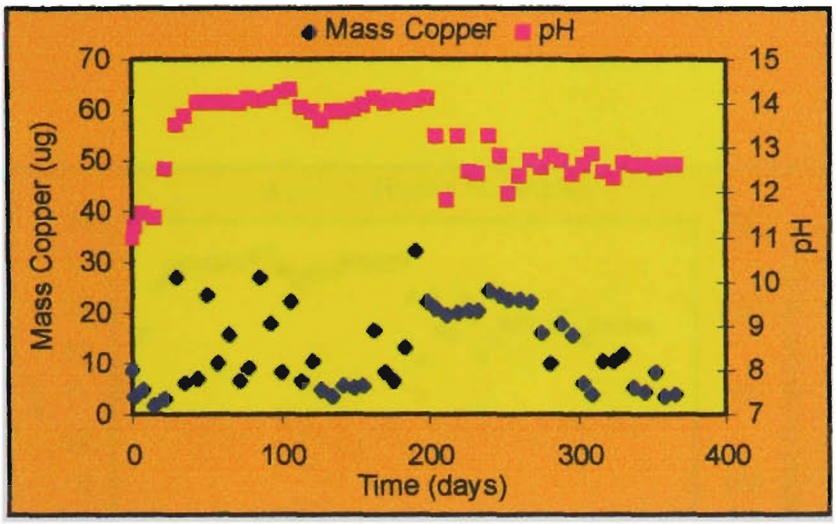


Figure 4.26: LCC100 – Mass Copper Leached and pH v's Time

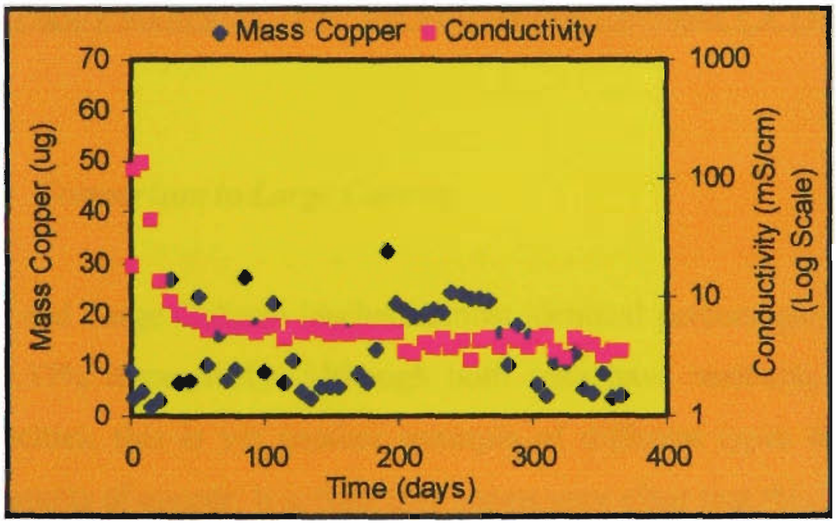


Figure 4.27: LCC100 – Mass Copper Leached and Conductivity v's Time

It is also interesting to compare the pH results with the leaching data observed for copper and zinc in Figure 4.24. Although both increase as a result of pH decreases, the copper increase is considerably weaker than that for zinc. This supports earlier data demonstrating zinc to be more easily leached by diffusion than copper, and that even a decrease in pH cannot necessarily free large amount of copper from the cement-waste matrix.

The redox data also shows a good reverse correlation with pH data, and, therefore, also with the mass of copper leached.

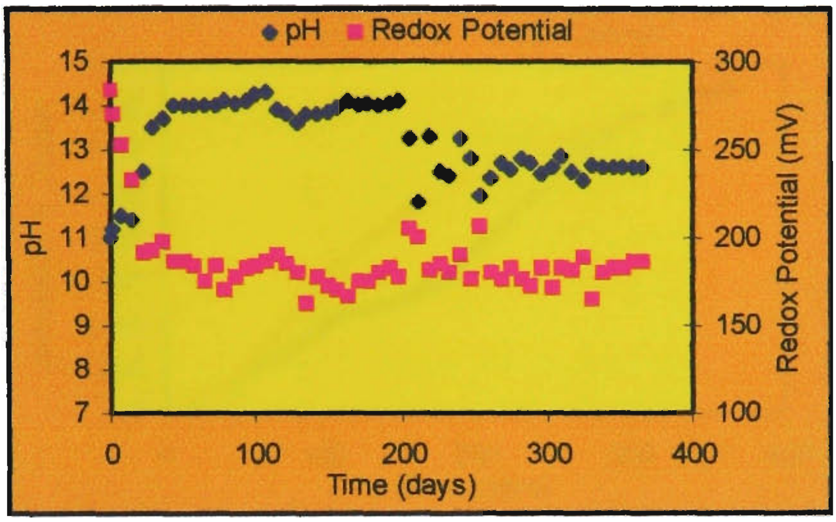


Figure 4.28: LCC100 – pH and Redox Potential v's Time

4.3.2.3.2 *Comparison to Large Column*

The LCC100 and Large Column leached almost identical percentages of copper, with 0.35% and 0.37% respectively. Although both tests have matching L/S ratios and leachant velocities, this is yet another example of different types of tests leaching negligible amounts of copper. It is therefore seems very clear that this waste would not pose any sort of threat for copper if disposed of to landfill.

Figure 4.29 depicts the leaching patterns for copper in each test. As with the LCC100, copper release from the Large Column had almost no <u>immediate</u> contribution from surface wash-off. Of course, as the Large Column experiment wore on, the effects of surface wash-off became apparent over the first two months. The LCC100, on the other hand, showed almost no surface wash-off whatsoever. Aside from the surface wash-off for zinc in the LCC100, a comparison of Figure 4.29 with Figure 3.29 (Section *3.3.2.3.2*) shows the leaching patterns for copper and zinc in both tests to be very similar. That is, as with zinc, the two trends of leaching for copper are reversed. At around the 150-200 day mark, the two trends stop moving in opposite directions and begin to converge until, after approximately 300 days, copper release from the LCC100 passes that from the Large Column.

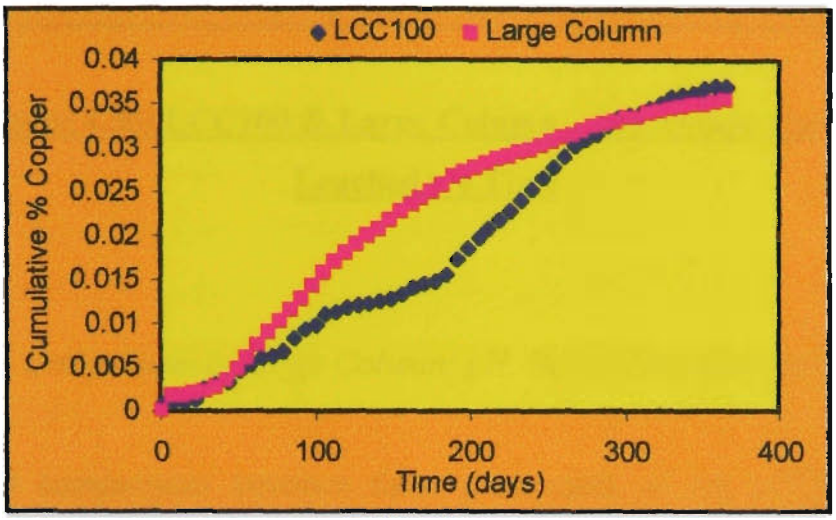


Figure 4.29: LCC100 & Large Column – Cumulative Percentage Copper Leached v's Time

Figure 4.30 clarifies this behaviour, clearly establishing that the Large Column releases copper at a much higher rate than the LCC100 in the first half of both tests, while the opposite occurs for the remainder of the tests.

Also similar to the results for zinc were the frequent release spikes for copper in the LCC100. These spikes were not observed for copper release from the Large Column, where the pattern of leachability was far steadier. It appears that this behaviour is due to increased channeling and wall-effects in the smaller column. The reasons for these effects, which have already been detailed in Section *3.3.2.3.2*, revolve primarily around column shape and method of leachant delivery.

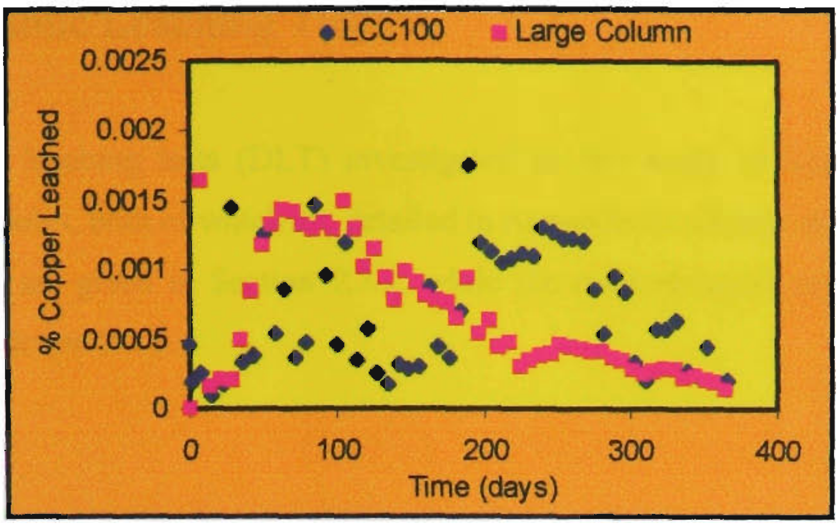


Figure 4.30: LCC100 & Large Column – Percentage Copper Leached v's Time

4.3.2.3.2.1 Comparison to Large Column; pH, Redox Potential, and Conductivity

The graphical comparisons between these parameters of the LCC100 and Large Column can be seen in Figures 3.31 – 3.33 in Section *3.3.2.3.2.1*. The observations regarding the startling similarities between the results were also covered in that section, and will, therefore, not be repeated here.

It *is* worth repeating, however, that regardless of the agreement in pH, redox, and conductivity in the LCC100 and the Large Column, the pattern of copper leaching was still quite different between the two tests. Had the tests run for another year, it is quite possible that any similarity in mass leached may have been non-existent, and the closeness of the electrode (pH, redox, and conductivity) data rendered insignificant. This, once again, demonstrates the value of a time-dependent test. Further, it shows that electrode data can contribute significantly to the elucidation of leaching mechanisms, only when analysed in combination with leachability data of the metal contaminant in question.

4.4 Dynamic Leaching Tests

The dynamic leaching tests (DLT) investigated in this study utilised two leachant renewal schedules, both of which are detailed in Appendix C. Details of the waste used in these tests are given in Section *2.3.2*, while the methodologies of these tests are provided in Section *2.4.3*.

4.4.1 Leaching Behaviour of Copper

Two DLTs were run for each renewal schedule. These were labelled 1A and 1B for the rapid renewal rate of 1 hour, and 4A and 4B for the slower renewal rate of 4 hours (Refer Section *2.4.3.2)*. The masses leached in each of these experiments are detailed in Table 4.8. The complete leaching data can be seen in Appendices K (i) – K (iv). All pH, redox, and conductivity data are shown in Appendices H (v) – H (viii).

Table 4.8: Copper DLT Test Data

Replicate	**t_n = 1A**	**t_n = 1B**	**t_n = 4A**	**t_n = 4B**
Mass Leached (mg)	0.107	0.108	0.135	0.130
% Leached	0.012	0.012	0.016	0.015

Table 4.8 shows the mass of copper leached from spheres 1A and 1B to be practically the same. Figure 4.31 also illustrates obvious similarities in the release trends of each sphere.

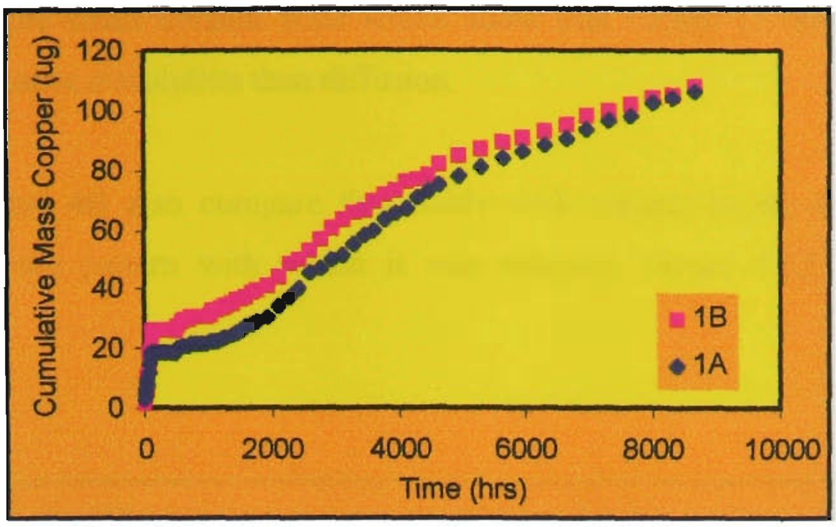


Figure 4.31: t_n = 1A & 1B – Cumulative Mass Copper Leached v's Time

The leaching from both spheres involved a surface wash-off, followed by a lengthy period of inactivity. If, as mentioned earlier, copper is solidified rather than stabilised within the matrix, this behaviour should be expected. As this is a leaching test with no agitation of any sort, the only form of leaching that can occur is surface washing and diffusion. For any effects of matrix dissolution to reveal themselves in the form of leached copper species, such a test would need to run for a greater length of time (>1 year). The period of inactivity, therefore, is the time taken for the copper to leach out of the sphere. Once copper leaching begins again, the rate increases until around 4500 hours before levelling off. This levelling off was starting to occur before this point but the drop is obvious here as the leaching schedule was stretched out to weekly at this time. This indicates that the rate of leaching is being limited through the accumulation of copper species in the leachate. Although it has not severely affected the mass of copper released, it has reduced it nonetheless.

When comparing Figure 4.31 to Figure 3.34 in Section *3.4.1*, it is also clear that zinc leaches by diffusion much more easily than copper. The surface wash-off for zinc leads into the diffusive aspect of the leaching process without a break in the pattern, whereas it took some time for copper to begin diffusing from the spheres. Further evidence of this is that only 0.012% of the available copper leached out. This is little more than 1/6 of the percentage of zinc leached from the same test. This data backs up results from the small column tests which show that copper is more likely to be released via matrix dissolution than diffusion.

Spheres 4A and 4B also compare favourably with respect to the mass of copper leached, and the pattern with which it was released. Figure 4.32 illustrates this comparison.

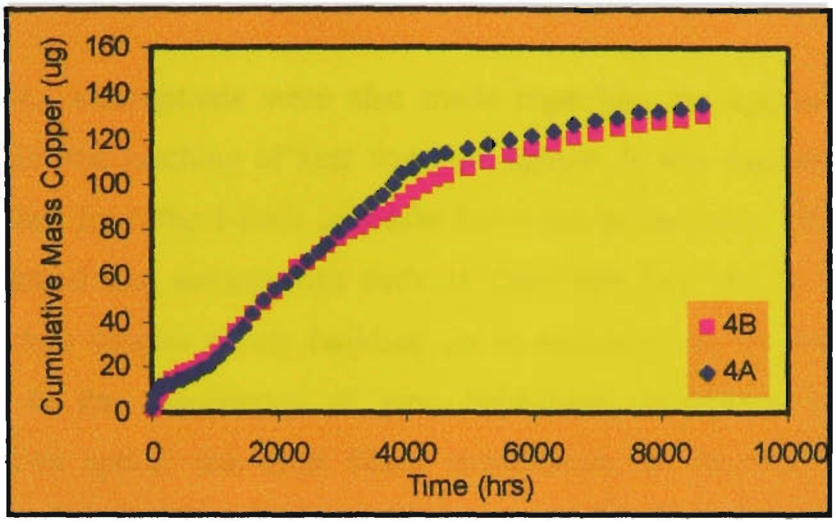


Figure 4.32: t_n = 4A & 4B – Cumulative Mass Copper Leached v's Time

What is remarkable about these results is that the split in sphere 4B (described in Section *3.4.1*) had no obvious effect on copper release. Further, as Table 4.8 details, even though sphere 4B had a much greater surface area available for leaching, it actually leached marginally less copper than did sphere 4A. Berardi *et al* (1997) investigated the matrix stability and leaching behaviour of ettringite-based stabilisation systems and noted similar behaviour. By tank leaching solid cylinders with a variety of leachants, they found that the more physically stable systems (although still monolithic) released amounts of calcium, aluminium and dopant metal greater or close to those released by the less physically stable systems. They suggested that the presence of needle-like ettringite microcrystals in the stable wastes provided a greater surface area available for leaching, thus facilitating greater release. The researchers concluded that 'it is often difficult to find direct correlation between physical and chemical characteristics of a binding matrix'.

The influence of a greater waste mass (and surface area) on reducing leachability was also observed with small columns ABLC100 and ABLC180 for copper. In both cases, one of the tests (ABLC180 and sphere 4B) had a greater amount of fixed waste available for leaching under the same leachant flow conditions as the other test (ABLC100 and sphere 4A), and yet it leached less copper. However, it should be reiterated that although a decrease in leaching was observed for sphere 4B, the difference was minimal. Therefore, small changes in waste surface area in the DLT do not appear to affect copper release.

In Section *3.4.1* assumptions were also made regarding the apparent reduction in driving-force for the leaching of zinc from the sphere. It was suggested that, as less zinc leached than from the 1-hour schedule this must be the case. The copper results have demonstrated that assumptions such as these can turn out to be false, where effects other than species purely building up in solution may be influencing metal release. Due to the consistency of zinc behaviour throughout most tests, that assumption does appear the most likely explanation for its DLT leaching data. However, the aforementioned slight variation in copper results between tests of different surface-areas makes any such statement for that metal a cautious one.

4.4.1.1 DLT; pH, Redox Potential, and Conductivity Results

Figures 3.36 to 3.41 in Section *3.4.1* illustrate the pH, redox, and conductivity results for spheres 1A, 1B, 4A and 4B. Although the data for spheres 1A & 1B and 4A & 4B correlate well for the electrode results, there are no significant correlations between that data and the copper leachability data, and, therefore, will not be discussed any further. As with previous tests, the increasing pH and decreasing conductivity at the beginning of both 1 and 4 hour tests corresponds to the high surface wash-off concentration observed for copper, before dropping to negligible levels. Both the 1 and 4 hour tests also show variations in conductivity levels as the leachate collection schedule changed to weekly and then fortnightly. Each change resulted in sudden increases in conductivity, no doubt a consequence of the build-up of alkalinity in the leachant over a longer period of time. If a decrease in driving force is a concern regarding estimation of rates of release for metals, these conductivity results imply that $Ca(OH)_2$, in contrast, is relatively unaffected by an increase in sampling time.

4.4.1.2 Mechanism of Copper Leaching

Plots of cumulative release of copper versus the square root of time are presented as Figures 4.33 and 4.34. As discussed in Section *3.4.1.1*, a straight line this type of plot is indicative of diffusive release.

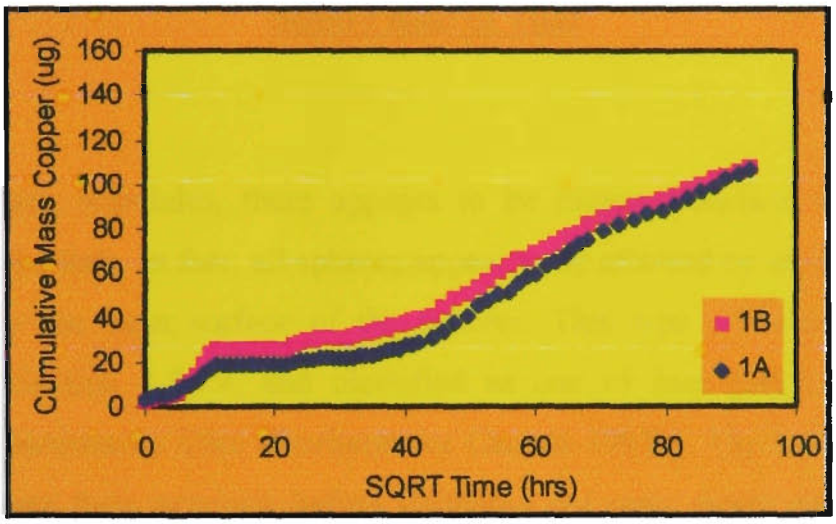


Figure 4.33: t_n = 1A & 1B – Cumulative Mass Copper Leached v's Square Root of Time

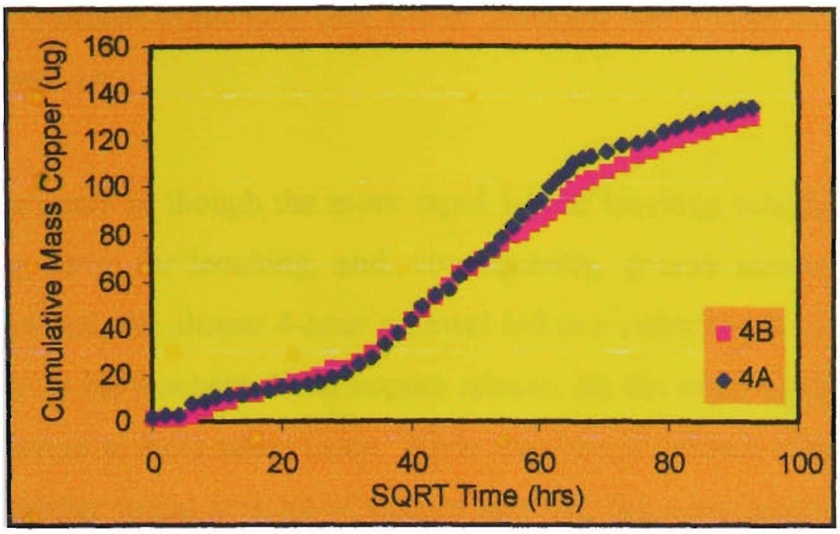


Figure 4.34: t_n = 4A & 4B – Cumulative Mass of Copper Leached v's Square Root of Time

In both leaching schedules, there appears to be minimal surface wash-off at the beginning of the tests. In fact, all spheres appear to be affected by an initial resistance to leaching to the outer surface of the spheres. This type of behaviour was first discussed in Section *1.3.4.4*, and identified as one of four general categories of leaching mechanisms by Côté (Environment Canada 1991b). The leaching of copper from all spheres then increases before flattening out once more, and this effect is certainly far more severe for the 1-hour test than the 4-hour test. Once again, a resistance to leaching is apparent, this time until approximately 1800 hours (where square root = ~42.5 hours) for the 1-hour test, and 1000 hours (where square root = ~31.5 hours) for the 4-hour test, after which copper release looks to be diffusion controlled in both cases. Quite possibly, this resistance to copper leaching from such a test is affected more by rapid leachant renewal than it is for leachant that is left in contact with the waste specimen for a longer period of time. Consequently, less frequent leachant renewal has resulted in the more rapid diffusion of copper from the 4-hour test, where this mechanism began to dominate leaching some 800 hours earlier than it did in the 1-hour test. Further, even though both renewal schedules were the same after 1764 hours (where square root = 42 hours), greater amounts of copper still leached from the spheres using the 4-hour schedule. What this data suggests, therefore, is that copper diffusion from the sphere will increase, immediately, and for some time after the leaching intervals employed in the DLT are, themselves, lengthened in duration. This contrasts to the zinc data where diffusion was greater in spheres 1A and 1B than in sphere 4A.

With zinc, it appears as though the more rapid 1-hour leaching schedule resulted in a greater driving force for leaching, and, consequently, greater concentrations in the leachate. In contrast, the slower 4-hour renewal led to a reduction in driving force and lower levels of in the leachate. With copper release, on the other hand, the reverse of this scenario seems to have taken place. While the 1-hour renewal schedule may have resulted in a greater initial amount of copper leached, the rapid leachant change may also have slowed the movement of copper species out of the sphere via diffusion. Once the leachant schedule stretched out to weekly, and then fortnightly, diffusion is occurring to a greater extent. For the 4-hour schedule, however, diffusion is obvious early in the piece. Considering that results from the column tests showed that copper release via diffusion appeared to be quite minimal, it makes sense that the 'faster' 1-hour test leached less copper via that mechanism. Consequently, once the rate of leachant renewal was slowed and the leachant was given time to penetrate the solid, the copper species were released from the sphere much more readily.

The plotting of release versus time on a log-log scale for both schedules in Figures 4.35 and 4.36 also clearly shows diffusion to be more dominant in the 4-hour schedule. An explanation of the utilisation of such a chart revolves around the slope of the subsequent plot, and is provided in Section *3.4.1.1.* Albino *et al* (1995) constructed similar log-log plots of their data after conducting dynamic leaching tests (ANS 16.1) for up to 6 months on metal-doped cement cylinders. Their results also produced slopes 'close enough to 0.5 to say that pore matrix diffusion is the main mechanism which effects the kinetics of (copper) leaching'.

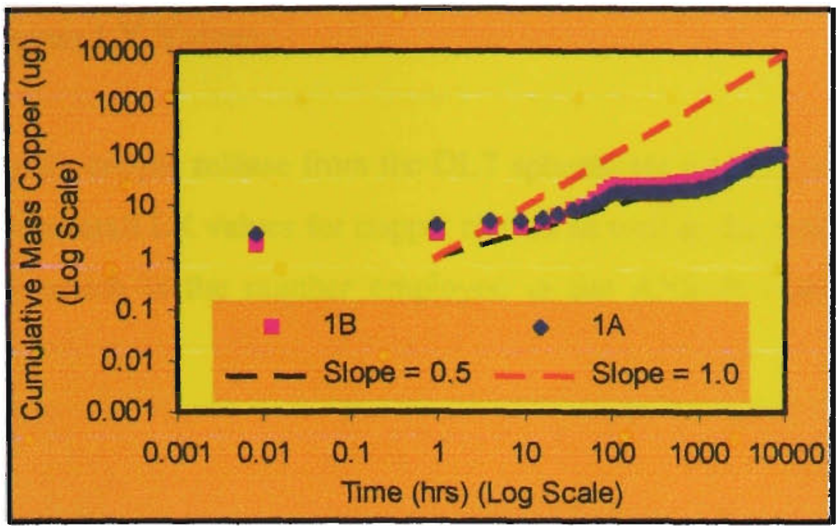


Figure 4.35: t_n = 1A & 1B – Cumulative Mass Copper Leached v's Time

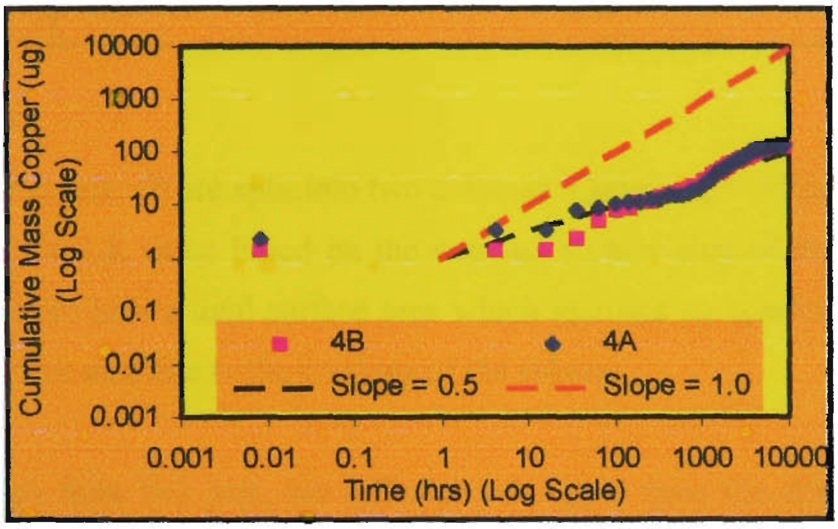


Figure 4.36: t_n = 4A & 4B – Cumulative Mass of Copper Leached v's Time

These plots also show dissolution to be non-existent in the DLT experiments. This is to be expected considering the benign nature of such water-based tests.

While it is important information that the mechanisms of release may vary depending upon the renewal schedule, equally important is the fact that the actual magnitude of copper release was shown to be minimal, with no more than 0.02% released from any of the DLTs after one year of leaching.

4.4.1.3 Copper LX Values

The LX values for copper release from the DLT spheres are detailed in Table 4.9. The table shows the overall LX values for copper release as well as the indexes for the first seven periods, which is the number employed in the ANS-16.1 protocol (USEPA 1989).

Table 4.9: Copper LX Data

Sphere	$t_n = 1A$	$t_n = 1B$	$t_n = 4A$	$t_n = 4B(a)$	$t_n = 4B(b)$
LX - 1st 7 Periods	13.49	14.00	13.75	14.14	14.50
LX - Total	14.50	15.00	14.62	15.00	15.35

The values for sphere 4B are split into two columns. Column $t_n = 4B(a)$ represents the calculation of the LX value based on the external surface area of the sphere, while column $t_n = 4B(b)$ uses a total surface area which includes an approximation for the increase in surface area due to the cracking of the sphere.

As can be seen from this data, the diffusion of copper from the spheres was quite minimal. As the range of overall LX data was 14.50 to 15.35, this certainly shows copper release from the spheres to be quite slow. These values are also approximately one LX unit higher than those for zinc, which further supports previous test data suggesting zinc can be leached more readily by diffusion than can copper.

The data in Table 4.9 shows the strength of diffusive leaching from all spheres to be very similar. The decrease in diffusivity of one order of magnitude (increase in LX of 1 unit) between the data for the first 7 periods of spheres 1A and B and the overall data for those spheres, clearly illustrates the influence surface wash-off had on the leaching of copper in the 1-hour test. For spheres 4A and B this decrease in diffusivity was not as significant, with an increase of only 0.85-0.87 LX units.

Another interesting point, already raised in Section *3.4.1.2.1*, is that LX values are expected to decrease with increasing renewal frequency. Although this appears to be the case for the copper data, the difference is only minor and cannot be used to support this proposition. In fact, the similarity between the results actually suggests that renewal frequency has not had a major effect on the *amount* of copper leached from the spheres. However, as discussed in Section *4.4.1.2*, the renewal frequency did affect the extent to which diffusion contributed to the overall amount of copper leached.

As with the zinc results, the copper data shows a higher LX value for sphere 4B(b) with the approximated surface area that included the cracking, than for the sphere 4B(a) calculation using the surface area of the outer surface of the sphere only. The reason for this is twofold, and thought to arise from a combination of a poorly approximated boundary condition of a zero surface concentration in the leachate, and an overestimation of an increase in surface area due to the cracking of the sphere (see Section *3.4.1.2.1*).

4.4.1.4 PIXE Analysis

Figure 4.37 illustrates the PIXE data for copper and, as with zinc, shows peaks in concentration at 388mm and 421mm, approximately 1mm in from the left edge and 2mm from the right. This supports suggestions made earlier in Section *3.4.1.3* that metal concentration will be present in higher amounts at the leaching boundary. Further, the concentration of copper drops sharply toward each edge of the sample, and to a much lesser extent toward the centre. In fact, as with zinc, the middle area of the plot demonstrates copper levels to be quite homogeneous throughout the sphere. It appears, therefore, that, as the copper has dissolved, the majority has diffused outward into the bulk solution, with a much smaller amount reprecipitating into the sphere.

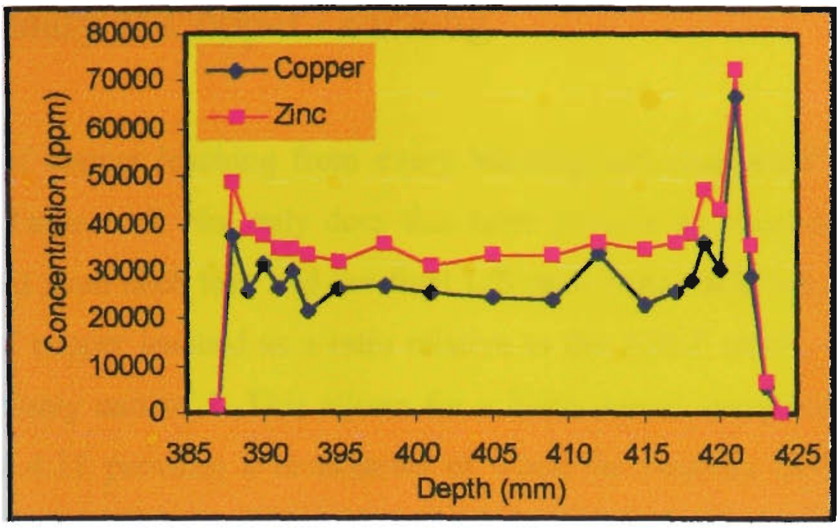


Figure 4.37: t_n = 4B – PIXE Data for Copper and Zinc

One of the most interesting features of this chart is that, like zinc, most of the copper appears to have been leached from the outer layer of the sphere. This was unexpected, as there is only approximately 20% more zinc in the waste than copper, and yet the percentage of zinc leached was 5-7 times greater than that for copper. Consequently, it was reasonable to expect a larger amount of copper in the outer layer of the sphere.

The most likely reason for this behaviour is that zinc leached more from sphere 4B due to the increase in surface area brought about by the split. Even though the cross section of the specimen shows a profile of metal leaching from one side of sphere 4B to the other, it does not show metal concentrations in the split section of the sphere. Therefore, considering species can leach from all available surfaces of the sphere and not just the section analysed via PIXE analysis, the leaching data would be expected to show the sorts of variations that have been observed for copper and zinc. In fact, considering zinc release has been shown to be affected more by surface area increases than copper, a much greater concentration of zinc in the leachates should be expected.

As a final point, the significance of the above discussion is not about why or how the zinc data does not match up with that for copper. Instead, it is that the PIXE data, while quite useful for establishing movement of species within the unfractured section sphere 4B, cannot be compared and contrasted to the leaching data with any great confidence due to the splitting that occurred early in the experiment.

4.5 Summary of Copper Leaching

A summary of copper leaching from every leaching test conducted in this work is presented in Table 4.10. Not only does this table provide an absolute percentage of copper leached from each test, and the final L/S ratio from each test, it also displays the amount of copper leached as a ratio relative to the ABLP result, which has been given the arbitrary unit of 1. This allows for a better visual comparison between the results. Table 4.11 provides a breakdown of when the majority of the copper was leached in the column and tank tests. That is, it shows how long was required for each 25% increment of the total amount of copper to be leached from the waste.

Table 4.10: Summary of Copper Results From All Tests

Test	**Percentage of Copper Leached**	**L/S Ratio**	**Ratio Leached (where ABLP = 1)**
MAT	26.7%	9.8:1	3337.5
TCLP	0.003%	20:1	0.375
ABLP	0.008%	20:1	1
Sequential ABLP	0.052%	200:1	6.5
Large Column	0.035%	19.1:1	4.375
LCC100	0.037%	17.6:1	4.625
ABLC100	0.34%	9571:1	42.5
ABLC180	0.14%	4873:1	17.5
DLT; T_n = 1A	0.012%	634.3:1	1.5
DLT; T_n = 1B	0.012%	626.2:1	1.5
DLT; T_n = 4A	0.016%	445.2:1	2
DLT; T_n = 4B	0.015%	447.5:1	1.875

Table 4.11: Leaching Breakdown of Copper From Column and Tank Tests

Test	Time to Leach 1st 25% of Total Copper (days)	Time to Leach 2nd 25% of Total Copper (days)	Time to Leach 3rd 25% of Total Copper (days)	Time to Leach 4th 25% of Total Copper (days)
Large Column	70	49	70	175
LCC100	100	105	56	105
ABLC100	4	49	142	168
ABLC180	95	77	78	112
DLT; T_n = 1A	66.7	69.8	84	140
DLT; T_n = 1B	22	93.5	77	168
DLT; T_n = 4A	60.2	48.3	56	196
DLT; T_n = 4B	54	47.5	77	182

As with the zinc data, the majority of the results have demonstrated that similar percentages of copper are released from tests in which the waste is allowed to establish its own leaching environment (i.e. all tests except the MAT). Further, Table 4.11 shows that, apart from the ABLC100 and Sphere 1A, copper release is fairly constant for the first 75% of release, with the last 25% taking a great deal longer to leach in all column and tank tests. Observations also reveal that, the greater the amount of agitation that occurs or the greater the L/S ratio, the greater the amount of copper released from the waste. This is most obvious in the ABLC100 and ABLC180 small columns, where a significant increase in L/S ratio in the 100g column led to a considerably greater mass of copper being leached from that column. Further, according to Table 4.11, the ABLC100 was the only column or tank test that showed a pronounced early release for copper. Nonetheless, the linearity of the leaching plots for both the ABLC100 and the ABLC180 columns suggest dissolution is the dominant leaching mechanism. As a consequence, it is suggested that the majority of the copper present in this waste is solidified rather than stabilised. This is further supported by the fact that greater amounts of copper were released in the Sequential ABLP compared to the earlier part of the ABLC100. Here, leaching by physical rather than chemical processes in the sequential test has been the more dominant release mechanism for copper. Agitation, therefore, may be more important for early release of copper from the waste than L/S ratio.

The DLT results showed that, when diffusion is the primary contributory leaching mechanism, minimal copper is released. The DLT data also showed that when the leachant renewal schedule is lengthened, the copper species were released from the sphere much more readily. This is thought to be due to the copper having a greater amount of time diffuse from further within the solid. While the leachant renewal schedule appeared to influence the amount of diffusive release that occurred, surface area did not seem as important. Even though zinc leaching was significantly affected by the increase in surface area of sphere 4B, the amount of copper released from spheres 4A and 4B was almost the same.

The PIXE work on sphere 4B showed the majority of the copper to diffuse out of the sphere, with only a minor amount moving inward and reprecipitating. This is an important finding because, as copper release appears to be dominated by matrix dissolution, a build-up of species within the waste could be a major concern if, over time, the waste was to break down and release the copper as a large concentration 'plug'.

All leaching results also showed conductivity, pH and redox potential yield little information on the leachability of copper under all test conditions. While it was initially thought that a lower system pH and higher Eh may have some influence on copper release, further testing showed the main driving forces for leaching to be waste agitation and L/S ratio. The main reason for the minimal effect of conductivity, pH and Eh on copper release is that the leachant employed in most tests was de-ionised water. Consequently, the waste itself controlled the leachate chemistry, as opposed to the leachant controlling waste leachability. In situations where a more aggressive leachant is employed, such as the MAT, this may not be the case. However, considering that, apart from the MAT, the highest amount of copper leached was 0.34% (ABLC100), it is unlikely such a waste would pose a copper-related contamination threat.

It is also important to emphasise that, apart from the MAT, 8 different types of leaching tests were investigated, all under varying conditions of L/S ratio, solid structure, leachant flow, column dimensions, test duration, etc. With all these variations, the overall difference between the lowest amount of copper leached (TCLP: 0.003%) and largest amount leached (ABLC100: 0.34%) was 113 times. That is, if a TCLP and any number of time-dependent tests (using de-ionised water) were run on this waste, the difference between the highest and lowest results would be approximately two orders of magnitude. Considering that, aside from the DLT tests, copper release has been shown to leach linearly with time, it is likely that a great deal more would be released the longer leaching was allowed to continue. Thus, presuming the leaching tests allow the waste to establish its own leaching environment, a 10^2 magnitude of difference between the highest and lowest results can be considered only as a minimum, and greater release of copper should be expected in the longer term as the matrix breaks down over time.

With this information in mind, a possible effective disposal scenario for the copper contaminant in this waste would be in a monofill where the waste can control its own leaching environment, and where matrix breakdown can be kept to a minimum.

5. Results and Discussion: Lead

5.1 Lead Analysis: Method Validation

Method validation for lead by DPASV was carried out according to the procedure described in Section *2.5.2.3.1* using a 17ml aliquot of a Large Column leachate of unknown concentration. Lead concentration by standard calibration was 33.10ppb and by standard additions was 32.72ppb. The difference is not significant. Accordingly, the method of standard calibrations was used throughout the leaching experiments for the analysis of lead. Lead recoveries were all between 97% and 106%. Method validation also demonstrated that no matrix effects were present in the analysis by standard calibration.

5.2 Batch Tests

The batch tests investigated in this study were the Maximum Availability Test, ABLP, Sequential ABLP, and TCLP. Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.4 – 2.4.6.*

5.2.1 Maximum Availability Test Results

The Maximum Availability Test was run in triplicate. An average of these results for mass and percentage of lead leached, pH, redox potential, and conductivity are detailed in Table 5.1. Results for each replicate for mass of lead leached, pH, redox, and conductivity, are shown in Appendix E (i). Volumes of acid added during the test are detailed in Section *3.2.1.*

Table 5.1: Lead Maximum Availability Test Data

Mass of Lead Leached (mg)	Percentage of Total Mass of Lead Leached (±1σ)	pH	Redox Potential (mV)	Conductivity (mScm^{-1})
303.03	21.8% (±0.14%)	4.68	564.1	6.6

This result demonstrates that no greater than 21.8% of the lead present in this solidified waste should leach out over time, with 79.2% remaining bound within the cement matrix.

5.2.2 TCLP Results

The average concentration, mass and percentage of lead leached, pH, redox potential, and conductivity in the TCLP are detailed in Table 5.2. Results for each of the four replicates for mass of lead leached, pH, redox, and conductivity, are shown in Appendix E (ii). The temperature during the extraction ranged from 20°C to 22°C.

Table 5.2: Lead TCLP Data

Concentration Leached (ppm)	Mass of Lead Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Lead Leached (±1σ)	pH	Redox Potential (mV)	Conductivity (mScm^{-1})
7.30	14.59	0.17% (±3.1 x 10^{-3}%)	12.11	232.1	12.8

The TCLP limit for lead is 5ppm (Table 1.5). Although only 0.17% of the lead present in the waste leached out in the TCLP, the concentration of lead in the leachate is still over the 5ppm TCLP limit.

A much higher percentage of lead leached out in the TCLP, than did copper or zinc (see Table 5.3). A possible reason for this may be that lead solubility is higher than that for copper and zinc in the initially low leachant pH. If that were the case, however, one would expect the percentages of lead leached in the primarily acidic Maximum Availability Test to be much higher than those leached for zinc and copper. As Table 5.3 clearly demonstrates, this was not the case.

Table 5.3: TCLP / MAT Results Comparison

Metal	Percentage Leached in Leaching Test	
	TCLP	MAT
Lead	0.168%	21.8%
Zinc	0.008%	49.3%
Copper	0.003%	26.7%

It is likely that the amphoteric behaviour of lead, combined with the higher final pH of the TCLP leachate, led to increased lead solubility, and, consequently, higher levels in the leachate. A comparison of the Pourbaix diagrams between lead, copper, and zinc, certainly shows lead to be more soluble at such pH and redox levels (pH = 12.1, Eh = 232mV) (Pourbaix 1974).

5.2.3 ABLP Results

The average concentration, mass and percentage of lead leached, pH, redox potential, and conductivity in the ABLP are detailed in Table 5.4. Results for each of the four replicates for mass of lead leached, pH, redox, and conductivity, are shown in Appendix E (iii). The temperature during the extraction ranged from 27°C to 29°C.

Table 5.4: Lead ABLP Data

Concentration Leached (ppm)	Mass of Lead Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Lead Leached ($\pm 1\sigma$)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
24.93	49.86	0.57% ($\pm 6.7 \times 10^{-3}$%)	11.60	210.3	8.20

These leaching results show that more than three times as much lead leached using the ABLP compared to the TCLP. Explanations for the neutral leachant of the ABLP releasing higher amounts of metals than the acidic TCLP revolve around acid-induced matrix attack and subsequent increased alkalinity release (see Section *3.2.3*).

The amphoteric nature of lead means that the high pH levels in the ABLP system can lead to much higher levels of lead in the leachates. A number of authors have shown lead to be easily leached at the high pH levels often encountered in cement-based wastes (Stegemann & Côté 1990; Fällman & Aurell 1996; Barna *et al* 1997; Sanchez *et al* 2000). Stegemann and Côté (1990) carried out equilibrium extractions on a number of treated and untreated wastes. They found that lead has a very low solubility in the high pH environment created by most S/S waste matrices, and that this is probably due to the formation of insoluble species of lead hydroxide. However, they do go on to point out that amphoteric metals, such as lead, tend to be somewhat more soluble at pH12 than pH10. This is supported by Barna *et al* (1997) in their investigation into the leaching behaviour of pollutants in S/S wastes. They solidified several industrial wastes in either ordinary Portland cement or blast furnace slag cement, before leaching the final products using a Dutch tank leaching test (NVN 7345). The results showed that solutions with pH of 12-13 gave the greatest release of lead. On the other hand, a solution saturated with carbon dioxide (pH 6-7) gave rise to the lowest release for lead. Similarly, Kamon *et* al (2000) subjected a cement stabilized waste sludge to column and batch leaching tests and found that, for lead, $Pb(OH)_2$ precipitates at weak alkali conditions, while a soluble complex ion ($Pb(OH)_4^{2-}$) is formed at a strong alkali condition. In their discussion on solid waste research, Ro *et al* (1997) point out that lead was solubilised more readily from MSW ash when extracted via the acidic leachants employed in the TCLP. They go on to further support Stegemann and Côté (1990) by pointing out that neutral to slightly alkaline environments appear to be the least conducive to metal leaching. Bin Shafique *et al* (1998) investigated the effects of carbonation on the leaching of cementitious wasteforms and showed lead to leach more at a higher pH. No mention is made, however, of the pHs encountered during the tests. Similar results were also obtained by Barna *et al* (1997) in their investigations into the leaching behaviour of pollutants in stabilized/solidified wastes. They leached a number of wastes using tank tests and a variety of leachants, and found that lime-saturated solutions (pH 12-13) gave the greatest flux of lead. Conversely, the solution saturated with carbon dioxide (pH 6-7) gave rise to the lowest flux of lead. Moskowicz *et al* (1997) also showed much greater release of lead from a Portland cement-based matrix using pH 12.5 leachant compared to pH 5 leachant. *Philipp et al* (1986) tested a number of variously fixed iron and steel industry wastes using a number of leaching tests. Their results revealed an increase in lead solubility when the system pH dropped from 7.5 down to 6 as a consequence of the addition of acetic acid. They also suggest the type of acid used in the leaching experiment can have a significant effect on metal leachability. In the case of a blast furnace sludge, more lead was leached using acetic acid than hydrochloric acid at the same pH. This is due to the very high solubility of lead acetate (552g/L H_2O) (American Mining Congress 1986). In a response to the (then proposed TCLP), the American Mining Congress (1986) argued a similar point. They stated that, although acetic acid is often described as a weak acid, it is a very aggressive acid in solubilising lead. This was supported by Baldi *et al* (source unknown) when they batch tested a waste treatment sludge with a variety of leachants, and found that significantly more lead was leached using a TCLP acetate buffer than was leached with CO_2 saturated water.

According to this research, there are two reasons the TCLP should have released higher amounts of lead than the ABLP. Firstly, the higher pH encountered in the TCLP (12.1 v's 11.6 in the ABLP), and secondly, the type of leachant used (acetic acid). One possible explanation for the fact that this did not occur is the time the TCLP leaching fluid may have taken to reach its final pH of 12.1. If the leachant was neutralised relatively quickly and then gradually climbed to a pH of 12.1, it could reasonably be expected that the system pH was neutral or only slightly alkaline for a significant time period of the test. As mentioned above, this would result in lower levels of lead release. Prange and Garvey (1990) investigated the impact of particle size on the TCLP leaching of cement-stabilised metallic wastes. They found that, in the extraction of the smaller particle sizes (1mm to 4mm), the pH of the TCLP leachant (Fluid #2, pH 2.88) attained a pH of 8.68 after 1 hour of leaching, 10.76 after 2 hours, and 11.66 by the end of the 18-hour test. Considering the waste type and particle size used in the research of Prange and Garvey is very similar to the one employed this work, it is possible, therefore, that the leachate pH in this TCLP experiment also followed a similar trend.

Another consideration is the form lead takes when solidified within a cement matrix. According to Herrera *et al* (1992), $Pb(OH)_3^-$ is the soluble species most likely to be present at the high pH found when cement is added to a lead-bearing waste. These ions then react to form lead polymers of aluminium and silicon hydrates that are less reactive, thus reducing the amount of lead available for leaching. It was also suspected that, unlike Cd^{2+} which was suspected of substituting for Ca^{2+} in the cement matrix, Pb^{2+} is not totally incorporated into the waste due to the size of the lead atom. Therefore, substitution for Ca^{2+} (in the CSH matrix) cannot take place, and the lead is not 'fixed' to any great extent in the matrix. Asavapisit *et al* (1997) also investigated the reactions of lead with cement during hydration, and they suggest a slightly different mechanism. They point out that in the basic environment present during cement hydration, the surfaces of cement particles will be negatively charged, and therefore able to adsorb metal cations. The most readily available cations in solution are Ca^{2+}, and these are believed to coat the silicate surfaces. Anionic species in solution (such as $Pb(OH)_3^-$) will then compete for Ca^{2+} adsorption sites forming a further layer, and are thus bound to the cement matrix. Zinc is also thought to behave in a very similar fashion, and is therefore expected to exhibit comparable release patterns to those for lead. This was only found to be the case for the Sequential ABLP, where the release patterns for both metals were quite similar (see Figures 3.1 and 5.1).

These theories of lead fixation are supported by research that shows lead and silicon release patterns to be very similar. Brown *et al* (1986) used a small upflow column to study the release patterns of heavy metals from S/S wastes. Their work showed lead release to coincide with silicate release in the lower section of the leaching column. These observations led them to suggest that lead may be bound into the silica matrix itself, rather than existing in the pores. Further, lead will not leach to any appreciable extent until the silica matrix breaks down, which is generally not until the leachate pH is very low. Research from Bishop (1988) also supports Brown *et al.* Therefore, according to the above suggestion, one would expect lead release to be controlled mainly by matrix dissolution. Both researchers further point out that metals that are trapped in the pores of a cement-based waste will be released as alkalinity ($Ca(OH)_2$) is released from the pores. Poon and Chen (1998) performed dynamic leaching tests on cement-stabilised wastes and found that, when the loss of calcium reached a certain level, matrix break–up at the waste surface contributed to greater release of some of the metals, particularly lead. Batchelor (1992) developed a numerical leaching model to describe leaching from S/S wastes based upon the interactions between hydrogen ion, calcium, lead, and acetate. His work showed that lower lead concentrations in the TCLP can be caused by changes in the solidified waste that would (normally) be associated with increased leachability. It was suggested that such non-intuitive behaviour was caused by interactions of lead chemistry with the acid-base chemistry of the leaching solution and alkalinity within the solid.

While the high pH assists in solubilising any available lead within the cement-waste matrix, it also retards acid-induced matrix dissolution and therefore the subsequent release of silicates and lead species. Complicating this are the initial pH level (and acetate concentration) in the TCLP leachate, and the effect this had on lead release over the course of the experiment. Another effect to take into account is the agitation that occurs in the TCLP and ABLP.

5.2.4 Sequential ABLP Results

The average concentration, mass and percentage of lead leached in the Sequential ABLP are detailed in Table 5.5. Results for each replicate for mass of lead leached, pH, redox, and conductivity, are shown in Appendix E (iv).

Table 5.5: Lead Sequential ABLP Data

Sequential Leach Number	Concentration Leached (ppm)	Mass of Lead Leached (mg)	Percentage of Total Mass of Lead Leached (±1σ)
1	24.93	49.86	0.57% (± 6.7 x 10^{-3}%)
2	21.47	42.95	0.50% (± 5.1 x 10^{-3}%)
3	16.52	33.04	0.38% (± 2.3 x 10^{-2}%)
4	12.85	25.70	0.30% (± 1.9 x 10^{-2}%)
5	12.86	25.73	0.30% (± 8.4 x 10^{-3}%)
6	13.76	27.51	0.32% (± 1.6 x 10^{-2}%)
7	14.02	28.03	0.32% (± 4.6 x 10^{-3}%)
8	3.61	7.22	0.08% (± 2.6 x 10^{-3}%)
9	3.17	6.33	0.07% (± 7.1 x 10^{-3}%)
10	4.28	8.57	0.10% (± 6.4 x 10^{-3}%)
Total	N/A*	**254.94**	**2.94%** (± 9.9 x 10^{-2}%)

*N/A = Not Applicable

The data, in Table 5.5, shows that approximately 2.94% of the lead present in the waste was removed after ten successive leaches. This demonstrates that the metal is reasonably well retained in the fixed waste system. It also demonstrates that the first ABLP leach acted as a worst case scenario test, since the maximum amount of lead leached in that particular extraction, and decreased steadily thereafter.

5.2.4.1 Leaching Behaviour of Lead

The data for the release of lead from the Sequential ABLP, depicted in Figure 5.1, shows lead to leach above the 5ppm TCLP/ABLP limit up to the 7th leaching interval (126 hours). At 144 hours the mass of lead released from the waste drops significantly, so that each of the last three leaches pass the TCLP/ABLP limit for lead.

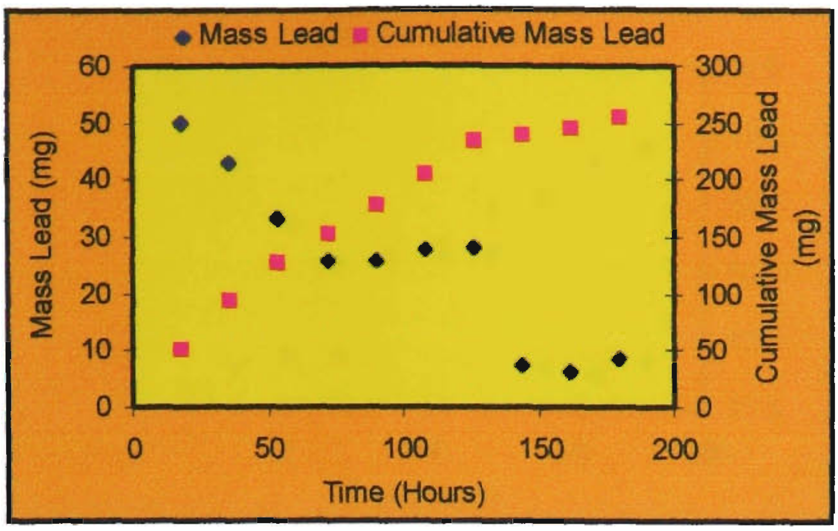


Figure 5.1: Sequential ABLP – Mass Lead Leached and Cumulative Mass Lead Leached v's Time

An examination of the lead/pH data in Figure 5.2 shows a broad reverse correlation between the two. The pH for the Sequential ABLP begins at 11.6, before climbing to 13.4 over the duration of the experiment. As has been stated previously, lead is expected to leach more at pH 12 than 10, although that is not what has occurred in this situation. Apart from the leaching period of 72 hours to 126 hours (where lead release was relatively constant), the amount of lead steadily decreases as leachate pH increases throughout the test. This disagrees with the notion that lead is more soluble at higher pH levels. In addition, inspection of the Pourbaix diagram for lead also shows that soluble hydroxides are expected to form under these conditions (Pourbaix 1974). Obviously, therefore, other mechanisms with a greater influence than pH are controlling lead leaching in the Sequential ABLP.

It was suggested earlier in Section *5.2.3* that, although lead is believed to be bound to the silicate matrix of the cement, the $Pb(OH)_3^-$ formed is not totally incorporated into the cement-matrix (Herrera *et al* 1992). Other research has shown metal trapped in the pores of a cement-based waste is released as alkalinity ($Ca(OH)_2$) is released from the pores (Brown *et al* 1986; Bishop 1988). For the most part (up to 176 hours), Figure 5.3 shows lead release to correspond well to the conductivity data observed in the Sequential ABLP.

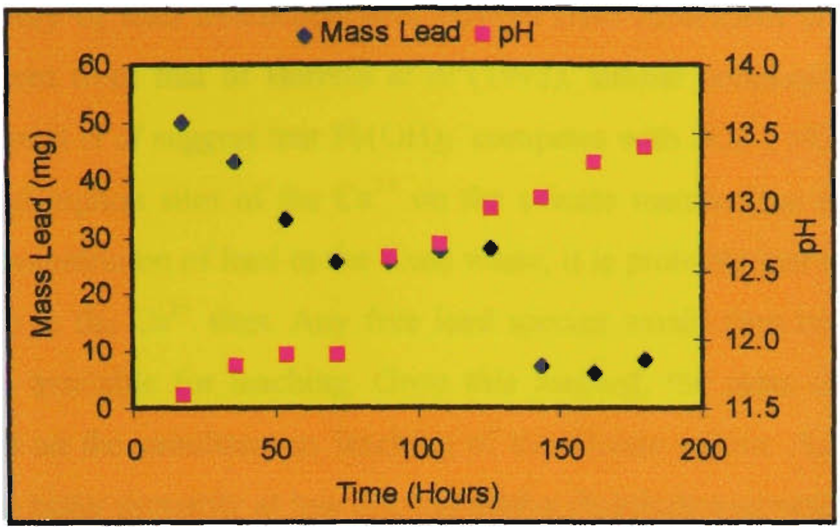


Figure 5.2: Sequential ABLP – Mass Lead Leached and pH v's Time

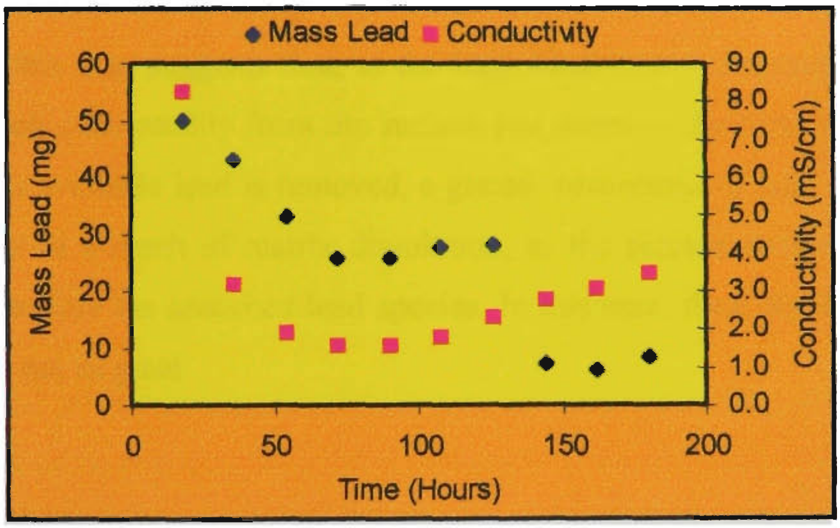


Figure 5.3: Sequential ABLP – Mass Lead Leached and Conductivity v's Time

Therefore, it appears that the lead is available for leaching from the surface and the pores of the waste for the first 126 hours, or seven extractions, of the test. After 126 hours, however, the mass of lead leached drops sharply suggesting that all of the readily available lead has been leached from the waste, and the only metal remaining is 'fixed' to the silicate matrix. This initial leachability would account for any lead, which, according to Herrera *et al*, was not totally incorporated into the cement-matrix.

While the theory of lead interaction with cement from Asavapisit *et al* (1997) was slightly different from that of Herrera *et al* (1992), similar conclusions can still be drawn. Asavapisit *et al* suggest that $Pb(OH)_3^-$ competes with SO_4^{2-}, NO_3^-, and OH^- for the cationic adsorption sites of the Ca^{2+} on the silicate matrix. Due to the relatively high initial concentration of lead in the fixed waste, it is probable that not all of it was able to adsorb to the Ca^{2+} sites. Any free lead species would then be trapped in the pores, readily available for leaching. Once this leached, the mass of lead released would depend on the simultaneous leaching of the silicate matrix. Although this has been shown to occur primarily at low pH, the matrix dissolution associated with such a physically aggressive test as the ABLP may lead to a more rapid breakdown of the silicate matrix. While the release of silicate (and lead) would not be as high as for a low pH system, it would still be significant, nonetheless.

In summary, this data suggests that, at the beginning of the Sequential ABLP, lead appears to leach quite readily from the surface and pores of the cement-waste matrix. In time, as this available lead is removed, a greater percentage of lead release is more likely to occur as a result of matrix dissolution, as the silicate matrix of the cement breaks down to free the adsorbed lead species. In this case, then, the effect of pH on lead release is not as great

5.2.4.1.1 Redox Potential Effects on Lead Leachability

As depicted in Figure 5.4, there appears to be only a broad correlation between lead release and redox potential. As explained previously in Section *3.2.4*, the lack of variation in redox potential precludes any conclusions being drawn from this data.

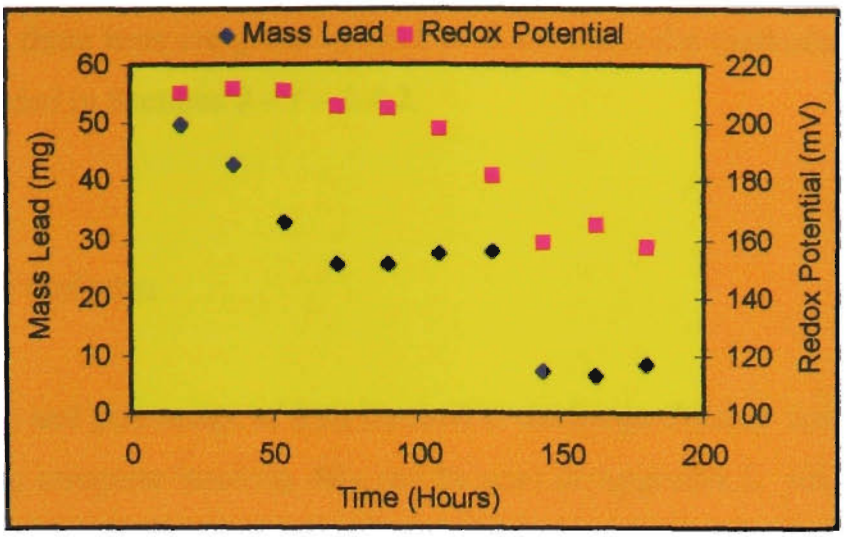


Figure 5.4: Sequential ABLP – Mass Lead Leached and Redox Potential v's Time

It is worth noting, however, that other research has shown that lead leaching has only a slight response to a change in leachant Eh. In 1985, Hermann and Neumann-Mahlkau analysed groundwater samples and concluded that lead concentrations appeared to be unaffected by changes in the redox potential (from +49mV to +347mV). Dusing *et al* (1992) investigated the effect of redox potential on leaching from S/S waste materials. They found that lead leaching appeared to increase with reducing conditions, although the lead leaching rates were very low. In a study on the effects of redox potential on waste testing, Standards Australia Working Group CH35 (1992) found that the influence of Eh on lead was unclear and was highly impacted by site-specific conditions. In contrast, Calmano *et al* (1993) carried out sequential chemical extractions on river sediments and found that more lead was released under oxidising conditions than reducing, for the same pH in the range 3 – 6.

5.3 Column Tests

One large column and several small column tests were investigated in this study. The small columns were the 100g Large Column Comparison (LCC100), 100g ABLP Comparison (ABLC100), and the 180g ABLP Comparison (ABLC180). Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.1 – 2.4.2.*

5.3.1 Large Column

The total mass and percentage of lead leached in the Large Column test are detailed in Table 5.6. The complete leaching data can be seen in Appendix L. All pH, redox and conductivity results are shown in Appendix F(ii).

Table 5.6: Large Column Test Data

Mass of Lead Leached (g)	Percentage of Total Mass of Lead Leached
36.90	1.12%

As for both zinc and copper, the percentage of lead released in the Large Column was greater than in the ABLP and TCLP, but less than in both the Sequential ABLP and the MAT (see Table 5.7). Further, as Table 5.8 reveals, a much greater percentage of lead was leached from the Large Column test compared to that for zinc and copper.

When read in combination with Tables 3.6 and 4.6, the data in Table 5.7 emphasises the point that much more lead than copper or zinc has leached from the waste in every test (including columns and DLT also), bar the MAT. This means that, in the only test where the pH of the leaching environment is rigorously controlled, the percentage of lead leached is less than copper, and much less than zinc.

Table 5.7: Percentages of Lead Leached in Batch Tests and Large Column

Leaching Test	Percentage of Total Mass of Lead Leached	Liquid to Solid Ratio	Method of Leachant Contact
Large Column	1.1%	19.1:1	Downflow Spraying
TCLP	0.2%	20:1	Rotary Agitation
ABLP	0.6%	20:1	Rotary Agitation
Sequential ABLP	2.9%	200:1	Rotary Agitation
Max. Avail. Test	21.8%	9.8:1	Stirring

Table 5.8: Percentages of Lead, Zinc, and Copper Leached in Large Column

Metal	Percentage of Total Mass of Metal Leached
Lead	1.12%
Zinc	0.09%
Copper	0.04%

5.3.1.1 Leaching Behaviour of Lead

Figure 5.5 illustrates the leaching pattern of lead from the Large Column. The figure clearly shows a surface wash-off period of approximately one-month, followed by around 150 days of steady leaching. After this, the mass of lead leached increases slowly, up until end of the test some 180 days later.

This pattern of release is actually quite different from that observed for both copper and zinc. Apart from an early, sharp spike for copper, both copper and zinc leached very similarly (refer Figure 4.5). There was an obvious period of rapidly increasing surface wash-off followed by gradually decreasing concentrations of each metal in the leachates.

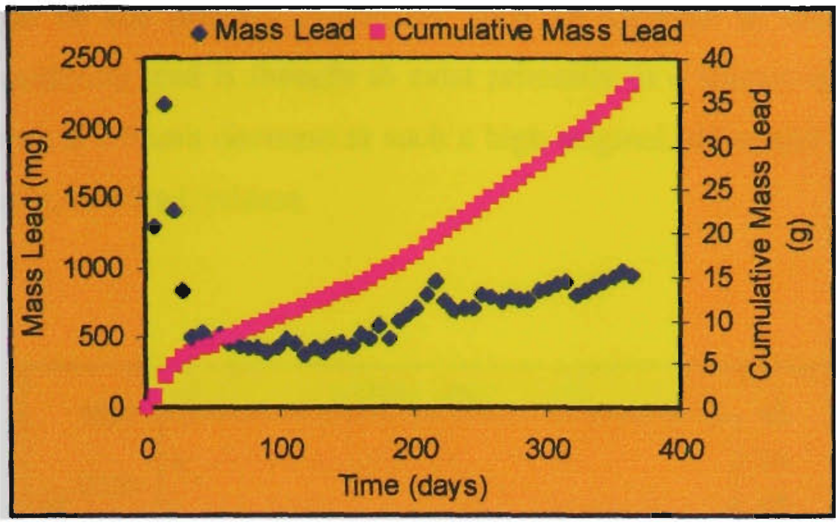


Figure 5.5: Large Column – Mass Lead Leached v's Time

The release for lead differed significantly in that the surface wash-off period increased only 2 weeks before the lead levels began to decrease. In addition, lead leaching increased at around 180 days, and continued increasing until the end of the experiment. This contrasted to the constant decrease in both zinc and copper concentrations in the leachates.

5.3.1.1.1 pH, Redox Potential, and Conductivity Effects on Lead Leachability

The results of the pH, redox and conductivity measurements (depicted in Figures *5.6 – 5.8*) provide valuable information on the possible mechanisms of lead leaching.

Note that, in order to better represent the conductivity data so that any patterns present may be easily identified, the first four points have been removed from the chart. The correlation between the mass of lead released and the conductivity measurements in the first four days of the test was excellent, as was the data for the remainder of the first month where surface wash-off predominates. After this, the lead levels stay relatively constant while the conductivity slowly decreases. At 180 days the lead levels begin to increase while, at the same time, the conductivity drops more sharply, before levelling off up to the end of the experiment. Similarly, at around the 200-day mark, the pH also drops sharply from approximately 14 down to 12.5. Ordinarily, such a pH decrease might be the primary reason for such an increase in metal leachability. However, considering lead is thought to exist primarily as a silicate-bound species in cement matrices, a 1.5 unit decrease at such a high original pH would have a minimal effect on silicate, and lead, release.

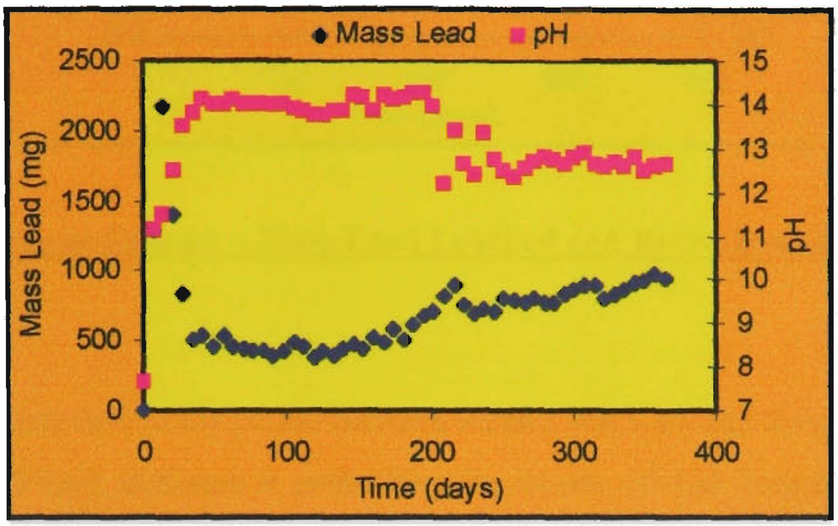


Figure 5.6: Large Column – Mass Lead Leached and pH v's Time

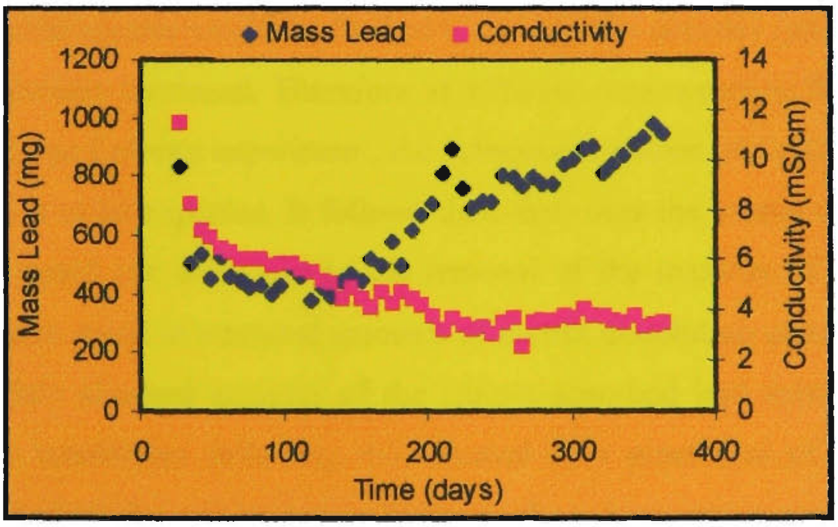


Figure 5.7: Large Column – Mass Lead Leached and Conductivity v's Time

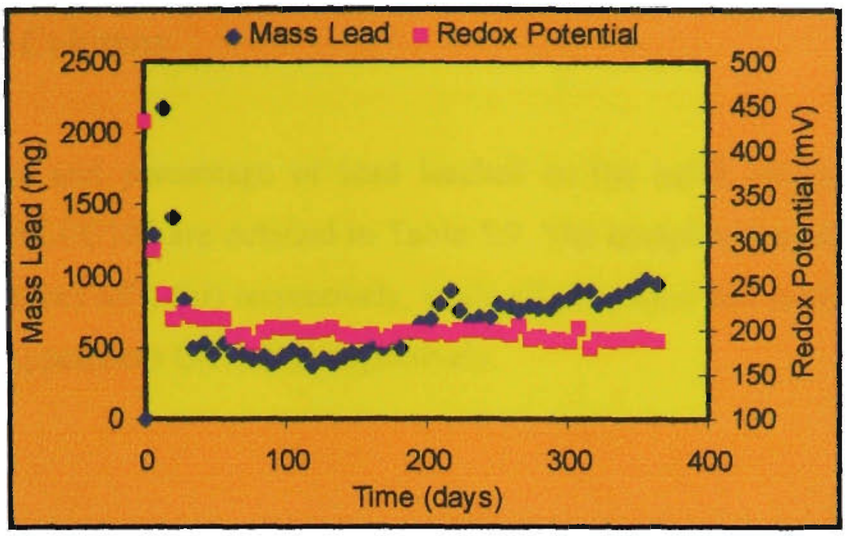


Figure 5.8: Large Column – Mass Lead Leached and Redox Potential v's Time

This data suggests that, in the period between surface wash-off and the increase in lead leaching at 180 days, diffusion is controlling the release of lead from the pores in the matrix. It was mentioned in Section *4.3.2.1.1* that there was a considerable period of time each day where the flow of liquid in the Large Column was relatively stagnant. During this period of no-flow, any liquid saturating the waste would be providing an environment conducive to leaching only by pore-based diffusion. Once the flow started again any diffused species would be flushed away, and the porosity (and tortuosity) of the waste fractionally increased. Therefore, if diffusion was occurring for a significant period of the Large Column experiment, the subsequent release of $Ca(OH)_2$, and pore-available lead, is to be expected. It follows then that, over the course of the yearlong leaching, this would not only lead to the removal of the majority of pore-available lead, but may also result in marginal amounts of matrix dissolution and the subsequent release of slightly elevated amounts of the silicate-adsorbed lead species. Therefore, gradual matrix breakdown following the removal of a great deal of pore-available $Ca(OH)_2$ is thought to be a contributing factor to the subsequent increase in available lead after 180 days.

