A Study of Leaching Tests for Cement Stabilised Waste

By

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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.

Jason Beard
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, \textit{AS 4493.3-1997}), Toxicity Characteristic Leaching Procedure (TCLP, \textit{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 irretreivable 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 landfiling.

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 Hock & 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.
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.

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).

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Symbol</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>Tricalcium Silicate</td>
<td>3CaO·SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>45</td>
</tr>
<tr>
<td>Belite</td>
<td>Dicalcium Silicate</td>
<td>2CaO·SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>27</td>
</tr>
<tr>
<td>Aluminate</td>
<td>Tricalcium Aluminate</td>
<td>3CaO·Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;A</td>
<td>11</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Tetracalcium Alumino Ferrite</td>
<td>4CaO·Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;·Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;AF</td>
<td>8</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td>9 (&lt;1 each)</td>
</tr>
</tbody>
</table>
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)**

<table>
<thead>
<tr>
<th>Type</th>
<th>Designation Characteristic</th>
<th>% C₃S</th>
<th>% C₂S</th>
<th>% C₃A</th>
<th>% C₄AF</th>
<th>% Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>General Purpose</td>
<td>45</td>
<td>27</td>
<td>11</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>II</td>
<td>Moderate Heat</td>
<td>44</td>
<td>27</td>
<td>11</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Evolution/ Sulphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>High Early Strength</td>
<td>53</td>
<td>19</td>
<td>11</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>IV</td>
<td>Low Heat Evolution</td>
<td>28</td>
<td>49</td>
<td>4</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Sulphate Resistance</td>
<td>38</td>
<td>43</td>
<td>4</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Rapid Hardening</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Super Rapid</td>
<td>66</td>
<td>11</td>
<td>8</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Hardening</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jet Cement</td>
<td>68</td>
<td>5</td>
<td>9</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52</td>
<td>0</td>
<td>22</td>
<td>5</td>
<td>21</td>
</tr>
</tbody>
</table>
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) $3\text{CaO.Al}_2\text{O}_3 + 12\text{H}_2\text{O} + \text{Ca(OH)}_2 \rightarrow 3\text{CaO.Al}_2\text{O}_3.\text{Ca(OH)}_2 + 12\text{H}_2\text{O}$
   (Aluminate) (Tricalcium aluminate hydrate)

2) $3\text{CaO.Al}_2\text{O}_3 + 30\text{H}_2\text{O} + 3\text{CaSO}_4.2\text{H}_2\text{O} \rightarrow 3\text{CaO.Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O}$
   (Aluminate) (Calcium trisulphate aluminate) (Ettringite)

3) $2(3\text{CaO.Si}_2\text{O}_2) + 6\text{H}_2\text{O} \rightarrow 3\text{CaO.2SiO}_2.3\text{H}_2\text{O} + 3\text{Ca(OH)}_2$
   (Alite) (Calcium silicate hydrate gel [CSH]) (Tobermorite gel)

4) $2\text{CaO.Si}_2\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 3\text{CaO.2SiO}_2.3\text{H}_2\text{O} + \text{Ca(OH)}_2$
   (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.
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 breaks 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 CaCl₂ 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 CO₂ to form Calcite (CaCO₃) (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.
Acetic Acid Solution

Leached Cement-Based Waste Form
Leached Layer
Unleached Kernel

Orange Color
Dark Grey
Medium Grey
Light Grey

pH=5.7
pH<5
pH>5
pH>12

Solid/solution Interface

While Remineralization Region (100 microns in width)

**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 lechant 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 CO₂, 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 lechant. 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 lechant 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 lechant and the other an acidic lechant (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)

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

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)

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Extraction Procedure (EP)</th>
<th>Toxicity Characteristic Leaching Procedure (TCLP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminants Covered</td>
<td>Metals, Pesticides, Herbicides</td>
<td>Metals, Pesticides, Herbicides, Semi-volatiles, Volatile organics</td>
</tr>
<tr>
<td>Extraction Fluid</td>
<td>16 x weight of solids with distilled water; 0.5M acetic acid added to maintain pH of 5</td>
<td>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</td>
</tr>
<tr>
<td>Method of Agitation</td>
<td>No specific form of agitation recommended</td>
<td>Rotary agitation only in an end over end fashion at 30 ± 2 RPM</td>
</tr>
<tr>
<td>Extraction Time</td>
<td>24 hours</td>
<td>18 hours</td>
</tr>
<tr>
<td>Temperature</td>
<td>20° – 40°C</td>
<td>22 ± 3°C</td>
</tr>
<tr>
<td>Filtration Pressures</td>
<td>Filtration to 75psi in 10psi increments</td>
<td>Filtration to 50psi in 10psi increments</td>
</tr>
<tr>
<td>Filter Material</td>
<td>0.45μm cellulose membrane with prefilter</td>
<td>0.6-0.8μm binderless glass fibre filter</td>
</tr>
</tbody>
</table>
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).
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).

