

# **Mine waste water treatment and acid recovery using membrane distillation and solvent extraction**

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## Abstract

Waste waters produced and disposed of at modern mine sites are problematic because they contain hazardous substances (e.g. heavy metals, metalloids, acids, process chemicals), and therefore require treatment before disposing to the environment. Three different kinds of mine waters are identified depending on their chemical composition and pH. They are acidic mine waters, alkaline mine waters and neutral mine waters. Acidic mine waters are of interest because they have greater environmental hazards compared to others. Other acidic waste solutions also considered are waste streams from mineral processing plants and smelter sites. The current approaches to manage acidic waste solutions includes, neutralization, flocculation, filtration and bioremediation. However, acid and water recovery using current technologies has not proven to be viable as most of these processes fail to produce sufficient volume and quality of water whereas others do not provide the selectivity necessary to create valuable product streams suitable for recycle or re-use. In these processes, the by-product sludge can itself become a disposal problem. Therefore a novel approach to acid and water recovery are needed to improve the sustainability of the mining industry.

The objective of this study is to explore the possibility for the novel combination of two technologies, membrane distillation (MD) and solvent extraction (SX) for water and acid recovery. The focus is the testing on acid and water recovery from industry spent acid streams and acidic mine wastes solutions and also modelling of the economic opportunities for MD to understand its cost sensitivities, in particular in the context of a carbon tax benchmarked against its more well-known application in seawater desalination.

In order to explore the concept for acid and water recovery by MD and SX, there were four stages of this project:

- (1) To confirm the viability of MD to concentrate real brine complexes to near saturation values without the presence of acid;
- (2) Develop a cost model for MD that explores its cost sensitivities, in particular with regards to carbon pricing and economic opportunity for using MD with waste heat;
- (3) Study the viability of MD to concentrate the spent acid ( $\text{H}_2\text{SO}_4$ ) in the waste stream and improve the efficiency of subsequent SX. This was carried out on model mine waste water from acid mine drainage and real leach solution containing  $\text{H}_2\text{SO}_4$  and HCl respectively; and
- (4) Study the viability of SX to selectively recover acids ( $\text{H}_2\text{SO}_4$ ) that would be pre concentrated by MD to assess the viability of the combined processes.

### *Viability of MD on real brine complexes and cost analysis*

In the first stage of the investigation, RO brine of approximately 3300 mg/L total dissolved solids (TDS) concentration was fed to the MD to concentrate the brine and recover fresh water. The experiment demonstrated MD to concentrate to hypersaline concentrations. MD showed high flux in the range of 20 to 37 kg/m<sup>2</sup>/h which is high for all salinities up to 361,000 mg/L TDS. The water recovery was > 90%. No scale was observed on the membrane, but was observed in the 0.5µm filter and was thus efficiently captured at the highest temperature point in the hot cycle to avoid membrane scaling. This is a novel finding for MD research, being of interest for hypersaline desalination applications. However the key finding for this research was the MD setup including a solids filter, which will be useful for concentrating mine waste waters prior to SX.

In the second stage, the cost model compared costs of MD to the common desalination technologies, multi-effect distillation (MED), multistage flash (MSF) and RO for seawater desalination. The results indicated that at any plant capacity when fed with fuel-fired steam and/or electricity, MSF is the most costly desalination process, while MED and MD are similar and RO has the best economics. With the inclusion of a carbon tax of \$23 per tonne carbon in Australia, the cost of all desalination technologies increased but RO remained the most economically favourable.

However, when heat comes at a cost equivalent of 10% of the value of the steam needed for MD and MED, under a carbon tax regime, the cost of MD is cheaper than RO and MED. The favour to MD was due to lower material cost. MD is highly sensitive to thermal energy, but offers a better opportunity for the use of waste thermal heat as compared with MED. Compared with RO, MD has lower reliance on electricity. MD can also cost effectively harness abundant low grade heat sources or be integrated into existing processes. This assessment has therefore guided the economically viable means of operating MD for mining water treatment.

#### *Performance of MD for concentrating mining waste waters*

The next stage of the investigation was to study the viability of MD to concentrate the spent acid ( $\text{H}_2\text{SO}_4$ ) in the waste stream and improve the efficiency of subsequent SX. This is because SX must have relatively high acid concentrations ( $\sim 200$  g/L) in order to extract the acids. MD testing was carried out on a synthetic model mine waste water from acid mine drainage and a real leach solution containing  $\text{H}_2\text{SO}_4$  and HCl respectively. The synthetic model mine water tests confirmed MD's viability to concentrate  $\text{H}_2\text{SO}_4$ . This was established from experiments on solution containing only acid ( $\text{H}_2\text{SO}_4$ ) and solutions containing both acid ( $\text{H}_2\text{SO}_4$ ) and salts. In all these solutions, the final concentration of  $\text{H}_2\text{SO}_4$  increased from as low as 40 g/L to at least 240 g/L. However in samples solution containing NaCl in the feed, HCl was found to enter the permeate due to its volatility. Thus MD worked well to concentrate  $\text{H}_2\text{SO}_4$ , but solutions containing Cl are likely to lead to HCl in the permeate.

MD was then tested on real leach solutions containing either  $\text{H}_2\text{SO}_4$  or HCl. For the  $\text{H}_2\text{SO}_4$  real leach solution, the salt rejection exceeded 99.9% and the free acid was concentrated from the initial concentration of 1.08 M to about 4.60 M. > 99.9% of the acid was rejected by the membrane. The concentrations factor for all metals except calcium was found to be greater than 4. This is attributable to the high water recovery achieved (>80%). As observed earlier in the groundwater benchmark test, the concentration factor achieved for calcium was limited because it was precipitating. The outcome of this testing showed that for a process waste leach solutions containing sulphuric acid, iron, aluminium, magnesium, scandium, nickel, cobalt, manganese and sulphates, MD is well suited to recover very clean water and concentrate sulphuric acid suitable for capture by SX. For the HCl real leach solution, HCl passes through the membrane to the permeate confirming the earlier finding on synthetic solutions containing Cl. Free acid in the permeate at the end of the MD experiment was higher than in the concentrate while salts were mostly rejected. Therefore, MD can be applied for the treatment of industrial effluents containing HCl and salts. The useful products might be hydrochloric acid and salts after crystallization from the supersaturated feed. Because MD can effectively remove HCl from the feed on its own, no SX testing was carried out on HCl rich waste waters.

### *SX for acid recovery*

The final stage of the research considered the viability of SX to selectively recover acids ( $\text{H}_2\text{SO}_4$ ) pre-concentrated by MD. This was carried out on a synthetic solution containing  $\text{H}_2\text{SO}_4$  and a model waste acidic solution from a copper smelting plant. Prior to the SX testing, the organic system required optimisation as SX for acids removal is not widely explored. Preliminary experiments were performed using extractants in the concentration range of 20–60% (v/v) TEHA and Alamine 336 and 20–100% (v/v) Cyanex 923. Initially, octanol was used as the diluent for all three systems. However, for Alamine 336 system, gel was formed with octanol as the diluent. The issues of gel formation was resolved for Alamine 336 system using Shellsol D70 (100% aliphatic) as a diluent and isodecanol as modifier. No phase separation problem was observed with the TEHA and Cyanex 923 systems. In terms of extraction, both TEHA and Alamine 336 systems performed well and much better than the Cyanex 923 system. With 60% concentration of TEHA and Alamine 336 acid extraction was 88%, and 91% respectively while 100% Cyanex 923 only 50% acid extraction. TEHA and Alamine 336 are amine extractants while Cyanex 923 is a neutral extractant. Amines are bases that naturally react with and extract acids. Therefore, the extractability for acid with TEHA and Alamine 336 is stronger than that with the neutral extractant Cyanex 923. The three extractant systems TEHA, Cyanex 923 and Alamine 336 were further examined for acid stripping. The loaded organic solutions were stripped with water at 60 °C. It was found that 97.6% and 95.3%  $\text{H}_2\text{SO}_4$  were stripped from the loaded TEHA and Cyanex 923 systems, respectively. In contrast, only 10.5%  $\text{H}_2\text{SO}_4$  was stripped from the Alamine336 system. Based on the extraction and stripping performance, the TEHA system was selected for further study due to higher acid extraction compared with the Cyanex 923 system and ease in stripping compared with the Alamine 336 system.

The selected organic system (TEHA) was optimized taking into account the effects of diluent, effect of modifiers, effect of organic composition, effect of agitation speed and effect of temperature on acid extraction. The organic system containing 50% TEHA and 20% octanol was tested with different diluents including Shellsol A150 (100% aromatic), Shellsol2046 (19% aromatic and 81% aliphatic) and Shellsol D70 (100% aliphatic). It was found that in terms of diluents type, the acid extractions were in the order of Shellsol A150 >>Shellsol 2046 > Shellsol D70, indicating that Shellsol A150 performed best. In the case of a modifier, octanol achieved better performance compared to isodecanol. To optimise the organic solution containing 50% TEHA, the concentrations of octanol and Shellsol A150 were varied with their total volume being 50% in the organic system. Best performance of the organic system for acid extraction was found to found to 50% TEHA, 40% octanol and 10% Shellsol A150.

The optimised TEHA system consisting of 50% TEHA, 40% octanol and 10% Shellsol A150 was tested under different temperatures using an O: A ratio of 2 at 22 °C. With the increase in temperature from 22 °C to 60 °C the acid extraction decreased from 82% to 72%. Investigating stripping and extracting kinetics, both were very fast and about between 1-2 mins. McCabe–Thiele extraction diagram showed that, three stages are required.

The optimised TEHA system was used to extract acid from a model waste acidic solution from copper smelting plant. It was found that the system effectively extracted acid and only a small amount of metals were entrained. After scrubbing the loaded organic solution in a single contact, almost all entrained metals were removed. In the case that the mining waste solution contains low concentration of acid, MD can be used to recover the water and concentrate the acid and metals. SX can be then used to recover the acid and metals.

*Major conclusions and opportunities for future work*

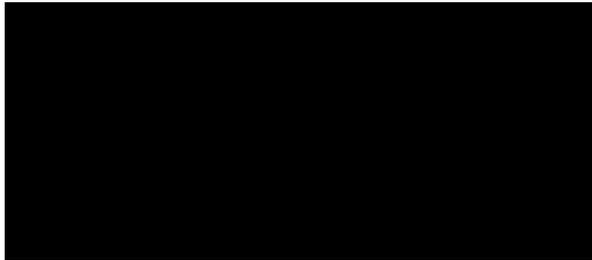
Through the four stages of study, it is concluded that the MD and SX can work well together for removal of clean acid and water from mining waste waters for potential reuse offering environmental benefits. MD can concentrate real mining waste waters and recover acids using either MD directly (HCl) or in conjunction with SX (H<sub>2</sub>SO<sub>4</sub>). For MD to work most cost effectively, harnessing process waste heat offsets the major cost of thermal energy required.

In future work, the application of MD may be coupled with the waste slag from mining operations as a source of thermal energy to produce freshwater from mining waste solutions and concentrate non-volatiles, such as H<sub>2</sub>SO<sub>4</sub>, heavy metal, metalloids etc., these are possibilities that need further research to prove the feasibility of MD for these applications. Further opportunities for future work would be to move towards the challenges of demonstrating the concept at a pilot scale using commercially available MSD and SX units. Such a trial will uncover the true costs and overall benefits that have so far been shown to be viable from this work.

### **Declaration**

“I, Uchenna Kennedy Kesieme, declare that the PhD thesis entitled Mine waste water treatment and acid recovery using membrane distillation and solvent extraction is not more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work”

Signature:



01-07-2015

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## Research Papers

### Published Journal Papers arising from PhD research

- [1] U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng, and M. Duke. Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation. *Desalination* 323(2013)66 – 74
- [2] U. K. Kesieme, H. Aral, M. Duke, N. Milne, and C.Y. Cheng. Recovery of sulphuric acids from waste and process solutions using solvent extraction. *Hydrometallurgy*, 138 (2013) 14– 20
- [3] U. K. Kesieme, N. Milne, C.Y. Cheng, H. Aral and M. Duke. Recovery of water and acid from leach solution using direct contact membrane distillation. *Water Science and Technology* 69(2014)868-875
- [4] U. K. Kesieme, N. Milne, C.Y. Cheng and M. Duke. Application of membrane distillation for the recovery of water from a synthetic waste alkaline solution. (Draft)

### Published Conference Paper:

- [1] U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng and M. Duke. Novel application of membrane distillation for acid and water recovery of mining waste waters. International Mine Water Association Annual Conference, IMWA, October, 2012, Bunbury, WA, Australia, 623 - 630
- [2] U. K. Kesieme, H. Aral, N. Milne, M. Duke, and C. Y. Cheng. Application of membrane distillation and solvent extraction for water and acid recovery from waste solution. Mine Water Solutions in Extreme Environment Annual Conference, 2013, Lima, Peru, Chapter 4, 424 – 433
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- [4] U. K. Kesieme, N. Milne, C. Y. Cheng, H. Aral and M. Duke. Recovery of fresh water, acid and metals from leach solution using membrane distillation. 7th IWA Specialised Membrane Technology Conference and Exhibition. Toronto, Canada, IWA: 2013, Paper 157

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- [3] U. K. Kesieme, N. Milne, H. Aral, H. and M. Duke. Membrane distillation for hydrochloric acid recovery from spent pickle liquor. Austpec Resources Industrial Project (2012)
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### **Oral presentations**

- [1] U. K. Kesieme, N. Milne, H. Aral, C. Y. Cheng, and M. Duke. Techno-economic analysis of different desalination technologies (MD, RO and MED) in the context of carbon pricing, and opportunities for membrane distillation. Early Career Membrane Society of Australasian (MSA) Annual Conference, Adelaide, Australia, 2011
- [2] U.K. Kesieme, H. Aral, N. Milne, M. Duke, and C. Y. Cheng. Application of membrane distillation and solvent extraction for water and acid recovery from waste solution. Early Career Membrane Society of Australasian (MSA) Annual Conference, Adelaide, Australia, 2012
- [3] U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng and M. Duke2012. Novel application of membrane distillation for acid and water recovery of mining waste waters. International Mine Water Association Annual Conference, IMWA, October, 2012, Bunbury, WA, Australia
- [4] U. K. Kesieme, N. Milne, C. Y. Cheng, C, H. Aral and M. Duke. Recovery of fresh water, acid and metals from leach solution using membrane distillation. 7th IWA Specialised Membrane Technology Conference and Exhibition. Toronto, Canada, IWA: 2013
- [5] U. K. Kesieme, N. Milne, C. Y. Cheng, C, H. Aral and M. Duke. Mine waste water treatment and acid recovery using membrane distillation and solvent extraction, International Membrane Science Technology Conference (IMSTEC), Melbourne, 25<sup>th</sup> -29<sup>th</sup> November, 2013

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# 1. Introduction (Chapter 1)

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## 1.1. Status of the mining industry and water use

Mining is a large industrial sector that is growing fast, and uses water in remote areas where it is often 'self-supplied' and more scarce. As the world's population grows, migrates towards cities, and improves its standard of living, the demand for mineral and metals will increase. There has been rapid increase in the production of most Australian metals and coal products since the 1950s[1, 2]. The highest production level in this sector is for coal, which since 1994 has almost doubled production from 456 Mt/year to approximately 815 Mt/year in 2008[3]. Iron ore also has a very high production rate, having grown from 129 Mt/year in 1944 to approximately 340 Mt/year in 2008[3]. There are strong prospects for further growth in ore mining in coming decades which is a major water user. Increasing production has used up most of the higher-grade ores so that the industry is increasingly accessing ores of lower quality, which require greater volumes of water to be used per tonne of metal produced. Both the increasing production and declining ore quality make continuing access to water a critical business imperative for the mining industry. The latest water account from the Australian Bureau of Statistics (ABS) report that water consumption in Australia decreased by nearly 14% between 2000-01 and 2004-05[4, 5]. Agricultural consumption went down by 23%, household by 8%, while household reuse or recycling increased from 11% to 16%[5]. However, over the same period: the mining industry's water use increased by 29% as a result of the increase in the level of mining activities, particularly in Western Australia[5]. The mining industry water usage in Australia account is about 10% of all the non-agricultural demand. Water is used by the minerals industry for operational activities that include[2, 6]:

- Transport of ore and waste in slurries and suspension;
- Separation of minerals through chemical processes;
- Physical separation of material such as in centrifugal separation;
- Cooling systems associated with power generation;
- Suppression of dust, both during mineral processing and around conveyors and roads; and
- Washing equipment.

For these applications, water is generally extracted from surface water bodies and ground water aquifers or from the by-product of the mine dewatering process[2]. At some stage of the mining operation, water is unwanted and has no value to the operation. At modern mine sites, water is collected and discharged to settling ponds and tailings dams. The exploitation of surface water and groundwater resources through mining activities is increasingly becoming a serious environmental issue. As a result, the amount to be used is often tightly regulated.

Metallic ore deposits (Cu, Pb, Zn, Au, Ni, U, and Fe), phosphate ores, coal seams, oil shales, and mineral sands may contain abundant sulphides. Large volumes of sulphide minerals can be exposed in: tailings dams; waste rock dumps; coal spoil heaps; heap leach piles; run-of-mine and low-grade ore stockpiles; open pit floors and faces; quarries; and other rock excavations[2, 7]. These sulphide mine wastes are in most cases polyminerale aggregates. The aggregates contain, apart from sulphides, a wide range of possible minerals including silicates, oxides, hydroxides, phosphates, halides, and carbonates[2]. Weathering of the minerals proceeds with

the help of atmospheric gases, water and microorganisms. The chemical weathering of an individual mineral within a polymineralic aggregate can be classified as acid producing (i.e. generation of  $H^+$ ), acid buffering (i.e. consumption of  $H^+$ ), or non-acid generating or consuming reaction (i.e. no generation or consumption of  $H^+$ ). For example, the degradation of pyrite is an acid producing reaction, whereas the weathering of calcite is acid buffering, and the dissolution of quartz does not consume or generate any acid[2, 8]. The balance of all chemical reactions, occurring within a particular waste at any time, will determine whether the material will produce acid and lead to acid mine drainage[2].

### **1.2. Acid mine drainage and case for acid recovery**

Acid mine drainage (AMD) is a persistent and potentially severe source of pollution from mine sites that can continue long after mining has ceased. An example of poor mine water quality that resulted to AMD is the waste rock dumps at the Mt. Lyell copper mine in Queenstown, Australia. The waste rock dumps and mine workings are significant contributors to AMD, leading to waste leaching into the Queen River[2]. It is estimated that AMD in this region will continue for another 600 years with the present copper load being 2000 kg per day[2]. In extreme cases, AMD may even continue for thousands of years[2, 7]. Other effluent generated from mining and metallurgical processes includes tailing waters and process acid streams from leaching and pickling applications. When such acid-laden waters reach receiving water bodies, such as lakes, streams or aquifers, the waters can cause undesirable turbidity and sedimentation, or their chemical composition may have toxic effects on plants and animals.

The increasingly stringent regulations regarding the discharge of acidic waste solutions and the increasing stress upon the recycling/reuse of these effluents after proper treatment poses strong challenges and high economic motivation for the development of new treatment methods. Until recently, the practice for treatment of acid-containing effluents from mining waste and metallurgical processes has been neutralization of which large amounts of alkaline reagents such as calcium carbonate; calcium oxide; calcium hydroxide; magnesium hydroxide and sodium hydroxide are used. This also produces a sludge containing heavy metal compounds that must be disposed of. Furthermore, valuable acid is lost during neutralization processes which could instead be recovered and reused. Industries are now giving serious consideration to acid recovery considering its economic and environmental benefits. Acids are extensively used for hydrometallurgical treatment of minerals and metals. The recovery of acid will not only benefit the environment and the economics of the operation, it can also provide a secondary source of valuable metals, and extend the life of the acid used[9]. Furthermore, recycling of acid would mean elimination of the safety problems associated with its transport to the site.  $H_2SO_4$  and  $HCl$  are acids of interest because that they are commonly used in mineral processing and hydrometallurgical extractions. Thus waste can be minimised by linking this acid demand to most acidic mine waste waters which generally contain  $H_2SO_4$ .