It is interesting that all three major mechanisms of release (surface wash-off, pore-based diffusion, matrix dissolution) appear to play a part in lead release from the large column. This contrasts with copper and zinc where surface wash-off is considered to be a dominant source of metal release from the waste.

5.3.2 Small Columns

The total mass and percentage of lead leached in the small columns ABLC100, ABLC180, and LCC100 are detailed in Table 5.9. The complete leaching data can be seen in Appendices M(i)-(iii) respectively, while all pH, redox and conductivity results are shown in Appendices G(iv)-(vi) respectively.

Table 5.9: Lead Small Column Test Data

Small Column	Mass of Lead Leached (mg)	Percentage of Total Mass of Lead Leached
ABLC100	240.46	2.7%
ABLC180	966.90	6.2%
LCC100	55.13	0.64%

5.3.2.1 ABLC100; Leaching Behaviour of Lead

Table 5.9 shows that the ABLC100 leached a relatively small amount of lead over the year the test was run. A far greater percentage of lead was, however, leached from the column than was leached for copper (0.34%) and zinc (0.32%).

Figure 5.9 clearly illustrates the substantial impact that surface wash-off had on the release of lead in the ABLC100. In fact, over ¼ of the total lead leached over the duration of the test, was leached inside the first 2 days. Further, after 4 days, more than ½ of the total was leached, and ¾ was leached after only 9 days. This demonstrates that leaching steadied to a constant level for the last 354 days of the test. The effect of surface wash-off is, therefore, much greater on lead leaching from the ABLC100 than from the Large Column which took 84 days to release ¼ of the total amount of lead leached over the duration of the test

A comparison between the leaching patterns of lead, copper, and zinc (Figure 5.10) illustrates the varying importance of surface wash-off on the release of those metals. While surface wash-off is responsible for negligible release of copper from the waste, it is shown to be a very important contributor to both zinc and lead release. This, no doubt, is a consequence of the suspected similarity in the fixation mechanisms of the metals to the cement matrix (See Section *5.2.3*).

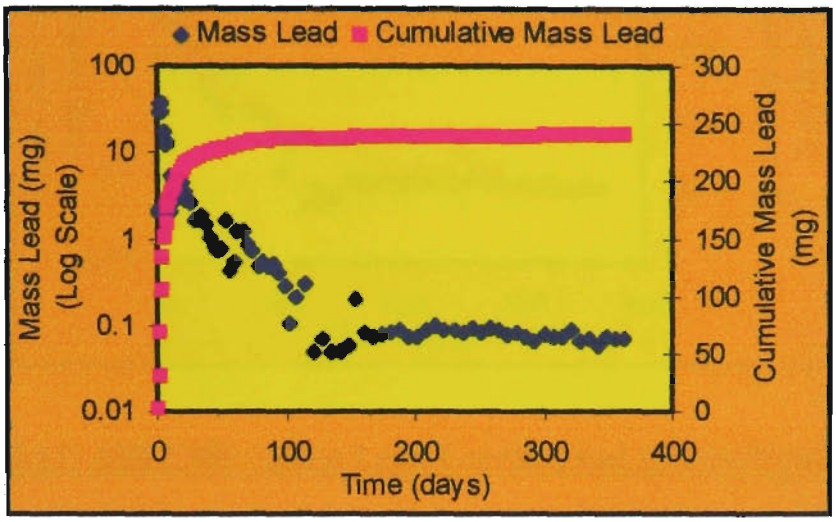


Figure 5.9: ABLC100 – Mass Lead Leached v's Time

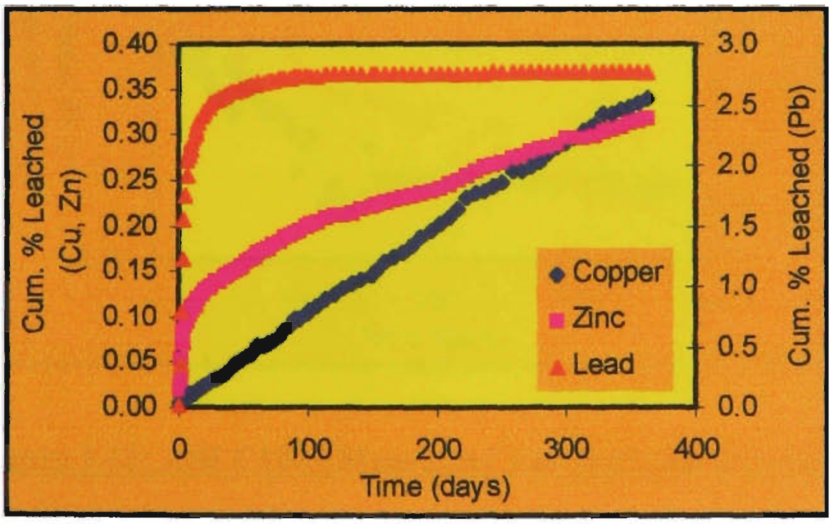


Figure 5.10: ABLC100 – Cumulative Percentage Lead, Copper, and Zinc Leached v's Time

Apart from the obvious period of surface wash-off, the leaching pattern for lead suggests release is dominated primarily by diffusion from the pores for the majority of the experiment. This is supported by the comparisons between release, conductivity and pH in Figures 5.11 and 5.12.

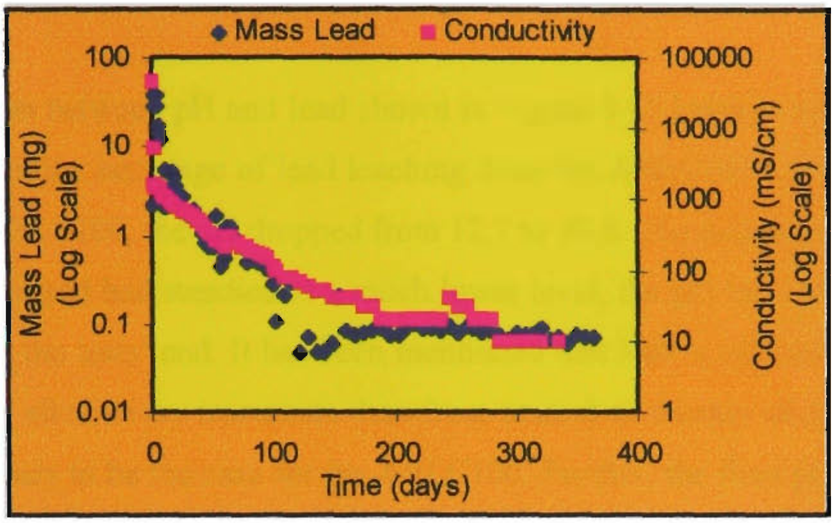


Figure 5.11: ABLC100 –Mass Lead Leached and Conductivity v's Time

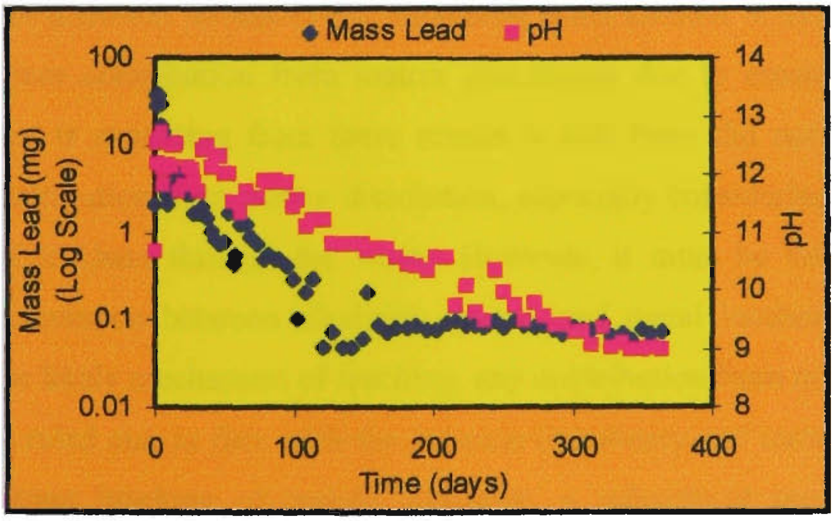


Figure 5.12: ABLC100 –Mass Lead Leached and pH v's Time

Figure 5.11 shows an excellent correlation between pattern of lead release and conductivity. While the influence of surface wash-off was not as great for the release of alkalinity as for lead, the following period of release until approximately 130 days was very similar. As stated earlier, this agreement between the release of alkalinity and lead suggests pore-initiated diffusion as the dominant leaching mechanism at this stage. The pattern of release for lead is also followed closely by the conductivity results for the final period of the experiment. At this stage it appears that the rate of diffusion has slowed as, not only has the conductivity dropped to less than 10μS cm^{-1}, but also the mass of lead leached has levelled off and is rather low.

The correlation between pH and lead shown in Figure 5.12 helps to explain what may be occurring in the last stage of lead leaching from the ABLC100. Over the first ~130 days of the ABLC100, the pH dropped from 12.7 to 10.8. Thereafter, when the mass of lead being released had steadied at a much lower level, the pH had dropped further to less than 9 by the tests' end. It has been mentioned that lead is expected to leach more from strongly alkaline environments than from neutral or weakly alkaline states. This certainly appears to be the case for the ABLC100. Further, the final pH, although low, will not contribute significantly to matrix dissolution and the subsequent release of any calcium silicate – adsorbed lead species. At such pH levels, and with the alkalinity release also quite low, it seems as though the majority of pore-available lead was released in the first 130 days of the test. In the following months, release is a combination of diffusion release of the remaining small amount of available lead, and a possible minor contribution from matrix dissolution due to erosion of the waste particles. What is surprising from these results is that there did not appear to be a significant contribution from matrix dissolution, especially considering the reasonably rapid flow of leachant through the waste. However, it must be stressed that even though the correlation between alkalinity release and metal leaching indicates that diffusion is the likely mechanism of leaching, any contribution from matrix dissolution should not be ruled out. In fact, with the increase in porosity and tortuosity from such apparently strong leaching of matrix alkalinity, a subsequent increase in matrix dissolution is inevitable. This, therefore, emphasises how difficult it can be to differentiate between mechanisms of diffusion and dissolution purely by observing time-dependent release plots for metals.

5.3.2.1.1 *Redox Potential Effects on Lead Leachability*

Figure 5.13 depicts a plot of redox potential and mass of lead leached in the ABLC100. As expected, it shows a reverse trend to that observed for pH (Figure 5.12).

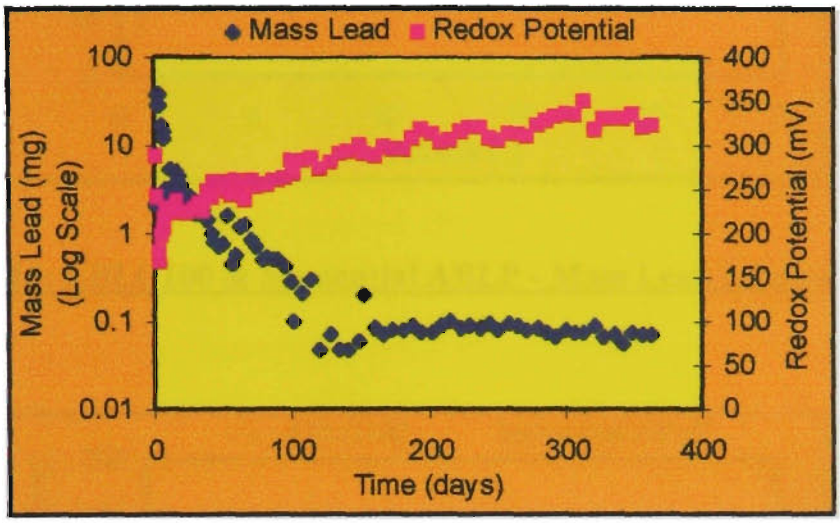


Figure 5.13: ABLC100 - Mass Lead Leached and Redox Potential v's Time

While the effect of Eh on lead release is, at times, quite contradictory (see Section *5.2.4.1.1*), there does not appear to be any significant change in the redox data to suggest it had a more pronounced effect on lead release than did surface wash-off. If anything, the suggestion by Hermann and Neumann-Mahlkau (1985) that changes in redox potential from +49mV to +347mV did not affect groundwater lead concentrations, is strongly supported by the ABLC100 Eh data.

5.3.2.1.2 *Comparison to Sequential ABLP*

Figures 5.14 and 5.15 illustrate moderate similarities for the leaching pattern of lead between the ABLC100 and the Sequential ABLP. The red data point indicates the combination of the first and second data points for the ABLC100 (See Section *3.3.2.1.2*).

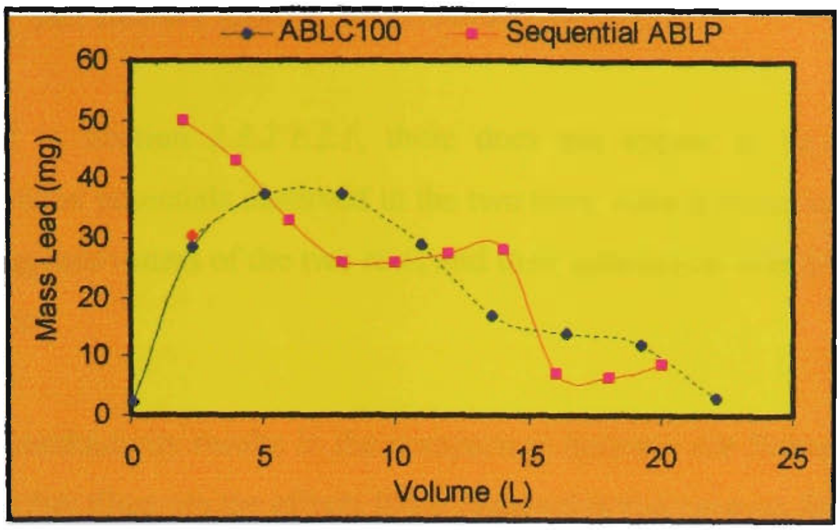


Figure 5.14: ABLC100 & Sequential ABLP - Mass Lead Leached v's Time

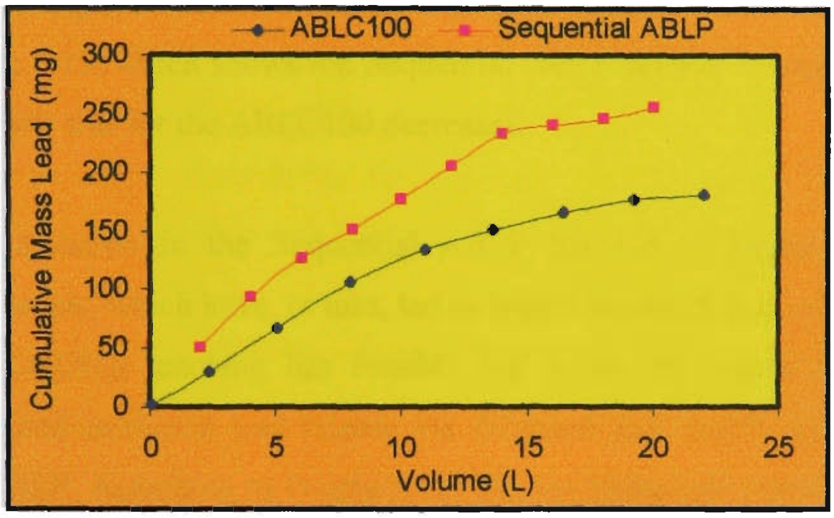


Figure 5.15: ABLC100 & Sequential ABLP - Cumulative Mass Lead Leached v's Time

While the patterns are quite similar, the obvious difference between the two tests is the actual mass of lead leached. In the Sequential ABLP, 2.94% of all lead present was leached. By comparison, only 2.04% leached from the ABLC100 for approximately the same volume of leachant. This is no doubt a consequence of the better contact of the leachant with the waste in the Sequential ABLP.

5.3.2.1.2.1 pH, Redox Potential, and Conductivity Effects

As discussed in Section *3.3.2.1.2.1*, there does not appear to be any correlation between the redox potentials observed in the two tests. Also detailed in that section are the relative aggressiveness of the two tests and their subsequent effects on conductivity and pH results.

The pH and conductivity results in the comparison between the Sequential ABLP and ABLC100 further illustrate the effects those parameters can have on lead leaching. The pH comparison in Figure 3.15 shows a dip in ABLC100 pH after the 10L mark, whereas the Sequential ABLP pH continues to climb. Similarly, after the 10L point, the conductivity for the Sequential ABLP climbs rapidly, in contrast to the very slightly decreasing ABLC100 values. This data corresponds well to the lead leaching data in Figure 5.15, which shows the Sequential ABLP release to increase from 10 to 15L point, while that for the ABLC100 decreases.

The greater agitation in the Sequential ABLP has led to higher pH (>13) and conductivity levels, which have, in turn, led to higher levels of lead released. Here, an increase in $Ca(OH)_2$ leaching has feasibly led to greater matrix porosity, higher leachate pH, and increased lead release via diffusion and matrix dissolution for the Sequential ABLP. According to Pourbaix (1974), the higher pH would also favour the formation of $Pb(OH)_3^-$ and $Pb(OH)_4^-$, thus solubilising lead. In contrast, release of lead from the ABLC100 was dominated by surface wash-off in the early part of the experiment.

5.3.2.2 ABLC180; Leaching Behaviour of Lead

After one year of leaching, the ABLC180 released 966.9mg of lead, or 6.205% of the original amount in the column. Although lead appears to have been only moderately retained within the matrix, when considering the overall trend of leaching illustrated in Figure 5.16, it is expected that little more lead will leach out in the medium term.

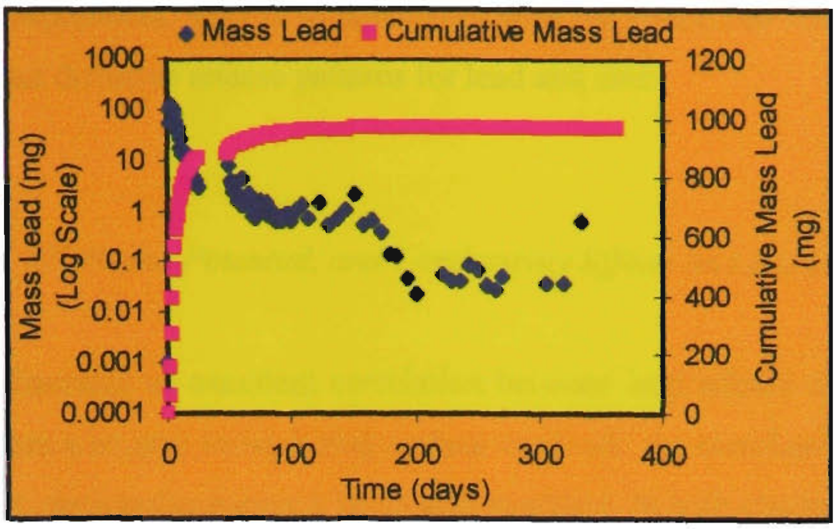


Figure 5.16: ABLC180 - Mass Lead Leached v's Time

After a significant amount of lead was released via surface wash-off, the mass of lead leached in the ABLC180 decreases sharply. Eventually, within 100 days of the commencement of the experiment, the mass leached had reached a plateau and minimal change in lead release was observed thereafter.

Figures 5.17 and 5.18 also illustrate the effect the break in leachant flow and sampling (explained in Section *3.3.2.2*) had on the pattern of lead leaching. Following the resumption of leachant flow, the level of lead released had risen to 14.75mg, up almost 490% from the pre-drought level of 3.02mg. The mass of lead released then took a total of 6 days to return to the pre-drought levels. As explained in Section *3.3.2.2*, this behaviour is indicative of a combination of pore-based diffusion, and the leaching of other, previously trapped, metal species in the solid matrix. However, the leaching of non-pore-available lead was not as significant as that for zinc, which took 21 days to drop back to pre-drought levels. The lead data also contrasted to the behaviour of copper, which dropped back the day after the resumption of leachant flow.

Foster (1998) demonstrated similar behaviour for lead in his small column work (refer to Section *3.3.2.2* for a description of his experiments). He showed that, as with zinc, the lead levels increased sharply in the second week of leaching for the 'constant soak' with the small particles, before slowly decreasing in concentration over the remaining weeks of the experiment. This is in agreement with the ABLC180 results which also provided similar diffusive release patterns for lead and zinc.

5.3.2.2.1 *pH, Redox Potential, and Conductivity Effects on Lead Leachability*

Figure 5.17 illustrates an excellent correlation between lead release and conductivity data. Aside from a reverse trend during surface wash-off, the correlation between lead release and pH, depicted in Figure 5.18, is also excellent. In both charts, the decreasing pH and conductivity levels are responses to a decrease in the amount of alkalinity being leached from the cement matrix. The mass of lead leached corresponds well to the removal of alkalinity, suggesting that, after surface wash-off, pore-based diffusion is the major mechanism controlling leaching of lead from the ABLC180. This is also similar to all other time-dependent experiments investigated thus far, which have indicated lead leaches primarily by surface wash-off and diffusion.

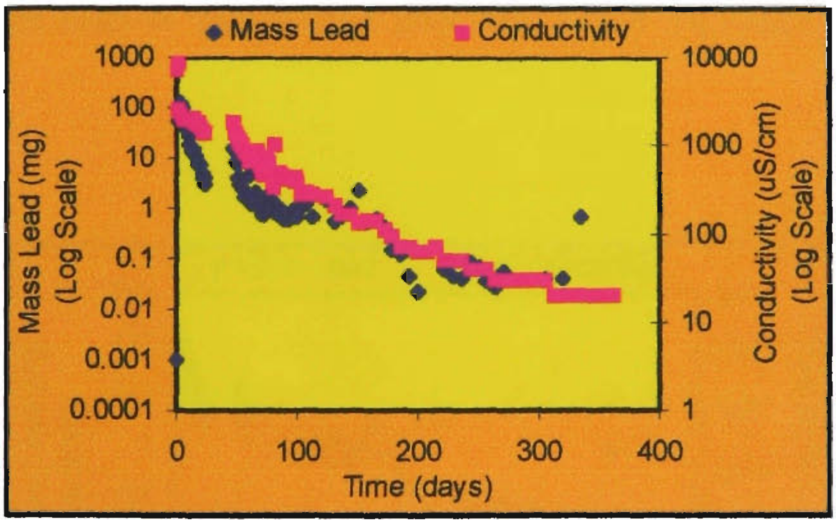


Figure 5.17: ABLC180 –Mass Lead Leached and Conductivity v's Time

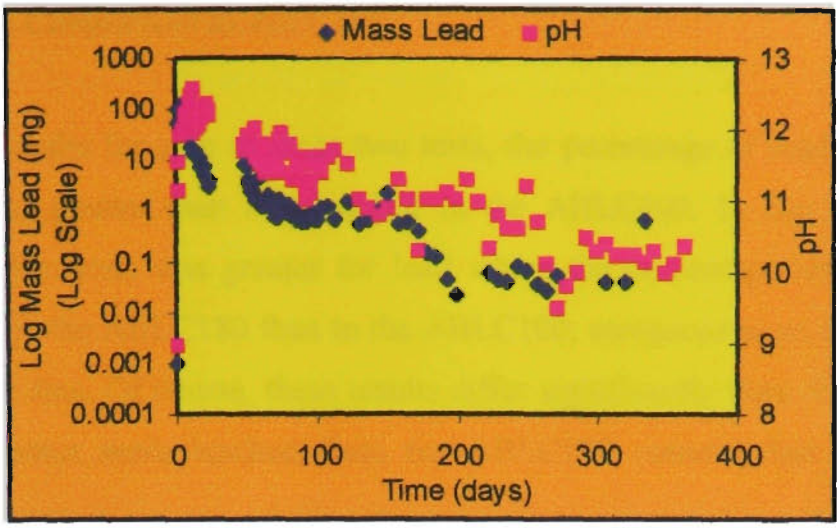


Figure 5.18: ABLC180 –Mass Lead Leached and pH v's Time

The redox results are interesting, as a correlation between them and lead leaching only became apparent following the end of the drought period. Figure 5.19 shows minimal correlation prior to the suspension of leachant flow. After it has resumed, the redox potential of the leachates rose steadily from approximately 200mV to over 300mV. Further, as the mass of lead leached plateaued, so did the redox potential of the leachates.

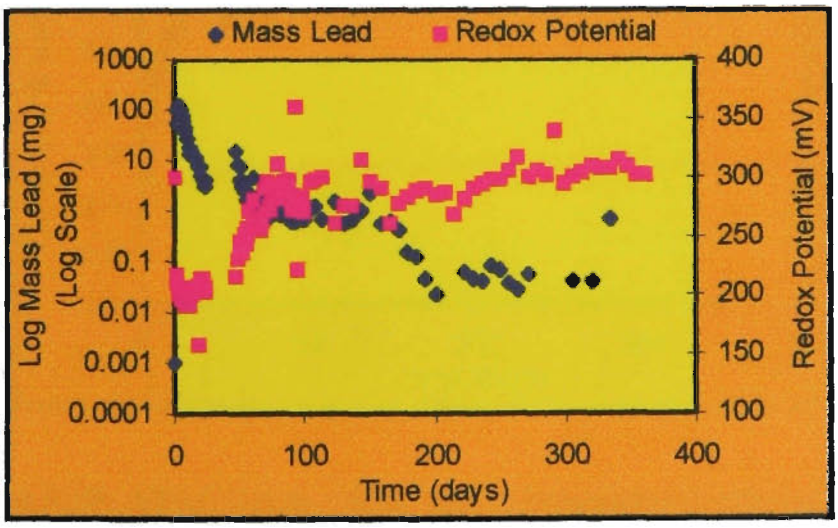


Figure 5.19: ABLC180 –Mass Lead Leached and Redox Potential v's Time

5.3.2.2.2 Comparison to ABLC100

As with the results for zinc in these two tests, the percentage of lead leached in the ABLC180 was greater than that leached in the ABLC100. In fact, the difference between the two tests was greater for lead where the percentage leached was 2.24 times greater in the ABLC180 than in the ABLC100, compared to an increase of only 1.34 times for zinc. Of course, these results differ significantly from those for copper, where 1.37 times more leached from the ABLC100 column than the ABLC180 column.

Aside from the difference in mass leached, the actual pattern of leaching for lead in the ABLC180 corresponds extremely well to that observed in the ABLC100. This comparison is illustrated in Figure 5.20. As with the other metals investigated so far, the only conclusion that can be drawn regarding the higher percentages leached in either test, is that the lower L/S ratio encountered in the ABLC180 has had a significant effect on lead leachability. It has not, however, influenced the actual pattern of lead leaching between the two tests.

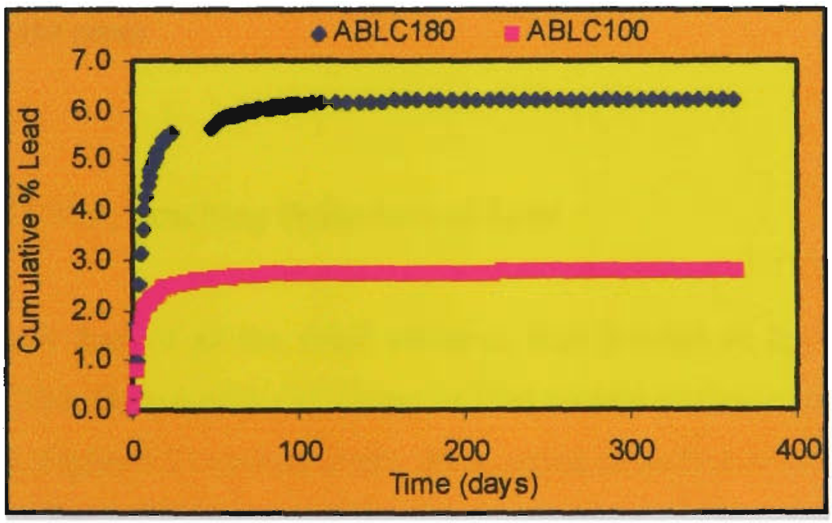


Figure 5.20: ABLC180 & ABLC100 – Cumulative Percentage Lead Leached v's Time

Also worth noting is that this increase in lead leaching at a lower L/S ratio contrasts with the conclusions of Philipp *et al* (1986). In their investigations into the leaching characteristics of iron and steel industry waste, they found that an increase in L/S ratio is conducive to greater concentrations of lead in the leachate.

5.3.2.2.2.1 Comparison to ABLC100; pH, Redox Potential, and Conductivity

Figure 3.21 (Section *3.3.2.2.2.1*) illustrates very similar patterns for redox potential for the two columns, with the ABLC100 recording slightly more oxidising conditions. Figures 3.22 and 3.23 (also in Section *3.3.2.2.2.1*) show the pH and conductivity levels in the ABLC180 to be slightly higher than the ABLC100. These results indicate that a greater amount of $Ca(OH)_2$ was removed from the ABLC180 than the ABLC100, no doubt a consequence of the higher amount of solids in the former test and, therefore, a lower L/S ratio. While the difference in the leaching of alkalinity and lead from the pores appears important early on in the two tests, where release of lead from the ABLC180 is much higher than from the ABLC100, after 100 days the effect is less obvious. At this point, the stable pattern of lead release from both columns indicates its release is relatively unaffected by elevated pH, or conductivity, once most of it has diffused from the pores.

5.3.2.3 LCC100; Leaching Behaviour of Lead

Table 5.9 shows that, of all the small columns, lead leached in the lowest amounts from the LCC100. Only 0.64% (55.13mg) of lead present in the column was released to the leachate. Figure 5.21 reveals a very short period of surface wash-off followed by steady leaching for the remainder of the test. In Figure 5.22, the leaching pattern for lead appears very similar to that for zinc, but different from copper where no distinct period of surface wash-off was evident. All three metals leached relatively steadily for the remainder of the test, although zinc and copper levels increased sharply at around 200 days, an increase that was not observed for lead.

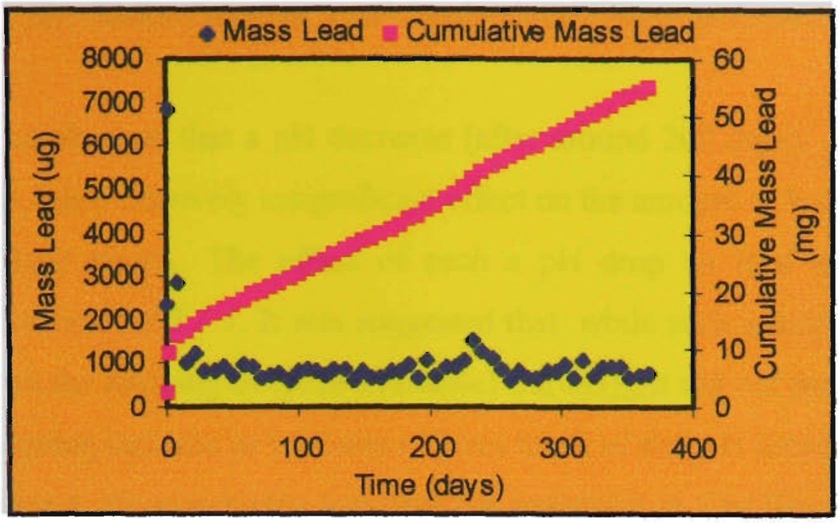


Figure 5.21: LCC100 - Mass Lead Leached v's Time

Of the total amount of lead released in the LCC100, the first 25% were leached in 22 days, the second 25% in 120 days, the third in 133 days, and the last 25% in 91 days. The slightly quicker release of the final 25% compared to the previous 50% is courtesy of a slight increase in lead leaching at around 230 days. This increase is, however, lower in intensity, and occurred at a later stage, than a similar increase observed for copper and zinc (see Figure 4.24).

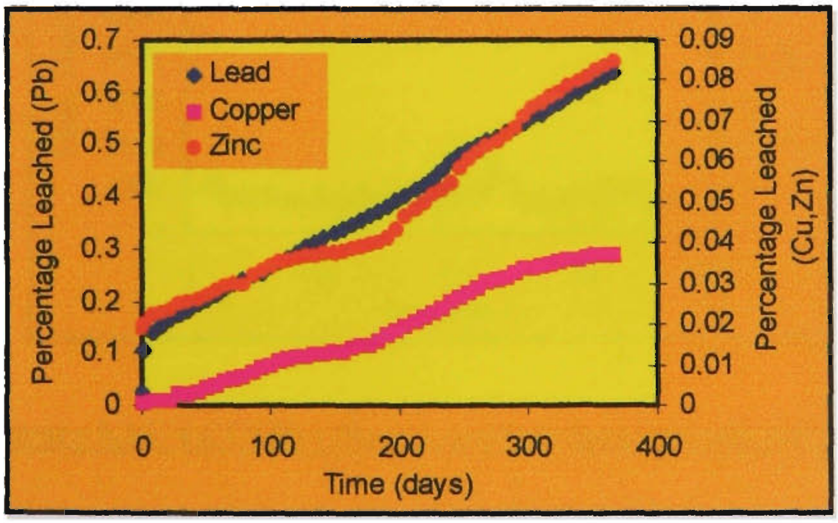


Figure 5.22: LCC100 – Cumulative Percentage Lead, Copper, and Zinc Leached v's Time

5.3.2.3.1 *pH, Redox Potential, and Conductivity Effects on Lead Leachability*

Figures 5.23 emphasises that a pH decrease (after around 200 days), at such initially high pH levels, has a relatively insignificant effect on the amount of lead released from the cement-based matrix. The effect of such a pH drop on lead leachability was discussed in Section *5.3.1.1.1*. It was suggested that, while such a drop was indicative of a decrease in the leaching of (pore-available) $Ca(OH)_2$, it did not necessarily follow that any subsequent increase in lead was a direct result of that pH decrease. Rather, for the Large Column, the conclusion was that the reduction in $Ca(OH)_2$ from the pores would lead to an increase in matrix porosity and tortuosity. While this would normally increase lead diffusion, the amount of lead readily available for leaching from the pores may already have been significantly depleted. Hence, the slight increase in matrix dissolution resulting from the initial diffusive processes was thought to provide a slight increase in lead leaching. This appears to be the case for the LCC100, where a decrease in pH at around 200 days corresponds to a decrease in conductivity at the same time. This is illustrated in Figure 5.24.

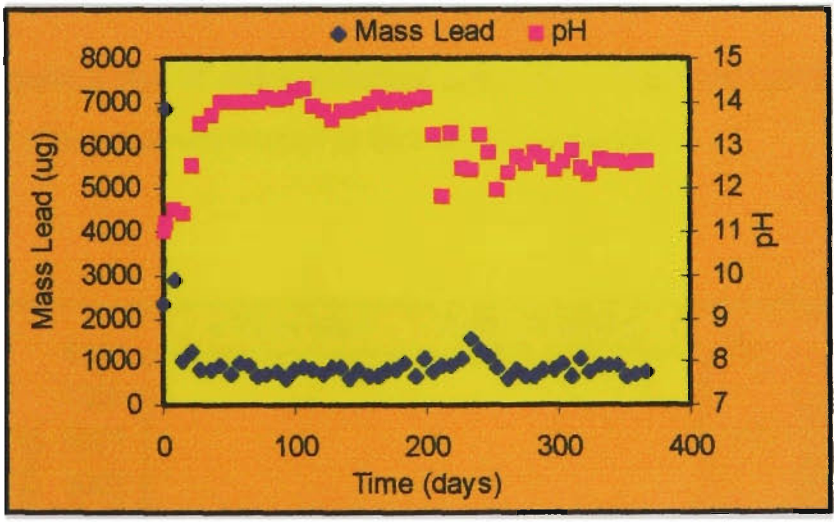


Figure 5.23: LCC100 - Mass Lead Leached and pH v's Time

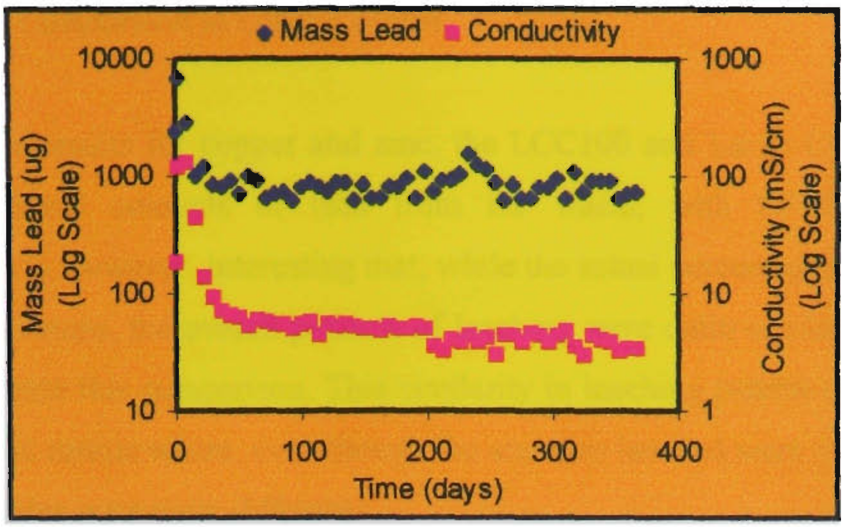


Figure 5.24: LCC100 - Mass Lead Leached and Conductivity v's Time

The increase in lead leaching soon after the pH and conductivity decrease may, indeed, be a consequence of a slight increase in matrix dissolution. If that is the case, the contribution is small and short lived as, within two weeks, the amount of lead leached returned to the levels observed prior to the increase. Just as likely is that the increase is purely coincidental, and the increase is a random spike in lead release.

Figure 5.25 depicts a plot of redox potential and mass of lead leached in the LCC100. As expected, it shows a reverse trend to that observed for pH.

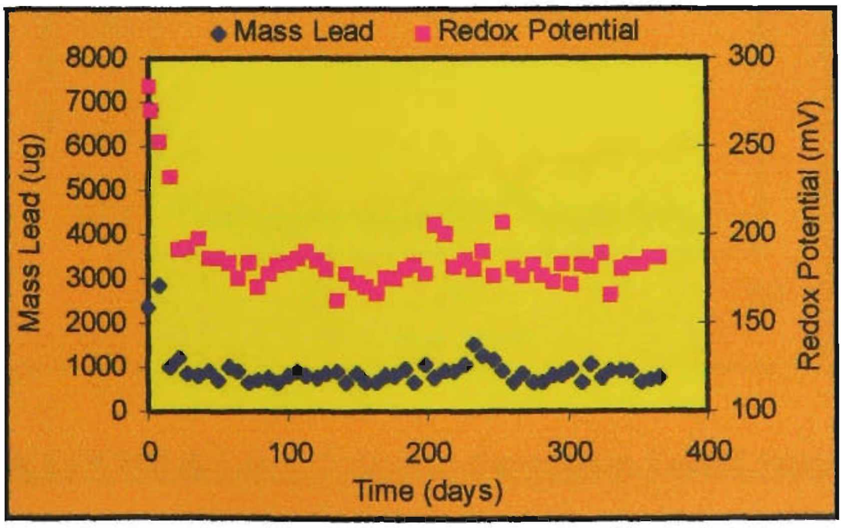


Figure 5.25: LCC100 - Mass Lead Leached and Redox Potential v's Time

5.3.2.3.2 Comparison to Large Column

Contrary to the results for copper and zinc, the LCC100 and Large Column leached markedly different amounts of lead from the waste, with 0.64% and 1.12% respectively. It is, however, interesting that, while the actual percentages of lead varied between the columns, the overall patterns of leaching were quite similar. Figures 5.26 and 5.27 illustrate this comparison. This similarity in leaching pattern contrasts to the copper and zinc results where, even though the amounts leached were comparable, the patterns of release were quite different.

While the amount leached via surface wash-off from each column is essentially the same, the Large Column leaches marginally greater amounts of lead from that point until around 200 days. After this the mass of lead leached from the Large Column increases significantly and climbs steadily until the end of the experiment. Lead release from the LCC100, on the other hand, remains constant throughout the remainder of the experiment following the period of surface wash-off. In contrast, the lead results from the LCC100 correspond with the other two small columns, which showed a period of surface wash-off followed by steady diffusive release.

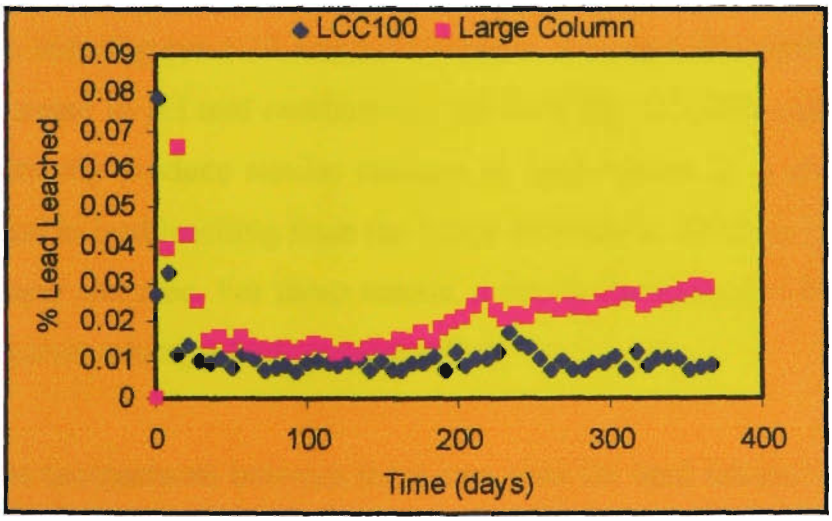


Figure 5.26: LCC100 & Large Column – Percentage Lead Leached v's Time

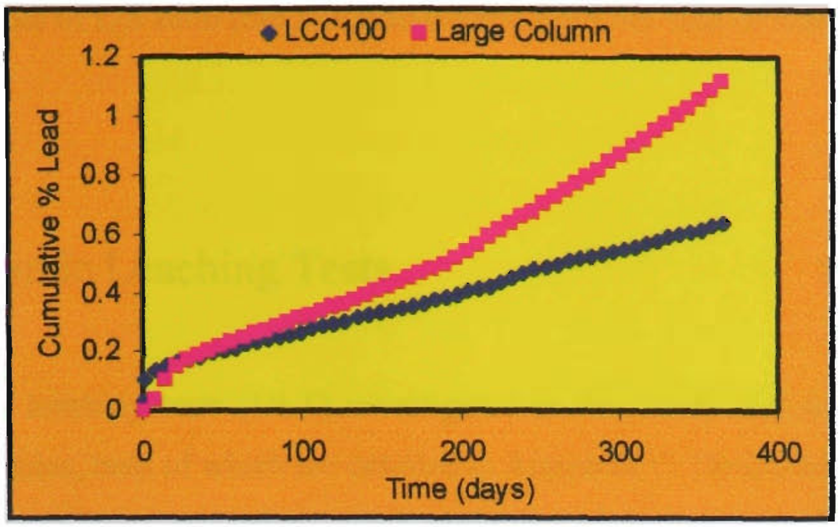


Figure 5.27: LCC100 & Large Column – Cumulative Percentage Lead Leached v's Time

5.3.2.3.2.1 Comparison to Large Column; pH, Redox Potential, and Conductivity

The graphical comparisons between these parameters of the LCC100 and Large Column can be seen in Figures 3.31 – 3.33 in Section *3.3.2.3.2.1*. The observations regarding the similarities between the results are also covered in that section, and will, therefore, not be repeated here.

In conjunction with Figures 5.26 and 5.27, Figures 3.31 and 3.32 demonstrate that an equivalent decrease in pH and conductivity for both the LCC100 and Large Column does not necessarily produce similar changes in lead release. It is also worth noting that the increase in lead leaching from the Large Column at 200 days contrasted to the results for copper and zinc. For those metals, a steady decrease was observed and the pH and conductivity changes had minimal effect.

Regardless, the comparisons between these two tests for lead release further illustrate that column size is important, not only for the amount of a metal released, but also for the manner in which it is released. Further, these differences can be amplified or diminished based on the type of metal leached, L/S ratio, flow rates, and pH, redox, and conductivity levels. Therefore, the work thus far has shown that scaling down a column in terms of L/S ratio (but not dimensions) does not lead to identical results for metal release.

5.4 Dynamic Leaching Tests

The dynamic leaching tests (DLT) investigated in this study utilised two leachant renewal schedules, both of which are detailed in Appendix C. Details of the waste used in these tests are given in Section *2.3.2*, while the methodologies of these tests are provided in Section *2.4.3*.

5.4.1 Leaching Behaviour of Lead

Two DLTs were run for each renewal schedule. These were labelled 1A and 1B for the rapid renewal rate of 1 hour, and 4A and 4B for the slower renewal rate of 4 hours (Refer Section *2.4.3.2)*. The masses leached in each of these experiments are detailed in Table 5.10. The complete leaching data can be seen in Appendices N (i) – N (iv). All pH, redox, and conductivity data are shown in Appendices H (v) – H (viii).

Table 5.10: Lead DLT Test Data

Replicate	$t_n = 1A$	$t_n = 1B$	$t_n = 4A$	$t_n = 4B$
Mass Leached (mg)	3.87	2.88	6.21	30.62
% Leached	0.10	0.07	0.15	0.76

Table 5.10 shows that approximately 35% more lead leached from sphere 1A than sphere 1B. This contrasts markedly from the results for both zinc and copper, where each metal was leached in similar amounts from both spheres. Figure 5.28 does, however, illustrate an obvious agreement between the pattern of leaching for lead from both spheres.

There is no obvious period of surface wash-off from either sphere, with both 1A and 1B appearing to leach lead via diffusion from the outset. Much has been discussed so far of the suspected mechanism of lead fixation via adsorption to the cement silicate surfaces. Further, in the many tests investigated thus far, the major mechanism of lead release is believed to be that of diffusion. That is, any lead that was not adsorbed onto the silicate surfaces during the cement setting was trapped in the pores and can only be released via diffusive processes. Therefore, the DLT provides a means of evaluating the extent to which the lead has been trapped in the pores of the waste, and not effectively adsorbed onto the silicate surfaces.

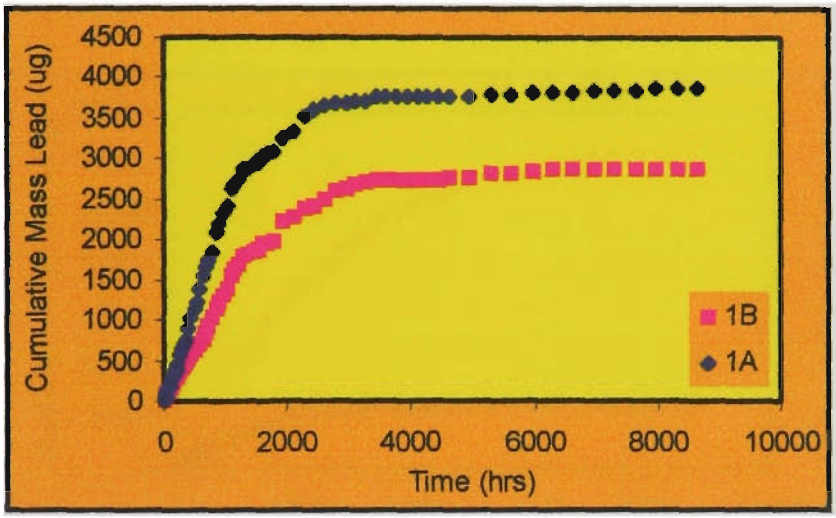


Figure 5.28: t_n = 1A & 1B – Cumulative Mass Lead Leached v's Time

In the case of spheres 1A and 1B, it is clear that the lead has been better retarded in the cement matrix of sphere 1B than 1A. It is, therefore, possible that, regardless of the care taken to produce spheres of equivalent homogeneity, the lead in sphere 1B has reacted differently during the cement setting reactions than the lead in sphere 1A. Obviously then, if the *mechanism* with which a metal is fixed into a cement matrix is easily affected by mild production changes, its magnitude of release from one specimen to the next may differ markedly. That is, if more lead is trapped in the pores of one sample, and more is fixed to the calcium silicate sites in another, the first sample will obviously leach more lead, regardless of the amounts of lead available or the homogeneity of the samples themselves. Consequently, even though the patterns of release for lead between spheres 1A and 1B were similar, this difference in magnitude of release has still occurred. In contrast, copper and zinc, which are each fixed by different mechanisms again, demonstrated almost identical release patterns and percentages of release between the two spheres.

The results for spheres 4A and 4B (illustrated in Figure 5.29) are also quite different. Although the pattern of lead release is effectively the same from the two spheres, the actual amount of lead leached differs significantly. While 0.154% of the lead present in sphere 4A leached out in one year, sphere 4B released 0.761% of the lead originally present, an increase of almost 500%.

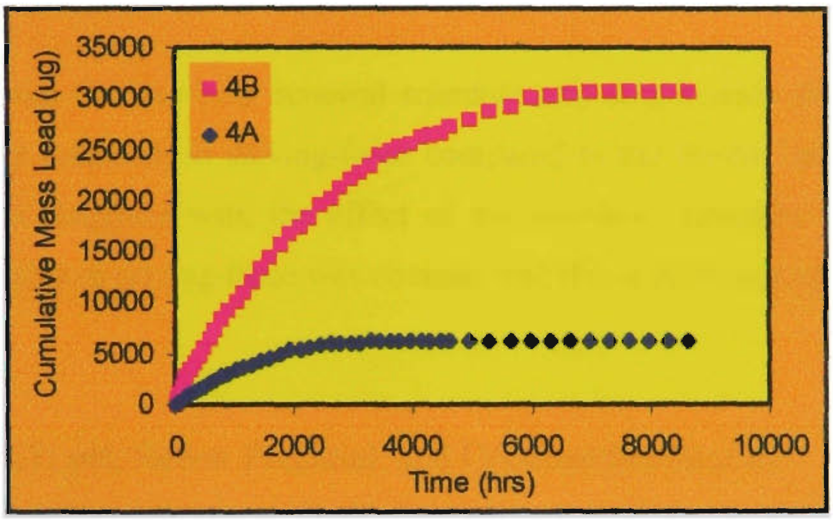


Figure 5.29: t_n = 4A & 4B – Cumulative Mass Lead Leached v's Time

The reason for such a difference is the split that appeared in sphere 4B earlier on in the test and increased the surface area available for leaching by approximately 50% (see Section *3.4.1*). However, while this split had no effect on copper release, and the increase in zinc leaching was only 50% (the equivalent of the surface area increase), the effect on lead leaching was far more extreme.

While the increase in surface area of sphere 4B demonstrated that surface wash-off contributes significantly to zinc release and little to copper release, it also revealed that surface wash-off is not necessarily the only mechanism that is affected by such an increase. Considering a 50% increase in surface area produced an equivalent 50% increase in zinc leaching, the obvious outcome is that release of zinc from the waste is dominated by surface interactions. Further, minimal difference in copper release shows that the mechanisms of surface wash-off and diffusion facilitate minimal copper release. However, the fact that the same increase in surface area led to a 500% increase in lead leaching further supports earlier suggestions that lead leaches predominantly by diffusion from the pores. Therefore, any increase in surface area will also lead to an increase in the volume of pore space available for leaching, and the subsequent amount of lead leached from those pores. Consequently, in the case of lead, the increase in surface wash-off is relatively insignificant compared to the increase in pore-based release. This, understandably, has significant implications with respect to the dangers of wastes degrading in landfills over time.

The results from the four-hour renewal schedule also demonstrate that there did not appear to be a reduction in driving-force compared to the results from the one-hour schedule. This disagrees with the effect of the four-hour schedule on zinc release where a reduction in driving-force was obvious, and this is discussed in Section *3.4.1*.

5.4.1.1 DLT; pH, Redox Potential, and Conductivity Results

Figures 3.36 - 3.41 in Section *3.4.1* illustrate the pH, redox, and conductivity results for all spheres. Although the data for spheres 1A & 1B and 4A & 4B correlate well for the electrode results, there are no significant correlations between that data and the lead leachability data. Both the 1 and 4 hour tests also show variations in conductivity levels as the leachate collection schedule changed to weekly and then fortnightly. These changes are discussed in Section *4.4.1.1*.

5.4.1.2 Mechanism of Lead Leaching

Plots of cumulative release of lead versus the square root of time are presented as Figures 5.30 and 5.31. As discussed in Section *3.4.1.1*, a straight line this type of plot is indicative of diffusive release.

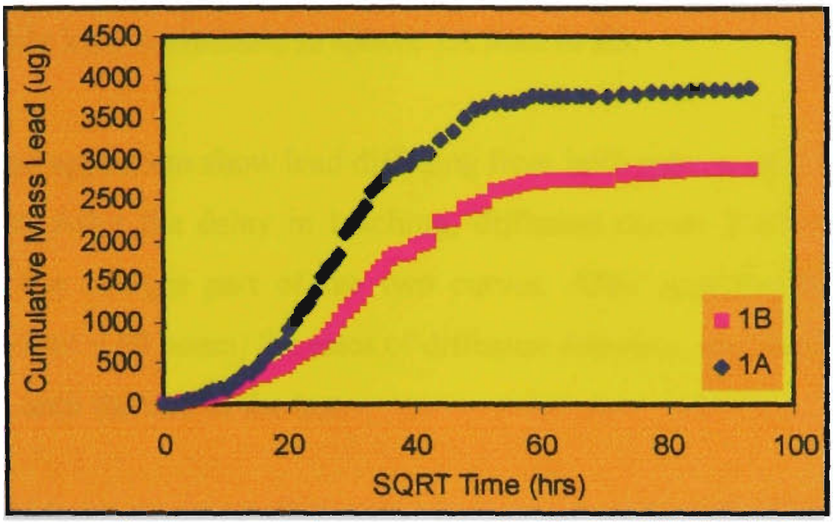


Figure 5.30: t_n = 1A & 1B – Cumulative Mass Lead Leached v's Square Root of Time

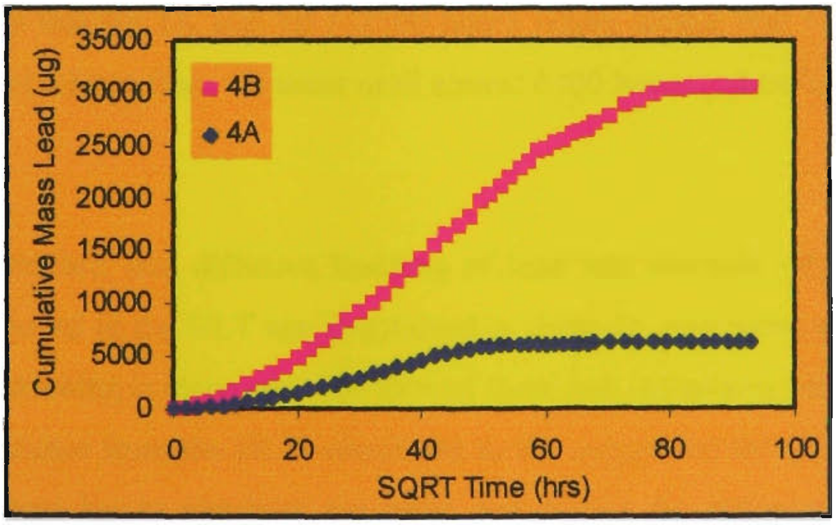


Figure 5.31: t_n = 4A & 4B – Cumulative Mass Lead Leached v's Square Root of Time

The pattern of lead release from spheres 1A and 1B, illustrated in Figure 5.30, shows practically no evidence of surface wash-off. Instead, both spheres appear to leach predominantly via diffusion following an initial resistance to leaching. This type of behaviour was first discussed in Section *1.3.4.4*, and identified as one of four general categories of leaching mechanisms by Côté (Environment Canada 1991b). It is interesting to note that sphere 1A is dominated by strong diffusive leaching at a much earlier stage than is 1B. As discussed in Section *5.4.1*, this suggests a greater amount of pore-available lead is available in sphere 1A than in 1B.

Figure 5.30 also appears to show lead diffusing from both spheres at much lower levels late in the test. After the delay in leaching, diffusion occurs from both spheres, as evidenced by the straight part of the two curves. After approximately 2500 hours (where square root = 50 hours) the rates of diffusion decrease, and much flatter straight lines continue until the end of the test.

Figure 5.31 also shows both of these trends for spheres 4A and 4B, however the effects do not seem as obvious. As with spheres 1A and 1B there is also a pattern of diffusion following an initial resistance to leaching. However, with the 4-hour renewal schedule, the delay at the beginning does not seem as marked as with the 1-hour schedule. Similarly, while the reduction in diffusive release of lead from sphere 4A occurs at a similar time to that for 1A and 1B (~2500 hours where square root = 50 hours), the slowing of lead release from 4B takes until almost 6400 hours (where square root = 80 hours).

It appears, therefore, that diffusive leaching of lead will increase when the leaching intervals employed in the DLT are lengthened in duration, and when the surface area available for leaching is increased. The first of these two influences was also observed with copper release from the DLT, which led to the suggestion the greater amount of time the leachant has to penetrate the solid, the greater the diffusive release of the copper (and lead). The fact that greater amounts of lead were released from sphere 4A than 1A or 1B also supports this suggestion. The second influence, a greater surface area leading to a much greater diffusion of lead from sphere 4B, was also observed (albeit to a much lesser extent) for zinc, and not at all for copper.

The plotting of cumulative release versus time on a log-log scale for both schedules in Figures 5.32 and 5.33 also clearly shows diffusion to be more dominant for the majority of the test in sphere 4B than for any of the other spheres. An explanation of the utilisation of such a chart revolves around the slope of the subsequent plot, and is provided in Section *3.4.1.1*.

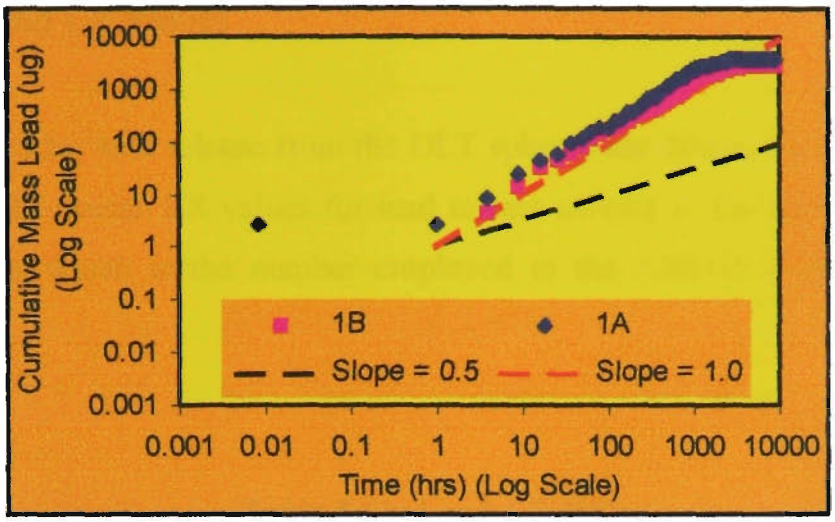


Figure 5.32: t_n = 1A & 1B – Cumulative Mass Lead Leached v's Time

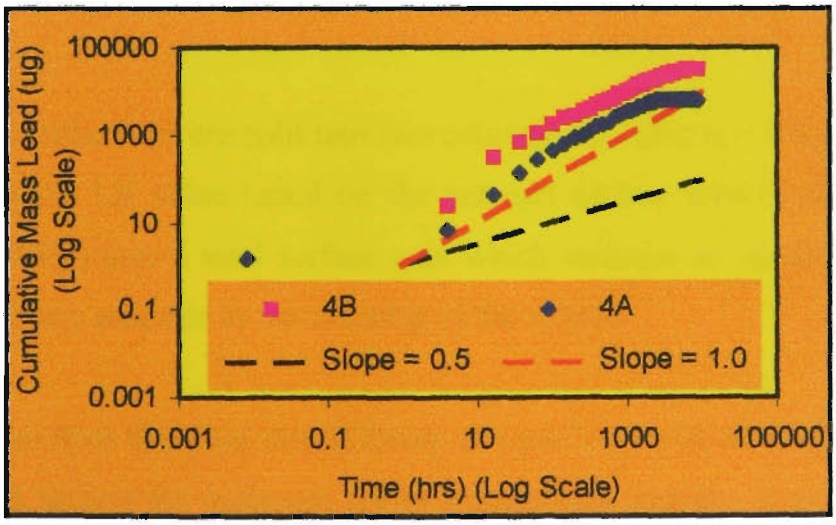


Figure 5.33: t_n = 4A & 4B – Cumulative Mass Lead Leached v's Time

Albino *et al* (1995) constructed similar plots of their data after conducting dynamic leaching tests (ANS 16.1) for up to 6 months on metal-doped cement cylinders. Their results also produced slopes 'close enough to 0.5 to say that pore matrix diffusion is the main mechanism which effects the kinetics of (lead) leaching'.

5.4.1.3 Lead LX Values

The LX values for lead release from the DLT spheres are detailed in Table 5.11. The table shows the overall LX values for lead release as well as the indexes for the first seven periods, which is the number employed in the ANS-16.1 protocol (USEPA 1989).

Table 5.11: Lead LX Data

Sphere	**t_n = 1A**	**t_n = 1B**	**t_n = 4A**	**t_n = 4B(a)**	**t_n = 4B(b)**
LX - 1st 7 Periods	14.80	15.78	14.39	13.27	13.62
LX - Total	14.91	15.34	14.50	13.39	13.75

The values for sphere 4B are split into two columns. Column t_n = 4B(a) represents the calculation of the LX value based on the external surface area of the sphere, while column t_n = 4B(b) uses a total surface area which includes an approximation for the increase in surface area due to the cracking of the sphere.

As can be seen from this data, the diffusion of lead from spheres 1A, 1B, and 4A was quite minimal. Sphere 4B, however, shows a significant increase in the amount of lead released, once again emphasising the importance of an increase in surface area on lead diffusion. Regardless of this increase, the fact that the range of total LX data was 13.39 to 15.34 shows lead release from the spheres to be quite slow. These values are also among the highest for the 1-hour schedule, yet the LX for sphere 4B is the lowest of the three metals investigated thus far. This also shows that an increase in surface area affects lead diffusion to a greater extent than it does zinc or copper.

Another interesting feature of the data in Table 5.11 is that, for all spheres except 1B, the LX values for the 1st 7 periods are actually less than the total LX values. This clearly illustrates the general lack of influence surface wash-off had on the leaching of lead in the DLT.
Once again, as with both the copper and zinc results, the lead data shows a higher LX value for sphere 4B(b) with the approximated surface area that included the cracking, than for the calculation using the surface area of the outer surface of the sphere only. As mentioned in Section *4.4.1.3*, this is thought to arise from a combination of a poorly approximated boundary condition of a zero surface concentration in the leachate, and an overestimation of an increase in surface area due to the cracking of the sphere.

5.4.1.4 PIXE Analysis

Figure 5.34 illustrates the PIXE data for lead and, as with both copper and zinc, shows peaks in concentration at 388mm and 421mm, approximately 1mm in from the left edge and 2mm from the right. This also supports suggestions made earlier in Section *3.4.1.3* that metal concentration will be present in higher amounts at the leaching boundary. Further, as demonstrated previously for copper and zinc, the concentration of lead drops sharply toward each edge of the sample, and to a much lesser extent toward the centre. The middle area of the plot also demonstrates lead levels to be quite homogeneous throughout the sphere. It appears, therefore, that, as the lead has dissolved, the majority has diffused outward into the bulk solution with a much smaller amount reprecipitating further into the sphere.

A comparison with Figure 3.53 also demonstrates a good correlation between the lead and silicon profiles from sphere 4B. Unlike zinc and copper, lead has a definite peak on the left side of the sphere where elevated levels of silicon also exist. This may be due to the greater likelihood of lead adsorption to silicon (detailed in Section *5.2.3*), which does not occur for copper, or to the same extent for zinc. It should, however, be reiterated that, as mentioned in Section *3.4.1.3*, the high level of silicon on the left side of the sphere might be due to experimental error.

Figure 5.35 clearly illustrates the similarities between the profiles of lead, copper and zinc across sphere 4B.

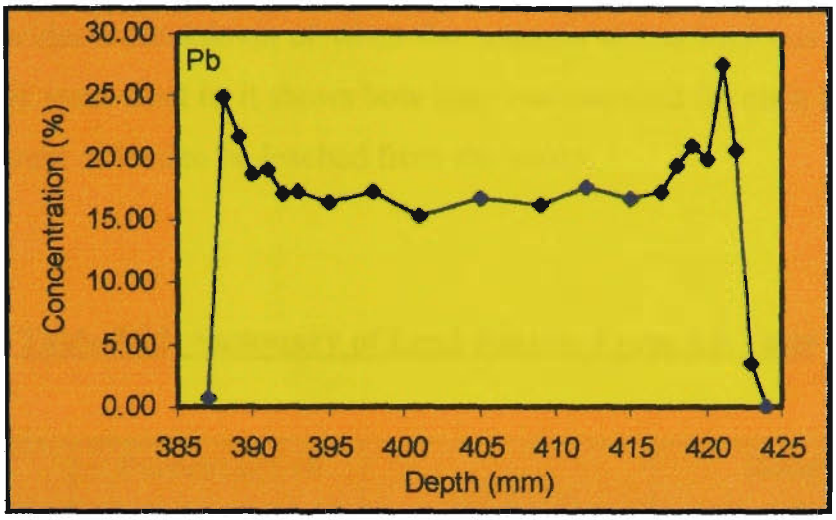


Figure 5.34: t_n = 4B – PIXE Data for Lead

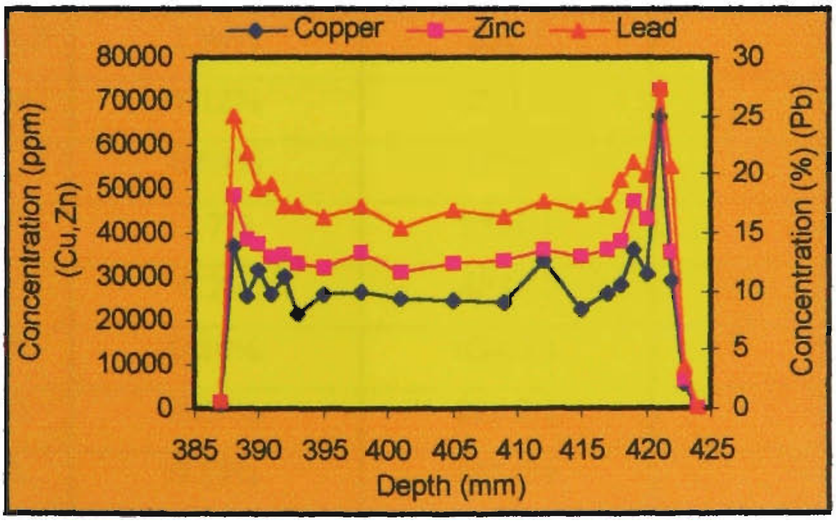


Figure 5.35: t_n = 4B – PIXE Data for Lead, Copper and Zinc

5.5 Summary of Lead Leaching

A summary of lead leaching from every leaching test conducted in this work is presented in Table 5.12. Not only does this table provide an absolute percentage of lead leached from each test, and the final L/S ratio from each test, it also displays the amount of lead leached as a ratio relative to the ABLP result, which has been given the arbitrary unit of 1. This allows for a better visual comparison between the results. Table 5.13 provides a breakdown of when the majority of the lead was leached in the column and tank tests. That is, it shows how long was required for each 25% increment of the total amount of lead to be leached from the waste.