### Table 1.7: Differences Between ABLP & TCLP

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ABLP</th>
<th>TCLP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allowable Leaching Fluids</td>
<td>pH = 2.88 &amp; 5.0 acetate leachant;</td>
<td>pH = 2.88 &amp; 5.0 acetate leachant</td>
</tr>
<tr>
<td></td>
<td>pH = 9.2 borate leachant;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>de-ionised water</td>
<td></td>
</tr>
<tr>
<td>Waste Particle Size</td>
<td>&lt;2.36mm diameter</td>
<td>&lt;9.5mm diameter</td>
</tr>
<tr>
<td>Method of Filtration</td>
<td>Positive Pressure Only</td>
<td>No specific method</td>
</tr>
<tr>
<td>Analysis of Leachate</td>
<td>Non-Combination of Liquids for</td>
<td>Combination Permitted</td>
</tr>
<tr>
<td></td>
<td>Analysis</td>
<td></td>
</tr>
</tbody>
</table>
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 deminerahsed 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, $D_e$ (cm$^2$/s), can then be calculated, and, from this, a leachability index ($L_X = -\log D_e$). The $L_X$ 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.

\[
\left( \frac{\Sigma a_n}{A_0} \right) \left( \frac{V}{S} \right) = 2 \left( \frac{D_e'}{\pi} \right)^{\frac{1}{2}} \frac{t_n}{n}^{\frac{1}{2}}
\]

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 \( D_{el} \) 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)
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 (<125 μm) 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 (Forstner 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 (Forstner 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)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extractant</th>
<th>Extracted Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>1M NH₄CH₃COO, pH 7</td>
<td>Exchangeable ions</td>
</tr>
<tr>
<td>Carbonatic</td>
<td>1M NaOAc, pH 5 w/ HOAc</td>
<td>Carbonates</td>
</tr>
<tr>
<td>Easily Reducible</td>
<td>0.01M NH₂OH HCl w/ 0.01M HNO₃</td>
<td>Mn-Oxides</td>
</tr>
<tr>
<td>Moderately Reducible</td>
<td>0.1M oxalate buffer pH 3</td>
<td>Amorphous Fe-oxides</td>
</tr>
<tr>
<td>Sulphidic/Organic</td>
<td>30% H₂O₂ pH 2 w/ 0.02M HNO₃ extr. w/ 1M NH₄OAc-6% HNO₃</td>
<td>Sulphides together with organic matter</td>
</tr>
<tr>
<td>Residual</td>
<td>Hot HNO₃ conc.</td>
<td>Lithogenic material</td>
</tr>
</tbody>
</table>

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 (ELEM), 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 ELEM 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 H₂SO₄ 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

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Dried Waste (g/kg)</th>
<th>Cement (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>2.055</td>
<td>59.6</td>
</tr>
<tr>
<td>Arsenic</td>
<td>15.8</td>
<td>0.035</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5.89</td>
<td>0.003</td>
</tr>
<tr>
<td>Calcium</td>
<td>5.755</td>
<td>409.7</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.086</td>
<td>0.06</td>
</tr>
<tr>
<td>Copper</td>
<td>67.9</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron</td>
<td>45.67</td>
<td>31.53</td>
</tr>
<tr>
<td>Lead</td>
<td>288.3</td>
<td>0.037</td>
</tr>
<tr>
<td>Magnesium</td>
<td>9.31</td>
<td>8.013</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.088</td>
<td>1.32</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.835</td>
<td>0.265</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.923</td>
<td>&lt;0.019</td>
</tr>
<tr>
<td>Silver</td>
<td>0.014</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Tin</td>
<td>0.685</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Zinc</td>
<td>78.33</td>
<td>0.434</td>
</tr>
</tbody>
</table>
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 CaCl₂ 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, CaCl₂ 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 (CaCl₂). Following the addition of CaCl₂ 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: CaCl₂: water (including that used to dissolve the CaCl₂) 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 CaCl₂ 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>
<thead>
<tr>
<th>Table 2.2: Ingredient Composition of Fixed Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (g)</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>5530</td>
</tr>
</tbody>
</table>

A 2.305L solution of CaCl₂ was prepared by adding 691.25g of granular CaCl₂ 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>
<thead>
<tr>
<th>Cement (g)</th>
<th>Waste (g)</th>
<th>CaCl₂ (ml)</th>
<th>H₂O (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>20</td>
<td>20</td>
<td>2</td>
</tr>
</tbody>
</table>