### **1.3. Alternative technologies for acid removal or recovery**

Besides neutralisation, other treatment methods involve both active and passive treatment technologies to mitigate the problems of acid and salt accumulation in process acidic waste solutions. Many of these treatment techniques are commercialized while others are not standard industry practice and still at the exploratory stage. These include ion exchange (i.e. metal removal using various ion exchange media such as resins or polymers)[2], electrolysis (i.e. metal recovery with electrodes), biosorption (i.e. metal removal using biological cell material), bioreactor tanks (i.e. vessels that contain colonies of metal immobilizing bacteria or contain

sulphate reducing bacteria causing the metal to precipitate as sulphides), aerated bioreactors and rock filters (i.e. removal of manganese from mine waters)[8], solvent extraction (i.e. removal of particular metals with solvents), and membrane distillation (i.e. that uses membrane to separate volatiles from non volatiles, example salts from water[10]. Both the established and innovative treatment techniques are generally designed to reduce volume, raise pH, lower dissolved metal and sulphate concentrations and the bioavailability of metals in solution, and also dispose or isolate the mine water or any metal-rich sludge generated. However, a more sustainable approach to deal with acidic effluents is to simultaneously recover the water, acid and valuable metals. A combination of treatment methods such as solvent extraction (SX) and membrane distillation (MD) may be applied to concentrate the acid and metals (inorganic salts), then extract the concentrated acid from the concentrated salts with a view to extract reusable fresh water and acid, as well as valuable metals.

#### **1.4. Solvent extraction and application for acid recovery**

SX is a well-established treatment method to purify and recover metals from waste solutions. It is used in hydrometallurgical processes to recover acids ( $H_2SO_4$ , HCl), precious heavy metals and treatment of metalloids present in a wastewater [9, 11, 12]. Nowadays, a very large number of stable solvents (extractants) are available for use in hydrometallurgy, showing excellent selectivity for a particular metal ion, coupled with advances in the engineering and increasing demands for higher purity products and more environmentally friendly routes. A number of extractants including TEHA (tris-2-ethylhexylamine), Alamine 336 (a mixture of tri-octyl/decyl amines), TBP (tri-butyl phosphate) and Cyanex 923 (a mixed alkyl phosphine oxides) are used to recover acids from acidic solutions [9, 11, 13, 14]. However work showing the optimal use of extractants for acid recovery in the presence of metals is not well known. Further, SX is economically viable when both the solute concentration and waste water flowrates are high but uneconomical when the concentration of the contaminant to be recovered is  $<0.6\text{g/L}$  [15]. To address this issue, MD maybe applied to preconcentrate the solute prior to SX.

MD is a thermally driven membrane process emerging commercially, and can be applied to concentrate acid and recover fresh water from acidic waste solutions[16]. MD processes have several configurations as follows (1) direct contact membrane distillation (DCMD), (2) air gap membrane distillation, (3) vacuum membrane distillation and (4) sweeping gas membrane distillation. DCMD, is the most widely used because it is convenient to set up, avoids the need for a separate condenser, and gives high water flux [17]. In the MD process, a microporous hydrophobic membrane is used to separate two aqueous solutions at different temperatures causing a vapour pressure drop and in turn a water flux. This process can take place at atmospheric pressure, and at temperatures which may be much lower than the boiling point of water. The hydrophobicity of the membrane prevents the transport of liquid while water vapour and volatiles can be transported from the warm side to the cold side. In comparison with other separations techniques, MD has several advantages including high rates of rejection for non-volatile components, lower operating pressure than pressure driven membrane processes (i.e. RO) and reduced vapour space and low feed temperature requirements ( $40\text{--}80\text{ }^\circ\text{C}$ ) compared to conventional distillation[17, 18]. The MD process is capable of treating highly concentrated solutions utilising low-grade heat for water distillation. It is promising technique for minimizing RO concentrate discharge[19], and can be applied for desalination and wastewater recycling in places where waste heat, solar or geothermal sources are available[17]. MD has been tested in the laboratory scale and applicable to a large number of areas including concentration of sulphuric acid, separation of non-volatile components and treatment of waste

water for removal of heavy metals[10, 20]. However the ability of MD to concentrate real saline waters to concentrations exceeding the limit of RO is not well described. Also, while the cost of desalinating water by MD is well known, it would be useful to explore its cost sensitivity, in particular when a price of carbon is applied to the energy source.

The concept however to combine SX and MD for acid and by-product recovery from acidic mining waste solution is novel, and not reported elsewhere. In bringing the two processes together, clean water is produced for reuse, and then acid is concentrated and recovered also for reuse leaving only concentrated brine rich in valuable metals. A conceptual flow-sheet to recover water, acid and metal values is shown in Figure 1. In Fig. 1a, for  $H_2SO_4$  waste solutions, DCMD can be applied to recover fresh water and concentrate sulphuric acid solution and metals. The concentrated acidic solution can be recovered using SX. The fresh water recovered by MD can be also used for scrubbing the entrained metals and stripping the extracted acid. The sulphuric acid concentration in the loaded strip liquor is usually lower than that in the feed. Therefore, a second MD is necessary to further increase the acid concentration. In Fig 1b, for HCl waste solutions, DCMD can be applied to recover HCl solution and also, concentrate the non-volatiles such a ferrous ion and SX is not needed.

### **1.5. Scope of this research**

The overview has identified knowledge gaps in exploring how MD and SX can be applied together for acid and water recovery in the mining industry. This study will address each of these knowledge gaps by:

1. Confirming the viability of MD to concentrate real brine complexes to near saturation values without the presence of acid;
2. Develop a cost model for MD that explores its cost sensitivities, in particular with regards to carbon pricing, for its better known application for seawater desalination. The economic opportunity for using MD with waste heat and different operation modes will then be explored;
3. Study the viability of MD to concentrate the spent acid in the waste stream and improve the efficiency of subsequent SX. This will be carried out on model mine waste water from acid mine drainage and leach solution containing  $H_2SO_4$  and HCl respectively;
4. Study the viability of SX to selectively recover acids ( $H_2SO_4$ ) that would be pre concentrated by MD to assess the viability of the combined processes.

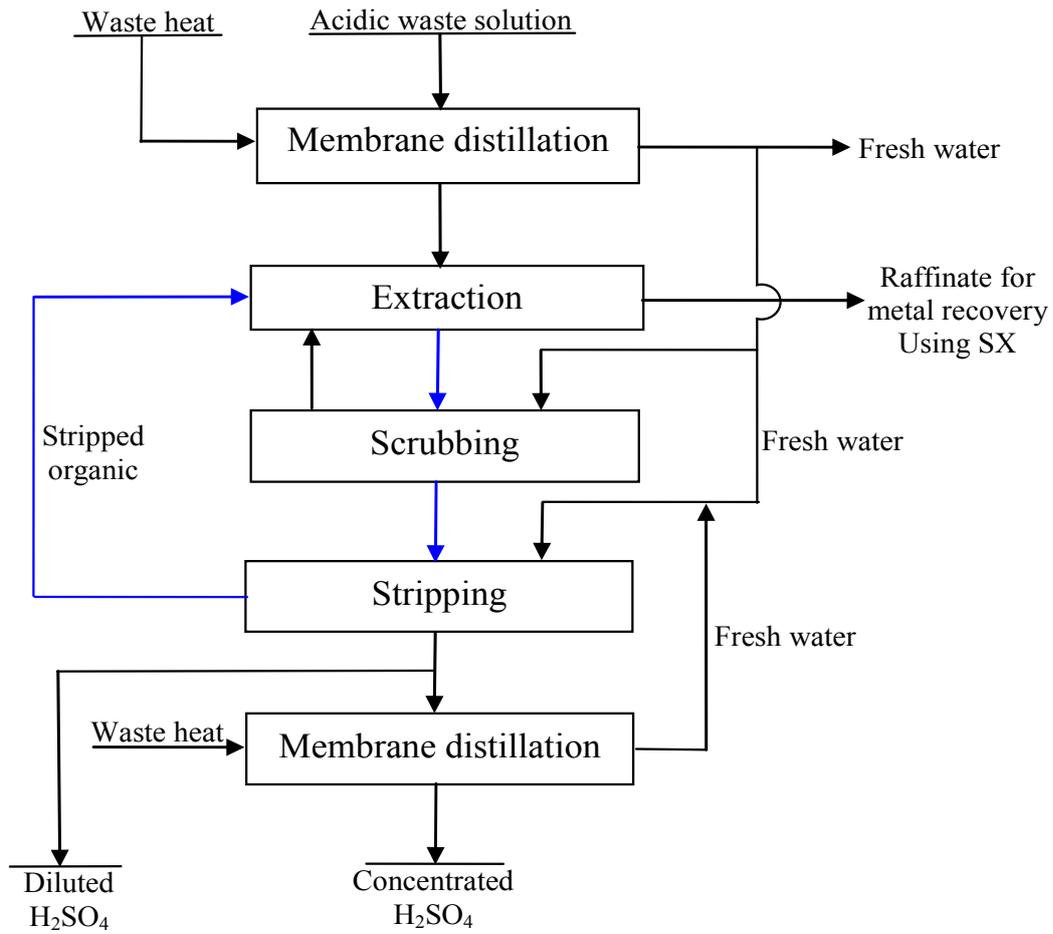


Fig. 1a: A conceptual flow-sheet to recover water, sulphuric acid and metal values by the novel combination of MD with SX

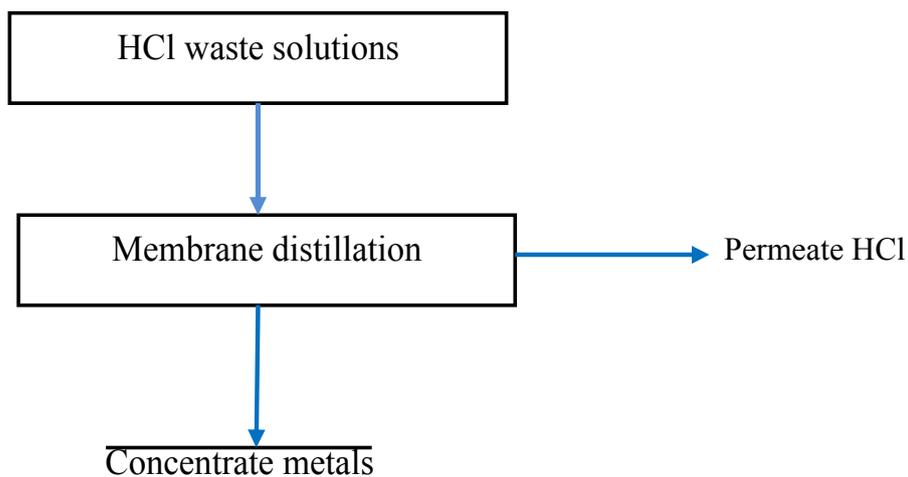


Fig. 1b: A flow-sheet to recover HCl and valuable metals

## **1.6. Project Aim and objective**

An acid-generating mine has the potential for long-term, devastating impacts on the environment. AMD is the biggest environmental threat from mining. The current approaches to manage AMD includes neutralization, which has not proven to be viable. Lime neutralisation of waste acid generates solid waste which causes environmental degradation and cost. Recycling acid and process water from waste streams of industry is an environmentally friendly method as it generates less waste and produces more fresh water. The overall aim is to explore how MD and SX can be applied together for acid and water recovery in the mining industry. In bringing the two processes together, clean water is produced for potential reuse, and then acid is concentrated and recovered also for reuse leaving only concentrated brine rich in valuable metals.

## 2. Literature review (Chapter 2)

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### 2.1. Identifying mine waters and process acidic streams for water and acid recovery

Mine waters are highly variable in their composition. The composition of mine waters varies depending on the mined ore and the chemical additives used during mineral processing and hydrometallurgical extraction. Regardless of the commodity extracted and the mineral processing and hydrometallurgical techniques applied, major cations (i.e.  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) and anions (i.e.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) are important constituents of any mine water[2]. Other constituents may include nitrogen or cyanide compounds[21]. Pyrite is the most abundant of the sulphide minerals, occurring in nearly all types of geological environments. When mining exposes pyrite and pyrrhotite to an oxidizing environment a series of complex chemical weathering reactions may occur. The chemical weathering of an individual mineral can be classified as acidic, such as AMD (i.e. generation of  $\text{H}^+$ ), acid buffering (i.e. consumption of  $\text{H}^+$ ), or non-acid generating or consuming reaction (i.e. non generation or consumption of  $\text{H}^+$ )[2]. Other waste waters generated from process and hydrometallurgical applications include leach and pickling solutions.

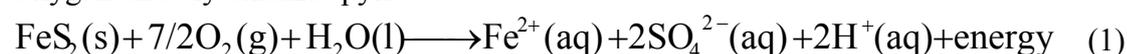
#### 2.1.1. Acidic mine water

Acidity of mine water is the total concentration of acidic species in an aqueous solution [22]. The net or total acidity of mine waters consists of proton acidity (i.e.  $\text{H}^+$ ) and latent acidity caused by the presence of other acidic components[22]. Acid mine water is resulting from oxidation pyrite which occurs in the presence of microorganisms is known as biotic[2]. Pyrite of oxidation can occur without microorganisms and is known as abiotic or inorganic chemical oxidation process. Biotic and abiotic degradation can be caused by oxygen (i.e. direct oxidation) or by oxygen and iron (i.e. indirect oxidation)[23]. Iron, both in its divalent and trivalent state, plays a central role in the indirect oxidation of pyrite. Different pyrite oxidation mechanisms can be summarized as[2, 23]:

- oxidation by oxygen (abiotic direct oxidation);
- oxidation by oxygen in the presence of microorganisms (biotic direct oxidation);
- oxidation by oxygen and iron (abiotic indirect oxidation);
- oxidation by oxygen and iron in the presence of microorganisms (biotic indirect oxidation)

Stoichiometric chemical reactions are commonly used to describe these different oxidation mechanisms. In the abiotic and biotic direct oxidation processes oxygen directly oxidizes pyrites [2, 24].

Oxygen directly oxidizes pyrite:

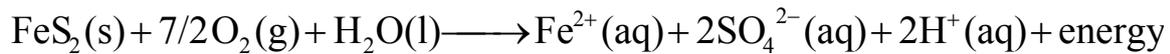


However, It is generally accepted, that pyrite oxidation is primarily accomplished by indirect oxidation [2]. The indirect oxidation of pyrite involves the chemical oxidation of pyrite by oxygen and ferric iron ( $\text{Fe}^{3+}$ ). The following chemical equations show the generally accepted sequence for such indirect oxidation of pyrite[2]:

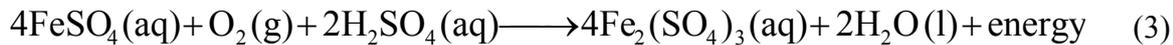
Oxidation of pyrite by oxygen (Step 1):



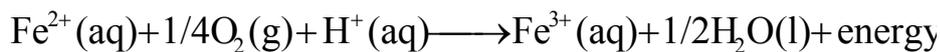
or



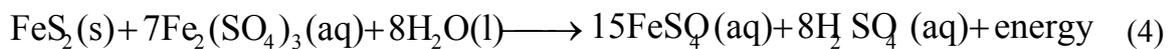
Oxidation of ferrous iron to ferric iron (Step 2):



or,



Oxidation of pyrite by ferric iron (Step 3):



or,



Equations 2, 3, and 4 release energy. Indirect pyrite oxidation is exothermic. In the initial step (Equation 2), pyrite is oxidized by oxygen to produce dissolved ferrous iron ( $\text{Fe}^{2+}$ ), sulphate and hydrogen ions. The dissolved iron sulphate ions cause an increase in the total dissolved solids of the water. The release of hydrogen ions with the sulphate anions results in an acidic solution unless other reactions occur to neutralize the hydrogen ions[2]. The second step (Equation 3) represents the oxidation of ferrous iron ( $\text{Fe}^{2+}$ ) to ferric iron ( $\text{Fe}^{3+}$ ) by oxygen and occurs at a low pH. In the third reaction (Equation 4) pyrite is oxidized with the help of  $\text{Fe}^{3+}$  generated in Equation 3. Thus,  $\text{Fe}^{3+}$  acts as the oxidizing agent of pyrite. The oxidation of pyrite by  $\text{Fe}^{3+}$  in turn generates more  $\text{Fe}^{2+}$ . This  $\text{Fe}^{2+}$  can then be oxidized to  $\text{Fe}^{3+}$  by oxygen via Equation 3. The  $\text{Fe}^{3+}$  in turn oxidizes pyrite via Equation 4, which in turn produces more  $\text{Fe}^{2+}$ , and so on. Equations 3 and 4 form a continuing cycle of  $\text{Fe}^{2+}$  conversion to  $\text{Fe}^{3+}$  and subsequent oxidation of pyrite by  $\text{Fe}^{3+}$  to produce  $\text{Fe}^{2+}$ . The above reactions describe the weathering of pyrite, highlight the need for water and oxygen, and illustrate the production of acid. The oxidation of sulphide minerals does not only create acid, but it also liberates metals and sulphate into waters and accelerates the leaching of other elements from gangue (spent) minerals. As a consequence, AMD is associated with the release of sulphate, heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), metalloids (As, Sb), and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F).

### 2.1.2. Alkaline and neutral mine waters

The pH of mine waters can extend to alkaline conditions. Alkalinity can be defined as the total concentration of basic species in an aqueous solution. Acid waters have sulphate as the principal anion, with iron, manganese and aluminium as major cations. However in alkaline mine waters, sulphate and bicarbonate are the principal anions, and concentrations of calcium, magnesium, potassium and sodium are generally elevated relative to iron and aluminium[25]. The oxidation of pyrite, the precipitation of iron and aluminium hydroxides, and the dissolution of some secondary minerals release acid protons to solution[7]. These processes increase the solution's acidity unless the proton is consumed through buffering reactions. Much of the buffering of the generated acidity is achieved through the reaction of the acid solution with

rock-forming minerals in the sulphide wastes. These gangue minerals have the capacity to buffer acid; that is, the minerals will react with and consume the hydrogen ions. Acid buffering is largely caused by the weathering of silicates, carbonates and hydroxides[2]. The buffering reactions occur under the same oxidizing conditions, which cause the weathering of sulphide minerals. However, unlike sulphide oxidation reactions, acid buffering reactions are independent of the oxygen concentration of the gas phase or water in which the weathering reactions take place[2]. The solubility of  $\text{Fe}^{3+}$  is very low in neutral and alkaline waters. Hence, the concentrations of  $\text{Fe}^{3+}$  are very low in these solutions, and pyrite oxidation by  $\text{Fe}^{3+}$  in neutral to alkaline waters is slow and insignificant. Also, the concentration of dissolved  $\text{Fe}^{3+}$  decreases with increasing pH as  $\text{Fe}^{3+}$  solubility is limited by the precipitation of ferric hydroxides ( $\text{Fe}(\text{OH})_3$ ) and oxyhydroxides ( $\text{FeOOH}$ ). Substantial concentrations of sulphate, metals (Cu, Cd, Fe, Hg, Mn, Mo, Ni, Pb, Tl, U, Zn), and metalloids (As, Sb, Se) have been documented in oxidized, neutral to alkaline mine[22, 25]. Mine waters of coal mines are not necessarily acidic. Many mine waters of coal mines have near neutral pH values. However, such waters typically contain elevated total dissolved solids and exhibit high electrical conductivities[22]. Substantial concentrations of manganese have been documented for some near-neutral coal mine waters[2]. Salt levels, particularly chloride concentrations, can be extreme[2]. These saline waters originate from saline aquifers as dewatering of the mine may intersect deep saline formation waters. Also, atmospheric exposure of saline coals and marine sediments within the stratigraphic sequence, containing abundant salt crystals, will lead to the generation of saline mine waters. Such waters are of environmental concern as they may adversely impact on the quality of receiving water bodies. Neutral to alkaline mine waters with high metal, metalloid, and sulphate contents can be caused by:

- Drainage from tailings repositories containing residues of alkaline leach processes or neutralized acidic tailings;
- Drainage from non-sulphuric ores and wastes;
- Drainage from sulphuric ores or wastes that have been completely oxidized during pre-mining weathering;
- Drainage from pyrite- or pyrrhotite-rich ores and wastes with abundant acid neutralizing minerals such as carbonate; and
- Drainage from sulphide ores or wastes depleted in acid producing sulphides (e.g. pyrite, pyrrhotite) and enriched in non-acid producing sulphides (e.g. galena, sphalerite, arsenopyrite, chalcocite, covellite, stibnite).

However, alkaline and neutral mine waters are not considered further. Acidic mine waters such as AMD and process acid streams are major issues in mining extractions and therefore of interest because of the environmental hazards compared to alkaline and neutral mine waters.