Table 5.12: Summary of Lead Results From All Tests

Test	Percentage of Lead Leached	L/S Ratio	Ratio Leached (where ABLP = 1)
MAT	21.8%	9.8:1	38.25
TCLP	0.17%	20:1	0.30
ABLP	0.57%	20:1	1
Sequential ABLP	2.94%	200:1	5.16
Large Column	1.12%	19.1:1	1.96
LCC100	0.64%	17.6:1	1.12
ABLC100	2.7%	9571:1	4.74
ABLC180	6.2%	4873:1	10.88
DLT; T_n = 1A	0.10%	634.3:1	0.18
DLT; T_n = 1B	0.07%	626.2:1	0.12
DLT; T_n = 4A	0.15%	445.2:1	0.26
DLT; T_n = 4B	0.76%	447.5:1	1.33

Table 5.13: Leaching Breakdown of Lead From Column and Tank Tests

Test	Time to Leach 1st 25% of Total Lead (days)	Time to Leach 2nd 25% of Total Lead (days)	Time to Leach 3rd 25% of Total Lead (days)	Time to Leach 4th 25% of Total Lead (days)
Large Column	84	126	84	70
LCC100	22	120	105	119
ABLC100	2	2	5	354
ABLC180	3	2	5	352
DLT; T_n = 1A	18.4	16.7	25.1	300.3
DLT; T_n = 1B	26.1	19.3	35.1	280
DLT; T_n = 4A	20.2	22.5	30.8	287
DLT; T_n = 4B	32.7	40.8	63	224

Similar to the zinc and copper results, the experimental data for lead shows that similar percentages of lead are released from tests in which the waste is allowed to establish its own leaching environment (i.e. all tests except the MAT). No doubt, the most important observation is that a lower L/S ratio and greater surface area result in greater release of lead from the fixed waste. Further, while surface wash-off, pore-based diffusion, and matrix dissolution were all shown to influence lead leaching, the diffusive mechanism was, by far, the most instrumental in effecting its release.

From the test results, it appears as though only a certain amount of lead could be adsorbed onto silicate surfaces during cement setting, with the remainder trapped in the pores of the fixed waste. Therefore, any lead that could not be released via pore-based diffusion tended to be leached via matrix dissolution, or, as more surface became available to leaching due to increases in matrix porosity and tortuosity. Considering that the majority of the lead leached did so via diffusion, the key to reducing lead release from this waste lies in the ability to increase the amount of lead able adsorb to the silicate sites. This may not be a simple process either, as evidenced by the DLT results for the 1-hour renewal frequency. It was observed that, even with the careful preparation of the spheres carried out for the DLT, sphere 1A still leached considerably more lead than 1B. It is thought that this was a consequence of greater adsorption of lead to the silicate sites in sphere 1B.

The evidence for the effects of L/S ratio and waste surface area on lead leaching was observed in a number of test comparisons made throughout the course of this chapter. The most obvious of these was the massive increase in lead leaching from the ABLC180 compared to the ABLC100, quite obviously due to the much lower L/S ratio in the latter test. Similarly, the Large Column, due to its short and wide design, has a much greater surface area available for immediate contact with fresh leachant. The LCC100, on the other hand, is longer and thinner. So, even though the L/S ratio was the same in those two tests, the Large Column released almost twice as much lead as the LCC100. The DLT results showed a massive difference between the amount of lead leached from the split sphere (4B) and sphere 4A. Once again, an increase in available surfaces, also effectively a decrease in L/S ratio, has led to an increase in lead release. Quite obviously therefore, under the test conditions observed, the greater the waste surface available for leaching to a specific volume of fluid, the greater the amount of lead leached.

The PIXE work on sphere 4B showed the majority of the lead present in that part of the sphere 4B to diffuse out of the sphere, with only a minor amount moving inward and reprecipitating. This profile also correlates well with those for copper and zinc, as illustrated earlier in Figure 5.35.

All leaching results also showed conductivity, pH and redox potential to have obvious but minor effects on the leachability of lead under all test conditions. While, at a lower pH, the amount of lead leached appears to increase due to the dissolution of the silicate outer shell, the leaching environments encountered in these tests generally precluded that situation from occurring. There also seemed to be a trend of greater release at higher pH levels (>10) as opposed to at a more neutral pH. However, compared to the influences of surface area and L/S ratio, the effects were relatively minor. The main reason for the minimal effect of conductivity, pH and Eh on lead release is that the leachant employed in most tests was de-ionised water. Consequently, the waste itself controlled the leachate chemistry, as opposed to the leachant controlling waste leachability.

With all this information in mind, a possible effective disposal scenario for the lead contaminant in this waste would be as a monolith in a monofill. However, while this may provide limited lead leaching in the short to medium term, over a longer period the breakdown of the waste may lead to sudden and massive increases in lead release due to increases in surface area.

6. Results and Discussion: Arsenic

6.1 Arsenic Analysis: Method Validation

Method validation for arsenic by HGAAS was carried out according to the procedure described in Section *2.5.1.1.4* using a 10ml aliquot of a Dynamic Leaching Test leachate of unknown concentration. Arsenic concentration by standard calibration was 3.60ppb and by standard additions was 3.66ppb. The difference is not significant. Accordingly, the method of standard calibrations was used throughout the leaching experiments for the analysis of arsenic. Selenium recoveries were all between 93% and 102%. Method validation also demonstrated that no matrix effects were present in the analysis by standard calibration.

6.2 Batch Tests

The batch tests investigated in this study were the Maximum Availability Test, ABLP, Sequential ABLP, and TCLP. Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.4 – 2.4.6*.

6.2.1 Maximum Availability Test Results

The Maximum Availability Test was run in triplicate. An average of these results for mass and percentage of arsenic leached, pH, redox potential, and conductivity are detailed in Table 6.1. Results for each replicate for mass of arsenic leached, pH, redox, and conductivity, are shown in Appendix E (i). Volumes of acid added during the test are detailed in Section *3.2.1*.

Table 6.1: Arsenic Maximum Availability Test Data

Mass of Arsenic Leached (mg)	Percentage of Total Mass of Arsenic Leached ($\pm 1\sigma$)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.22	0.32% ($\pm 5.2 \times 10^{-3}$ %)	4.68	564.1	6.6

This result demonstrates that no greater than 0.32% of the arsenic present in this solidified waste should leach out over time, with 99.68% remaining bound within the cement matrix. It also contrasts strongly with the results for the other metals studied, as can be seen below in Table 6.2.

Table 6.2: Maximum Availability Test Data

Metal	Percentage of Total Mass of Metal Leached
Arsenic	0.32%
Copper	26.7%
Lead	21.8%
Zinc	43.9%

This MAT result for arsenic indicates that it is well retained in the matrix and, thus, would be expected to leach poorly from all tests. However, as seen in the following sections, this is simply not the case, as in tests where the waste controls its environment, arsenic leaching is substantial. The reason for such a massive restriction of arsenic release must, therefore, be based on the pH and Eh conditions imposed upon the MAT. These reasons, including their relevance in a comparison between the results from both the MAT and the TCLP, are discussed in depth in Section *6.2.2*.

6.2.2 TCLP Results

The average concentration, mass and percentage of arsenic leached, pH, redox potential, and conductivity in the TCLP are detailed in Table 6.3. Results for each of the four replicates for mass of arsenic leached, pH, redox, and conductivity, are shown in Appendix E (ii). The temperature during the extraction ranged from 20°C to 22°C.

Table 6.3: Arsenic TCLP Data

Concentration Leached (ppm)	Mass of Arsenic Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Arsenic Leached ($\pm 1\sigma$)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.14	0.28	0.064% ($\pm 1.6 \times 10^{-3}$%)	12.11	232.1	12.8

The TCLP limit for arsenic is 5ppm (Table 1.5). As only 0.14ppm of the arsenic was present in the TCLP leachate, it can be said that the waste passes the TCLP requirements for that contaminant.

As with the other metals studied, only a small amount of arsenic was released from the waste over the duration of the test. Unlike the other metals, however, the percentage leached was only about five times less than that leached from the MAT. The reasons for such behaviour are many and varied, and primarily revolve around the species formed by arsenic in the cement-based environment. Although the following information will help to explain the behaviour of arsenic in these experiments, it is worth pointing out that no speciation analyses have been conducted in this research. Therefore, any observations regarding the leaching of arsenic will encompass all species released during the tests.

Unlike many cations, arsenic does not form an insoluble hydroxide. Therefore, the mechanism that operates during S/S of many heavy metals does not apply for As. The two most common valence states, As^{3+} and As^{5+}, are commonly observed in solution as AsO_2^{3-} (arsenite) and AsO_4^{3-} (arsenate), respectively, and as protonated forms of these oxy-anions, depending on pH. Although these anions form a variety of water-soluble salts, many insoluble metal arsenates are well known. Arsenate may be precipitated with lime to produce $Ca_3(AsO_4)_2$, which has very low water solubility. Unfortunately, this type of arsenate can react with atmospheric CO_2 introduced via fresh leachant, to produce $CaCO_3$ and release soluble arsenate (Cartledge 1993; Büchler *et al* 1996; Akhter *et al* 1997; Leist *et al* 2000).

Similar behaviour is also evident for As^{3+}. As Côté *et al* (1987) showed in their work on the diffusion testing of cement-based wastes, arsenic was precipitated as basic calcium arsenite [$Ca(AsO_2)_2.Ca(OH)_2$] in the cement matrix. This precipitate is converted to the more soluble calcium arsenite [$Ca(AsO_2)_2$] and to arsenite ion by reaction with CO_2 according to the following reactions:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \ldots(1)$$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \qquad \ldots(2)$$

$$Ca(AsO_2)_2.Ca(OH)_2 + H_2CO_3 \rightarrow Ca(AsO_2)_2 + CaCO_3 + 2H_2O \qquad \ldots(3)$$

$$Ca(AsO_2)_2 + H_2CO_3 \rightarrow 2HAsO_2 + CaCO_3 \qquad \ldots(4)$$

As with the release of arsenate, the rate of conversion is limited by the availability of the carbonates that are introduced with the fresh leachant. According to Stronach *et al* (1997), however, such reactions are not likely to take place immediately. In their investigations into the reactions between cement and arsenic (III) oxide, it was shown that, while carbonate may neutralise cement pH, arsenic solubilisation is unlikely to be significant as long as free $Ca(OH)_2$ remains to condition the aqueous phase to low carbonate concentrations.

It should also be mentioned that the influence of carbon dioxide is not limited to the formation of soluble arsenic salts, as described above. The effects of carbon dioxide on the carbonation of cements and the lowering of leachant pH are well known (discussed in Section *1.2.3.4.3.4*). In their work on the development of quick leaching tests for monolithic wastes, Wahlström *et al* (1998) found that the pH was, on average, 0.4

units higher in a closed leaching vessel than in an open vessel. It was believed that the uptake of CO_2 from the air was the main reason for the difference.

Not only can the availability of fresh leachant dictate arsenic leaching, the pH and redox potential are also thought to have significant effects on its release. Förstner *et al* (1990) reviewed the mobility of metals in sludges and solid wastes and found arsenic to be solubilised at neutral to alkaline pH conditions. Earlier work by Blakey (1984) on the behaviour of arsenical wastes co-disposed with domestic solid wastes also indicated arsenic solubility was greatest at pH 5-9 under slightly reducing conditions. This was supported by de Groot *et al* (1989) who found arsenic to leach more from coal fly ash at neutral pH levels. In contrast, work by Ozaki *et al* (1997) on heavy metal release from various ashes in batch tests demonstrated that, the lower the pH value of leachate after the leaching test, the higher the concentration of As observed. Similarly, Twidwell *et al* (1992) point out that arsenic has a low solubility at the pH levels found in natural waters.

Regardless of the effect of pH on arsenic release, the majority of research conducted thus far has clearly shown arsenic to leach more from reducing environments than oxidising ones (Hermann & Neumann-Mahlkau 1985; Dusing *et al* 1992; Standards Australia 1992). Further complicating this, and the fact that arsenic can be easily solubilised from a cement matrix, Conner (1990) points out that the valence state of arsenic can change easily and reversibly with redox potential. This is important as it has been demonstrated that, not only is As^{3+} more mobile than As^{5+}, it is also more toxic (Conner 1990; Hermann & Neumann-Mahlkau 1985; Dusing *et al* 1992). Côté *et al* (1987) suggest that more reducing conditions may increase leaching due to a greater conversion of basic calcium arsenite ($Ca(AsO_2)_2.Ca(OH)_2$) to the much more mobile arsenite ion ($HAsO_2$) (see reactions (3) and (4) previously). Examination of Pourbaix diagrams for arsenic also show that As^{3+} would appear to be the dominant species in reducing conditions (Pourbaix 1974). Glasser (1997) suggests that, while most elements with a formal charge of +3 or more are well-retained in cement matrices, anionic species are less-well bound. He also explains that, even though some arsenate, AsO_4^{3-}, will substitute for the sulphate phases of cement hydration products, the partition coefficients between aqueous and solid phases do not indicate good binding for large, tetrahedral species. This is more pronounced for species having the structure

MO_3**:** (where **:** corresponds to an electron pair occupying a tetrahedral vertex). Thus AsO_4^{2-}, arsenate, is somewhat better fixed than AsO_3^{2-}, arsenite.

In the case of the MAT and TCLP, it appears that the pH (MAT = 4.68, TCLP = 12.11) and Eh (MAT = 564.1mV, TCLP = 232.1mV) of the two tests have had noticeable effects on the final release of arsenic from the fixed waste. Although the first step in the MAT was extraction at pH 7, where arsenic may be expected to leach appreciably, the final step involved addition of acid, which produced a final pH of 4.7. Consequently, the Eh of the system would also have risen significantly, finishing up in excess of 550mV. Since the valence state of arsenic can change easily with redox potential, it is most likely that arsenic remained in the +5 form, thus limiting its leaching from the matrix. The much lower final Eh observed in the TCLP (232mV) would have been more conducive to arsenic release, regardless of the high pH (12.11) that eventuated from the test.

Even though a comparison of the conditions between the two tests suggests that the TCLP may have been more conducive to arsenic leaching, the particle size difference between the two tests may also be significant. Prange and Garvey (1990) investigated the effect of particle size on the amount of arsenic removed from cement S/S wastes via the TCLP. Their results disagree with the above assumption, as they found that the larger particle sizes released arsenic in an amount approximately 2 orders of magnitude greater than for the smaller particles. They also showed that, although the pH of the final solutions was practically the same (~11) for all particle sizes, it took far longer to get to this level for the larger particles. Contrasting this, Ozaki *et al* (1997) conducted a series of leaching tests on a variety of ashes and sludges. They found that arsenic release was up to 4 times greater for particle sizes <5mm in diameter, as opposed to those of diameter 20-50mm. They also demonstrated that the amount of arsenic leached varied according to the test method used.

The most important point in the comparison of the MAT and TCLP is that, regardless of the low percentages leached in these two tests, the results were very close to one another. This contrasts strongly with the results observed thus far for copper, lead, and zinc.

6.2.3 ABLP Results

The average concentration, mass and percentage of arsenic leached, pH, redox potential, and conductivity in the ABLP are detailed in Table 6.4. Results for each of the four replicates for mass of arsenic leached, pH, redox, and conductivity, are shown in Appendix E (iii). The temperature during the extraction ranged from 27°C to 29°C.

This result demonstrates that similar amounts of arsenic leached using the ABLP and the TCLP, where the only difference between the two tests was the type of leaching fluid employed.

Table 6.4: Arsenic ABLP Data

Concentration Leached (ppm)	Mass of Arsenic Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Arsenic Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.11	0.22	0.051% (±3.6 x 10^{-4}%)	11.60	210.3	8.20

A comparison of the electrode data, detailed in Table 6.5, shows minor differences between the two tests. The slightly higher pH and conductivity observed in the acidic TCLP is no doubt a consequence of the greater levels of alkalinity in the leachate.

Table 6.5: Comparison of Electrode Data Between the ABLP and TCLP

Parameter	ABLP	TCLP
pH	11.60	12.11
Eh (mV)	210.25	232.05
Conductivity ($mScm^{-1}$)	8.23	12.78

The fact that the redox potential in both tests finished up at similar levels is the most likely reason for such similar percentages of arsenic release from the ABLP and the TCLP. This has been discussed previously in Section *6.2.2*.

6.2.4 Sequential ABLP Results

The average concentration, mass and percentage of arsenic leached in the Sequential ABLP are detailed in Table 6.6. Results for each replicate for mass of arsenic leached, pH, redox, and conductivity, are shown in Appendix E (iv).

Table 6.6: Arsenic Sequential ABLP Data

Sequential Leach Number	Concentration Leached (ppb)	Mass of Arsenic Leached (μg)	Percentage of Total Mass of Arsenic Leached (±1σ)
1	109.9	219.8	0.051% (± 3.6 x 10^{-4}%)
2	48.9	97.8	0.023% (± 5.4 x 10^{-4}%)
3	26.9	53.8	0.012% (± 6.8 x 10^{-4}%)
4	32.4	64.9	0.015% (± 1.9 x 10^{-4}%)
5	40.6	81.1	0.019% (± 7.5 x 10^{-4}%)
6	55.3	110.5	0.026% (± 1.6 x 10^{-3}%)
7	94.3	188.5	0.044% (± 2.1 x 10^{-3}%)
8	141.5	283.1	0.065% (± 2.4 x 10^{-3}%)
9	169.5	338.9	0.078% (± 2.0 x 10^{-3}%)
10	117.1	234.1	0.054% (± 3.2 x 10^{-3}%)
Total	N/A*	**1672.5**	**0.387%** (± 0.014 %)

*N/A = Not Applicable

The data, in Table 6.6, shows that 0.39% of the arsenic present in the waste was removed after ten successive leaches. This demonstrates that the arsenic is very well retained in the fixed waste system. It also demonstrates that the first ABLP leach did not act as a worst case scenario test, since higher amounts of arsenic were shown to leach in the last three sequential extractions of the test.

It is also worth noting that the amount leached from the waste in the Sequential ABLP exceeded that predicted by the MAT. This suggests, therefore, that the MAT is a poor predictor of maximum arsenic leachability for this particular waste.

6.2.4.1 Leaching Behaviour of Arsenic

Following a brief period of surface washing over the first three extractions, Figure 6.1 shows arsenic release to increase as the test wears on. Although the final point of the Sequential ABLP appears to signify a slowing of the leaching rate, further extractions would be required to show longer-term behaviour. This type of behaviour seems to support the earlier suggestion that arsenic leaching will increase as fresh leachant comes into contact with the waste. Vela *et al* (1994) batch tested a variety of incinerator and coal ashes with pH5 acetate buffer at a 20:1 L/S ratio. After sampling at various intervals during the five days of testing, they also found that arsenic leached in high amounts at the beginning of the test, before levelling off, and then increasing until the end of the extraction.

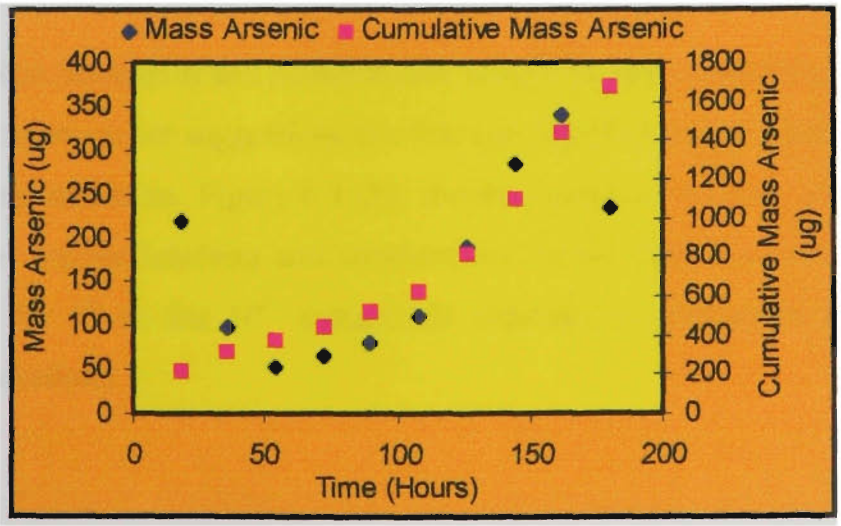


Figure 6.1: Sequential ABLP – Mass Arsenic Leached v's Time

6.2.4.1.1 *pH, Redox Potential, and Conductivity Effects on Arsenic Leachability*

Figure 6.2 illustrates a good correlation between the pH levels observed in the Sequential ABLP, and the mass of arsenic leached. Regardless of this correlation, there is no absolute evidence pointing to the control of arsenic leachability by pH in such an alkaline system. In fact, research detailed earlier (Section *6.2.2*) suggests that the actual *amount* of arsenic leached over the course of the experiment would most likely be greater if the experiment had been conducted at a more neutral pH.

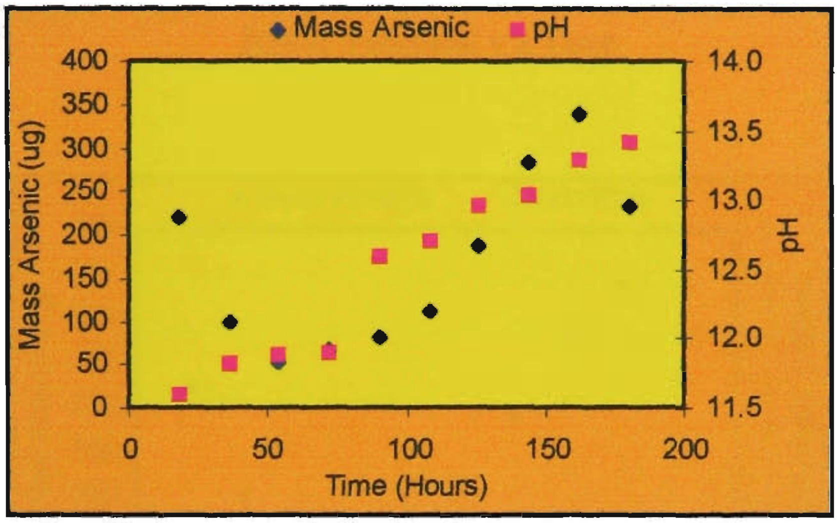


Figure 6.2: Sequential ABLP – Mass Arsenic Leached and pH v's Time

The comparison between redox potential and arsenic release, represented in Figure 6.3, appears to support earlier suggestions that the amount of arsenic leached increases with more reducing conditions. Figure 6.4 also shows a good correlation, this time between the pattern of arsenic leaching and conductivity levels. The increase in conductivity levels from the 5th to the 10th extractions indicates a subsequent increase in the leaching of alkalinity.

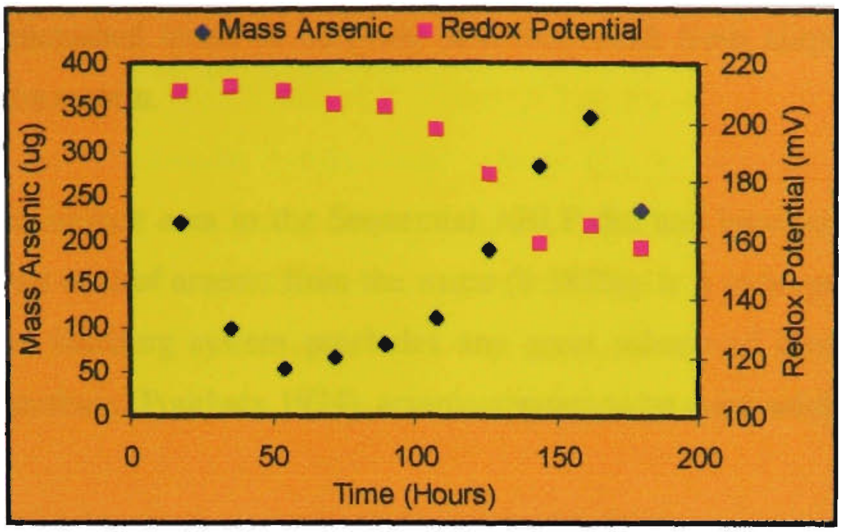


Figure 6.3: Sequential ABLP – Mass Arsenic Leached and Redox Potential v's Time

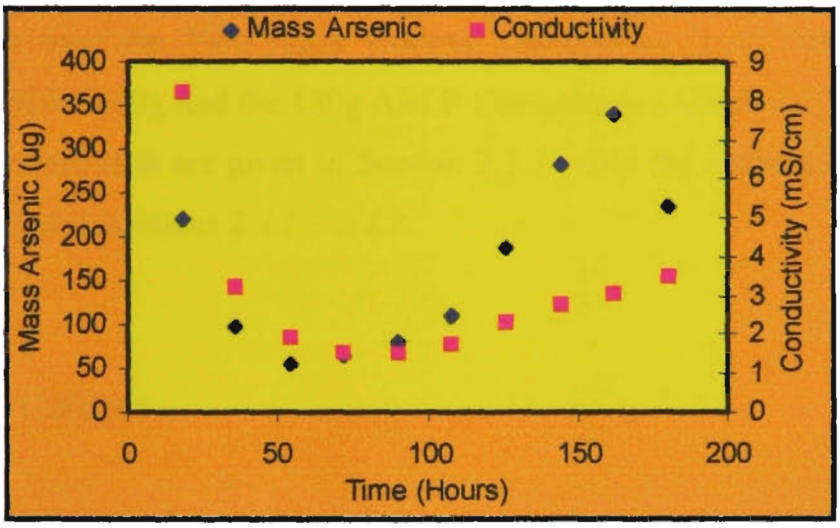


Figure 6.4: Sequential ABLP – Mass Arsenic Leached and Conductivity v's Time

While a correlation between alkalinity and metal release is normally indicative of leaching via pore-based diffusion, this is unlikely to be the case in such an aggressive test as the Sequential ABLP. Here, the massive release of alkalinity is due mainly to an increase in the surface area available for leaching due to the break-up of the waste matrix. Considering the reactions detailed in Section *6.2.2*, this increase in surface area may also result in more rapid release of arsenic from the waste, as the calcium arsenite reacts with replenished levels of carbonic acid from each fresh aliquot of leachant introduced to the system.

The increase in surface area in the Sequential ABLP did not, however, result in the release of a great deal of arsenic from the waste (0.387%). It is quite possible that the high pH of the leaching system precludes any great release of arsenic. However, according to Pourbaix (Pourbaix 1974), arsenic appears to be quite soluble under those conditions.

6.3 Column Tests

One large column and several small column tests were investigated in this study. The small columns were the 100g Large Column Comparison (LCC100), 100g ABLP Comparison (ABLC100), and the 180g ABLP Comparison (ABLC180). Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.1 – 2.4.2*.

6.3.1 Large Column

The total mass and percentage of arsenic leached in the Large Column test are detailed in Table 6.7 The complete leaching data can be seen in Appendix O. All pH, redox and conductivity results are shown in Appendix F(ii).

Table 6.7: Large Column Test Data

Mass of Arsenic Leached (mg)	Percentage of Total Mass of Arsenic Leached
67.6	0.04%

In contrast with copper, lead, and zinc, the percentage of arsenic released from the Large Column was less than in the ABLP and TCLP. However, the arsenic results agreed with those for the other metals tested, where the mass leached from the Large Column was less than from both the Sequential ABLP and the MAT (see Table 6.8). Further, as Table 6.9 reveals, a much greater percentage of lead was leached from the Large Column test compared to that for arsenic, zinc and copper.

Table 6.8: Percentages of Arsenic Leached in Batch Tests and Large Column

Leaching Test	Percentage of Total Mass of Arsenic Leached	Liquid to Solid Ratio	Method of Leachant Contact
Large Column	0.04%	19.1:1	Downflow Spraying
TCLP	0.06%	20:1	Rotary Agitation
ABLP	0.05%	20:1	Rotary Agitation
Sequential ABLP	0.39%	200:1	Rotary Agitation
Max. Avail. Test	0.32%	9.8:1	Stirring

Table 6.9: Percentages of Arsenic, Lead, Zinc, and Copper Leached From Large Column

Metal	Percentage of Total Mass of Metal Leached
Arsenic	0.041%
Lead	1.12%
Zinc	0.093%
Copper	0.035%

Interestingly, the percentage of arsenic leached, with respect to the L/S ratio, is very similar for all tests except the MAT and the Sequential ABLP. That is, the TCLP, ABLP, and Large Column, all with similar L/S ratios, released similar percentages of arsenic. However, at ten times the L/S ratio of those two tests, the Sequential ABLP also leached approximately ten times the amount of arsenic. The MAT is the odd test out, and this is the only test in which the waste cannot control its own leaching environment. It appears, therefore, that, MAT excepted, arsenic leaching may be reasonably correlated with the L/S ratio of the method employed to test it.

6.3.1.1 Leaching Behaviour of Arsenic

Figure 6.4 illustrates both the normal and cumulative leaching patterns of arsenic. Analysis of this diagram shows a short surface wash-off period at the beginning of the experiment, followed by a steadily decreasing leaching rate until approximately 200 days into the test. After this point the leaching rate remains constant.

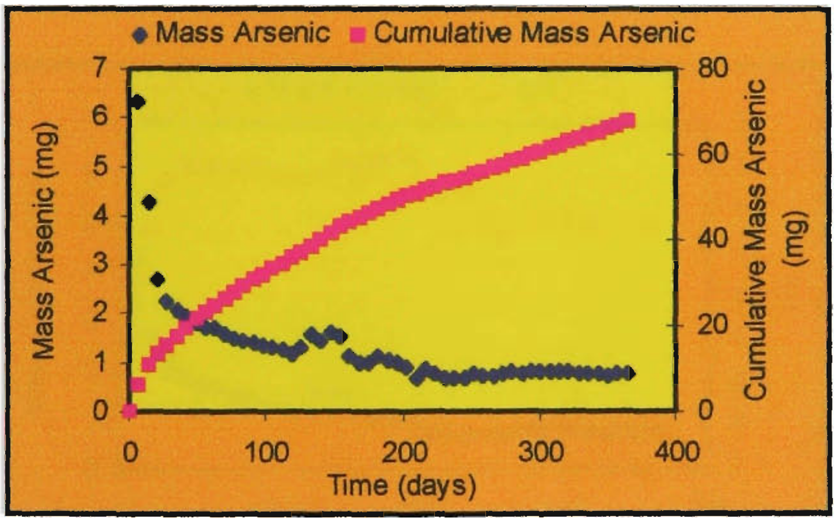


Figure 6.5: Large Column – Mass Arsenic Leached v's Time

This pattern of leaching for arsenic is different from that observed for copper and zinc, where there was a significant period of surface wash-off followed by a decreasing rate of leaching for the remainder of the test (refer Figure 4.5). The release pattern of lead matched that of arsenic a lot more closely, in that the surface wash-off period was relatively short, and release was fairly constant thereafter. The only difference was that, while lead leaching increased at around 200 days, arsenic leaching decreased slightly.

6.3.1.1.1 pH, Redox Potential, and Conductivity Effects on Arsenic Leachability

Figure 6.6 shows that the levelling off in arsenic leaching after 200 days of running the Large Column coincides with a significant decrease in pH at the same time.

It was explained, in Section *5.3.1.1.1*, that this sudden decrease in pH, along with a less severe drop in conductivity levels, signified a reduction in available $Ca(OH)_2$. While it is thought that this led to greater lead leachability, due to an increase in surface area of the waste, a reduction in available $Ca(OH)_2$ would more likely effect arsenic by slowing the reaction process detailed in Section *6.2.2*.

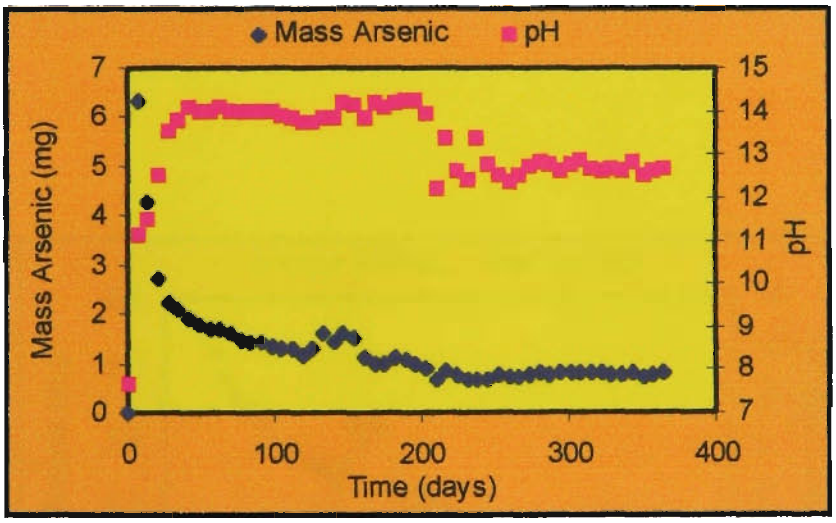


Figure 6.6: Large Column – Mass Arsenic Leached and pH v's Time

Even though fresh carbon dioxide is still being introduced with new leachant, the formation of basic calcium arsenite in the cement matrix would be clearly retarded due to a reduction in the level of $Ca(OH)_2$ from that available at the beginning of the reaction series. Although the decrease in arsenic release is minor at that point, it is significant nonetheless.

The correlation between arsenic leaching and conductivity, depicted in Figure 6.7, is very good, and suggests pore-based diffusion is the primary leaching mechanism following the early period of surface wash-off. It also shows a slight drop in leached alkalinity at the 200-day mark, around the same time as pH and arsenic levels decreased. Note that the first four points have been removed from the data in Figure 6.7 in order to better demonstrate the pattern of leaching.

Redox potential also demonstrates good correlation with the pattern of arsenic release, and this is illustrated in Figure 6.8. The fact that arsenic leaching decreases early in the experiment as Eh drops from oxidising to more neutral conditions appears to contrast with an earlier suggestion that the leachability of arsenic is higher at neutral to slightly reducing redox potentials. However, under these conditions, where negligible arsenic is being released from the matrix, it is more likely that the reduction in release is related solely to the solubilisation of fines throughout the column, rather than to redox potential.

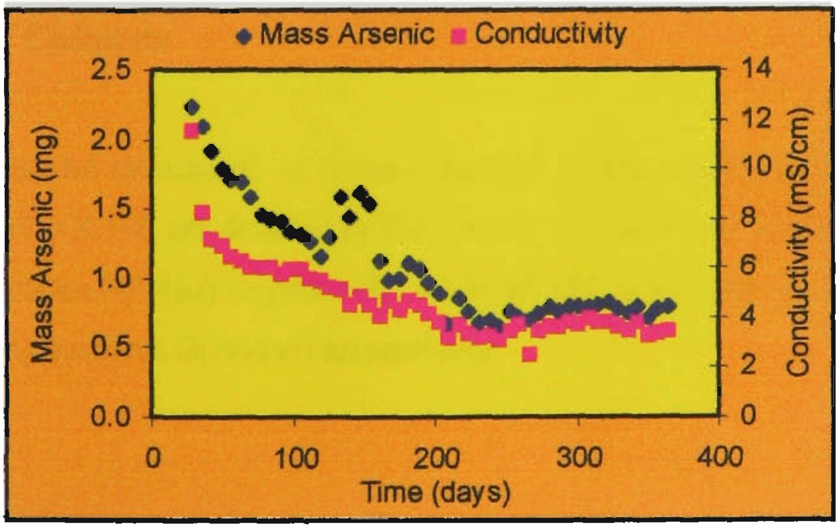


Figure 6.7: Large Column – Mass Arsenic Leached and Conductivity v's Time

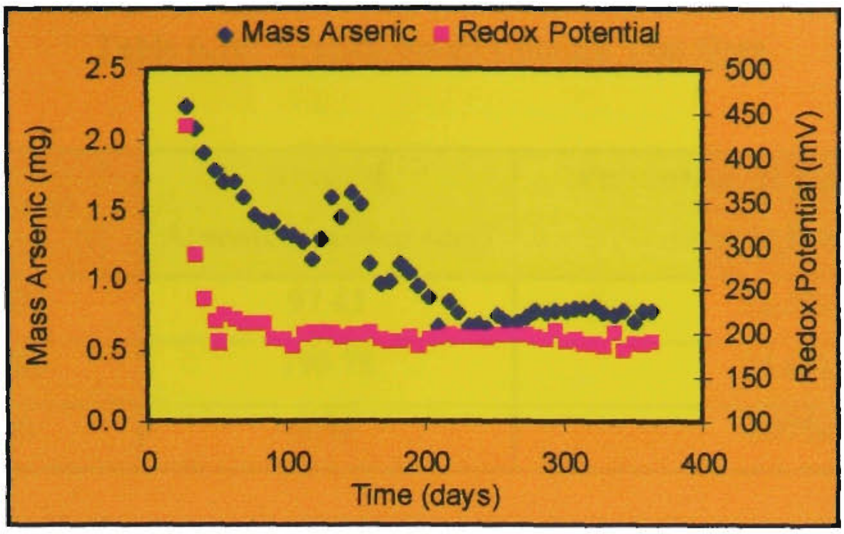


Figure 6.8: Large Column – Mass Arsenic Leached and Redox Potential v's Time

While pH, Eh, and conductivity are possibly responsible for changes in arsenic behaviour, they have not been significant enough to have any real effect on arsenic leaching. This, however, does not also mean that pH, Eh, and conductivity played a lesser role in keeping arsenic leaching to the very low final level observed in this experiment.

6.3.2 Small Columns

The total mass and percentage of arsenic leached in the small columns ABLC100, ABLC180, and LCC100 are detailed in Table 6.10. The complete leaching data can be seen in Appendices P(i)-(iii) respectively, while all pH, redox and conductivity results are shown in Appendices G(iv)-(vi) respectively.

Table 6.10: Arsenic Small Column Test Data

Small Column	Mass of Arsenic Leached (mg)	Percentage of Total Mass of Arsenic Leached
ABLC100	97.45	22.5%
ABLC180	190.78	24.6%
LCC100	0.32	0.07%

6.3.2.1 ABLC100; Leaching Behaviour of Arsenic

As detailed in Table 6.10, a massive amount of arsenic was leached from the ABLC100. This is easily the largest amount of any metal leached from a test thus far, and clearly exceeds the maximum leachable amount predicted by the MAT of 0.32%.

Figure 6.9, which presents the leaching data over the entire year of the experiment, shows a minimal period of surface wash-off at the beginning of the test. In fact, the practically straight plot of cumulative mass leached indicates arsenic was dominated by diffusion/dissolution mechanisms for the entire experiment. This pattern of release was very similar to that observed for copper, as illustrated in Figure 6.10. Although based on tank leaching tests, Andrés' *et al* (1995) suggests that a linear relationship between cumulative mass (or fraction) leached and time is indicative of matrix dissolution. While this certainly may have been the case for copper in the ABLC100 where the mechanism of containment was primarily solidification, no evidence has been presented to suggest that arsenic release is controlled by matrix dissolution.

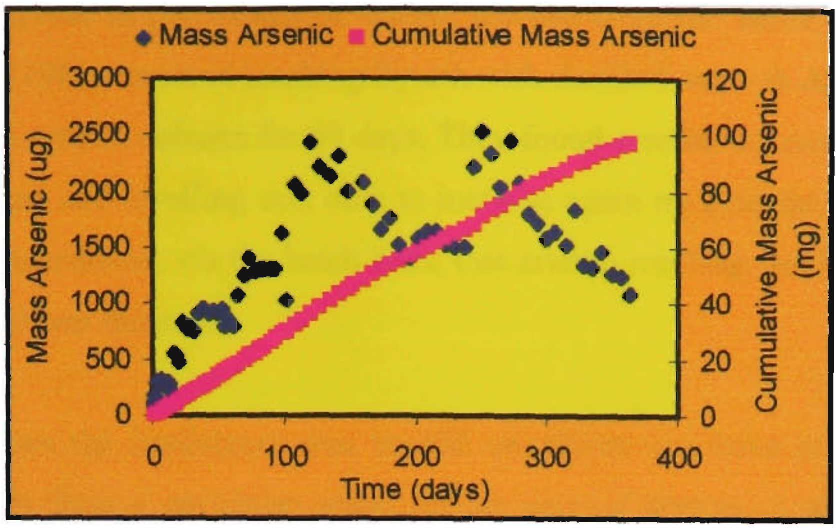


Figure 6.9: ABLC100 – Mass Arsenic Leached v's Time

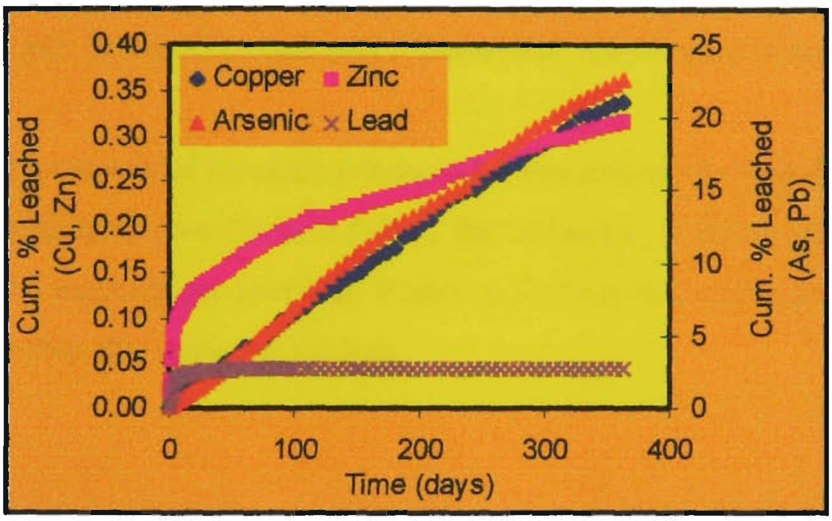


Figure 6.10: ABLC100 – Cumulative Percentage Arsenic, Lead, Copper, and Zinc Leached v's Time

It was suggested in Section *6.3.1* that arsenic leaching may be significantly influenced by the L/S ratio of the test method employed. The L/S ratio of the ABLC100 is 9571:1, which is approximately 479 times greater than the ratio for the TCLP and ABLP. If the percentage of arsenic leached in the ABLC100 (22.5%) is divided by 479, an answer of 0.047% is obtained. This is also quite similar to those percentages leached in the batch and column tests already reported (except the MAT). This finding was similar to that for the Sequential ABLP, where an increase in L/S ratio has provided an equivalent increase in percentage of arsenic leached from the waste. Early work by Jackson *et al* (1981) involved leaching fly ash with distilled water in ABLP-type batch tests, and also a small column for 60 days. They found arsenic leached rapidly at first before declining and levelling out, only to increase again up until the end of the test. They also demonstrated, via the batch tests, that arsenic leaching increased as the L/S ratio of the test was increased.

This emphasises the importance that landfill conditions can have on the release of specific metals from a particular waste. In the case of arsenic, it appears obvious, therefore, that if the volume of liquid passing around the waste is kept to a minimum, the amount released should also be small.

6.3.2.1.1 pH, Redox Potential, and Conductivity Effects on Arsenic Leachability

Considering the amount of research conducted investigating the effects of pH and Eh on arsenic leachability (see Section *6.2.2*), the influence of these parameters in the ABLC100 were surprisingly minimal. Figure 6.11 depicts a comparison of pH with arsenic release over the course of the test.

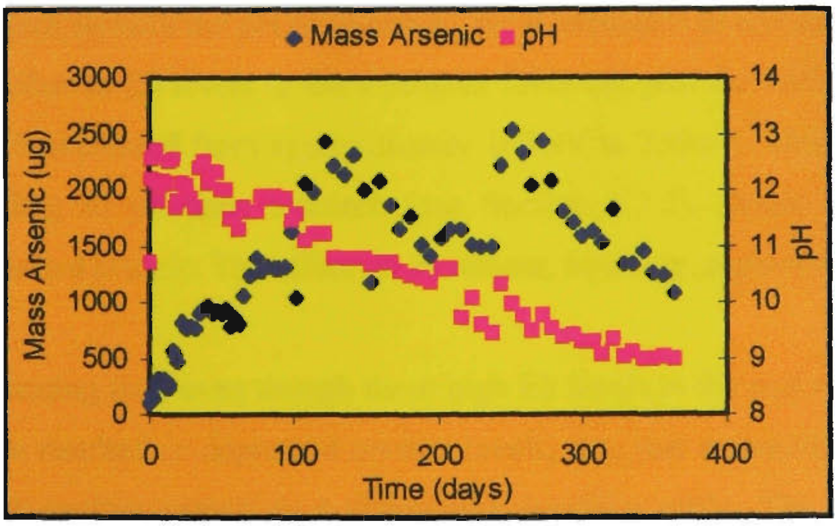


Figure 6.11: ABLC100 – Mass Arsenic Leached and pH v's Time

The release pattern shows two distinct decreases in arsenic leaching. The first decrease begins at 120 days and lasts until the 200-day mark. After this, leaching is constant for a few weeks until a sharp increase in the mass of arsenic leached occurs at around 240 days. This was followed by a gradual decrease in arsenic release until the conclusion of the experiment. At no time during this period of fluctuating release did the pH trend deviate from its decreasing path. Further, the total drop in pH of almost 4 units signified the gradually reducing availability of alkalinity in the matrix, yet the arsenic pattern appeared relatively unaffected by the drop. A possible reason for this is that arsenic has been shown to leach more freely from wastes at more neutral pH levels (see Section *6.2.2*).

Another point to consider here is that, just because arsenic release is decreasing at the end of the test, this trend may not necessarily continue. The mass leached increased between 170 and 230 days, so there is no reason why that could not happen again. This is extremely important information, as, had the test been terminated early based upon the assumption that the arsenic decrease continued, the conclusions of the test would effectively be invalid. Further, these same conclusions may incorrectly categorise the waste as fit for landfill when a great deal more arsenic was still available for leaching.

A similar type of behaviour was also observed with redox potential. A comparison of the pattern of arsenic leaching to redox potential during the ABLC100 is illustrated in Figure 6.12. Here, as with the pH comparison, the fluctuations in arsenic release do not appear to correlate to Eh levels in the leachates. Over the year the ABLC100 was run, the redox levels increased from approximately 160mV to 350mV. This is an increase, which, according to previous research (see Section *6.2.2*), should have led to a decrease in leached arsenic. The effect on its release, however, appeared minimal.

It is worth repeating that, even though these high Eh levels at the end of the test could very well have resulted in depressed arsenic levels, it is just as possible that the low levels are just another trough in a fluctuating leaching cycle. The most probable scenario is that the pH and Eh changes observed during this experiment had minimal effect on arsenic leachability, with L/S ratio presumably the major influence on arsenic release.

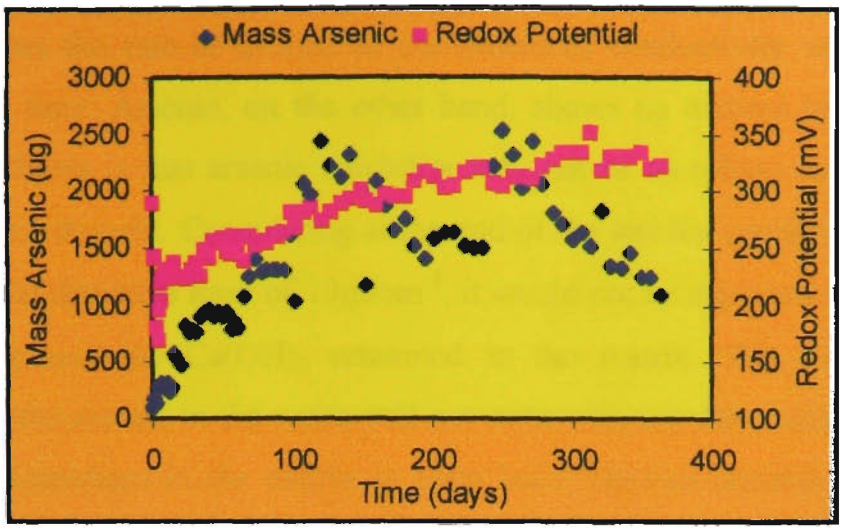


Figure 6.12: ABLC100 – Mass Arsenic Leached and Redox Potential v's Time

Figure 6.13 shows a plot of arsenic release versus conductivity. The first two measurements of conductivity (46,500μScm^{-1} and 5,500μScm^{-1} respectively) have been removed from the plotted data to permit better observation of the pattern of alkalinity release.

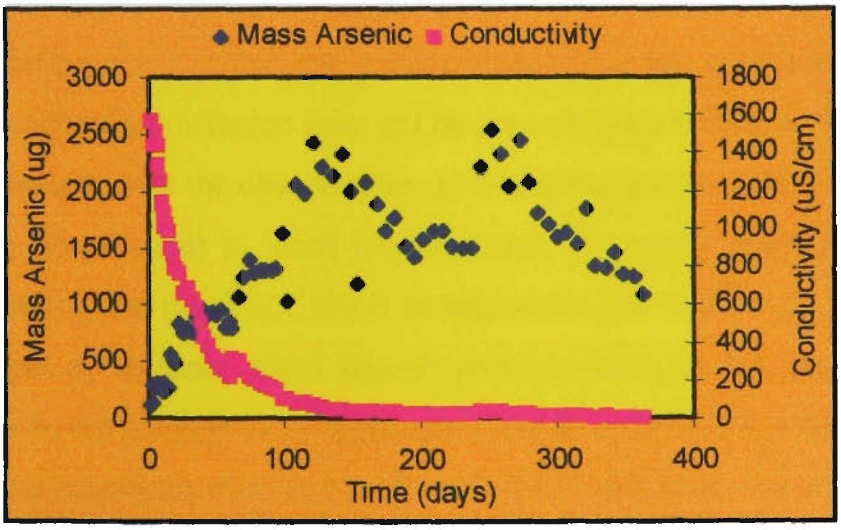


Figure 6.13: ABLC100 – Mass Arsenic Leached and Conductivity v's Time

This plot shows the rate of decline in the measured conductivity values to slowly decrease with time. Arsenic, on the other hand, shows no distinct leaching pattern. What it also shows is that arsenic solubility may not be as reliant on pore-available $Ca(OH)_2$ as first thought. Considering at the end of the test the conductivity levels are approaching the detection limit of $10\mu Scm^{-1}$, it would not be expected that any readily available pore-available $Ca(OH)_2$ remained in the matrix. This does not mean, however, that the arsenic in the waste will not react with any other calcium hydroxide salts present elsewhere in the matrix to form basic calcium arsenite. Further, there would certainly be no shortage of carbon dioxide present in the leachant to contribute to the reaction process (detailed earlier in Section *6.2.2*). Therefore, regardless of the lack of alkalinity in the leachate, the solubilising of arsenic does not seem to have been impeded.

The most likely reason for the low levels of conductivity is the possibility of the formation of calcium arsenate, discussed earlier in Section *6.2.4.1.* Such a reaction would lead to a reduction in available Ca^{2+} in the leachate, and, therefore, reduce the conductivity levels in the leachates. Further, the steady pH decrease, observed in Figure 6.11, raises the possibility of the protonation of the ionised oxyanions of arsenic, which would lead to an even greater reduction in leachate conductivity.

Another interesting point is that the arsenic release did not correlate well with the conductivity, suggesting diffusion may not be the only major mechanism of leaching. This is in agreement with the observations, and leaching pattern (see Figure 6.10), for copper, which was thought to leach predominantly by matrix dissolution. It is also worth remembering that the ABLC100 is an aggressive test with a high L/S ratio and a rapid throughput of leachant. Even though previous research has suggested arsenic leaches mainly by diffusion in DLT-type tests (Côté & Isabel 1984; Stegemann & Côté 1990), under the conditions observed in the ABLC100, diffusion would not necessarily be expected to be the dominant mechanism of arsenic release.

6.3.2.1.2 *Comparison to Sequential ABLP*

Figures 6.14 and 6.15 illustrate moderate similarities for the leaching pattern of arsenic between the ABLC100 and the Sequential ABLP. The dashed line indicates the combination of the first and second data points for the ABLC (see Section *3.3.2.1.2*).

The figures show that a greater amount of arsenic was released from the ABLC100 over the first 10L of the experiment before plateauing off, while the Sequential ABLP release increased over the second 10L. This late increase in arsenic release from the Sequential ABLP may be due to the eventual breakdown of the matrix in the more aggressive test. Overall, there was little separating the final cumulative mass leached from each test after approximately 20L of leachant had been used.

Although there is a good correlation between the cumulative trends of release, especially for the first 8L, this does not necessarily mean that the Sequential ABLP is a substitute for the ABLC100. Observing the complete data for the ABLC100, which demonstrated that arsenic could be released in large amounts up to 10 months after the test had begun, supports this suggestion.

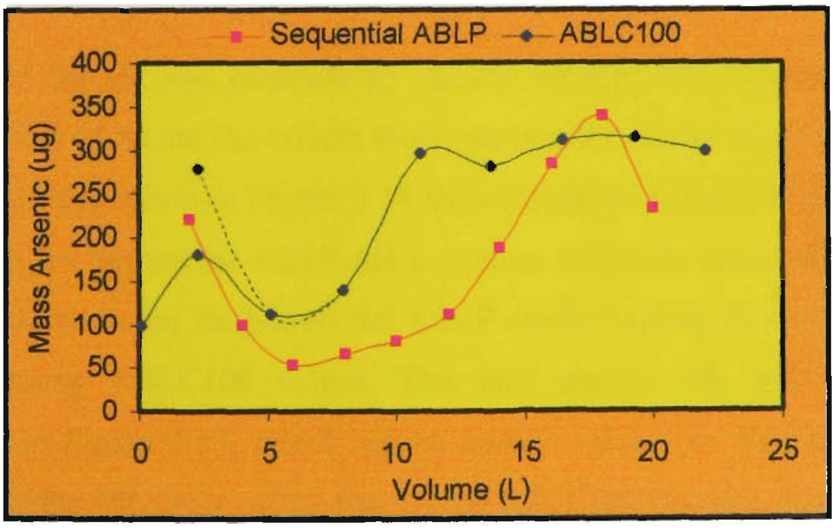


Figure 6.14: ABLC100 & Sequential ABLP – Mass Arsenic Leached v's Time

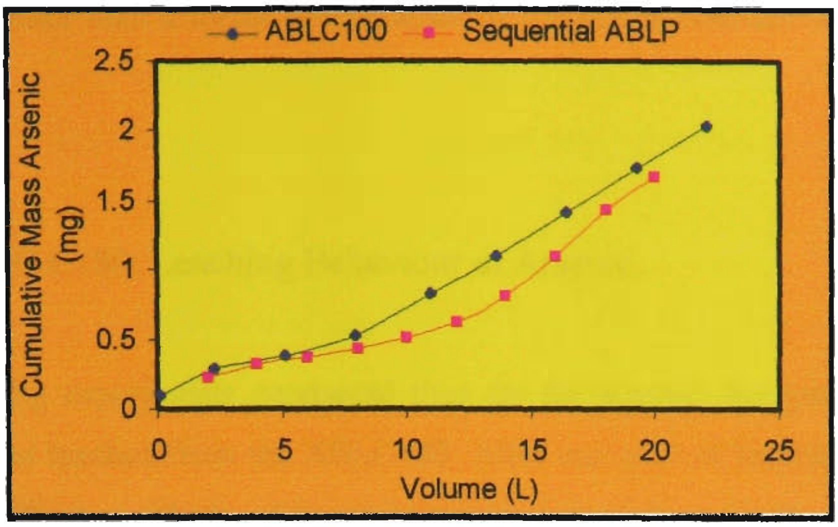


Figure 6.15: ABLC100 & Sequential ABLP – Cumulative Mass Arsenic Leached v's Time

6.3.2.1.2.1 pH, Redox Potential, and Conductivity Effects

As covered in Section *3.3.2.1.2.1*, there does not appear to be any correlation between the redox potentials observed in the two tests. Also detailed in that section is the relative aggression of the two tests and their subsequent effects on conductivity and pH results.

Comparison of the pH and conductivity results between the Sequential ABLP and ABLC100 further illustrate the effects those parameters can have on arsenic leaching trends. The pH comparison in Figure 3.14 shows a dip in ABLC100 pH after the 10L mark, whereas the Sequential ABLP pH continues to climb. Similarly, after the 10L point, the conductivity for the Sequential ABLP climbs rapidly, in contrast to the very slightly decreasing ABLC100 values. This data corresponds well to the arsenic leaching data in Figure 6.14, which shows arsenic release in the Sequential ABLP increasing after the 10L point, while that for the ABLC100 remains much the same.

While the greater agitation in the Sequential ABLP has led to higher pH (>13) and conductivity levels, significant changes in conditions of these systems have been shown to have minimal effect on the masses of arsenic leaching in the tests conducted. Therefore, it is more likely that the increase in arsenic release is due to matrix breakdown, rather than a direct consequence of the pH or conductivity levels in the leachates.

6.3.2.2 ABLC180; Leaching Behaviour of Arsenic

Of the leaching experiments conducted thus far for arsenic, the greatest mass and percentage was leached from the ABLC180. After one year of leaching, this column released 190.78mg, or 24.6% of its total arsenic content. As with the ABLC100, this result demonstrates that arsenic is poorly retained within the cement-based waste at high L/S ratios. The leaching trend, illustrated in Figure 6.16, appears to show that a great deal more arsenic is yet to be leached, even though a release plateau has slowly developed toward the end of the experiment. Once again, note that leachates were sampled from this column at gradually increasing intervals, therefore creating the illusion of a massive increase in arsenic release between 100 and 150 days. Observation of the cumulative plot certainly shows an increase in arsenic release at this time, however the change in not as great as that suggested by the plot of mass leached.

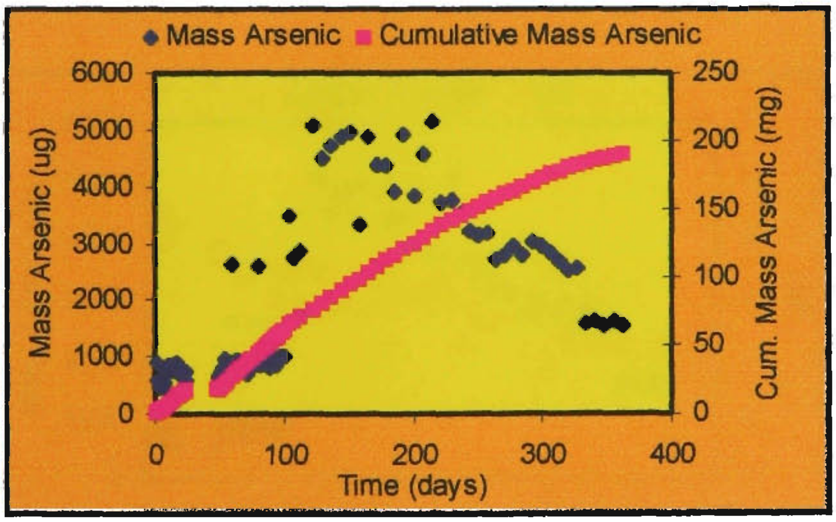


Figure 6.16: ABLC180 – Mass Arsenic Leached v's Time

It can be seen that the break in leachant flow had a minimal effect on the pattern of arsenic leaching as the difference between the mass of arsenic leached from the 24th to the 48th day samples ('stop-start' period) is a decrease of less than 20%. Foster also demonstrated that this type of break in leachant flow had little effect on arsenic leachability (1998) (refer to Section *3.3.2.2* for a description of his experiments).

6.3.2.2.1 pH, Redox Potential, and Conductivity Effects on Arsenic Leachability

Figures 6.17 and 6.18 illustrate broad correlations between arsenic release and pH and also redox potential. It can be seen that mass of arsenic leached steadily decreases after 200 days of leaching, as the pH of the leachates drop, and redox potential rises. While the response to the increase in Eh is in agreement with the work of previous authors (Hermann & Neumann-Mahlkau 1985; Dusing *et al* 1992; Standards Australia 1992), the opposite is true for the pH data. Here, arsenic was expected to increase in leachability as the pH decreased to more neutral levels (Förstner *et al* 1990; de Groot *et al* 1989; Blakey 1984). However, as with the behaviour of arsenic in the ABLC100, it seems most likely that the pH and Eh changes observed during this experiment had minimal effect on arsenic leachability, with L/S ratio, presumably, being the major influence on arsenic release.

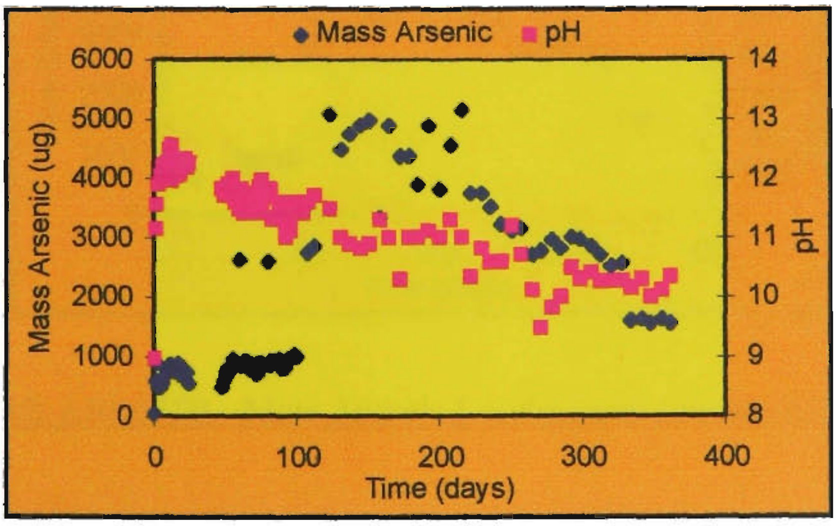


Figure 6.17: ABLC180 – Mass Arsenic Leached and pH v's Time

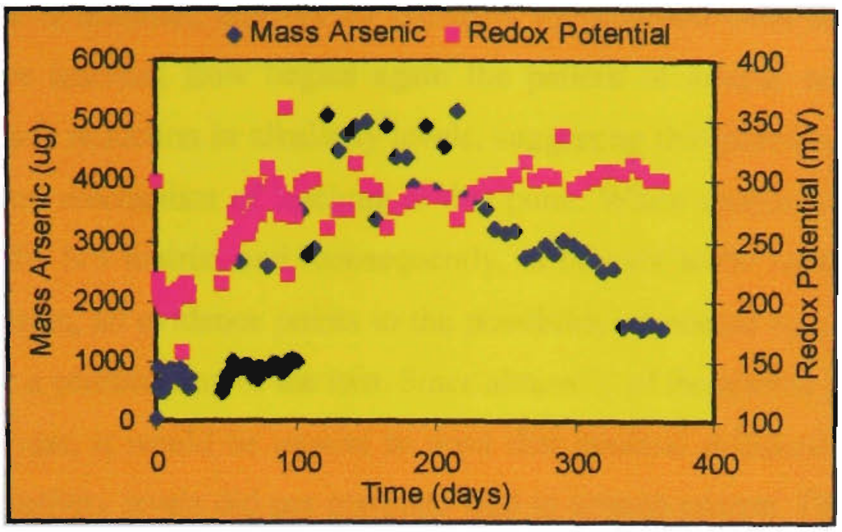


Figure 6.18: ABLC180 – Mass Arsenic Leached and Redox Potential v's Time

The response of arsenic to measured conductivity is similar to that observed for copper, and is illustrated in Figure 6.19.

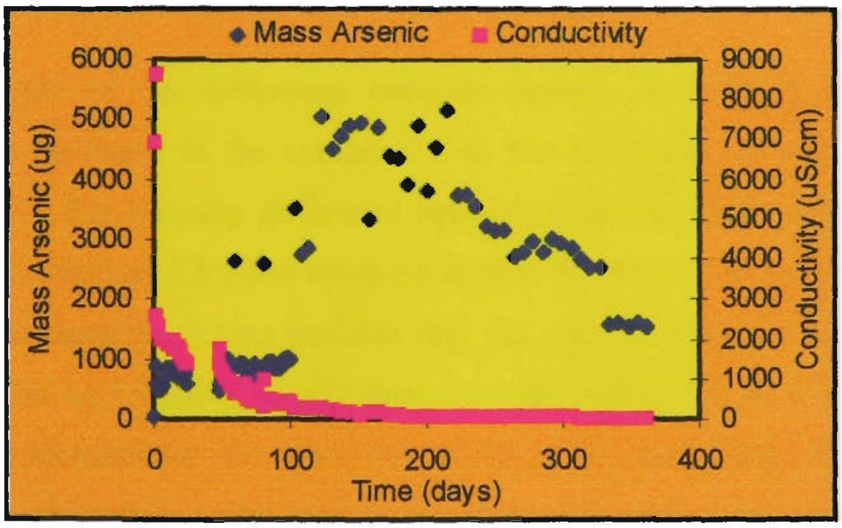


Figure 6.19: ABLC180 – Mass Arsenic Leached and Conductivity v's Time

As with copper, when the mass of arsenic dropped back to pre-drought levels following the resumption of leachant flow, the conductivity levels followed suit. This differs from the results for both zinc and lead, which took some time to drop back to their pre-drought levels. This data suggests that, under such stagnant conditions, arsenic release is minimal, and occurs primarily by diffusion from the waste pores. However, once leachant flow begins again the pattern of arsenic release does not follow the steady reduction in alkalinity levels, suggesting that pore-based diffusion is not a significant mechanism of leaching at this point. While copper is believed to be well held in the S/S matrix, and, consequently, is thought to be released mainly by matrix dissolution, all evidence points to the possibility of release by either diffusion, dissolution, or a combination of the two. Since almost ¼ of the arsenic present leached out over one year, it would be unwise to posit that minimal diffusion occurs, purely because conductivity levels did not correlate well to arsenic release. The suggestion is that, while surface wash-off is minimal for arsenic, the combination of diffusion and matrix dissolution release substantial amounts of the oxy-anion of arsenic. Therefore, while the minimal copper release suggests that dissolution is the primary release mechanism, the large amount of arsenic released precludes the same conclusion, regardless of the similarity in the release patterns.

6.3.2.2.2 Comparison to ABLC100

Another example of the difference between arsenic and copper release in the ABLC180 can be found in the comparison to the ABLC100. It was mentioned in Section *3.3.2.2.2* that the only difference between these two small columns was that the ABLC180 contained 1.8 times more waste than the ABLC100 (and hence a lower L/S ratio). Consequently, it was possible that the mass of arsenic released from the ABLC180 would be 1.8 times greater than from the ABLC100, with the percentages released being identical for the two columns. However, each metal investigated has behaved quite differently under these contrasting L/S ratio conditions. Table 6.11 details these differences, listing the amounts of each metal leached from the two columns. The table shows that arsenic was the only metal leaching to practically the same extent from both columns. This similarity between the columns is illustrated in Figure 6.20.

Table 6.11: Metal Release From the ABLC180 and ABLC100

Metal	Percentage Leached	
	ABLC180	ABLC100
Arsenic	24.6%	22.5%
Copper	0.14%	0.34%
Lead	6.21%	2.77%
Zinc	0.43%	0.32%

This further emphasises that, regardless of the similarity of leaching patterns between copper and arsenic in the small columns, the actual behaviour of arsenic has been shown to be quite different. While copper was the only metal to leach in greater amounts from the ABLC100 than from the ABLC180, arsenic leaching was essentially the same from both columns.

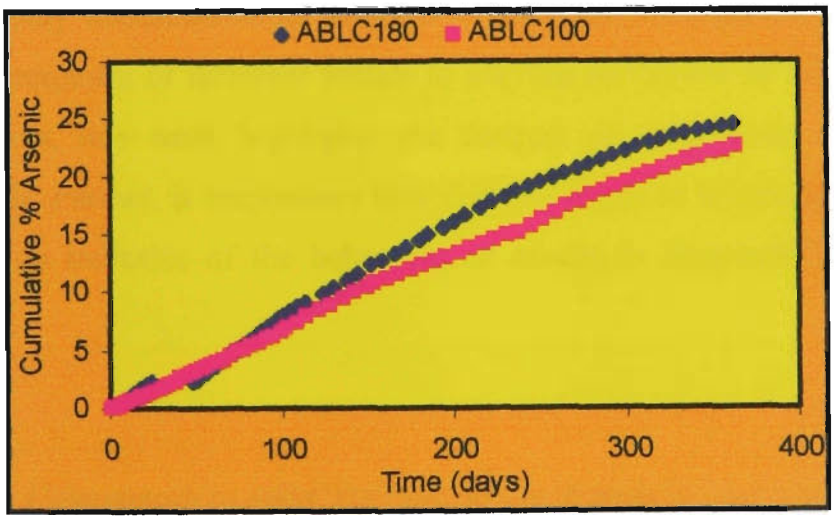


Figure 6.20: ABLC180 & ABLC100 – Cumulative Percentage Arsenic Leached v's Time

This information also highlights the different response to the change in L/S ratio between the columns. Earlier, in Section *6.3.2.1*, it was pointed out that arsenic leaching increased with an increase in L/S ratio. This was the case for all leaching tests, expect for the MAT. While this trend has not continued between the ABLC180 and the ABLC100, the ABLC180 has still leached an amount of arsenic that is reasonably close to that released from the earlier tests, corrected for L/S ratio. That is, if the L/S ratio of the ABLC180 (4859:1) is divided by 243 in order to equate it to the 20:1 L/S ratio, the amount of arsenic leached becomes 0.10%. Even though this seems close to the arsenic release of 0.03% – 0.07% from the earlier batch and columns tests, it is important to use caution with this sort of comparison to predict column results based on results from simple batch tests.

In this case, while results from the ABLC180 and ABLC100 demonstrated a similar response of arsenic release to different L/S ratios, the response can vary significantly, depending upon the mass of waste used and the type of tests being compared. Up until the review of the ABLC180 data, an increase in L/S ratio had led to an equivalent increase in arsenic release. However, as has been clarified, a decrease in the L/S ratio of the ABLC180 relative to the ABLC100 has led to the *same* percentage of arsenic being leached, as opposed to the anticipated decrease. If, based on a single batch type test, a prediction of leaching from the ABLC180 had been made, the result would have been significantly underestimated. Therefore, while such comparisons are useful in assessing the response of different metals to varying conditions of L/S ratio between contrasting tests, this work highlights the dangers of using such comparisons as predictive tools. Further, it emphasises how difficult it can be to employ a single-point batch test as an indicator of the behaviour of metals in long-term, time-dependent leaching tests.

6.3.2.2.2.1 Comparison to ABLC100; pH, Redox Potential, and Conductivity

Figure 3.21 (Section *3.3.2.2.2.1*) illustrates very similar patterns for redox potential for the two columns, with the ABLC100 recording slightly more oxidising conditions. Figures 3.22 and 3.23 (also in Section *3.3.2.2.2.1*) show the pH and conductivity levels in the ABLC180 were slightly higher than the ABLC100. These results indicate that a greater amount of $Ca(OH)_2$ was removed from the ABLC180 than the ABLC100, a consequence of the higher amount of solids in the former test and, therefore, a lower L/S ratio. Since the amount of arsenic released correlates well with the increase in waste mass in the ABLC180, it appears unlikely that any slight differences in pH, Eh, or conductivity have significantly affected the correlation.

6.3.2.3 LCC100; Leaching Behaviour of Arsenic

Table 6.10 indicated that the lowest percentage of arsenic (0.07%) was released from the LCC100 column. Figure 6.21 reveals that, of this amount, over 43% was released in the initial surface wash-off step. This differs from the other small columns, which had negligible amounts of arsenic released via surface wash-off. Note that the first point in the plot of mass of arsenic leached (137.6μg) has been removed to better observe the pattern of the other points in the chart. (It has <u>not</u>, however, been removed from the plot of cumulative mass of arsenic leached). This is the same for all subsequent plots of arsenic mass in the LCC100.