A 200ml solution of CaCl₂ was also prepared by adding 50g of granular CaCl₂, 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 crashed 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>
<thead>
<tr>
<th>Metal</th>
<th>Crushed Fixed Waste (g/kg)</th>
<th>Spherical Fixed Waste (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>4.325</td>
<td>4.361</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.264</td>
<td>0.267</td>
</tr>
<tr>
<td>Copper</td>
<td>18.542</td>
<td>18.70</td>
</tr>
<tr>
<td>Lead</td>
<td>86.821</td>
<td>87.713</td>
</tr>
<tr>
<td>Zinc</td>
<td>22.59</td>
<td>22.68</td>
</tr>
</tbody>
</table>

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 HNO₃ 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% HNO₃ 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
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:

\[
\pi \cdot (25\text{cm})^2 \cdot 75\text{cm}
\]

\[
= 147.26 \text{ dm}^3/\text{year}
\]

\[
= 403.46 \text{ cm}^3/\text{day}
\]

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 HNO₃ 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](image)

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>
<thead>
<tr>
<th>Column</th>
<th>LCC100</th>
<th>ABLC100</th>
<th>ABLC180</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Waste Mass (g)</td>
<td>100.00</td>
<td>100.00</td>
<td>179.48</td>
</tr>
<tr>
<td>Flow Rate (L/Day)</td>
<td>$4.65 \times 10^{-3}$</td>
<td>2.67</td>
<td>2.67</td>
</tr>
<tr>
<td>Direction of Flow Through Column</td>
<td>Down</td>
<td>Up</td>
<td>Up</td>
</tr>
</tbody>
</table>
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; \[ \text{flow rate} = \pi \cdot (1.2\text{cm})^2 \cdot (75\text{cm} \cdot 5) \]
\[ = 1696.46 \text{ cm}^3/\text{year} \]
\[ = 4.65 \text{ cm}^3/\text{day} \]

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 HNO₃ 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](image-url)
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 \( t_1 = 1 \)hr was selected, and for less mobile contaminants \( t_1 = 4 \)hr.

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 \( 10 \times 40.7 \), 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 HNO₃ 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% HNO₃ 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 HNO₃ 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 HNO₃ solution was prepared by adding 45ml of concentrated HNO₃ 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 (NaBH₄) solution for the arsenic analyses consisted of 1g of NaBH₄ and 6.5ml of 0.5M sodium hydroxide made up to 250ml in a volumetric flask. For selenium analyses, 0.75g of AR NaBH₄ 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

<table>
<thead>
<tr>
<th>Element</th>
<th>ARSENIC</th>
<th>SELENIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>193.7</td>
<td>196.0</td>
</tr>
<tr>
<td>Lamp Current (mA)</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Slit Width (nm)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Background Correction</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>Flame Type</td>
<td>Air/Acetylene</td>
<td>Air/Acetylene</td>
</tr>
<tr>
<td>Air Flow Rate (L/min.)</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Acetylene Flow Rate (L/min.)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Reductant</td>
<td>4g/L NaBH₄</td>
<td>3g/L NaBH₄</td>
</tr>
<tr>
<td>Carrier</td>
<td>100ml/L HCl</td>
<td>100ml/L HCl</td>
</tr>
<tr>
<td>Purge Gas</td>
<td>N₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Reductant Flow Rate (ml/min.)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Carrier Flow Rate (ml/min.)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sample Flow Rate (ml/min.)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Purge Gas Pressure (kPa)</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

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 0μL, 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 H₂SO₄ addition to give a final concentration of 1%v/v H₂SO₄. 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

<table>
<thead>
<tr>
<th>U_{start}</th>
<th>-1.2V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔU</td>
<td>+1.5V</td>
</tr>
<tr>
<td>Pulse Amplitude (U_{DP})</td>
<td>40mV</td>
</tr>
<tr>
<td>mm/t_{drop}</td>
<td>1</td>
</tr>
<tr>
<td>t_{drop} [s]</td>
<td>0.8</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>7.5mV/sec</td>
</tr>
<tr>
<td>Stirrer Speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Mercury Drop Size</td>
<td>2</td>
</tr>
<tr>
<td>Nitrogen Pressure (psi)</td>
<td>50</td>
</tr>
<tr>
<td>Purge Gas</td>
<td>N₂</td>
</tr>
</tbody>
</table>

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 HNO₃ 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 HNO₃ solution was prepared prior to every analysis by adding 50ml of concentrated HNO₃ 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 HNO₃ 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 Metal Standards

Following analysis of the blank solution, the stirrer was turned back on and 50\mu L 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 50\mu L and 100\mu L 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\textsubscript{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\textsubscript{3} for 15 minutes. It was then removed and rinsed with deionised water until the washings were pH neutral.