### **2.1.3. Waters and process acidic solutions from hydrometallurgical applications**

Often during the design of a new hydrometallurgical refinery, engineers primarily focus on the metals to be extracted while residual water is considered later. The use of water in hydrometallurgical processes has an impact on the environment as the residual waste water often contain high concentrations of acids, heavy metals and metalloids. The chemical solutions used in hydrometallurgical processes are usually an acid or base dissolved in water. This application is commonly used in leaching of metal ore and pickling applications. In leaching applications HCl and  $\text{H}_2\text{SO}_4$  are often used as leaching fluid to dissolve mineral or metal from their ores. After treatment, the loaded leach solution often contains high concentration of residual acid and valuable metals. Both the loaded leach and pickling liquor

contain high concentration of residual acid, valuable metal and water that can be treated and reused.

## **2.2. Review of acid and metal recovery and applications**

MD, SX and ion exchange (IX) are common techniques to recover metals and acids from waste solutions [9, 15]. At low solute feed concentrations, SX loses its advantages and does not perform well [15]. This is an issue for mining waters where acids are in the order of 10 g/L concentration, and SX performs best at above 200 g/L acid. Often under the conditions of low solute concentration, the loss of solvent into the aqueous wastewater phase through solubility or entrainment is greater than the quantity of solute recovered [15]. In this instance, an alternative technology such as MD may be required to concentrate the solution for acid or metal recovery.

### **2.2.1. Ion exchange for acid and metal recovery**

IX is a technology that enables the recovery of good quality process water along with the recovery of valuable metals, metal salts and acids from the tailings water generated by the minerals industry [26]. With IX it is possible to recover some of the acids from discharge waters containing, for example, ferric chloride or ferric sulphate [26, 27]. In most cases the acid can be reclaimed at least approximately half of the original concentration [26]. Acid is recovered by selectively adsorbing the hydronium ( $H_3O^+$ ) ion on an anion exchange resin. Once the salts and impurities are removed, the acid could be reused. The economics of ion exchange is driven mostly by the cost of resin regeneration chemicals, which increases proportionately with the increase in the amount of dissolved salts in the water. However, the resin regeneration costs decrease significantly when cheaper regeneration chemicals such as  $H_2O$ ,  $NaCl$  and  $Na_2SO_4$  are used. IX is more cost effective when used to treat water with  $\leq 1500$  mg/L dissolved salts [15]. At lower TDS, IX is extremely attractive for its low capital and operational costs, and high recovery (90-95%) rates [26].

The advantages of IX are summarised as follows [26]:

- High loading (adsorption) capacity;
- Very low metal losses i.e., high metal recovery;
- Treatment (Sorption/Desorption) takes place at ambient temperature and pressure; and
- Extremely low toxicity risks (compared with solvent extraction).

There are a number of IX methods that are applied commercially around the world. These methods can be either batch or continuous or a combination of both with the resin bead bed classified as fixed, moving or mixed. Each of the above processes can further be classified as co-current or counter-current depending on how the waste water is contacted with the resin.

IX has been used by the minerals industry for one or more of the following reasons [26]:

- water recovery;
- De-colorization and de-mineralization (pollutant removal) of tailings water;
- Acid recovery;
- Effluent polishing; and
- Valuable metal recovery from the tailing or process waters.

While IX is good for removing acids or metals at low concentrations, for reuse an additional concentration step is also needed. In comparison to SX, IX also requires the addition of chemicals to regenerate the exchange beds.

### 2.2.2. Solvent extraction for acid and metal recovery

SX is a well-established technology to separate, purify and concentrate metals.[28, 29], while research into acid recovery is a new area of application [12, 13, 28, 30, 31]. An example flow diagram to recover metal as currently practiced in the industry is shown in Figure 2. SX is a simple operation that requires shift in the equilibrium between the extractions and stripping processes[28]. Acidic waste streams normally contain low concentrations of acids in the range of 10-20 g/L. SX is a method applied in large and medium scale operations when solute concentrations are high. The general requirements of an extractant suitable for use in commercial solvent extraction are as follows[29]:

- Be relatively inexpensive;
- Have a very low solubility in the aqueous phase;
- Will not form stable emulsions with an aqueous phase when mixed, for example a mixer;
- Have good coalescing properties when mixed with a diluent (and modifier if necessary);
- Have high metal loading capacity; and
- Be easily stripped of the loaded metal.

SX is economically viable method when both the solute concentration and waste water flowrates are high but uneconomical when contaminate concentration is low [15]. At low solute feed concentrations, the use of solvent extraction loses its advantage. Different solvents (extractants) for acid extraction are listed in the next section.

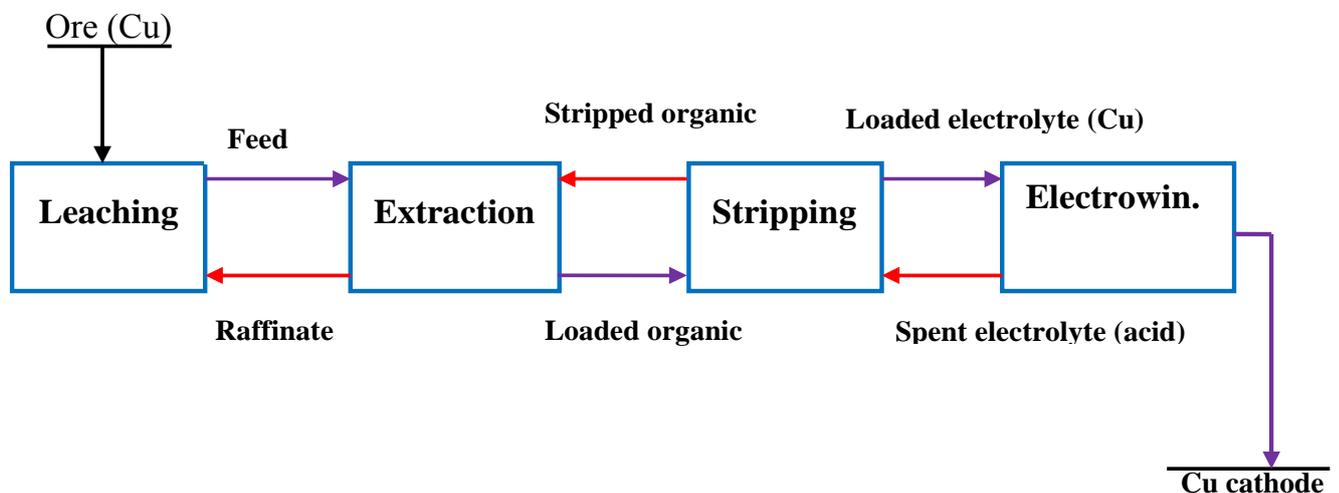


Fig. 2: An example of SX: Cu leach-solvent extraction-electrowinning processes

### 2.2.2.1. Solvents for H<sub>2</sub>SO<sub>4</sub> extraction

List of commercial reagents together with their manufacturers and common uses are given in the literature[32]. Extractants are often trialkylamines or trialkylphosphine oxides and include the commercial compounds TEHA, Alamine-336 and Cyanex-923. A number of organic extractants have been tested to recover sulphuric acid from waste streams including TEHA, Alamine 336 and Cyanex 923.

#### **TEHA:**

TEHA is a tertiary amine with a molecular formulae of  $(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2)_3\text{N}$ . Several authors have studied TEHA for sulphuric acid extraction from acidic effluents. Agrawal et al. [14] reported extraction of acid from zinc electrowinning bleed stream containing 173.5 g/L of sulphuric acid using 75% TEHA in kerosene. It was found that TEHA had a very good acid extraction capacity even in the presence of a large amount of zinc. The extraction of H<sub>2</sub>SO<sub>4</sub> increased with the increasing TEHA concentration. The plot of Log [H<sub>2</sub>SO<sub>4</sub>] vs. Log [TEHA] gave straight line with a slope value of 1.063, indicating that 1 mole of TEHA extracted 1 mole of sulphuric acid[14]. Three extraction stages were required to extract 90% acid at an A: O ratio of 1:2 based on McCabe Thiele diagram. The loaded acid was stripped with hot distilled water at 60°C[14]. In a similar study in 2009, Haghshenas et al.[9] investigated the separation of sulphuric acid from aqueous media in terms of thermodynamics and other conditions. The effect of TEHA concentration in octanol and the acid concentration in the aqueous feed on acid extraction was examined. It was shown that the acid extraction increased with the increase in the relative amount of TEHA in the organic solution and reached a maximum depending on the initial acid concentration in the feed solution. With the TEHA concentration of 64.5%, the highest acid extraction of 58% was obtained, but the organic solution started to separate into two phases. However, with 43% TEHA in octanol a maximum acid extraction of 49% was observed at acid concentration of 150 g/L[9]. A comparison was made between TEHA and Cyanex 923 for H<sub>2</sub>SO<sub>4</sub> recovery. It was reported that the relative amount of the reaction enthalpy is more sensitive with TEHA than Cyanex 923[9]. The authors concluded that TEHA may be more feasible for recovery of H<sub>2</sub>SO<sub>4</sub> from aqueous media than Cyanex 923[9]. They also reported that acid extraction improved significantly when octanol is used as a modifier in the organic solution containing TEHA and the effect was more significant when the acid concentration was less than 150 g/L. It was also reported that presence of octanol in the organic phase prevented third phase formation although octanol itself did not extract sulphuric acid[9]. The effect of diluents such as n-dodecane, n-heptane, toluene and benzole on extraction conditions was examined no significant effect was observed on the acid extraction when kerosene was substituted by other types of diluents. In 2000, Gottlieb et al.[12] also reported that the presence of octanol as a modifier gave higher acid extraction by TEHA in Shellsol 2046. It was found that the increase in temperature slightly lowered the sulphuric acid extraction. The temperature effect was more significant at lower acid concentrations in the feed solution.

#### **Alamine 336:**

Alamine 336 is a mixture of tri-octyl/decyl amine. In 2007 Agrawal et al. [11] studied the extraction of sulphuric acid using Alamine 336. It was reported that the extraction of sulphuric acid increased with the increase in the Alamine 336 concentration. The acid extracted increased from 17 g/L to 37 g/L with the increase in the solvent concentration from 10% to 35% using A:O ratio of 1 in a single contact[11, 33]. After 4 contacts, the loaded acid concentration in the organic solution increased from 40.5g/L to 80.8 g/L with the increase in the Alamine 336 concentration from 10% to 35%. Phase separation problem was reported when the

concentration of Alamine is above 35% (v/v) in kerosene using 10% isodecanol as phase modifier[11]. The acid extraction was unchanged using tri-n-butyl phosphate or isodecanol as modifier when keeping other parameters constant, but the phase separation time was shorter using isodecanol[11, 33]. The plot of logD vs. Log (extractant concentration) gave a straight line with a slope value of 0.94, indicating that 1 mole of the extractant extracted 1 mole of acid. The McCabe –Thiele diagram indicated that about 90% H<sub>2</sub>SO<sub>4</sub> extraction could be reached with three counter current stages using an A:O ratio of 1:2[11]. A comparative equilibrium datum for the extraction of H<sub>2</sub>SO<sub>4</sub> using Cyanex 923, Alamine 336 and Tributyl phosphate (TBP) was discussed. Alamine 336 showed higher acid extraction than Cyanex923, but the acid extracted could not be stripped using distilled water at 60°C while the acid extracted by Cyanex 923 was readily stripped using distilled water at 60°C[11].

Tait [34] investigated in 1993 the effect of different binary systems on acid extraction. The following six binary extractant systems were studied: Alamine 336/D2EHPA, Alamine 336/PC-88A, Alamine 336/Cyanex 272, Aliquat 336/D2EHPA, Primene JMT/D2EHPA and Adogen 283/D2EHPA in Shellsol AB. The reaction of extraction of sulphuric acid by a binary extractant system could be expressed according to:



Where HA donates the organic acid and RA is the extractant. The reaction stoichiometry was two extractant molecules per sulphuric acid molecule. Thus, relatively high extractant concentrations were necessary to achieve efficient acid extraction. The binary extractant systems studied had a concentration range of 1.4 – 1.6 M when undiluted [34]. However, these mixtures were viscous and required dilution. Consequently, to obtain effective extraction at relatively high acid concentrations, high organic to aqueous phase ratio was required. In strong acid media, bisulphate anions predominate over sulphate anions and the extraction equilibrium becomes:



The binary system consisting of 50% Alamine 336/D2EHPA in Shellsol AB with an O:A volume ratio of 5:1 was the best amongst the binary systems tested in term of acid extraction, which reached almost 100% in the range of initial acid concentration of 0.2 – 0.4 M. However, the extracted acid could not be stripped from the loaded solvent using water. Instead, dilute base was required to strip the extracted acid, which made the application of these binary systems uneconomical and impossible.

### **Cyanex 923:**

Cyanex 923 is a mixture of four trialkyl phosphine oxides. The extraction of acid by Cyanex 923 has been investigated by several authors because of its desirable properties including low tendency to hydrolysis and low solubility in water [30]. The advantage over other phosphine oxides is that it can be readily used without dilution. Haghshenas et al.[9] proposed the use of Cyanex 923 as a potential extractant for recovery of sulphuric acid because Cyanex 923 displayed a good compromise between its ability to extract sulphuric acid and to be stripped by water. Liao et al. [30]reported that when the acid concentration was less than 500 g/L H<sub>2</sub>SO<sub>4</sub>, third phase did not appear with the organic systems containing 40% and 50% (w/w) Cyanex 923. Haghshenas et al.[9]reported that sulphuric acid extraction increased with increasing concentration of Cyanex 923.

Alquacil and Lopez [35] investigated the effect of diluents such as decane and toluene on the extraction equilibrium of sulphuric acid with Cyanex 923. It was found that diluent type did not affect the acid extraction. However, third phase formed with aliphatic diluents for 10-20% Cyanex 923 concentration when acid concentration was over 3 M. It was also found that the extraction of sulphuric acid decreased with increase in temperature. Gottlieb et al. [12] reported that the extraction of mineral acids by Cyanex 923 was generally represented by Equation 7:



where X donates the dissociated acid anion and TRPO is Cyanex 923.

A similar equation was stated by Haghshenas et al. [9] as shown in Equation 8:



The reaction mechanism of  $\text{H}_2\text{SO}_4$  and Cyanex923 in equation 8 is showing one extractant molecules per sulphuric acid molecule. The top bars denote the organic phases. Wisniewski et al. [36] investigated the extraction of sulphuric acid from solution containing hydroxylamine sulphate and ammonium sulphate using Cyanex 923 at 20 and 50°C. The authors reported that the increase in temperature had no significant effect on sulphuric acid extraction. In contrast, the phase separation time increased with increasing temperature. The presence of hydroxylamine sulphate and ammonium sulphate did not affect both the rate and amount of sulphuric acid extracted with Cyanex 923. The stripping of sulphuric acid with water from 100% Cyanex 923 using an O: A ratio of 1 at 25 and 50°C, indicated that the temperature had almost no effect on acid stripping from Cyanex 923. It was reported that the acid stripping kinetics was fast with the equilibrium being obtained after 4 - 5 minutes of mixing. Haghshenas et al. [9] reported that the extraction reaction of acid by TEHA and Cyanex 923 was exothermic and the enthalpy change was -6.34 and -2.24 kJ, respectively, indicating that the acid extraction by Cyanex 923 was less sensitive to temperature compared to that by TEHA. The extraction kinetics for both TEHA and Cyanex 923 showed that the time needed for equilibrium extraction of sulphuric acid with both extractants was 1.5 min. It was also found that the extraction at equilibrium using 43% (v/v) TEHA was higher compared to that using 50% (v/v) Cyanex 923 in kerosene. Unlike other tertiary amines such as Alamine 336, the acid extracted by TEHA can be easily stripped using water at 60°C compared to Cyanex 923.

### **Comparison of TEHA, Cyanex 923 and Alamine 336 for $\text{H}_2\text{SO}_4$ extraction**

The extraction and stripping performance of the three extractants, TEHA, Alamine 336 and Cynaex 923, are summarised and compared in Table 1 in terms of temperature, O: A ratio, concentration of the extractant, concentration of the acid and extraction reaction enthalpies

Table 1: Comparison of TEHA, Alamine 336 and Cyanex 923

Name of extractant	TEHA	Alamine 336	Cyanex 923	Ref
Type of extractant	Tertiary amine	Tertiary amine	Phosphine oxide	[14, 32]
Diluents tested and effect	Kerosene and Shellsol 2046.	Kerosene	Kerosene, Shellsol 2046 and D70. Higher Acid extraction with 100% Cyanex 923	[9, 11, 12, 32, 33, 35]
Modifier tested and effect	Octanol. Acid extraction improved by increasing the concentration of octanol	Isodecanol and TBP. No effect on acid extraction. Shorter phase separation time with isodecanol than with TBP.	Octanol. Acid extraction was higher with 100% Cyanex 923.	[9, 12, 14, 32-34]
H <sub>2</sub> SO <sub>4</sub> extraction and effect of reagent concentration	Good H <sub>2</sub> SO <sub>4</sub> extraction with 50% TEHA. Further concentration increases resulted in phase separation problem.	Good H <sub>2</sub> SO <sub>4</sub> extraction with 35% Alamine 336. Further concentration increase resulted in phase separation problem.	Good H <sub>2</sub> SO <sub>4</sub> extraction with 100% Cyanex 923 and no phase separation problem.	[9, 12, 14]
Temperature effect on extraction	High extraction at room temperatures. Acid extraction decreased with increasing temperatures. In terms of H <sub>2</sub> SO <sub>4</sub> extraction: TEHA > Alamine 336 > Cyanex 923			[9, 12]
Extraction reaction	Exothermic. Enthalpy change - 6.34 kJmol <sup>-1</sup>	Unknown	Exothermic. Enthalpy change -2.24 kJ mol <sup>-1</sup>	[9, 12, 14]
Stripping using H <sub>2</sub> O	Easy stripping using H <sub>2</sub> O.	Not stripped completely using H <sub>2</sub> O	Easy striping using H <sub>2</sub> O	[12, 14]
Temperature effect on stripping	Higher striping at higher temperatures.	Poor striping at higher temperatures.	Higher striping at higher temperatures.	[9, 12]

All extractants (TEHA, Alamine 336 and Cyanex 923) can extract H<sub>2</sub>SO<sub>4</sub>. However, for Alamine 336 systems; the extracted acid cannot be stripped while in TEHA and Cyanex 923 systems can be stripped using water at 60°C. TEHA was selected because it has highest degree of acid extraction and stripping compared to Cyanex 923 and almost 99.9% of the acid can be stripped from the loaded organic. A proposed flowsheet to recover sulphuric acid is shown in Figure 3. TEHA can be applied to extract H<sub>2</sub>SO<sub>4</sub> from a concentrated waste acidic solution, then the loaded organic is scrubbed to remove metal entrainment before stripping using H<sub>2</sub>O to recover the acid (H<sub>2</sub>SO<sub>4</sub>).