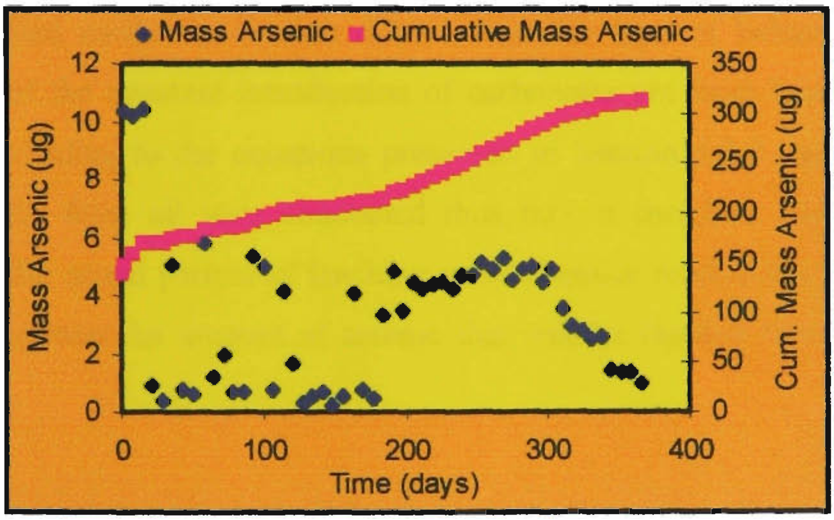


Figure 6.21: LCC100 – Mass Arsenic Leached v's Time

Of the other metals investigated, only the behaviour of zinc was similar, although only 22.5% leached in the surface wash-off step as opposed to an amount almost twice that for arsenic. In the case of lead, surface wash-off lasted for 3 leachate samples, while that for copper was relatively non-existent.

Aside from the high amount leached via surface wash-off, the arsenic release is, for the most part, fairly erratic. For each of the first 3 weeks after surface wash-off, approximately 10µg of arsenic leached from the waste. From this point until the sample taken on the 184th day of the test, no more than 2µg of arsenic per week leached from the waste (aside from 5 release spikes during that time). The arsenic levels then increased to around 4 - 5µg per sample, and remained at that level until 300days, after which they decreased until the end of the test.

This sudden increase in arsenic release half way through the LCC100 is similar to the leaching pattern for the ABLC100, which also demonstrated a sudden increase in arsenic levels at around 200 days. Further, the Sequential ABLP demonstrated an increase in arsenic leaching after the 3rd extraction. In fact, other than for the ABLC180 and Large Column, all time – related tests clearly show arsenic to be capable of leaching strongly, and suddenly, after as much as 7 months of a leaching test has passed.

It was suggested earlier in Section *6.2.4.1* that this type of behaviour may be a consequence of the constant introduction of carbonates via fresh leachant, which in turn reacts according to the equations presented in Section *6.2.2.* According to this (and the results from all tests conducted thus far), it therefore makes sense that, regardless of the actual pattern of leaching or mechanism responsible, the greater the L/S ratio the greater the amount of arsenic that will be leached from this particular waste type.

6.3.2.3.1 pH, Redox Potential, and Conductivity Effects on Arsenic Leachability

Figure 6.22 illustrates a no significant correlation between arsenic release and redox potential in the LCC100.

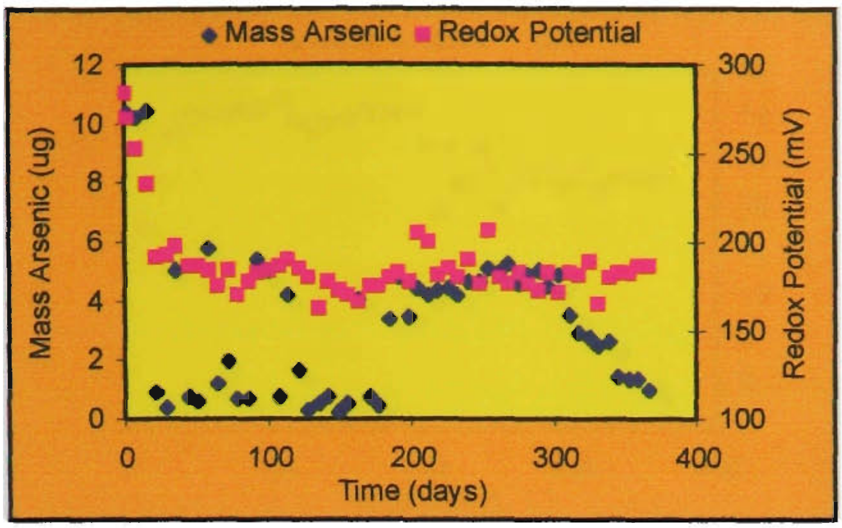


Figure 6.22: LCC100 – Mass Arsenic Leached and Redox Potential v's Time

While the Eh data does not, in this case, appears to correspond to the mass of arsenic leached, the changes in potential were so minor that any subsequent effects are probably quite minimal. It is most likely that the L/S ratio, method of leachant introduction, and column dimensions had far greater impact on arsenic release, than minor variations in redox potential.

Apart from the decrease in arsenic leaching observed after 300 days, Figures 6.23 and 6.24 illustrate good correlations between arsenic release from the LCC100 and pH and conductivity results respectively. Note that the first four points have been removed from the data in Figure 6.24 in order to better demonstrate the pattern of leaching. Of most significance is the sudden increase in arsenic release that coincided with sudden decreases in pH and conductivity after approximately 200 days. A similar decrease in pH and conductivity was observed in the Large Column (see Figures 3.31 & 3.32). However, this led to a decrease in arsenic release, as opposed to the increase observed for the LCC100. Since such pH and conductivity changes are indicative of a reduction in pore-available $Ca(OH)_2$, this was thought to reduce the amount of arsenic leached in the Large Column by slowing the reaction processes detailed in Section *6.2.2*. This, however, is obviously not the case for the LCC100.

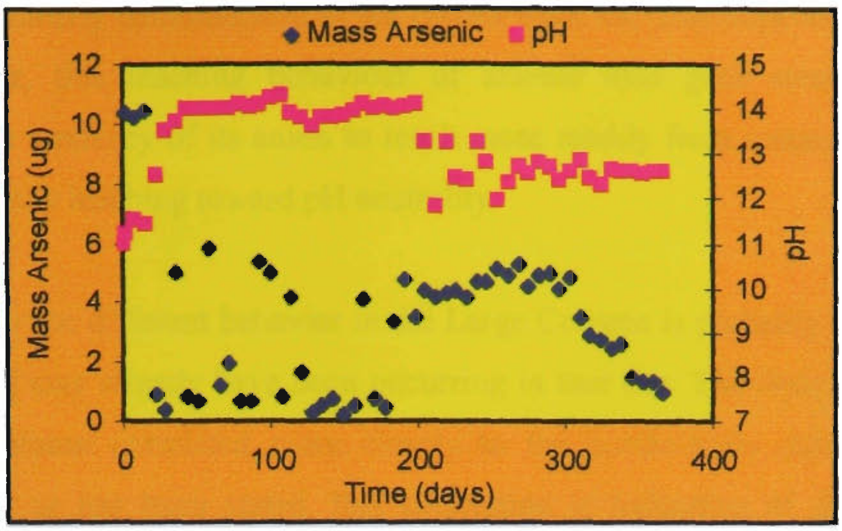


Figure 6.23: LCC100 – Mass Arsenic Leached and pH v's Time

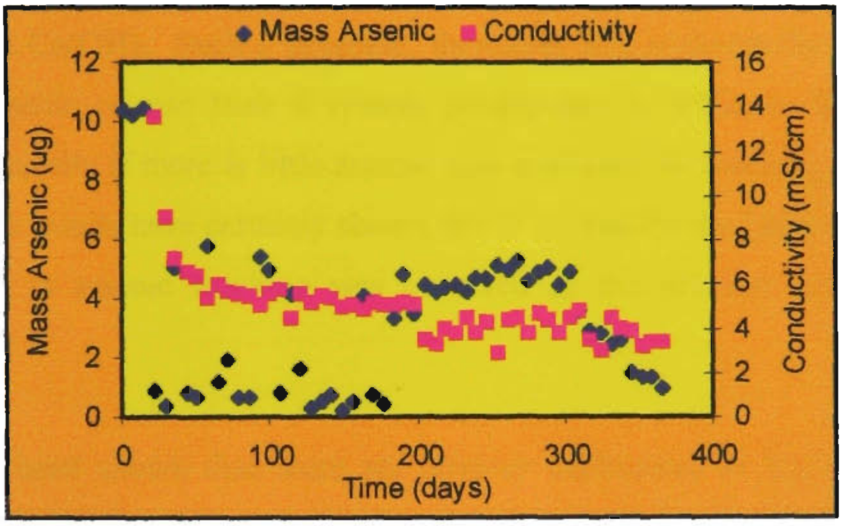


Figure 6.24: LCC100 – Mass Arsenic Leached and Conductivity v's Time

One possible explanation for the increase in arsenic levels is that, as stated in Section *6.3.2.2.1*, even though the pore-available $Ca(OH)_2$ levels appear to be dropping, this does not mean that the arsenic in the waste can not react with any other $Ca(OH)_2$ elsewhere in the matrix, forming basic calcium arsenite. Further, any pore-based leaching also serves to increase matrix porosity and tortuosity, so that any soluble calcium arsenite that had been previously *physically* trapped within the waste can now be leached far more easily. This type of behaviour, therefore, demonstrates that large surges of arsenic leaching can, and will, occur, as the waste becomes more porous, and this has been clearly demonstrated in the results from the time-dependent tests in this study. Further, this leaching behaviour of arsenic also goes some way toward explaining the tendency of its anion to leach more readily from cement-based wastes that are gradually leaching toward pH neutrality.

The reason for the different behavior in the Large Column is probably due to the type of release that may already have been occurring in that test. The arsenic release from the Large Column correlated more closely to the conductivity data than did the LCC100 and, as has been stated, this correlation is indicative of diffusion as the dominant mechanism of leaching. In contrast, the absence of a correlation between the arsenic and conductivity data for the LCC100 suggests leaching will occur via a combination of diffusion *and* dissolution. Further, according to earlier discussion, any decrease in pH and conductivity signifies a similar decrease in the leaching of any pore-available $Ca(OH)_2$. Such a decrease, therefore, will undoubtedly have a greater impact on arsenic release from a system predisposed to diffusive leaching (Large Column), especially if there is little arsenic also available for leaching via dissolution processes. The results have certainly shown this to be true for the Large Column where the reduction in arsenic leaching was observed as the pH and conductivity also decreased.

While it has been shown that there are obvious differences in the mechanisms of arsenic release from the two columns, the reason for such differences requires discussion. Probably, the most significant reason relates to the dimensions of the columns and their respective methods of leachant introduction (spraying v's pipetting). It appears therefore, that the method of leachant introduction and the dimensions of the leaching column (as well as the L/S ratio) can have a significant impact on arsenic release from a specific leaching test.

6.3.2.3.2 *Comparison to Large Column*

A comparison of the cumulative percentage of arsenic leached from the LCC100 and the Large Column is presented in Figure 6.25.

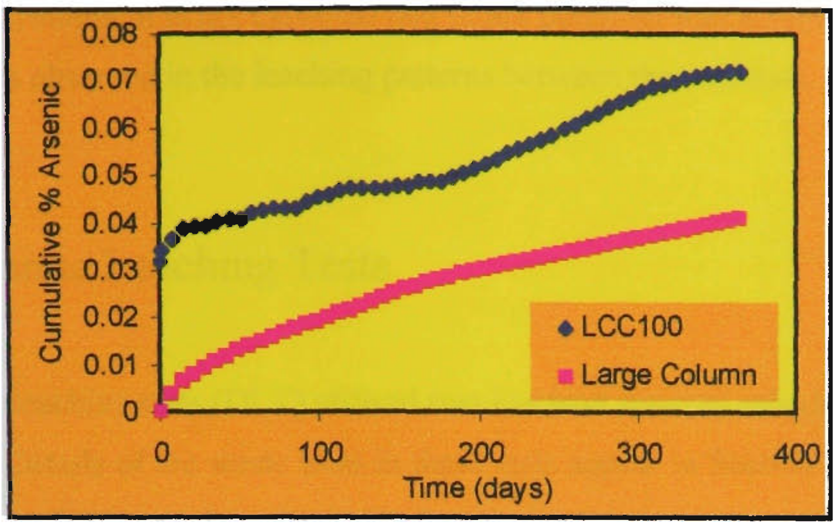


Figure 6.25: LCC100 & Large Column – Cumulative Percentage Arsenic Leached v's Time

As with lead, the LCC100 and Large Column leached markedly different amounts of arsenic from the waste, releasing 0.0725 and 0.041% respectively. However, in contrast to the lead results, the major discrepancy in leaching was via surface wash-off between these two tests. In fact, if it weren't for this significant difference in early release, both tests would have leached almost exactly the same percentage of arsenic, regardless of the mechanisms that actually facilitated the release. With that in mind, there were, of course, other contributing factors to the overall difference in release patterns, and these have already been discussed in Section *6.3.2.3.1*.

6.3.2.3.2.1 Comparison to Large Column; pH, Redox Potential, and Conductivity

The graphical comparisons between these parameters of the LCC100 and Large Column can be seen in Figures 3.31 – 3.33 in Section *3.3.2.3.2.1*. The observations pertaining to the similarities between the results are also covered in that section. Similarly, the effects of pH and conductivity on leaching from the two columns have also been discussed previously (Section *6.3.2.3.1*).

As already stated, redox potential had a minimal effect on leachability from the LCC100. Further, while the correlation between Eh and arsenic release appeared better for the Large Column, it is not expected that redox potential was a major contributor to the differences observed in the leaching patterns between the two tests.

6.4 Dynamic Leaching Tests

The dynamic leaching tests (DLT) utilised two leachant renewal schedules, detailed in Appendix C. Details of the waste used in these tests appear in Section *2.3.2*, while the methodologies of the tests are provided in Section *2.4.3*.

6.4.1 Leaching Behaviour of Arsenic

Two DLTs were run for each renewal schedule. These were labelled 1A and 1B for the rapid renewal rate of 1 hour, and 4A and 4B for the slower renewal rate of 4 hours (Refer Section *2.4.3.2)*. The masses leached in each of these experiments are detailed in Table 6.12. The complete leaching data can be seen in Appendices Q (i) – Q (iv). All pH, redox, and conductivity data are shown in Appendices H (v) – H (viii).

Table 6.12: Arsenic DLT Test Data

Replicate	t_n = 1A	t_n = 1B	t_n = 4A	t_n = 4B
Mass Leached (mg)	3.00	2.69	1.68	1.65
% Leached	1.50	1.33	0.83	0.82

Table 6.12 shows that the amount of arsenic leached from sphere 1A was only 11% more than that from 1B. This result is similar to zinc and copper, where each metal was leached in similar amounts from both spheres, but contrasts with the lead data which showed a great deal more to leach from 1B than 1A. Figure 6.26 illustrates the similarities in arsenic release between the two spheres.

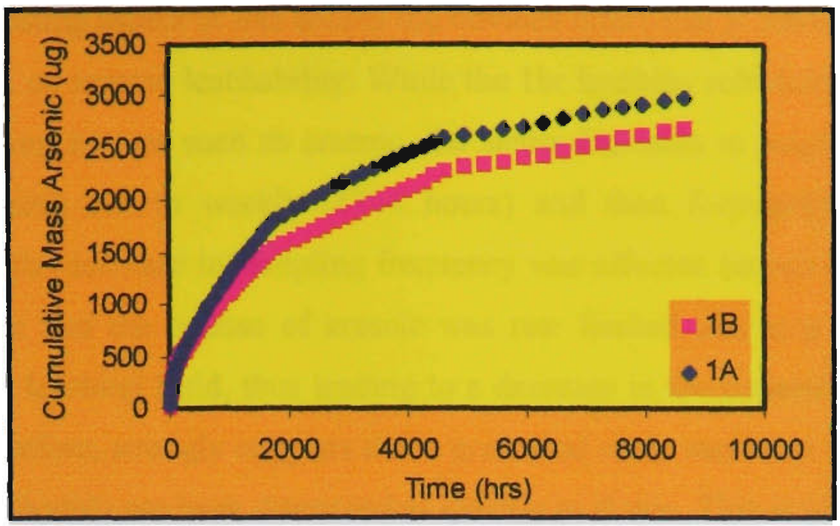


Figure 6.26: t_n = 1A & 1B – Cumulative Mass Arsenic Leached v's Time

What appears to be an early period of surface wash-off is visible in the release patterns of both spheres, followed by diffusion control. Côté and Isabel (1984) applied 28 day DLTs to cement solidified synthetic waste solutions and found arsenic to behave in a similar fashion to that seen in Figure 6.26. In a shorter length DLT (7 – 9 leaching intervals), Stegemann and Côté (1990) found arsenic release was linear with time. The reason for this, however, is due to the shorter length of the test, which would not provide an accurate longer-term leaching trend. In fact, any seven sequential points taken from Figure 6.26 would provide a linear relationship between arsenic and time, even though arsenic release was shown to decrease over time. Andac and Glasser (1998) used an extended NEN475 tank leaching test (544 days of leaching) to evaluate the effect of test conditions on the leaching of a cement stabilised fly ash. Their results contrasted the general assertion that longer leach tests show the same trend as the shorter tests. It was shown that, for the first 10 to 100 days of leaching, release was dominated by exchange of pore-water with the leachant. Thereafter, a semi-protective leached layer accumulated, which was also densified by $CaCO_3$ precipitation, and this was believed to be one of the main controls limiting leaching rates. Some of this resistance to leaching was offset by the formation of cracks a few μm below the exposed surface which exerted a major influence on leaching. Further, this cracking was exacerbated by increased concentrations of CO_2 in the leachant. As a result of this work they concluded that short-term tests could very much overpredict the actual course of leaching.

Another interesting aspect of this data is the obvious effect that a decrease in sampling frequency had on arsenic leachability. While the 1hr leaching schedule is intended for rapidly diffusing species such as arsenic, the sharp decreases in mass leached as the renewal stretches out to weekly (1764 hours) and then fortnightly (4620 hours) suggests that the decrease in sampling frequency was effected far too quickly. This is clear evidence that the release of arsenic was rate limited due to a build-up of its species in the leaching fluid, thus leading to a decrease in the concentration gradient. This data, therefore, strongly suggests that a great deal more may have leached out had the renewal schedule not been decreased as quickly as it was. This is unfortunate since it means the final masses leached may not be an accurate representation of what could be potentially released via diffusion.

While the rate-limiting effect may be significant enough for other metals, it is even more so for arsenic due to the added influence fresh leachant has on its rate of release. Côté *et al* (1987) noted as much in their work on two years of dynamic leaching of cement-based waste forms. While they found that arsenic release was primarily diffusion controlled, they also suggested that the rate of arsenic release was effectively controlled by the rate of leachant renewal (in particular the rate of CO_2 renewal). This was proven to be the case when they compared the amount of arsenic leached to the amount of carbonates added with the leachant to the DLT systems. Basing their calculations on a CO_2 partial pressure of $10^{-3.5}$ atm, they estimated the H_2CO_3 concentration in the distilled water leachant to be $10^{-5.65}$M, which is equivalent to 360μmol of H_2CO_3 over the duration of the experiments. The estimated amount of carbonates that reacted with each specimen was found to be of the same order of magnitude as the amount of arsenic mobilised. They, therefore, concluded that, given the stoichiometry of the reactions presented in Section *6.2.2*, the postulate that leachant renewal rate limited the release of arsenic was true.

Spheres 4A and 4B demonstrated similar behaviour to that of 1A and 1B, where leaching was diffusion controlled following an initial period of surface wash-off (Figure 6.27). The amounts released from 4A and 4B were also very similar, with only 0.01% of arsenic leached separating the two spheres.

The fact that a great deal less arsenic was leached from the 4-hour schedule than the 1-hour schedule also shows the effect of rate limiting leaching. Lower levels of metal in the 4-hour schedule compared to the 1-hour schedule were also observed for zinc. Of course, as stated previously, the lower amount of CO_2 introduced to the 4-hour system would be a contributing factor in the reduction of leached arsenic compared to the 1-hour system. Therefore, once again, the rate of leachant renewal has been shown to have a very strong influence on the amount of arsenic released from the spheres in the DLT.

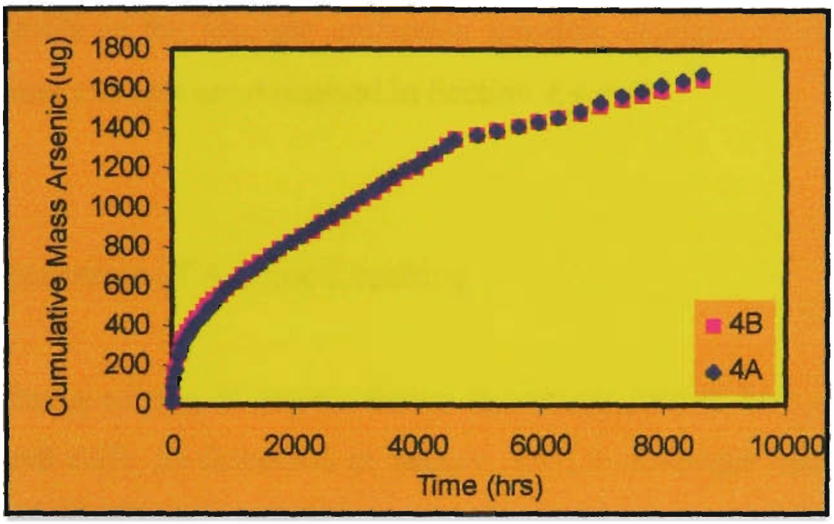


Figure 6.27: t_n = 4A & 4B – Cumulative Mass Arsenic Leached v's Time

Also of interest is that no more arsenic was released from the fractured sphere (4B) than was leached from the intact one (4A). Obviously then, while L/S ratio and leachant renewal appear to be extremely important parameters in governing arsenic release, the external surface area available for leaching is not as significant. In the ABLC180, where leaching occurs as much by dissolution as diffusion, it was suggested than some of the previously trapped arsenic was released as the waste matrix broke down. However, the 4-hour renewal DLT showed no significant increase in arsenic release when the crack appeared after two weeks of leaching in sphere 4B. It may be, therefore, that a significant flow of leachant is required to free any such trapped arsenic species. This would also explain why such behaviour was observed only in the ABLC180, where the test conditions and flow rate facilitated this type of release.

6.4.1.1 DLT; pH, Redox Potential, and Conductivity Results

Figures 3.36 – 3.41 in Section *3.4.1* illustrate the pH, redox, and conductivity results for all spheres. Although the data for spheres 1A & 1B and 4A & 4B correlate well with the electrode results, there are no significant correlations between that data and the arsenic leachability data. Both the 1 and 4 hour tests also show variations in conductivity levels as the leachate collection schedule changed to weekly and then fortnightly. These changes are discussed in Section *4.4.1.1*.

6.4.1.2 Mechanism of Arsenic Leaching

Plots of cumulative release of arsenic versus the square root of time are presented as Figures 6.28 and 6.29. As discussed in Section *3.4.1.1*, a straight line of this type of plot is indicative of diffusive release.

These charts provide the best example yet of purely diffusive release in the DLT. It was originally thought that the sharp increase at the beginning of the test was the influence of surface wash-off. However, as these charts show, the high levels of arsenic leached appear to be merely the beginnings of the diffusive process. Any surface wash-off that did occur would have been insignificant relative to the amounts leached via diffusion.

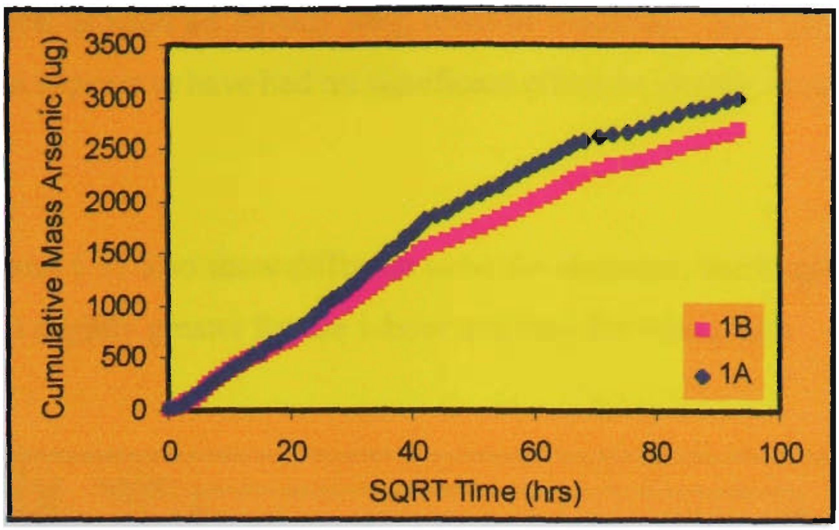


Figure 6.28: t_n = 1A & 1B – Cumulative Mass Arsenic Leached v's Square Root of Time

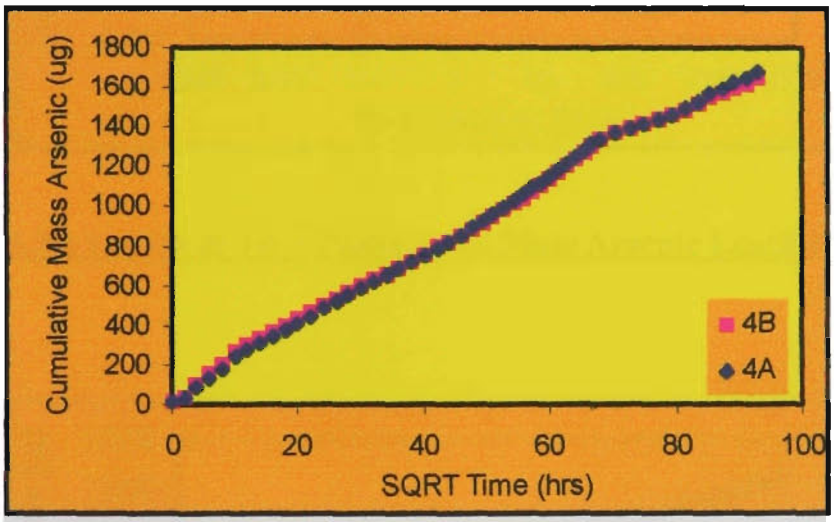


Figure 6.29: t_n = 4A & 4B – Cumulative Mass Arsenic Leached v's Square Root of Time

Spheres 1A and 1B both show the effects of a reduced driving force for leaching due to an increase in sampling time. However, this has simply produced three distinct zones of diffusion, each with a rate slightly lower than the previous one. As discussed in Section *6.4.1*, the reason for such a decrease in arsenic release can be directly correlated to the renewal frequency of the leachant and the subsequent introduction of carbonates to the DLT system. The diffusion of arsenic from spheres 4A and 4B, on the other hand, shows almost no overall effect due to the change in leachant renewal time. Therefore, at such an already long renewal frequency, any further reduction in sampling time appears to have had no significant effect on arsenic release from spheres 4A and 4B.

Figures 6.30 and 6.31 also show diffusion to be the dominant leaching mechanism, and that the rate is slightly greater for the 1-hour test than the 4-hour test.

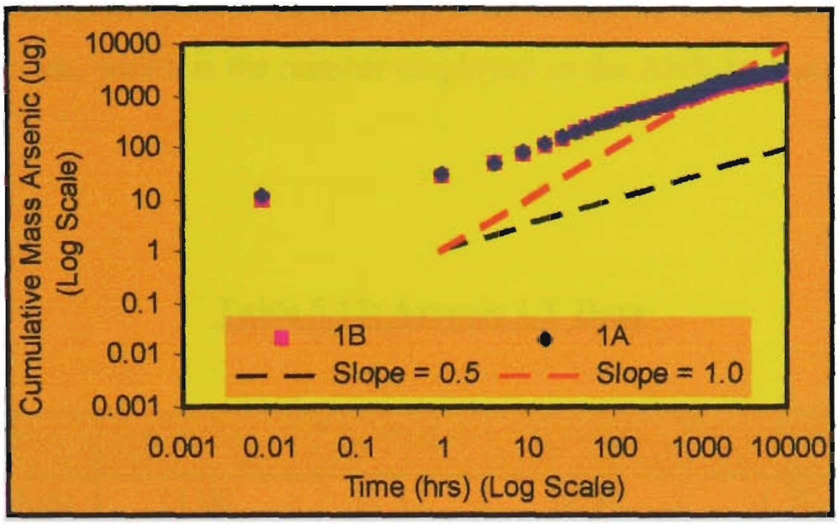


Figure 6.30: t_n = 1A & 1B – Cumulative Mass Arsenic Leached v's Time

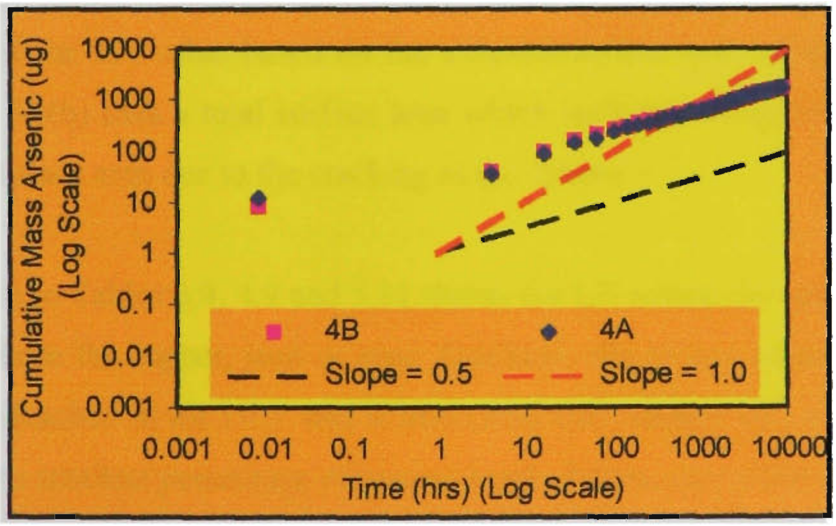


Figure 6.31: t_n = 4A & 4B – Cumulative Mass Arsenic Leached v's Time

An explanation of the utilisation of such a chart on a log-log scale revolves around the slope of the subsequent plot, and is provided in Section *3.4.1.1*.

6.4.1.3 Arsenic LX Values

The LX values for arsenic release from the DLT spheres are detailed in Table 6.13. The table shows the overall LX values for arsenic release as well as the indexes for the first seven periods, which is the number employed in the ANS-16.1 protocol (USEPA 1989).

Table 6.13: Arsenic LX Data

Sphere	t_n = 1A	t_n = 1B	t_n = 4A	t_n = 4B(a)	t_n = 4B(b)
LX - 1st 7 Periods	11.00	11.17	10.99	11.30	11.65
LX - Total	11.97	12.12	11.85	12.15	12.50

The values for sphere 4B are split into two columns. Column t_n = 4B(a) represents the calculation of the LX value based on the external surface area of the sphere, while column t_n = 4B(b) uses a total surface area which includes an approximation for the increase in surface area due to the cracking of the sphere.

A comparison to Tables 3.9, 4.9 and 5.11 shows the LX values for arsenic to be much lower than those for copper, lead or zinc. Similarly, the largest percentage of any of those metals leached in the DLT was 0.76% (lead from sphere 4B), and this was still lower than the smallest percentage of arsenic leached from any of the spheres. Further, although LX values between 10 and 15 are indicative of slow leaching rates (USEPA 1989), the fact that such a large amount of arsenic was released, relative to the other metals, is important information with respect to the ultimate disposal of this waste.

Regardless of the fact that spheres 1A and 1B leached a great deal more arsenic than 4A or 4B, the LX values for all spheres were quite similar. Also, the decrease in LX values of 0.85 to 0.97 units between the total data and that for the first 7 periods clearly illustrates the influence surface wash-off had on arsenic leaching. While it was mentioned earlier that surface wash-off had practically no effect on arsenic release in the DLT, the influence only needs to occur in the first one or two points for it to be evidenced in decreased LX data.

Once again, as with the other metals, the arsenic data shows a higher LX value for sphere 4B(b) with the approximated surface area that included the cracking, than for the calculation using the surface area of the outer surface of the sphere only. As mentioned in Section *4.4.1.3*, this is thought to arise from a combination of a poorly approximated boundary condition of a zero surface concentration in the leachate, and an overestimation of an increase in surface area due to the cracking of the sphere.

6.5 Summary of Arsenic Leaching

A summary of arsenic leaching from every leaching test conducted in this work is presented in Table 6.14. Not only does this table provide an absolute percentage of arsenic leached from each test, and the final L/S ratio from each test, it also displays the amount of arsenic leached as a ratio relative to the ABLP result, which has been given the arbitrary unit of 1. This allows for a better visual comparison between the results. Table 6.15 provides a breakdown of when the majority of the arsenic was leached in the column and tank tests. That is, it shows how long was required for each 25% increment of the total amount of arsenic to be leached from the waste.

Table 6.14: Summary of Arsenic Results From All Tests

Test	Percentage of Arsenic Leached	L/S Ratio	Ratio Leached (where ABLP = 1)
MAT	0.32%	9.8:1	6.27
TCLP	0.064%	20:1	1.25
ABLP	0.051%	20:1	1
Sequential ABLP	0.387%	200:1	7.59
Large Column	0.04%	19.1:1	0.78
LCC100	0.07%	17.6:1	1.37
ABLC100	22.5%	9571:1	441
ABLC180	24.6%	4873:1	482
DLT; T_n = 1A	1.50%	634.3:1	29.4
DLT; T_n = 1B	1.33%	626.2:1	26.1
DLT; T_n = 4A	0.83%	445.2:1	16.3
DLT; T_n = 4B	0.82%	447.5:1	16.1

Table 6.15: Leaching Breakdown of Arsenic From Column and Tank Tests

Test	Time to Leach 1st 25% of Total Arsenic (days)	Time to Leach 2nd 25% of Total Arsenic (days)	Time to Leach 3rd 25% of Total Arsenic (days)	Time to Leach 4th 25% of Total Arsenic (days)
Large Column	35	77	98	154
LCC100	0 (Surface Wash)	8	211	147
ABLC100	86	81	91	105
ABLC180	85	73	78	126
DLT; T_n = 1A	18.4	38.7	79.4	224
DLT; T_n = 1B	16.7	43.5	97.3	203
DLT; T_n = 4A	20.2	67.3	91	182
DLT; T_n = 4B	16.7	70.8	84	189

Unlike the results for all other metals investigated thus far, Table 6.14 shows that minimal arsenic was leached in the MAT. This information is vitally important because, although the MAT is designed as a predictor of maximum leaching rates primarily for DLT-type tests, all spheres in the DLT were shown to leach arsenic at levels greater than that predicted by the MAT. Similarly, a number of other tests also leached greater levels of arsenic than the MAT (Sequential ABLP, ABLC100, and ABLC180). It appears that the low level observed in the MAT is a consequence of pH and Eh levels in the final leachate.

The greatest amounts of arsenic were leached from the small column up-flow tests, the ABLC100 and ABLC180, where a combination of dissolution and pore-based diffusion was shown to control leaching. For the batch tests, redox potential was believed to be the most important parameter in determining the dominant species of arsenic present in the waste and, therefore, the leaching rate of that species from the waste. However, as the small column results show, a rapid leachant velocity and high L/S ratio is far more important when it comes to removing arsenic from this particular waste. The main reason for such behaviour is thought to derive from the constant renewal of carbonates via the frequent introduction of fresh leachant. The reaction of those carbonates with arsenic species to form soluble arsenates and arsenites may certainly have been a key factor in greater release of those species from the waste. Hence, as the velocity (small upflow columns compared to the downflow columns and batch tests) or frequency of the leachant renewal is increased (DLT; 1 hour tests compared to the 4 hour tests), arsenic release is also increased. This effect can impact even further on predictions of arsenic release as, in a number of the experiments, levels increased at some stage well after it was thought that arsenic leaching was stable. The fact that arsenic leaching did not decrease in the 180g column relative to the 100g column, however, means that an increase in L/S ratio is not all that is required to increase arsenic release.

The results of the two columns also raise an interesting point about the possibility of test comparisons based upon a simple L/S ratio to mass leached correlation. It was found that the TCLP, ABLP, Sequential ABLP, Large Column, LCC100, and ABLC100 all correlated well for arsenic release (<1 order of magnitude) when L/S ratios were taken into account. If a prediction of arsenic release was made for the

ABLC180 based on this data, the number would have been underestimated, as the reduction in L/S ratio of the ABLC180 was expected to lead to a lower amount of arsenic leached from the waste than was actually released.

Apart from the LCC100 where surface wash-off contributed more than 43% of all arsenic leached, all experiments showed that arsenic was released via either pore-based diffusion, dissolution, or a combination of the two. Considering Table 6.15 shows that surface wash-off did not appear to be a major contributor to arsenic leaching in the Large Column, the LCC100 result clearly demonstrates the effect that column dimensions and method of leachant delivery can have on the amount, mechanism, and pattern of arsenic release.

The DLT results demonstrated an excellent pattern of diffusive leaching of arsenic from the spheres which correlates well with earlier research (Côté & Isabel 1984, Stegemann & Côté 1990). Further, although the amounts leached were not large, they were, by far the greatest leached of any metal thus far. The DLT results also showed the effects of an increase in renewal frequency, where the 1-hour schedule leached approximately 70% more arsenic than did the 4-hour schedule. Surprisingly, the crack in sphere 4B did not appear to affect arsenic release at all, as both spheres 4A and 4B released practically identical amounts. This result was similar to that observed in the comparison between the ABLC100 and ABLC180 small columns, where a decrease in L/S ratio was effected by an increase in mass of waste available for leaching. Considering the amount and flow of liquid was the same, it is quite possible that, under such conditions, increases in waste mass may not greatly affect arsenic leaching in the short to medium term. Considering arsenic release has shown potential to increase over time, the long-term trend may, however, prove to be quite different.

In order to minimise the impact of arsenic release from this waste, therefore, the ideal disposal scenario would be one in which any introduction of liquid to the landfill was minimal. That is, based on the previous data, any sudden influx of liquid could lead to surges in arsenic release in the short term. In the longer term, the effects may be even more deleterious.

7. Results and Discussion: Selenium

7.1 Selenium Analysis: Method Validation

Method validation for selenium by HGAAS was carried out according to the procedure described in Section *2.5.1.2* using a 20ml aliquot of a Dynamic Leaching Test leachate of unknown concentration. Selenium concentration by standard calibration was 12.60ppb and by standard additions was 12.76ppb. The difference is not significant. Accordingly, the method of standard calibrations was used throughout the leaching experiments for the analysis of selenium. Selenium recoveries were all between 95% and 104%. Method validation also demonstrated that no matrix effects were present in the analysis by standard calibration.

7.2 Batch Tests

The batch tests investigated in this study were the Maximum Availability Test, ABLP, Sequential ABLP, and TCLP. Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.4 – 2.4.6*.

7.2.1 Maximum Availability Test Results

The Maximum Availability Test was run in triplicate. Averages of these results for mass and percentage of selenium leached, pH, redox potential, and conductivity are detailed in Table 7.1. Results for each replicate for mass of selenium leached, pH, redox, and conductivity, are shown in Appendix E (i). Volumes of acid added during the test are detailed in Section *3.2.1*.

Table 7.1: Selenium Maximum Availability Test Data

Mass of Selenium Leached (mg)	Percentage of Total Mass of Selenium Leached (±1σ)	pH	Redox Potential (mV)	Conductivity (mScm^{-1})
0.068	1.62% (±0.03%)	4.68	564.1	6.6

This result demonstrates that no greater than 1.62% of the selenium present in this solidified waste should leach out over time, with 98.38% remaining bound within the cement matrix. As with arsenic, the percentage of selenium leached via this test is much less than that released for copper, lead, and zinc. A comparison of these results can be seen in Table 7.2.

Table 7.2: Maximum Availability Test Data

Metal	Percentage of Total Mass of Metal Leached
Selenium	1.62%
Arsenic	0.32%
Copper	26.7%
Lead	21.8%
Zinc	43.9%

7.2.2 TCLP Results

The average concentration, mass and percentage of selenium leached, pH, redox potential, and conductivity in the TCLP are detailed in Table 7.3. Results for each of the four replicates for mass of selenium leached, pH, redox, and conductivity, are shown in Appendix E (ii). The temperature during the extraction ranged from 20°C to 22°C.

Table 7.3: Selenium TCLP Data

Concentration Leached (ppm)	Mass of Selenium Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Selenium Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.027	0.054	0.21% (±0.02%)	12.11	232.1	12.8

As detailed in Table 7.3, the 1ppm TCLP limit for selenium (see Table 1.5) was not exceeded. As with the other metals studied, only a small amount of selenium was released from the waste over the duration of the test. This result is not unexpected as selenium is rarely found in industrial wastes (except for coal fly ashes) in appreciable amounts, and when it is present in large amounts it is not generally leached to any great extent (Conner 1990).

7.2.3 ABLP Results

The average concentration, mass and percentage of selenium leached, pH, redox potential, and conductivity in the ABLP are detailed in Table 7.4. Results for each of the four replicates for mass of selenium leached, pH, redox, and conductivity, are shown in Appendix E (iii). The temperature during the extraction ranged from 27°C to 29°C.

Table 7.4: Selenium ABLP Data

Concentration Leached (ppm)	Mass of Selenium Leached per 100g Fixed Waste (mg)	Percentage of Total Mass of Selenium Leached (±1σ)	pH	Redox Potential (mV)	Conductivity ($mScm^{-1}$)
0.104	0.209	0.79% (±5.4 x 10^{-5}%)	11.60	210.3	8.20

This result demonstrates that almost four times as much selenium leached from the ABLP compared to the TCLP. A comparison of the electrode data (see Appendices E(ii) and E(iii)) between the ABLP and TCLP shows that a conductivity level almost twice as great for the TCLP, did not lead to a corresponding increase in solubilised selenium. It must be pointed out that, in contrast to the non-conducting leachant used in the ABLP, the acetate leachant used in the TCLP contributed 0.50mScm^{-1} to the final leachate conductivity. Therefore, the small contribution to conductivity from the acetate leachate does not have a significant bearing on this discussion. The fact that an acidic system such as the TCLP possibly releases a greater amount of $Ca(OH)_2$, but not selenium, suggests that the selenium species are not readily available for leaching in large amounts from the waste pores. In fact, it may be that a significant portion of the selenium present in the matrix is physically trapped and available only as the waste structure deteriorates.

The pH of the final leachate in the ABLP was around 11.6, approximately one half of a pH unit lower than that observed in the TCLP. de Groot *et al* (1989) assessed the leaching characteristics of coal fly ash and found selenium to leach more at neutral pH, with decreases in concentration towards lower and higher pH. In fact, a pH diagram in that paper shows a maximum concentration for selenium at pH11, and significant drops as the pH decreases below pH7, and increases to pH12. According to the above, at this pH, it is expected that a greater amount of selenium will be available for leaching. This was observed in the results, which showed selenium levels almost four times as great in the ABLP compared to the TCLP. The MAT would also be expected to leach less selenium than both the TCLP and ABLP based on pH considerations alone, but this was not the case. As mentioned earlier, if most of the selenium is physically trapped within the matrix, more would be available for leaching in a test like the MAT (due to its much smaller particle size) compared to the TCLP and ABLP.

The most common water-soluble selenium species are salts of the selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) anions (U.S. National Research Council 1983). A World Health Organisation publication on drinking-water guidelines (1996) states that most selenate salts are appreciably more soluble than the corresponding selenite compounds. Further, their solubility and stability are greatest in alkaline environments, and the conversion of selenates to the less stable selenites and to elemental selenium is very slow. In a study on the effects of redox potential on waste testing, Standards Australia Working Group CH35 (1992) also found selenium to be more stable at higher pH, particularly under oxidising conditions. An example of the solubility of selenium can be found in the natural environment where, in alkaline soils, selenium is present as water-soluble selenate and is available to plants, while, in acid soils, it is usually found as selenite bound to iron and aluminium oxides in compounds of very low solubility (World Health Organisation 1996). Similarly, in his work on trace element leachability of Australian coals, Killingley (2001) presents evidence that suggests the adsorptive properties of the selenium ion (selenate or selenite) can have a significant effect on its leachability. He has shown selenium leaching to be dependent on the iron content of the ash. Further, it is suggested that selenium leaches quickly, but then re-adsorbs onto iron oxides present in the ash, and the greater the iron content of the ash, the lower the selenium leachability. Conde and Sanz Alaejos (1997) reviewed selenium concentrations in natural and environmental waters. They found that, under natural conditions, selenite is stable and can pass into solution especially when the pH values are high, but it is easily adsorbed by solid phases.

No speciation studies were performed in this work, but the information presented above suggests that if selenium is being leached from the waste, it may just as quickly be re-adsorbed, from solution, back onto the surface of the waste. Further, both selenite *and* selenate are capable of the leaching/readsorption process, especially at the high pH levels encountered in this waste. In fact, considering the fixed waste used in this work contains approximately 26g/kg of iron and 30g/kg of aluminium (and selenium is present in roughly 1/100th those amounts), the readsorption of selenium is a very real possibility.

The slightly lower pH of the ABLP to that of the TCLP was used to help explain why the ABLP leached four times more selenium than the TCLP, even though the TCLP conductivity was twice that of the ABLP. The readsorption of selenium may be another important contributing factor. The higher conductivity level observed in the TCLP is, of course, indicative of the increased matrix attack that occurs in an acidic leaching system. This increased matrix attack would, therefore, also result in an increase in porosity and surface area available for leaching as $Ca(OH)_2$ is leached from the pores. If selenium is being leached along with alkalinity, the higher surface area made available in the TCLP compared to the ABLP has actually resulted in a greater amount of selenium readsorbing to the waste particles, thus leading to lower levels in the leachate.

7.2.4 Sequential ABLP Results

The average concentration, mass and percentage of selenium leached in the Sequential ABLP are detailed in Table 7.5. Results for each replicate for mass of selenium leached, pH, redox, and conductivity, are shown in Appendix E (iv).

Table 7.5: Selenium Sequential ABLP Data

Sequential Leach Number	Concentration Selenium Leached (ppm)	Mass of Selenium Leached (mg)	Percentage of Total Mass of Selenium Leached (±1σ)
1	104.4	208.8	0.79% (±9.3 x 10^{-3}%)
2	61.4	122.9	0.46% (±4.9 x 10^{-2}%)
3	59.0	118.1	0.45% (±9.8 x 10^{-2}%)
4	54.9	109.7	0.42% (±8.3 x 10^{-2}%)
5	73.0	146.1	0.55% (±7.9 x 10^{-2}%)
6	61.7	123.3	0.47% (±2.9 x 10^{-2}%)
7	85.4	170.8	0.65% (±1.1 x 10^{-1}%)
8	41.6	83.2	0.31% (±4.3 x 10^{-2}%)
9	37.7	75.3	0.29% (±2.5 x 10^{-2}%)
10	54.5	109.0	0.41% (±3.0 x 10^{-2}%)
Total	N/A*	**1.27**	**4.80%** (±0.56%)

*N/A = Not Applicable

The data, in Table 7.5, shows that 4.80% of the selenium present in the waste was removed after ten successive leaches. This demonstrates that the metal is well retained in the fixed waste system. It also demonstrates that the first ABLP leach acted as a worst case scenario test, since this was the highest amount of selenium leached over the duration of the test.

It is also worth noting that the amount leached from the waste in the Sequential ABLP far exceeded that predicted by the MAT of 1.62%. This suggests, therefore, that the MAT is a poor predictor of maximum selenium leachability for this particular waste.

7.2.4.1 Leaching Behaviour of Selenium

Following a slightly elevated period of surface wash-off, Figure 7.1 shows the amount of selenium released decreased only marginally for the remainder of the extractions.

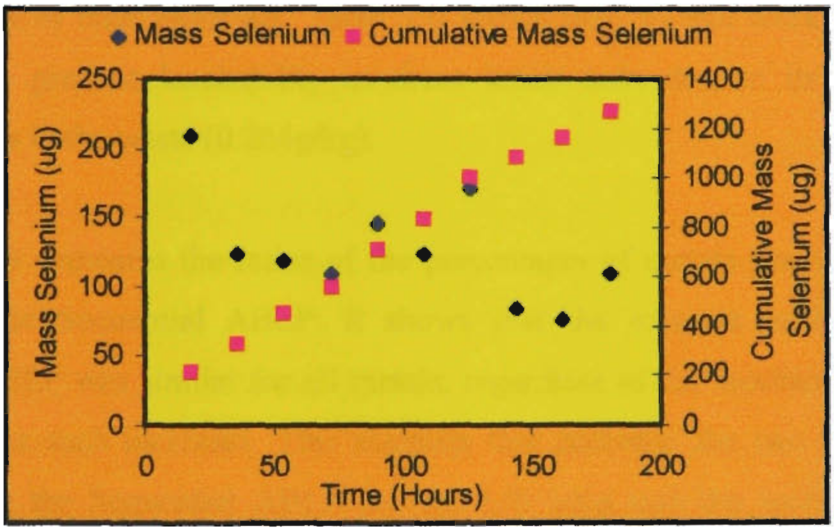


Figure 7.1: Sequential ABLP – Mass Selenium Leached v's Time

The steady release of selenium during the sequential ABLP supports the suggestion that only the species unable to re-adsorb to the waste particles will leach into solution, and may be a consequence of any increase in surface area encountered during the test, either caused by particle abrasion or an increase in porosity as $Ca(OH)_2$ is leached from the waste. Such an increase, while possibly facilitating the physical release of any trapped selenium, could also have led to a reduction in species via adsorption.

In addition to the effect of surface area increases, any increase in the mass of solids tested (a decrease in L/S ratio) may also bring about the same result. Jackson *et al* (1981) leached fly ash with distilled water in ABLP-type batch tests, and also from a small column for 60 days. They demonstrated, via the batch tests, that the percentage of selenium released from the waste increased as the L/S ratio of the test was increased. That is, the fewer solids there are for adsorption to take place, the more selenium will be in the leachate.

In contrast to the behaviour of selenium in Figure 7.1, Wadge and Hutton (1987) employed a sequential batch shaking test using distilled water in order to evaluate the potential leachability of refuse and coal fly ashes. They also found that the amount of selenium released peaked in the first extraction. However, rather than dropping slightly and then steadying, the amount of selenium leached declined rapidly in successive extractions. It is worth adding, though, that selenium displayed the greatest leachability of all metal species in each ash type, despite being present at relatively low concentrations in both materials. Table 7.6 shows that, in this work, selenium also displayed the greatest leachability in these batch tests despite its relatively low concentrations in the waste (0.264g/kg).

Table 7.6 also compares the ratios of the percentages of metals leached between the ABLP and the Sequential ABLP. It shows that the increase in leaching in the Sequential ABLP was similar for all metals, regardless of the mechanism(s) believed responsible for such increases. This suggests that probably the two most important parameters in the Sequential ABLP are the L/S ratio and the increase in particle abrasion over 10 successive leaches (compared to the abrasion that occurs during a single extraction).

Table 7.6: Ratio of the Percentage of Metals Leached From the Sequential ABLP to the ABLP

Metal	Percentage Leached		Ratio of Sequential ABLP : ABLP
	Sequential ABLP (ten extractions)	ABLP	
Selenium	4.80%	0.79%	6.1:1
Arsenic	0.39%	0.05%	7.8:1
Copper	0.05%	0.008%	6.3:1
Lead	2.94%	0.57%	5.2:1
Zinc	0.17%	0.035%	4.9:1

In the case of selenium, the increase in L/S ratio has led to a decrease in matrix adsorption and a subsequent overall increase in leachability (compared to the ABLP). Combating this is the gradual increase in surface area, which appears to have brought about a slight overall decrease in the amount of selenium leached over the last nine extractions in the Sequential ABLP. Of course, these mechanisms are further affected (and dictated) by the pH/Eh conditions of the system and any insoluble species formed as a consequence of those conditions.

Compare this to arsenic, where the increase in leaching is thought to be a response to the constant renewal of carbonates in the fresh leachant introduced for each extraction. In the case of copper an increase in matrix dissolution is believed to be the controlling factor in the subsequent increases in leachability later on in the Sequential ABLP. Different again are the conclusions for lead, and zinc, where the greater L/S ratio and number of extractions have led to increases in both diffusive and dissolution processes, thereby increasing the amounts of each metal released.

This is an extremely important finding as it emphasises that, in this case, regardless of the chemical or physical mechanisms that have led to increases in metal release, the degree of that increase is practically the same for all metals. Further, such behaviour is a consequence of the increase in L/S ratio, an obviously significant variable whose importance should not be taken lightly.

7.2.4.1.1 pH, Redox Potential, and Conductivity Effects on Selenium Leachability

It was mentioned earlier that selenium was believed to leach a lot more readily in alkaline environments of pH 7 to 11, and this is supported by the data presented in Figure 7.2. As the pH increased from 11.6 to 13.41 over the course of the experiment, the mass of selenium leached slightly decreased. This trend is in agreement with the suggestion that a highly alkaline environment (>pH 11) is not conducive to selenium release.

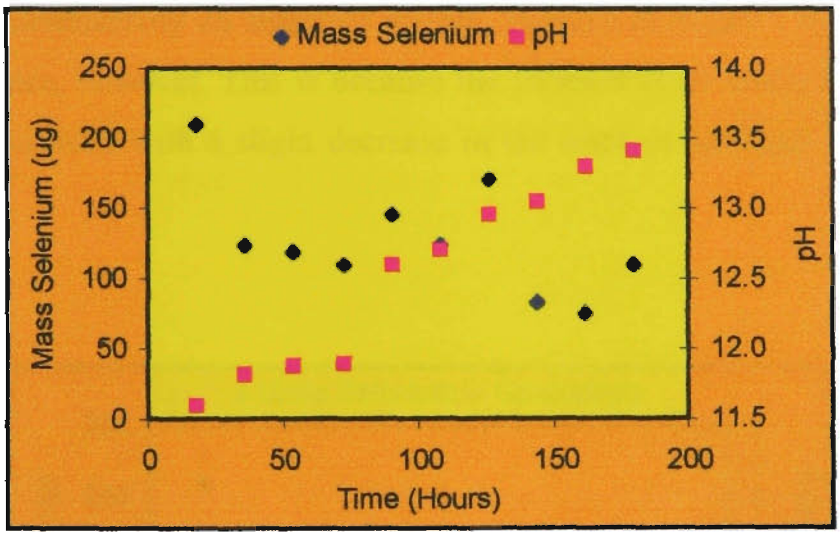


Figure 7.2: Sequential ABLP – Mass Selenium Leached and pH v's Time

Similarly, while there appears to be a broad trend in Figure 7.3, the effect of redox potential is assumed to be minimal.

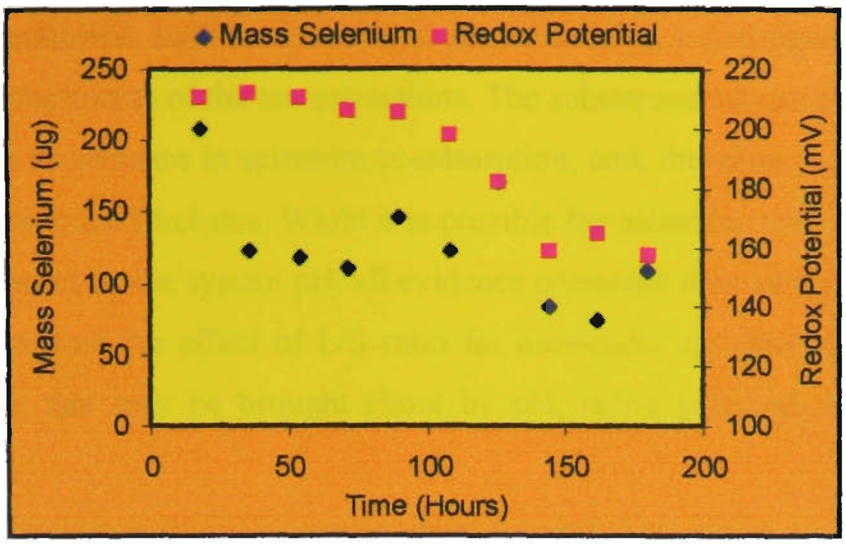


Figure 7.3: Sequential ABLP – Mass Selenium Leached and Redox Potential v's Time

The effect of conductivity on selenium release, pictured in Figure 7.4, seems to have greater relevance, however. This is because the increase in its levels for most of the extractions coincided with a slight decrease in the mass of selenium detected in the leachates.

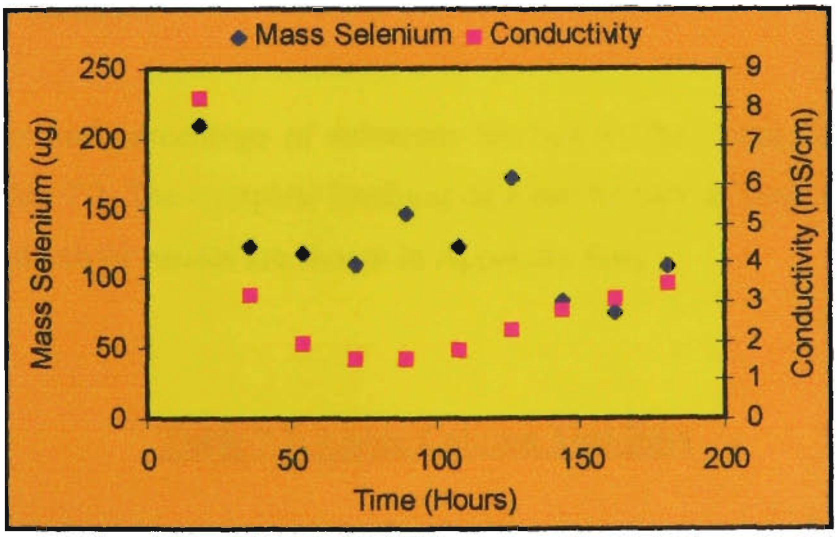


Figure 7.4: Sequential ABLP – Mass Selenium Leached and Conductivity v's Time

As already mentioned, such an increase in conductivity is a consequence of particle abrasion over the course of the ten extractions. The subsequent increase in surface area has resulted in an increase in selenium re-adsorption, and, therefore, a decrease in the amount present in the leachates. While it is possible the selenium release may, indeed, have been affected by the system pH, all evidence presented thus far for the Sequential ABLP suggests that the effect of L/S ratio far outweighs any possible alteration in release pattern that may be brought about by pH, redox potential, or conductivity changes.

7.3 Column Tests

One large column and several small column tests were investigated in this study. The small columns were the 100g Large Column Comparison (LCC100), 100g ABLP Comparison (ABLC100), and the 180g ABLP Comparison (ABLC180). Details of the waste used in these tests are given in Section *2.3.3* while the methodologies of these tests are provided in Sections *2.4.1 – 2.4.2*.

7.3.1 Large Column

The total mass and percentage of selenium leached in the Large Column test are detailed in Table 7.7. The complete leaching data can be seen in Appendix R. All pH, redox and conductivity results are shown in Appendix F(ii).

Table 7.7: Large Column Test Data

Mass of Selenium Leached (mg)	Percentage of Total Mass of Selenium Leached
12.92	0.13%

As with arsenic (and in contrast with copper, lead, and zinc), the percentage of selenium released from the Large Column was less than in the ABLP and TCLP. However, the selenium results agreed with those for the other metals tested, where the mass leached from the Large Column was less than from both the Sequential ABLP and the MAT (see Table 7.8). Further, as Table 7.9 reveals, the percentage of selenium released was greater than all other metals except lead.

Table 7.8: Percentages of Selenium Leached in Batch Tests and Large Column

Leaching Test	Percentage of Total Mass of Selenium Leached	Liquid to Solid Ratio	Method of Leachant Contact
Large Column	0.13%	19.1:1	Downflow Spraying
TCLP	0.21%	20:1	Rotary Agitation
ABLP	0.79%	20:1	Rotary Agitation
Sequential ABLP	4.80%	200:1	Rotary Agitation
Max. Avail. Test	1.62%	9.8:1	Stirring

Table 7.9: Percentages of Metals Leached From Large Column

Metal	Percentage of Total Mass of Metal Leached
Selenium	0.13%
Arsenic	0.04%
Lead	1.12%
Zinc	0.09%
Copper	0.04%

7.3.1.1 Leaching Behaviour of Selenium

It is not surprising that the Large Column released the lowest amount of selenium from all the tests investigated. Not only is the test relatively benign with respect to its flow rate and aggressiveness, the L/S ratio is not large either. Therefore, as mentioned in previous chapters, the conditions imposed upon the Large Column test encourage an increased residence time of the liquid in the column, and hence promote diffusive leaching processes. Figure 7.5 provides a clear depiction of this behaviour where there is an extended surface wash-off period of approximately 110 days. Following this, the mass of selenium released steadies, and slightly rises for the remaining 250 days of the experiment. The fact that the mass leached does not continue to drop indicates diffusive processes are still occurring, albeit slowly. The low amount of selenium leached, however, appears to suggest that the low L/S ratio has led to a reduction in selenium leaching, possibly due to the greater opportunity for re-adsorption at such low flow rates (refer to discussion in Section *7.2.3*). This data, therefore, implies that selenium release from the Large Column is minimal, and does not appear to pose a threat in the medium term. However at a higher L/S ratio, where the rate of diffusion is likely to increase, this may not be the case.

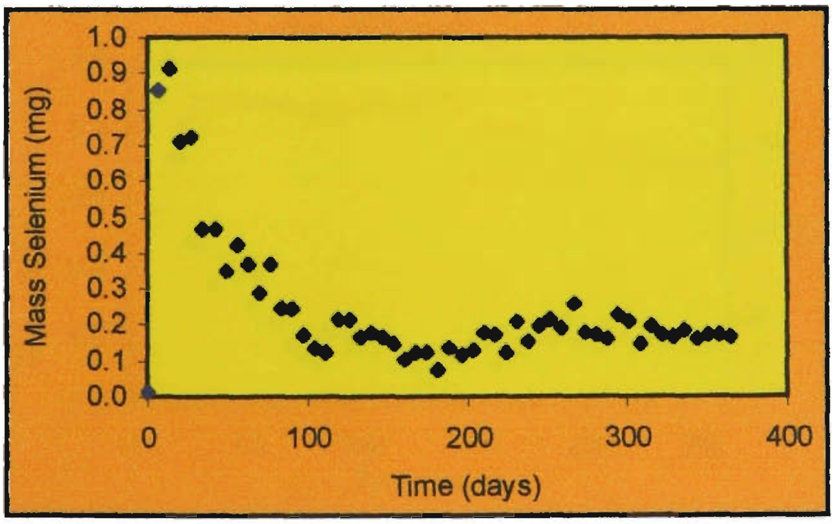


Figure 7.5: Large Column – Mass Selenium Leached v's Time

7.3.1.1.1 pH, Redox Potential, and Conductivity Effects on Selenium Leaching

The diagrams illustrating pH and conductivity responses to selenium release are illustrated in Figures 7.6 and 7.7 respectively.

The conductivity chart is missing the first four points of very high readings to provide a better comparison between alkalinity release and selenium. The decrease in both pH and conductivity levels at around 200 days has been discussed previously (see Section *5.3.1.1.1*) and is believed to signify a reduction in the availability of $Ca(OH)_2$ for leaching. It was suggested, in that section, that these conditions led to greater lead leachability due to an increase in surface area of the waste. While this may be the case for lead, which was present in massive amounts in the waste, any increase in surface area has obviously not had a similar effect on selenium release. It was believed that such an opening of pore space, while possibly facilitating the release of any trapped selenium, would more likely lead to an increase in its adsorption to the new surfaces, thus reducing the levels released. This, however, is clearly not the case. In fact, as Figures 7.6 and 7.7 illustrate, after approximately 200 days, any increase or decrease in pH and conductivity has actually resulted in a small increase for selenium release.

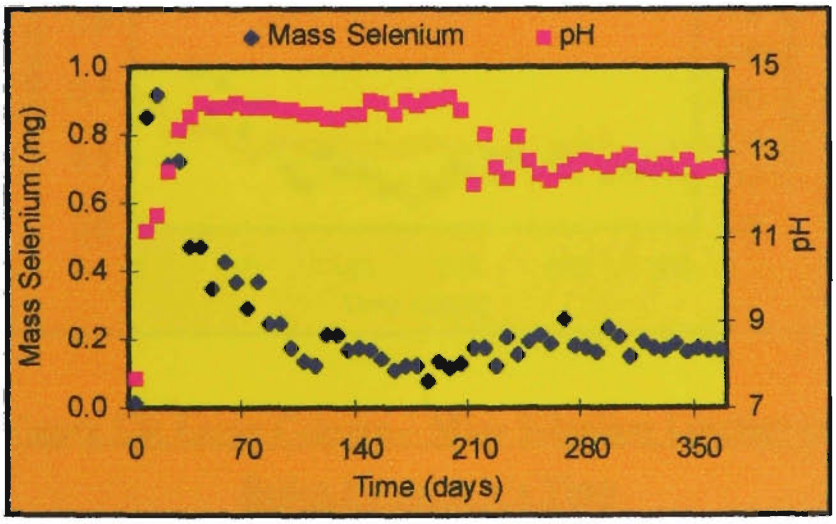


Figure 7.6: Large Column – Mass Selenium Leached and pH v's Time

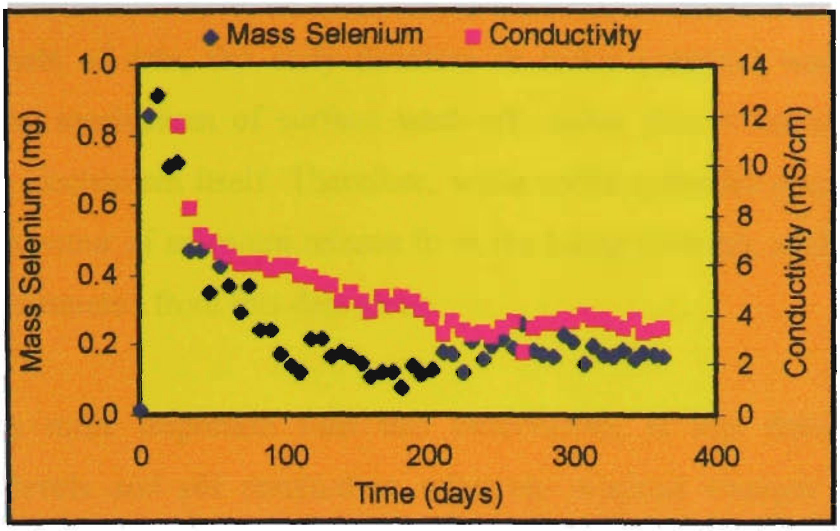


Figure 7.7: Large Column – Mass Selenium Leached and Conductivity v's Time

Redox potential also correlates well with the pattern of selenium release, and this is illustrated in Figure 7.8.

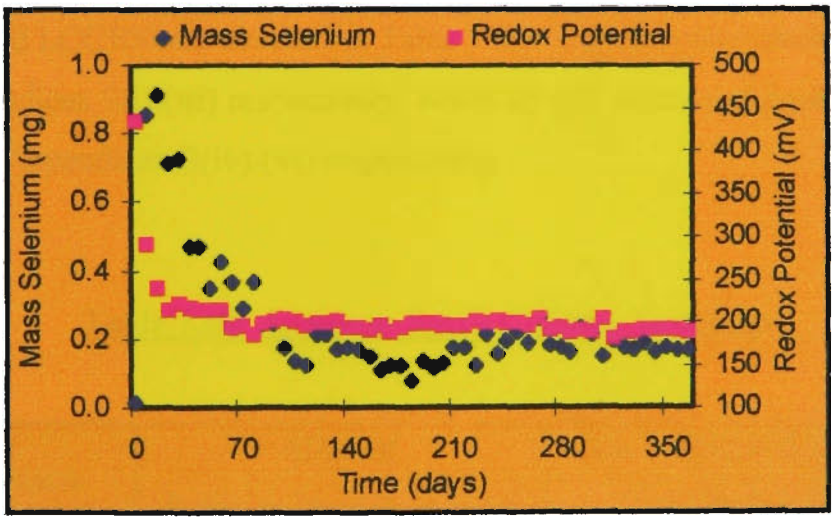


Figure 7.8: Large Column – Mass Selenium Leached and Redox Potential v's Time

It was mentioned earlier that the more soluble selenate salts are believed to have a greater stability and solubility than the selenites under oxidising conditions. Considering no speciation studies were performed, it is practically impossible to qualify that assessment based on this data alone. Also, regardless of the agreement between the sets of data, the early decrease in redox potential would be a direct response to the mechanism of surface wash-off, rather than it having any obvious effect on that mechanism itself. Therefore, while redox potential may have played a part in the behaviour of selenium release from the Large Column, such a contribution cannot be substantiated from this data alone.

What is even more important than this observation, is that these variations in conductivity levels and pH resulted in relatively minimal changes in the rate of selenium leaching. From earlier batch testing, this seems to suggest that, while the surface area of the waste is obviously important, it is nowhere near as critical to selenium leaching as the L/S ratio of the leaching test employed.

7.3.2 Small Columns

The total mass and percentage of selenium leached in the small columns ABLC100, ABLC180, and LCC100 are detailed in Table 7.10. The complete leaching data can be seen in Appendices S(i)-(iii) respectively, while all pH, redox and conductivity results are shown in Appendices G(iv)-(vi) respectively.

Table 7.10: Selenium Small Column Test Data

Small Column	Mass of Selenium Leached (mg)	Percentage of Total Mass of Selenium Leached
ABLC100	16.98	64.3%
ABLC180	16.27	34.3%
LCC100	0.04	0.16%

7.3.2.1 ABLC100; Leaching Behaviour of Selenium

Table 7.10 shows that the ABLC100 leached a massive amount of selenium over the year the test was run. A comparison of the metals released in this test can be seen in Table 7.11, and it demonstrates that, not only was selenium the most easily leached metal, but the two metals which exist as anions were released in much greater amounts than the cationic species of metals. Further, the amount of selenium leached far exceeded that predicted by the MAT.

Table 7.11: ABLC100 Test Data for all Metals

Metal	Mass of Metal Leached (mg)	Percentage of Total Mass of Metal Leached
Selenium	16.98	64.3%
Arsenic	97.45	22.5%
Copper	6.27	0.3%
Lead	240.46	2.8%
Zinc	7.15	0.3%

The pattern of selenium release, depicted in Figure 7.9, appears to show a short period of surface wash-off followed by a somewhat erratic release pattern until approximately 160 days. After this, the mass released suddenly, and sharply, drops, before steadily declining until the end of the test. The sudden decrease in release is made even more obvious when one takes into consideration that 87% of all selenium leached was released in the first half of the test. It must be emphasised, once again, that when viewing the plot of mass leached v's time for the small columns, the increase in sampling time at around 100 days must be taken into account. Any sharp increases in mass leached at this point should, therefore, be checked against the cumulative plot to ascertain whether the increase is due to the lengthened sampling regime, or an actual greater release of the metal in question. In the case of selenium an increase in leaching is observed in the cumulative plot at 120 days and, therefore, the increase in selenium release was not due to an increase in sampling time.