2.5.2.3 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 TDScant 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 58.31 ml (29.15 meq) of 0.5M HNO₃ in the first part of the extraction to keep the solution at pH 7, while 98.57 ml (49.28 meq) of 0.5M HNO₃ was added in the second part to maintain a solution pH of 4.

### Table 3.1: Zinc Maximum Availability Test Data

<table>
<thead>
<tr>
<th>Mass of Zinc Leached (mg)</th>
<th>Percentage of Total Mass of Zinc Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>158.6</td>
<td>43.9% (±0.3%)</td>
<td>4.68</td>
<td>564.1</td>
<td>6.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration Leached (ppm)</th>
<th>Mass of Zinc Leached per 100g Fixed Waste (mg)</th>
<th>Percentage of Total Mass of Zinc Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.095</td>
<td>0.19</td>
<td>0.01% (±2.0 x 10⁻⁴%)</td>
<td>12.11</td>
<td>232.1</td>
<td>12.8</td>
</tr>
</tbody>
</table>

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.
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

---

**Table 3.3: Zinc ABLP Data**

<table>
<thead>
<tr>
<th>Concentration Leached (ppm)</th>
<th>Mass of Zinc Leached per 100g Fixed Waste (mg)</th>
<th>Percentage of Total Mass of Zinc Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.80</td>
<td>0.04% (±8.1 x 10⁻²%)</td>
<td>11.60</td>
<td>210.3</td>
<td>8.20</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Sequential Leach Number</th>
<th>Concentration leached (ppm)</th>
<th>Mass of Zinc Leached (mg)</th>
<th>Percentage of Total Mass of Zinc Leached (±1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40</td>
<td>0.80</td>
<td>0.036% (±8.1 x 10⁻⁴%)</td>
</tr>
<tr>
<td>2</td>
<td>0.31</td>
<td>0.63</td>
<td>0.028% (±1.6 x 10⁻³%)</td>
</tr>
<tr>
<td>3</td>
<td>0.26</td>
<td>0.52</td>
<td>0.023% (±1.7 x 10⁻³%)</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.40</td>
<td>0.018% (±8.3 x 10⁻⁴%)</td>
</tr>
<tr>
<td>5</td>
<td>0.18</td>
<td>0.37</td>
<td>0.016% (±3.5 x 10⁻⁴%)</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.33</td>
<td>0.015% (±8.9 x 10⁻⁴%)</td>
</tr>
<tr>
<td>7</td>
<td>0.12</td>
<td>0.24</td>
<td>0.011% (±1.7 x 10⁻⁴%)</td>
</tr>
<tr>
<td>8</td>
<td>0.07</td>
<td>0.14</td>
<td>0.006% (±1.5 x 10⁻⁴%)</td>
</tr>
<tr>
<td>9</td>
<td>0.07</td>
<td>0.14</td>
<td>0.006% (±5.1 x 10⁻⁴%)</td>
</tr>
<tr>
<td>10</td>
<td>0.13</td>
<td>0.25</td>
<td>0.011% (±5.9 x 10⁻⁴%)</td>
</tr>
<tr>
<td>Total</td>
<td>N/A</td>
<td>3.83</td>
<td>0.169% (±7.6 x 10⁻³%)</td>
</tr>
</tbody>
</table>

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](image)

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.

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

<table>
<thead>
<tr>
<th>Mass of Zinc Leached (mg)</th>
<th>Percentage of Total Mass of Zinc Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>796.2</td>
<td>0.09%</td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Leaching Test</th>
<th>Percentage of Total Mass of Zinc Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Column</td>
<td>0.09%</td>
</tr>
<tr>
<td>TCLP</td>
<td>0.01%</td>
</tr>
<tr>
<td>ABLP</td>
<td>0.04%</td>
</tr>
<tr>
<td>Sequential ABLP</td>
<td>0.17%</td>
</tr>
<tr>
<td>Max. Avail. Test</td>
<td>43.9%</td>
</tr>
</tbody>
</table>

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.

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.