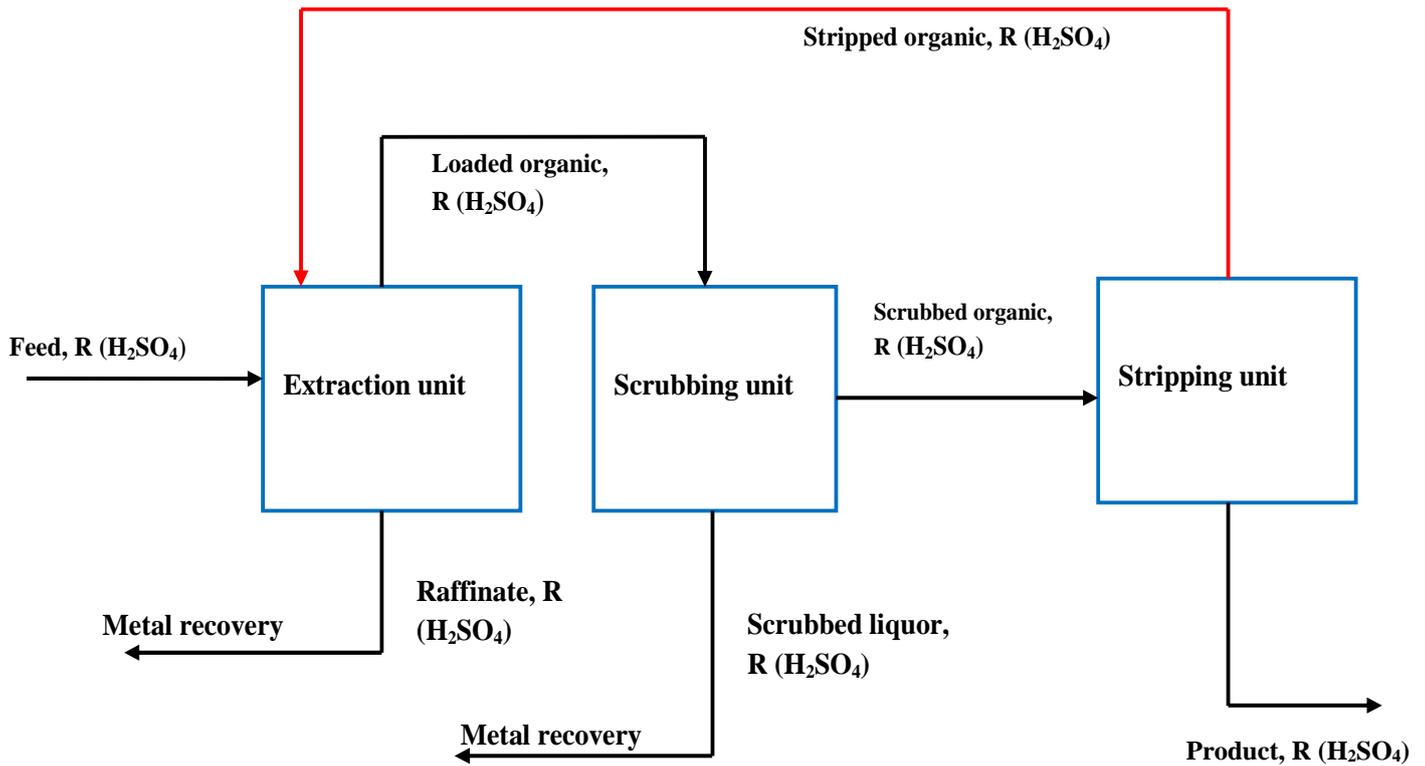


Fig. 3: Proposed flow sheet to recover H<sub>2</sub>SO<sub>4</sub> using SX

#### 2.2.2.2. Solvent for HCl extractions

HCl is applied in a wide range of metallurgical processes for various treatments such as leaching, etching and steel pickling [33]. Alamine 336, Aliquat 336, Cyanex 923 and TBP (tributyl phosphate), are the common extractants used for HCl extraction and recovery. Eyal and Canari [37] reported that HCl can be extracted using straight chain aliphatic amines diluted in alcoholic diluents due to ion pair formation. This mechanism may be represented by a two-step process of amine protonation and anion addition. Sarangi et al. [31] investigated the removal and recovery of hydrochloric acid from a leach liquor of a secondary resource using extractants such as TBP, Cyanex 923, Alamine 336 and Aliquat 336. It was reported that extraction of HCl increased with the increase in extractant concentration. When the Alamine 336 concentration increased from 10% to 100% (v/v) at an A:O ratio of 1:1, the extraction of HCl increased from 5.1% to 31.5%. The time for phase separation also increased with the increase in Alamine 336 concentration from 0.75 to 30 minutes. The logD vs. log(extractant concentration) plots (with all extractants) were straight lines with slope value ~1, indicating that 1 mole of extractant extracted 1 mole of acid. The McCabe–Thiele diagram constructed with Alamine 336 indicated > 99.5% HCl extraction in two counter current stages using an A:O of 1:4.

The extraction equation of HCl using Alamine 336 is as shown:



Where A336-denotes Alamine 336.

The extraction of HCl with Aliquat 336, Cyanex 923 and TBP also follows the same mechanism as in equation 9. Sarangi et al. [31] reported increase in acid extraction with

increases in the extractants concentrations for Aliquat 336, Cyanex 923 and TBP. For Aliquat 336, HCl extraction increases from 1.88 to 11.74% with the increase of Aliquat 336 concentration from 10 to 80 vol. %. The slope of log D vs. log [Aliquat 336] plot for extraction of acid with Aliquat 336 is 0.918, indicating the association of one Aliquat 336 molecule with the extracted species. For TBP, the percentage extraction of acid increased from 0.99 to 9.20% with the increase of TBP concentration from 13.66 to 100%. The log [TBP] vs. log D plot gives slope of 1.21 and confirms the association of one TBP molecule with the extracted species. For Cyanex 923, HCl extraction increased from 9.28 to 27.36% with the increase of Cyanex 923 concentration from 10 to 100%. The plot of log [Cyanex 923] vs. log D is a straight line with a slope of 0.573 indicating an association of one Cyanex 923 molecule with the extracted species. The McCabe Thiele diagram constructed with Cyanex 923 indicated that the quantitative extraction of HCl could be reached using four counter current stages and an A/O ratio of 1:5. Sarangi et al. [31] found that the extraction of HCl follows the order as shown below:

$$\text{Alamine 336} > \text{Cyanex 923} > \text{Aliquat 336} > \text{TBP} \quad (10)$$

Although Alamine 336 was the most efficient extractant for HCl, the extracted acid could not be stripped from the loaded organic with water. In contrast, the acid can be readily stripped with water from other extractants including Aliquat 336, TBP and Cyanex 923. Cyanex 923 is the best option for HCl recovery in terms of extraction and stripping.

However due to the volatile nature of HCl compared to H<sub>2</sub>SO<sub>4</sub>, the HCl is likely to transfer to the permeate during MD which will be discussed later.

### 2.3. Review of MD and applications

MD is a hybrid of membrane and thermal desalination. The energy consumption in MD systems include both thermal energy necessary to heat the feed solution and the electrical energy required to run the circulation pumps. As an energy intensive process, the interest in the technology faded quickly because it was observed that the energy required for MD is higher than that of RO whilst the cost of electricity needed for RO was also lower[38]. However, the cost of electricity has risen making RO appear unsustainable due to its reliance on high value electricity, where MD can make use of waste heat or solar thermal energy more conveniently. Also, the advantages of MD over its conventional thermal equivalent, MED is not clear and needs to be established. MED has no membrane. It consists of multiple stages or "effects". In each stage the feed water is heated by steam in tubes. Some of the water evaporates, and this steam flows into the tubes of the next stage, heating and evaporating more water. Each stage essentially reuses the energy from the previous stage. MD is more compact and can use a cheaper material for constructing the membrane module (i.e. polymer based materials) while MED consist of metals that can lead to corrosion unless expensive anticorrosive materials are used. Also MD is cost competitive to MED and more convenient to use especially when a low grade heat is available [18, 39, 40]. The electrical energy requirement for a MD system is potentially lower than the MED. In MD processes, the mass transfer in gas phase is driven by a vapour pressure difference, arising from a temperature difference or reduced pressure, across the membrane, and from the feed side to the permeate side[41]:

In general MD has several advantages and disadvantages [42]:

Advantages of MD:

- 100% (theoretical) rejection of ions, macromolecules, colloids, cells, and other non-volatiles;
- Lower operating temperatures than conventional distillation;
- Lower operating pressures than conventional pressure-driven membrane separation processes;
- Low sensitivity to variations in process variables (e.g. pH and salts);
- Good to excellent mechanical properties and chemical resistance;
- Reduced vapour spaces compared to conventional distillation processes; and
- It can be used after RO for recovery of additional fresh water from brine.

Disadvantages of MD:

- High energy intensity (although energy, i.e. heat, is usually low grade);
- Sensitive to surfactants; and
- Volatiles such as ammonia or carbonates pass through the membrane and must be treated separately.

### 2.3.1. Configurations of MD

Four configurations of the MD system are identified in the literature, which differ based on how the cold side permeate is processed [43].

- Direct contact MD (DCMD) in which the membrane is in direct contact with liquid phases. This is the simplest configuration capable of producing reasonably high flux. It is best suited for applications such as desalination and concentration of aqueous solutions (e.g. acid) [10];
- Air gap MD (AGMD) in which an air gap is interposed between the membrane and a condensation surface. The configuration has the highest energy efficiency, but the flux obtained is generally low. The air gap configuration can be widely employed for most MD applications [44], particularly where thermal energy availability is low or high cost;
- Vacuum MD (VMD) in which the permeate side is vapour or air under reduced pressure, and if needed, permeate is condensed in a separate device. This configuration is useful when volatiles are being removed from an aqueous solution [45]; and
- Sweep Gas MD (SGMD), in which stripping gas is used as a carrier for the produced vapour. It is used when volatiles are removed from an aqueous solution [46].

Of the four configurations, DCMD is the most popular for MD laboratory research, with more than half of the published references for MD based on DCMD[43]. The DCMD configuration was selected for most experimental work because of its simplicity and high water flux [43]. The main disadvantage for DCMD in commercial applications is its low energy efficiency due to increased conductive losses through the membrane. Although polymeric membranes generally have low thermal conductivity, the driving force (temperature difference between the feed and permeate sides) for mass transfer will also lead to significant conductive heat transfer through the membrane due to the small membrane thickness, so only part of the supplied heat

energy is used for production[47, 48]. However, AGMD is more popular in commercial applications because of its high energy efficiency and capability for latent heat recovery.

### **2.3.2. Configurations of MD modules**

There are two major MD module configurations, which are the hollow fibre and plate and frame. Both of these configuration shave been used in pilot plant trials [54, 55].The hollow fibre module has a very high packing density[55]. In this configuration, the feed is introduced into the shell side or into lumen side of the hollow fibre, and cooling fluid, sweeping gas, or negative pressure can be applied on the other side to form VMD, SGMD, or DCMD. Because of its large active area combined with a small footprint, hollow fibre modules have great potential in commercial applications [56]. Although broken hollow fibre cannot be replaced, they can be detected by the liquid decay test (LDT) [39, 57]and pinned to remove broken fibre from service. The plate and frame module is suitable for flat sheet membranes and can be used for DCMD, AGMD, VMD, and SGMD. Although this configuration has a relatively smaller effective area for the same volume when compared to the hollow fibre modules, it is easy to construct and multiple layers of flat sheet MD membranes can be used to increase the effective area. It is easy to change damaged membranes from this configuration. Thus, this module is widely employed in laboratory experiments for testing the influence of membrane properties and process parameters on the flux or energy efficiency of MD [56]. Also the flow dynamics can be improved by the use of spacers that increase turbulence and reduce temperature polarization.

### **2.3.3. Membrane Materials**

The most common materials used for MD membranes are poly(tetrafluoroethylene) (PTFE),poly(propylene) (PP) and poly(vinylidene fluoride) (PVDF) [58]. The porosity of the membranes used is in the range of 0.60 to 0.95, the pore size is in the range of 0.2 to 1.0  $\mu\text{m}$ , and the thickness is in the range of 0.04 to 0.25 mm[17]. Of these materials, PTFE has the highest hydrophobicity (largest contact angle with water), good chemical and thermal stability and oxidation resistance, but it has the highest conductivity which will cause greater heat transfer through PTFE membranes. PVDF has good hydrophobicity, thermal resistance and mechanical strength and can be easily prepared into membranes with versatile pore structures by different methods. PP also exhibits good thermal and chemical resistance [56]. Recently, new membrane materials, such as carbon nanotubes, fluorinated copolymer materials [59, 60] have been developed to make MD membranes with good mechanical strength and high hydrophobicity and porosity. Sintering, stretching, and phase inversion are some of the methods to fabricate MD membranes from these materials[61].

### **2.3.4. Membranes for MD Applications**

Hollow fibre membranes are mainly prepared from PP, PVDF, and PVDF-PTFE composite material[62],while flat sheet membrane-mainly prepared from PP, PTFE, and PVDF. Compared with flat sheet membranes, hollow fibre membranes have relatively large specific surface areas [63], but the main issue of the hollow fibre module is its typically low flux [64]. The low flux is related to its poor flow dynamics and the resultant high degree of temperature polarization. However, high-flux hollow fibre membranes with different features suitable for MD have been developed recently, such as dual-layer hydrophilic-hydrophobic fibre with a very thin effective hydrophobic PVDF layer (50 $\mu\text{m}$ ), and hollow fibre membranes with a sponge-like structure and thin walls [65], which have flux of about 50–70  $\text{kg m}^{-2} \text{h}^{-1}$  at about 80–90  $^{\circ}\text{C}$ . This flux is as high as that from flat sheet membrane. The reported flux from flat sheet membranes is typically 20–30  $\text{L m}^{-2} \text{h}^{-1}$ [43]at inlet temperatures of hot 60 $^{\circ}\text{C}$  and cold 20 $^{\circ}\text{C}$ . In general, the polymeric membranes are composed of a thin active layer and a porous

support layer. This structure is able to provide sufficient mechanical strength for the membrane to enable the active layer to be manufactured as thin as possible, which reduces the mass transfer resistance.

PTFE membranes were selected for further studies because they have the highest hydrophobicity (largest contact angle with water), good chemical and thermal stability and oxidation resistance, and also high flux, better salt rejection, and higher energy efficiency compared to PVDF and PP. Additionally it was shown that PTFE membranes with larger pore size and structured support layer (scrim) had a better performance in MD.

### **2.3.5. Membrane Fouling and Wetting**

Fouling and scaling are two important mechanisms that affect stability of the MD process and lead to reduce the overall efficiency. The foulant, e.g., bio-film, precipitations of organic and inorganic matter, can reduce the permeability of a membrane by clogging the membrane surface and/or pores. In addition, such build-up of fouling and scaling surfaces reduce the flow channel area which causes a pressure drop and lower flow rates. Such reduction will increase the temperature polarization effect and consequentially, reduces the flux[66]. Furthermore, fouling and scaling may cause membrane partial wetting or severe membrane damage. The current treatment process is chemical dosing of anti-scalants to control scaling [67-69]. Since the hydrophobic MD membrane is the barrier between the feed and permeate, membrane wetting will reduce the rejection of the non-volatiles. Membrane wetting can occur under the following conditions:

- The hydraulic pressure applied on the surface of the membrane is greater than the minimum Liquid Entry Pressure(LEP);
- The foulant depositing on the membrane surface can effectively reduce the hydrophobicity of the membrane [66], which was generally found in a long-term operation or in treating high-concentration feeds such as for brine crystallisation; and
- In the presence of high organic content or surfactant in the feed, which can lower the surface tension of feed solution and/or reduce the hydrophobicity of the membrane via adsorption and lead to membrane wetting [70].

There are several types of fouling and scaling, including biological, particulate and scale.

Biological fouling is caused by microorganisms' growth on the membrane surface forming a biofilm[66, 71]. The hydrodynamic conditions and the chemical composition of feed liquid and operation conditions have significant effects on membrane fouling[72]. At MD typical temperature operational conditions, high salt concentration, and low pH due to acids (for scaling control), there is a low biofouling potential. However it is well known that bacteria are able to grow under extreme conditions such as high temperatures as 110°C and pH values as low as 0.5[71, 73].

Particulate fouling is caused by the deposition of solid particles on the membrane. The rate and type of deposition is dependent on the size of these suspended solids[38]. Mechanical pretreatment with on-line coagulation, sand filtration and/or rapid sand filtration and cartridge filtration are well practiced method to reduce particular fouling agents.

Scale formation results from formation of crystals on membrane surfaces[38]. Scale formation also causes clogging of membrane pores and reduces its surface area, contributing to

temperature polarization. Gryta et al. [73] reported rapid crystallization of salt on the membrane surface during the concentration of saturated solutions using DCMD configuration. Li et al. reported sharp flux decrease using a novel MD bioreactor to treat waste water from a petrochemical plant [74].

### **2.3.6. Economic assessment of MD and carbon tax**

Desalinated water cost by MD, like the benchmark RO and MED systems, is sensitive to several economic and technical factors such as energy source, plant capacity, salinity, and design features. Among those factors, energy source and plant capacity have a dominating influence in addition to feed seawater salinity for the RO process. Unlike RO, energy consumption in MD systems includes both thermal as well as electrical energy. The thermal energy requirement of MD is around 90% of the total energy but can come at a relatively low cost and offers an opportunity for the use of low cost waste thermal heat. An extensive study of MD by Obaidani et al. [75], reports exergy analysis, sensitivity study and economical evaluation carried out to assess the feasibility of the direct contact membrane distillation (DCMD) process with heat recovery. They estimated a water cost \$1.17/m<sup>3</sup>, which is comparable to the cost of water produced by conventional thermal processes, i.e. \$1.00/m<sup>3</sup> for MED and \$1.40/m<sup>3</sup> for Multi-stage flash (MSF) [76]. The study also revealed a high possibility of significant savings when a low-grade thermal energy source is used. The study claims that the cost is competitive to the cost of water produced by RO, which is about \$0.5/m<sup>3</sup> [77]. The Memstill project presented in 2006 by Hanemaier et al. [78] claims to have the potential to reduce the cost of existing desalination technologies for seawater and brackish water, by replacing MSF and MED modules by an air gap MD module. The process proposes to reduce the desalination costs to \$0.26/m<sup>3</sup> using low grade thermal steam or heat as the driving force. The principle reason for this observed saving was cheaper plant materials to build their module in comparison to RO (RO uses high pressure vessels), and ability to utilise low cost heat sources (i.e., waste heat) as the principle energy source. Memstill pilots have been operating since 2006 fed with raw seawater, with the first in Singapore, two in the Netherlands at the E.ON Benelux Power Plant, then a more recent trial at BASF, Port of Antwerp running until March 2011. Similarly, in a recent (2012) study by M.R. Qtaishat and F. Banat [79] the costs in sourcing the heat from solar energy were explored. The economics were found to be dependent on the cost and efficiency of the solar panels indicating that waste heat for MD is currently a more economically viable concept. While it is well known that energy plays a major role in the overall cost of MD, how its costs compare to other desalination technologies when a tax on carbon is imposed is still unknown. The mining industry is a major source of CO<sub>2</sub> emissions, so studies on options for potential adoption into the mining industry should include the forecast increase in cost with carbon tax applied.

### **2.3.7. Applications of MD for desalination and acid recovery**

MD has potential applications in many areas of scientific and industrial interest to obtain highly purified permeates from solutions containing contaminants. Although MD is currently studied mostly at the laboratory scale, it has potentially distinctive advantages in some particular areas [43, 56]. There are several pilot plants currently undergoing field trials: for treating wastewater from a power plant (in Singapore) [80], wastewater in a chemical plant (The Netherlands) by Memstill, and other wastewaters are currently being investigated at laboratory stage, i.e., the RO concentrate treatment, ground water treatment and solar heat utilisation [81-83]. Testing of MD on RO groundwater concentrates revealed that the concept is indeed viable, but suffers from practical issues such as scaling on MD membranes [84]. A similar result was found for an RO-MD trial on a solar powered direct contact MD system in rural Victoria, Australia [85]. Membrane scaling led to flux declines, but flux was easily restored using an acid clean. Scaling

was found to be effectively managed by cleaning or the addition of anti-scalant. However in remote mining operations, the concept to minimise use of additional chemicals is of interest. As the scaling salts are likely to form in the higher temperature zone of the DCMD hot cycle loop, they may be intercepted prior to the membrane using a filter. However this opportunity for reducing scaling on MD membranes has not yet been explored.

Producing high-purity water from salty water is one of the many MD applications. MD also can be used for water treatment, such as removing heavy metals from waste water [86], recovering HCl from cleaning solution in electroplating [16], concentrating sulphuric acid to recover lanthanide compounds in apatite phosphogypsum extraction process[87], eliminating radioisotopes, reducing the waste volume from nuclear industry[88] and removing volatile organic components from dilute aqueous solutions[89, 90]. Tomaszewska and Mientka[10] also studied separation of H<sub>2</sub>SO<sub>4</sub> and HCl from a synthetic solution containing only H<sub>2</sub>SO<sub>4</sub> and HCl. It was reported that the presence of sulphuric acid in the feed decreases the solubility of HCl, and hence increases HCl flux as H<sub>2</sub>SO<sub>4</sub> concentration increases in the feed. In the work reported by Zhang et al.[91]and Tang and Zhou [92], acid recovery from different process acidic solutions using MD technique was also reported. These studies of DCMD for acid recovery focus on treatment of primarily synthetic and specific real solutions and thus further work on utilising MD for both HCl removal and H<sub>2</sub>SO<sub>4</sub> concentration of real mining waters is not reported.