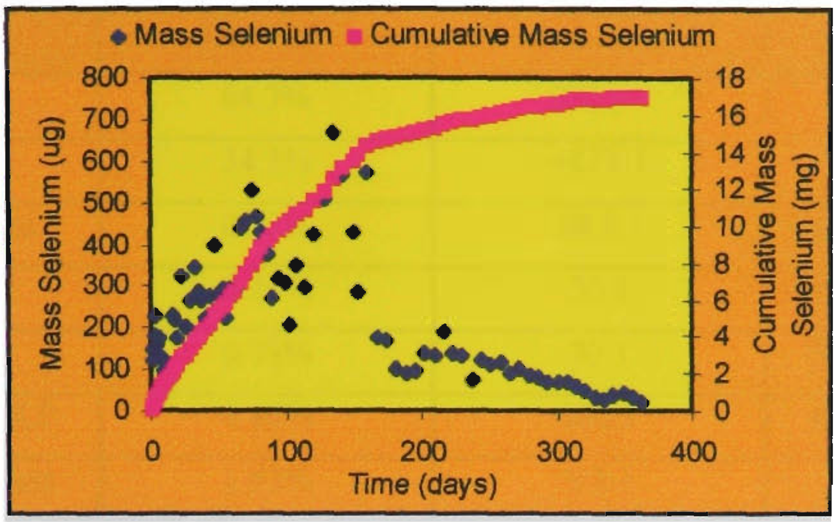


Figure 7.9: ABLC100 – Mass Selenium Leached v's Time

It is no surprise the ABLC100 released a large amount of selenium due to the extremely high L/S ratio and leachant velocity employed in that test. Further, the results in Table 7.12 show that, regardless of the adsorptive properties of its anions, an increase in L/S ratio will lead to a significant increase in the amount of selenium leached.

This is certainly shown to be the case in a comparison between the tests presented above where no agitation is used. An increase in L/S ratio of 255 times between the Large Column and the ABLC180, and 501 times between the Large Column and the ABLC100, has resulted in increases of 264 and 495 times the percentage leached, respectively, from the Large Column.

Table 7.12: Percentages of Selenium Leached in Batch Tests and Columns

Leaching Test	Percentage of Total Mass of Selenium Leached	Liquid to Solid Ratio	Method of Leachant Contact
ABLC100	64.3%	9571:1	Upflow
ABLC180	34.3%	4873:1	Upflow
Large Column	0.13%	19.1:1	Downflow Spraying
TCLP	0.21%	20:1	Rotary Agitation
ABLP	0.79%	20:1	Rotary Agitation
Sequential ABLP	4.80%	200:1	Rotary Agitation
Max. Avail. Test	1.62%	9.8:1	Stirring

7.3.2.1.1 pH, Redox Potential, and Conductivity Effects on Selenium Leaching

Figures 7.10 – 7.12, which illustrate comparisons of selenium leaching to the electrode results, provide no obvious correlations, or explanations for the erratic release patterns observed.

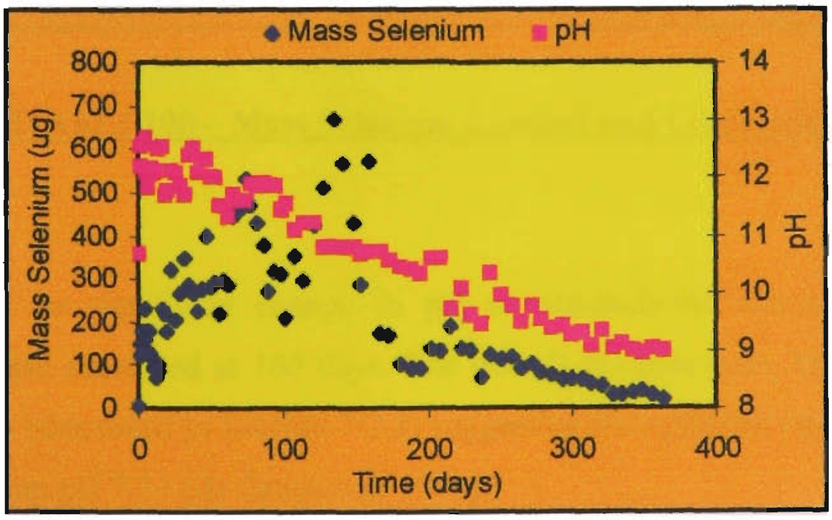


Figure 7.10: ABLC100 – Mass Selenium Leached and pH v's Time

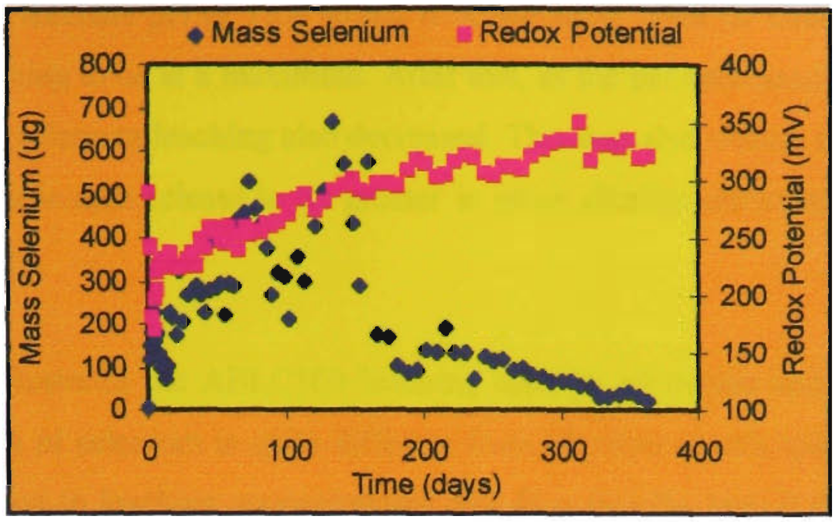


Figure 7.11: ABLC100 – Mass Selenium Leached and Redox Potential v's Time

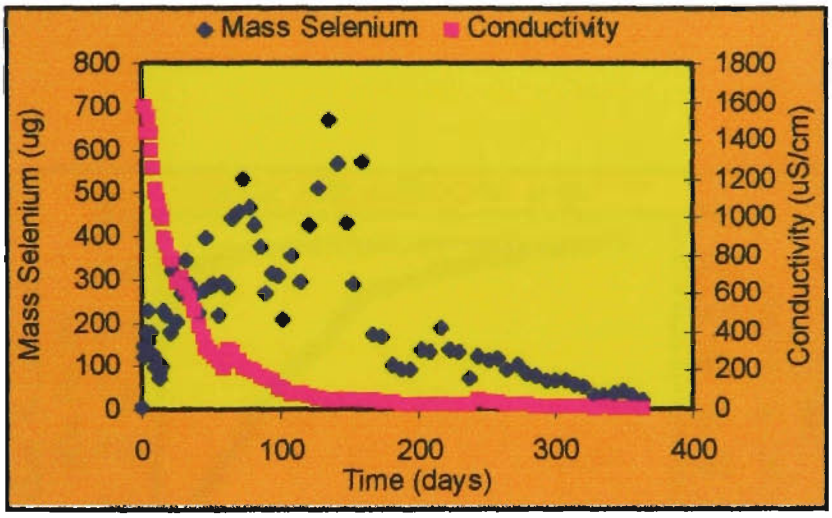


Figure 7.12: ABLC100 – Mass Selenium Leached and Conductivity v's Time

For example, no significant change in pH or conductivity was observed where selenium release decreased at 160 days. The overall pH data does, however, support previous work (discussed in Section *7.2.3*) suggesting the optimum leaching range for selenium is from pH 7-11 (de Groot *et al* 1989).

As Figure 7.10 clearly shows, the mass of selenium leached starts off low when the pH is at around 12.5. As the experiment progresses and the pH slowly decreases, the levels of selenium in the leachate, in contrast, increase. The maximum levels of selenium are observed at a leachate pH of 10.8 which is at the same point de Groot *et al* showed selenium leaching to be at a maximum. After this, as the pH decreased toward its final value of 8.99, selenium leaching also decreased. This was also similar to de Groot *et al* who showed selenium release to be greater in more alkaline environments in the pH range of 7 to 11.

Figure 7.13 illustrates the ABLC100 leaching data for all metals and shows that the release pattern of selenium is quite different from all other metals studied, due to the sudden decrease in leaching approximately 160 days into the test. It can be seen that selenium release was constant and strong to this point before dropping, meaning that there was no apparent retardation of the leaching process in these early stages. Therefore, once all the readily available selenium was removed from the waste (~60%), the rate of release dropped suddenly and then levelled out until the end of the test.

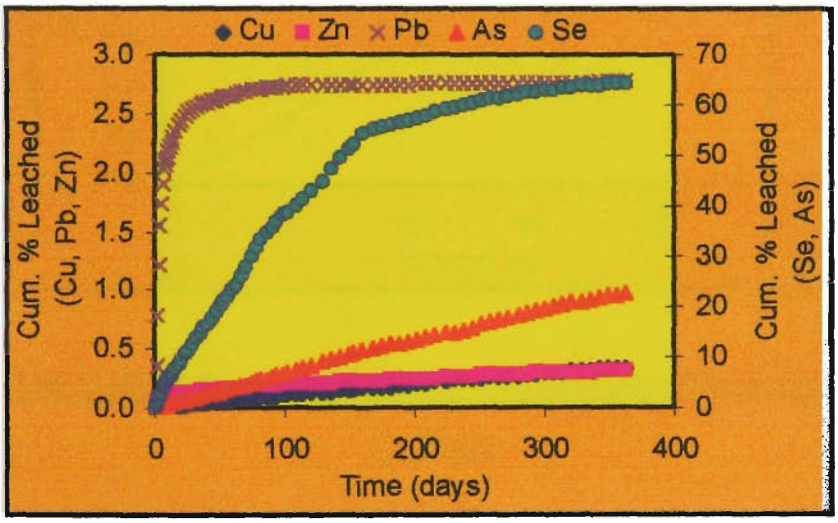


Figure 7.13: ABLC100 – Mass of all Metals Released v's Time

7.3.2.1.2 *Comparison to Sequential ABLP*

A comparison of data between the ABLC100 and the Sequential ABLP is illustrated in Figures 7.14 and 7.15 for the first 20L of leaching. While the release patterns may appear somewhat erratic, the cumulative leaching trends are quite similar.

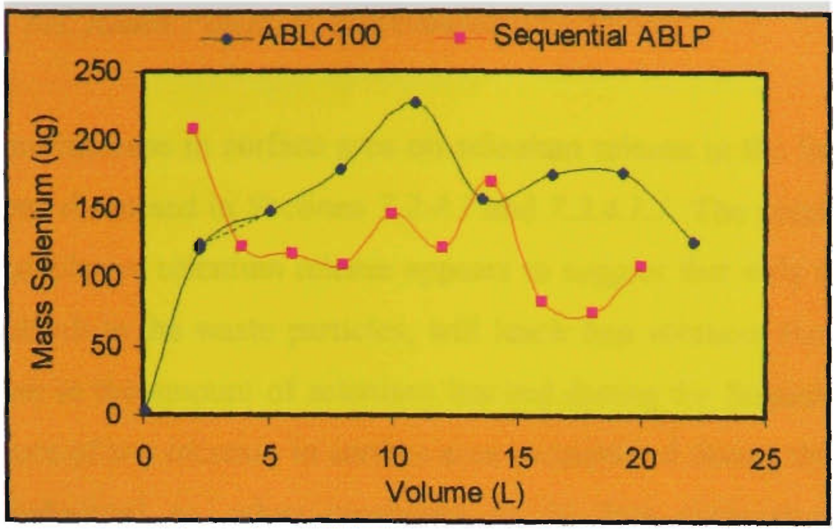


Figure 7.14: ABLC100 & Sequential ABLP – Mass Selenium Leached v's Time

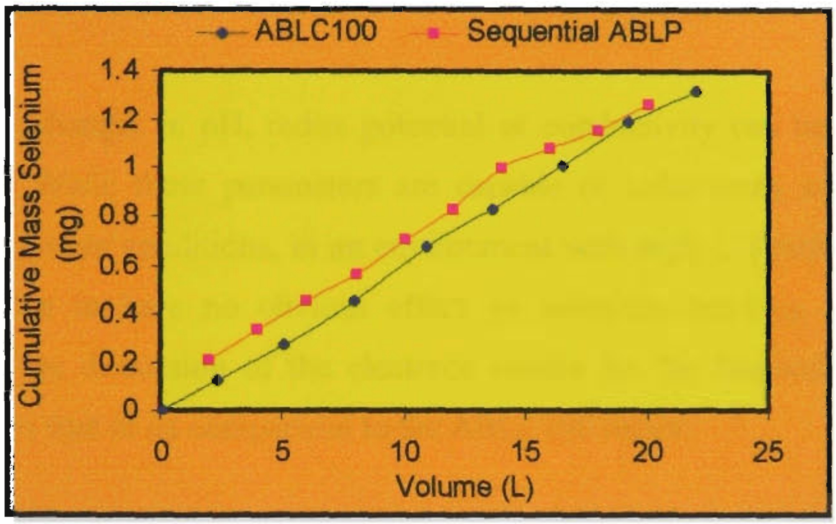


Figure 7.15: ABLC100 & Sequential ABLP – Cumulative Mass Selenium Leached v's Time

Even though the Sequential ABLP is a far more aggressive test than the ABLC100, the masses leached are still much the same. This is because the L/S ratios in the two tests are also similar up to that point in the ABLC100. Consequently, this data further strengthens the view that L/S ratio is the most important parameter with respect to selenium release.

7.3.2.1.2.1 pH, Redox Potential, and Conductivity Effects

The effect of an increase in surface area on selenium release in the Sequential ABLP has already been discussed in Sections *7.2.4.1* and *7.2.4.1.1*. The point was made that the trend of cumulative selenium release appears to suggest that only the free species, unable to re-adsorb to the waste particles, will leach into solution. Further, the *slight*, overall decrease in the amount of selenium leached during the Sequential ABLP may be a consequence of any increase in surface area encountered during the test. The word 'slight' is emphasised as, when compared to the less aggressive ABLC100, it obviously had minimal bearing on overall selenium release. If the leachant is high enough in volume, and its contact with the waste is 'complete', any increase in selenium adsorption that occurs may be inconsequential, relative to the effect of L/S ratio, under such conditions

Similarly, any changes in pH, redox potential or conductivity can be viewed in the same context. While these parameters are capable of influencing selenium release under certain system conditions, in an environment with high L/S ratio, the electrode data was shown to have no obvious effect on selenium leaching. This was also mentioned in the discussion of the electrode results for the Sequential ABLP, and obviously holds true in its comparison to the ABLC100 results.

7.3.2.2 ABLC180; Leaching Behaviour of Selenium

After one year of leaching, the ABLC180 released 16.27mg of selenium, or 34.3% of the original amount in the column. At such a high flow rate of leachant, this result demonstrates selenium to be poorly retained within the matrix.

Figure 7.16 also illustrates that the break in leachant flow (explained in Section *3.3.2.2*) had a significant effect on selenium leachability. In fact, the increase in leachability after the period of no-flow was the greatest of all metals investigated. As also discussed in Section *3.3.2.2*, this is indicative of contributory leaching mechanisms other than only pore-based diffusion.

Following a surface wash-off period in the early part of the experiment, the leachant flow was halted for 24 days. After its resumption, selenium levels increase markedly, taking approximately 60 days to return to their previous levels, before increasing again, then decreasing in intensity, and then levelling out at the end of the test.

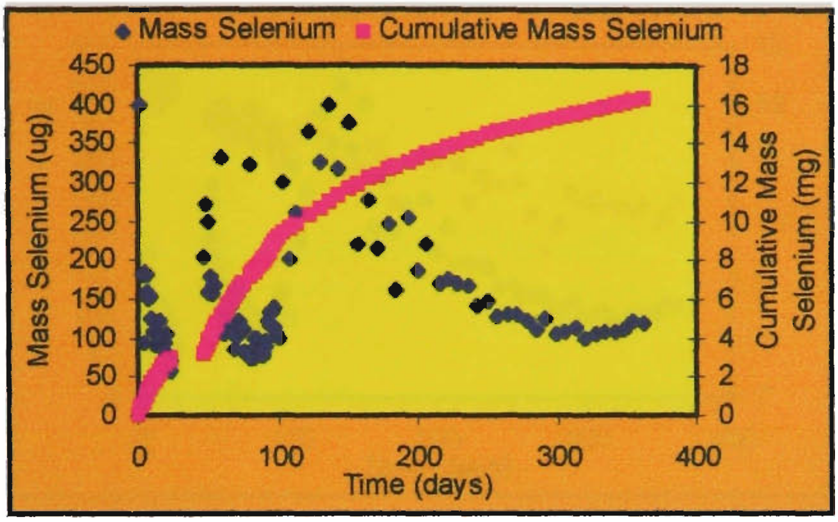


Figure 7.16: ABLC180 – Mass Selenium Leached v's Time

What is important here, though, is that significant amounts of selenium were still being released at the end of the test. In fact, the cumulative trend of release appears to suggest that the rate of selenium release remained unchanged from day 250. This column, therefore, would need to be run for a great deal longer to determine when the selenium leaching rate would begin to decline.

7.3.2.2.1 pH, Redox Potential, and Conductivity Effects on Selenium Leachability

Figures 7.17 and 7.18 illustrate broad correlations between selenium release and pH and also redox potential. Aside from the increase in selenium leaching following the period of no-flow in the ABLC180, there is a constant decrease in release as pH also decreases. While this makes sense considering selenium is thought to be more soluble at higher pH (see Section *7.2.3*), it is contradicted by the fact that the pH remained unchanged following the period of no-flow, yet a great deal of selenium was released in the following weeks. A reverse correlation is observed for redox potential, which increases marginally as selenium levels decrease. This is in disagreement with the information presented earlier on selenium (Section *7.2.3*) regarding its proclivity for leaching in more oxidising environments.

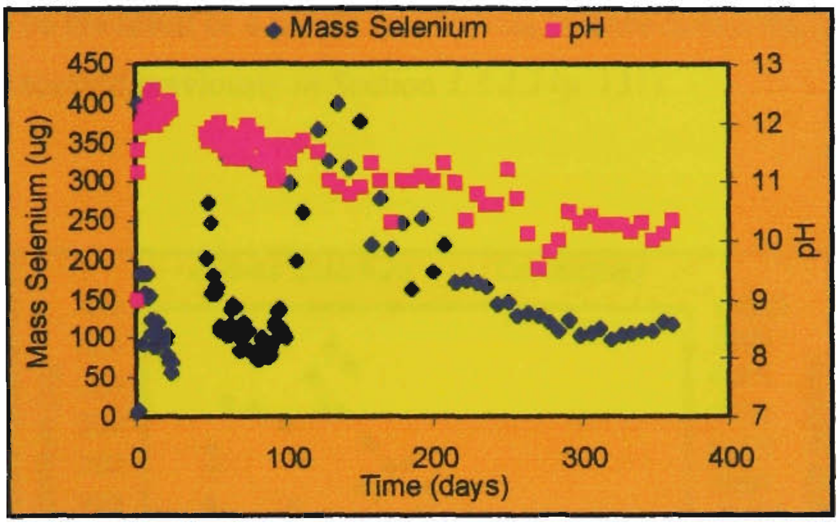


Figure 7.17: ABLC180 – Mass Selenium Leached and pH v's Time

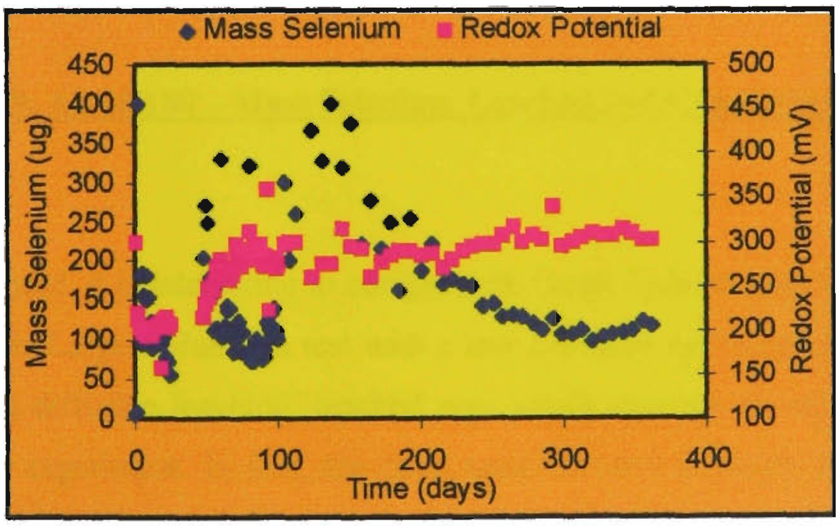
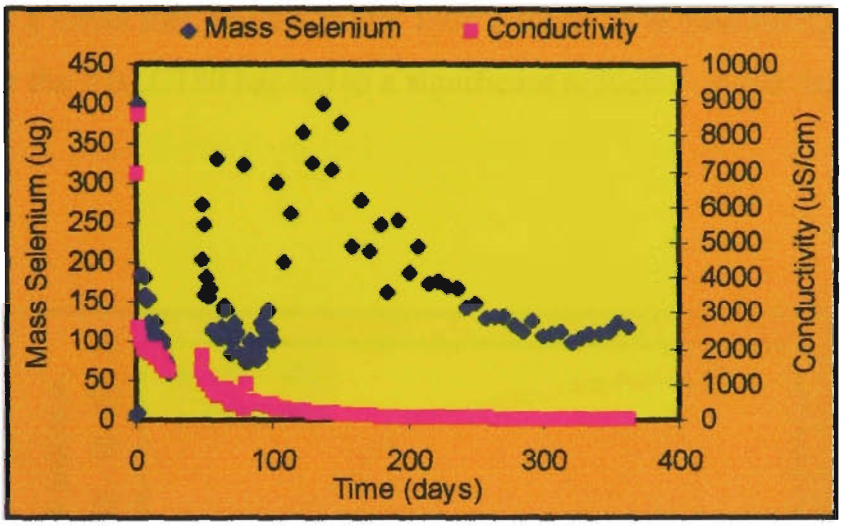


Figure 7.18: ABLC180 – Mass Selenium Leached and Redox Potential v's Time

Figure 7.19 depicts a plot of selenium leaching and conductivity data. While, as with the pH and Eh data, the correlation is broad, it clearly shows a lack of agreement after the period of no-flow. Following the resumption of leachant flow, selenium takes approximately two months to drop back to pre-drought levels, whereas the conductivity levels decrease almost immediately. It appears, therefore, that selenium is being leached by mechanisms other than just pore-based diffusion. Note that this may, at least partly, be the result of a simple equilibrium balance across the leachate-particle interface, as discussed previously in Section *3.3.2.2* (p. 131).



<u>**Figure 7.19: ABLC180 – Mass Selenium Leached and Conductivity v's Time**</u>

With this in mind, it is interesting to compare the Large Column data to that from the ABLC180. The Large Column, a test with a low L/S ratio and conditions that would seem to assist diffusive leaching, leached very small amounts of selenium over the course of the experiment. In fact, the final samples were releasing little more than 150µg of selenium. Compare this to the 100µg released for the ABLC180, which has a mass some 380 times less than the Large Column. It is, therefore, obvious from this data that, while pore-based diffusion of selenium may be a very minor contributor to selenium release in tests with low L/S ratios, it can combine with other mechanisms under high L/S conditions to release massive amounts of selenium to the leachate. Further to this point, Batchelor (1999) noted that when sorption plays a major role, larger volumes of leaching fluid will affect the desorption of contaminants by dilution as well. Therefore, it would be expected that, in high-flow tests such as the ABLC180 and ABLC100, massive amounts of selenium might indeed be desorbed from the matrix resulting in high levels in the leachate.

7.3.2.2.2 Comparison to ABLC100

Figure 7.20 illustrates the cumulative leaching patterns of selenium in both the ABLC180 and the ABLC100. It shows that the percentage leached in the ABLC100 is 1.87 times greater than that leached in the ABLC180. Since the mass of waste in the ABLC180 is 1.8 times that amount in the 100g column, it is obvious that the decrease in L/S ratio for the ABLC180 has led to a significant reduction in the mass of selenium released.

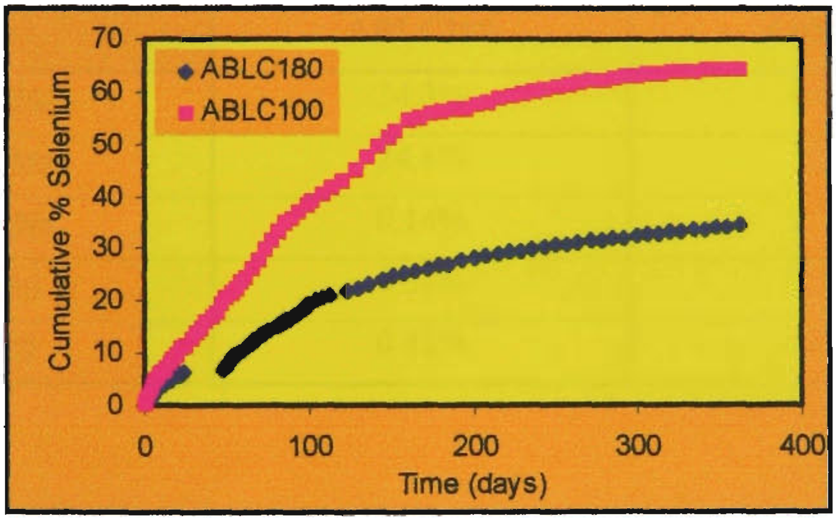


Figure 7.20: ABLC180 & ABLC100 – Cumulative Percentage Selenium Leached v's Time

It is also worth noting that, regardless of the increase in leaching from the 100g column, the actual patterns of selenium release from both columns are still quite similar. Obviously then, while an increase in L/S ratio speeds up the release of selenium species, the pattern of release remains, essentially, the same.

Table 7.13 details a comparison between the columns for all metals leached. It shows that copper was the only other metal to leach significantly more from the ABLC100 than the ABLC180. This is interesting because the behaviour of copper during the period of no-flow in the ABLC180 was very different from that for selenium. While selenium took some time to drop back, the copper levels decreased immediately. Yet, in a comparison between the two up-flow columns, selenium and copper both recorded similar increases in levels leached for the ABLC100. This information also highlights the fact that, while the period of no-flow may cause immediate effects in the release patterns of copper and selenium in the ABLC180, in the end the stop-start conditions did not greatly alter the mass of either metal leached.

Table 7.13: Metal Release From the ABLC180 and ABLC100

Metal	Percentage Leached	
	ABLC180	ABLC100
Selenium	34.3%	64.3%
Arsenic	24.6%	22.5%
Copper	0.14%	0.34%
Lead	6.21%	2.77%
Zinc	0.43%	0.32%

7.3.2.2.2.1 *Comparison to ABLC100; pH, Redox Potential, and Conductivity*

Figure 3.21 (Section *3.3.2.2.2.1*) illustrates very similar patterns for redox potential for the two columns, with the ABLC100 recording slightly more oxidising conditions. Figures 3.22 and 3.23 (also in Section *3.3.2.2.2.1*) show the pH and conductivity levels in the ABLC180 were slightly higher than the ABLC100. These results indicate that a greater amount of $Ca(OH)_2$ was removed from the ABLC180 than the ABLC100, a consequence of the higher amount of solids in the former test. Further, since the electrode results from those two columns were so similar, and the actual percentages of selenium released so different, it appears that any change in pH, Eh, and conductivity has resulted in minimal changes to the pattern of selenium leaching.

7.3.2.3 LCC100; Leaching Behaviour of Selenium

Table 7.10 shows that, of all the small columns, selenium clearly leached in the lowest amounts from the LCC100. Only 0.16% of selenium present in the column was released to the leachate, which is over 200 times less than from the ABLC180, and over 400 times less than from the ABLC100.

Figure 7.21 illustrates the normal and cumulative leaching trends of selenium from the LCC100. It reveals a moderate period of surface wash-off, followed by a steadily decreasing release trend for the remainder of the experiment. A comparison of cumulative metal release patterns is depicted in Figure 7.22. While the cumulative release pattern for other metals was shown to be primarily linear, the trend for selenium is one of a gradual decrease in percentage leached.

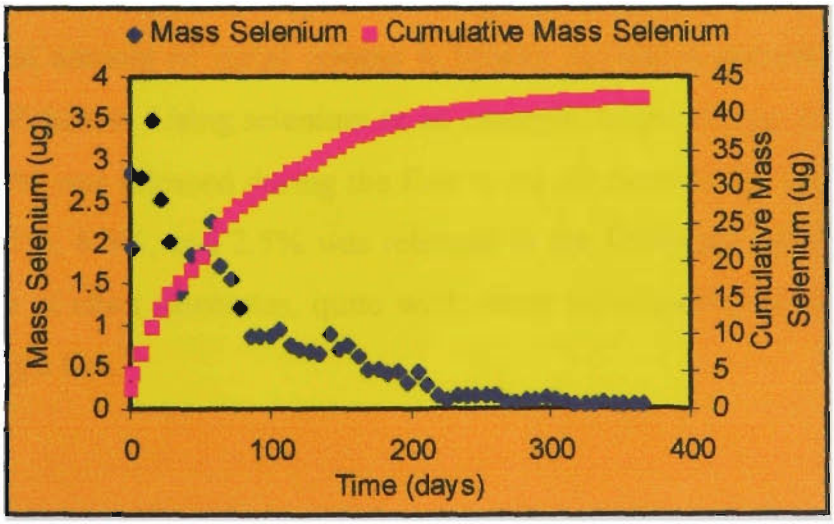


Figure 7.21: LCC100 – Mass Selenium Leached v's Time

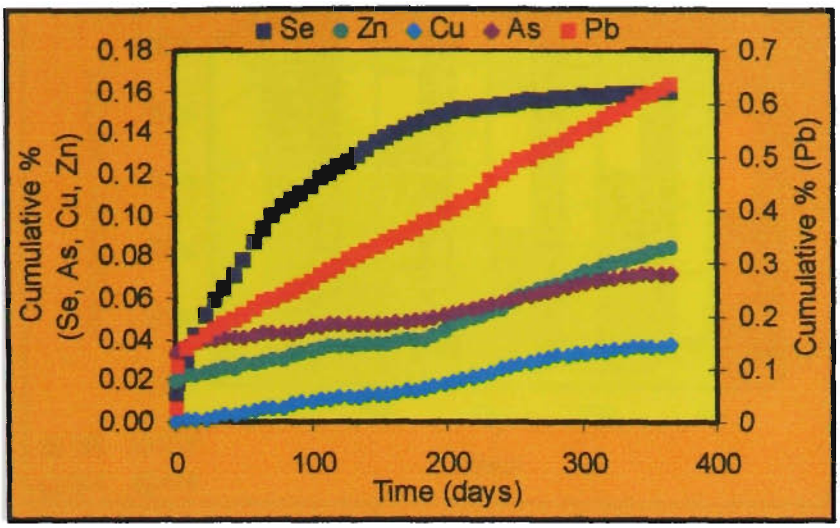


Figure 7.22: LCC100 – Cumulative Percentage of all Metals v's Time

The only metal to demonstrate a similar leaching characteristic to selenium was copper, in that those two were the only species not to start leaching in high amounts at the very beginning of the test. It is worth noting that the similarity ends there, however, as selenium went on to leach significant amounts via surface wash-off in the following few weeks.

Figure 7.23 also illustrates a comparison of metal leaching in the LCC100. In this figure, the total amount of metal release is broken up into a percentage leached for each quarter of the test. Using selenium as an example, of the 42.1µg released from the LCC100, 69.4% was released during the first ¼ (or 93 days) of the test. Following on from this, 21.5%, 6.6%, and 2.5% was released in the following three quarters of the test. This type of chart illustrates, quite well, when the majority of a metal has been released during a test.

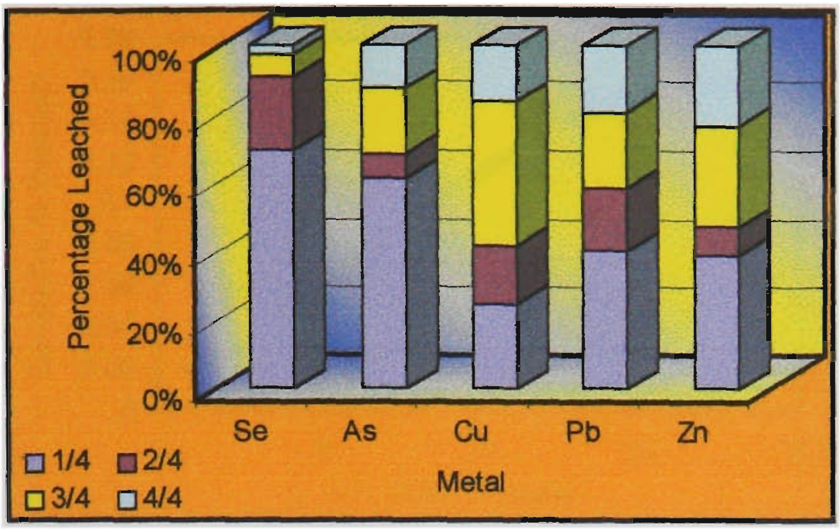


Figure 7.23: LCC100 – Release Breakdown for all Metals

Of all the metals investigated, the percentage of total release was greatest for selenium in the first ¼ of the test. However, it is important to qualify this observation by pointing out that, unlike arsenic, lead, and zinc, the selenium was not leached as one big 'plug' within the first couple of weeks of the test. As shown in Figure 7.22, while the surface wash-off for arsenic, lead, and zinc was concentrated and immediate, the surface leaching of selenium was more gradual. This means that, even though selenium will tend to leach more in the early stages, the amount leached at the very beginning may not pose as much of an environmental problem as it could for arsenic, lead, and zinc.

Further, the levels of selenium constantly decreased over the course of the experiment, whereas, after surface wash-off, the release patterns for all other metals showed either periods of increasing leaching, or relatively steady release throughout the test. According to de Groot and Van der Sloot (1992), a plot of a steadily decreasing release pattern versus the square root of time should provide a straight line and be, therefore, indicative of diffusion controlled release. Figure 7.24 certainly shows this to be the case from the end of the first month up until the 200th day of the test, after which the curve flattens. Of course, under such low-flow test conditions, diffusion would be expected to dominate release for most metals.

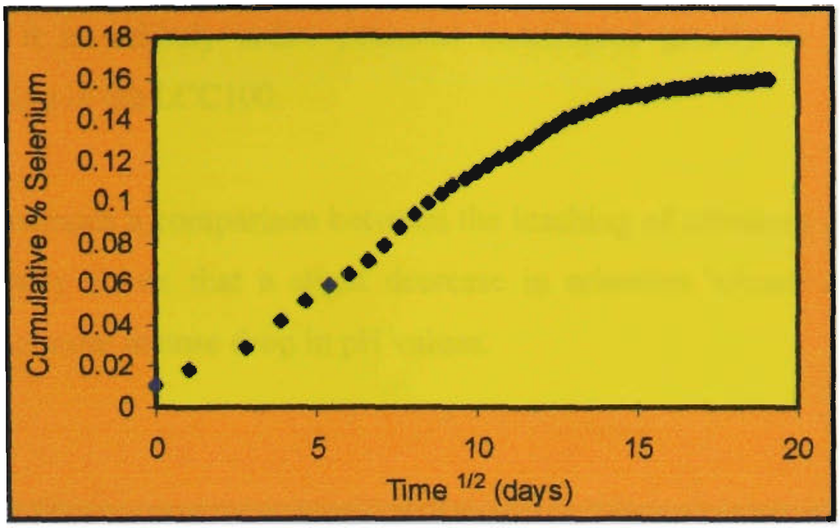


Figure 7.24: LCC100 – Mass Selenium Leached v's Square Root of Time

7.3.2.3.1 pH, Redox Potential, and Conductivity Effects on Selenium Leachability

Figure 7.25 illustrates a broad correlation between selenium release and redox potential in the LCC100.

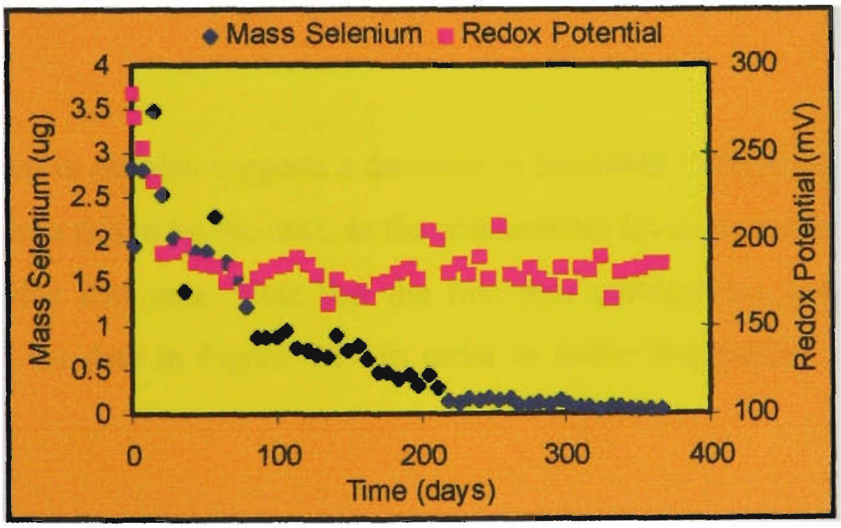


Figure 7.25: LCC100 – Mass Selenium Leached and Redox Potential v's Time

It has been mentioned that selenium release is thought to be greater under more oxidising conditions. However, since the levels of selenium continued to drop once the

Eh stabilised, it is unlikely redox potential contributed greatly to the pattern of selenium leaching in the LCC100.

Figure 7.26 illustrates a comparison between the leaching of selenium in the LCC100 and pH. It clearly shows that a slight decrease in selenium release after 200 days coincides with a more intense drop in pH values.

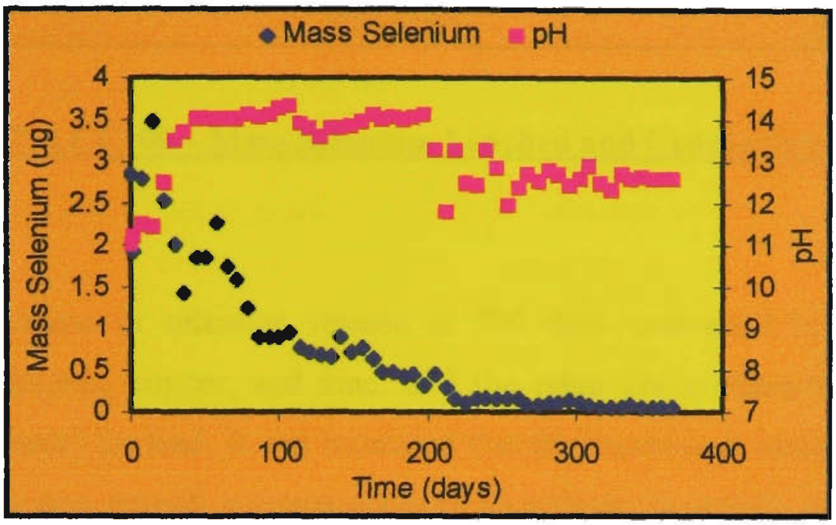


Figure 7.26: LCC100 – Mass Selenium Leached and pH v's Time

The sudden drop in pH also suggests a decrease in leachable $Ca(OH)_2$ from the waste. Figure 7.27 shows this to be the case, as the conductivity levels decrease from 5000μS to 3500μS during that time. Note that the first four conductivity points have been removed from the data in Figure 7.27 in order to better demonstrate the pattern of leaching.

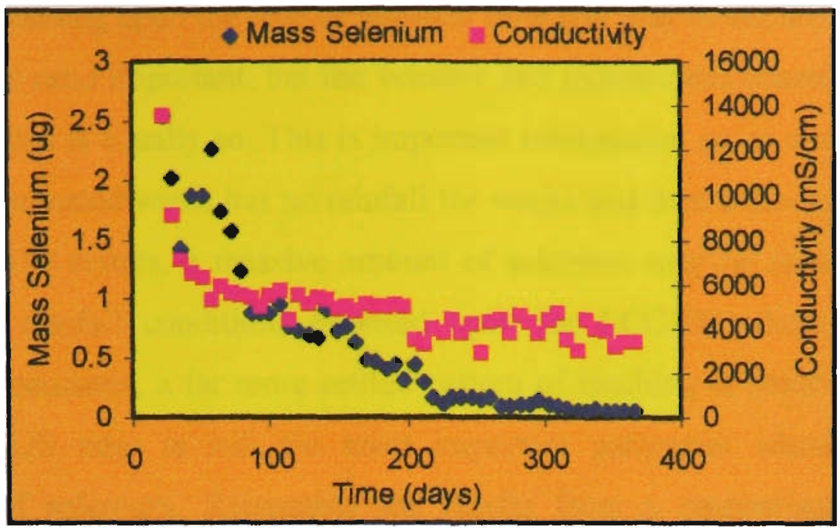


Figure 7.27: LCC100 – Mass Selenium Leached and Conductivity v's Time

The slight decrease in selenium release at 200 days contrasted to the increases observed for arsenic, copper, and zinc, and the relatively unchanged trend (slight temporary increase) for lead. It was intimated that any increase in leaching of arsenic, copper and zinc was, overall, a consequence of an increase in porosity arising from the leaching of $Ca(OH)_2$. Lead, on the other hand, was thought to increase only slightly due to the fact that the majority of the pore-based species had already leached. The effect on selenium is similar to lead in that, once the majority of available $Ca(OH)_2$ had leached from the pores, so too had the selenium.

This is interesting because it contrasts with the ABLC180 data which shows selenium to leach strongly in contrast to $Ca(OH)_2$, following the resumption of leachant flow. It was thought that, because of this behaviour, selenium was leaching less from the pores, and more from the solid matrix by further diffusive and dissolution processes. This, of course, depended heavily on the unique flow conditions employed during that test.

Obviously, the reason for the difference in selenium release from the two columns lay in the method, volume, and velocity of leachant introduction. In the LCC100, the waste was constantly saturated with leachant once the flow of liquid had finished after each day's addition. Similarly, the ABLC180 had a stagnant period of 4 weeks. However, this led to increased levels of selenium in the leachate for two months after the flow resumed. These observations infer that the mechanism of selenium release can alter markedly, depending upon the type of leachant flow that may be occurring. That is, not only is the L/S ratio important, but the velocity and incremental quantity at which the leachant is added is equally so. This is important information as, in a landfill situation where a contaminated waste has no rainfall for weeks and then a downpour, according to the ABLC180 results, a massive amount of selenium may be released. However, under steady rainfall conditions imposed upon the LCC100 where pore-diffusive leaching predominates, a far more settled pattern of leaching is observed. Of course, once again, L/S ratio is still the most important parameter when assessing the leachability of selenium. Reiterating the results from a comparison between the ABLC100 and ABLC180 data proves this, where, under conditions of steady leachant introduction in the 100g column (yet at 1.8 times the L/S ratio), approximately 1.9 times as much selenium was leached.

7.3.2.3.2 Comparison to Large Column

The percentage of selenium released in the LCC100 (0.16%) was similar to that in the Large Column (0.13%). This was also the case for copper and zinc, but contrary to the results for arsenic and lead. Figure 7.28 illustrates a comparison of the leaching patterns of selenium from the two columns, and shows the trends to be reasonably similar.

Following surface wash-off, the leaching of selenium from the Large Column was constant until 200 days, when it increased slightly, before continuing to leach at those levels until the end of the experiment. The release patterns from the LCC100, however, showed the rate of release to slowly drop over the course of the test. In contrast to the Large Column, at 200 days there was a noticeably stronger decrease in the amount of selenium leached, after which the rate of release steadied. Overall, it can be said that the LCC100 leached more at the beginning of the experiment and less at the end, with opposite holding true for the Large Column. Further, like lead, zinc, and copper, the selenium levels appear to be drawing toward one another by the end of both leaching tests.

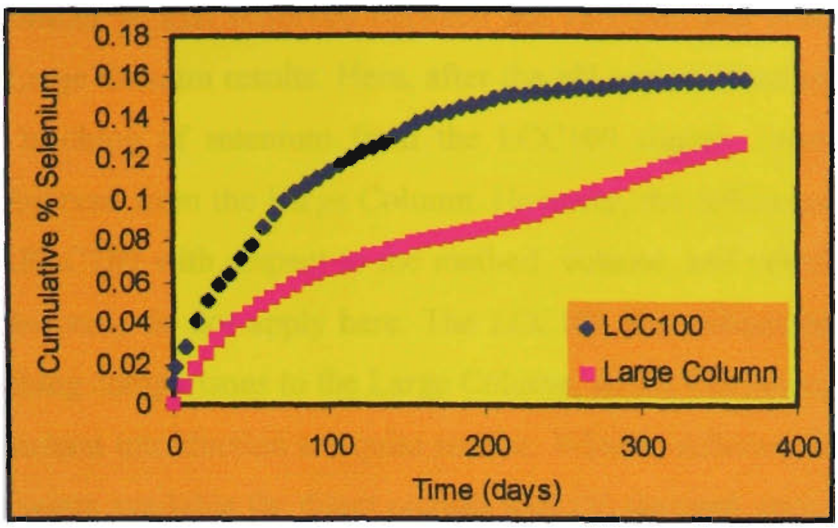


Figure 7.28: LCC100 & Large Column – Percentage Selenium Leached v's Time

7.3.2.3.2.1 Comparison to Large Column; pH, Redox Potential, and Conductivity

The graphical comparisons between these parameters of the LCC100 and Large Column can be seen in Figures 3.31 – 3.33 in Section *3.3.2.3.2.1.* The observations regarding the similarities between the results are also covered in that section, and will, therefore, not be repeated here.

As already stated, it is unlikely that redox potential had a significant effect on leachability from either the LCC100 or Large Column. Consequently, it is not expected that redox potential was a major contributor to any differences observed in the leaching patterns between the two tests.

In conjunction with Figure 7.28, Figures 3.31 and 3.32 demonstrate that an equivalent decrease in pH and conductivity does not necessarily produce an equivalent response in selenium leaching from the LCC100 and the Large Column. The behaviour of selenium, following the decrease in pH and conductivity at 200 days, was extensively discussed in Section *7.3.2.3.1.* After comparing the LCC100 results with those for the ABLC180, it was concluded that pore-based diffusion was the controlling mechanism of release from the LCC100. The reason for such a difference was believed to lie, not only in the L/S ratio of the two tests, but also the method, volume, and velocity of leachant introduction.

A difference, similar to that observed between the LCC100 and ABLC180, is also evident in the Large Column results. Here, after the pH and conductivity decreases at 200 days, the leaching of selenium from the LCC100 slightly increased, while a decrease was observed from the Large Column. However, the differences between the LCC100 and ABLC180 with respect to the method, volume, and velocity of leachant introduction, obviously do not apply here. The LCC100 was deliberately designed to investigate leaching comparisons to the Large Column, so the L/S ratios, methods, and velocities of leachant introduction are quite similar. What is different, however, is the surface area of waste available for direct contact with the leachant once it is applied to each column. While leachant was sprayed onto approximately 1963cm^2 of waste in the Large Column, the top surface area available in the LCC100 was only 4.52cm^2. This is, quite obviously, a massive difference, and one that has had a noticeable effect on determining the dominant mechanisms of selenium leaching in each test. Such leaching effects have already been discussed in Section *3.3.2.3.2*, and are believed to be at least partly due to the different types of channelling and wall surface effects in each column.

Although the percentages of selenium leached in each test were similar, it is to be expected that such a difference in column design would affect the trends of leaching in each test. While the L/S ratios were practically identical for each column, the important point is that a much greater area of waste comes into *immediate* contact with fresh leachant after each addition to the Large Column compared to the LCC100. In the smaller column, the liquid must travel for some time before the contact of the liquid to the surface area (and mass) of the solid is similar between the two tests. It is obvious, therefore, that such a variation in column dimensions *must* lead to differences in leaching patterns.

In light of the above discussion, one final point should be emphasised. Since the LCC100 and Large Column leached similar percentages of selenium, and the changes in selenium release (at 200 days) between the two tests were relatively small, L/S ratio remains the most important parameter when evaluating the leachability of selenium in column tests.

7.4 Dynamic Leaching Tests

The dynamic leaching tests (DLT) utilised two leachant renewal schedules, detailed in Appendix C. Details of the waste used in these tests appear in Section *2.3.2*, while the methodologies of the tests are provided in Section *2.4.3*.

7.4.1 Leaching Behaviour of Selenium

Two DLTs were run for each renewal schedule. These were labelled 1A and 1B for the rapid renewal rate of 1 hour, and 4A and 4B for the slower renewal rate of 4 hours (Refer Section *2.4.3.2)*. The masses leached in each of these experiments are detailed in Table 7.14. The complete leaching data can be seen in Appendices T (i) – T (iv). All pH, redox, and conductivity data are shown in Appendices H (v) – H (viii).

Table 7.14: Selenium DLT Test Data

Replicate	$t_n = 1A$	$t_n = 1B$	$t_n = 4A$	$t_n = 4B$
Mass Leached (mg)	0.44	0.53	0.39	0.46
% Leached	3.64	4.25	3.19	3.74

Table 7.14 shows that in excess of 3% of the selenium present leached from all spheres, values far greater than the 1.62% predicted by the MAT. In fact, selenium along with arsenic, leached poorly from the MAT (see Table 7.2), yet was shown to diffuse readily from the spheres in the DLTs. Table 7.15 compares the percentages of all the metals leached in the DLT and shows that, in an environment where diffusion is the controlling mechanism of metal release, selenium leaches in massive amounts compared to the other metals.

Table 7.15: Percentage of Metals Released in the DLT

Metal	$t_n = 1A$	$t_n = 1B$	$t_n = 4A$	$t_n = 4B$
Selenium	3.64	4.25	3.19	3.74
Arsenic	1.50	1.33	0.83	0.82
Copper	0.012	0.012	0.016	0.015
Lead	0.10	0.07	0.15	0.76
Zinc	0.07	0.07	0.06	0.09

This is important because it demonstrates that, since the DLT is a better representation of the type of slow, diffusive leaching that is more likely to occur in a landfill, the more aggressive MAT is therefore a poor choice as a predictor for long-term leaching of selenium from this waste.

Table 7.14 also shows that the amount of selenium leached from sphere 1A was approximately 17% less than from 1B. This is the only metal which has leached in greater amounts from sphere 1B than 1A while, for arsenic and lead, this trend is reversed. Figure 7.29 illustrates the similarities in selenium release between the two spheres.

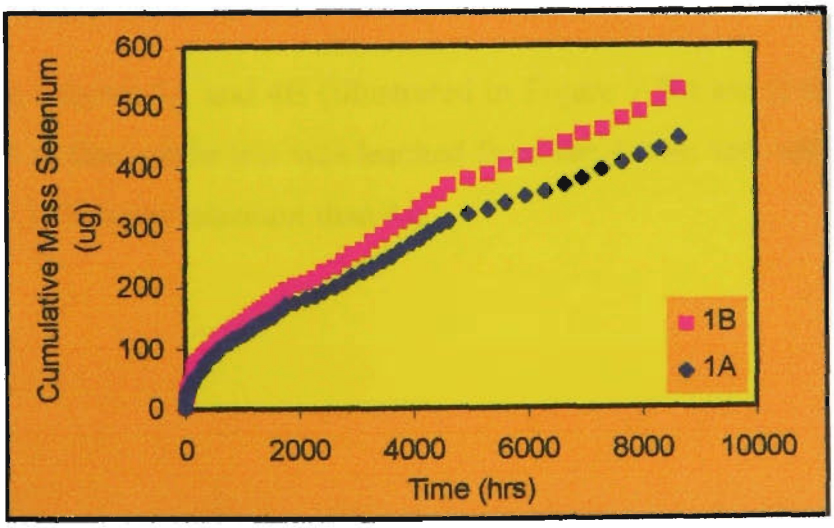


Figure 7.29: t_n = 1A & 1B – Cumulative Mass Selenium Leached v's Time

A relatively short, early period of surface wash-off is visible in the release trend of both spheres, followed by diffusion control for the remainder of the experiment. Closer inspection of the plot also reveals slight, temporary decreases in selenium leaching following the reduction in sampling frequency after 1764 hours and 4620 hours. This is clear evidence that the release of selenium was rate-limited due to a build-up of its species in the leaching fluid, thus leading to a decrease in the concentration gradient. The reduction in driving force, however, is not as severe as was observed for arsenic and, consequently, does not appear to have affected the final masses leached to any great extent.

The fact that a greater amount of selenium leached from sphere 1B does not necessarily suggest that the spheres were heterogeneous. If that were the case, the results for copper and zinc would not be so similar. Instead, as was discussed in Section *5.4.1* for lead, the selenium appears to have been better retarded in the cement matrix of sphere 1A than 1B. That is, regardless of the care taken to produce spheres of equivalent homogeneity, the selenium in sphere 1A has reacted differently to 1B during the cement setting reactions. In the case of lead this was believed to be due to greater amounts of the metal being fixed to the calcium silicate sites in sphere 1B, leading to lower leaching from that sphere. The case for selenium may be similar, where the greater adsorption of its species to iron and aluminium in sphere 1A during the setting process has resulted in a slightly lower percentage of release from that sphere.

The results for spheres 4A and 4B (illustrated in Figure 7.30) are similar to those for the 1-hour test in that, while less was leached from the 4-hour test, sphere 4B leached approximately 17% more selenium than 4A.

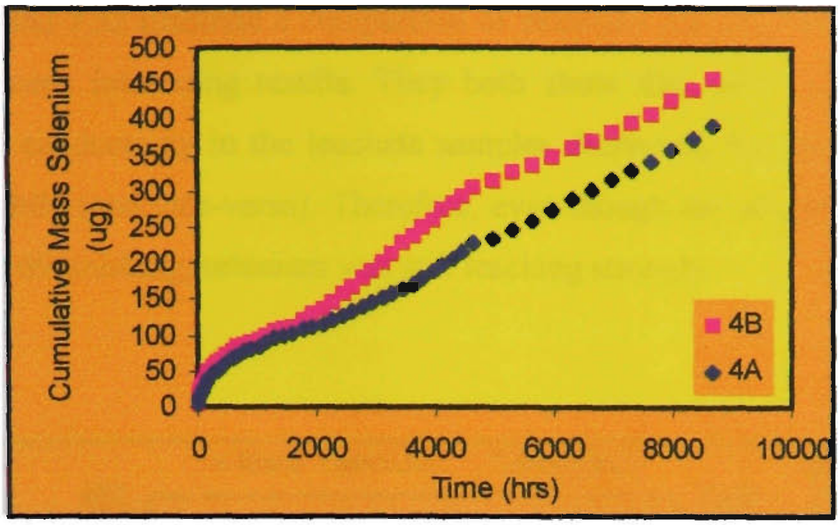


Figure 7.30: t_n = 4A & 4B – Cumulative Mass Selenium Leached v's Time

In the 4-hour test, there is also a clear period of surface wash-off, followed by diffusion from both spheres. What is most interesting about these results, however, is the sudden slight increase in selenium release from sphere 4B after approximately 1800 hours. This does eventually occur for sphere 4A, but not until approximately 4000 hours have passed. An explanation for this phenomenon lies in the change in sampling frequency that occurred at 1764 hours and 4620 hours. If the renewal frequency had actually continued according to the formula detailed in Section *2.4.3.2*, from 1764 hours the sampling would have been less frequent. That is, considering the renewal frequency was weekly for a great deal of time, a higher amount of liquid has contacted the spheres than otherwise would have occurred by continuing the use of the leachant renewal formula. These results lend weight to the argument that any increase in L/S ratio will lead to a greater amount of selenium release from the waste. This may also explain why selenium leached in greater amounts from the 1-hour tests compared to the 4-hour tests.

The former argument is, however, contradicted by the fact that more selenium leached from sphere 4B, where 50% more of the surface was available for leaching, than in 4A. Reasons for this, though, may lie in the type of diffusive leaching that is occurring from the spheres. Considering both spheres in the 4-hour test were leached at the same L/S ratio, the surface area has, indeed, had an effect on the selenium leaching that has occurred.

Figures 7.31 and 7.32 illustrate a comparison of selenium leaching with conductivity, and present some interesting results. They both show that, after surface wash-off, whenever the conductivity in the leachate samples decreased, the levels of selenium increased slightly (and vice-versa). Therefore, even though the alkalinity available in the pores was diminishing, selenium was still leaching strongly.

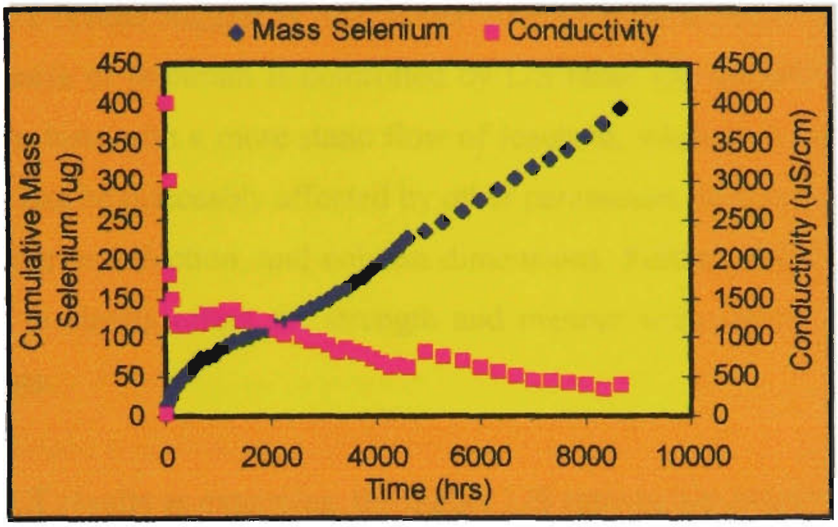


Figure 7.31: t_n = 4A – Cumulative Mass Selenium and Conductivity v's Time

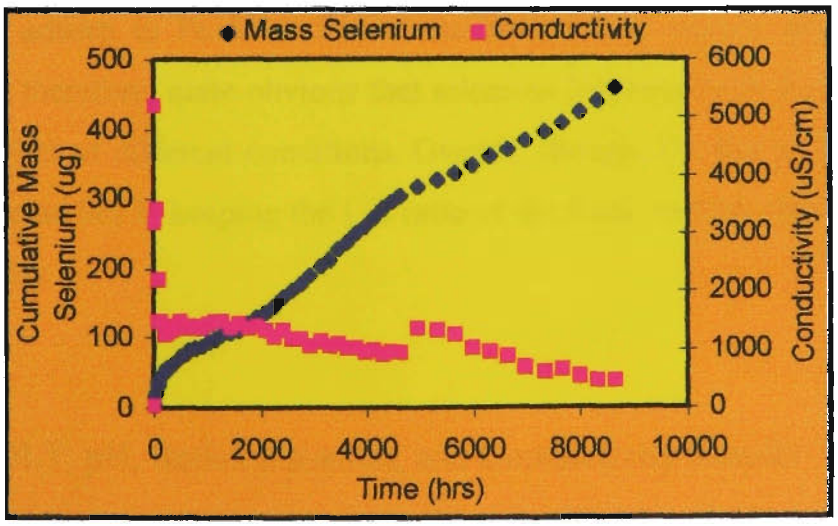


Figure 7.32: t_n = 4B – Cumulative Mass Selenium and Conductivity v's Time

This behaviour was even more pronounced in sphere 4B, suggesting that the greater surface area may lead to greater diffusive release from areas in the matrix other than just the pores. These results are also similar to those for the Large Column (see Section *7.3.1.1.1*) which leached less selenium as the conductivity levels increased, and vice-versa, and was thought to leach more from matrix diffusive / dissolution processes than purely pore-based diffusion.

What all these results suggest is that, under conditions of constant and high leachant flow, the release of selenium is controlled by L/S ratio. On the other hand, selenium leaching from tests with a more static flow of leachant, while also governed primarily by L/S ratio, can be noticeably affected by other parameters, such as surface area of the waste, leachant introduction, and column dimensions. Further, these parameters have been shown to clearly affect the strength and manner with which selenium diffuses from the waste.

Using the DLT results as examples, the higher L/S ratio in the 1-hour test led to higher values of selenium release compared to those from the 4-hour test. Within the 4-hour test itself, the change of renewal frequency resulted in elevated levels of selenium for short times, while the greater surface area in sphere 4B led to greater diffusion from that matrix than occurred in 4A. Further complicating these issues is the propensity for selenium to adsorb to Fe/Al and solid surfaces in the matrix, thus preventing its release. It is, therefore, quite obvious that selenium leaching from this waste can occur under a number of different conditions. Overall, though, the key to the prevention of selenium release lies in keeping the L/S ratio of the final 'resting place' of the waste as low as possible.

7.4.1.1 DLT; pH, Redox Potential, and Conductivity Results

Figures 3.36 – 3.41 in Section *3.4.1* illustrate the pH, redox, and conductivity results for all spheres. Although the data for spheres 1A & 1B and 4A & 4B correlate well with the electrode results, aside from the slight variations in selenium release due to conductivity changes (see Section *7.4.1*), there are no significant correlations between that data and the selenium leachability data. Both the 1 and 4 hour tests also show variations in conductivity levels as the leachate collection schedule changed to weekly and then fortnightly. These changes were discussed in Section *4.4.1.1*.

7.4.1.2 Mechanism of Selenium Leaching

Plots of cumulative release of selenium versus the square root of time are presented as Figures 7.33 and 7.34. As discussed in Section *3.4.1.1*, a straight line for this type of plot is indicative of diffusive release. Although the lines in these charts appear to have curved significantly upwards, results show that each plot has three distinct linear sections, and these relate to the change in renewal schedules at 1764 hours and 4620 hours. The increase in leaching from one section to the next may be a consequence of the alteration of renewal frequencies, and has affected both the 1-hour and 4-hour tests. While the change in renewal frequencies has affected both tests, selenium leaching was seen to increase most in the 4-hour schedule, and, within this schedule, was more intense for sphere 4B than 4A. The reasons for such increases in selenium release have already been discussed in Section *7.4.1*. Therefore, it seems not unreasonable that, for all spheres, diffusion appears to be the controlling mechanism of leaching for selenium in the DLT.

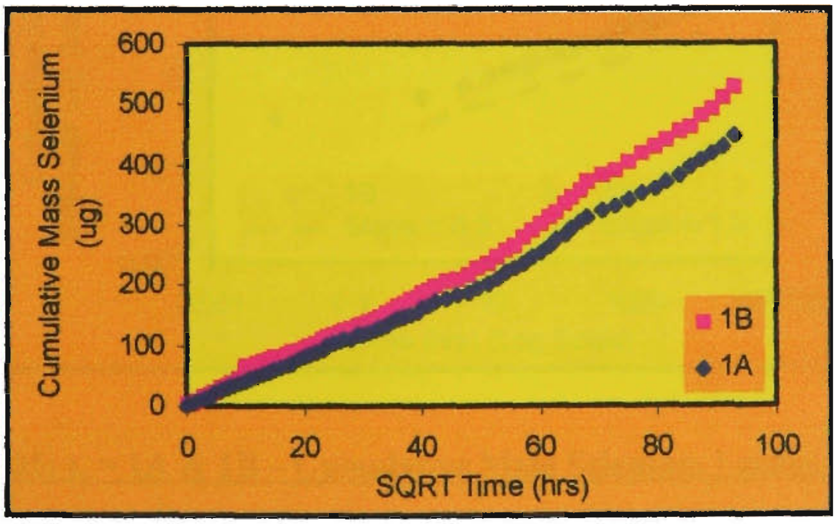


Figure 7.33: t_n = 1A & 1B – Cumulative Mass Selenium Leached v's Square Root of Time

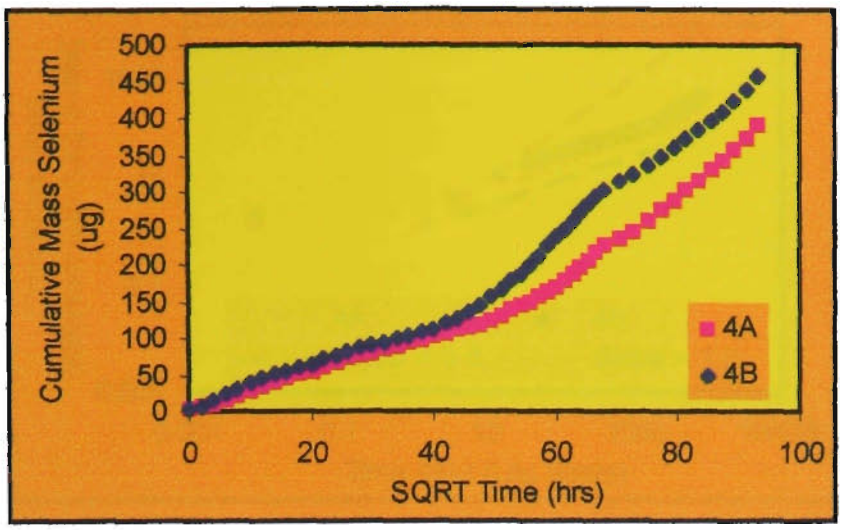


Figure 7.34: t_n = 4A & 4B – Cumulative Mass Selenium Leached v's Square Root of Time

Figures 7.35 and 7.36 also indicate the likelihood of diffusion as the dominant leaching mechanism, and that the rate is slightly greater for the 4-hour test than the 1-hour test. An explanation of the utilisation of such a chart on a log-log scale revolves around the slope of the subsequent plot, and is provided in Section *3.4.1.1*.

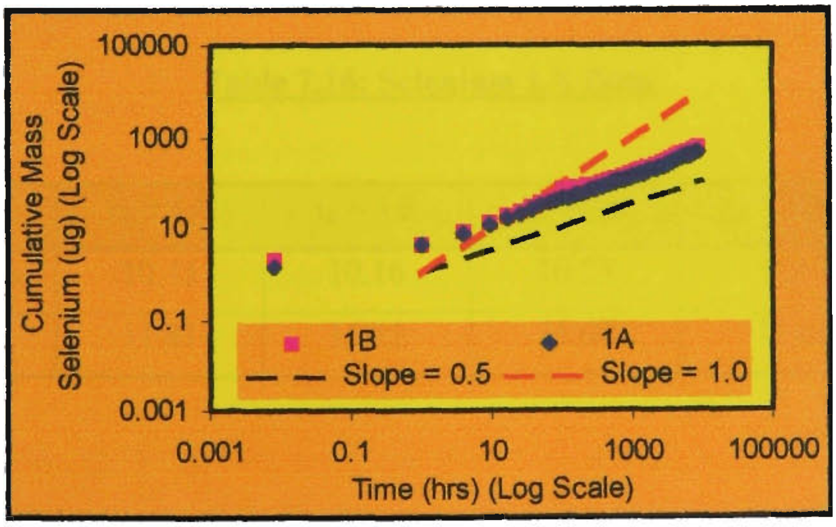


Figure 7.35: t_n = 1A & 1B – Cumulative Mass Selenium Leached v's Time

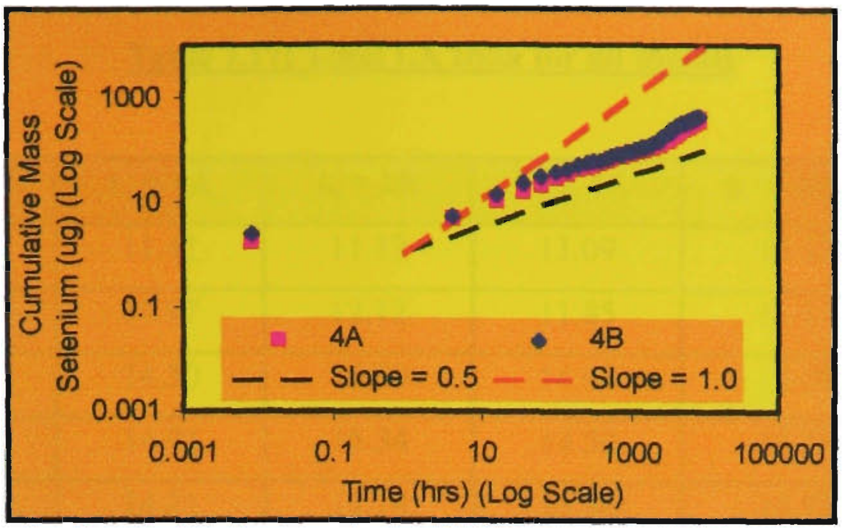


Figure 7.36: t_n = 4A & 4B – Cumulative Mass Selenium Leached v's Time

7.4.1.3 Selenium LX Values

The LX values for selenium release from the DLT spheres are detailed in Table 7.16. The table shows the overall LX values for selenium release as well as the leaching indexes for the first seven periods, which is the number employed in the ANS-16.1 protocol (USEPA 1989).

Table 7.16: Selenium LX Data

Sphere	t_n = 1A	t_n = 1B	t_n = 4A	t_n = 4B(a)	t_n = 4B(b)
LX - 1st 7 Periods	10.45	10.16	10.25	9.97	10.32
LX - Total	11.41	11.12	11.09	10.82	11.17

Table 7.17 clearly shows that selenium was released far more readily via diffusive processes from all spheres than any other metal. This was to be expected, considering that the leaching data detailed in Table 7.15 revealed a much greater percentage of selenium leached from all spheres in the DLT. In fact, of the metals investigated in this work, the two that leached most readily in the DLT were arsenic and selenium, both of which exist in this type of environment predominantly as anionic species.

Table 7.17: Total LX Data for all Metals

LX – Total	t_n = 1A	t_n = 1B	t_n = 4A	t_n = 4B(a)	t_n = 4B(b)
Selenium	11.41	11.12	11.09	10.82	11.17
Arsenic	11.97	12.12	11.85	12.15	12.50
Copper	14.50	15.00	14.62	15.00	15.35
Lead	14.91	15.34	14.50	13.39	13.75
Zinc	14.21	14.18	13.46	13.92	14.27

Although the LX values for selenium are indicative of slow leaching rates (USEPA 1989), and only 3-4% was released from the spheres, these results are important because they demonstrate the propensity of selenium to leach at a much greater rate via diffusion than any of the other metals studied. It has already been demonstrated that, at high flow rates and L/S ratios, selenium release from this waste type can be dramatic. Therefore, if the flow of liquid around this waste was significant in a landfill, selenium leaching could end up posing quite a problem. Further, the fact that the initial level of selenium in the waste was quite low, especially compared to the concentrations of the other metals investigated, means there is a danger of overlooking its potential for excessive release.