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 \( K_{sp} \text{Zn(OH)}^2 = 3.3 \times 10^{-17} \) (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.
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

<table>
<thead>
<tr>
<th>Small Column</th>
<th>Mass of Zinc Leached (mg)</th>
<th>Percentage of Total Mass of Zinc Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABLC100</td>
<td>7.15</td>
<td>0.32%</td>
</tr>
<tr>
<td>ABLC180</td>
<td>17.27</td>
<td>0.43%</td>
</tr>
<tr>
<td>LCC100</td>
<td>1.75</td>
<td>0.08%</td>
</tr>
</tbody>
</table>

#### 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 \( \frac{1}{4} \) of the total zinc leached over the duration of the test, was leached in the first 4 days. Further, after 53 days \( \frac{1}{2} \) of the total was leached, and \( \frac{3}{4} \) 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.
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](image)

**Figure 3.12: ABLC100 & Sequential ABLP – 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](image)

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](image)

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, 17.265 mg, 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 $\frac{1}{4}$ 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 $\frac{3}{4}$. 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](image)
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 40\(\mu\)g leached, following the period of no flow, the mass of zinc in the leachate jumped back up to over 400\(\mu\)g. It was a further 21 days before the levels of zinc dropped back down to 40\(\mu\)g 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 317 days 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.
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 100 days 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.
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.
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.
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).
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).
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.
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.
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](image1)

![Figure 3.32: LCC100 & Large Column – Conductivity](image2)
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

<table>
<thead>
<tr>
<th>Replicate</th>
<th>t_n = 1A</th>
<th>t_n = 1B</th>
<th>t_n = 4A</th>
<th>t_n = 4B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Leached (mg)</td>
<td>0.71</td>
<td>0.74</td>
<td>0.60</td>
<td>0.90</td>
</tr>
<tr>
<td>% Leached</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.09</td>
</tr>
</tbody>
</table>

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](image)

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 40.7 cm$^2$ to approximately 61 cm$^2$, 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
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.

![Cumulative Mass Zinc Leached vs Square Root of Time](image)

**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_e = 4A & 4B – Cumulative Mass Zinc Leached v’s Square Root of Time](image)

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**
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:

- \( \Delta t_n \) = 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
- \( \beta \) = 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>
<thead>
<tr>
<th>Sphere</th>
<th>( t_n = 1A )</th>
<th>( t_n = 1B )</th>
<th>( t_n = 4A )</th>
<th>( t_n = 4B(a) )</th>
<th>( t_n = 4B(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LX - 1(^{st}) 7 Periods</td>
<td>13.21</td>
<td>13.19</td>
<td>12.60</td>
<td>13.08</td>
<td>13.42</td>
</tr>
<tr>
<td>LX - Total</td>
<td>14.21</td>
<td>14.18</td>
<td>13.46</td>
<td>13.92</td>
<td>14.27</td>
</tr>
</tbody>
</table>

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**

![Sphere 1A](image)

**Figure 3.47: Sphere 1A**
Figure 3.48: Sphere 1B

Figure 3.49: Sphere 4A

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 PDXE 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
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: tₚ = 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: t₁ = 4B – PIXE Data for Calcium](image)

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

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

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

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

<table>
<thead>
<tr>
<th>Mass of Copper Leached (mg)</th>
<th>Percentage of Total Mass of Copper Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79.34</td>
<td>26.7% (±0.19%)</td>
<td>4.68</td>
<td>564.1</td>
<td>6.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration Leached (ppm)</th>
<th>Mass of Copper Leached per 100g Fixed Waste (mg)</th>
<th>Percentage of Total Mass of Copper Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.050</td>
<td>0.003% (±3.1 x 10⁻⁵%)</td>
<td>12.11</td>
<td>232.1</td>
<td>12.8</td>
</tr>
</tbody>
</table>

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

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

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>
<thead>
<tr>
<th>Sequential Leach Number</th>
<th>Copper Concentration Leached (ppm)</th>
<th>Mass of Copper Leached (mg)</th>
<th>Percentage of Total Mass of Copper Leached (±1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.08</td>
<td>0.15</td>
<td>0.008% (± 2.5 x 10⁻⁴%)</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.10</td>
<td>0.005% (± 4.3 x 10⁻⁴%)</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>0.08</td>
<td>0.004% (± 1.5 x 10⁻⁴%)</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>0.06</td>
<td>0.003% (± 6.0 x 10⁻⁴%)</td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>0.06</td>
<td>0.003% (± 8.2 x 10⁻⁴%)</td>
</tr>
<tr>
<td>6</td>
<td>0.04</td>
<td>0.08</td>
<td>0.004% (± 1.9 x 10⁻⁴%)</td>
</tr>
<tr>
<td>7</td>
<td>0.04</td>
<td>0.08</td>
<td>0.004% (± 6.0 x 10⁻⁴%)</td>
</tr>
<tr>
<td>8</td>
<td>0.03</td>
<td>0.06</td>
<td>0.003% (± 5.8 x 10⁻⁴%)</td>
</tr>
<tr>
<td>9</td>
<td>0.06</td>
<td>0.12</td>
<td>0.007% (± 2.4 x 10⁻⁴%)</td>
</tr>
<tr>
<td>10</td>
<td>0.09</td>
<td>0.18</td>
<td>0.009% (± 4.5 x 10⁻⁴%)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>N/A</strong></td>
<td><strong>0.97</strong></td>
<td><strong>0.052% (± 5.7 x 10⁻³%)</strong></td>
</tr>
</tbody>
</table>

*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).