### **2.3.8. Conclusions from the literature**

The overview has identified knowledge gaps in exploring how MD and SX can be applied together for acid and water recovery in the mining industry. Based on the above review, the novel concept for MD and SX for water and acid recovery in mining will be explored by:

- Performing MD experiments on RO brine from real ground water for water recovery confirming the ability of a filter to remove scaling membrane foulants;
- Develop a cost model to determine cost sensitivities of MD compared to other desalination techniques, in particular RO and MED, so propose economically viable ways for MD to be used. This is made in context of a tax on carbon and comparing for the more common seawater desalination application;
- Application of MD to concentrate the spent acid (HCl and H<sub>2</sub>SO<sub>4</sub>) in the waste stream and improve the efficiency of subsequent SX);
- Perform SX experiments and optimize solvents for selective acid recovery; and
- Perform MD and SX trial experiments for acid and water recovery from waste acidic solutions.

### **3. MD testing on RO brine to recover beyond the limit of RO systems and economic assessment (Chapter 3)**

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The aim of this work is to assess the viability of MD to concentrate beyond the limit of RO from real ground water for water recovery and to confirm the ability of a filter to remove scaling membrane foulants. Furthermore, to develop a cost model for MD that explores its cost sensitivities, in particular with regards to carbon pricing. The mining industry is a major source of CO<sub>2</sub> emissions, so studies on options for potential adoption into the mining industry should include the forecast increase in cost with carbon tax applied. The economic opportunity for using MD with waste heat and different operation modes will then be explored.

This work was published in the journal *Desalination* as follows:

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## **Response from the thesis examination**

### **Examiner's comment:**

The authors state that precipitation was occurring but that no scale was observed on the membrane. SEM or other evidence to support the statements of observed fouling would be useful

### **Response**

While scale precipitation was evident by the change in Ca values in proportion to other salts shown in Table 3 of the paper, future work is suggested in Chapter 9 (i.e. Future work section), to explore the membrane scaling by techniques such as SEM

### **Examiner's comment:**

Also, a very simplified method was used to assess the capital cost – could something more realistic be substituted here

### **Response**

The cost assessment found heat cost was most significant utilising current known plant prices enabling reliable conclusions to be made. However while RO and MED plant costs can be more reliable due to the wide availability of plant data, MD plant costs have to be estimated. However as they are emerging in application, future work will require a revised cost assessment to improve on the present cost information

### **Examiner's comment:**

It is also doubtful that MD has electricity consumptions the same as MED (2 kWh/m<sup>3</sup>).

### **Response**

The electrical consumption of MD of 2 kWh/m<sup>3</sup> assumed in this work was found to be close to more recently available work on MD trials when considering the additional pumping energy required for pretreatment. In Doung et al, Desalination, Accepted Oct 2014, they determined electrical consumption of 1.1 kWh/m<sup>3</sup> for the MD unit alone without pretreatment. Therefore our value closely represents a whole plant value.

**Declaration of co-authors enclosed**

**DECLARATION BY CO-AUTHORS**

The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. There are no other authors of the publication according to these criteria;
4. Potential conflicts of interest have been disclosed to a) granting bodies, b) the editor or publisher of journals or other publications, and c) the head of the responsible academic unit; and
5. The original data is stored at the following location(s):

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and will be held for at least five years from the date indicated below:

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Signature 4		18/11/2013
Signature 5		18/11/2013



# Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation

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## HIGHLIGHTS

- Carbon tax increases water cost by 16% to 28%, with RO being least sensitive.
- With waste heat and carbon tax, MD is the most cost effective technology.
- Direct contact MD was shown to concentrate RO brine up to 361,000 mg/L TDS.
- MD cost can be as low as \$0.57 per m<sup>3</sup> water treated.
- We proposed a cost effective MD mode for harnessing low grade heat (<50 °C).

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## ABSTRACT

The economics of membrane distillation (MD) and common seawater desalination methods including multi effect distillation (MED), multistage flash (MSF) and reverse osmosis (RO) are compared. MD also has the opportunity to enhance RO recovery, demonstrated experimentally on RO concentrate from groundwater. MD concentrated RO brine to 361,000 mg/L total dissolved solids, an order of magnitude more saline than typical seawater, validating this potential. On a reference 30,000 m<sup>3</sup>/day plant, MD has similar economics with other thermal desalination techniques, but RO is more cost effective. With the inclusion of a carbon tax of \$23 per tonne carbon in Australia, RO remained the economically favourable process. However, when heat comes at a cost equivalent of 10% of the value of the steam needed for MD and MED, under a carbon tax regime, the cost of MD reduces to \$0.66/m<sup>3</sup> which is cheaper than RO and MED. The favour to MD was due to lower material cost. On low thermally, high electrically efficient installations MD can desalinate water from low temperature (<50 °C) heat sources at a cost of \$0.57/m<sup>3</sup>. Our assessment has found that generally, MD opportunities occur when heat is available at low cost, while extended recovery of RO brine is also viable.

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## 1. Introduction

Desalination is a means of producing fresh water from saline or brackish water by removing dissolved salts to make it suitable for human use, agricultural and industrial or manufacturing purposes [1]. With water shortages emerging across the world, communities are turning to desalination as a solution to reliable water supply. Cost and energy reductions for desalination are therefore considered an important factor to minimise the environmental impact of desalinated fresh water supply especially in arid and semi arid regions where there is little alternative. Commercial technologies for desalination include membrane separation processes such as reverse osmosis (RO) and electrodialysis (ED), as well

as thermal processes, specifically multi effect distillation (MED), multi stage flash (MSF) and vapour compression distillation (VCD). These technologies are the most widely used desalination processes with MSF and RO dominating the market for both brackish and sea water with a total share of about 78% [2].

The techno-economic performance of these processes favours RO due to the continual advances made to reduce energy consumption and lower cost of water produced [3,4]. While most authors report RO as the less expensive process to recover fresh water these studies do not take into account imminent rises in energy prices. RO uniquely relies on electricity to operate, while the thermal processes can utilise waste heat or solar thermal energy more conveniently [3–6].

The US Bureau of Reclamation Desalination Roadmap 2003 [7] indicated that in RO, energy consumption accounts for 44% of the produced water cost, and fixed charges account for 37%. Together, these account for over 81% of the total desalination cost [7,8]. Similarly, it

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is known that for thermally driven desalination processes MSF and MED, the capital cost of the large metallic evaporators is very high, in the range of 40% to 50% of the total cost of water produced [1–9]. These systems thus conform to very different economics, and it is of interest to know where they fit economically under rising energy prices and the recent emergence of carbon pricing. Furthermore, alternative desalination processes that are not commercialised (or widely used) may be more economical from the perspective of capital and energy costs. They may also be easier to use and can potentially utilise a low grade heat source making them of considerable interest. One commercially emerging desalination technology that has different cost metrics and can harness waste heat sources is membrane distillation.

Membrane distillation (MD) is a thermally driven membrane process and may find an economically feasible niche amongst the commercialised desalination processes (MSF, MED and RO) which are considered to be technologically mature and therefore have very little space for major performance improvements [2]. The advantages of MD over commercialised desalination technologies are as follows [6]: (i) lower operating temperatures and vapour space required than MSF and MED (ii) lower operating pressure than RO (iii) more than 99.9% theoretical salt rejection (iv) the performance is not limited by high osmotic pressure or concentration polarisation. Four MD configurations have been identified: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) and sweep gas membrane distillation (SGMD) [5]. The DCMD configuration was selected in our experimental work because of its simplicity and high water flux.

To date the commercial uptake of MD has not been significant and further work is needed to uncover real opportunities. Furthermore, other emerging technologies which are still in the research and development phase such as forward osmosis and freeze/thawing [1] indicate that despite the variety of commercial desalination systems, there is still a driver for more diversity in desalination options. In order to foresee the 'economic niche' of these emerging technologies, a cost analysis is needed to understand how they will fit within the desalination industry. The emerging technology that is the focus in this economic assessment is MD.

A desalinated water cost model for MD, like the benchmark RO and MED systems, is sensitive to several economic and technical factors such as energy source, plant capacity, salinity, and design features [5]. Among those factors, energy source and plant capacity have a dominating influence in addition to feed seawater salinity for the RO process [5–11]. The energy requirement of desalination has an important effect on the overall process economics that is more prone to suffer from variation in the cost of fossil fuels [12].

An extensive study of membrane distillation by Obaidani et al. [3], reports exergy analysis, sensitivity study and economical evaluation carried out to assess the feasibility of the direct contact membrane distillation (DCMD) process with heat recovery. They estimated a water cost of \$1.17/m<sup>3</sup>, which is comparable with the cost of water produced by conventional thermal processes, i.e. \$1.00/m<sup>3</sup> for MED and \$1.40/m<sup>3</sup> for MSF [10]. The study also reveals that there is a high possibility of significant savings when a low-grade thermal energy source is used. The study claims that the cost is competitive with the cost of water produced by RO, which is about \$0.5/m<sup>3</sup> [11].

The Memstill project presented in 2006 by Hanemaijer et al. [13] claims to have the potential to reduce the cost of existing desalination technologies for seawater and brackish water, by replacing MSF and MED modules by an air gap MD module. The process proposes to reduce the desalination costs to \$0.26/m<sup>3</sup> using low grade thermal steam or heat as the driving force. Similarly, in a recent (2012) study by M.R. Qtaishat and F. Banat [14], the costs in sourcing the heat from solar energy was explored. The economics were found to be dependent on the cost and efficiency of the solar panels indicating

that waste heat for MD is currently a more economically viable concept.

Despite these costing reports in literature, it is uncertain what desalinated water by any technology will cost in a carbon constrained society. In 2012, Australia implemented a \$23 per tonne carbon cost. A variable price will commence in 2015 when the Australian Government converts this to an Emission Trading Scheme [15]. With policies coming into practice to tax carbon emissions, the economics of each desalination process is therefore undergoing change particularly with the concept of MD using waste heat. Therefore one of the purposes of this work is to explore how carbon taxing will influence the cost of desalination and how the waste heat concept can give opportunities for MD.

### 1.1. Membrane distillation progress and technological challenges

MD is a hybrid of membrane and thermal desalination. The MD process classically uses membranes that are hydrophobic and microporous. The driving force is a vapour pressure difference across the membrane. The vapour evolved from the feed solution passes through the pores of the membrane and is collected as the condensate. Liquid water is prevented from passing the membrane thus creating a desalination effect over a very small space. Due to the convenient containment of the liquid surface using the membrane, higher packing densities bring it in line with state of the art RO compactness. This is typically achieved via different MD configurations, which are DCMD, VMD, AGMD and SGMD, which have been well described in the literature [16–19].

The standard thermal energy required to operate an MD system is 628 kWh/m<sup>3</sup> [20]. This value equates to a performance ratio (PR), or gain output ratio (GOR) of 1, being the mass ratio of water produced to the amount of steam energy (i.e., latent heat) fed to the process. This can be compared with state-of-the-art MED requiring about 2 kWh/m<sup>3</sup> of electric energy and 60 kWh/m<sup>3</sup> thermal energy as shown in Table 1. In the last few years, MD has emerged with numerous commercially oriented devices and novel process integrations to try to match MED thermal efficiencies. The most notable organisations specialising in MD modules or high efficiency systems are: Fraunhofer ISE (AGMD), Memstill and Aquastill (AGMD), Scarab (AGMD), Memsys (vacuum enhanced multi effect AGMD) [20]. The thermal energy required through Memstill's trials, is as low as 56 to 100 kWh/m<sup>3</sup> of water produced (GOR up to 11.2). This is the lowest value reported from real testing (or highest GOR), but to achieve this, the water must be heated to 80–90 °C.

In addition to high energy requirements, the other technological challenges of MD include module design, membrane fouling and scaling. These are well described in the literature [16,17,21–23]. Attractive advantages of MD are related to the possibility of overcoming the RO limit of around 70,000 mg/L (due to trans-membrane flux independent from feed concentration), process intensification and also its ability to operate at relatively low temperatures [7,17]. This enables MD to be a compact operation for further recovery of RO brines at low pressure, and reduce discharge volumes in areas where this is a significant cost (e.g. inland groundwater desalination).

Despite the potential of MD, it has not been significantly implemented since it was patented in the late 1960s. Research intensity picked up in the 1980s [5] due to rising water, energy and environmental issues. We have previously explored polymer and ceramic membranes for desalination, and explored MD in dairy processing and industrial process integration [24–28]. While MD researchers have already focussed on relative technology costs, process optimisation, module design and fouling, this paper presents results on a niche operation of extended RO recovery, as well as the relative price of MD under a carbon tax and in a modified operational mode.

## 1.2. Objectives of the study

The objectives of this study are as follows:

1. To carry out testing on RO brines to explore potential to recover beyond the limit of RO systems (70,000 mg/L). This is done in the context of inland groundwater desalination to reduce discharge volumes;
2. To assess the potential impact of a carbon price on the cost of desalination technologies as well as the impact of utilising waste heat to drive MED and MD; and
3. To assess opportunities for low thermally/high electrically efficient MD setups that can effectively harness abundant lower grade heat sources.

## 2. Methodology

### 2.1. Desalination testing on groundwater RO concentrate

Experiments were conducted in DCMD mode to confirm the viability of MD to further concentrate beyond the limit of RO at 70,000 mg/L. The flow diagram of the experimental rig is shown in Fig. 1. In this test, 20 L of feed solution was initially added to the feed reservoir. Following batch concentration, another 20 L of raw feed water was added after each run for five different experimental runs; making a total of 100 L raw feed solution processed using DCMD. The membranes used were flat sheet PTFE supported on polypropylene scrim backing as optimised in previous work [16]. The membranes had an active area of 0.0169 m<sup>2</sup>, pore size of 0.45 μm and were supplied by Ningbo Chanqi, China. A cartridge filter with filtration size of 0.5 μm was used on the hot loop to collect precipitated matter prior to entering the MD module. The flow rate into the module hot and cold sides was 900 mL/min, the feed temperature was 60 °C and the cold temperature was maintained at 20 °C. Permeate build-up was measured by the accumulated mass of water in the permeate tank. Electrical conductivity was measured using a conductivity metre in the permeate tank to ensure membrane intactness (conductivity < 100 μS/cm). The concentrated brine for the MD experiments was obtained from a RO plant operating in Edenhope, Victoria, Australia. Groundwater is fed to the RO plant with total dissolved solids (TDS) of around 1400 mg/L, and the brine TDS concentration was approximately 3300 mg/L. The RO concentrate was further concentrated by an in-house RO rig using a 2.5 in. DOW FILMTEC BW30 membrane operating at pressures between 1.5 and 1.8 MPa to achieve a TDS of approximately 11,000 mg/L. This became the feed water to the MD experiment. TDS was determined gravimetrically on 5 mL aliquots of sample dried at 105 °C overnight. Cations in samples were determined by ICP-OES analysis, which was performed on a range of serial dilutions to reduce the concentration of each species to a suitable level. Cs matrix buffering at ~5 g/L and a Cs internal standard was employed to accommodate the wide range of matrix variation in the dilutions. Chloride concentration was determined via titration with AgNO<sub>3</sub> after acidification with 1:1 nitric acid solution. The end point was detected electrochemically.

### 2.2. Cost modelling

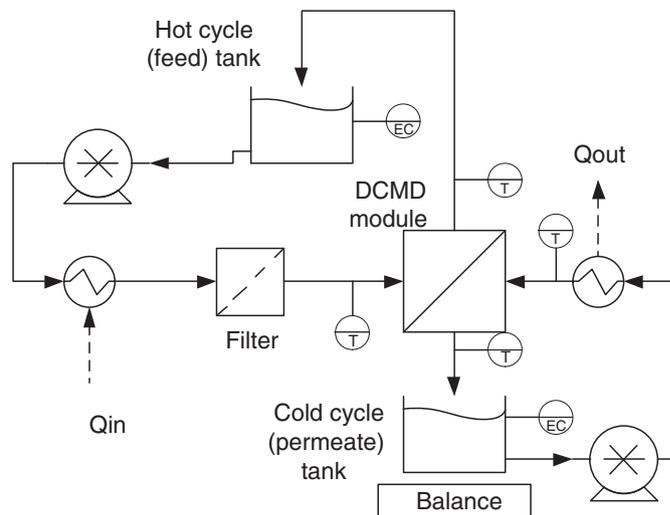
#### 2.2.1. Thermal and electrical energy usage and emissions of established desalination

Energy consumption in MD systems includes both the thermal energy necessary to heat the feed solution and the electrical energy required to run the circulation pumps, vacuum pumps or compressors. The thermal energy requirement is around 90% of the total energy but can come at a relatively low cost. Meanwhile electrical energy is more expensive than low grade heat. Desalination requires about 0.8 kWh/m<sup>3</sup> energy for seawater desalination based on a thermodynamic minimum [12,14,29,30].

**Table 1**

Data and assumptions used in the economic study.

Input Parameter	MD	RO	MED	Reference
Plant availability (%)	90	90	90	[3,31,32]
Interest rate (%)	5	5	5	[3,5,33]
Amortisation	0.08	0.08	0.08	[3,5,33]
Electrical cost (\$/kWh)	0.09	0.09	0.09	[30,33]
Steam cost (\$/kg)	0.007	0.007	0.007	[3]
Labour cost (\$/m <sup>3</sup> )	0.03	0.02	0.03	[3,5,34,35]
Brine disposal (\$/m <sup>3</sup> )	0.0015	0.04	0.0015	[3,36,37]
Maintenance cost (%)	2	2	2	[32,34,38]
Pre-treatment cost (\$/m <sup>3</sup> )	0.019	0.05	0.03	[3,32,39,40]
Thermal energy requirement (kWh/m <sup>3</sup> )	100	0	60	[2,41–43]
Emission factor for natural gas (kg CO <sub>2</sub> -e/kWh)	0.184	0.184	0.184	[44,45]
Emission factor for electricity (kg CO <sub>2</sub> -e/kWh)	1.22	1.22	1.22	[44,45]
Electrical energy requirement (kWh/m <sup>3</sup> )	2	3.5	2	[2,33,46,47]
Carbon tax (\$/tonne carbon)	23	23	23	[15]
Exponent 'm' (scale index)	0.8	0.81	0.83	[30]



**Fig. 1.** DCMD experimental flow diagram.

The energy values and carbon intensity used in our economic study are shown in Table 1. Here the total energy requirement for seawater desalination is at least an order of magnitude higher than the thermodynamic minimum, and mostly sourced from fossil fuel (electric power generation and by-product steam). The pollution associated with energy production from fossil fuel is as follows: NO<sub>x</sub>, SO<sub>2</sub>, volatile compounds, particulates, and CO<sub>2</sub>. Other environmental impacts include cost from effluent disposal, including chemicals, brine and possible sludge. The CO<sub>2</sub> emission from fossil fuel is the pollution of greatest interest in this work and also considered to be the highest contributor to greenhouse gas emissions (largest volume emitted). The carbon footprint of desalination systems is a combination of emissions associated with power used in the desalination process and the embodied associated chemicals used in production, treatment and disposal of solid waste and manufacture and replacement of membrane components. In our cost model, a carbon tax of \$23 per tonne carbon was used reflecting the initial fixed price of carbon introduced in Australia on 1 July 2012. This will increase gradually, then transition to a cap-and-trade emission trading system by 2015.

#### 2.2.2. Economic model setup

The major cost elements for desalination plants are capital cost and annual operating costs.

Capital cost covers purchasing cost of equipment, auxiliary equipment, land and installation charges [5]. Annual operating cost represents the total yearly costs of owning and operating a desalination plant. These include amortisation or fixed charges, operating and maintenance costs, energy costs and membrane replacement costs. This cost study is only for isolated plant cases and does not include distribution. The combined environmental impact of desalination includes on and off site pumping. However, this report focusses only on the impact of CO<sub>2</sub> emission from the desalination plant itself to allow weighing up of the truly different aspects. Other environmental costs would include effluent disposal, chemicals, brine and sludge.

The calculation setup is presented in the following sections. A sample calculation of water production cost using the MD system based on this setup, when a low grade heat source is available and carbon tax applied is presented in Appendix A.