Regardless of the fact that spheres 1A and 1B leached a great deal more selenium than 4A or 4B, the LX values for all spheres were quite similar. Also, the decrease in LX values of 0.85 to 0.96 units between the total data and that for the first 7 periods clearly illustrates the influence a minimal amount of surface wash-off had on the LX values.

As with the other metals results, selenium shows a higher LX value for sphere 4B(b) with the approximated surface area that included the cracking, than for the calculation using the surface area of the outer surface of the sphere only. The reason for such behaviour has already been explained (see Section *4.4.1.3*) and is thought to arise from a combination of a poorly approximated boundary condition of a zero surface concentration in the leachate, and an overestimation of an increase in surface area due to the cracking of the sphere.

7.4.1.4 PIXE Analysis

Figure 7.37 illustrates the PIXE data for selenium and, as for the other metals (except arsenic), shows peaks in concentration at 388mm and 421mm, approximately 1mm in from the left edge and 2mm from the right.

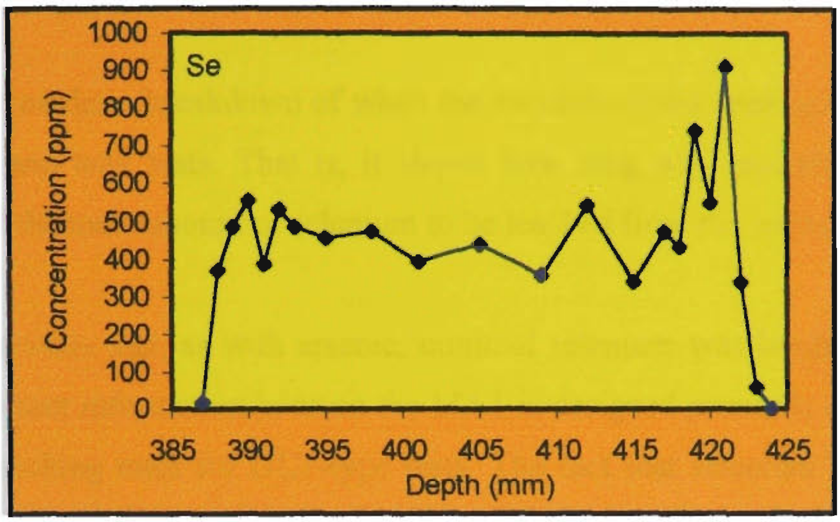


Figure 7.37: t_n = 4B – PIXE Data for Selenium

This also supports suggestions made earlier in Section *3.4.1.3* that metal concentration will be present in higher amounts at the leaching boundary. Further, as also demonstrated previously to a certain extent for the other metals, the concentration of selenium drops sharply toward each edge of the sample, and to a much lesser extent toward the centre. It appears, therefore, that the majority of the selenium has diffused outward into the bulk solution with a much smaller amount reprecipitating further into the sphere. Such reprecipitation would certainly make sense, considering that selenium has maximal solubility at pH 11. Therefore, if selenium were to diffuse inwardly through the sphere, as soon as it encountered the higher pH in the matrix it would be expected to reprecipitate.

7.5 Summary of Selenium Leaching

A summary of selenium leaching from every leaching test is presented in Table 7.18. Not only does this table provide an absolute percentage of selenium leached from each test, and the final L/S ratio from each test, it also displays the amount of selenium leached as a ratio relative to the ABLP result, which has been given the arbitrary unit of 1. This allows for a better visual comparison between the results.

Table 7.19 provides a breakdown of when the majority of the selenium was leached in the column and tank tests. That is, it shows how long was required for each 25% increment of the total amount of selenium to be leached from the waste.

Table 7.18 reveals that, as with arsenic, minimal selenium was leached in the MAT. This is important information because the MAT is designed primarily as a predictor of maximum leaching rates for DLT-type tests. The fact that selenium release from all spheres was at least twice this number suggests the MAT is a poor predictor of selenium leaching. Further examination of the tabulated results also shows that any test with a L/S ratio greater than 200:1 far exceeded the predicted selenium level in the MAT.

Table 7.18: Summary of Selenium Results From All Tests

Test	Percentage of Selenium Leached	L/S Ratio	Ratio Leached (where ABLP = 1)
MAT	1.62%	9.8:1	2.05
TCLP	0.21%	20:1	0.27
ABLP	0.79%	20:1	1
Sequential ABLP	4.80%	200:1	6.08
Large Column	0.13%	19.1:1	0.16
LCC100	0.16%	17.6:1	0.20
ABLC100	64.30%	9571:1	81.39
ABLC180	34.30%	4873:1	43.42
DLT; T_n = 1A	3.64%	634.3:1	4.61
DLT; T_n = 1B	4.25%	626.2:1	5.38
DLT; T_n = 4A	3.19%	445.2:1	4.04
DLT; T_n = 4B	3.74%	447.5:1	4.73

Table 7.19: Leaching Breakdown of Selenium From Column and Tank Tests

Test	Time to Leach 1st 25% of Total Selenium (days)	Time to Leach 2nd 25% of Total Selenium (days)	Time to Leach 3rd 25% of Total Selenium (days)	Time to Leach 4th 25% of Total Selenium (days)
Large Column	35	63	147	119
LCC100	15	43	56	252
ABLC100	41	41	60	221
ABLC180	53	39	80	190
DLT; T_n = 1A	32.7	96.8	105	126
DLT; T_n = 1B	35	94.5	105	126
DLT; T_n = 4A	66.7	104.8	105	84
DLT; T_n = 4B	73.5	77	98	112

These results are not surprising, considering the significant effects both L/S ratio and leachant velocity were shown to have on selenium release from this waste. The largest amounts of selenium released from this waste were from the small columns, ABLC100 and ABLC180, both of which have massive L/S ratios and quite rapid flow rates. The reasons for such behaviour revolve around the relative ease with which selenium can be removed from the matrix, and also reflect the poor leachability of selenium at low L/S ratios and flow rates.

It was suggested earlier in the chapter that the primary mechanism of selenium fixation involved adsorption of both the selenite and selenate species to the solid surfaces in the waste, specifically iron and aluminium oxides. However, at high flow rates, it was expected that the selenium would be easily desorbed to the leachant resulting in high levels in the leachate. The effects of adsorption were evident in the MAT, ABLP, and TCLP where, regardless of the agitation of the tests, minimal levels of selenium were released. It is thought that such tests may have actually hindered selenium leaching by providing gradually increasing surface areas and available pore space via matrix break-up. These increased surface areas, while normally facilitating the greater release of other species, may facilitate a greater amount of adsorption. Similar behaviour was also observed in the Sequential ABLP where selenium release was shown to slightly decrease over the course of the ten extractions. These adsorption effects were also observed in the Large Column and the LCC100. Although the trends of release were slightly different between the two tests, the percentages leached were still much the same. In both cases the slow leachant flow through the waste and low L/S ratio were thought to contribute to minimal selenium release.

As mentioned previously, the large amounts leached using the ABLC100 and ABLC180 clearly demonstrate how important both L/S ratio and leachant flow are to selenium release. Even between these two tests the same effect can be seen, where a decrease in L/S ratio of 1.8 from the ABLC180 to the ABLC100 has led to a similar decrease in percentage leached.

The DLT data also showed that increased leachant renewal frequencies lead to increased levels of selenium release (effectively a higher L/S ratio). The DLT results, therefore, show that leachant flow is not necessary to achieve increases in selenium leaching, and the high L/S ratios employed in the DLT certainly resulted in high levels of selenium in the leachates compared to the other metals. However, it must be pointed out that the Sequential ABLP was a far shorter test at approximately 1/2 to 1/3 the L/S ratio and yet it still leached more selenium than any of the DLT spheres. Therefore, while L/S ratio has certainly been shown to be the dominant factor in the leaching of selenium from this waste, the type of leachant contact with the waste, and the speed or aggressiveness with which it interacts with the waste are also important.

Therefore, in order to minimise the impact of selenium release from this waste, the ideal disposal scenario would be one in which any introduction of liquid to the landfill was minimal. The lower the liquid levels, the lower the L/S ratio and, therefore, the less selenium released.

8. Correlations and Conclusions

8.1 Introduction

This chapter draws together the results presented and discussed in Chapters 3 to 7 inclusive. The chapter aims to explore correlations between leaching tests and leachate properties, as well as providing overall conclusions to the work suggestions for further experimentation.

8.2 Complete Leaching Data

Table 8.1 details the percentages of metals leached from all tests conducted in this work. It has been placed here to allow convenient access to all relevant data when comparisons are made between tests.

A comparative measure of retention of the various species in the matrix can be made by comparing the cumulative percentages leached from all the tests (apart from the MAT). The MAT was removed from this assessment because it is an extremely aggressive test whose conditions would not be seen in a real landfill situation. While the individual environments manufactured for the other tests are also unlikely to be observed in the field, together they encompass a range of possibilities for final landfill disposal conditions that are well within the realms of possibility. The complete totals detailed in the table above show the order of decreasing leachability to be:

$$\mathbf{Se > As > Pb > Zn > Cu}$$

This simple assessment of leachability, therefore, shows selenium to have the greatest leachability, and copper the best retention, of all metals from this particular waste. Further, the difference between selenium and copper is in excess of two orders of magnitude.

Table 8.1: Complete Leaching Data Summary

EXPERIMENT	PERCENTAGE LEACHED				
	Arsenic	Copper	Lead	Selenium	Zinc
MAT	0.32%	26.7%	21.8%	1.62%	43.9%
TCLP	0.064%	0.003%	0.17%	0.21%	0.01%
ABLP	0.051%	0.008%	0.57%	0.79%	0.04%
Seq. ABLP	0.387%	0.052%	2.94%	4.80%	0.169%
Batch Tests Total	0.502%	0.063%	3.68%	5.80%	0.219%
Large Column	0.04%	0.04%	1.12%	0.13%	0.09%
LCC100	0.07%	0.04%	0.64%	0.16%	0.08%
Slow-Flow Columns Total	0.11%	0.08%	1.76%	0.29%	0.17%
ABLC100	22.5%	0.34%	2.7%	64.3%	0.32%
ABLC180	24.6%	0.14%	6.2%	34.3%	0.43%
Rapid-Flow Columns Total	47.1%	0.48%	8.9%	98.6%	0.75%
DLT: 1A	1.50%	0.012%	0.10%	3.64%	0.07%
DLT: 1B	1.33%	0.012%	0.07%	4.25%	0.07%
DLT: 4A	0.83%	0.016%	0.15%	3.19%	0.06%
DLT: 4B	0.82%	0.015%	0.76%	3.74%	0.09%
DLT Total	4.48%	0.055%	1.08%	14.82%	0.29%
TOTAL (no MAT)	**52.2**	**0.7**	**15.4**	**119.6**	**1.4**

Considering the basis of this work was the interpretation of the regulatory batch tests, a more appropriate comparison may, therefore, involve adding the TCLP and ABLP percentages. This would produce a number that takes into account the range of initial leachant pH levels expected in a landfill. As Table 8.1 shows, such a comparative assessment produces an order of leachability similar to that shown above, with only arsenic and lead changing positions. Other comparisons for the different test types provide similar results, with only the low-flow column tests showing major variation where lead leached the strongest, followed by selenium, zinc, arsenic, and copper.

8.2.1 Leaching Comparisons Between the ABLP and the TCLP

Figure 8.1 illustrates a graphical comparison between the amounts of metals leached from the waste using the two regulatory tests, the ABLP and TCLP.

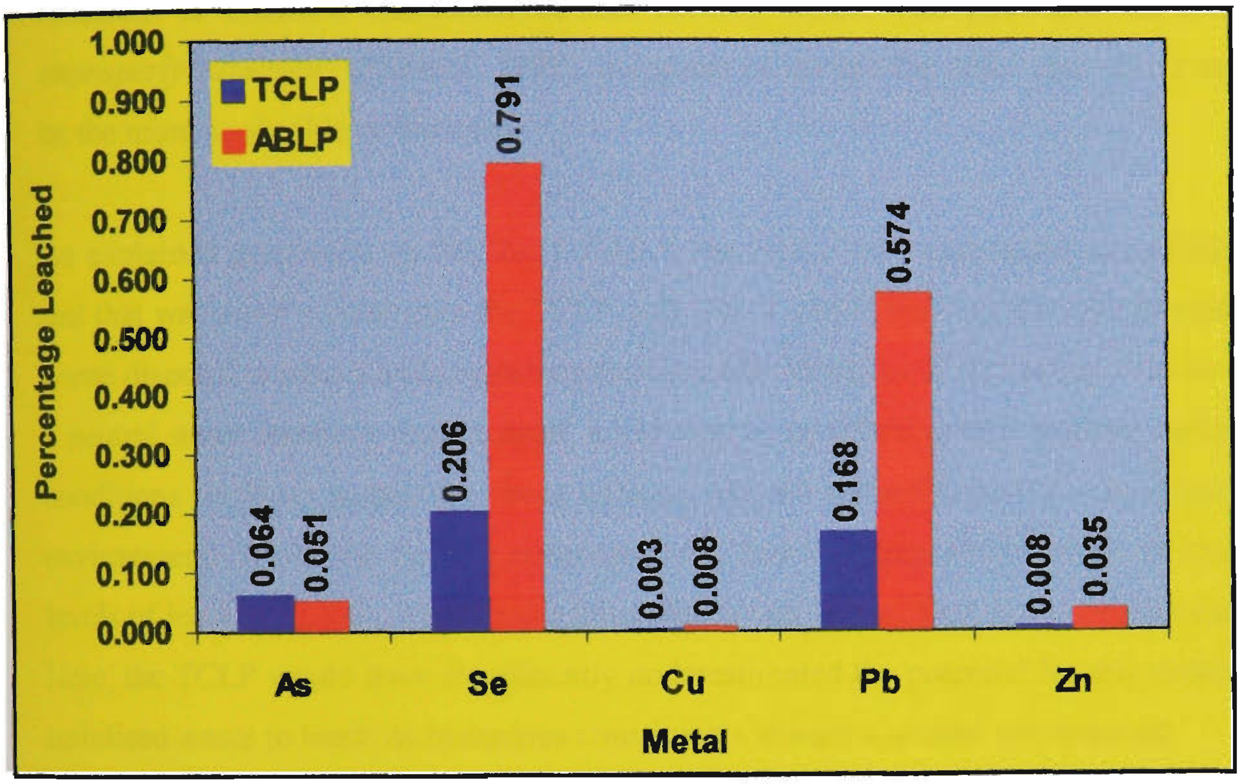


Figure 8.1: ABLP / TCLP Comparison

This figure clearly illustrates the relative influences of de-ionised water and acetate leachant on increasing metal release. The only exception to this trend was arsenic, which leached in slightly greater amounts from the TCLP than from the ABLP. Another interesting feature of this data was that lead leached far more appreciably from the ABLP, when it was thought that the reverse would be the case due to the high solubility of lead acetate. Overall, apart from arsenic, the ABLP leached between 2.7 and 4.4 times more of the species of interest compared to the TCLP. This is an interesting finding as debate over TCLP has generally focussed on the acidic leachant, yet this data shows that water tends to release greater concentrations of metals over the duration of the test.

The most difficult aspect of evaluating this type of single point test is the ultimate interpretation of what the results actually mean. In this case, the data could be portrayed in a number of ways. For example, depending upon the application of the results, some may find it to their advantage to conclude that, in this case, the ABLP overestimates leaching, while others may take the opposite view that TCLP underestimates the final values. Considering that the TCLP data was originally intended 'to establish characteristics that identify wastes that pose a threat *when improperly managed*' (Kimmell 1999), it appears as though the latter assessment may be the more applicable in this case.

As explained previously in Section *1.3.4.3.3*, the ABLP was introduced to provide a test that was more precise than the TCLP, and which was better suited to the particular waste disposal practices and regulatory requirements that exist in Australia. The use of a neutral water leachant was, in itself, a key step in establishing site specific leaching conditions for those wastes (eg. mine tailings) that are seldom buried in a co-disposal environment. While the general consensus was that this step would result in lower levels of leached metals, these results have shown that this will not always be the case. Here, the TCLP would have significantly underestimated the potential for this cement-stabilised waste to leach its hazardous constituents in such a neutral environment.

Of course, it has already been established that a key-contributing factor to such leaching behaviour is the waste particle size used in both tests. While the maximum allowable particle sizes in the TCLP and ABLP are 9.5mm and 2.36mm respectively, neither has a minimum particle size requirement. Therefore, for comparison, all tests were run with a waste particle size of less than 2.36mm. While the various possible effects and resultant mechanisms of release have already been discussed in previous chapters, the key point here is that, at the designated particle size of the ABLP, the use of a leachant which allowed the waste to establish its own leaching environment facilitated the release of much greater amounts of hazardous metals than did the use of a far more aggressive leachant.

Regardless of the difference between the TCLP and ABLP results, a single data point can only reveal so much about a waste's propensity for longer term leaching. If, indeed, the intention of these tests is to identify 'problem wastes', the value obtained would surely need to represent a maximum leachable amount for the medium to long-term. If it cannot do this effectively or accurately, then one of these so-called 'problem wastes' may pass undetected. Therefore, while the ABLP may appear to provide a better assessment of leaching potential in neutral environments for this waste, the only acceptable way to evaluate such data is to run longer time-dependent tests and compare the results obtained. In fact, the key objective of this work was to compare metal leaching within and between longer-term tests and the ABLP with a view to developing a more meaningful interpretation of what that single data point actually means. While the TCLP/ABLP comparison is useful, the key to understanding the data better lies in the comparisons discussed in the following sections.

8.2.2 Leaching Comparisons Between the ABLP and the Sequential ABLP

Figures 8.2 and 8.3 illustrate graphical comparisons between the amounts and patterns of metals leached from the waste in the ABLP and the Sequential ABLP. Figure 8.2 shows that, for all metals, an ABLP with ten sequential extractions did not provide a final leached amount that was ten times greater than the first extraction. In fact, the ratio of metal leaching between the ABLP and Sequential ABLP ranged from 4.83 to 7.56 times the percentage of metal released in the first extraction. What this simple interpretation suggests is that, for this waste, the leachability of the species of interest will tend to decrease over time.

This is certainly the case for lead, selenium, and zinc, where the highest amount of all these metals was released in the first extraction. Therefore, for those metals, a single-point batch test provides a worst-case leaching scenario from this waste. In contrast, copper and, more significantly, arsenic, were shown to leach in greater amounts later in the Sequential ABLP. While the increase was minimal for copper, any increase is still cause for concern when it is considered that regulatory tests are employed to assess potentially problematic wastes for the immediate and long term.

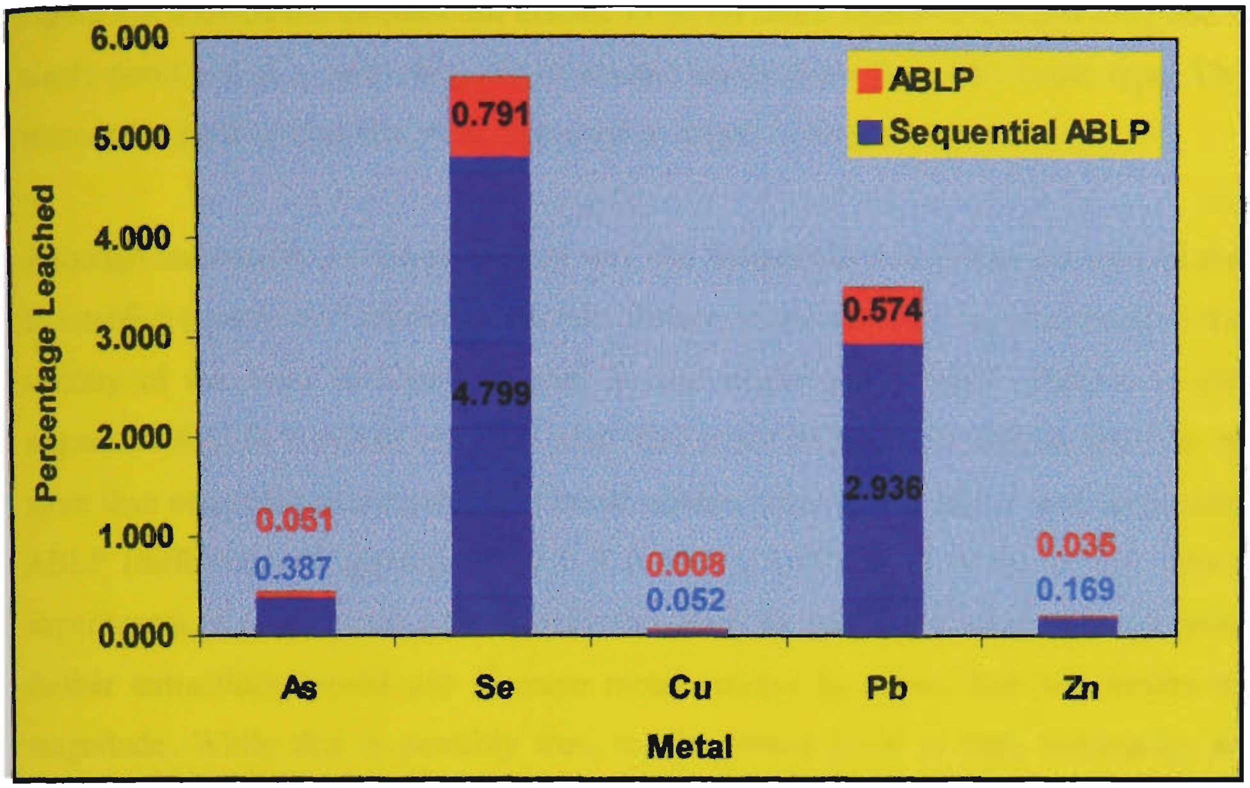


Figure 8.2: ABLP / Sequential ABLP Percentage Leached Comparison

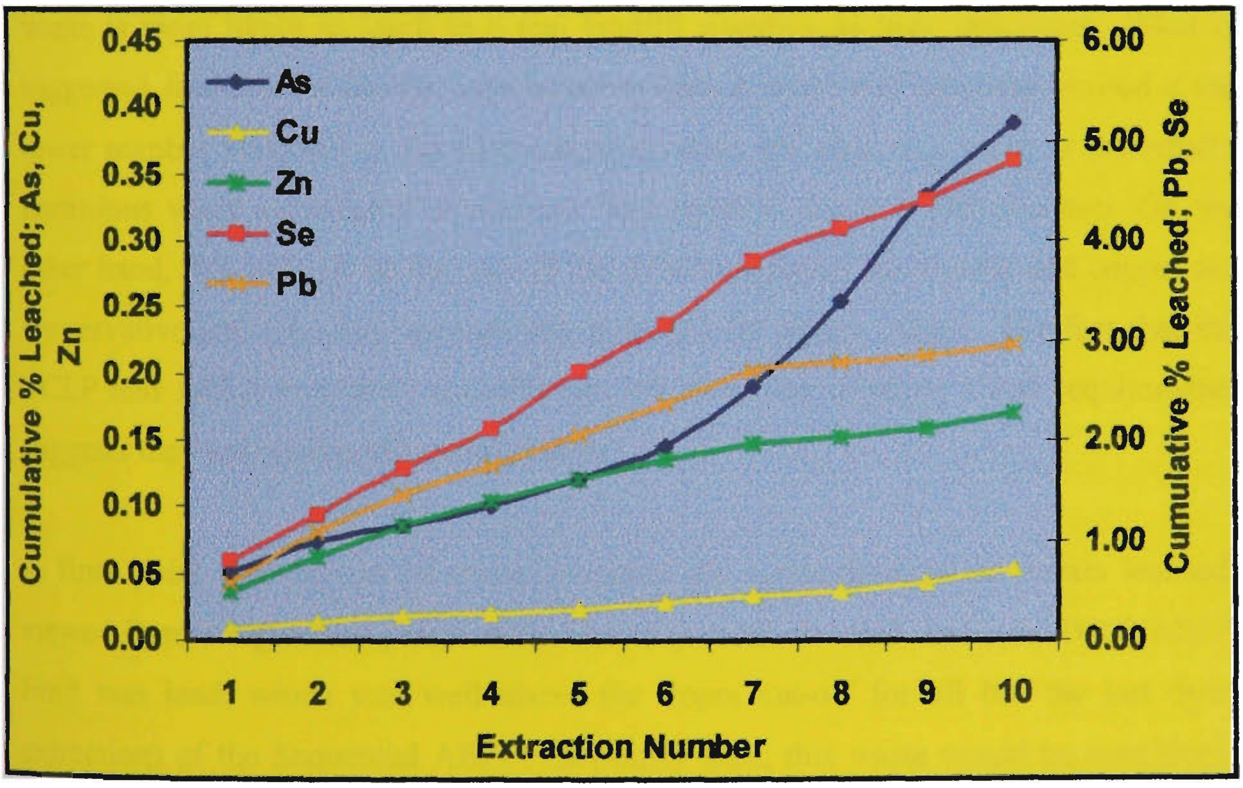


Figure 8.3: ABLP / Sequential ABLP Leaching Pattern Comparison

Figure 8.3 showed the increase for arsenic to be far more significant, suggesting that a single point test is a poor predictor of arsenic leachability from this waste type. The reasons for such an increase were discussed at length in Section *6.2.4.1*.

Although technically a time-dependent test, the Sequential ABLP was not carried out to establish a pattern of release for metals. Rather, it was more of an assessment of the validity of the final number produced by the single point ABLP. Perusal of the sequential data in previous chapters may lead some to conclude that an increase of more than one-order of magnitude in metal release between the ABLP and Sequential ABLP (difference of approximately 5-8 times) is unlikely to occur in any future experiments. A single point ABLP could, therefore, be run, in the knowledge that nine further extractions would not increase metal release by more than two orders of magnitude. While this is possibly true, the important point is that, eventually, an amount of arsenic (or copper) greater than that predicted in the ABLP may be leached from the waste.

It is also important to clarify that these results do not automatically suggest that the waste is more likely to leach in a real landfill situation as time progresses. What is suggested, however, is that the assessment of such a waste may be compromised if the lower number observed in the first extraction does not class the waste as potentially hazardous when subsequent extractions may point to the opposite situation. On the other hand, this will not be the case if the reference points for arsenic and copper are conservative and take into account any potential for future release. The fact that the TCLP and ABLP regulatory cut-offs are 100 times the drinking water requirements suggests they are realistically conservative.

A final point that should be made concerns the concentrations of metals leached, viewed from a regulatory perspective. The only metal to leach above its TCLP/ABLP limit was lead, which was well above the 5ppm cut-off for all but the last three extractions of the Sequential ABLP. Obviously then, this waste would be considered unfit for landfill disposal based on that criteria alone. However, in the case of arsenic, regardless of its future potential for leaching, the limit was not exceeded in any of the extractions. Further, just because arsenic release increased as the test wore on, it does not necessarily follow that, if greater amounts of arsenic were present in this waste, it would pose a regulatory concern. This certainly holds true considering that the patterns and mechanisms of metal release have varied markedly even though they leached from the same waste under the same conditions. An increase in arsenic levels in this particular waste, therefore, would change solution chemistries, solubilities, and physical structure to such an extent that completely different patterns of leaching may be observed, not only for arsenic but for all the other metals as well. Hence, although there may be a temptation to suggest the possibility for greater problems with this waste if its arsenic concentration were higher, such an assumption may be completely false.

8.2.3 Leaching Comparisons Between the Sequential ABLP and the ABLC100

Figures 8.4 and 8.5 illustrate graphical comparisons between the amounts and patterns of metals leached from the waste in the Sequential ABLP and the ABLC100.

The data is interesting because it clearly illustrates that, while the cumulative patterns of release between the two tests are fairly similar for all metals, the amounts leached are not. The exceptions to this statement are arsenic and selenium, both of which leached in similar amounts from the Sequential ABLP and ABLC100, and had similar leaching patterns. Also, arsenic was the only metal to leach more from the less aggressive ABLC100 than from the sequential test.

Probably the most important information gained from these tests revolves around the comparison of leaching patterns. While such information cannot be used to predict actual amounts of metals leached from one test simply by running the other, it does present a model for establishing short to medium term trends for this waste. That is, based on the above information, one could run a Sequential ABLP and be fairly safe in assuming that the release trend would be similar in the ABLC100 over the first 20L, and that the amounts leached would be either the same or less for all metals. Of course, the reverse also holds true: running an ABLC100 trial can provide predictive guidance on Sequential ABLP.

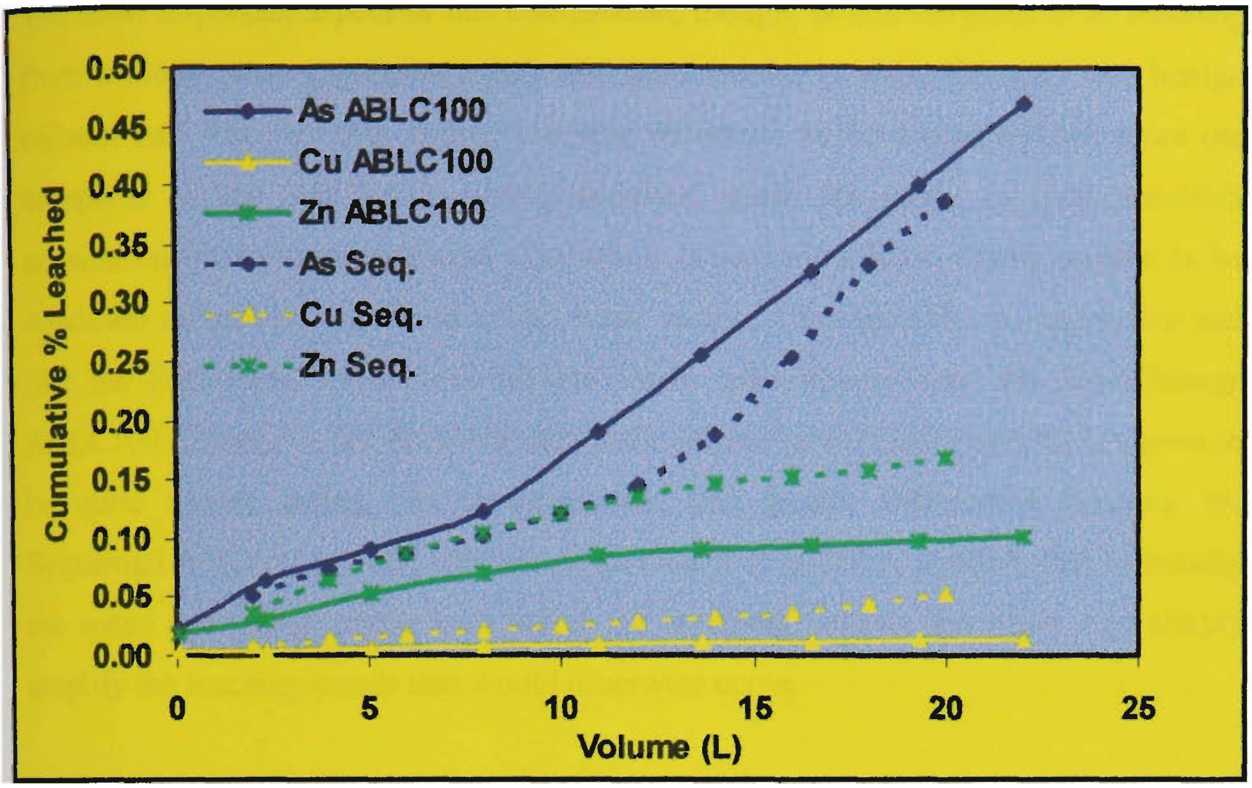


Figure 8.4: Sequential ABLP / ABCL100 Leaching Pattern Comparison; Arsenic, Copper, and Zinc

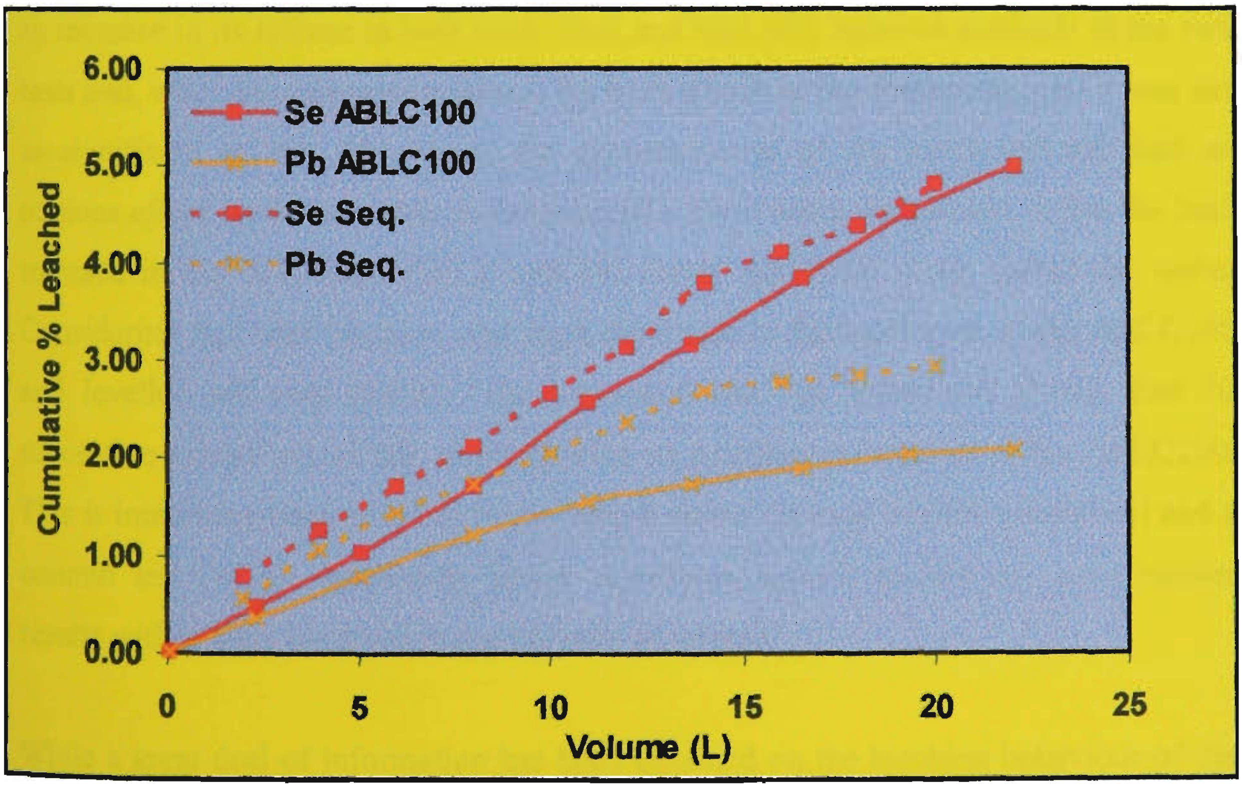


Figure 8.5: Sequential ABLP / ABCL100 Leaching Pattern Comparison; Lead and Selenium

The most important aspect of this comparison, though, is that the patterns of leaching from a much more aggressive batch test were similar to those from a more benign column test. The fact that copper leaching increased as the sequential test wore on, compared to the ABCL100, which remained much the same, is understandable considering that the experiments conducted in this work have shown copper to be solidified rather than stabilised in the waste matrix. Consequently, an aggressive test like the Sequential ABLP will always leach more copper than the more benign ABLC100. However, for the other metals the release mechanisms have been shown to be quite varied during the investigations, and greater differences between the Sequential ABLP and ABLC100 were expected. It is therefore possible that increasing the speed and completeness with which the leachant contacts the waste may simply amplify the leaching trends that would otherwise occur.

The fact that selenium and arsenic leached similar amounts from both tests further illustrates the effects that different test parameters can have on metal release. Regardless of any pH, Eh, or conductivity changes observed in the Sequential ABLP, the most important parameter for the release of these metals from those tests appears to be L/S ratio. This was most obvious for arsenic, where an increase in L/S ratio led to an increase in its release in both tests. Zinc and lead also behaved similarly in the two tests and, while the increase in release for both metals in the Sequential ABLP was not as significant as that for copper, the aggressiveness of the batch test still had an obvious effect on the leaching of those metals. Even more remarkable is that the lead released in the Sequential ABLP and the *entire* ABLC100 were almost the same. Considering that lead leaching was most dominant in the early part of the ABLC100 and levelled off very quickly, the sequential test has effectively shown that 10 successive extractions of this waste provide an excellent correlation to the ABLC100. This is interesting because a batch test (which doesn't mimic landfill conditions) and a column test (which supposedly better represents landfill conditions) gave similar results with respect to amounts and patterns of release.

While a great deal of information has been obtained on the leaching behaviour of the metals of interest from these two tests, more work still needs to be done to facilitate better comparisons between batch and column tests. It has certainly been shown that the cumulative leaching patterns are similar between these two tests over the first 20L, however, it is the actual degree of amplification in leaching between the less and more aggressive tests that is really important. If a consistent correlation could be obtained, for a specific waste type, under varying conditions, it would enable prediction of a release trend and amount leached via either test depending upon the capabilities of a particular laboratory. Further, not only could a sequential test be used to determine the applicability of a single point regulatory test, the very same data could also be used to predict leaching results similar to those from a small column test.

8.2.4 Leaching Comparisons Between the ABLC100 and the ABLC180

Figures 8.6 and 8.7 illustrate graphical comparisons between the amounts and patterns of metals leached from the waste in the ABLC100 and the ABLC180 small columns.

The only difference between these two tests was that the ABLC180 contained approximately 80g more waste than the ABLC100. It is, therefore, quite remarkable that it induced such varied leaching behaviour between the metals. Figures 8.6 and 8.7 show that, while the percentage of arsenic released from the two columns was much the same, lead and zinc were leached in much greater amounts from the 180g column. Contrasting those results, the percentages of selenium and copper leached from the ABLC100 far exceeded those from the ABLC180. Of even greater interest is the fact that, in all cases, regardless of the amounts leached, the patterns of release from the two columns were very similar for each metal.

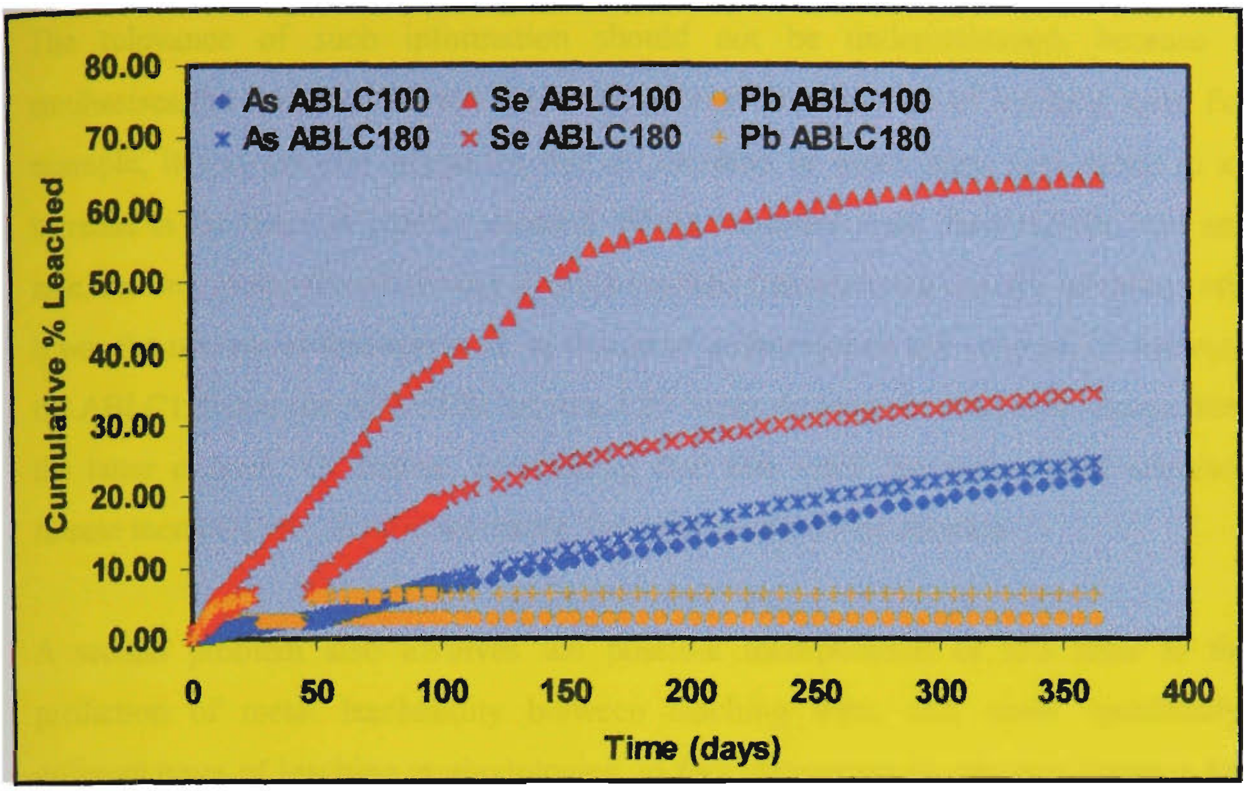


Figure 8.6: ABCL100 / ABLC180 Leaching Pattern Comparison; Arsenic, Lead and Selenium

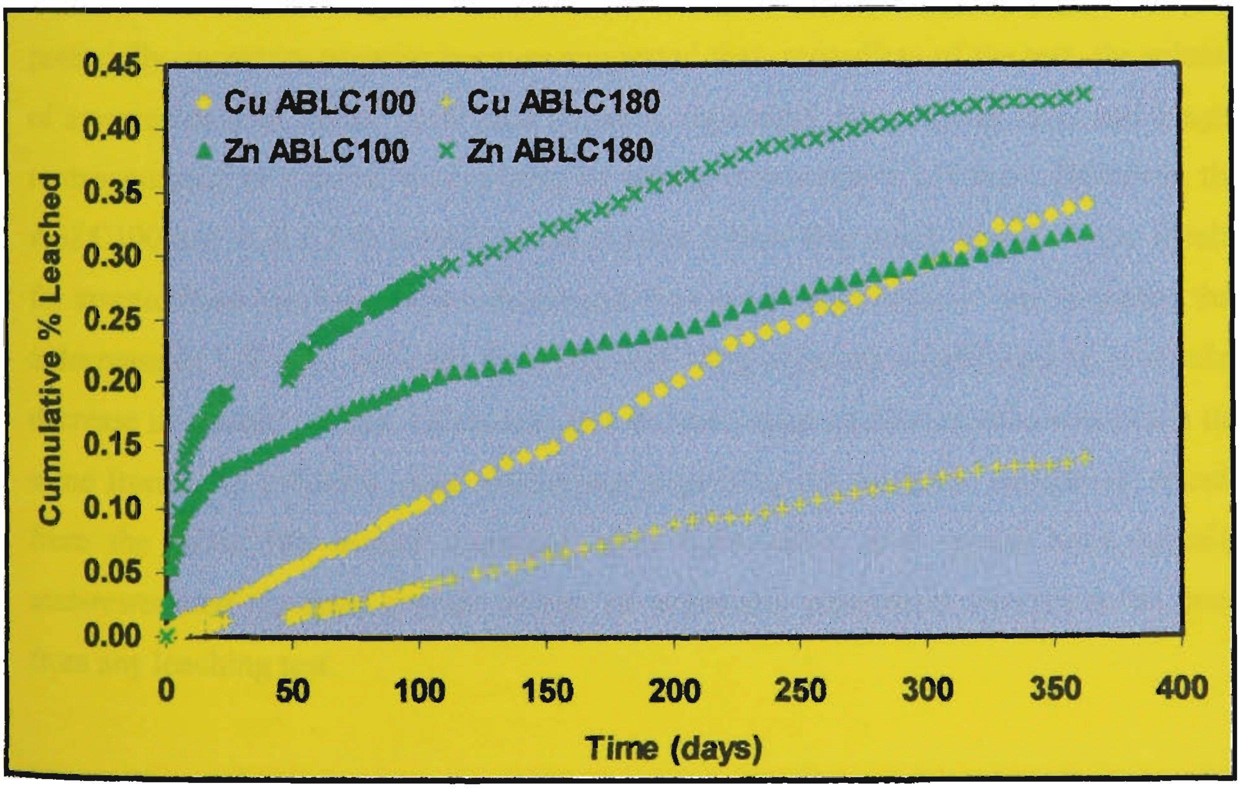


Figure 8.7: ABCL100 / ABLC180 Leaching Pattern Comparison; Copper and Zinc

The relevance of such information should not be underestimated, because it emphasises the dangers inherent in the design and interpretation of leaching tests. For example, it was initially suggested that an increase in waste mass may result in an increase in the mass of metals released. While increases were observed for lead and zinc, the only proportional change in mass leached that occurred was for selenium, and it was the reverse of that expected. In this case, a decrease in L/S ratio of 1.8 between the ABLC100 and the ABLC180 led to a 1.87 times decrease in selenium release from the latter column. Of course, considering that this work has shown that selenium release increases as L/S ratio increases, this now comes as no surprise.

A second problem also involves the possible incorporation of L/S ratio in the prediction of metal leachability between leaching tests, and, more specifically, different types of leaching methodologies. In fact, discussion in previous chapters has certainly shown that, of all parameters varied in these tests, L/S ratio has had the most significant influence on the release of *all* metals. The majority of the early work for arsenic appeared to suggest that, for this waste, leaching results could be correlated one to another by incorporating L/S ratio, and that the subsequent 'modified' leaching results would all be within one order of magnitude. Consequently, this was a potentially important premise because suggested that, regardless of the test, the release of arsenic could be better correlated between regulatory single-point tests and longer term sequential or column tests, purely by taking into account L/S ratio. However, the ABLC100 and ABLC180 leaching data did not follow this trend. Based on the results for arsenic from the ABLC100 column and the earlier batch tests, it was expected that a decrease in L/S ratio between the 100g and 180g columns would lead to as similar decrease in arsenic release. Of course, this did not occur and the release was much the same from both columns. Any predictions regarding the potential release of arsenic from the ABLC180 would therefore have been false, and would have actually *underestimated* the final arsenic levels, an extremely dangerous conclusion to draw from any leaching test.

The results of this comparison are, in some ways, similar to those for the Sequential ABLP and the ABLP, discussed in Section *8.2.2.* In that comparison, it was observed that the cumulative patterns of release of the metals were quite alike, yet the intensity of the release varied between the tests. So it is for the ABLC100 and the ABLC180 comparison.

Therefore, while varying L/S ratio, the mass of waste in the test, or waste agitation results in different amounts of metals being released, the patterns of release remain fairly consistent. Although this is useful information, the challenge is in finding correlations between percentage released, in order for these tests to have useful predictive capabilities. However, even the most casual interpretation of the data for the Sequential ABLP, ABLC100, and ABLC180 reveals how difficult a task this would be. For example, copper release seemed to be favoured most by the conditions in the Sequential ABLP, followed by the 100g and 180g small columns respectively. This is due to the fact that copper is released primarily by matrix break-up, and, as the sequential test and ABLC100 are the most aggressive in terms of particle abrasion and leachant velocity, they leached the copper far more readily than did the ABLC180. Selenium was also leached better via those two tests, although the reason for its leachability was associated with the desorption of the anionic species from the waste at higher flow rates, rather than matrix break-up. Contrasting those results, the leaching of zinc and lead was greater for the 180g column due to a combination of surface wash-off, diffusion and dissolution mechanisms, while arsenic leaching was much the same from all three tests. The reason for reiterating these leaching results is to emphasise the fact that *all metals have shown that they will leach differently from one another between and within tests, from the same waste, and under identical conditions*. Therefore, if a simple change in a test of increasing the waste content by 80% can produce such variation in leaching data and, consequently, in the ability to compare and contrast tests, then the use of laboratory leaching tests to predict the leaching of metals from wastes will prove far more difficult than first suspected. In addition, the possibility of ascribing more meaning to a single point laboratory test has also been shown to be a very complex goal.

8.2.5 Leaching Comparisons Between the Large Column and the LCC100

Figures 8.8 and 8.9 illustrate graphical comparisons between the amounts and patterns of metals leached from the waste in the Large Column and the LCC100 small columns.

Figure 8.8 presents the leaching data of all metals from the Large Column and the LCC100. Figure 8.9, on the other hand, shows all metals except for lead in order to facilitate a better comparison between the release trends of those weaker leaching metals.

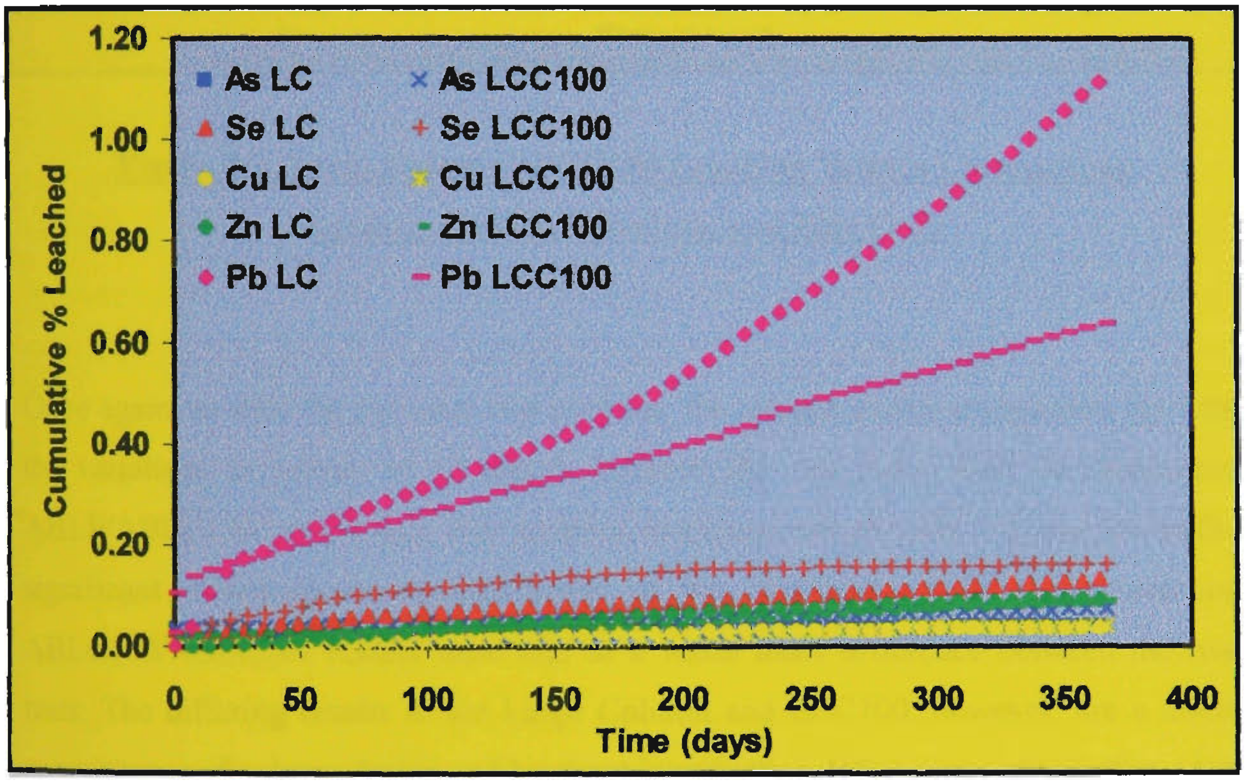


Figure 8.8: Large Column / LCC100 Leaching Pattern Comparison

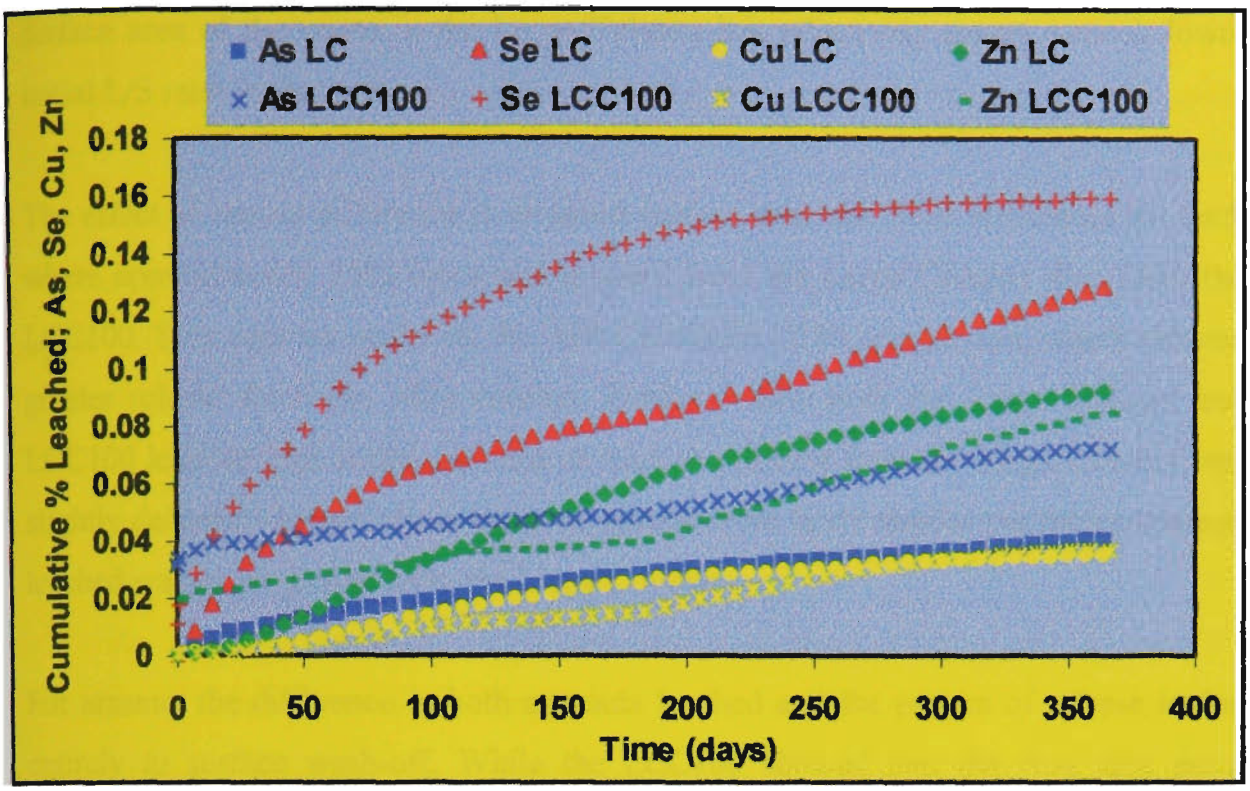


Figure 8.9: Large Column / LCC100 Leaching Pattern Comparison; Arsenic, Copper, Selenium, and Zinc Only

Once again, as with the previous two sections, the interest in this comparison lay with the variations in release of all metals between the two tests. With the Sequential ABLP/ABLC100 comparison, any variation in release over the first 20L was due to the significant difference in aggressiveness of the two tests, while the contrasting ABLC100/ABLC180 results were due to a waste mass difference between the two tests. The differing results in the Large Column and LCC100, however, are a direct consequence of column design and leachant introduction. What this means is that, even though L/S ratio is a most significant parameter in a leaching test in terms of controlling species release, the shape of the column is also critical to the amount of species released, and the trend with which it is leached.

The major effect of column design in this instance was the resultant difference in waste surface area that came into immediate contact with the leachant that was introduced daily to the columns. While the waste mass and leachant volume employed in the Large Column had been scaled down to accommodate the LCC100, the higher initial surface area of the waste in the Large Column has effectively meant a much lower initial L/S ratio in that test.

The effect of such a difference in exposed surface area was most noticeable for lead, where approximately 75% more was leached from the Large Column than from the LCC100. This concurs well with the ABLC100/ABLC180 comparison, which showed greater release from the 180g column. Further, while both the Large Column and LCC100 leached high initial amounts of lead, the release from the Large Column was slightly delayed. Overall, the patterns of release were fairly similar yet the percentage leached was much greater from the Large Column.

For arsenic, the difference in both amounts leached and the pattern of release is due entirely to surface wash-off. While the LCC100 showed that the first data point comprised approximately 43% of all arsenic leached, the same point for the Large Column was only a fraction of that number. Once again, the overall cumulative patterns of release are quite similar, so it is the surface wash-off for arsenic that had the most effect on its release. This demonstrates the effect that the exposed surface area of the waste in contact with fresh leachant can have on arsenic leachability.

The increase in surface wash-off in the LCC100 was also observed for zinc where 22.5% of the total amount leached was released in the column washing step, compared to less than 1% for the Large Column. The comparative patterns of release were also interesting because, although the patterns of leaching were shown to be quite varied, by the end of the test the percentages of zinc leached from the two tests were practically the same. Similar trends of release were also observed for copper, with a higher initial release from the Large Column and lower for the LCC100, with the reverse occurring after 200 days. Once again, as with zinc, the final percentages leached were almost identical. Further, for both metals, after one year of leaching the release from both columns appeared to be levelling off suggesting that little more of either metal would leach in the medium term from both the LCC100 and the Large Column.

Selenium, together with arsenic, showed higher release from the LCC100 than the Large Column. Unlike arsenic and zinc, however, there was no significant amount of surface wash-off of selenium in either test. Also, as opposed to the release trends for zinc and copper, the percentage of selenium leached early in the LCC100 was quite high, and it decreased steadily as the test wore on. The pattern in the Large Column was the opposite, and actually increased at 200 days. By the end of both tests, the release patterns appeared to be drawing toward one another. Although not as close as for both zinc and copper, the final amounts of selenium leached from the two columns were fairly similar while, once again, the patterns were quite different.

Therefore, as the percentages of copper, selenium, and zinc leached from these columns were quite concordant, it can be said that, in terms of amounts leached, the LCC100 produced similar results to the much larger column. However, had the experiments taken place over a shorter time frame, the effects of such varied column design and leachant introduction method would most certainly have led to different conclusions. This emphasises how vitally important the pattern of metals' release is in determining potential leachability in both laboratory, and field-testing. While changes to the physical design of all leaching tests will have their own immediate consequences with respect to leachability, the more pressing problem may be to do with the *length of the test itself*. That is, if a column A is constructed with a greater diameter than column B, how long must the test be run before the true effects of such a change are made obvious to the analyst? Further, how does this affect any possible comparison with regulatory tests such as the ABLP and TCLP?

8.2.6 Leaching Comparisons Between the MAT and the DLT

Figure 8.10 illustrates a graphical comparison between the amounts of metals leached from the waste in the MAT and the DLT experiments.

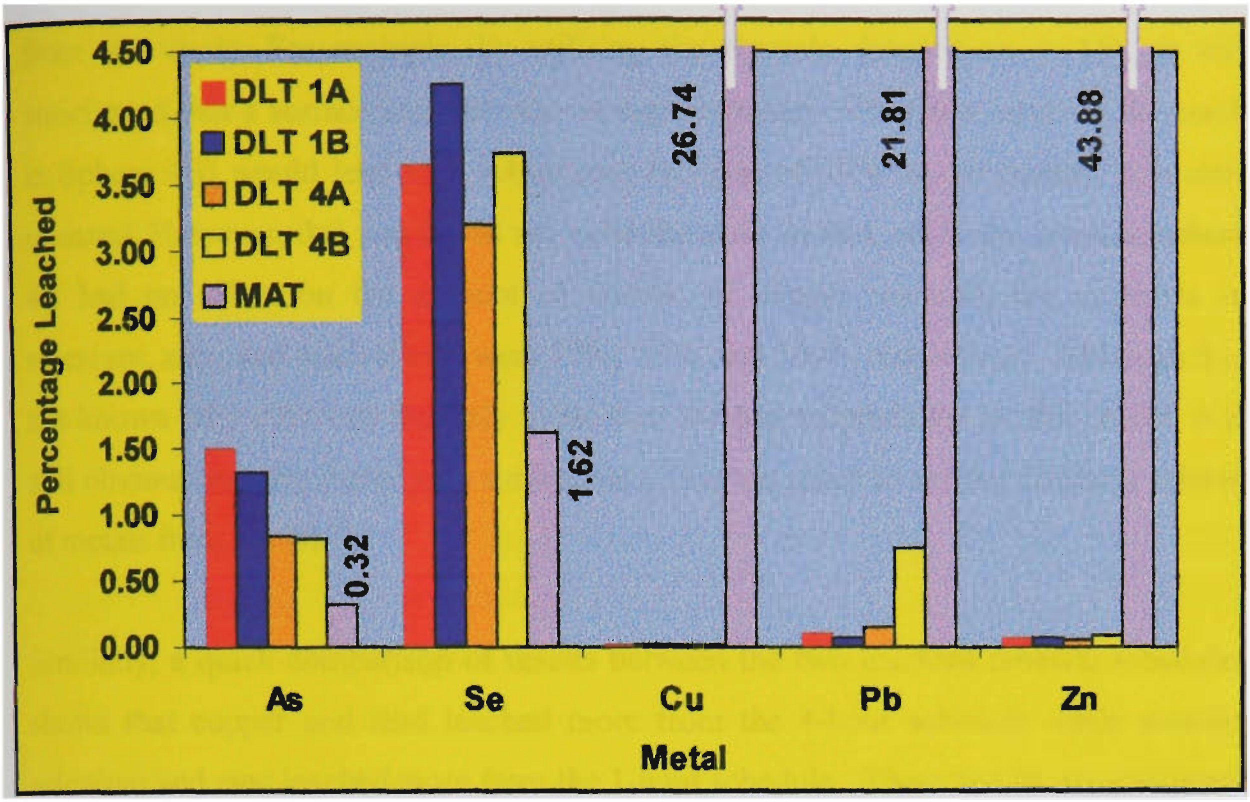


Figure 8.10: MAT / DLT Comparison

The DLT was run in order to establish the diffusive capabilities of the metals, and was not intended for the purpose of any extensive cross-test comparisons. However, basic comparisons can be made within the test itself and between the DLT and the MAT. This is because, while the MAT is an extreme worst case scenario test, it is most frequently employed as a tool for establishing the maximum leachable amounts from short-term dynamic leaching tests. From the data above it can be seen that, after one year of leaching in the DLT, copper, lead and zinc have all leached much less than the amounts predicted by the MAT. Conversely, both arsenic and selenium leached in far greater amounts from all DLT spheres.

Therefore, as with the order of leaching ability from this waste presented earlier in this chapter, the ease with which metals diffused from this waste was:

Se > As > Pb > Zn > Cu

The data and discussion presented in previous chapters also emphasised the various effects that renewal schedules and waste surface area had on the diffusion of metals from the waste. For example, by utilising the formula detailed on p. 158, it was anticipated that a surface area increase of approximately 50% (as a result of the crack in Sphere 4B) would lead to a subsequent increase of 50% in the amount of metals released. However, this was found not to be the case. In fact, while the crack in sphere 4B had no effect on the amount of arsenic or copper released, the increases in selenium, zinc, and lead release were 17%, 50%, and 500% respectively. Although it is not known why zinc was the only metal that leached as predicted by the model, it is still obvious that any increase in surface area does not result in similar diffusive release of metals from the DLT.

Similarly, a quick comparison of results between the two leachant renewal schedules shows that copper and lead leached more from the 4-hour schedule while arsenic, selenium and zinc leached more from the 1-hour schedule. These results are consistent with the other comparisons (such as the ABLC100 v's ABLC180), where the changing of a single test parameter resulted in vastly different leaching trends for most, if not all the metals.

8.3 Conclusions and the Need for Further Work

Although the intention of the work was to look for correlations between different types of leaching tests and, more specifically, between regulatory single-point and long-term tests, significant correlations were elusive. However, the various leaching experiments have clearly demonstrated that *minor changes in test methodology, design, and/or construction, led to significant differences in both the mass of metal species released, and the trends with which they were leached from the waste.*

This work has also demonstrated that it is extremely difficult to find any obvious and simple correlations between short and long-term leaching tests. While the tests were water-based leaching experiments in which the variables were kept to a minium, the waste and contaminant chemistries were found to be far too complex to allow basic cross-test comparisons. If such simple tests, with minor differences in methodologies, can produce such diverse behaviours in five metals, then predictions made about contaminant fate in the far more complex environments found in real landfills are fraught with uncertainty. It therefore follows that, for just one waste type contaminated with many metals, it is extremely difficult to find a suitable disposal environment that will be optimal for all contaminants, not only in the short term, but the medium to long-term as well.

While no one conclusion can be made about the predictive efficacy of any particular test, there is, however, one broad conclusion that *can* be made about all of these experiments: the L/S ratio is the key driving force in determining the amount and trend of metals released from the waste. In fact, the possibility of using L/S ratio for predictive purposes was suggested and trialed with the data produced from these experiments. It was shown that arsenic leaching corresponded well with changes in L/S ratio for the most part. However, once the mass of waste, rather than the liquid volume, was altered in the small column tests, the correlation did not follow suit.

In terms of the leaching patterns between batch and column tests and between different column tests themselves, the results showed that, while the patterns of metal release were quite similar, the amounts leached varied considerably between metals and within the tests. That is, an increase in waste mass resulted in a variety of leaching behaviours from the different metals, while the individual metals themselves frequently behaved unexpectedly based on observations of previous test data. Further, for all comparisons, the major differences between the methodologies of the tests, which led to varied behaviour, were the method of leachant contact and the L/S ratio. Unfortunately, only so many variables could be investigated in the time frame available, meaning that more extensive studies of L/S effects could not be investigated. Consequently, the analysis of metal(s) release from a waste using many different L/S ratios (by changing both leachant volume and waste mass), as well as varying the method and area of leachant contact, would be key variables to investigate in any future work. Further to this, any future investigations should also focus on determining what constitutes an 'adequate test length', since, depending upon when the tests were halted, markedly different conclusions on leaching behaviours could have been drawn.

Finally, the question of what the ABLP or TCLP result really means is still a matter of conjecture. Nonetheless, if the results of these regulatory tests were applied, the waste could not be disposed of in this form due to the excessive levels of lead in the leachates. However, the more realistic column tests based on rainfall data have shown that lead, copper, and zinc leach in greater amounts than those observed in the ABLP and TCLP, while selenium leached less from the columns and arsenic remained unchanged. Obviously then, regardless of the aggressiveness of the batch tests, a more realistic assessment of the waste in question has shown that some metals will leach at far greater levels than those predicted by the ABLP and TCLP. While no correlations were found between the batch and column tests, the applicability of single-point leaching data as a basis for decisions on disposal has certainly been further questioned. The more benign (and realistic) rainfall-based column tests suggest the waste may pose more of a hazard in a real landfill than would have been otherwise suspected based solely upon the results of regulatory testing.