[Graph showing Mass Copper Leached and pH v's Time]

**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 halfway 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](image)

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

<table>
<thead>
<tr>
<th>Mass of Copper Leached (mg)</th>
<th>Percentage of Total Mass of Copper Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>250.5</td>
<td>0.04%</td>
</tr>
</tbody>
</table>

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 $4.5 \times 10^{-21}$ mol L$^{-1}$ as compared to $3.3 \times 10^{-17}$ 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.

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

<table>
<thead>
<tr>
<th>Leaching Test</th>
<th>Percentage of Total Mass of Copper Leached</th>
<th>Liquid to Solid Ratio</th>
<th>Method of Leachant Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Column</td>
<td>0.035%</td>
<td>19.1:1</td>
<td>Downflow Spraying</td>
</tr>
<tr>
<td>TCLP</td>
<td>0.003%</td>
<td>20:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>ABLP</td>
<td>0.008%</td>
<td>20:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>Sequential ABLP</td>
<td>0.052%</td>
<td>200:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>Max. Avail. Test</td>
<td>26.7%</td>
<td>9.8:1</td>
<td>Stirring</td>
</tr>
</tbody>
</table>
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 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](image)

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](image)
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.
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

<table>
<thead>
<tr>
<th>Small Column</th>
<th>Mass of Copper Leached (mg)</th>
<th>Percentage of Total Mass of Copper Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABLC100</td>
<td>6.27</td>
<td>0.34%</td>
</tr>
<tr>
<td>ABLC180</td>
<td>4.59</td>
<td>0.14%</td>
</tr>
<tr>
<td>LCC100</td>
<td>0.69</td>
<td>0.04%</td>
</tr>
</tbody>
</table>

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](image)

![Figure 4.10: ABLC100 – Cumulative Percentage Copper and Zinc Leached v’s Time](image)

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 day's leachate, and the spraying of the following day's 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
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 1OL mark, whereas the Sequential ABLP pH continues to climb. Similarly, after the 1OL 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 1OL 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](image)

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).
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](image)

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.

![Graph showing cumulative percentage copper leached vs time for ABLC180 and ABLC100](image)

**Figure 4.21: ABLC180 & ABLC100 – Cumulative Percentage Copper Leached vs 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.
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.
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.
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 \( \text{Ca(OH)}_2 \) available for leaching. If the majority of the \( \text{Ca(OH)}_2 \) 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.

![Graph: LCC100 - pH and Redox Potential v's Time](image)

**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 immediate 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.

![Graph showing cumulative percentage copper leached vs time](image)

**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.
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**

<table>
<thead>
<tr>
<th>Replicate</th>
<th>t_n = 1A</th>
<th>t_n = 1B</th>
<th>t_n = 4A</th>
<th>t_n = 4B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Leached (mg)</td>
<td>0.107</td>
<td>0.108</td>
<td>0.135</td>
<td>0.130</td>
</tr>
<tr>
<td>% Leached</td>
<td>0.012</td>
<td>0.012</td>
<td>0.016</td>
<td>0.015</td>
</tr>
</tbody>
</table>

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.
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](image)

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: tᵣ = 1A & 1B – Cumulative Mass Copper Leached v’s Square Root of Time](image-url)
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’.
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

<table>
<thead>
<tr>
<th>Sphere</th>
<th>$t_n = 1A$</th>
<th>$t_n = 1B$</th>
<th>$t_n = 4A$</th>
<th>$t_n = 4B(a)$</th>
<th>$t_n = 4B(b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LX - 1st 7 Periods</td>
<td>13.49</td>
<td>14.00</td>
<td>13.75</td>
<td>14.14</td>
<td>14.50</td>
</tr>
<tr>
<td>LX - Total</td>
<td>14.50</td>
<td>15.00</td>
<td>14.62</td>
<td>15.00</td>
<td>15.35</td>
</tr>
</tbody>
</table>

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.
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**