2.2.3. Capital cost (CAPEX) of a plant

The CAPEX is estimated using a Capacity Factored Estimate. The cost of new plant is derived from the cost of a similar plant of known capacity, with similar production route, but not necessarily the same end product (the product should be relatively similar, however). It relies on the nonlinear relationship between capacity and cost as shown in Eq. (1) [34,39]:

$$\left[ \frac{\text{capital cost plant 1}}{\text{capital cost plant 2}} \right] = \left[ \frac{\text{plant capacity 1}}{\text{plant capacity 2}} \right]^m \tag{1}$$

m = the scale index [exponent]. The m used in the capacity factor equation is the slope of the log curve that has been drawn to reflect the change in the cost of a plant as it is made larger or smaller [34]. The value varies depending on the type of plant as shown in Table 1. The methodology of using capacity factor is sometimes referred to as the “six tenth factor” method because of the reliance on an exponent of 0.6 if no other information is available [39]. However, for desalination plants the exponent m is usually closer to 0.8 [48]. The capital cost of various desalination plants as reported in the literature is as shown in Table 2.

2.2.4. The cost of capital

The annual capital cost reflects the cost associated with servicing the capital cost used to build the new desalination plant. This is estimated by multiplying the total capital cost of treatment and conveyance by appropriate capital recovery factor [30,36,45].

The capital recovery factor (CRF) is calculated using the net present value (NPV) method. The net present value (NPV) of the asset is defined for a given discount rate (r), and (n), a series of future payments over a defined period of time:

$$CRF = \left[ \frac{r(1+r)^n}{(1+r)^n - 1} \right] \tag{2}$$

**Table 2**  
Capital cost of various desalination processes.

Process	Plant capacity m <sup>3</sup> /day	Unit-capital cost \$/(m <sup>3</sup> /day)	Reference
MD	24,000	1131	[3]
MED	37,850	1860	[5]
MSF	37,850	1598	[5]
RO	37,850	1313	[5]

In terms of cost per amount of water produced, the capital cost is then determined by:

$$\text{Normalised capital cost} \left[ \frac{\$}{\text{m}^3} \right] = \frac{CRF \times \text{Capital cost} \left[ \frac{\$}{\text{y}} \right]}{\text{Plant capacity} \left[ \frac{\text{m}^3}{\text{y}} \right]} \tag{3}$$

2.2.5. Operating cost for the desalination process

Operating costs are those expenditures incurred after plant commissioning and during the actual operation. These include energy, brine disposal, membrane replacement, pre-treatment, labour, and maintenance cost determined as follows:

2.2.5.1. Electrical and thermal energy. Determining the electrical energy requirement requires the current industrial cost of electricity as shown in Table 1. However thermal energy requirement is less obvious since this energy is typically taken from low pressure steam lines in a thermal process as opposed to specifically burning fuel for desalination [46]. A value of \$0.007 per kg steam wash used in 2008 [3], which indexed to 2012 is \$0.0078 per kg. Using latent heat, this value converts to \$0.0124 per kWh. The energy (electricity or thermal) cost is determined by:

$$\text{Energy cost} \left[ \frac{\$}{\text{m}^3} \right] = \text{Cost of energy} \left[ \frac{\$}{\text{kWh}} \right] \times \text{Specific energy consumption} \left[ \frac{\text{kWh}}{\text{m}^3} \right] \tag{4}$$

2.2.5.2. Emission cost. Carbon costs for both electrical and thermal (via natural gas) is given as follows:

$$\begin{aligned} \text{Carbon cost} \left[ \frac{\$}{\text{m}^3} \right] &= \text{Energy requirement} \left[ \frac{\text{kWh}}{\text{m}^3} \right] \times \text{Emission factor} \left[ \frac{\text{kg CO}_2\text{-e}}{\text{kWh}} \right] \\ &\times \text{Carbon tax} \left[ \frac{\$}{\text{tonne CO}_2\text{-e}} \right] \times \frac{1}{1000} \left[ \frac{\text{tonne}}{\text{kg}} \right] = \end{aligned} \tag{5}$$

Both electrical and thermal emissions are determined separately and added to produce the total emission cost.

2.2.5.3. Membrane replacement cost. In this analysis, the membrane cost for MD is estimated based on principle flux of 6 kg/m<sup>2</sup>/h, a membrane cost of \$9 per m<sup>2</sup>, and 20% replacement per year. This leads to the operating cost of \$0.034 per m<sup>3</sup> water treated:

$$\begin{aligned} \text{Membrane cost} \left[ \frac{\$}{\text{m}^3} \right] &= \\ \text{Membrane price} \left[ \frac{\$}{\text{m}^2} \right] \times \text{Replacement rate} \left[ \frac{1}{\text{y}} \right] &\times \frac{1000 \left[ \frac{\text{l}}{\text{m}^3} \right]}{\text{Membrane flux} \left[ \frac{\text{l}}{\text{m}^2 \text{h}} \right] \times 8760 \left[ \frac{\text{h}}{\text{y}} \right]} \end{aligned} \tag{6}$$

2.2.5.4. Brine disposal cost/pre-treatment cost/maintenance cost/labour cost. The specific cost for brine disposal, pre-treatment costs, maintenance costs and labour costs for various desalination technologies is given in Table 1.

3. Results and discussion

3.1. Experimental viability of MD for RO brine reduction

Fig. 2 shows the flux as a function of time (and increasing concentration) for three batch DCMD processes, while Table 3 shows the concentration of various species at the start and end of each batch

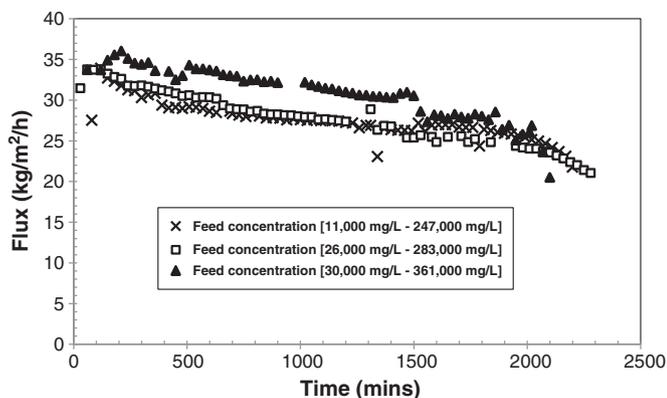


Fig. 2. Flux over time during DCMD experiment fed with RO groundwater concentrate.

concentration. In each run 20 L of feed was concentrated until a volume of <2 L was achieved. This represents a recovery greater than 90%. Fluxes were in the range of 20 to 37 kg/m<sup>2</sup>/h which were largely consistent and quite high for all salinities (up to 361,000 mg/L TDS) in these experiments. Importantly, this data shows that the flux is not significantly dependent on the feed water salinity in this concentration range. While flux declined during the run, since it returned to the original value as the previous run at lower concentration after replacing the membrane, we conclude this is due to changes in the new membrane's performance, and not salinity. This is strong evidence to support the concept that the flux of MD (and hence capital cost) is not as strongly linked to concentration as in the case of RO.

It is also important to note that the fluxes are higher than the value chosen in our economic model (Section 2.2.5.3) since practical MD installations typically have heat recovery systems or operate at lower temperatures, which tend to reduce flux. These experiments were performed, not to determine an appropriate flux but to validate to potential for RO brine concentration using MD.

The results in Table 3 also show that the majority of the TDS was sodium chloride, which accounted for 72% to 77% of the TDS for all samples with the exception of the initial feed of Feed 1. In this case the NaCl represented 99% of the TDS. We believe, based on a mass balance that this higher value is likely due to an underestimate of the TDS. Comparison of the concentration factors of sodium and chloride, measured by different techniques, reveals similar values for all three runs (17, 11 and 11 respectively). This implies that the elemental analysis is more reliable than TDS. We also see that sodium chloride concentration for the final concentrated solution (Feed 3) was 259,000 mg/L which is below the saturation concentration of approximately 373,000 mg/L at 60 °C [49]. As stated earlier, the NaCl enrichment was very high. An approximate 17 fold increase was measured in the first batch concentration process, while 11 fold increases were seen in the second and third batch concentration processes. This aligns well with the greater than 90% water recovery estimated. The calcium concentration factor on the other hand was more limited. A 4.5-fold increase was observed in the first experiment reducing to a

1.6-fold increase for the third experiment. This is a strong indication that precipitation was occurring. No scale was observed on the membrane, but was observed in the 0.5 µm filter and was thus efficiently captured at the highest temperature point in the hot cycle to avoid membrane scaling. MD can therefore operate at salinities well beyond where RO fails, showing increasing potentials to enhance water recovery. Similar results have been demonstrated experimentally, using MD process to concentrate feed water salinity up to 76,000 mg/L TDS, which is twice the salinity of seawater [6,21]. Our costing in this work is benchmarked using seawater desalination to allow comparison to RO, but clearly MD can exceed the limitations of RO due to its non-reliance on overcoming osmotic pressure. MED could also achieve such high salinities, but is limited due to scaling issues. An interesting feature of MD as a thermal process is the separation of the saline water heating zone (heat exchanger) from the evaporation zone (membrane). The separation has allowed the convenient placement of the filter between the zones to capture precipitating salts immediately after heating, but prior to evaporation. As the water enters the membrane module, it begins to cool due to evaporation effectively enhancing the solubility of common scale species as they concentrate. Also, the membrane surface itself is cooled by the cold permeate side leading to the temperature polarisation effect. Both effects assist in the avoidance of calcium scaling of the membrane.

### 3.2. Desalination technology costing

Fig. 3 shows the treated water cost as a function of plant size. At a production capacity of 30,000 m<sup>3</sup>/day, the cost of MD is \$1.72/m<sup>3</sup> while the MED cost is \$1.48/m<sup>3</sup> and RO cost is \$0.69/m<sup>3</sup>, indicating that as a plant supplied with steam, MD is not economically favourable against RO or MED for seawater desalination. In this comparison, the higher cost of MD is due to the assumption that waste heat is not available on site and water is heated to high temperatures (>60 °C) by steam. Fig. 3 also shows the economy of scale for all MD, RO, MED and MSF. MSF has a strong economy of scale compared with others, but at any scale was determined the most expensive method to desalinate seawater and the most energy intensive. MD costs are slightly higher than the cost of MED. Similar results were reported by Obaidani et al. [3] in 2008, where the cost of MD was estimated at \$1.17/m<sup>3</sup> and MED is \$1.00/m<sup>3</sup>. MED and MD consume greater amounts of energy (thermal and electrical combined) than RO. However, both MED and MD can utilise waste heat or solar thermal energy.

The cost comparison of both technologies presented in Fig. 4 shows that a large cost saving is expected when a high temperature (~60 °C) waste heat source is available for MD desalination. In such a case, the cost of water produced by MD decreases to \$0.61/m<sup>3</sup> and MED \$0.81/m<sup>3</sup>. MD is now cheaper and more competitive than the cost of water produced by RO. We assumed that waste heat costs 10% of the price of steam used in this analysis. Therefore, MD appears cheaper for desalination if a low cost (i.e. waste) heat source is available.

Table 3  
Concentration of TDS and major species in the concentrated groundwater samples.

Sample solution	Feed solution (mg/L)	TDS (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Sulphur (mg/L)	Calcium (mg/L)	Magnesium (mg/L)
Feed 1	Initial feed concentration (mg/L)	11,000	3820	7080	260	250	520
	Final feed concentration (mg/L)	247,000	63,700	120,000	4340	1130	8110
Feed 2	Initial feed concentration (mg/L)	26,000	6880	12,700	440	330	910
	Final feed concentration (mg/L)	283,000	76,000	143,000	5040	750	10,300
Feed 3	Initial feed concentration (mg/L)	30,000	8080	14,800	540	320	–
	Final feed concentration (mg/L)	361,000	91,200	168,000	5410	500	13,100

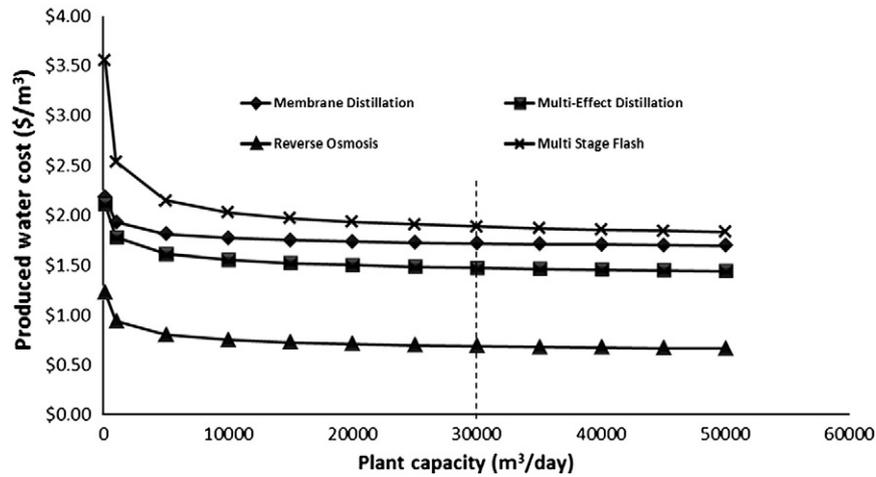


Fig. 3. Water production cost of MD, RO, MED and MSF driven by steam and/or electricity. Dotted line indicates reference plant capacity of 30,000 m<sup>3</sup>/day used in this study.

3.3. Cost composition of MD and MED

Figs. 5 and 6 show the cost break down for each contributor to the water price for MD and MED respectively. At any capacity, the cost is highly sensitive to thermal energy, but is more significant for MD and hence offers a better opportunity for the use of waste thermal heat as compared with MED (Fig. 7). Although our choice of the nominal 100 kWh/m<sup>3</sup> thermal energy requirement is higher than the 60 kWh/m<sup>3</sup> value used for MED (Table 1), the advantage of MD over MED is its ability to be built from cheaper materials than the MED.

3.4. Cost impact of carbon tax on MD, RO and MED

The amount of carbon dioxide emitted to produce a cubic metre of potable water by desalination will depend on the source of energy used for both thermal and electrical energy, the amount of chemical used in the process and life of consumable items such as the membrane. Offsetting the carbon emissions associated with energy increases the total cost of desalination for MD, MED and RO as shown in Fig. 7. With the inclusion of tax of \$23 per tonne carbon, and production capacity of 30,000 m<sup>3</sup>/day, the overall production cost for MD is \$2.20/m<sup>3</sup>, MED is \$1.77/m<sup>3</sup> and RO is \$0.80/m<sup>3</sup>. Again, RO is

still the most cost effective desalination technology when a carbon tax is applied when no waste energy is used. In this context, RO would be most viable for desalination but reaches its TDS limit of around 70,000 mg/L where the thermal processes like MED and MD (demonstrated by data in Fig. 2 and Table 3) can concentrate much beyond this. If the thermal energy had to be produced for these processes (i.e. as steam in Fig. 3), the higher thermal energy requirement for MD over MED means it is more sensitive to the carbon tax. However this assessment does not take into account changes in emissions produced from the different construction materials of MD systems (utilising mostly polymeric materials) compared with MED (mostly metallic materials). A life cycle assessment (LCA) is therefore needed to assess this possibility for reduced carbon emissions of MD. Such assessments have already been conducted, and indicate for MD and RO that energy still accounts for >90% of the environmental impact. [50]. So while construction materials contribute little to overall impact, a comparison to MED is still needed.

However, there is a cost saving for the thermal technologies when they are driven by a waste heat source while a carbon tax is applied. As shown in Fig. 7, the cost of MD desalinated water is still more economical, with a total cost of \$0.66/m<sup>3</sup>, compared with \$0.88/m<sup>3</sup> for MED and \$0.80/m<sup>3</sup> for RO. Again, MD becomes the cost effective desalination technology when waste heat is applied due to the cheaper

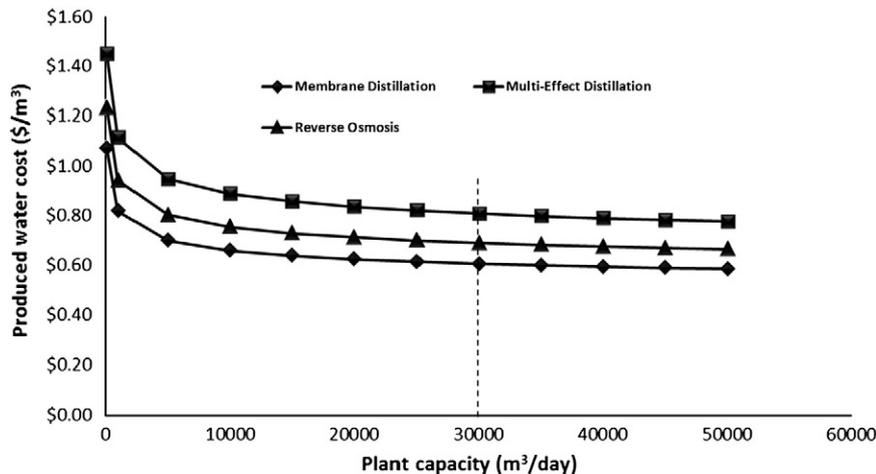


Fig. 4. Cost of MD, RO and MED when high temperature waste heat (at 10% steam cost) is available for both MD and MED. Dotted line indicates reference plant capacity of 30,000 m<sup>3</sup>/day used in this study.

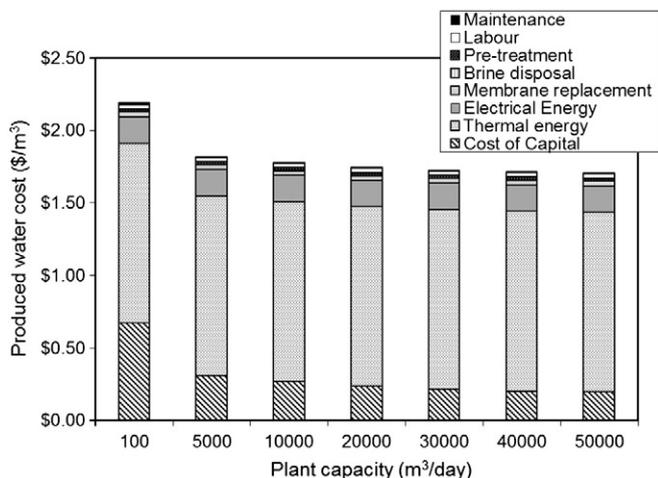


Fig. 5. Breakdown of water production cost treated by MD.

materials of construction and strongest sensitivity to thermal energy cost.

### 3.5. Thermal vs. electrical efficiency in MD: case for low grade waste heat

State of the art MD systems feature innovative arrangements which minimise the loss of the latent heat that is an essential part of the MD process. The internal heat recycling systems borrow from the thinking in conventional thermal processes [46]. These are ideally placed when the cost of the thermal energy is higher, for example higher temperature sources, or when supplied from solar panels (i.e. high grade). However thermal processes have optimal economics depending on the balance between the cost of the energy (operating cost) and the system complexity (capital cost) [45].

Based on this concept, when the cost of low grade heat is low due to lower temperature (<50 °C), a less thermally efficient system is therefore more economical. Further, heat recycling becomes less efficient when lower temperatures are supplied. Such cases are significant in industry, as less thermally efficient MED has better economics if it leads to cheaper capital [46]. For example in closed cycle power station condensers, anaerobic digesters, and industry heating services, exhaust heat is available at much lower temperatures and can be relatively abundant. As an example of this abundance, 500 MW of thermal energy from power station condensers can (assuming 100% to latent heat) evaporate 19 million L of water per day even at low temperature (<50 °C). This is a significant desalinated water

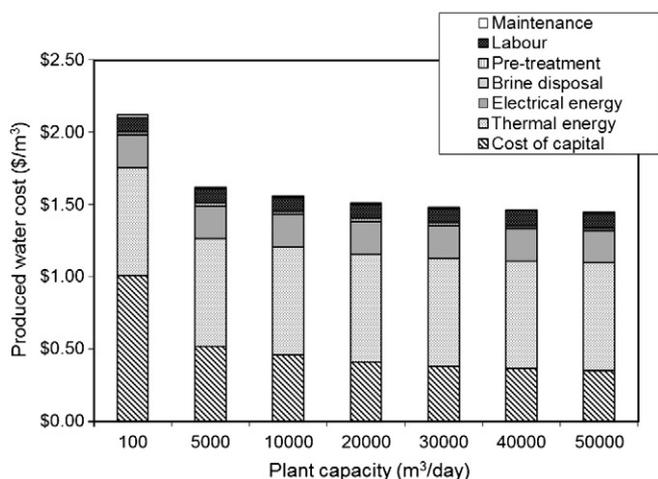


Fig. 6. Breakdown of water production cost treated by MED.