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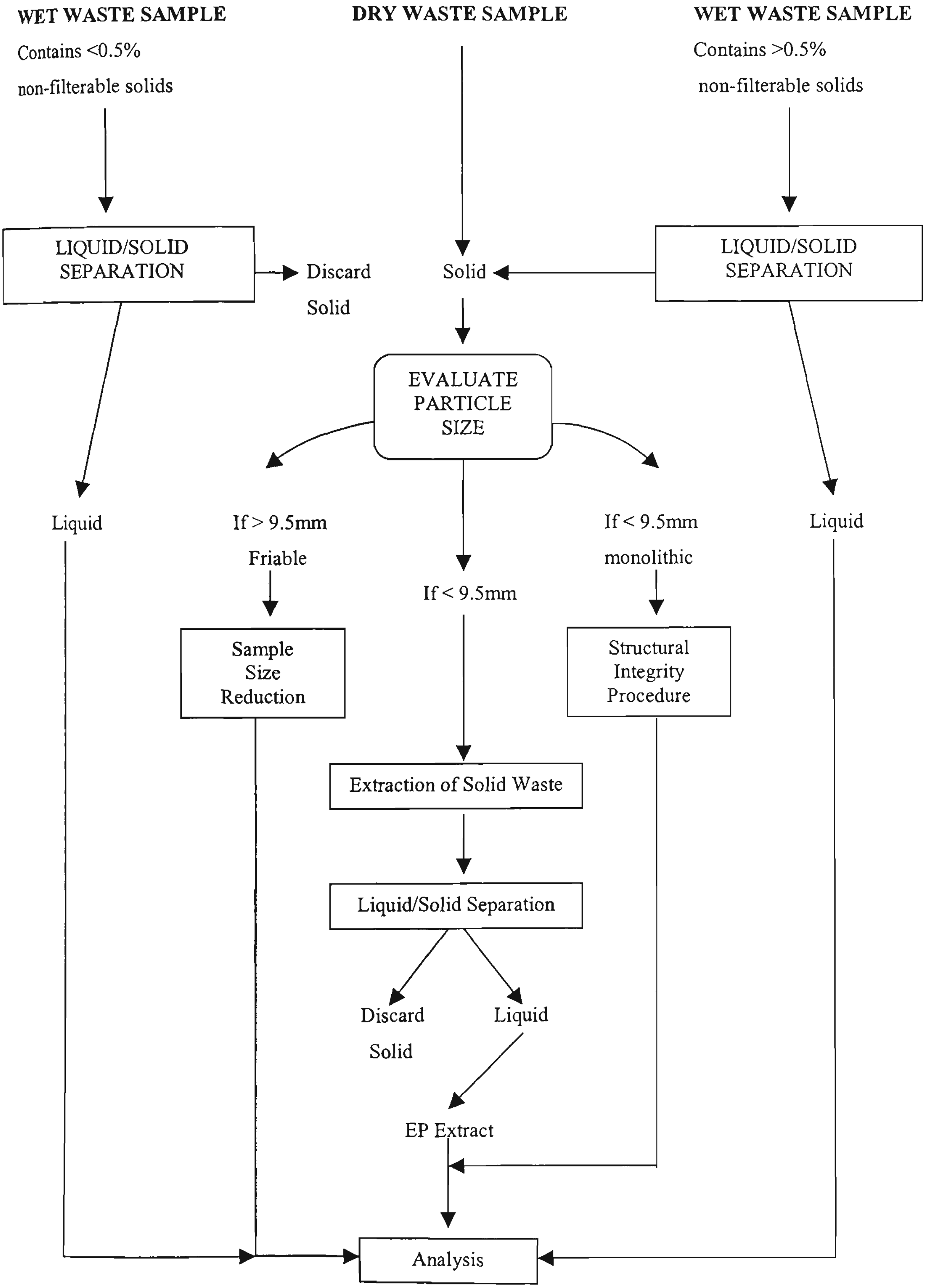
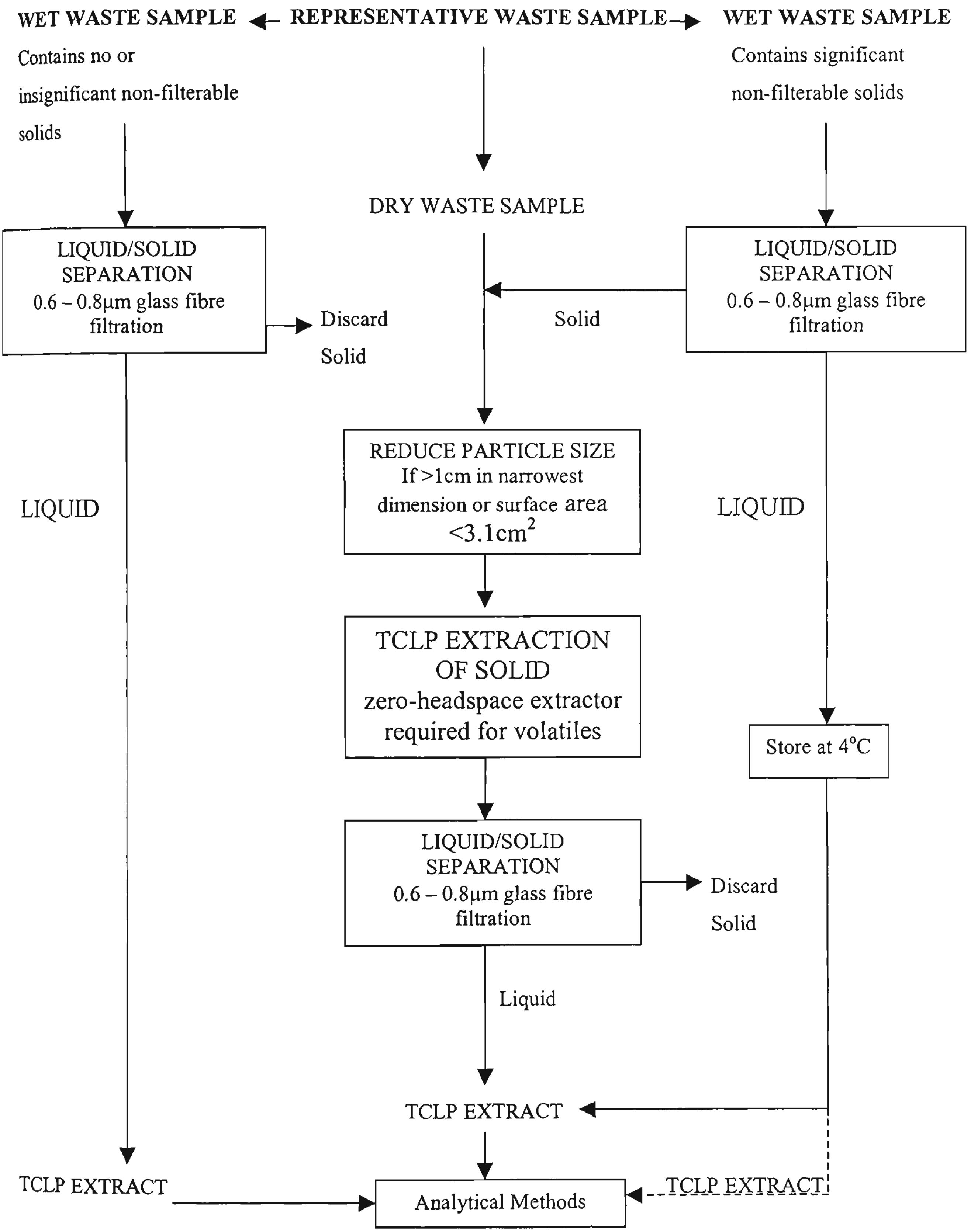
Appendix A: Extraction Procedure Flow Chart (Perket & Webster 1981)



Appendix B: Toxicity Characteristic Leaching Procedure Flow Chart (Federal Register, *vol. 261*, 29 Mar. 1990)



Appendix C: DLT Leachant Renewal Schedules

t_1 = 1 hour (very mobile)

t=	Time From Start	Time Increment	Day No.	Clock Time
0	30 sec. Wash off	30 sec.	1st	30 sec.
1	1hr	1 hr.	1st	6am
2	4hr	3hr	1st	9am
3	9hr	5hr	1st	2pm
4	16hr	7hr	1st	9pm
5	25hr	9hr	2nd	6am
6	36hr	11hr	2nd	5pm
7	49hr	13hr	3rd	6am
8	64hr	15hr	3rd	9pm
9	81hr	17hr	4th	2pm
10	100hr	19hr	5th	9am
11	121hr	21hr	6th	6am
12	144hr	23hr	7th	5am
13	169hr	25hr	8th	6am
14	196hr	27hr	9th	9am
15	225hr	29hr	10th	2pm
16	256hr	31hr	11th	9pm
17	289hr	33hr	13th	6am
18	324hr	35hr	14th	5pm
19	361hr	37hr	16th	6am
20	400hr	39hr	17th	9pm
21	441hr	41hr	19th	2pm
22	484hr	43hr	21st	9am
23	529hr	45hr	23rd	6am
24	576hr	47hr	25th	5am
25	625hr	49hr	27th	6am
26	676hr	51hr	29th	9am
27	729hr	53hr	31st	2pm
28	784hr	55hr	33rd	9pm
29	841hr	57hr	36th	6am
30	900hr	59hr	38th	5pm
31	961hr	61hr	41st	6am
32	1024hr	63hr	43rd	9pm
33	1089hr	65hr	46th	2pm
34	1156hr	67hr	49th	9am
35	1225hr	69hr	52nd	6am
36	1296hr	71hr	55th	5am
37	1369hr	73hr	58th	6am
38	1444hr	75hr	61st	9am
39	1521hr	77hr	64th	2pm
40	1600hr	79hr	67th	9pm
41	1681hr	81hr	71st	6am
42	1764hr	83hr	74th	5pm

t_1 = 4 hour (less mobile)

t=	Time From Start	Time Increment	Day No.	Clock Time
0	30 sec. wash off	30 sec.	1st	30 sec.
1	4hr	4hr	1st	9am
2	16hr	12hr	1st	9pm
3	36hr	20hr	2nd	5pm
4	64hr	28hr	3rd	9pm
5	100hr	36hr	5th	9am
6	144hr	44hr	7th	5am
7	196hr	52hr	9th	9am
8	256hr	60hr	11th	9pm
9	324hr	68hr	14th	5pm
10	400hr	76hr	17th	9pm
11	484hr	84hr	21st	9am
12	576hr	92hr	25th	5am
13	676hr	100hr	29th	9am
14	784hr	108hr	33rd	9pm
15	900hr	116hr	38th	5pm
16	1024hr	124hr	43rd	9pm
17	1156hr	132hr	49th	9am
18	1296hr	140hr	55th	5pm
19	1444hr	148hr	61st	9am
20	1600hr	156hr	67th	9pm
21	1764hr	164hr	74th	5pm

- Following the collection of samples t = 42 and t = 21 from the 1 hour and 4 hour renewal schedules respectively, samples were then taken weekly at 12pm until 4620 hours had passed, and then fortnightly until a total sampling time of 1 year had passed.

Appendix D: Chemicals Information

Chemical	Grade	Manufacturer
1000ppm Arsenic (as As_2O_3)	AR	BDH
1000ppm Copper (as $Cu(NO_3)_2.3H_2O$)	AR	BDH
1000ppm Lead (as $Pb(NO_3)_2$	AR	BDH
1000ppm Selenium (as SeO_2)	AR	BDH
1000ppm Zinc (as $Zn(NO_3)_2.4H_2O$)	AR	BDH
Activated Carbon	Pure	Merck
Ammonium Fluoride	AR	BDH
Anhydrous Disodium Hydrogen Phosphate	AR	BDH
(L) Ascorbic Acid	AR	BDH
Calcium Chloride	LR	APS
Elemental Mercury	AR	BDH
Ferric Ammonium Sulphate	AR	Merck
Ferrous Ammonium Sulphate	AR	Merck
Glacial Acetic Acid	AR	BDH
Hydrochloric Acid (Conc.)	AR	BDH
Hydrofluoric Acid (40%)	AR	BDH
Hydrogen Peroxide (30%)	AR	APS
Nitric Acid (Conc.)	AR	APS
Potassium Chloride	AR	APS
Potassium Dihydrogen Phosphate	AR	BDH
Potassium Hydrogen Phthalate	AR	APS
Potassium Iodide	AR	BDH
Quinhydrone	AR	BDH
Silver Chloride	AR	Merck
Sodium Acetate	AR	BDH
Sodium Borohydride	GR	Merck
Sodium Carbonate	AR	BDH
Sodium Hydroxide	AR	BDH
Sodium Peroxide	AR	APS
Sulphuric Acid (Conc.)	AR	APS
pH Buffers; 4.01, 7.01, 10.01	LR	APS

KEY

AR = Analytical Reagent
LR = Laboratory Reagent
GR = General Reagent
BDH = British Drug Houses
APS = Asia Pacific Specialty Chemicals

Appendix Ei: Maximum Availability Test Data

Result	Replicate		
	1	2	3
pH	4.7	4.63	4.71
Redox Potential (mV)	562.2	578.6	551.5
Conductivity (mScm^{-1})	6.80	6.70	6.20
Mass As (mg)	0.229	0.220	0.223
Mass Se (mg)	0.067	0.068	0.070
Mass Cu (mg)	79.041	78.865	80.116
Mass Pb (mg)	303.499	305.110	300.495
Mass Zn (mg)	158.421	157.268	160.140

Appendix Eii: TCLP Test Data

Result	Replicate				
	Blank	1	2	3	4
pH	3.00	12.09	12.11	12.14	12.10
Redox Potential (mV)	600.0	230.0	233.2	233.4	231.6
Conductivity ($mScm^{-1}$)	0.50	12.80	12.90	12.60	12.80
Mass As (mg)	B.D.	0.267	0.280	0.276	0.286
Mass Se (mg)	B.D.	0.050	0.056	0.054	0.057
Mass Cu (mg)	B.D.	0.049	0.051	0.050	0.051
Mass Pb (mg)	B.D.	15.010	14.560	14.270	14.520
Mass Zn (mg)	B.D.	0.184	0.188	0.184	0.195

- B.D. = Below Detection

Appendix Eiii: ABLP Test Data

Result	Replicate				
	Blank	1	2	3	4
pH	6.35	11.59	11.59	11.62	11.59
Redox Potential (mV)	415.0	207.3	207.7	210.5	215.5
Conductivity (mScm^{-1})	0.00	8.30	8.20	8.20	8.20
Mass As (mg)	0.002	0.222	0.219	0.220	0.218
Mass Se (mg)	B.D.	0.210	0.209	0.210	0.207
Mass Cu (mg)	0.004	0.154	0.154	0.159	0.146
Mass Pb (mg)	0.002	49.964	49.852	50.632	48.996
Mass Zn (mg)	0.004	0.832	0.795	0.799	0.782

- B.D. = Below Detection

Appendix Eiv: Sequential ABLP Test Data

Electrode Data

Extraction No.	Replicate	pH	Redox (mV)	Conductivity (mScm^{-1})	Temp. Range (°C)
1	Blank	6.35	415	0.00	27 - 29
	1	11.59	207.3	8.30	
	2	11.59	207.7	8.20	
	3	11.62	210.5	8.20	
	4	11.59	215.5	8.20	
2	Blank	6.75	423	0.00	24 - 30
	1	11.81	210.5	3.20	
	2	11.8	211.6	3.20	
	3	11.82	212.2	3.20	
	4	11.82	213.3	3.10	
3	Blank	7	430	0.00	22 - 25
	1	11.89	211.9	1.92	
	2	11.88	212.6	1.91	
	3	11.87	209.9	1.92	
	4	11.89	207.4	1.90	
4	Blank	Spilt Sample	Spilt Sample	Spilt sample	20 - 23
	1	11.88	207.3	1.54	
	2	11.88	204.8	1.50	
	3	11.9	204.8	1.55	
	4	11.89	205.3	1.52	
5	Blank	6.95	425	0.00	20 - 23
	1	12.58	204.5	1.53	
	2	12.6	206.5	1.52	
	3	12.59	204.3	1.52	
	4	12.6	204.8	1.54	
6	Blank	6.95	415	0.00	20 - 22
	1	12.72	198	1.74	
	2	12.71	198	1.78	
	3	12.63	199.91	1.71	
	4	12.72	194.9	1.82	
7	Blank	7	415	0.00	20 - 22
	1	12.93	183.4	2.30	
	2	12.96	182	2.20	
	3	12.94	183	2.30	
	4	12.97	180	2.30	
8	Blank	6.9	400	0.00	19 - 22
	1	13.03	161	2.80	
	2	13.05	158	2.70	
	3	13	157.8	2.70	
	4	13.06	159.5	2.80	

Electrode Data (contd.)

Extraction No.	Replicate	pH	Redox (mV)	Conductivity (mScm^{-1})	Temp. Range (°C)
9	Blank	7	400	0.00	22 - 23
	1	13.28	165.7	3.00	
	2	13.28	166.1	3.00	
	3	13.28	165.4	3.00	
	4	13.32	162.8	3.10	
10	Blank	6.94	400	0.00	19 - 22
	1	13.39	159.2	3.50	
	2	13.4	157.2	3.40	
	3	13.43	156	3.50	
	4	13.43	157.2	3.50	

Metals Data

Extraction No.	Replicate	Mass Zn (mg)	Mass Cu (mg)	Mass Pb (mg)	Mass As (mg)	Mass Se (mg)
1	Blank	0.019	0.005	0.003	0.002	0.002
	1	0.832	0.154	49.964	0.222	0.210
	2	0.795	0.154	49.852	0.219	0.209
	3	0.799	0.159	50.632	0.22	0.210
	4	0.782	0.146	48.996	0.218	0.207
2	Blank	0.014	0.006	0.003	0.002	0.002
	1	0.566	0.087	42.689	0.096	0.118
	2	0.638	0.108	43.714	0.097	0.125
	3	0.655	0.105	42.689	0.102	0.106
	4	0.644	0.099	42.689	0.097	0.142
3	Blank	0.016	0.005	0.003	0.002	0.003
	1	0.555	0.094	32.785	0.054	0.134
	2	0.560	0.099	35.517	0.055	0.109
	3	0.466	0.054	30.053	0.057	0.112
	4	0.516	0.032	33.810	0.049	0.117
4	Blank	0.020	0.003	B.D.	0.001	0.001
	1	0.433	0.059	27.662	0.064	0.095
	2	0.388	0.042	25.613	0.065	0.093
	3	0.388	0.061	23.222	0.066	0.104
	4	0.394	0.073	26.296	0.066	0.147
5	Blank	0.009	0.003	B.D.	0.002	0.002
	1	0.356	0.037	25.294	0.081	0.159
	2	0.377	0.068	24.947	0.077	0.147
	3	0.370	0.045	25.779	0.080	0.112
	4	0.373	0.073	26.888	0.086	0.166

Metals Data (Contd.)

Extraction No.	Replicate	Mass Zn (mg)	Mass Cu (mg)	Mass Pb (mg)	Mass As (mg)	Mass Se (mg)
6	Blank	0.016	B.D.	B.D.	0.002	B.D.
	1	0.352	0.080	29.384	0.111	0.117
	2	0.334	0.081	27.720	0.101	0.127
	3	0.348	0.083	27.443	0.109	0.115
	4	0.301	0.089	25.502	0.120	0.134
7	Blank	0.012	B.D.	B.D.	0.004	B.D.
	1	0.240	0.079	27.443	0.182	0.136
	2	0.239	0.068	28.552	0.189	0.214
	3	0.249	0.081	27.997	0.180	0.172
	4	0.243	0.099	28.136	0.203	0.161
8	Blank	0.009	0.004	B.D.	B.D.	B.D.
	1	0.132	0.071	6.882	0.273	0.088
	2	0.141	0.067	7.519	0.276	0.097
	3	0.134	0.057	7.185	0.283	0.082
	4	0.135	0.061	7.279	0.300	0.066
9	Blank	0.012	0.008	B.D.	0.004	B.D.
	1	0.127	0.120	5.426	0.327	0.073
	2	0.159	0.123	7.125	0.344	0.085
	3	0.138	0.131	6.579	0.350	0.075
	4	0.141	0.120	6.189	0.335	0.067
10	Blank	0.009	0.009	B.D.	0.004	B.D.
	1	0.237	0.163	7.822	0.220	0.104
	2	0.250	0.174	8.368	0.247	0.106
	3	0.274	0.186	9.339	0.249	0.104
	4	0.254	0.178	8.737	0.220	0.123

- B.D. = Below Detection

Appendix Fi: Large Column Data – Zinc

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	35.72	0.04	0.0000041
7	5108.42	5.14	0.0005977
14	8752.64	13.90	0.0016146
21	14775.19	28.67	0.0033313
28	19442.35	48.11	0.0055903
35	20337.42	68.45	0.0079532
42	23981.64	92.43	0.0107396
49	23022.63	115.46	0.0134145
56	24320.49	139.78	0.0162403
63	25599.16	165.38	0.0192146
70	25132.44	190.51	0.0221346
77	23981.64	214.49	0.0249210
84	24269.34	238.76	0.0277408
91	24173.44	262.93	0.0305494
98	21584.13	284.52	0.0330572
105	21123.80	305.64	0.0355115
112	21123.80	326.76	0.0379659
119	19762.02	346.53	0.0402620
126	20241.52	366.77	0.0426138
133	20912.82	387.68	0.0450436
140	17076.80	404.76	0.0470277
147	19698.08	424.46	0.0493164
154	19474.32	443.93	0.0515790
161	18994.81	462.92	0.0537860
168	18707.11	481.63	0.0559595
175	17076.80	498.71	0.0579436
182	18994.81	517.70	0.0601506
189	17927.12	535.63	0.0622335
196	16648.45	552.28	0.0641678
203	15062.89	567.34	0.0659179
210	11226.87	578.57	0.0672224
217	14199.79	592.77	0.0688722
224	10939.17	603.71	0.0701432
231	10574.75	614.28	0.0713718
238	11009.50	625.29	0.0726510
245	10881.63	636.17	0.0739153
252	12121.95	648.30	0.0753237
259	12249.81	660.55	0.0767470
266	11039.78	671.59	0.0780297
273	10617.17	682.20	0.0792633
280	10106.24	692.31	0.0804375
287	10588.82	702.90	0.0816678
294	9826.42	712.72	0.0828095
301	9790.55	722.51	0.0839470
308	9019.58	731.53	0.0849950

Appendix Fi: Large Column Data – Zinc (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
315	9197.97	740.73	0.0860637
322	9034.03	749.77	0.0871133
329	8239.64	758.01	0.0880706
336	8417.29	766.42	0.0890486
343	8040.97	774.46	0.0899829
350	7759.23	782.22	0.0908844
357	6987.74	789.21	0.0916963
364	6989.29	796.20	0.0925084

Appendix Fii: Large Column Electrode Data

Day No.	Conductivity (mScm^{-1})	Redox Potential (mV)	pH
Wash Off	72.0	434.0	7.67
7	210.0	289.0	11.12
14	78.0	239.0	11.50
21	26.4	212.0	12.50
28	11.5	219.9	13.50
35	8.2	215.0	13.80
42	7.2	211.9	14.10
49	6.9	211.8	14.00
56	6.5	211.7	14.00
63	6.3	193.0	14.10
70	6.0	194.2	14.00
77	6.0	184.3	14.00
84	6.0	197.5	14.00
91	5.8	200.7	13.98
98	5.9	201.8	13.99
105	5.9	201.1	13.89
112	5.6	195.8	13.85
119	5.5	197.8	13.75
126	5.2	198.4	13.75
133	5.1	201.0	13.85
140	4.5	193.5	13.85
147	4.9	191.4	14.18
154	4.5	190.8	14.13
161	4.1	195.3	13.85
168	4.7	186.5	14.20
175	4.3	192.7	14.08
182	4.7	196.6	14.16
189	4.5	197.3	14.25
196	4.2	196.8	14.26
203	3.8	195.3	13.95
210	3.2	196.0	12.20
217	3.7	195.4	13.39
224	3.4	199.1	12.62
231	3.2	198.7	12.38
238	3.3	199.1	13.36
245	3.1	197.4	12.76
252	3.5	196.7	12.48
259	3.7	194.1	12.33
266	2.5	203.2	12.51

Appendix Fii: Large Column Electrode Data (contd.)

Day No.	Conductivity (mScm^{-1})	Redox Potential (mV)	pH
273	3.5	189.4	12.70
280	3.6	192.5	12.79
287	3.6	187.2	12.75
294	3.8	188.5	12.63
301	3.7	186.3	12.78
308	4.0	201.6	12.88
315	3.8	180.3	12.65
322	3.8	188.4	12.60
329	3.6	187.2	12.67
336	3.5	190.0	12.60
343	3.8	189.0	12.80
350	3.3	191.0	12.50
357	3.4	189.8	12.60
364	3.5	187.1	12.65

Appendix Gi: ABLC100 Data – Zinc

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	411.90	0.41	0.0182
1	269.99	0.68	0.0302
2	527.91	1.21	0.0536
3	359.43	1.57	0.0695
4	325.52	1.89	0.0839
5	136.77	2.03	0.0899
6	92.07	2.12	0.0940
7	93.23	2.22	0.0981
8	64.96	2.28	0.1010
9	60.49	2.34	0.1037
10	50.62	2.39	0.1059
11	60.85	2.45	0.1086
12	40.50	2.49	0.1104
13	50.24	2.54	0.1126
14	46.71	2.59	0.1147
16	100.13	2.69	0.1191
18	103.32	2.79	0.1237
20	81.00	2.88	0.1273
23	89.09	2.96	0.1312
26	64.00	3.03	0.1341
29	67.28	3.10	0.1371
32	49.65	3.15	0.1393
35	59.77	3.21	0.1419
38	74.75	3.28	0.1452
41	55.05	3.34	0.1476
44	63.17	3.40	0.1504
47	51.54	3.45	0.1527
50	67.52	3.52	0.1557
53	88.58	3.61	0.1596
56	59.96	3.67	0.1623
59	63.65	3.73	0.1651
62	79.76	3.81	0.1686
66	84.62	3.89	0.1724
70	72.37	3.97	0.1756
74	81.30	4.05	0.1792
78	79.05	4.13	0.1827
82	64.43	4.19	0.1855
86	75.35	4.27	0.1889
90	65.90	4.33	0.1918
94	66.34	4.40	0.1947
99	88.80	4.49	0.1987
102	43.49	4.53	0.2006
108	75.85	4.61	0.2039
114	103.97	4.71	0.2085
121	29.42	4.74	0.2098

Appendix Gi: ABLC100 Data – Zinc (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
128	18.73	4.76	0.2107
135	58.73	4.82	0.2133
142	89.08	4.91	0.2172
149	80.63	4.99	0.2208
153	38.16	5.03	0.2225
160	89.77	5.12	0.2264
167	57.83	5.17	0.2290
174	46.86	5.22	0.2311
181	57.83	5.28	0.2336
188	56.20	5.33	0.2361
195	52.58	5.39	0.2385
202	60.06	5.45	0.2411
209	72.89	5.52	0.2443
216	95.11	5.61	0.2485
223	132.56	5.75	0.2544
230	113.99	5.86	0.2595
237	87.36	5.95	0.2633
244	70.14	6.02	0.2664
251	86.01	6.10	0.2702
258	93.33	6.20	0.2744
265	67.97	6.27	0.2774
272	66.65	6.33	0.2803
279	92.56	6.43	0.2844
286	45.56	6.47	0.2864
293	72.53	6.54	0.2897
300	112.65	6.66	0.2946
307	18.65	6.67	0.2955
314	24.55	6.70	0.2966
321	50.00	6.75	0.2988
328	92.56	6.84	0.3029
335	78.65	6.92	0.3064
342	38.53	6.96	0.3081
349	89.25	7.05	0.3120
356	52.55	7.10	0.3143
363	48.52	7.15	0.3165

Appendix Gii: ABLC180 Data – Zinc

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	2.99	0.0030	0.000074
1	871.79	0.8748	0.021576
2	1490.72	2.3655	0.058343
3	219.05	2.5846	0.063745
4	201.71	2.7863	0.068720
5	1229.67	4.0159	0.099049
6	844.55	4.8605	0.119879
7	542.86	5.4033	0.133268
8	338.26	5.7416	0.141611
9	229.92	5.9715	0.147281
10	219.44	6.1910	0.152694
11	178.30	6.3693	0.157091
12	159.88	6.5291	0.161035
13	94.81	6.6240	0.163373
14	145.26	6.7692	0.166956
15	124.20	6.8934	0.170019
16	109.95	7.0034	0.172731
17	129.42	7.1328	0.175923
18	101.31	7.2341	0.178422
19	109.82	7.3439	0.181130
20	168.97	7.5129	0.185298
21	92.01	7.6049	0.187567
22	66.31	7.6712	0.189202
23	79.51	7.7507	0.191163
24	39.57	7.7903	0.192139
48	403.07	8.1934	0.202080
49	223.29	8.4166	0.207588
50	158.38	8.5750	0.211494
51	102.48	8.6775	0.214021
52	107.24	8.7847	0.216666
53	102.55	8.8873	0.219196
54	95.31	8.9826	0.221546
55	103.97	9.0866	0.224111
56	68.60	9.1552	0.225802
57	68.83	9.2240	0.227500
60	183.29	9.4073	0.232021
61	57.83	9.4651	0.233447
62	54.44	9.5196	0.234790
63	53.51	9.5731	0.236110
64	64.95	9.6380	0.237711
65	63.62	9.7016	0.239280
66	69.67	9.7713	0.240999
67	58.58	9.8299	0.242444
68	50.58	9.8805	0.243691
69	41.43	9.9219	0.244713
70	32.82	9.9547	0.245523

Appendix Gii: ABLC180 Data – Zinc (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
71	36.63	9.9913	0.246426
72	39.95	10.0313	0.247411
73	54.74	10.0860	0.248761
74	58.58	10.1446	0.250206
75	47.64	10.1922	0.251381
76	52.52	10.2448	0.252677
80	171.27	10.4160	0.256901
81	46.96	10.4630	0.258059
82	47.29	10.5103	0.259225
83	44.39	10.5547	0.260320
84	44.72	10.5994	0.261423
85	42.58	10.6420	0.262473
86	51.35	10.6933	0.263740
87	42.86	10.7362	0.264797
88	45.42	10.7816	0.265917
89	48.76	10.8304	0.267120
90	50.29	10.8807	0.268360
91	55.80	10.9365	0.269736
92	48.15	10.9846	0.270924
93	52.57	11.0372	0.272220
94	53.55	11.0907	0.273541
95	52.43	11.1432	0.274834
96	52.37	11.1955	0.276126
97	59.89	11.2554	0.277603
98	55.59	11.3110	0.278974
99	53.16	11.3642	0.280285
100	54.46	11.4186	0.281628
104	161.87	11.5805	0.285621
108	128.35	11.7088	0.288786
113	116.37	11.8252	0.291657
123	233.25	12.0585	0.297409
130	190.45	12.2489	0.302107
137	224.60	12.4735	0.307646
144	230.30	12.7038	0.313326
151	270.31	12.9741	0.319993
158	177.88	13.1520	0.324380
165	241.37	13.3934	0.330333
172	233.85	13.6272	0.336101
179	225.22	13.8524	0.341656
185	252.50	14.1049	0.347883
193	249.20	14.3541	0.354030
200	239.34	14.5935	0.359933
207	145.55	14.7390	0.363523
215	219.02	14.9580	0.368925
222	206.01	15.1641	0.374006
229	170.27	15.3343	0.378205

Appendix Gii: ABLC180 Data – Zinc (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
236	221.32	15.5556	0.383664
243	114.54	15.6702	0.386489
250	105.21	15.7754	0.389084
257	109.01	15.8844	0.391772
264	100.62	15.9850	0.394254
271	138.58	16.1236	0.397672
278	133.24	16.2568	0.400958
285	116.77	16.3736	0.403838
292	123.25	16.4969	0.406878
299	128.10	16.6250	0.410037
306	118.96	16.7439	0.412971
313	84.46	16.8284	0.415054
320	78.50	16.9069	0.416991
327	65.21	16.9721	0.418599
334	49.75	17.0218	0.419826
341	0.00	17.0218	0.419826
348	0.00	17.0218	0.419826
355	106.90	17.1287	0.422462
362	136.11	17.2648	0.425819

Appendix Giii: LCC100 Data – Zinc

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	430.95	0.43	0.0191
1	20.82	0.45	0.0200
8	55.22	0.51	0.0224
15	5.07	0.51	0.0227
22	9.11	0.52	0.0231
29	36.15	0.56	0.0247
36	12.25	0.57	0.0252
44	12.79	0.58	0.0258
51	35.61	0.62	0.0274
58	16.75	0.63	0.0281
65	23.60	0.66	0.0291
72	11.16	0.67	0.0296
79	7.21	0.68	0.0300
86	41.19	0.72	0.0318
93	31.53	0.75	0.0332
100	22.33	0.77	0.0342
107	24.32	0.80	0.0352
114	17.56	0.81	0.0360
121	7.37	0.82	0.0363
128	7.89	0.83	0.0367
135	7.34	0.84	0.0370
142	5.89	0.84	0.0373
149	4.96	0.85	0.0375
156	6.18	0.85	0.0378
163	21.57	0.87	0.0387
170	10.88	0.89	0.0392
177	6.47	0.89	0.0395
184	12.55	0.90	0.0400
191	28.42	0.93	0.0413
198	49.22	0.98	0.0435
205	75.70	1.06	0.0468
212	37.60	1.10	0.0485
219	33.42	1.13	0.0500
226	42.25	1.17	0.0519
233	34.99	1.21	0.0534
240	32.26	1.24	0.0548
247	78.49	1.32	0.0583
254	58.51	1.38	0.0609
261	32.21	1.41	0.0623
268	32.36	1.44	0.0638
275	32.55	1.47	0.0652
282	32.56	1.51	0.0666
289	35.76	1.54	0.0682
296	65.10	1.61	0.0711
303	47.99	1.65	0.0732
310	26.86	1.68	0.0744

Appendix Giii: LCC100 Data – Zinc (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
317	31.00	1.71	0.0758
324	29.90	1.74	0.0771
331	29.00	1.77	0.0784
338	30.20	1.80	0.0797
345	24.70	1.83	0.0808
352	32.40	1.86	0.0823
359	28.80	1.89	0.0835
366	26.00	1.91	0.0847

Appendix Giv: ABLC100 Electrode Data

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0	46500	288	10.69
1	5500	241.4	12.19
2	1570	240.4	12.54
3	1440	180	12.59
4	1440	168.7	12.71
5	1510	196.4	12.1
6	1440	203.8	11.82
7	1340	218.5	12.07
8	1250	225	12.14
9	1140	226.3	12.16
10	1130	222.5	12.1
11	1080	223.2	12.12
12	1010	230.1	12.12
13	1020	222.6	12.5
14	990	230.8	12.5
16	890	237	12.54
18	860	225	11.7
20	790	225	11.8
23	770	222.5	12.13
26	660	225	12.08
29	680	230.6	11.85
32	630	235.7	11.7
35	580	225	12.4
38	510	247.3	12.5
41	430	240.6	12.1
44	380	256.8	12.3
47	320	253.8	12.3
50	300	258.4	12
53	270	246.5	12
56	250	243.3	11.5
59	220	260	11.5
62	310	251.4	11.31
66	300	238	11.7
70	250	259.5	11.6
74	220	251.9	11.6
78	210	255	11.9
82	190	254	11.85
86	170	260.8	11.9
90	160	260.1	11.85
94	150	262.7	11.85
99	110	281.4	11.45
102	100	268.5	11.55
108	80	281.9	11.1
114	80	285.7	11.2
121	70	273.1	11.2

Appendix Giv: ABLC100 Electrode Data (contd.)

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
128	60	281.2	10.8
135	50	289.8	10.8
142	50	293.6	10.8
149	40	300.1	10.78
153	40	290.3	10.68
160	40	287.6	10.72
167	40	296.4	10.7
174	30	295.5	10.55
181	30	294.1	10.46
188	20	307.7	10.42
195	20	317.1	10.35
202	20	312.7	10.58
209	20	301.9	10.58
216	20	304.2	9.72
223	20	315.5	10.06
230	20	320.2	9.61
237	20	319.9	9.47
244	40	306.3	10.33
251	30	304	9.96
258	30	312.5	9.75
265	20	311.4	9.48
272	20	310	9.76
279	20	321.4	9.54
286	10	327.3	9.39
293	10	332.8	9.4
300	10	334.2	9.28
307	10	333.9	9.3
314	10	350.7	9.06
321	10	317.9	9.34
328	0	330	9.03
335	10	330	9.1
342	0	329.4	9
349	0	334.2	8.97
356	0	319.2	9.02
363	0	322.1	8.99

Appendix Gv: ABLC180 Electrode Data

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0	6900	299.5	8.97
1	8600	210.8	11.55
2	2600	218.1	11.15
3	2300	201.5	11.9
4	2200	200.5	12
5	1990	196.4	12.02
6	1950	205.4	12.22
7	1960	197	12.2
8	2000	192	12.07
9	1970	194	12.25
10	1940	194	12.36
11	1940	191.6	12.48
12	1860	191	12.55
13	1920	204.8	11.95
14	1960	200.7	12.02
15	1750	206	12.05
16	1760	202.7	12.16
17	1810	206.5	12.12
18	1750	208.6	12.06
19	1690	210	12.15
20	1570	212	12.18
21	1470	213	12.24
22	1400	213.7	12.35
23	1380	203	12.2
24	1380	207	12.25
48	1780	214.9	11.8
49	1370	230	11.7
50	1200	236	11.7
51	1110	246	11.8
52	1120	236.9	11.9
53	1000	237	11.7
54	990	251	11.8
55	970	243.2	11.85
56	830	256.2	12
57	820	272.2	11.6
60	660	280	11.5
61	700	260	11.6
62	750	262.7	11.8
63	740	265	11.4
64	810	260.5	11.6
65	850	258.8	11.6
66	870	255.3	11.6
67	860	261.2	11.7
68	630	265	11.4
69	560	270	11.65
70	520	290	11.5

Appendix Gv: ABLC180 Electrode Data (contd.)

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
71	480	295.7	11.55
72	460	290.3	11.6
73	690	274.8	11.75
74	730	271.8	11.85
75	670	284.3	11.4
76	630	284.6	11.95
80	320	310	11.7
81	990	280	11.65
82	490	284.3	11.8
83	490	294.3	11.3
84	490	292.2	11.3
85	480	295.4	11.3
86	470	292.3	11.35
87	445	297.3	11.45
88	440	290	11.5
89	430	274.3	11.6
90	430	271.1	11.55
91	410	284	11.55
92	420	279	11.2
93	430	280	11
94	430	280	11.3
95	410	280	11.2
96	440	278.2	11.1
97	430	280	11.5
98	430	282.3	11.6
99	380	270	11.5
100	380	273	11.6
104	280	296	11.4
108	290	298	11.6
113	270	300	11.7
123	260	260	11.5
130	200	275	11
137	160	275	10.9
144	160	313.7	10.8
151	130	295	10.9
158	140	290.5	11.3
165	140	260	11
172	110	277	11
179	90	283	11
185	70	288	11
193	70	290	11.1
200	60	285	11
207	60	286	11.3
215	70	268.2	10.99
222	50	280	10.33
229	50	290	10.8

Appendix Gv: ABLC180 Electrode Data (contd.)

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
236	50	294.7	10.6
243	40	296.7	10.6
250	40	296.6	11.2
257	40	305	10.7
264	30	316.1	10.1
271	30	300	9.5
278	30	305	9.8
285	30	301.7	10
292	30	310	10.5
299	30	293	10.3
306	30	299.5	10.4
313	20	302.6	10.25
320	20	308.4	10.25
327	20	307.4	10.25
334	20	306.4	10.15
341	20	313.8	10.3
348	20	307.8	10
355	20	301.5	10.1
362	20	301.1	10.35

Appendix Gvi: LCC100 Electrode Data

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0	18300	284	11
1	118000	269.5	11.2
8	132000	252.6	11.5
15	44000	232.8	11.4
22	13500	191.7	12.5
29	9000	193	13.5
36	7100	196.9	13.7
44	6500	186.5	14
51	6300	186	14
58	5300	183.8	14
65	5900	175.5	14
72	5600	183.6	14
79	5500	170.1	14.1
86	5400	177.8	14.05
93	5000	182.2	14.1
100	5500	184	14.25
107	5700	186.1	14.3
114	4400	189.4	13.9
121	5500	185	13.8
128	5100	179.6	13.6
135	5400	162.4	13.8
142	5300	177.3	13.8
149	4900	172.1	13.86
156	5000	170.5	13.96
163	4800	166.4	14.11
170	5100	174.6	14
177	5000	175.6	14.05
184	5000	180	14
191	5100	182.8	14.05
198	5000	177	14.1
205	3500	204.9	13.24
212	3300	199.7	11.81
219	4000	181	13.28
226	3800	185.4	12.48
233	4400	179.7	12.41
240	3800	189.8	13.25
247	4200	176.4	12.82
254	2900	206.7	11.97
261	4300	179.8	12.36
268	4400	176.6	12.7
275	3800	182.8	12.55
282	4600	176.6	12.81
289	4300	172.4	12.7
296	3800	182.9	12.44
303	4400	171.3	12.6
310	4700	183	12.87

Appendix Gvi: LCC100 Electrode Data (contd.)

Time (days)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
317	3500	181.3	12.49
324	3000	188.7	12.3
331	4400	165.1	12.67
338	4000	180	12.6
345	3900	182.3	12.62
352	3200	182.7	12.58
359	3400	186	12.6
366	3400	186	12.6

Appendix Hi: DLT t_n = 1A Data – Zinc

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	4.93	4.93	0.00047
1	2.58	7.51	0.00072
4	4.63	12.13	0.00116
9	4.55	16.68	0.00160
16	6.90	23.58	0.00226
25	13.49	37.07	0.00355
36	10.54	47.61	0.00456
49	13.26	60.87	0.00583
64	8.05	68.93	0.00660
81	10.15	79.08	0.00758
100	1.00	80.08	0.00767
121	10.57	90.64	0.00868
144	11.17	101.81	0.00975
169	11.97	113.78	0.01090
196	11.70	125.48	0.01202
225	12.77	138.25	0.01325
256	12.23	150.48	0.01442
289	10.64	161.11	0.01544
324	10.64	171.75	0.01646
361	9.04	180.79	0.01732
400	10.10	190.89	0.01829
441	13.30	204.19	0.01956
484	12.23	216.42	0.02074
529	9.57	225.99	0.02165
576	6.91	232.90	0.02231
625	13.30	246.20	0.02359
676	9.30	255.50	0.02448
729	10.23	265.73	0.02546
784	9.97	275.70	0.02642
841	11.25	286.96	0.02749
900	11.25	298.21	0.02857
961	10.74	308.95	0.02960
1024	11.76	320.71	0.03073
1089	11.76	332.47	0.03185
1156	11.25	343.72	0.03293
1225	13.80	357.53	0.03426
1296	14.83	372.35	0.03568
1369	9.72	382.07	0.03661
1444	6.14	388.21	0.03720
1521	9.21	397.42	0.03808
1600	13.80	411.23	0.03940
1681	9.97	421.20	0.04036
1764	9.97	431.18	0.04131
1932	16.61	447.79	0.04290

Appendix Hi: DLT t_n = 1A Data – Zinc (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	9.47	457.26	0.04381
2268	9.90	467.16	0.04476
2436	10.54	477.70	0.04577
2604	7.98	485.68	0.04653
2772	8.84	494.52	0.04738
2940	7.56	502.07	0.04811
3108	9.90	511.97	0.04905
3276	9.69	521.66	0.04998
3444	11.81	533.47	0.05111
3612	7.56	541.03	0.05184
3780	7.35	548.38	0.05254
3948	11.39	559.76	0.05363
4116	10.54	570.30	0.05464
4284	10.54	580.83	0.05565
4452	9.47	590.31	0.05656
4620	14.36	604.66	0.05793
4956	18.80	623.47	0.05974
5292	26.00	649.47	0.06223
5628	14.99	664.46	0.06366
5964	5.67	670.14	0.06421
6300	5.46	675.60	0.06473
6636	6.95	682.55	0.06540
6972	7.16	689.70	0.06608
7308	4.62	694.32	0.06652
7644	3.56	697.87	0.06687
7980	7.16	705.03	0.06755
8316	1.35	706.39	0.06768
8652	1.44	707.83	0.06782

Appendix Hii: DLT t_n = 1B Data – Zinc

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	5.08	5.08	0.00049
1	6.97	12.05	0.00115
4	5.16	17.21	0.00165
9	6.07	23.28	0.00223
16	7.05	30.33	0.00291
25	13.26	43.59	0.00418
36	9.78	53.37	0.00511
49	9.32	62.69	0.00601
64	1.76	64.45	0.00618
81	13.71	78.17	0.00749
100	12.67	90.83	0.00870
121	18.33	109.16	0.01046
144	12.77	121.93	0.01168
169	10.90	132.83	0.01273
196	9.57	142.40	0.01364
225	14.36	156.76	0.01502
256	10.90	167.66	0.01606
289	14.10	181.76	0.01742
324	10.10	191.86	0.01838
361	12.55	204.42	0.01959
400	14.10	218.51	0.02094
441	12.23	230.75	0.02211
484	10.64	241.38	0.02313
529	7.71	249.09	0.02387
576	8.51	257.59	0.02468
625	11.17	268.76	0.02575
676	15.96	284.72	0.02728
729	12.27	296.99	0.02846
784	11.25	308.25	0.02953
841	14.83	323.07	0.03095
900	13.04	336.11	0.03220
961	10.74	346.85	0.03323
1024	10.23	357.08	0.03421
1089	13.29	370.37	0.03549
1156	12.78	383.16	0.03671
1225	10.74	393.90	0.03774
1296	12.78	406.68	0.03897
1369	10.48	417.16	0.03997
1444	7.68	424.84	0.04071
1521	11.76	436.60	0.04183
1600	12.27	448.87	0.04301
1681	21.21	470.08	0.04504
1764	10.74	480.82	0.04607
1932	17.89	498.71	0.04778

Appendix Hii: DLT t_n = 1B Data – Zinc (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	9.26	507.97	0.04867
2268	9.26	517.23	0.04956
2436	10.11	527.34	0.05053
2604	10.54	537.88	0.05154
2772	10.11	547.99	0.05250
2940	8.41	556.40	0.05331
3108	7.98	564.38	0.05408
3276	10.75	575.13	0.05511
3444	12.24	587.37	0.05628
3612	11.60	598.97	0.05739
3780	10.96	609.93	0.05844
3948	9.69	619.62	0.05937
4116	7.77	627.39	0.06011
4284	11.60	638.99	0.06122
4452	13.94	652.92	0.06256
4620	15.03	667.96	0.06400
4956	11.85	679.81	0.06513
5292	15.67	695.48	0.06664
5628	13.76	709.24	0.06795
5964	10.10	719.34	0.06892
6300	3.91	723.25	0.06930
6636	3.43	726.67	0.06962
6972	4.38	731.06	0.07004
7308	3.11	734.17	0.07034
7644	2.32	736.48	0.07056
7980	0.57	737.05	0.07062
8316	0.73	737.77	0.07069
8652	2.32	740.09	0.07091

Appendix Hiii: DLT t_n = 4A Data – Zinc

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	10.17	10.17	0.00097
4	9.02	19.19	0.00184
16	9.17	28.37	0.00272
36	12.51	40.87	0.00391
64	13.11	53.98	0.00517
100	14.89	68.87	0.00659
144	13.78	82.64	0.00791
196	12.66	95.30	0.00912
256	10.87	106.18	0.01016
324	12.66	118.84	0.01138
400	18.24	137.07	0.01312
484	11.77	148.84	0.01425
576	13.33	162.17	0.01552
676	14.22	176.39	0.01688
784	12.88	189.27	0.01812
900	15.78	205.06	0.01963
1024	14.68	219.73	0.02103
1156	16.26	235.99	0.02259
1296	21.48	257.47	0.02465
1444	14.90	272.37	0.02607
1600	15.81	288.18	0.02759
1764	16.49	304.67	0.02916
1932	18.30	322.98	0.03092
2100	11.73	334.70	0.03204
2268	12.41	347.11	0.03323
2436	14.45	361.56	0.03461
2604	12.18	373.74	0.03577
2772	8.10	381.84	0.03655
2940	11.73	393.57	0.03767
3108	11.50	405.07	0.03877
3276	15.36	420.42	0.04024
3444	12.86	433.29	0.04147
3612	4.47	437.76	0.04190
3780	14.45	452.21	0.04329
3948	12.09	464.30	0.04444
4116	10.91	475.21	0.04549
4284	11.91	487.12	0.04663
4452	18.44	505.56	0.04839
4620	15.83	521.39	0.04991
4956	16.28	537.67	0.05147
5292	14.94	552.61	0.05290
5628	8.91	561.52	0.05375
5964	6.01	567.53	0.05432
6300	3.78	571.31	0.05469

Appendix Hiii: DLT t_n = 4A Data – Zinc (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	5.56	576.87	0.05522
6972	5.56	582.44	0.05575
7308	4.22	586.66	0.05616
7644	3.78	590.44	0.05652
7980	2.21	592.65	0.05673
8316	1.99	594.64	0.05692
8652	2.44	597.08	0.05715

Appendix Hiv: DLT t_n = 4B Data – Zinc

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	5.84	5.84	0.00056
4	8.72	14.56	0.00139
16	13.26	27.82	0.00266
36	17.20	45.02	0.00431
64	15.34	60.36	0.00578
100	17.79	78.15	0.00748
144	21.81	99.96	0.00957
196	19.80	119.76	0.01146
256	18.46	138.22	0.01323
324	18.91	157.12	0.01504
400	18.01	175.14	0.01676
484	18.91	194.04	0.01857
576	18.01	212.06	0.02030
676	18.46	230.52	0.02207
784	16.45	246.97	0.02364
900	18.46	265.43	0.02541
1024	11.73	277.16	0.02653
1156	17.63	294.80	0.02822
1296	21.77	316.56	0.03030
1444	16.65	333.21	0.03190
1600	17.44	350.65	0.03356
1764	21.96	372.61	0.03567
1932	22.75	395.36	0.03784
2100	16.06	411.42	0.03938
2268	17.24	428.67	0.04103
2436	22.75	451.42	0.04321
2604	17.04	468.46	0.04484
2772	23.14	491.60	0.04706
2940	20.78	512.39	0.04905
3108	25.11	537.50	0.05145
3276	20.98	558.48	0.05346
3444	25.11	583.59	0.05586
3612	20.59	604.18	0.05783
3780	21.57	625.75	0.05990
3948	24.72	650.47	0.06226
4116	18.22	668.69	0.06401
4284	22.36	691.05	0.06615
4452	28.65	719.70	0.06889
4620	28.56	748.26	0.07162
4956	32.80	781.07	0.07476
5292	36.60	817.66	0.07827
5628	29.45	847.12	0.08109
5964	10.92	858.04	0.08213
6300	9.14	867.17	0.08301

Appendix Hiv: DLT t_n = 4B Data – Zinc (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	8.69	875.86	0.08384
6972	8.24	884.11	0.08463
7308	8.24	892.35	0.08542
7644	4.00	896.35	0.08580
7980	1.32	897.67	0.08593
8316	1.10	898.77	0.08603
8652	2.66	901.43	0.08629

Appendix Hv: DLT t_n = 1A Electrode Data

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0.008	30	490	6.44
1	350	356	8.67
4	1150	298.8	10.5
9	2100	268	10.58
16	2300	270.6	10.8
25	2300	268.9	11
36	2000	260	11
49	1730	266	11
64	1450	224.6	11.2
81	1180	241.4	11.1
100	970	242.2	11.6
121	910	251.5	11.3
144	840	238.1	11.3
169	790	253	11.6
196	780	238	11.5
225	750	247	11.4
256	740	261	11.9
289	770	236.5	11.5
324	770	253	11.4
361	780	252	11.5
400	830	250	11.5
441	840	238	11.47
484	840	214	11.7
529	830	251	11.8
576	800	228	11.9
625	850	232	11.9
676	800	232	12.1
729	850	157	12.1
784	840	230	12.3
841	840	218	12.4
900	780	219	12.5
961	840	236.5	12.45
1024	840	250	12.6
1089	880	237.9	11.1
1156	900	243.9	11.5
1225	910	242.1	11.7
1296	750	268.1	11.7
1369	740	256.5	11.8
1444	710	261.2	11.6
1521	710	267	11.3
1600	770	268.8	11.6
1681	730	271.8	11.6
1764	740	272.5	11.6
1932	1050	269.2	12.25

Appendix Hv: DLT t_n = 1A Electrode Data (contd.)

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
2100	970	281.2	11.7
2268	910	305.1	11.5
2436	940	247	12
2604	880	259	12.1
2772	840	258.5	12.3
2940	770	268	11.8
3108	790	258.8	11.7
3276	720	270	11.5
3444	750	264	11.6
3612	630	262	11.3
3780	630	260	12.1
3948	660	261	11.4
4116	590	268.3	10.9
4284	550	243	11.8
4452	600	260	11.4
4620	570	259.5	11.7
4956	820	246.5	12.3
5292	680	227.3	11.4
5628	670	226.8	11.6
5964	580	242.5	12.2
6300	510	236.7	12.5
6636	530	226.1	11.8
6972	480	221.7	12.4
7308	460	229.2	12.6
7644	470	232.7	12.75
7980	450	241.7	12.65
8316	430	230.3	12.3
8652	450	236.8	12.5

Appendix Hvi: DLT t_n = 1B Electrode Data

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0.008	40	525	6.11
1	390	345	9
4	1140	283.2	10.5
9	1960	262.5	10.66
16	2300	262.1	10.8
25	2300	261.6	10.8
36	1970	252.6	11
49	1785	246	11
64	1520	227	11.2
81	1190	245	11.1
100	980	242	11.5
121	930	245.3	11.45
144	850	240	11.3
169	820	242.5	11.2
196	780	232.3	11.5
225	770	240	11.5
256	740	253	11.9
289	780	234.8	11.4
324	780	248.5	11.3
361	790	247.3	11.5
400	820	243	11.5
441	860	244.7	11.5
484	840	227.5	11.9
529	810	248.5	11.8
576	790	234.3	12.1
625	820	228.5	12.1
676	780	231	12
729	830	162	12.3
784	850	228	12.3
841	850	218.8	12.4
900	750	218.5	12.5
961	830	234.5	12.6
1024	840	255	12.7
1089	880	239.4	11.6
1156	900	243.5	11.5
1225	910	241.3	11.7
1296	780	255	11.6
1369	810	256.2	11.8
1444	795	262	11.6
1521	780	259	11.4
1600	800	265.7	11.6
1681	780	269.6	11.65
1764	760	270	11.7
1932	1170	263.4	12.3

Appendix Hvi: DLT t_n = 1B Electrode Data (contd.)

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
2100	1010	271.2	11.75
2268	980	287	11.7
2436	1000	241	12
2604	930	252	12.1
2772	890	253	12.4
2940	900	260	11.8
3108	830	254.9	11.5
3276	810	262	11.6
3444	830	248	11.6
3612	730	247.1	11.4
3780	780	254	12.3
3948	680	250	11.6
4116	700	264.1	11.1
4284	630	236	11.9
4452	650	251	11.5
4620	620	254	11.8
4956	980	232.2	12.3
5292	920	215.5	11.6
5628	850	220.4	11.7
5964	730	231.9	12.5
6300	660	223.7	12.8
6636	540	223.8	11.8
6972	520	215.4	12.5
7308	480	220.2	12.65
7644	510	227.4	12.75
7980	440	237.6	12.65
8316	430	228.6	12.25
8652	440	231.7	12.45

Appendix Hvii: DLT t_n = 4A Electrode Data

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0.008	30	380	7.88
4	1370	300	10.1
16	4000	251	11
36	4000	251	11
64	3000	242.5	11.3
100	1790	233	11.3
144	1500	231.6	11.3
196	1220	224.6	11.7
256	1140	247	11.9
324	1150	241.8	11.5
400	1190	236.5	11.6
484	1210	231	11.9
576	1200	228.4	12.3
676	1190	221	12.1
784	1300	210	12.5
900	1230	207	12.7
1024	1290	235	12.8
1156	1340	234	12.8
1296	1360	240.1	11.8
1444	1210	247	11.7
1600	1230	240.3	11.8
1764	1200	255.5	11.85
1932	1200	259.9	12.25
2100	1100	265.3	11.8
2268	1050	276.8	11.7
2436	1120	236.5	12
2604	1020	248	12.1
2772	950	252.3	12.2
2940	950	256.5	11.9
3108	900	252.5	11.5
3276	810	260.9	11.6
3444	860	234.8	11.6
3612	820	223.5	11.5
3780	790	253.2	12.3
3948	720	257.9	11.6
4116	670	264	11.1
4284	630	236	11.86
4452	640	247	11.5
4620	630	255	11.8
4956	820	237.3	12.2
5292	770	223.1	11.47
5628	710	224.6	11.7
5964	620	234.2	12.5
6300	560	228.6	12.6

Appendix Hvii: DLT t_n = 4A Electrode Data (contd.)

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
6636	520	222.3	11.8
6972	460	216.4	12.44
7308	460	221.2	12.65
7644	410	231.9	12.6
7980	390	240.2	12.5
8316	350	233.3	12.1
8652	380	237.7	12.35

Appendix Hviii: DLT t_n = 4B Electrode Data

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
0.008	30	530	6.33
4	3200	268.8	10.5
16	5200	242.5	11.1
36	3400	238.8	11.2
64	2200	235	11.5
100	1500	230	11.4
144	1480	224	11.45
196	1240	222	11.7
256	1280	251.2	12
324	1340	235.2	11.5
400	1410	233	11.7
484	1470	226.5	12
576	1370	225	12.4
676	1360	217	12.4
784	1400	220	12.5
900	1380	202.2	12.7
1024	1440	230	13
1156	1470	229.2	11.7
1296	1480	233.5	11.8
1444	1370	235.7	11.7
1600	1430	247.6	11.6
1764	1360	252	11.9
1932	1400	252.5	12.3
2100	1320	258	11.95
2268	1200	261	11.8
2436	1320	230	12.2
2604	1180	238	12.3
2772	1160	244.3	12.5
2940	1050	250	11.6
3108	1150	247.5	11.6
3276	1070	261	11.8
3444	1120	222.9	11.8
3612	1020	216	11.7
3780	1040	238.6	12.4
3948	950	250.2	11.8
4116	980	247	11.4
4284	910	230	12.14
4452	940	236	11.55
4620	950	242	12
4956	1360	224.3	12.5
5292	1330	208.8	11.76
5628	1250	213.1	12
5964	1040	222.4	12.8
6300	950	212.4	13.1

Appendix Hviii: DLT t_n = 4B Electrode Data (contd.)

Time (hours)	Conductivity (μScm^{-1})	Redox Potential (mV)	pH
6636	880	207	12.1
6972	670	207.6	12.8
7308	600	218.2	12.85
7644	630	223.5	12.95
7980	530	232.1	12.85
8316	460	226.6	12.3
8652	460	230.8	12.5

Appendix I: Large Column Data – Copper

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	18.98	0.02	0.000003
7	11593.62	11.61	0.001644
14	1176.84	12.79	0.001810
21	1415.87	14.21	0.002011
28	1478.77	15.68	0.002220
35	3538.86	19.22	0.002721
42	5907.16	25.13	0.003557
49	8272.33	33.40	0.004728
56	9360.55	42.76	0.006053
63	10140.55	52.90	0.007489
70	9983.29	62.89	0.008902
77	9291.36	72.18	0.010217
84	9102.65	81.28	0.011506
91	9480.07	90.76	0.012847
98	9102.65	99.86	0.014136
105	10593.46	110.46	0.015636
112	9134.10	119.59	0.016928
119	7215.55	126.81	0.017950
126	8071.03	134.88	0.019092
133	6687.16	141.56	0.020039
140	5554.90	147.12	0.020825
147	6989.10	154.11	0.021815
154	6385.23	160.49	0.022718
161	5781.36	166.28	0.023537
168	5479.42	171.75	0.024312
175	5403.94	177.16	0.025077
182	4649.10	181.81	0.025735
189	6624.26	188.43	0.026673
196	3831.36	192.26	0.027215
203	4535.87	196.80	0.027858
210	3139.42	199.94	0.028302
217	3365.87	203.30	0.028778
224	2158.13	205.46	0.029084
231	2485.23	207.95	0.029436
238	2736.84	210.68	0.029823
245	2862.65	213.55	0.030228
252	3240.06	216.79	0.030687
259	3202.32	219.99	0.031140
266	3012.89	223.00	0.031567
273	2896.27	225.90	0.031977
280	2884.36	228.78	0.032385
287	2563.31	231.35	0.032748
294	2444.88	233.79	0.033094
301	1987.26	235.78	0.033375
308	1744.33	237.52	0.033622

Appendix I: Large Column Data – Copper (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
315	1955.66	239.48	0.033899
322	1993.66	241.47	0.034181
329	2003.33	243.48	0.034465
336	1544.33	245.02	0.034683
343	1655.33	246.68	0.034918
350	1432.23	248.11	0.035120
357	1322.70	249.43	0.035308
364	1020.31	250.45	0.035452

Appendix Ji: ABLC100 Data – Copper

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	69.47	0.07	0.00375
1	0.00	0.07	0.00375
2	27.69	0.10	0.00524
3	42.00	0.14	0.00751
4	34.72	0.17	0.00938
5	17.91	0.19	0.01034
6	14.65	0.21	0.01113
7	24.94	0.23	0.01248
8	12.34	0.24	0.01314
9	10.93	0.25	0.01373
10	0.00	0.25	0.01373
11	23.17	0.28	0.01498
12	12.37	0.29	0.01565
13	18.20	0.31	0.01663
14	18.07	0.33	0.01761
16	22.49	0.35	0.01882
18	54.74	0.40	0.02177
20	29.95	0.43	0.02339
23	46.34	0.48	0.02589
26	64.61	0.54	0.02937
29	45.88	0.59	0.03184
32	49.42	0.64	0.03451
35	35.44	0.68	0.03642
38	64.88	0.74	0.03992
41	51.49	0.79	0.04270
44	84.99	0.88	0.04728
47	45.21	0.92	0.04972
50	68.80	0.99	0.05343
53	44.71	1.04	0.05584
56	64.07	1.10	0.05930
59	52.14	1.15	0.06211
62	87.36	1.24	0.06682
66	18.88	1.26	0.06784
70	41.60	1.30	0.07008
74	71.15	1.37	0.07392
78	69.04	1.44	0.07764
82	115.31	1.55	0.08386
86	115.73	1.67	0.09010
90	107.17	1.78	0.09588
94	39.07	1.82	0.09799
99	92.29	1.91	0.10297
102	58.81	1.97	0.10614
108	86.80	2.05	0.11082
114	127.39	2.18	0.11769
121	117.60	2.30	0.12403

Appendix Ji: ABLC100 Data – Copper (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
128	105.22	2.41	0.12971
135	116.80	2.52	0.13601
142	101.94	2.62	0.14150
149	85.04	2.71	0.14609
153	60.60	2.77	0.14936
160	183.20	2.95	0.15924
167	122.80	3.08	0.16586
174	89.20	3.16	0.17067
181	115.02	3.28	0.17688
188	195.01	3.47	0.18739
195	104.57	3.58	0.19303
202	151.79	3.73	0.20122
209	124.17	3.86	0.20792
216	194.09	4.05	0.21838
223	203.51	4.25	0.22936
230	89.96	4.34	0.23421
237	84.31	4.43	0.23876
244	55.12	4.48	0.24173
251	113.85	4.60	0.24787
258	201.46	4.80	0.25874
265	0.00	4.80	0.25874
272	108.04	4.91	0.26456
279	103.69	5.01	0.27015
286	170.58	5.18	0.27935
293	116.31	5.30	0.28563
300	119.73	5.42	0.29208
307	79.98	5.50	0.29640
314	138.56	5.63	0.30387
321	125.91	5.76	0.31066
328	214.98	5.98	0.32225
335	0.00	5.98	0.32225
342	72.04	6.05	0.32614
349	76.25	6.12	0.33025
356	87.09	6.21	0.33495
363	63.62	6.27	0.33838

Appendix Jii: ABLC180 Data – Copper

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	0.23	0.000	0.00001
1	13.10	0.013	0.00040
2	27.10	0.040	0.00121
3	24.80	0.065	0.00196
4	5.07	0.070	0.00211
5	33.95	0.104	0.00313
6	16.08	0.120	0.00362
7	12.17	0.133	0.00398
8	24.30	0.157	0.00471
9	22.02	0.179	0.00537
10	4.78	0.184	0.00552
11	32.82	0.216	0.00650
12	15.59	0.232	0.00697
13	2.67	0.235	0.00705
14	17.98	0.253	0.00759
15	20.01	0.273	0.00819
16	7.24	0.280	0.00841
17	13.71	0.294	0.00882
18	16.95	0.311	0.00933
19	14.98	0.326	0.00978
20	13.15	0.339	0.01018
21	22.55	0.361	0.01086
22	20.34	0.382	0.01147
23	17.22	0.399	0.01198
24	28.66	0.427	0.01285
48	63.07	0.491	0.01474
49	27.10	0.518	0.01555
50	14.84	0.532	0.01600
51	16.63	0.549	0.01650
52	15.54	0.565	0.01697
53	20.01	0.585	0.01757
54	27.10	0.612	0.01838
55	35.10	0.647	0.01944
56	15.87	0.663	0.01991
57	6.67	0.669	0.02011
60	20.00	0.689	0.02072
61	21.19	0.711	0.02135
62	4.68	0.715	0.02149
63	0.00	0.715	0.02149
64	22.79	0.738	0.02218
65	6.80	0.745	0.02238
66	6.88	0.752	0.02259
67	22.95	0.775	0.02328
68	12.53	0.787	0.02365
69	6.83	0.794	0.02386
70	12.13	0.806	0.02422

Appendix Jii: ABLC180 Data – Copper (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
71	7.40	0.814	0.02445
72	7.80	0.821	0.02468
73	20.47	0.842	0.02530
74	5.82	0.848	0.02547
75	8.54	0.856	0.02573
76	10.44	0.867	0.02604
80	52.39	0.919	0.02762
81	24.79	0.944	0.02836
82	6.24	0.950	0.02855
83	4.99	0.955	0.02870
84	18.74	0.974	0.02926
85	0.00	0.974	0.02926
86	11.61	0.985	0.02961
87	25.83	1.011	0.03039
88	9.11	1.020	0.03066
89	8.98	1.029	0.03093
90	27.51	1.057	0.03176
91	14.21	1.071	0.03218
92	26.01	1.097	0.03297
93	10.97	1.108	0.03329
94	18.12	1.126	0.03384
95	30.38	1.157	0.03475
96	16.02	1.173	0.03523
97	16.32	1.189	0.03572
98	31.78	1.221	0.03668
99	14.54	1.235	0.03712
100	24.01	1.259	0.03784
104	107.30	1.366	0.04106
108	49.48	1.416	0.04255
113	57.07	1.473	0.04426
123	171.31	1.644	0.04941
130	57.95	1.702	0.05115
137	115.68	1.818	0.05463
144	81.47	1.899	0.05708
151	215.20	2.115	0.06354
158	72.08	2.187	0.06571
165	93.51	2.280	0.06852
172	108.43	2.389	0.07178
179	130.52	2.519	0.07570
185	108.88	2.628	0.07897
193	161.18	2.789	0.08381
200	141.35	2.931	0.08806
207	132.20	3.063	0.09203
215	20.00	3.083	0.09264
222	39.79	3.123	0.09383
229	0.00	3.123	0.09383

Appendix Jii: ABLC180 Data – Copper (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
236	105.93	3.229	0.09701
243	112.30	3.341	0.10039
250	113.31	3.454	0.10379
257	110.64	3.565	0.10712
264	84.29	3.649	0.10965
271	105.28	3.754	0.11281
278	59.07	3.813	0.11459
285	64.51	3.878	0.11653
292	71.55	3.949	0.11868
299	85.90	4.035	0.12126
306	98.59	4.134	0.12422
313	83.61	4.218	0.12673
320	76.32	4.294	0.12903
327	77.27	4.371	0.13135
334	78.61	4.450	0.13371
341	0.00	4.450	0.13371
348	0.00	4.450	0.13371
355	70.41	4.520	0.13583
362	74.79	4.595	0.13807

Appendix Jiii: LCC100 Data – Copper

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0	8.52	8.52	0.00046
1	3.46	11.98	0.00065
8	4.70	16.68	0.00090
15	1.68	18.36	0.00099
22	3.23	21.59	0.00116
29	26.79	48.38	0.00261
36	6.30	54.68	0.00295
44	7.10	61.78	0.00333
51	23.37	85.15	0.00459
58	10.03	95.18	0.00513
65	15.86	111.04	0.00599
72	6.70	117.74	0.00635
79	8.97	126.71	0.00683
86	27.04	153.74	0.00829
93	17.68	171.42	0.00924
100	8.48	179.90	0.00970
107	22.17	202.07	0.01090
114	6.52	208.59	0.01125
121	10.60	219.19	0.01182
128	4.82	224.01	0.01208
135	3.27	227.28	0.01226
142	5.79	233.07	0.01257
149	5.40	238.48	0.01286
156	5.65	244.12	0.01317
163	16.38	260.51	0.01405
170	8.17	268.68	0.01449
177	6.67	275.35	0.01485
184	13.10	288.45	0.01556
191	32.37	320.82	0.01730
198	22.21	343.04	0.01850
205	20.85	363.89	0.01963
212	19.49	383.38	0.02068
219	20.08	403.46	0.02176
226	20.61	424.07	0.02287
233	20.46	444.54	0.02397
240	24.16	468.69	0.02528
247	23.57	492.27	0.02655
254	22.79	515.06	0.02778
261	22.73	537.79	0.02900
268	22.31	560.09	0.03021
275	15.91	576.00	0.03106
282	10.07	586.08	0.03161
289	17.78	603.86	0.03257
296	15.55	619.40	0.03341
303	6.12	625.52	0.03374
310	3.98	629.50	0.03395

Appendix Jiii: LCC100 Data – Copper (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
317	10.56	640.06	0.03452
324	10.49	650.55	0.03509
331	11.90	662.45	0.03573
338	5.12	667.57	0.03600
345	4.44	672.01	0.03624
352	8.35	680.36	0.03669
359	3.62	683.98	0.03689
366	3.98	687.96	0.03710

Appendix Ki: DLT t_n = 1A Data – Copper

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	2.96	2.96	0.00035
1	1.30	4.25	0.00050
4	0.92	5.17	0.00060
9	0.00	5.17	0.00060
16	0.81	5.99	0.00070
25	1.24	7.23	0.00084
36	1.24	8.47	0.00099
49	1.35	9.82	0.00115
64	2.04	11.86	0.00138
81	2.92	14.78	0.00172
100	2.18	16.96	0.00198
121	1.89	18.85	0.00220
144	0.00	18.85	0.00220
169	0.00	18.85	0.00220
196	0.00	18.85	0.00220
225	0.00	18.85	0.00220
256	0.00	18.85	0.00220
289	0.00	18.85	0.00220
324	0.00	18.85	0.00220
361	0.00	18.85	0.00220
400	0.00	18.85	0.00220
441	0.00	18.85	0.00220
484	0.00	18.85	0.00220
529	1.39	20.23	0.00236
576	0.77	21.00	0.00245
625	0.00	21.00	0.00245
676	0.00	21.00	0.00245
729	0.25	21.25	0.00248
784	0.00	21.25	0.00248
841	0.00	21.25	0.00248
900	0.08	21.33	0.00249
961	0.00	21.33	0.00249
1024	0.76	22.08	0.00258
1089	0.42	22.50	0.00263
1156	0.00	22.50	0.00263
1225	0.42	22.91	0.00267
1296	0.76	23.67	0.00276
1369	0.93	24.60	0.00287
1444	0.76	25.35	0.00296
1521	0.42	25.77	0.00301
1600	2.11	27.88	0.00325
1681	0.25	28.13	0.00328
1764	0.76	28.88	0.00337
1932	1.77	30.66	0.00358

Appendix Ki: DLT t_n = 1A Data – Copper (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	3.39	34.05	0.00397
2268	3.08	37.13	0.00433
2436	3.08	40.20	0.00469
2604	5.24	45.44	0.00530
2772	1.85	47.29	0.00552
2940	2.77	50.06	0.00584
3108	1.69	51.75	0.00604
3276	3.08	54.83	0.00640
3444	3.54	58.37	0.00681
3612	0.92	59.30	0.00692
3780	3.85	63.14	0.00737
3948	2.46	65.61	0.00766
4116	1.23	66.84	0.00780
4284	3.70	70.53	0.00823
4452	2.46	73.00	0.00852
4620	2.38	75.38	0.00880
4956	3.16	78.53	0.00917
5292	3.00	81.53	0.00952
5628	2.38	83.92	0.00980
5964	2.69	86.61	0.01011
6300	1.76	88.37	0.01032
6636	2.54	90.90	0.01061
6972	3.00	93.90	0.01096
7308	3.00	96.90	0.01131
7644	1.61	98.51	0.01150
7980	4.24	102.75	0.01199
8316	1.92	104.66	0.01222
8652	2.07	106.74	0.01246

Appendix Kii: DLT t_n = 1B Data – Copper

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	1.67	1.67	0.00019
1	1.24	2.91	0.00034
4	0.92	3.83	0.00044
9	0.00	3.83	0.00044
16	0.92	4.76	0.00055
25	1.51	6.27	0.00072
36	2.53	8.79	0.00101
49	1.88	10.68	0.00123
64	3.51	14.19	0.00163
81	4.62	18.80	0.00217
100	4.54	23.35	0.00269
121	2.77	26.12	0.00301
144	0.00	26.12	0.00301
169	0.00	26.12	0.00301
196	0.00	26.12	0.00301
225	0.00	26.12	0.00301
256	0.00	26.12	0.00301
289	0.00	26.12	0.00301
324	0.00	26.12	0.00301
361	0.00	26.12	0.00301
400	0.00	26.12	0.00301
441	0.00	26.12	0.00301
484	0.00	26.12	0.00301
529	1.69	27.81	0.00321
576	1.23	29.04	0.00335
625	0.77	29.81	0.00344
676	0.00	29.81	0.00344
729	0.42	30.23	0.00348
784	0.59	30.82	0.00355
841	0.00	30.82	0.00355
900	0.00	30.82	0.00355
961	0.00	30.82	0.00355
1024	0.59	31.40	0.00362
1089	1.43	32.84	0.00378
1156	0.25	33.08	0.00381
1225	0.76	33.84	0.00390
1296	0.42	34.26	0.00395
1369	0.59	34.84	0.00402
1444	1.60	36.45	0.00420
1521	0.25	36.69	0.00423
1600	0.59	37.28	0.00430
1681	1.43	38.71	0.00446
1764	0.76	39.47	0.00455
1932	1.43	40.91	0.00471

Appendix Kii: DLT t_n = 1B Data – Copper (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	3.08	43.98	0.00507
2268	4.62	48.60	0.00560
2436	1.69	50.30	0.00580
2604	2.62	52.91	0.00610
2772	3.70	56.61	0.00652
2940	4.00	60.61	0.00698
3108	2.62	63.23	0.00729
3276	2.46	65.69	0.00757
3444	0.92	66.62	0.00768
3612	2.77	69.39	0.00800
3780	1.85	71.24	0.00821
3948	1.69	72.93	0.00840
4116	2.77	75.70	0.00872
4284	0.92	76.62	0.00883
4452	1.69	78.32	0.00903
4620	3.40	81.72	0.00942
4956	2.90	84.62	0.00975
5292	2.39	87.01	0.01003
5628	2.52	89.53	0.01032
5964	1.26	90.79	0.01046
6300	2.27	93.06	0.01072
6636	2.02	95.07	0.01096
6972	3.02	98.10	0.01130
7308	2.14	100.24	0.01155
7644	2.14	102.38	0.01180
7980	1.76	104.14	0.01200
8316	1.26	105.40	0.01215
8652	2.52	107.92	0.01244

Appendix Kiii: DLT t_n = 4A Data – Copper

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	2.21	2.21	0.00026
4	1.03	3.23	0.00037
16	0.00	3.23	0.00037
36	4.24	7.48	0.00086
64	1.27	8.75	0.00101
100	1.56	10.31	0.00119
144	1.13	11.44	0.00132
196	0.00	11.44	0.00132
256	1.42	12.86	0.00149
324	0.00	12.86	0.00149
400	1.85	14.71	0.00170
484	0.00	14.71	0.00170
576	1.27	15.99	0.00185
676	0.99	16.97	0.00196
784	2.28	19.26	0.00223
900	1.42	20.68	0.00239
1024	3.78	24.46	0.00283
1156	3.26	27.72	0.00321
1296	5.85	33.57	0.00388
1444	4.47	38.04	0.00440
1600	5.16	43.20	0.00500
1764	5.85	49.05	0.00567
1932	4.47	53.52	0.00619
2100	3.61	57.13	0.00661
2268	4.99	62.11	0.00719
2436	4.81	66.93	0.00774
2604	3.44	70.36	0.00814
2772	3.95	74.32	0.00860
2940	4.30	78.61	0.00909
3108	4.47	83.08	0.00961
3276	4.81	87.90	0.01017
3444	3.78	91.68	0.01061
3612	3.44	95.11	0.01100
3780	5.23	100.34	0.01161
3948	4.26	104.61	0.01210
4116	2.75	107.35	0.01242
4284	3.16	110.51	0.01278
4452	2.19	112.70	0.01304
4620	1.26	113.96	0.01318
4956	1.43	115.39	0.01335
5292	2.64	118.03	0.01365
5628	1.43	119.46	0.01382
5964	1.95	121.41	0.01404
6300	2.29	123.70	0.01431

Appendix Kiii: DLT t_n = 4A Data – Copper (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	2.12	125.82	0.01456
6972	2.12	127.95	0.01480
7308	1.60	129.55	0.01499
7644	2.12	131.67	0.01523
7980	0.00	131.67	0.01523
8316	1.60	133.27	0.01542
8652	1.43	134.70	0.01558

Appendix Kiv: DLT t_n = 4B Data – Copper

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	1.40	1.40	0.00016
4	0.00	1.40	0.00016
16	0.00	1.40	0.00016
36	0.92	2.32	0.00027
64	2.43	4.75	0.00055
100	3.15	7.90	0.00092
144	0.99	8.89	0.00103
196	2.43	11.32	0.00132
256	0.41	11.73	0.00136
324	2.28	14.01	0.00163
400	1.56	15.57	0.00181
484	1.85	17.42	0.00203
576	0.70	18.12	0.00211
676	1.56	19.68	0.00229
784	2.72	22.40	0.00260
900	0.41	22.81	0.00265
1024	2.98	25.79	0.00300
1156	3.67	29.46	0.00343
1296	6.31	35.77	0.00416
1444	2.42	38.19	0.00444
1600	4.92	43.11	0.00501
1764	4.64	47.76	0.00555
1932	5.06	52.82	0.00614
2100	4.78	57.60	0.00670
2268	5.61	63.21	0.00735
2436	2.01	65.22	0.00758
2604	4.09	69.31	0.00806
2772	3.67	72.98	0.00849
2940	2.98	75.96	0.00883
3108	3.53	79.49	0.00924
3276	1.45	80.95	0.00941
3444	3.26	84.20	0.00979
3612	2.42	86.63	0.01007
3780	2.28	88.91	0.01034
3948	3.39	92.31	0.01073
4116	3.81	96.12	0.01118
4284	3.26	99.37	0.01156
4452	3.12	102.49	0.01192
4620	1.95	104.44	0.01214
4956	2.64	107.08	0.01245
5292	3.16	110.24	0.01282
5628	2.99	113.22	0.01317
5964	2.47	115.69	0.01345
6300	2.29	117.99	0.01372

Appendix Kiv: DLT t_n = 4B Data – Copper (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
6636	2.29	120.28	0.01399
6972	2.12	122.40	0.01423
7308	1.95	124.35	0.01446
7644	1.60	125.95	0.01465
7980	1.26	127.21	0.01479
8316	1.43	128.64	0.01496
8652	1.26	129.90	0.01510

Appendix L: Large Column Data – Lead

Time (days)	Mass Leached (mg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	0.11	0.11	0.000003
7	1292.54	1292.65	0.039078
14	2172.52	3465.17	0.104755
21	1405.73	4870.91	0.147252
28	836.12	5707.03	0.172528
35	503.85	6210.87	0.187760
42	534.88	6745.76	0.203930
49	452.73	7198.48	0.217616
56	526.75	7725.23	0.233540
63	454.32	8179.55	0.247275
70	445.42	8624.98	0.260740
77	419.86	9044.84	0.273433
84	430.82	9475.66	0.286457
91	394.31	9869.96	0.298377
98	430.82	10300.78	0.311401
105	483.95	10784.73	0.326031
112	454.32	11239.05	0.339766
119	372.40	11611.45	0.351024
126	419.86	12031.31	0.363717
133	390.65	12421.97	0.375526
140	439.58	12861.55	0.388815
147	464.41	13325.96	0.402855
154	443.60	13769.56	0.416265
161	518.45	14288.01	0.431939
168	492.89	14780.90	0.446839
175	580.53	15361.43	0.464389
182	496.54	15857.97	0.479400
189	612.34	16470.31	0.497911
196	668.30	17138.61	0.518115
203	704.67	17843.28	0.539417
210	810.56	18653.84	0.563921
217	894.54	19548.39	0.590964
224	759.44	20307.83	0.613923
231	689.80	20997.63	0.634776
238	715.77	21713.40	0.656414
245	712.06	22425.46	0.677941
252	804.76	23230.23	0.702269
259	793.63	24023.86	0.726262
266	765.69	24789.55	0.749409
273	796.51	25586.06	0.773488
280	774.58	26360.63	0.796904
287	773.27	27133.90	0.820281
294	839.49	27973.39	0.845659
301	857.24	28830.63	0.871574
308	893.87	29724.49	0.898596

Appendix L: Large Column Data –Lead (contd.)