<table>
<thead>
<tr>
<th>Test</th>
<th>Percentage of Copper Leached</th>
<th>L/S Ratio</th>
<th>Ratio Leached (where ABLP = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAT</td>
<td>26.7%</td>
<td>9.8:1</td>
<td>3337.5</td>
</tr>
<tr>
<td>TCLP</td>
<td>0.003%</td>
<td>20:1</td>
<td>0.375</td>
</tr>
<tr>
<td>ABLP</td>
<td>0.008%</td>
<td>20:1</td>
<td>1</td>
</tr>
<tr>
<td>Sequential ABLP</td>
<td>0.052%</td>
<td>200:1</td>
<td>6.5</td>
</tr>
<tr>
<td>Large Column</td>
<td>0.035%</td>
<td>19.1:1</td>
<td>4.375</td>
</tr>
<tr>
<td>LCC100</td>
<td>0.037%</td>
<td>17.6:1</td>
<td>4.625</td>
</tr>
<tr>
<td>ABLC100</td>
<td>0.34%</td>
<td>9571:1</td>
<td>42.5</td>
</tr>
<tr>
<td>ABLC180</td>
<td>0.14%</td>
<td>4873:1</td>
<td>17.5</td>
</tr>
<tr>
<td>DLT; T_n = 1A</td>
<td>0.012%</td>
<td>634.3:1</td>
<td>1.5</td>
</tr>
<tr>
<td>DLT; T_n = 1B</td>
<td>0.012%</td>
<td>626.2:1</td>
<td>1.5</td>
</tr>
<tr>
<td>DLT; T_n = 4A</td>
<td>0.016%</td>
<td>445.2:1</td>
<td>2</td>
</tr>
<tr>
<td>DLT; T_n = 4B</td>
<td>0.015%</td>
<td>447.5:1</td>
<td>1.875</td>
</tr>
</tbody>
</table>
Table 4.11: Leaching Breakdown of Copper From Column and Tank Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Time to Leach 1$^{st}$ 25% of Total Copper (days)</th>
<th>Time to Leach 2$^{nd}$ 25% of Total Copper (days)</th>
<th>Time to Leach 3$^{rd}$ 25% of Total Copper (days)</th>
<th>Time to Leach 4$^{th}$ 25% of Total Copper (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Column</td>
<td>70</td>
<td>49</td>
<td>70</td>
<td>175</td>
</tr>
<tr>
<td>LCC100</td>
<td>100</td>
<td>105</td>
<td>56</td>
<td>105</td>
</tr>
<tr>
<td>ABLCl00</td>
<td>4</td>
<td>49</td>
<td>142</td>
<td>168</td>
</tr>
<tr>
<td>ABLCl80</td>
<td>95</td>
<td>77</td>
<td>78</td>
<td>112</td>
</tr>
<tr>
<td>DLT; $T_n = 1A$</td>
<td>66.7</td>
<td>69.8</td>
<td>84</td>
<td>140</td>
</tr>
<tr>
<td>DLT; $T_n = 1B$</td>
<td>22</td>
<td>93.5</td>
<td>77</td>
<td>168</td>
</tr>
<tr>
<td>DLT; $T_n = 4A$</td>
<td>60.2</td>
<td>48.3</td>
<td>56</td>
<td>196</td>
</tr>
<tr>
<td>DLT; $T_n = 4B$</td>
<td>54</td>
<td>47.5</td>
<td>77</td>
<td>182</td>
</tr>
</tbody>
</table>

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 PDCE 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

<table>
<thead>
<tr>
<th>Mass of Lead Leached (mg)</th>
<th>Percentage of Total Mass of Lead Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.03</td>
<td>21.8% (±0.14%)</td>
<td>4.68</td>
<td>564.1</td>
<td>6.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration Leached (ppm)</th>
<th>Mass of Lead Leached per 100g Fixed Waste (mg)</th>
<th>Percentage of Total Mass of Lead Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30</td>
<td>14.59</td>
<td>0.17% (±3.1 x 10⁻³%)</td>
<td>12.11</td>
<td>232.1</td>
<td>12.8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Percentage Leached in Leaching Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TCLP</td>
</tr>
<tr>
<td>Lead</td>
<td>0.168%</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.008%</td>
</tr>
<tr>
<td>Copper</td>
<td>0.003%</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration Leached (ppm)</th>
<th>Mass of Lead Leached per 100g Fixed Waste (mg)</th>
<th>Percentage of Total Mass of Lead Leached (±1σ)</th>
<th>pH</th>
<th>Redox Potential (mV)</th>
<th>Conductivity (mScm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.93</td>
<td>49.86</td>
<td>0.57% (±6.7 x 10⁻³%)</td>
<td>11.60</td>
<td>210.3</td>
<td>8.20</td>
</tr>
</tbody>
</table>