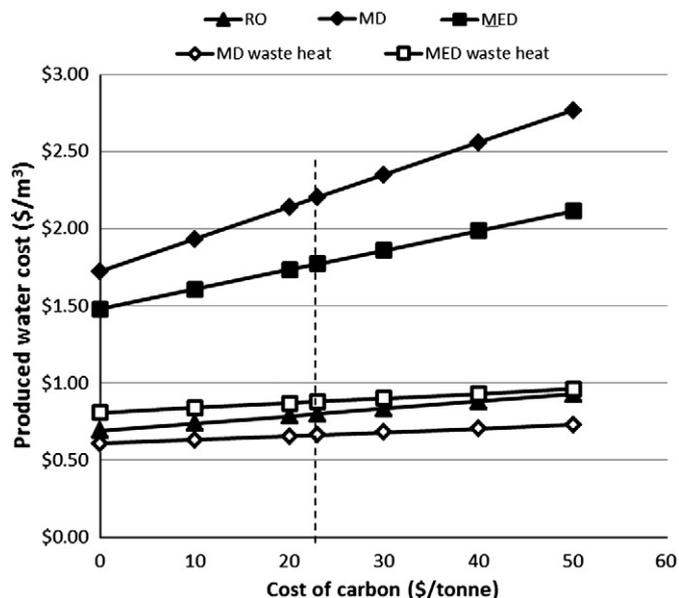


Fig. 7. Impact of carbon tax on water price for RO, MED and MD with steam (solid symbols) and with waste heat (hollow systems). Dotted line indicates \$23 per tonne carbon tax.

volume from a low temperature waste heat that is commonly discharged to the sea or other large water body.

To apply this opportunity to MD, the MD plant works better without heat recycling. This is because lost flux due to the lower temperature can be restored by operating at higher membrane cross flow velocity. This however means heat recycling is not possible. A recent trial of MD on a sea water cooled power station's waste heat from our group [51] demonstrated that electrical efficiency can be 1.9 kWh/m<sup>3</sup> based on: DCMD with no heat recovery, a heat supply of around 35 °C, cooled by seawater, and flux of 4 kg/m<sup>2</sup>/h (membrane replacement cost of \$0.051/m<sup>3</sup> by Eq. (6)). If this system required 1200 kWh/m<sup>3</sup> of this 35 °C heat, the 500 MW thermal load to the sea could desalinate 10 million L of water per day. This quantity would take 0.8 MW of the power station's 500 MW electrical capacity to run the circulation pumps. Assuming the equivalent of 1% of the full price of steam to pay for this heat, the desalinated water cost becomes \$0.57/m<sup>3</sup> (carbon tax applied, scaled to 30,000 m<sup>3</sup>/day reference plant). Further electrical energy reductions are possible through MD, for example in a MDHX module; electrical demand can be as low as 0.01 kWh/m<sup>3</sup> [28,52]. Assuming that this electrical demand is in practice 1 kWh/m<sup>3</sup>, under a carbon tax and reference plant scale, we see cost drop to \$0.45/m<sup>3</sup>. Therefore, MD seems economically viable in cases where low thermally efficient, but high electrically efficient systems are employed to make the best use of abundant lower temperature heat. For this low grade waste heat case, MED has not been included in the costing as it is assumed that MED will not effectively function at such low temperatures. A simple evaporator would be the technical equivalent, but subject to similar economics as MED due to the greater cost of the materials of construction.

This investigation acknowledges the efforts to offset greenhouse gas emissions by constructing renewable energy harnessing facilities (such as solar collectors and wind turbines). However despite these efforts, it is valid to argue that the power from these facilities would be better offsetting emissions of the existing high value electricity demand instead of a newly constructed desalination plant. Unless our electricity is sourced in a major way from renewables, the power grid still is supplied by 90% fossil fuels [46,53], so although a positive outcome of building a desalination plant is the construction of a renewable energy power station, the power delivered to the desalination plant from the grid is still majority supplied by fossil fuels, and

**Table 4**

Summary costing of MD, RO and MED desalination for 30,000 m<sup>3</sup>/day reference plant. Units in \$/m<sup>3</sup>. Carbon tax of \$23 per tonne carbon used when applied to costing.

Desalination case	MD	RO	MED
No carbon tax and driven with low pressure steam and electricity	1.72	0.69	1.48
Carbon tax applied and driven with low pressure steam and electricity	2.20	0.80	1.77
No carbon tax and driven with high temperature waste heat and electricity	0.61	0.69	0.81
Carbon tax applied and driven with high temperature waste heat and electricity	0.66	0.80	0.88
Carbon tax applied and driven with low temperature waste heat and electricity (low thermally, high electrically efficient mode)	0.57	0.80	N/A

realistically will be the major proportion for decades to come. This makes the ability to desalinate water from existing energy sources that are currently discarded more attractive as a means to produce low carbon treated water today. This is the outcome we have found in our economic assessment that compares MD with the more established desalination technologies RO, MSF and MED. It is therefore concluded that MD is viable both economically and environmentally (low carbon context) to desalinate water when a low cost waste heat source is found. However this heat source would need to be considered as ‘waste’, i.e. it cannot be minimised by the source process’ efficiency improvements. A water treatment operation could be considered a valuable use of currently discarded heat. Despite efforts to improve process efficiencies, there are viable sources of such heat, for example the abundant waste heat exhausted from a power station at 40 °C, which has no other value internally, but valuable as a source of energy for MD. With increased process integration, it is possible to explore options on utilising the existing heat paths in processes to become the heat source and sink to treat a separate process stream by MD [28]. Therefore the constraint to find ‘waste’ heat sources is lifted, but the compromise is increased process complexity.

**4. Conclusion**

- The cost of desalination schemes will increase by introduction of a price for carbon, but RO still remains lowest cost;
- Under a carbon tax, MD has the best economics when the heat source has a low cost (e.g. waste heat). Specifically compared with MED, MD has lower cost materials. Compared with RO, MD has lower reliance in electricity;
- When fed with steam, MSF is the most costly desalination process, while MED and MD are similar and RO has the best economics;
- MD has the capacity to desalinate RO groundwater concentrate to hypersaline concentrations demonstrating its viability as a high recovery desalination technology;
- MD can also cost effectively harness abundant low grade heat sources or be integrated into existing processes.

Table 4 summarises the outcomes of the cost modelling.

**Acknowledgements**

The authors would like thank CSIRO for the funding through CSIRO, Minerals Down Under Flagship Award and Victoria University for providing the PhD scholarship for Mr Uchenna Kennedy Kesieme. The authors acknowledge Paul Atherton of GWM Water for providing the RO brines from the Edenhope drinking water plant used in this work.

**Appendix A**

A sample calculation of water production cost using MD system when a low grade heat source is available and a carbon tax

*Plant capacity:* 30,000 m<sup>3</sup>/day

*The annual production capacity:*

$$30,000 \frac{\text{m}^3}{\text{day}} \times 365 \frac{\text{days}}{\text{y}} \times 0.9 = 9855000 \frac{\text{m}^3}{\text{y}}$$

*Capital cost:* The capital cost is estimated using Eq. (1), capacity based factor equation (see Section 2.2.3)

$$= 1131 \times 24,000 \left[ \frac{30,000}{24,000} \right]^{0.8} = \$32,449,040.$$

*Normalised capital cost:* The cost of capital per m<sup>3</sup> water produced is estimated using Eqs. (2) and (3) in Section 2.2.4, the Net present Value method

$$\frac{0.05 \times (1 + 0.05)^{30}}{(1 + 0.05)^{30} - 1} \times \frac{32,449,040}{9,855,000} = \frac{\$0.21}{\text{m}^3}$$

*Cost of electricity:* The cost of electricity is estimated using Eq. (4):

$$0.09 \times 2 = \frac{\$0.18}{\text{m}^3}$$

*Thermal energy cost:* Thermal energy cost is estimated using the same method for annual cost of electricity. However, when a low or high grade heat is available, we assumed the cost is equal to 10% of the total cost of thermal energy.

$$0.0124 \times 100 \times 10\% = \frac{\$0.124}{\text{m}^3}$$

*Brine disposal cost:* The brine disposal cost from Table 1 is \$0.0015/m<sup>3</sup>.

*Membrane replacement cost:* The membrane replacement cost is estimated using Eq. (6)

$$9 \times 20\% \times \frac{1,000}{6 \times 8760} = \frac{\$0.034}{\text{m}^3}$$

*Pre-treatment cost:* The pre-treatment cost from Table 1 is \$0.019/m<sup>3</sup>.

*Labour cost:* The labour cost taken from Table 1 is \$0.03/m<sup>3</sup>.

*Maintenance cost:* maintenance cost is estimated as 2% of the normalised capital cost.

$$0.21 \times 2\% = \frac{\$0.0043}{\text{m}^3}$$

*Emission cost*

Emission cost takes into account both the thermal and electrical energy. However, when waste heat is available, the cost of emission using thermal energy is assumed to be zero. Only electrical energy is therefore considered. This is estimated using Eq. (5)

$$2 \times 1.22 \times \frac{23}{1000} = \frac{\$0.056}{\text{m}^3}$$

*Total water treatment cost:*

$$= 0.21 + 0.12 + 0.18 + 0.0015 + 0.034 + 0.019 + 0.03 + 0.0043 + 0.056 = \$0.66/\text{m}^3.$$

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#### **4. Application of MD for acid and water recovery of mining waste waters (Chapter 4)**

---

A preliminary experiment was conducted in DCMD mode to assess the viability of MD to concentrate acid and recover fresh water from mining waste solutions. The experimental study were carried out on a synthetic model mine waste water from acid mine drainage.

The paper was published in a proceeding, International Mine Water Association Annual Conference (IMWA) as follows:

U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng and M. Duke. Novel application of membrane distillation for acid and water recovery of mining waste waters. International Mine Water Association Annual Conference, IMWA, October, 2012, Bunbury, WA, Australia, 623 - 630

## **Response from the thesis examination**

### **Examiner's comment:**

Testing of the three groups (0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M NaCl, and 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 0.2 M NaCl) allows for clear comparison. However, there is no statement before the test as to why these three combinations were selected

### **Response:**

In the Abstract section of the IMWA paper

“U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng and M. Duke. Novel application of membrane distillation for acid and water recovery of mining waste waters. International Mine Water Association Annual Conference, IMWA, October, 2012, Bunbury, WA, Australia, 623 – 630”

It stated that “The influence of acid concentration and the presence of inorganic salts in the feed were investigated using DCMD for three different synthetic solutions: (A) 0.5 M H<sub>2</sub>SO<sub>4</sub> (B) 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M NaCl (C) 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 0.2 M NaCl”

Furthermore, the Introduction section of the paper stated that “Many ores contain sulphide minerals such as pyrite (FeS<sub>2</sub>) [1]. Mining of these ores has the potential to expose sulphide minerals to atmosphere and water to generate and release acidic solutions containing sulphate, heavy metals and metalloids.” And “Membrane distillation (MD) is a new technology that may offer advantages of low energy consumption, operating at low temperature and high efficiency especially when waste heat is available to concentrate acids and metals for recovery [2- 4]”

The rationale for the selection of H<sub>2</sub>SO<sub>4</sub> and salts is that H<sub>2</sub>SO<sub>4</sub> is produced when sulphide minerals are exposed to air and water. In addition, sulphate, heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), metalloids (As, Sb), and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F) are also released depending on the ore. The concentrations of acid (H<sub>2</sub>SO<sub>4</sub>) and salts selected for synthetic acidic solutions (A to C) are based on expert advice received from the industries collaborating on the project (Jervois mining) and CSIRO”.

Furthermore, the concentration of acid and salts present in a typical acidic mine water is well described in the paper:

Nordstrom D.K (2011). Mine Waters: Acidic to Circumneutral. ELEMENTS, VOL. 7, PP. 393–398. DOI: 10.2113/gselements.7.6.393.

The values of pH reported for acid mine waters are in range of –3.5 to 5. Therefore our value is similar to that of a real mine water

**Examiner's comment:**

and there is also no discussion about why NaCl and Na<sub>2</sub>SO<sub>4</sub> will affect the passage of HCl into the distillate after the test.

**Response:**

In Page 627 of the IMWA conference paper published as “U. K. Kesieme, N. Milne, H. Aral, C.Y. Cheng and M. Duke. Novel application of membrane distillation for acid and water recovery of mining waste waters. International Mine Water Association Annual Conference, IMWA, October, 2012, Bunbury, WA, Australia, 623 – 630”.

It was stated “In the case of solution B and C, the final pH recorded in the permeate tank was within the range of 2.0 – 2.5 due to HCl vapour, obtaining the Cl<sup>-</sup> from the NaCl added to the feed (Table 2). This also had the effect of increasing the conductivity in the permeate for solutions B and C”

The point of this was to use the representative components in the synthetic solution to show what happens to sulphuric acid in the presence of chloride. It was shown chloride goes through the membrane which has been quantified

**Examiner's comment:**

2 M NaCl was stated to be used in feed 2 (0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M NaCl) in the abstract, but actually 0.1 M was reported in Tables 1 and 2. If 0.1 M NaCl was used, then there is no direct comparison among the three groups any more, which makes the work less interesting

**Response:**

The overall aim of the experiment is to understand the effect of different salt concentration on H<sub>2</sub>SO<sub>4</sub> concentrating in the feed using DCMD. The 0.2M NaCl in the abstract is typo error. However, the actual concentration of 0.1 M NaCl was reported in Table 1 and 2.

**Examiner's comment**

Why is the chloride concentration in the distillate higher since the feed water only contains H<sub>2</sub>SO<sub>4</sub>

**Response:**

This is an interesting observation, but while the increase is not significant in the context of the work (chloride values still very low at <50 mg/L), it does show some chloride increase due to operation. We suspect that because the value is so small, the increase could be due to experimental error and/or residual chloride in the equipment.

**Examiner's comment:**

The statement that “MD can utilize a low-grade heat source...” is not a conclusion and should be moved to the introduction instead

**Response:**

The paper is already published. However the purpose to mention in the conclusion is still valid, as it relates to the point made earlier in the paper our choice of temperature (60°C) being in the waste heat range. In the main body of the paper, references are cited about MD using waste heat supporting the statement in the conclusion that waste heat can be used for acid recovery MD.

**Declaration of co-authors enclosed**

**DECLARATION BY CO-AUTHORS**

The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. There are no other authors of the publication according to these criteria;
4. Potential conflicts of interest have been disclosed to a) granting bodies, b) the editor or publisher of journals or other publications, and c) the head of the responsible academic unit; and
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Signature 4		18/11/2013
		19/11/2013

Signature 5:

19/11/2013

*Novel application of membrane distillation for acid and water recovery of mining waste waters* by U. K. Kesieme, N. Milne, H. Aral, C. Y. Cheng, and M. Duke was published in *International Mine Water Association Symposium*, 623-630, 2012.

The full-text of this article is subject to copyright restrictions, and cannot be included in the online version of the thesis.

The conference paper is available from:

<https://www.imwa.info/imwaconferencesandcongresses/proceedings/264-proceedings-2012.html>

## **5. Recovery of water and acid from leach solutions using DCMD (Chapter5)**

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DCMD experiments were conducted on a real leach solutions that's contain  $H_2SO_4$  and HCl respectively to access the viability of MD to recover acid and water and to confirm the ability of a filter to remove scaling membrane foulants from mining waste solutions

The paper was accepted in the journal Water Science and Technology as follows:

U. K. Kesieme, N. Milne, C.Y. Cheng, H. Aral and M. Duke. Recovery of water and acid from leach solution using direct contact membrane distillation. Journal of Water Science and Technology 69 (2014) 668-875

**Declaration of co-authors enclosed**

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The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
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Signature 1		
Signature 2		18/11/2013
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Signature 4		18/11/2013
Signature 5:		18/11/2013

*Recovery of water and acid from leach solution using direct contact membrane distillation* by U. K. Kesieme, N. Milne, C.Y. Cheng, H. Aral and M. Dukerwas published in the peer review journal, *Journal of Water Science and Technology*, 69/4, 868-875, 2014.

The full-text of this article is subject to copyright restrictions, and cannot be included in the online version of the thesis.

The article is available from: <https://doi.org/10.2166/wst.2013.788>

## **6. Recovery of sulphuric acid from waste and process solutions using SX (Chapter 6)**

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The aim of this work is to perform SX experiments and optimize solvents for selective acid recovery. The most suitable extractant for sulphuric acid recovery was selected in terms of extraction and stripping, and also optimised and characterised. The composition of the extracted species was investigated using slope analysis. This was carried out on a synthetic solution containing H<sub>2</sub>SO<sub>4</sub> and a model waste acidic solution from copper smelting plant.

The paper is published in the journal Hydrometallurgy as follows:

U. K. Kesieme, H. Aral, M. Duke, N. Milne, and C.Y. Cheng. Recovery of sulphuric acids from waste and process solutions using solvent extraction. *Hydrometallurgy*, 138 (2013) 14 – 20

**Declaration of co-authors enclosed**

**DECLARATION BY CO-AUTHORS**

The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. There are no other authors of the publication according to these criteria;
4. Potential conflicts of interest have been disclosed to a) granting bodies, b) the editor or publisher of journals or other publications, and c) the head of the responsible academic unit; and
5. The original data is stored at the following location(s):

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Signature 3		19-11-2013
Signature 4		18-11-2013
Signature 5:		18/11/2013



## Recovery of sulphuric acid from waste and process solutions using solvent extraction



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### ABSTRACT

TEHA (tris-2-ethylhexylamine) was selected as the extractant in the current study due to high acid extraction and ease in stripping. An optimum organic system consisting of 50% TEHA, 40% octanol and 10% Shellsol A150 was determined. It was found that the acid extraction decreased with the increase in temperature. The change in enthalpy ( $\Delta H$ ) was  $-13.2 \text{ kJ mol}^{-1}$ , indicating exothermic extraction reaction. Both extraction and stripping kinetics was very fast. McCabe–Thiele extraction diagram showed that for a feed solution containing 200 g/L  $\text{H}_2\text{SO}_4$ , three stages are required. McCabe–Thiele stripping diagram showed that three stages are required. Using slope analysis, it was found that the extracted species consisted of one acid molecule, one TEHA (A) molecule and two octanol (O) molecules with a formulae of  $(\text{H}_2\text{SO}_4)_1\text{AO}_2$ .

The optimised TEHA system was used to extract acid from a synthetic process solution containing a number of metals. It was found that the system only extracted acid with a small amount of metals entrained. After scrubbing the loaded organic solution in a single contact, almost all entrained metals were removed. In the case that the mining waste solution contains low concentration of acid, membrane distillation (MD) technology can be used to recover the water and concentrate the acid and metals. Solvent extraction can be then used to recover the acid and metals. A conceptual process flowsheet has been developed using a combination of MD and SX.

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### 1. Introduction

Solvent extraction (SX) is a well established technology to separate, purify and concentrate metals. It has been also applied for acid recovery from waste solutions and bleeding streams of copper, zinc and precious metals (Agrawal and Sahu, 2009; Agrawal et al., 2007, 2008; Gottlieb et al., 2000a,b). The use of SX to recover various acids has been reviewed by Ritcey (2006).

Extractants including TEHA (tris-2-ethylhexylamine), Alamine 336 (tri-octyl/decyl amines), TBP (tributyl phosphate) and Cyanex 923 (hexyl/octyl phosphine oxides) have been tested and applied to recover acids using solvent extraction (Agrawal et al., 2007; Alguacil and Lopez, 1996; Gottlieb et al., 2000a,b; Liao et al., 2002; Rickelton, 1993; Sarangi et al., 2006). Agrawal et al. (2008) studied the extraction of sulphuric acid from zinc electrowinning bleed stream containing 174 g/L  $\text{H}_2\text{SO}_4$  using TEHA in kerosene. It was found that TEHA had very good acid extraction capacity even in the presence of a large amount of zinc. In a similar study, Haghshenas et al. (2009) investigated the extraction of sulphuric acid in terms of thermodynamics and other conditions. It was reported that the acid extraction increased with the increase in the TEHA concentration in the organic solution and reached

a maximum depending on the initial acid concentration in the feed solution. Furthermore, a comparison of TEHA and Cyanex 923 for sulphuric acid extraction was studied in terms of thermodynamics. It was found that stripping of sulphuric acid from TEHA is more readily than from Cyanex 923 while the stripping of acid was easier from Cyanex 923 than from amine extractants (Wolter et al., 2002). Agrawal et al. (2007) studied the extraction of sulphuric acid using Alamine 336 and found that the extraction of sulphuric acid increased with the increase in the Alamine 336 concentration. Although, Alamine 336 showed higher extraction ability for sulphuric acid than Cyanex 923, the acid extracted could not be stripped completely using hot water.