Time (days)	Mass Leached (mg)	Cumulative Mass Leached (mg)	Cumulative % Leached
315	900.57	30625.07	0.925822
322	808.97	31434.03	0.950277
329	840.31	32274.34	0.975681
336	869.71	33144.05	1.001973
343	904.22	34048.27	1.029308
350	928.66	34976.94	1.057382
357	978.24	35955.18	1.086955
364	944.85	36900.03	1.115519

Appendix Mi: ABLC100 Data – Lead

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	2.11	2.11	0.02432
1	28.35	30.46	0.35084
2	37.41	67.87	0.78170
3	37.46	105.33	1.21319
4	28.82	134.15	1.54516
5	16.98	151.13	1.74069
6	13.91	165.04	1.90092
7	11.86	176.90	2.03754
8	3.13	180.03	2.07363
9	2.55	182.59	2.10301
10	2.04	184.63	2.12651
11	5.29	189.92	2.18747
12	3.21	193.13	2.22446
13	3.27	196.40	2.26209
14	2.86	199.26	2.29506
16	5.04	204.30	2.35312
18	4.48	208.78	2.40467
20	3.53	212.31	2.44538
23	2.72	215.03	2.47676
26	2.70	217.73	2.50782
29	1.67	219.41	2.52710
32	1.64	221.05	2.54603
35	1.89	222.94	2.56784
38	1.42	224.37	2.58423
41	1.02	225.39	2.59603
44	0.80	226.19	2.60521
47	0.73	226.91	2.61357
50	0.75	227.66	2.62222
53	1.62	229.29	2.64093
56	0.44	229.73	2.64599
59	0.55	230.27	2.65230
62	1.19	231.47	2.66606
66	1.24	232.71	2.68034
70	0.86	233.57	2.69025
74	0.72	234.29	2.69851
78	0.49	234.78	2.70419
82	0.53	235.31	2.71032
86	0.49	235.81	2.71601
90	0.50	236.30	2.72172
94	0.41	236.71	2.72647
99	0.28	237.00	2.72973
102	0.10	237.10	2.73092
108	0.21	237.31	2.73330
114	0.30	237.60	2.73671
121	0.05	237.65	2.73726

Appendix Mi: ABLC100 Data – Lead (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
128	0.07	237.72	2.73808
135	0.05	237.77	2.73863
142	0.05	237.82	2.73918
149	0.06	237.88	2.73986
153	0.20	238.08	2.74219
160	0.08	238.16	2.74316
167	0.07	238.24	2.74400
174	0.08	238.32	2.74491
181	0.08	238.40	2.74585
188	0.09	238.48	2.74685
195	0.07	238.56	2.74771
202	0.08	238.63	2.74857
209	0.09	238.72	2.74959
216	0.10	238.82	2.75072
223	0.09	238.91	2.75171
230	0.09	238.99	2.75271
237	0.08	239.08	2.75366
244	0.09	239.17	2.75473
251	0.08	239.25	2.75566
258	0.10	239.34	2.75676
265	0.09	239.43	2.75776
272	0.08	239.51	2.75866
279	0.08	239.59	2.75963
286	0.07	239.67	2.76049
293	0.07	239.73	2.76125
300	0.08	239.81	2.76217
307	0.08	239.89	2.76304
314	0.07	239.96	2.76390
321	0.09	240.05	2.76492
328	0.07	240.12	2.76568
335	0.07	240.19	2.76647
342	0.06	240.25	2.76714
349	0.07	240.32	2.76800
356	0.07	240.39	2.76880
363	0.07	240.46	2.76961

Appendix Mii: ABLC180 Data – Lead

Time (days)	Mass Leached (mg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	0.00097	0.00097	0.00001
1	56.38	56.38	0.36181
2	97.54	153.92	0.98779
3	115.32	269.24	1.72785
4	120.25	389.50	2.49956
5	97.10	486.60	3.12270
6	77.44	564.04	3.61968
7	58.40	622.44	3.99448
8	45.09	667.53	4.28383
9	35.07	702.61	4.50891
10	27.69	730.30	4.68661
11	18.35	748.64	4.80434
12	13.31	761.95	4.88977
13	13.80	775.76	4.97835
14	14.64	790.40	5.07231
15	12.71	803.11	5.15389
16	10.85	813.96	5.22351
17	11.19	825.15	5.29533
18	7.32	832.47	5.34229
19	7.98	840.45	5.39349
20	7.36	847.81	5.44074
21	4.98	852.79	5.47271
22	3.87	856.66	5.49751
23	3.88	860.53	5.52239
24	3.02	863.56	5.54179
48	14.75	878.30	5.63642
49	8.10	886.40	5.68841
50	7.77	894.18	5.73830
51	3.91	898.09	5.76339
52	3.55	901.64	5.78617
53	2.99	904.63	5.80538
54	2.45	907.08	5.82110
55	2.37	909.45	5.83632
56	1.64	911.09	5.84685
57	1.61	912.70	5.85717
60	4.43	917.13	5.88559
61	1.24	918.37	5.89354
62	1.27	919.64	5.90168
63	1.33	920.97	5.91025
64	1.69	922.67	5.92112
65	1.76	924.43	5.93244
66	2.09	926.52	5.94585
67	1.77	928.29	5.95719
68	1.37	929.65	5.96596
69	1.04	930.69	5.97265
70	0.77	931.46	5.97757

Appendix Mii: ABLC180 Data – Lead (contd.)

Time (days)	Mass Leached (mg)	Cumulative Mass Leached (mg)	Cumulative % Leached
71	0.71	932.17	5.98211
72	0.75	932.92	5.98693
73	1.31	934.23	5.99536
74	1.60	935.83	6.00560
75	1.30	937.13	6.01395
76	1.11	938.24	6.02107
80	1.42	939.66	6.03017
81	0.79	940.45	6.03524
82	0.91	941.36	6.04108
83	0.85	942.21	6.04653
84	0.84	943.05	6.05192
85	0.97	944.01	6.05813
86	0.82	944.83	6.06338
87	0.67	945.50	6.06765
88	0.69	946.19	6.07211
89	0.63	946.82	6.07613
90	0.62	947.44	6.08013
91	0.71	948.16	6.08471
92	0.63	948.79	6.08877
93	0.77	949.55	6.09368
94	0.80	950.36	6.09883
95	0.78	951.14	6.10383
96	0.84	951.98	6.10922
97	0.88	952.85	6.11485
98	0.71	953.56	6.11939
99	0.68	954.24	6.12375
100	0.64	954.88	6.12786
104	1.07	955.95	6.13474
108	1.25	957.21	6.14279
113	0.69	957.90	6.14722
123	1.42	959.32	6.15634
130	0.55	959.87	6.15986
137	0.70	960.57	6.16435
144	1.04	961.61	6.17104
151	2.24	963.85	6.18541
158	0.53	964.37	6.18879
165	0.63	965.00	6.19283
172	0.40	965.40	6.19538
179	0.15	965.55	6.19631
185	0.12	965.67	6.19710
193	0.05	965.72	6.19740
200	0.02	965.74	6.19754
207	0.00	965.74	6.19754
215	0.00	965.74	6.19754
222	0.06	965.80	6.19792
229	0.04	965.84	6.19820

Appendix Mii: ABLC180 Data – Lead (contd.)

Time (days)	Mass Leached (mg)	Cumulative Mass Leached (mg)	Cumulative % Leached
236	0.04	965.88	6.19846
243	0.08	965.96	6.19899
250	0.07	966.03	6.19942
257	0.04	966.07	6.19965
264	0.03	966.09	6.19983
271	0.05	966.15	6.20017
278	0.00	966.15	6.20017
285	0.00	966.15	6.20017
292	0.00	966.15	6.20017
299	0.00	966.15	6.20017
306	0.04	966.19	6.20042
313	0.00	966.19	6.20042
320	0.04	966.23	6.20068
327	0.00	966.23	6.20068
334	0.67	966.90	6.20497
341	0.00	966.90	6.20497
348	0.00	966.90	6.20497
355	0.00	966.90	6.20497
362	0.00	966.90	6.20497

Appendix Miii: LCC100 Data – Lead

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	2344.80	2.34	0.02701
1	6829.08	9.17	0.10566
8	2872.46	12.05	0.13875
15	1002.65	13.05	0.15030
22	1213.93	14.26	0.16428
29	834.52	15.10	0.17389
36	808.78	15.91	0.18321
44	902.27	16.81	0.19360
51	693.60	17.50	0.20159
58	980.86	18.48	0.21289
65	904.98	19.39	0.22331
72	661.08	20.05	0.23092
79	712.57	20.76	0.23913
86	747.80	21.51	0.24774
93	625.85	22.14	0.25495
100	807.42	22.94	0.26425
107	875.17	23.82	0.27433
114	820.91	24.64	0.28379
121	727.10	25.37	0.29216
128	861.96	26.23	0.30209
135	879.55	27.11	0.31222
142	627.43	27.73	0.31945
149	832.64	28.57	0.32904
156	650.88	29.22	0.33654
163	645.02	29.86	0.34396
170	797.46	30.66	0.35315
177	791.60	31.45	0.36227
184	944.04	32.40	0.37314
191	645.02	33.04	0.38057
198	1073.04	34.11	0.39293
205	738.83	34.85	0.40144
212	914.73	35.77	0.41197
219	914.73	36.68	0.42251
226	1055.45	37.74	0.43467
233	1512.78	39.25	0.45209
240	1254.80	40.51	0.46654
247	1137.53	41.64	0.47965
254	879.55	42.52	0.48978
261	627.43	43.15	0.49700
268	832.64	43.98	0.50659
275	650.88	44.63	0.51409
282	645.02	45.28	0.52152
289	797.46	46.08	0.53070
296	791.60	46.87	0.53982
303	944.04	47.81	0.55070
310	645.02	48.46	0.55812

Appendix Miii: LCC100 Data – Lead (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
317	1073.04	49.53	0.57048
324	738.83	50.27	0.57899
331	914.73	51.18	0.58953
338	914.73	52.10	0.60007
345	904.98	53.00	0.61049
352	661.08	53.66	0.61810
359	712.57	54.38	0.62631
366	752.12	55.13	0.63497

Appendix Ni: DLT t_n = 1A Data – Lead

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	2.69	2.69	0.00007
1	0.00	2.69	0.00007
4	5.83	8.52	0.00021
9	15.73	24.25	0.00060
16	22.00	46.25	0.00115
25	13.10	59.35	0.00148
36	34.41	93.76	0.00234
49	28.77	122.53	0.00305
64	31.85	154.37	0.00385
81	36.95	191.33	0.00477
100	2.48	193.81	0.00483
121	67.05	260.85	0.00650
144	28.70	289.56	0.00722
169	81.75	371.30	0.00926
196	19.40	390.70	0.00974
225	80.17	470.87	0.01174
256	102.24	573.10	0.01429
289	75.51	648.62	0.01617
324	60.17	708.79	0.01767
361	48.79	757.58	0.01889
400	145.29	902.87	0.02251
441	128.96	1031.83	0.02572
484	114.61	1146.44	0.02858
529	84.42	1230.86	0.03069
576	153.70	1384.56	0.03452
625	170.03	1554.59	0.03876
676	102.73	1657.32	0.04132
729	67.02	1724.34	0.04299
784	121.04	1845.38	0.04601
841	243.52	2088.90	0.05208
900	120.05	2208.95	0.05507
961	110.15	2319.11	0.05782
1024	105.21	2424.31	0.06044
1089	195.76	2620.07	0.06532
1156	76.50	2696.58	0.06723
1225	52.75	2749.33	0.06854
1296	117.58	2866.91	0.07147
1369	11.97	2878.88	0.07177
1444	45.82	2924.70	0.07292
1521	25.02	2949.72	0.07354
1600	90.87	3040.59	0.07580
1681	28.89	3069.48	0.07652
1764	7.89	3077.37	0.07672
1932	165.58	3242.95	0.08085

Appendix Ni: DLT t_n = 1A Data – Lead (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
2100	86.18	3329.13	0.08300
2268	186.59	3515.72	0.08765
2436	91.79	3607.51	0.08994
2604	40.82	3648.33	0.09096
2772	39.29	3687.62	0.09194
2940	8.40	3696.02	0.09214
3108	9.01	3705.03	0.09237
3276	11.66	3716.70	0.09266
3444	46.93	3763.63	0.09383
3612	2.29	3765.92	0.09389
3780	3.51	3769.43	0.09397
3948	5.55	3774.97	0.09411
4116	1.47	3776.44	0.09415
4284	0.00	3776.44	0.09415
4452	0.04	3776.49	0.09415
4620	2.99	3779.47	0.09423
4956	0.00	3779.47	0.09423
5292	27.53	3807.00	0.09491
5628	0.00	3807.00	0.09491
5964	11.67	3818.67	0.09520
6300	7.52	3826.18	0.09539
6636	7.14	3833.32	0.09557
6972	21.86	3855.19	0.09611
7308	3.36	3858.55	0.09620
7644	3.36	3861.91	0.09628
7980	1.48	3863.39	0.09632
8316	3.17	3866.56	0.09640
8652	1.55	3868.11	0.09644

Appendix Nii: DLT t_n = 1B Data – Lead

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	0.00	0.00	0.00000
1	0.00	0.00	0.00000
4	4.32	4.32	0.00011
9	9.90	14.23	0.00035
16	18.99	33.22	0.00082
25	13.85	47.07	0.00116
36	15.61	62.67	0.00154
49	15.48	78.15	0.00192
64	35.13	113.28	0.00279
81	24.00	137.29	0.00338
100	30.39	167.67	0.00412
121	24.73	192.41	0.00473
144	30.28	222.69	0.00548
169	37.01	259.70	0.00639
196	36.82	296.52	0.00729
225	47.70	344.22	0.00846
256	14.45	358.67	0.00882
289	37.01	395.69	0.00973
324	26.52	422.21	0.01038
361	39.39	461.60	0.01135
400	51.27	512.86	0.01261
441	57.40	570.27	0.01402
484	62.35	632.62	0.01555
529	43.35	675.97	0.01662
576	37.90	713.87	0.01755
625	47.80	761.67	0.01873
676	72.05	833.72	0.02050
729	87.10	920.82	0.02264
784	109.02	1029.84	0.02532
841	115.13	1144.97	0.02815
900	76.90	1221.87	0.03004
961	80.98	1302.85	0.03203
1024	86.08	1388.93	0.03415
1089	154.38	1543.31	0.03795
1156	76.90	1620.22	0.03984
1225	57.03	1677.24	0.04124
1296	111.56	1788.81	0.04398
1369	31.54	1820.35	0.04476
1444	11.97	1832.32	0.04505
1521	32.36	1864.68	0.04585
1600	80.88	1945.56	0.04784
1681	10.75	1956.30	0.04810
1764	28.08	1984.38	0.04879
1932	242.04	2226.42	0.05474

Appendix Nii: DLT t_n = 1B Data – Lead (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	48.46	2274.89	0.05593
2268	119.31	2394.20	0.05887
2436	28.18	2422.38	0.05956
2604	68.85	2491.23	0.06125
2772	119.31	2610.54	0.06419
2940	24.00	2634.54	0.06478
3108	42.25	2676.78	0.06581
3276	23.29	2700.07	0.06639
3444	26.34	2726.41	0.06703
3612	7.18	2733.59	0.06721
3780	8.40	2741.99	0.06742
3948	1.06	2743.06	0.06744
4116	3.51	2746.56	0.06753
4284	1.27	2747.83	0.06756
4452	0.45	2748.28	0.06757
4620	8.52	2756.80	0.06778
4956	3.08	2759.88	0.06786
5292	54.89	2814.77	0.06921
5628	8.82	2823.59	0.06942
5964	15.47	2839.05	0.06980
6300	23.92	2862.98	0.07039
6636	4.44	2867.42	0.07050
6972	9.73	2877.14	0.07074
7308	1.87	2879.01	0.07079
7644	0.36	2879.37	0.07079
7980	1.57	2880.94	0.07083
8316	1.42	2882.36	0.07087
8652	1.27	2883.63	0.07090

Appendix Niii: DLT t_n = 4A Data – Lead

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	1.50	1.50	0.00004
4	5.45	6.96	0.00017
16	36.79	43.75	0.00108
36	89.34	133.09	0.00329
64	152.52	285.61	0.00706
100	141.95	427.55	0.01056
144	185.20	612.76	0.01514
196	205.39	818.15	0.02021
256	150.60	968.75	0.02393
324	219.09	1187.84	0.02935
400	297.67	1485.51	0.03670
484	299.11	1784.62	0.04409
576	259.94	2044.56	0.05051
676	294.79	2339.35	0.05780
784	357.27	2696.62	0.06662
900	335.64	3032.26	0.07492
1024	358.49	3390.75	0.08377
1156	262.87	3653.61	0.09027
1296	281.22	3934.83	0.09721
1444	306.33	4241.16	0.10478
1600	354.62	4595.78	0.11354
1764	399.05	4994.83	0.12340
1932	294.74	5289.57	0.13068
2100	134.41	5423.98	0.13400
2268	151.31	5575.30	0.13774
2436	305.85	5881.14	0.14530
2604	76.46	5957.60	0.14719
2772	23.82	5981.43	0.14778
2940	50.00	6031.42	0.14901
3108	37.63	6069.06	0.14994
3276	76.85	6145.90	0.15184
3444	16.39	6162.29	0.15225
3612	3.64	6165.93	0.15234
3780	5.18	6171.11	0.15246
3948	4.41	6175.52	0.15257
4116	3.25	6178.77	0.15265
4284	0.35	6179.12	0.15266
4452	0.74	6179.86	0.15268
4620	16.31	6196.17	0.15308
4956	0.00	6196.17	0.15308
5292	5.63	6201.79	0.15322
5628	0.00	6201.79	0.15322
5964	0.93	6202.72	0.15324
6300	0.93	6203.65	0.15327

Appendix Niii: DLT t_n = 4A Data – Lead (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
6636	0.00	6203.65	0.15327
6972	3.06	6206.71	0.15334
7308	0.00	6206.71	0.15334
7644	0.00	6206.71	0.15334
7980	1.78	6208.50	0.15339
8316	0.00	6208.50	0.15339
8652	0.00	6208.50	0.15339

Appendix Niv: DLT t_n = 4B Data – Lead

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	0.00	0.00	0.00000
4	25.01	25.01	0.00062
16	291.93	316.94	0.00787
36	385.38	702.32	0.01744
64	449.79	1152.11	0.02861
100	493.05	1645.16	0.04086
144	674.00	2319.16	0.05759
196	529.82	2848.98	0.07075
256	555.77	3404.75	0.08455
324	639.40	4044.15	0.10043
400	714.38	4758.53	0.11817
484	858.57	5617.09	0.13949
576	872.99	6490.08	0.16117
676	838.38	7328.46	0.18199
784	973.92	8302.38	0.20618
900	956.62	9258.99	0.22993
1024	816.14	10075.14	0.25020
1156	892.47	10967.61	0.27237
1296	1145.30	12112.91	0.30081
1444	1111.91	13224.82	0.32842
1600	1113.50	14338.32	0.35607
1764	1248.66	15586.98	0.38708
1932	1057.85	16644.83	0.41335
2100	803.42	17448.25	0.43330
2268	843.18	18291.43	0.45424
2436	1340.10	19631.52	0.48752
2604	608.63	20240.15	0.50264
2772	911.55	21151.70	0.52527
2940	873.39	22025.09	0.54696
3108	794.68	22819.77	0.56670
3276	549.00	23368.77	0.58033
3444	1057.85	24426.61	0.60660
3612	391.58	24818.19	0.61633
3780	446.44	25264.63	0.62741
3948	386.81	25651.43	0.63702
4116	453.59	26105.02	0.64828
4284	336.72	26441.74	0.65664
4452	246.08	26687.82	0.66275
4620	553.58	27241.40	0.67650
4956	608.06	27849.45	0.69160
5292	979.77	28829.22	0.71593
5628	469.20	29298.42	0.72759
5964	774.68	30073.10	0.74682
6300	213.91	30287.01	0.75214

Appendix Niv: DLT t_n = 4B Data – Lead (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	204.30	30491.31	0.75721
6972	110.30	30601.62	0.75995
7308	5.09	30606.71	0.76008
7644	14.17	30620.88	0.76043
7980	1.35	30622.24	0.76046
8316	1.35	30623.59	0.76049
8652	0.00	30623.59	0.76049

Appendix O: Large Column Data – Arsenic

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	17.71	0.02	0.00001
7	6335.62	6.35	0.00386
14	4263.25	10.62	0.00644
21	2700.90	13.32	0.00808
28	2236.63	15.55	0.00944
35	2081.02	17.64	0.01070
42	1907.08	19.54	0.01186
49	1780.57	21.32	0.01294
56	1701.51	23.02	0.01397
63	1693.07	24.72	0.01500
70	1587.65	26.31	0.01596
77	1461.14	27.77	0.01685
84	1418.98	29.19	0.01771
91	1408.43	30.59	0.01857
98	1334.64	31.93	0.01938
105	1313.55	33.24	0.02017
112	1271.39	34.51	0.02094
119	1155.42	35.67	0.02165
126	1292.47	36.96	0.02243
133	1585.43	38.55	0.02339
140	1446.36	39.99	0.02427
147	1620.20	41.61	0.02525
154	1533.28	43.15	0.02618
161	1123.01	44.27	0.02687
168	975.25	45.24	0.02746
175	992.63	46.24	0.02806
182	1114.32	47.35	0.02874
189	1053.48	48.41	0.02938
196	966.56	49.37	0.02996
203	888.33	50.26	0.03050
210	671.03	50.93	0.03091
217	853.56	51.78	0.03143
224	766.64	52.55	0.03189
231	679.72	53.23	0.03230
238	688.41	53.92	0.03272
245	655.03	54.57	0.03312
252	752.38	55.33	0.03358
259	710.66	56.04	0.03401
266	703.68	56.74	0.03443
273	746.67	57.49	0.03489
280	791.08	58.28	0.03537
287	765.50	59.04	0.03583
294	791.08	59.84	0.03631
301	791.08	60.63	0.03679
308	796.20	61.42	0.03727

Appendix O: Large Column Data –Arsenic (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
315	801.32	62.22	0.03776
322	816.67	63.04	0.03826
329	770.61	63.81	0.03872
336	748.33	64.56	0.03918
343	785.25	65.34	0.03966
350	715.33	66.06	0.04009
357	780.00	66.84	0.04056
364	784.24	67.62	0.04104

Appendix Pi: ABLC100 Data – Arsenic

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	99.30	0.10	0.02296
1	179.50	0.28	0.06446
2	111.08	0.39	0.09014
3	139.75	0.53	0.12246
4	295.48	0.83	0.19078
5	280.61	1.11	0.25566
6	312.30	1.42	0.32787
7	314.19	1.73	0.40051
8	298.43	2.03	0.46951
9	294.91	2.33	0.53770
10	281.73	2.61	0.60284
11	305.37	2.91	0.67344
12	232.64	3.15	0.72723
13	243.80	3.39	0.78360
14	277.58	3.67	0.84778
16	559.15	4.23	0.97707
18	531.82	4.76	1.10003
20	476.48	5.23	1.21020
23	823.88	6.06	1.40069
26	762.98	6.82	1.57710
29	786.24	7.61	1.75889
32	759.80	8.37	1.93457
35	899.39	9.27	2.14252
38	939.72	10.21	2.35980
41	954.11	11.16	2.58040
44	901.57	12.06	2.78886
47	930.83	12.99	3.00408
50	900.43	13.89	3.21227
53	943.14	14.84	3.43034
56	787.61	15.62	3.61244
59	854.07	16.48	3.80991
62	798.38	17.28	3.99451
66	1066.19	18.34	4.24103
70	1240.79	19.58	4.52792
74	1393.96	20.98	4.85022
78	1283.69	22.26	5.14703
82	1305.37	23.57	5.44885
86	1301.02	24.87	5.74966
90	1296.20	26.16	6.04936
94	1309.84	27.47	6.35221
99	1618.04	29.09	6.72633
102	1031.00	30.12	6.96471
108	2056.24	32.18	7.44014
114	1976.69	34.16	7.89717
121	2425.53	36.58	8.45799

Appendix Pi: ABLC100 Data – Arsenic (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
128	2214.15	38.79	8.96993
135	2128.11	40.92	9.46198
142	2318.08	43.24	9.99796
149	2002.16	45.24	10.46088
153	1172.69	46.42	10.73203
160	2079.48	48.50	11.21283
167	1869.18	50.36	11.64501
174	1654.62	52.02	12.02758
181	1756.41	53.78	12.43369
188	1514.92	55.29	12.78396
195	1404.66	56.70	13.10874
202	1575.11	58.27	13.47292
209	1637.50	59.91	13.85154
216	1644.75	61.55	14.23183
223	1510.99	63.06	14.58119
230	1490.88	64.55	14.92590
237	1496.53	66.05	15.27192
244	2214.16	68.27	15.78386
251	2533.92	70.80	16.36974
258	2323.91	73.12	16.90706
265	2030.22	75.15	17.37648
272	2438.92	77.59	17.94039
279	2074.50	79.67	18.42004
286	1804.43	81.47	18.83725
293	1710.47	83.18	19.23274
300	1581.94	84.76	19.59850
307	1629.33	86.39	19.97523
314	1521.80	87.91	20.32709
321	1831.74	89.75	20.75061
328	1339.81	91.09	21.06040
335	1325.26	92.41	21.36681
342	1457.24	93.87	21.70375
349	1254.70	95.12	21.99385
356	1239.25	96.36	22.28038
363	1085.32	97.45	22.53132

Appendix Pii: ABLC180 Data – Arsenic

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	20.30	0.02	0.00262
1	884.25	0.90	0.11653
2	581.81	1.49	0.19148
3	468.71	1.96	0.25186
4	483.00	2.44	0.31408
5	476.60	2.91	0.37548
6	548.78	3.46	0.44618
7	669.08	4.13	0.53237
8	679.21	4.81	0.61987
9	773.66	5.59	0.71954
10	833.66	6.42	0.82693
11	824.18	7.24	0.93311
12	844.98	8.09	1.04196
13	845.25	8.93	1.15085
14	789.45	9.72	1.25255
15	862.63	10.59	1.36368
16	861.06	11.45	1.47460
17	876.30	12.32	1.58749
18	687.28	13.01	1.67603
19	725.93	13.74	1.76955
20	747.92	14.48	1.86590
21	743.71	15.23	1.96171
22	752.86	15.98	2.05869
23	746.67	16.73	2.15488
24	570.37	17.30	2.22836
48	468.13	17.77	2.28867
49	602.10	18.37	2.36623
50	662.62	19.03	2.45159
51	736.34	19.77	2.54645
52	808.07	20.57	2.65055
53	815.19	21.39	2.75557
54	846.24	22.24	2.86458
55	977.50	23.21	2.99051
56	831.92	24.05	3.09768
57	870.86	24.92	3.20987
60	2635.25	27.55	3.54935
61	868.04	28.42	3.66118
62	882.49	29.30	3.77486
63	910.39	30.21	3.89215
64	917.68	31.13	4.01037
65	895.71	32.03	4.12575
66	906.08	32.93	4.24248
67	895.30	33.83	4.35782
68	792.13	34.62	4.45986
69	786.96	35.41	4.56124
70	730.63	36.14	4.65536

Appendix Pii: ABLC180 Data – Arsenic (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
71	728.75	36.87	4.74925
72	714.29	37.58	4.84126
73	883.91	38.46	4.95513
74	901.79	39.37	5.07131
75	830.94	40.20	5.17835
76	886.84	41.08	5.29260
80	2592.06	43.68	5.62652
81	862.22	44.54	5.73759
82	908.95	45.45	5.85469
83	893.84	46.34	5.96984
84	943.41	47.28	6.09137
85	920.97	48.21	6.21002
86	934.96	49.14	6.33046
87	954.24	50.09	6.45339
88	844.91	50.94	6.56224
89	825.35	51.76	6.66856
90	835.45	52.60	6.77619
91	832.29	53.43	6.88341
92	832.29	54.26	6.99063
93	869.86	55.13	7.10269
94	960.99	56.10	7.22648
95	981.45	57.08	7.35292
96	956.28	58.03	7.47611
97	991.05	59.02	7.60378
98	1018.85	60.04	7.73504
99	1004.13	61.05	7.86439
100	995.76	62.04	7.99267
104	3498.50	65.54	8.44336
108	2747.87	68.29	8.79736
113	2863.64	71.15	9.16626
123	5066.10	76.22	9.81890
130	4488.84	80.71	10.39717
137	4737.27	85.45	11.00745
144	4895.58	90.34	11.63812
151	4952.48	95.29	12.27612
158	3338.74	98.63	12.70623
165	4880.83	103.51	13.33500
172	4376.16	107.89	13.89876
179	4371.20	112.26	14.46188
185	3906.12	116.17	14.96508
193	4899.49	121.07	15.59625
200	3816.60	124.88	16.08792
207	4552.49	129.44	16.67440
215	5163.90	134.60	17.33963
222	3729.75	138.33	17.82012
229	3735.61	142.06	18.30135

Appendix Pii: ABLC180 Data – Arsenic (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
236	3535.19	145.60	18.75677
243	3204.78	148.80	19.16963
250	3128.41	151.93	19.57264
257	3158.66	155.09	19.97956
264	2711.58	157.80	20.32887
271	2781.22	160.58	20.68716
278	2954.39	163.54	21.06776
285	2797.14	166.34	21.42810
292	3008.88	169.34	21.81572
299	2945.01	172.29	22.19511
306	2843.67	175.13	22.56144
313	2685.95	177.82	22.90746
320	2508.07	180.33	23.23056
327	2539.18	182.87	23.55767
334	1586.47	184.45	23.76204
341	1614.43	186.07	23.97002
348	1551.72	187.62	24.16992
355	1623.46	189.24	24.37906
362	1541.58	190.78	24.57766

Appendix Piii: LCC100 Data – Arsenic

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0	137.61	137.61	0.03182
1	10.36	147.97	0.03421
8	10.20	158.18	0.03657
15	10.44	168.62	0.03899
22	0.87	169.49	0.03919
29	0.36	169.86	0.03927
36	5.03	174.89	0.04044
44	0.78	175.67	0.04062
51	0.64	176.30	0.04076
58	5.79	182.10	0.04210
65	1.21	183.31	0.04238
72	1.95	185.26	0.04283
79	0.68	185.94	0.04299
86	0.65	186.59	0.04314
93	5.37	191.96	0.04438
100	4.99	196.95	0.04554
107	0.78	197.74	0.04572
114	4.17	201.91	0.04668
121	1.66	203.57	0.04707
128	0.33	203.90	0.04715
135	0.55	204.46	0.04727
142	0.71	205.17	0.04744
149	0.24	205.42	0.04749
156	0.50	205.91	0.04761
163	4.07	209.99	0.04855
170	0.77	210.76	0.04873
177	0.43	211.19	0.04883
184	3.34	214.54	0.04960
191	4.80	219.34	0.05071
198	3.47	222.81	0.05152
205	4.42	227.23	0.05254
212	4.20	231.44	0.05351
219	4.36	235.80	0.05452
226	4.42	240.22	0.05554
233	4.20	244.42	0.05651
240	4.68	249.10	0.05759
247	4.68	253.77	0.05868
254	5.13	258.90	0.05986
261	4.93	263.83	0.06100
268	5.27	269.10	0.06222
275	4.56	273.66	0.06327
282	4.90	278.56	0.06441
289	5.01	283.57	0.06557
296	4.47	288.04	0.06660
303	4.88	292.92	0.06773
310	3.53	296.46	0.06855

Appendix Piii: LCC100 Data – Arsenic (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
317	2.92	299.38	0.06922
324	2.79	302.17	0.06987
331	2.45	304.62	0.07043
338	2.59	307.21	0.07103
345	1.46	308.67	0.07137
352	1.34	310.01	0.07168
359	1.36	311.37	0.07199
366	0.99	312.36	0.07222

Appendix Qi: DLT t_n = 1A Data – Arsenic

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	11.70	11.70	0.00585
1	18.32	30.01	0.01502
4	20.99	51.00	0.02552
9	35.45	86.46	0.04327
16	38.13	124.58	0.06235
25	38.40	162.98	0.08156
36	44.41	207.40	0.10379
49	43.76	251.16	0.12569
64	42.45	293.61	0.14694
81	43.11	336.71	0.16851
100	41.47	378.18	0.18926
121	47.68	425.87	0.21313
144	29.81	455.68	0.22804
169	31.49	487.17	0.24380
196	34.30	521.47	0.26097
225	34.30	555.77	0.27814
256	35.98	591.76	0.29614
289	34.86	626.62	0.31359
324	34.86	661.48	0.33104
361	38.23	699.71	0.35017
400	33.74	733.45	0.36705
441	36.55	769.99	0.38534
484	38.79	808.78	0.40476
529	44.97	853.75	0.42726
576	63.49	917.24	0.45903
625	47.21	964.46	0.48266
676	44.41	1008.86	0.50488
729	43.28	1052.14	0.52655
784	44.41	1096.55	0.54877
841	45.53	1142.08	0.57155
900	42.16	1184.24	0.59265
961	47.21	1231.45	0.61628
1024	67.69	1299.14	0.65016
1089	48.54	1347.68	0.67445
1156	48.74	1396.42	0.69884
1225	51.93	1448.35	0.72483
1296	48.74	1497.09	0.74922
1369	49.14	1546.23	0.77381
1444	51.53	1597.77	0.79960
1521	51.93	1649.70	0.82559
1600	55.32	1705.02	0.85328
1681	55.52	1760.55	0.88107
1764	53.53	1814.08	0.90785
1932	53.19	1867.26	0.93447

Appendix Qi: DLT t_n = 1A Data – Arsenic (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	51.59	1918.86	0.96029
2268	54.39	1973.24	0.98751
2436	53.19	2026.43	1.01413
2604	51.19	2077.63	1.03975
2772	46.81	2124.43	1.06317
2940	43.61	2168.05	1.08500
3108	49.20	2217.24	1.10962
3276	47.60	2264.85	1.13344
3444	44.10	2308.95	1.15551
3612	39.05	2348.00	1.17506
3780	45.36	2393.36	1.19776
3948	44.10	2437.45	1.21982
4116	46.37	2483.82	1.24303
4284	36.53	2520.35	1.26131
4452	38.55	2558.90	1.28060
4620	37.79	2596.69	1.29951
4956	30.98	2627.67	1.31502
5292	24.92	2652.59	1.32749
5628	28.20	2680.80	1.34161
5964	32.75	2713.54	1.35799
6300	41.57	2755.11	1.37880
6636	46.12	2801.23	1.40188
6972	46.87	2848.10	1.42533
7308	26.78	2874.88	1.43874
7644	27.82	2902.70	1.45266
7980	30.94	2933.64	1.46814
8316	31.11	2964.76	1.48371
8652	33.72	2998.47	1.50059

Appendix Qii: DLT t_n = 1B Data – Arsenic

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	9.66	9.66	0.00477
1	19.92	29.58	0.01462
4	20.46	50.04	0.02472
9	28.76	78.80	0.03893
16	37.59	116.39	0.05750
25	37.59	153.99	0.07608
36	48.99	202.98	0.10028
49	45.07	248.05	0.12255
64	45.07	293.11	0.14481
81	45.40	338.51	0.16724
100	37.87	376.38	0.18595
121	47.68	424.07	0.20951
144	25.66	449.73	0.22219
169	29.66	479.39	0.23684
196	28.01	507.40	0.25068
225	28.95	536.35	0.26498
256	28.95	565.30	0.27929
289	29.89	595.19	0.29405
324	31.30	626.49	0.30952
361	31.30	657.79	0.32498
400	31.53	689.33	0.34056
441	32.47	721.80	0.35660
484	33.18	754.98	0.37300
529	35.76	790.74	0.39066
576	35.76	826.50	0.40833
625	34.82	861.32	0.42553
676	33.88	895.21	0.44227
729	37.40	932.61	0.46075
784	36.00	968.61	0.47854
841	35.06	1003.67	0.49586
900	34.59	1038.25	0.51295
961	39.52	1077.77	0.53247
1024	36.23	1114.00	0.55037
1089	43.41	1157.41	0.57182
1156	41.23	1198.65	0.59219
1225	43.41	1242.06	0.61364
1296	41.48	1283.54	0.63413
1369	40.75	1324.28	0.65426
1444	41.96	1366.24	0.67499
1521	41.96	1408.20	0.69572
1600	43.90	1452.10	0.71741
1681	47.05	1499.15	0.74065
1764	44.62	1543.77	0.76270
1932	40.99	1584.76	0.78295

Appendix Qii: DLT t_n = 1B Data – Arsenic (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	40.75	1625.51	0.80308
2268	41.48	1666.99	0.82357
2436	46.56	1713.55	0.84657
2604	42.93	1756.48	0.86778
2772	41.72	1798.20	0.88839
2940	43.66	1841.85	0.90996
3108	40.51	1882.36	0.92997
3276	40.99	1923.35	0.95022
3444	42.20	1965.55	0.97107
3612	43.48	2009.03	0.99255
3780	46.03	2055.06	1.01529
3948	42.20	2097.26	1.03614
4116	46.54	2143.80	1.05914
4284	43.48	2187.27	1.08062
4452	45.26	2232.54	1.10298
4620	47.31	2279.84	1.12635
4956	36.32	2316.17	1.14430
5292	30.19	2346.36	1.15921
5628	31.47	2377.83	1.17476
5964	29.68	2407.51	1.18942
6300	31.73	2439.24	1.20510
6636	42.45	2481.69	1.22607
6972	44.75	2526.45	1.24818
7308	44.50	2570.94	1.27017
7644	26.26	2597.20	1.28314
7980	28.51	2625.71	1.29723
8316	31.46	2657.18	1.31277
8652	33.02	2690.20	1.32908

Appendix Qiii: DLT $t_n = 4$A Data – Arsenic

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	12.18	12.18	0.00604
4	24.21	36.38	0.01804
16	49.64	86.03	0.04267
36	49.91	135.94	0.06742
64	42.95	178.89	0.08872
100	60.77	239.65	0.11886
144	33.91	273.56	0.13568
196	33.77	307.33	0.15242
256	34.54	341.87	0.16955
324	34.02	375.89	0.18643
400	34.02	409.92	0.20330
484	34.88	444.80	0.22060
576	35.97	480.77	0.23844
676	35.46	516.23	0.25603
784	35.46	551.69	0.27361
900	34.95	586.64	0.29095
1024	34.19	620.83	0.30790
1156	29.86	650.69	0.32271
1296	30.12	680.81	0.33765
1444	35.71	716.52	0.35536
1600	34.70	751.22	0.37257
1764	33.68	784.90	0.38928
1932	35.71	820.61	0.40699
2100	34.95	855.56	0.42432
2268	36.22	891.79	0.44229
2436	34.19	925.97	0.45924
2604	32.41	958.38	0.47532
2772	31.39	989.77	0.49088
2940	32.66	1022.43	0.50708
3108	32.66	1055.09	0.52328
3276	34.19	1089.28	0.54024
3444	30.79	1120.08	0.55551
3612	31.06	1151.14	0.57091
3780	32.67	1183.80	0.58712
3948	31.60	1215.40	0.60279
4116	31.86	1247.26	0.61859
4284	31.86	1279.13	0.63439
4452	32.67	1311.79	0.65059
4620	27.85	1339.64	0.66441
4956	28.92	1368.56	0.67875
5292	25.44	1394.00	0.69136
5628	20.35	1414.35	0.70146
5964	24.37	1438.71	0.71354
6300	20.89	1459.60	0.72390

Appendix Qiii: DLT t_n = 4A Data – Arsenic (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
6636	32.93	1492.53	0.74023
6972	36.15	1528.68	0.75816
7308	37.75	1566.44	0.77689
7644	26.26	1592.69	0.78991
7980	27.30	1619.99	0.80345
8316	26.43	1646.43	0.81656
8652	29.73	1676.15	0.83130

Appendix Qiv: DLT $t_n = 4B$ Data – Arsenic

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	8.21	8.21	0.00410
4	29.56	37.78	0.01883
16	61.69	99.47	0.04959
36	56.07	155.54	0.07754
64	46.16	201.70	0.10055
100	57.82	259.52	0.12938
144	36.68	296.21	0.14767
196	35.61	331.82	0.16542
256	33.74	365.56	0.18224
324	34.27	399.83	0.19933
400	33.53	433.36	0.21604
484	31.49	464.85	0.23174
576	33.78	498.63	0.24858
676	31.75	530.38	0.26441
784	29.97	560.34	0.27935
900	32.51	592.85	0.29555
1024	32.00	624.85	0.31151
1156	29.97	654.82	0.32645
1296	32.51	687.33	0.34265
1444	33.27	720.60	0.35924
1600	35.31	755.91	0.37684
1764	33.78	789.69	0.39368
1932	32.00	821.69	0.40964
2100	30.98	852.67	0.42508
2268	28.69	881.36	0.43939
2436	37.34	918.71	0.45800
2604	28.44	947.14	0.47218
2772	33.14	980.29	0.48870
2940	30.64	1010.93	0.50398
3108	32.46	1043.39	0.52016
3276	29.50	1072.89	0.53487
3444	36.11	1109.00	0.55287
3612	31.78	1140.77	0.56871
3780	32.69	1173.46	0.58501
3948	30.64	1204.10	0.60028
4116	36.56	1240.66	0.61851
4284	31.32	1271.99	0.63412
4452	33.60	1305.59	0.65087
4620	34.51	1340.10	0.66808
4956	26.77	1366.86	0.68142
5292	22.44	1389.30	0.69261
5628	21.53	1410.83	0.70334
5964	21.98	1432.81	0.71430
6300	24.72	1457.53	0.72662

Appendix Qiv: DLT t_n = 4B Data – Arsenic (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
6636	25.17	1482.70	0.73917
6972	31.78	1514.48	0.75501
7308	31.32	1545.80	0.77063
7644	21.23	1567.03	0.78121
7980	23.31	1590.34	0.79283
8316	26.78	1617.12	0.80618
8652	28.86	1645.98	0.82057

Appendix R: Large Column Data – Selenium

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	14.71	0.01	0.00015
7	852.17	0.87	0.00862
14	913.04	1.78	0.01770
21	709.13	2.49	0.02475
28	724.35	3.21	0.03195
35	468.70	3.68	0.03661
42	468.70	4.15	0.04127
49	346.96	4.50	0.04472
56	423.04	4.92	0.04892
63	365.22	5.29	0.05255
70	289.13	5.58	0.05543
77	365.22	5.94	0.05906
84	243.48	6.18	0.06148
91	243.48	6.43	0.06390
98	173.48	6.60	0.06562
105	136.96	6.74	0.06699
112	121.74	6.86	0.06820
119	213.04	7.07	0.07031
126	213.04	7.29	0.07243
133	167.39	7.45	0.07410
140	175.00	7.63	0.07584
147	167.39	7.80	0.07750
154	144.57	7.94	0.07894
161	106.52	8.05	0.08000
168	121.74	8.17	0.08121
175	121.74	8.29	0.08242
182	76.09	8.37	0.08317
189	136.96	8.50	0.08454
196	114.13	8.62	0.08567
203	129.35	8.75	0.08696
210	176.27	8.92	0.08871
217	173.45	9.10	0.09043
224	121.45	9.22	0.09164
231	208.59	9.43	0.09371
238	155.18	9.58	0.09526
245	194.54	9.78	0.09719
252	215.62	9.99	0.09934
259	187.51	10.18	0.10120
266	257.79	10.44	0.10376
273	180.48	10.62	0.10556
280	173.45	10.79	0.10728
287	162.21	10.95	0.10889
294	229.68	11.18	0.11118
301	208.59	11.39	0.11325
308	145.34	11.54	0.11470

Appendix R: Large Column Data –Selenium (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
315	194.54	11.73	0.11663
322	173.45	11.90	0.11835
329	166.43	12.07	0.12001
336	184.24	12.26	0.12184
343	158.37	12.41	0.12342
350	174.24	12.59	0.12515
357	169.24	12.76	0.12683
364	167.14	12.92	0.12849

Appendix Si: ABLC100 Data – Selenium

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	3.05	0.00	0.01154
1	120.43	0.12	0.46772
2	148.08	0.27	1.02861
3	178.71	0.45	1.70554
4	226.92	0.68	2.56509
5	158.05	0.84	3.16377
6	175.97	1.01	3.83032
7	177.06	1.19	4.50099
8	126.98	1.32	4.98198
9	117.69	1.43	5.42778
10	97.41	1.53	5.79676
11	90.22	1.62	6.13851
12	70.84	1.69	6.40685
13	86.19	1.78	6.73333
14	103.73	1.88	7.12625
16	228.17	2.11	7.99054
18	216.76	2.33	8.81159
20	176.83	2.50	9.48142
23	321.03	2.82	10.69745
26	203.08	3.03	11.46668
29	266.26	3.29	12.47524
32	345.37	3.64	13.78345
35	287.69	3.93	14.87317
38	264.75	4.19	15.87600
41	224.73	4.42	16.72723
44	275.30	4.69	17.77003
47	394.95	5.09	19.26605
50	282.79	5.37	20.33723
53	290.15	5.66	21.43628
56	220.21	5.88	22.27041
59	293.11	6.17	23.38066
62	285.81	6.46	24.46329
66	440.89	6.90	26.13332
70	458.09	7.36	27.86852
74	529.17	7.89	29.87296
78	467.30	8.35	31.64303
82	427.16	8.78	33.26106
86	374.88	9.16	34.68105
90	268.24	9.42	35.69710
94	316.00	9.74	36.89406
99	308.48	10.05	38.06255
102	207.83	10.26	38.84978
108	352.28	10.61	40.18418
114	295.61	10.90	41.30393
121	424.49	11.33	42.91185

Appendix Si: ABLC100 Data – Selenium (contd.)

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
128	509.72	11.84	44.84261
135	668.64	12.51	47.37535
142	568.10	13.08	49.52725
149	428.23	13.50	51.14933
153	287.02	13.79	52.23654
160	572.54	14.36	54.40525
167	172.54	14.54	55.05880
174	167.93	14.70	55.69490
181	102.24	14.81	56.08216
188	89.58	14.90	56.42149
195	92.95	14.99	56.77358
202	137.46	15.13	57.29425
209	132.06	15.26	57.79448
216	188.85	15.45	58.50982
223	135.41	15.58	59.02274
230	131.21	15.71	59.51975
237	72.49	15.79	59.79434
244	123.05	15.91	60.26045
251	111.14	16.02	60.68143
258	118.21	16.14	61.12919
265	90.00	16.23	61.47011
272	99.83	16.33	61.84824
279	83.25	16.41	62.16358
286	78.16	16.49	62.45963
293	67.76	16.56	62.71631
300	67.51	16.62	62.97202
307	66.67	16.69	63.22457
314	57.11	16.75	63.44088
321	49.88	16.80	63.62983
328	29.83	16.83	63.74283
335	28.78	16.86	63.85183
342	35.22	16.89	63.98522
349	40.19	16.93	64.13745
356	29.25	16.96	64.24824
363	22.26	16.98	64.33254

Appendix Sii: ABLC180 Data – Selenium

Time (days)	Mass Leached (μg)	Cumulative Mass Leached (mg)	Cumulative % Leached
0	5.38	0.01	0.01136
1	399.51	0.40	0.85457
2	8.96	0.41	0.87348
3	182.43	0.60	1.25852
4	94.02	0.69	1.45695
5	183.95	0.87	1.84519
6	157.80	1.03	2.17824
7	181.94	1.21	2.56224
8	150.54	1.36	2.87996
9	153.69	1.52	3.20433
10	123.52	1.64	3.46503
11	106.98	1.75	3.69083
12	90.36	1.84	3.88154
13	89.77	1.93	4.07102
14	108.51	2.04	4.30005
15	121.43	2.16	4.55633
16	96.82	2.26	4.76069
17	102.27	2.36	4.97655
18	101.36	2.46	5.19048
19	94.51	2.55	5.38995
20	103,83	2.66	5.60910
21	78.63	2.74	5.77506
22	69.94	2.81	5.92267
23	71.64	2.88	6.07388
24	57.23	2.94	6.19467
48	202.78	3.14	6.62266
49	272.44	3.41	7.19768
50	247.82	3.66	7.72072
51	157.16	3.82	8.05241
52	179.28	3.99	8.43079
53	167.07	4.16	8.78341
54	156.45	4.32	9.11361
55	166.20	4.48	9.46439
56	110.59	4.59	9.69781
57	113.91	4.71	9.93823
60	330.78	5.04	10.63638
61	105.35	5.14	10.85874
62	104.01	5.25	11.07827
63	117.05	5.37	11.32531
64	137.90	5.50	11.61635
65	143.44	5.65	11.91910
66	140.08	5.79	12.21477
67	109.13	5.90	12.44510
68	103.53	6.00	12.66360
69	84.23	6.08	12.84136
70	101.19	6.19	13.05494

Appendix Sii: ABLC180 Data – Selenium (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
71	100.69	6.29	13.26746
72	112.43	6.40	13.50476
73	122.30	6.52	13.76288
74	107.89	6.63	13.99058
75	110.16	6.74	14.22309
76	83.38	6.82	14.39907
80	322.41	7.14	15.07954
81	72.20	7.22	15.23192
82	85.57	7.30	15.41253
83	72.41	7.37	15.56535
84	99.98	7.47	15.77636
85	98.12	7.57	15.98346
86	90.46	7.66	16.17439
87	87.53	7.75	16.35914
88	86.67	7.84	16.54206
89	75.30	7.91	16.70100
90	78.52	7.99	16.86671
91	86.44	8.08	17.04915
92	96.51	8.17	17.25284
93	121.73	8.30	17.50976
94	115.27	8.41	17.75305
95	134.06	8.55	18.03600
96	134.36	8.68	18.31959
97	138.52	8.82	18.61195
98	113.04	8.93	18.85053
99	105.48	9.04	19.07316
100	100.06	9.14	19.28434
104	298.81	9.44	19.91501
108	200.74	9.64	20.33870
113	261.23	9.90	20.89006
123	365.09	10.26	21.66060
130	325.82	10.59	22.34827
137	399.54	10.99	23.19155
144	317.37	11.31	23.86139
151	375.81	11.68	24.65457
158	220.05	11.90	25.11901
165	277.47	12.18	25.70463
172	214.17	12.39	26.15665
179	247.41	12.64	26.67884
185	162.31	12.80	27.02140
193	253.49	13.06	27.55641
200	186.92	13.24	27.95093
207	220.21	13.46	28.41570
215	171.14	13.63	28.77691
222	175.66	13.81	29.14767
229	170.82	13.98	29.50820

Appendix Sii: ABLC180 Data – Selenium (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (mg)	Cumulative % Leached
236	166.59	14.15	29.85980
243	142.29	14.29	30.16013
250	146.68	14.44	30.46971
257	128.08	14.56	30.74002
264	130.88	14.70	31.01626
271	129.81	14.83	31.29023
278	120.46	14.95	31.54448
285	110.53	15.06	31.77777
292	124.53	15.18	32.04061
299	105.03	15.29	32.26228
306	107.15	15.39	32.48843
313	112.45	15.51	32.72576
320	98.61	15.60	32.93389
327	103.60	15.71	33.15255
334	107.32	15.81	33.37905
341	108.64	15.92	33.60835
348	111.09	16.03	33.84282
355	121.67	16.16	34.09961
362	117.53	16.27	34.34767

Appendix Siii: LCC100 Data – Selenium

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0	2.83	2.83	0.01072
1	1.93	4.76	0.01802
8	2.79	7.54	0.02857
15	3.47	11.01	0.04170
22	2.53	13.53	0.05127
29	2.01	15.54	0.05887
36	1.41	16.95	0.06421
44	1.85	18.81	0.07123
51	1.85	20.66	0.07826
58	2.26	22.92	0.08681
65	1.73	24.65	0.09338
72	1.57	26.22	0.09933
79	1.23	27.45	0.10399
86	0.88	28.34	0.10733
93	0.88	29.22	0.11067
100	0.88	30.10	0.11402
107	0.95	31.05	0.11761
114	0.76	31.81	0.12049
121	0.72	32.53	0.12322
128	0.68	33.21	0.12579
135	0.66	33.87	0.12831
142	0.91	34.78	0.13174
149	0.72	35.50	0.13447
156	0.77	36.27	0.13739
163	0.64	36.91	0.13981
170	0.48	37.39	0.14162
177	0.47	37.86	0.14340
184	0.41	38.27	0.14496
191	0.45	38.72	0.14668
198	0.32	39.04	0.14788
205	0.45	39.49	0.14960
212	0.30	39.79	0.15073
219	0.16	39.95	0.15134
226	0.12	40.07	0.15178
233	0.17	40.24	0.15241
240	0.16	40.40	0.15301
247	0.17	40.56	0.15365
254	0.15	40.72	0.15422
261	0.17	40.88	0.15485
268	0.09	40.97	0.15520
275	0.09	41.06	0.15554
282	0.12	41.18	0.15598
289	0.11	41.28	0.15638
296	0.14	41.42	0.15691
303	0.11	41.53	0.15731
310	0.09	41.62	0.15764

Appendix Siii: LCC100 Data – Selenium (contd.)

Time (days)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
317	0.07	41.68	0.15788
324	0.06	41.74	0.15811
331	0.07	41.81	0.15836
338	0.07	41.88	0.15862
345	0.06	41.94	0.15885
352	0.06	42.00	0.15908
359	0.05	42.05	0.15929
366	0.06	42.11	0.15950

Appendix Ti: DLT t_n = 1A Data – Selenium

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	1.34	1.34	0.01098
1	2.58	3.92	0.03216
4	3.46	7.39	0.06054
9	4.34	11.73	0.09612
16	4.34	16.07	0.13170
25	4.49	20.55	0.16848
36	4.34	24.90	0.20406
49	4.19	29.09	0.23844
64	4.12	33.21	0.27223
81	4.27	37.48	0.30721
100	2.66	40.14	0.32904
121	2.66	42.81	0.35087
144	3.97	46.78	0.38341
169	4.24	51.01	0.41815
196	4.26	55.27	0.45303
225	4.02	59.29	0.48601
256	3.24	62.53	0.51256
289	3.76	66.29	0.54334
324	4.22	70.51	0.57793
361	5.04	75.55	0.61925
400	3.93	79.48	0.65150
441	5.01	84.49	0.69253
484	4.29	88.78	0.72770
529	4.13	92.91	0.76156
576	4.18	97.09	0.79586
625	3.99	101.08	0.82855
676	4.11	105.20	0.86226
729	3.22	108.42	0.88865
784	3.04	111.46	0.91359
841	4.29	115.75	0.94876
900	1.79	117.54	0.96345
961	2.51	120.05	0.98399
1024	2.86	122.91	1.00746
1089	3.83	126.74	1.03883
1156	4.92	131.65	1.07913
1225	5.58	137.23	1.12484
1296	3.85	141.08	1.15636
1369	5.40	146.47	1.20060
1444	4.02	150.50	1.23358
1521	4.65	155.15	1.27169
1600	5.31	160.45	1.31520
1681	5.74	166.19	1.36223
1764	5.82	172.01	1.40993
1932	4.01	176.02	1.44279

Appendix Ti: DLT t_n = 1A Data – Selenium (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
2100	5.22	181.24	1.48555
2268	5.62	186.86	1.53160
2436	6.22	193.08	1.58260
2604	7.43	200.51	1.64349
2772	8.43	208.94	1.71261
2940	9.54	218.48	1.79081
3108	8.03	226.51	1.85664
3276	9.04	235.55	1.93071
3444	8.33	243.88	1.99901
3612	9.34	253.22	2.07556
3780	10.34	263.56	2.16035
3948	10.65	274.21	2.24760
4116	8.33	282.54	2.31591
4284	9.54	292.08	2.39410
4452	11.25	303.33	2.48630
4620	8.84	312.16	2.55873
4956	9.34	321.50	2.63527
5292	8.74	330.24	2.70687
5628	10.65	340.88	2.79413
5964	8.84	349.72	2.86656
6300	10.65	360.37	2.95381
6636	10.85	371.21	3.04272
6972	10.75	381.96	3.13080
7308	11.95	393.91	3.22878
7644	10.75	404.66	3.31686
7980	10.75	415.40	3.40494
8316	13.76	429.17	3.51775
8652	15.37	444.54	3.64374

Appendix Tii: DLT t_n = 1B Data – Selenium

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	1.93	1.93	0.01558
1	2.36	4.29	0.03471
4	4.05	8.34	0.06746
9	4.56	12.90	0.10435
16	4.63	17.53	0.14184
25	5.22	22.75	0.18407
36	5.15	27.90	0.22570
49	5.80	33.70	0.27267
64	4.49	38.19	0.30897
81	4.49	42.68	0.34528
100	21.52	64.20	0.51943
121	2.50	66.70	0.53964
144	4.38	71.08	0.57510
169	3.02	74.10	0.59952
196	2.09	76.19	0.61642
225	3.42	79.61	0.64407
256	2.29	81.90	0.66258
289	2.09	83.98	0.67948
324	2.89	86.87	0.70283
361	3.09	89.96	0.72780
400	3.52	93.47	0.75626
441	5.25	98.72	0.79871
484	5.25	103.97	0.84116
529	4.25	108.22	0.87554
576	4.42	112.63	0.91127
625	3.95	116.58	0.94323
676	3.75	120.33	0.97358
729	3.78	124.12	1.00419
784	4.42	128.53	1.03992
841	2.99	131.52	1.06408
900	4.42	135.94	1.09981
961	3.92	139.85	1.13150
1024	3.42	143.27	1.15915
1089	4.15	147.42	1.19273
1156	5.25	152.67	1.23518
1225	6.24	158.91	1.28570
1296	4.81	163.73	1.32466
1369	5.91	169.64	1.37249
1444	5.08	174.72	1.41360
1521	4.95	179.67	1.45363
1600	6.31	185.98	1.50469
1681	5.75	191.73	1.55118
1764	5.61	197.34	1.59659
1932	6.29	203.62	1.64744

Appendix Tii: DLT t_n = 1B Data – Selenium (contd.)

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
2100	5.91	209.53	1.69525
2268	6.10	215.63	1.74459
2436	10.04	225.67	1.82581
2604	8.58	234.25	1.89520
2772	10.45	244.70	1.97977
2940	10.19	254.89	2.06221
3108	9.85	264.74	2.14192
3276	11.84	276.58	2.23773
3444	13.23	289.81	2.34478
3612	9.48	299.29	2.42145
3780	10.60	309.89	2.50723
3948	10.04	319.93	2.58846
4116	12.29	332.23	2.68792
4284	11.54	343.77	2.78130
4452	11.35	355.12	2.87316
4620	12.86	367.98	2.97717
4956	11.35	379.33	3.06903
5292	10.00	389.33	3.14995
5628	13.98	403.32	3.26308
5964	12.18	415.50	3.36162
6300	12.86	428.35	3.46563
6636	9.85	438.20	3.54534
6972	13.98	452.19	3.65847
7308	9.93	462.11	3.73878
7644	16.05	478.16	3.86862
7980	13.72	491.88	3.97961
8316	15.86	507.74	4.10793
8652	17.36	525.10	4.24839

Appendix Tiii: DLT t_n = 4A Data – Selenium

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
0.008	1.75	1.75	0.01425
4	3.16	4.91	0.03992
16	5.39	10.31	0.08373
36	5.64	15.95	0.12956
64	6.22	22.17	0.18010
100	5.81	27.98	0.22727
144	5.57	33.55	0.27255
196	6.88	40.43	0.32846
256	5.09	45.52	0.36979
324	4.53	50.05	0.40656
400	4.64	54.69	0.44424
484	6.70	61.38	0.49864
576	5.01	66.40	0.53936
676	5.91	72.31	0.58737
784	4.11	76.42	0.62080
900	3.70	80.12	0.65089
1024	3.70	83.83	0.68097
1156	5.20	89.03	0.72321
1296	5.46	94.49	0.76758
1444	3.55	98.04	0.79645
1600	4.34	102.38	0.83170
1764	4.26	106.65	0.86634
1932	4.11	110.76	0.89977
2100	4.26	115.03	0.93441
2268	3.89	118.92	0.96601
2436	6.13	125.05	1.01585
2604	6.51	131.56	1.06873
2772	6.32	137.88	1.12008
2940	6.70	144.58	1.17448
3108	5.39	149.96	1.21824
3276	6.88	156.85	1.27415
3444	7.07	163.92	1.33158
3612	6.73	170.65	1.38628
3780	7.63	178.28	1.44828
3948	9.13	187.41	1.52242
4116	8.75	196.16	1.59353
4284	9.15	205.32	1.66789
4452	11.44	216.76	1.76083
4620	11.82	228.58	1.85686
4956	6.87	235.45	1.91264
5292	11.44	246.89	2.00558
5628	13.73	260.61	2.11709
5964	13.73	274.34	2.22859
6300	14.49	288.83	2.34629

Appendix Tiii: DLT t_n = 4A Data – Selenium (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	14.87	303.70	2.46709
6972	12.96	316.66	2.57241
7308	12.39	329.06	2.67308
7644	12.39	341.45	2.77375
7980	15.94	357.39	2.90322
8316	16.51	373.89	3.03733
8652	18.49	392.39	3.18753

Appendix Tiv: DLT t_n = 4B Data – Selenium

Time (hours)	Mass Leached (µg)	Cumulative Mass Leached (µg)	Cumulative % Leached
0.008	2.42	2.42	0.01973
4	2.91	5.33	0.04352
16	9.53	14.86	0.12138
36	8.29	23.15	0.18910
64	7.46	30.61	0.25006
100	7.88	38.48	0.31440
144	5.53	44.02	0.35961
196	6.87	50.88	0.41572
256	5.04	55.92	0.45688
324	4.47	60.39	0.49336
400	4.58	64.97	0.53079
484	6.68	71.65	0.58534
576	4.96	76.61	0.62587
676	5.88	82.48	0.67388
784	4.05	86.53	0.70695
900	3.63	90.16	0.73659
1024	3.63	93.79	0.76623
1156	5.15	98.94	0.80832
1296	5.42	104.36	0.85259
1444	3.48	107.83	0.88099
1600	4.28	112.11	0.91592
1764	8.09	120.20	0.98204
1932	8.38	128.58	1.05051
2100	8.38	136.96	1.11899
2268	8.31	145.27	1.18687
2436	11.80	157.07	1.28325
2604	10.54	167.61	1.36934
2772	10.57	178.18	1.45573
2940	11.11	189.30	1.54653
3108	12.01	201.31	1.64467
3276	11.98	213.28	1.74251
3444	13.77	227.06	1.85505
3612	11.47	238.53	1.94878
3780	11.26	249.79	2.04075
3948	10.36	260.15	2.12538
4116	13.41	273.56	2.23497
4284	10.03	283.60	2.31696
4452	10.47	294.06	2.40246
4620	10.29	304.35	2.48650
4956	11.44	315.79	2.57994
5292	9.86	325.64	2.66046
5628	10.61	336.25	2.74714
5964	12.73	348.98	2.85116
6300	12.34	361.32	2.95194

Appendix Tiv: DLT t_n = 4B Data – Selenium (contd.)

Time (hours)	Mass Leached (μg)	Cumulative Mass Leached (μg)	Cumulative % Leached
6636	10.29	371.60	3.03598
6972	12.48	384.08	3.13794
7308	12.05	396.13	3.23637
7644	12.34	408.47	3.33715
7980	16.18	424.65	3.46937
8316	15.97	440.62	3.59982
8652	17.01	457.63	3.73879