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; Bara 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 Bara 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 H2O) (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 CO2 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)\textsuperscript{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\textsuperscript{2+} which was suspected of substituting for Ca\textsuperscript{2+} in the cement matrix, Pb\textsuperscript{2+} is not totally incorporated into the waste due to the size of the lead atom. Therefore, substitution for Ca\textsuperscript{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\textsuperscript{2+}, and these are believed to coat the silicate surfaces. Anionic species in solution (such as Pb(OH)\textsuperscript{3-}) will then compete for Ca\textsuperscript{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)\textsubscript{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

<table>
<thead>
<tr>
<th>Sequential Leach Number</th>
<th>Concentration Leached (ppm)</th>
<th>Mass of Lead Leached (mg)</th>
<th>Percentage of Total Mass of Lead Leached (±1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.93</td>
<td>49.86</td>
<td>0.57% (± 6.7 x 10^{-3}% )</td>
</tr>
<tr>
<td>2</td>
<td>21.47</td>
<td>42.95</td>
<td>0.50% (± 5.1 x 10^{-3}% )</td>
</tr>
<tr>
<td>3</td>
<td>16.52</td>
<td>33.04</td>
<td>0.38% (± 2.3 x 10^{-3}% )</td>
</tr>
<tr>
<td>4</td>
<td>12.85</td>
<td>25.70</td>
<td>0.30% (± 1.9 x 10^{-3}% )</td>
</tr>
<tr>
<td>5</td>
<td>12.86</td>
<td>25.73</td>
<td>0.30% (± 8.4 x 10^{-3}% )</td>
</tr>
<tr>
<td>6</td>
<td>13.76</td>
<td>27.51</td>
<td>0.32% (± 1.6 x 10^{-3}% )</td>
</tr>
<tr>
<td>7</td>
<td>14.02</td>
<td>28.03</td>
<td>0.32% (± 4.6 x 10^{-3}% )</td>
</tr>
<tr>
<td>8</td>
<td>3.61</td>
<td>7.22</td>
<td>0.08% (± 2.6 x 10^{-3}% )</td>
</tr>
<tr>
<td>9</td>
<td>3.17</td>
<td>6.33</td>
<td>0.07% (± 7.1 x 10^{-3}% )</td>
</tr>
<tr>
<td>10</td>
<td>4.28</td>
<td>8.57</td>
<td>0.10% (± 6.4 x 10^{-3}% )</td>
</tr>
<tr>
<td>Total</td>
<td>N/A*</td>
<td>254.94</td>
<td>2.94% (± 9.9 x 10^{-3}% )</td>
</tr>
</tbody>
</table>

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.
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.
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.
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>
<thead>
<tr>
<th>Mass of Lead Leached (g)</th>
<th>Percentage of Total Mass of Lead Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.90</td>
<td>1.12%</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Leaching Test</th>
<th>Percentage of Total Mass of Lead Leached</th>
<th>Liquid to Solid Ratio</th>
<th>Method of Leachant Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Column</td>
<td>1.1%</td>
<td>19.1:1</td>
<td>Downflow Spraying</td>
</tr>
<tr>
<td>TCLP</td>
<td>0.2%</td>
<td>20:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>ABLP</td>
<td>0.6%</td>
<td>20:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>Sequential ABLP</td>
<td>2.9%</td>
<td>200:1</td>
<td>Rotary Agitation</td>
</tr>
<tr>
<td>Max. Avail. Test</td>
<td>21.8%</td>
<td>9.8:1</td>
<td>Stirring</td>
</tr>
</tbody>
</table>

Table 5.8: Percentages of Lead, Zinc, and Copper Leached in Large Column

<table>
<thead>
<tr>
<th>Metal</th>
<th>Percentage of Total Mass of Metal Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>1.12%</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.09%</td>
</tr>
<tr>
<td>Copper</td>
<td>0.04%</td>
</tr>
</tbody>
</table>

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.
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 \textit{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
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

<table>
<thead>
<tr>
<th>Small Column</th>
<th>Mass of Lead Leached (mg)</th>
<th>Percentage of Total Mass of Lead Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABLC100</td>
<td>240.46</td>
<td>2.7%</td>
</tr>
<tr>
<td>ABLC180</td>
<td>966.90</td>
<td>6.2%</td>
</tr>
<tr>
<td>LCC100</td>
<td>55.13</td>
<td>0.64%</td>
</tr>
</tbody>
</table>

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](image)

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).
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 \textit{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)$_4^{2-}$, 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.
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](image)

*Figure 5.17: ABLC180 - Mass Lead Leached and Conductivity 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.
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](image)

**Figure 5.20: ABLC180 & ABLC100 – Cumulative Percentage Lead Leached v’s Time**