The acid concentrations in mining waste solutions are usually low and can be concentrated using membrane distillation (MD) technology in which the vapour of volatile constituents including water in the feed solution of the hot side can pass through the pores of the hydrophobic membrane to the cold side for condensation. As a result, fresh water is recovered and the other constituents are concentrated. MD offers advantages of low energy consumption, high efficiency and operating at low temperatures to recover fresh water and concentrate the acid and metals (Tomaszewska, 2000; Tomaszewska et al., 1995). After concentrating, solvent extraction can be applied to selectively recover the sulphuric acid and valuable metals.

In the current paper, the most suitable extractant for sulphuric acid recovery in terms of extraction and stripping was selected, optimised

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and characterised. The composition of the extracted species was investigated using slope analysis and a process flowsheet to recover water, acid and metals proposed.

## 2. Experimental

### 2.1. Organic solutions

Organic solvents TEHA and octanol were purchased from Sigma-Aldrich. Alamine 336 was supplied by BASF, Cyanex 923 by Cytec and Shellsol A150, Shellsol 2046 and Shellsol D70 by Shell Chemicals, Australia. All reagents were used without further purification.

### 2.2. Aqueous solutions

The feed solution containing only sulphuric acid was prepared by diluting AR grade concentrated sulphuric acid using deionised water. The feed solution containing sulphuric acid and metals was prepared by adding required amounts of AR grade concentrated sulphuric acid and AR grade metal sulphate salts in deionised water.

### 2.3. Procedures

All batch solvent extraction tests were carried out in 100 mL hexagonal glass vessels immersed in a temperature controlled water bath. Eurostar digital overhead stirrers with 30 mm diameter impellers were used for mixing and the typical mixing time was 10 min for equilibrium. After separation, the organic solution was stripped twice using water at 60 °C. The loaded strip liquors and the aqueous sample were titrated to determine acid extraction, stripping and mass balance.

#### 2.3.1. Batch extraction

The extractants TEHA, Alamine 336 and Cyanex 923 in various concentrations in a temperature range of 22–60 °C were tested at an O/A ratio of 2 for the extraction of sulphuric acid.

#### 2.3.2. Extraction and stripping distribution isotherms

To determine acid extraction distribution isotherms, the selected organic system was contacted with the synthetic acid feed solution using different O/A ratios at 22 °C. To determine acid stripping distribution isotherms, the pre-loaded organic solution was stripped with water using different A/O ratios at 60 °C.

#### 2.3.3. Extraction and stripping kinetics

To determine extraction kinetics, timing started immediately when the selected organic solution was mixed with the synthetic acid feed solution at an O/A ratio of 2 and 22 °C. Mixed solution samples were taken at different times for acid titration. To determine stripping kinetics, timing started immediately when the pre-loaded organic solution was mixed with deionised water at 60 °C. Samples were taken at different times for acid titration.

#### 2.3.4. Slope analysis

Organic solutions containing various concentrations of TEHA and Shellsol A150 with 40% octanol were used for extraction slope analysis in terms of TEHA composition. Organic solutions containing various concentrations of octanol and Shellsol A150 with 50% TEHA were used for extraction slope analysis in terms of octanol composition. Different organic solutions and a synthetic feed solution containing low concentration of sulphuric acid were mixed at an O/A ratio of 1 and 22 °C to obtain data for slope analysis.

#### 2.3.5. Acidity titration

An automatic titration instrument (Titrand 842) was used to determine the concentration of sulphuric acid in aqueous solutions taken from extraction and stripping tests. Stock solution of 20 mL containing

280 g/L potassium oxalate was diluted to 40 mL using deionised water. The solution was stirred and the pH measured and adjusted to 6.5 before adding 0.250 mL of the sample solution. The resultant aqueous solution was titrated using NaOH to estimate the concentration of free acid in the aqueous sample.

## 3. Results and discussion

### 3.1. Selection of organic system

#### 3.1.1. Selection of organic system in terms of extraction

Three organic extractants including TEHA, Alamine 336 and Cyanex 923 were used to extract acid in the feed solution containing 200 g/L H<sub>2</sub>SO<sub>4</sub> at an O/A ratio of 2 and 22 °C. Preliminary experiments were performed using extractants in the concentration range of 20–60% (v/v) TEHA and Alamine 336 and 20–100% (v/v) Cyanex 923 (Table 1). Initially, octanol was used as the diluent for all three systems. For the Alamine 336 system, gel was formed with octanol as the diluent. Agrawal et al. (2007) met the same problem and used a system containing modifier isodecanol in diluent kerosene to solve it. Therefore in this study, Shellsol D70 (100% aliphatic) was used as diluent and isodecanol as modifier for the Alamine 336 system. No phase separation problems were observed with the TEHA and Cyanex 923 systems. In fact, the 100% Cyanex 923 system without diluent also performed well in terms of phase separation.

For the systems tested in Table 1, the acid extraction all increased with the increase in the extractant concentration (Fig. 1). This is in agreement with the observation reported by Gottlieb et al. (2000a,b), Agrawal et al. (2007, 2008), Haghshenas et al. (2009) and Agrawal and Sahu (2009). When the TEHA concentration increased from 20% to 60%, the acid extraction increased from 44% to 88%. When the Alamine 336 concentration increased from 20% to 60%, the acid extraction increased from 38% to 91%. The acid extraction was much lower with the Cyanex 923 systems. When the Cyanex 923 concentration increased from 20% to 60%, the acid extraction increased from 7.6% to 20%. With the 100% Cyanex 923 system, the acid extraction reached only 50%. It can be concluded that in terms of extraction, both TEHA and Alamine 336 systems performed well and much better than the Cyanex 923 system. TEHA and Alamine 336 are amine extractants and Cyanex 923 neutral extractant consisting of hexyl/octyl phosphine oxides. Amines are bases that naturally react with and extract acids. Therefore, the extractability for acid with TEHA and Alamine 336 is stronger than that with the neutral extractant Cyanex 923.

#### 3.1.2. Selection of organic system in terms of stripping

Three organic systems – (1) 50% TEHA and 50% octanol, (2) 50% Alamine 336, 30% Shellsol D70 and 20% isodecanol and (3) 100% Cyanex 923 – were loaded with the feed solution containing 200 g/L H<sub>2</sub>SO<sub>4</sub>

**Table 1**  
Compositions and extractions with the organic systems preliminarily tested.

Compositions of organic system	Extraction (%)
20% TEHA and 80% octanol	44.17
30% TEHA and 70% octanol	60.44
40% TEHA and 60% octanol	73.30
50% TEHA and 50% octanol	84.23
60% TEHA and 40% octanol	87.83
20% Alamine 336, 60% Shellsol D70 and 20% isodecanol	38.00
30% Alamine 336, 50% Shellsol D70 and 20% isodecanol	52.05
40% Alamine 336, 40% Shellsol D70 and 20% isodecanol	72.29
50% Alamine 336, 30% Shellsol D70 and 20% isodecanol	84.57
60% Alamine 336, 20% Shellsol D70 and 20% isodecanol	91.37
20% Cyanex 923 and 80% octanol	7.55
30% Cyanex 923 and 70% octanol	9.10
40% Cyanex 923 and 60% octanol	11.89
50% Cyanex 923 and 50% octanol	13.56
60% Cyanex 923 and 40% octanol	19.98
100% Cyanex 923 and 0% octanol	50.24

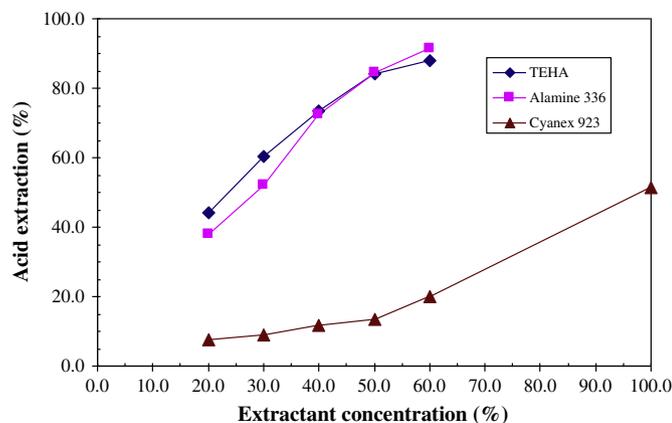


Fig. 1. Effect of extractant concentration on  $H_2SO_4$  extraction in a single contact at an O/A ratio of 2 and 22 °C.

using an O/A ratio of 2 at 22 °C. The loaded organic solutions were stripped with water at 60 °C. It was found that 97.6% and 95.3%  $H_2SO_4$  were stripped from the loaded TEHA and Cyanex 923 systems, respectively. In contrast, only 10.5%  $H_2SO_4$  was stripped from the Alamine 336 system (Table 2). The difficulty in stripping the acid from the Alamine 336 system was also reported by Agrawal et al. (2007).

Based on the extraction and stripping performance, the TEHA system was selected for further study due to higher acid extraction compared with the Cyanex 923 system and ease in stripping compared with the Alamine 336 system.

### 3.2. Effect of TEHA organic system composition and temperature on acid extraction

#### 3.2.1. Effect of diluent on acid extraction

The organic system containing 50% TEHA and 20% octanol was tested with different diluents including Shellsol A150 (100% aromatic), Shellsol 2046 (19% aromatic and 81% aliphatic) and Shellsol D70 (100% aliphatic). It was found that in terms of diluent type, the acid extractions were in the order of Shellsol A150 > Shellsol 2046 > Shellsol D70 (Table 3) with Shellsol A150 performed best. Moreover, the organic solutions separated into two layers with Shellsol D70 and Shellsol 2046 as the diluent, indicating third phase formation. Therefore, further optimisation was carried out using Shellsol A150 as diluent for the TEHA system.

#### 3.2.2. Effect of modifier on acid extraction

Another modifier, isodecanol, was also tested with the three diluents. It was found that although no third phase formation was observed with Shellsol 2046 and Shellsol D70 as the diluent, the acid extraction was

Table 2  
Stripping of acid from three loaded organic systems using deionised water at 60 °C.

Organic system	TEHA	Alamine 336	Cyanex 923
Acid in loaded organic (g/L)	84.3	71.0	51.5
Acid in stripped organic (g/L)	2.02	63.2	2.42
Stripping (%)	97.61	10.50	95.30

Table 3  
Effect of diluent on acid extraction at O/A ratio of 2 at 22 °C.

Organic composition			Extraction (%)
TEHA	Octanol	Diluent	
50%	20%	30% Shellsol A150	72.34
50%	20%	30% Shellsol 2046	69.02
50%	20%	30% Shellsol D70	67.76

Table 4  
Effect of modifier on acid extraction at O/A ratio of 2 at 22 °C.

Organic composition			Extraction (%)
TEHA	Isodecanol	Diluent	
50%	20%	30% Shellsol A150	71.02
50%	20%	30% Shellsol 2046	67.31
50%	20%	30% Shellsol D70	66.35

slightly lower with all three organic systems compared with octanol as the modifier (Tables 3 and 4). For example, the acid extraction was 72.3% with octanol as the modifier compared with 71.0% with isodecanol as the modifier when Shellsol A150 was used as the diluent.

#### 3.2.3. Effect of organic composition on acid extraction

When TEHA was used as the extractant, the presence of octanol in the organic phase was necessary to prevent third phase formation. To optimise the organic solution containing 50% TEHA, the concentrations of octanol and Shellsol A150 were varied with their total volume being 50% in the organic system. The increase in concentration of octanol from 20% to 50% resulted in the increase in acid extraction from 72.34% to 84.23% (Table 5). Although the highest acid extraction was obtained with the system containing 50% TEHA and 50% octanol, the slightly viscous mixture and slow phase separation (5–6 min) prevented it from practical operation. Therefore, the system consisting of 50% TEHA, 40% octanol and 10% Shellsol A150 with slightly lower extraction, but less viscosity and faster phase separation (about 2 min) was chosen as the optimum composition for further investigation.

#### 3.2.4. Effect of temperature on acid extraction

The optimised TEHA system consisting of 50% TEHA, 40% octanol and 10% Shellsol A150 was tested under different temperatures using an O/A ratio of 2 at 22 °C. With the increase in temperature from 22 °C to 60 °C, the acid extraction decreased from 82.13% to 72.46% for the initial acid concentration of 200 g/L in the feed solution (Table 6). Gottlieb et al. (2000a), Agrawal et al. (2008) and Haghshenas et al. (2009) also found the same phenomenon with the TEHA system. Further extraction studies were performed at 22 °C or room temperature.

The effect of temperature was also demonstrated thermodynamically using the Van't Hoff Equation (Gottlieb et al., 2000b; Haghshenas et al., 2009). The enthalpy change ( $\Delta H$ ) of the extraction process can be obtained from the following equations.

$$\text{Log}(D) = \frac{-\Delta H}{2.303 RT} + C \quad (1)$$

Table 5  
Effect of organic composition on  $H_2SO_4$  extraction at O/A ratio of 2 at 22 °C.

Organic composition			Extraction (%)
TEHA	Octanol	Shellsol A150	
50%	50%	0%	84.23
50%	40%	10%	82.24
50%	30%	20%	76.37
50%	20%	30%	72.34

Table 6  
Acid extractions and distribution coefficients (D) at different temperatures.

t (°C)	T (K)	1000/K	D	log(D)	Extraction (%)
22	295	3.390	2.30	0.36173	82.13
30	303	3.300	2.09	0.32015	80.68
40	313	3.195	1.75	0.24304	77.78
50	323	3.096	1.38	0.13988	73.43
60	333	3.003	1.32	0.12057	72.46

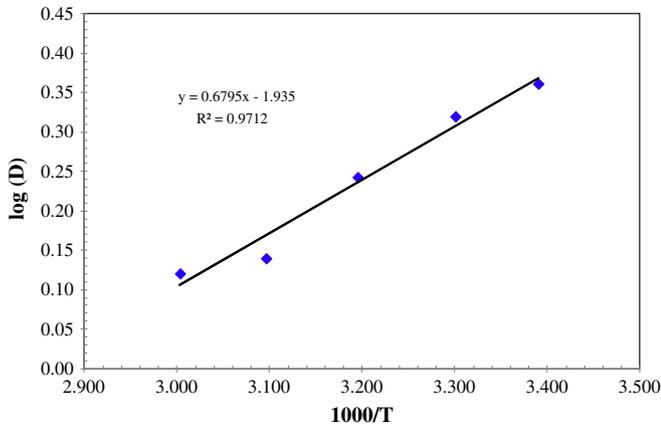


Fig. 2. A plot of log(D) vs. 1000/T.

where R is the gas constant, D the distribution coefficient, K the absolute temperature and C the integration constant. Eq. (1) can be re-written as Eq. (2):

$$\text{Log}(D) = \frac{1000}{T}A + C \quad (2)$$

where

$$A = \frac{-\Delta H}{2303R} \quad (3)$$

If a plot of log(D) against (1000/T) forms a straight line, then A will be the slope of the line and  $\Delta H$  can be calculated from the slope using Eq. (4):

$$\Delta H = -2303RA \quad (4)$$

A slope of 0.68 was obtained (Fig. 2) with a calculated change in enthalpy ( $\Delta H$ ) of  $-13.2 \text{ kJ mol}^{-1}$ . The negative value indicates the extraction is exothermic and hence the increase in temperature decreases acid extraction and increases acid stripping. Haghshenas et al. (2009) reported that the extraction reaction of sulphuric acid by TEHA was exothermic with the enthalpy change of  $-6.34 \text{ kJ mol}^{-1}$ . The difference is probably caused by the different compositions of the organic systems. Haghshenas et al. (2009) used 43% TEHA, 20% octanol and 37% kerosene while the current system consisted of 50% TEHA, 40% octanol and 10% Shellsol A150.

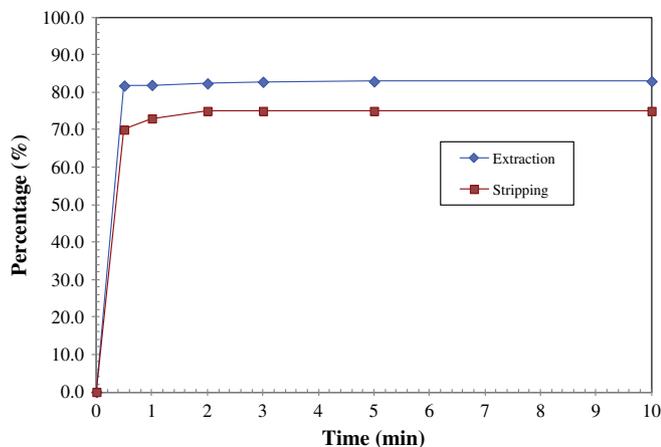


Fig. 3. Extraction and stripping kinetics with the optimised TEHA organic system.

Table 7  
Successive extraction of H<sub>2</sub>SO<sub>4</sub> using the optimised TEHA system.

Stage	Solution	Acid concentration (g/L)	Accumulative extraction (%)
	Feed	203.9	–
1	Raffinate 1	36.39	82.15
2	Raffinate 2	8.09	96.03
3	Raffinate 3	2.03	99.00

### 3.3. Characterisation of the selected TEHA organic system

#### 3.3.1. Extraction kinetics

The optimised TEHA organic system was tested for extraction kinetics at an O/A ratio of 2 and 22 °C. Solution mixture samples were taken at 0.5, 1, 2, 3, 5 and 10 min. The acid extraction reached 81.8% after mixing for 0.5 min and was kept almost constant after that, indicating that the acid extraction reached equilibrium very quickly and the extraction kinetics was very fast (Fig. 3).

#### 3.3.2. Stripping kinetics

The optimised organic system was loaded at an O/A ratio of 2 and 22 °C. The pre-loaded organic solution was subjected to stripping with distilled water at an A/O ratio of 2 and 60 °C (Fig. 3). Solution mixture samples were taken at 0.5, 1, 2, 3, 5 and 10 min. The acid stripping reached 75% after 2 min of mixing and was kept almost constant after that, indicating that the acid stripping reached equilibrium quickly and the stripping kinetics was fast.

#### 3.3.3. Successive extraction using the TEHA organic system

The optimised TEHA organic system was subjected to successive extraction with the synthetic feed solution containing 204 g/L H<sub>2</sub>SO<sub>4</sub> for three times at an O/A ratio of 2 and 22 °C. The first extraction test was conducted with both fresh organic and fresh feed solutions. The second and third extraction tests were conducted using the fresh organic solution and the raffinate from the previous extraction test. The accumulative acid extraction after the three extraction stages was 82.2%, 96.0% and 99.0%, respectively, with only 2 g/L H<sub>2</sub>SO<sub>4</sub> left in the last raffinate, indicating that in a counter current operation, only very small amount of acid would remain in the raffinate after three stages of extraction (Table 7).

#### 3.3.4. Acid extraction distribution isotherms and McCabe–Thiele diagram

The optimised TEHA organic system was used to determine acid extraction distribution isotherm with different O/A ratios at 22 °C. McCabe–Thiele diagram of H<sub>2</sub>SO<sub>4</sub> extraction was constructed to estimate the number of theoretical extraction stages required using the

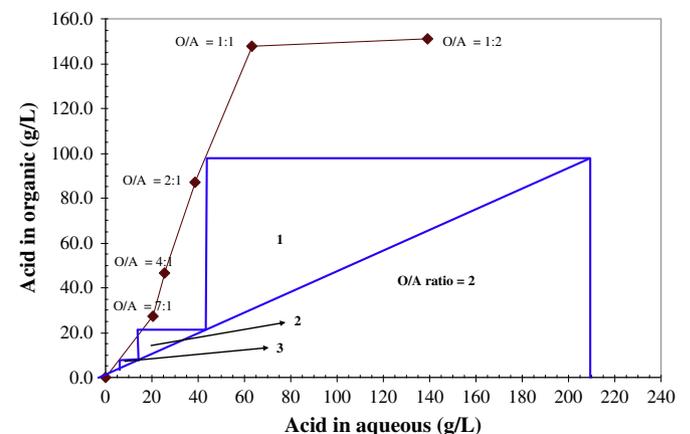


Fig. 4. Acid extraction distribution isotherm and McCabe–Thiele diagram with the TEHA system at operating O/A ratio of 2.

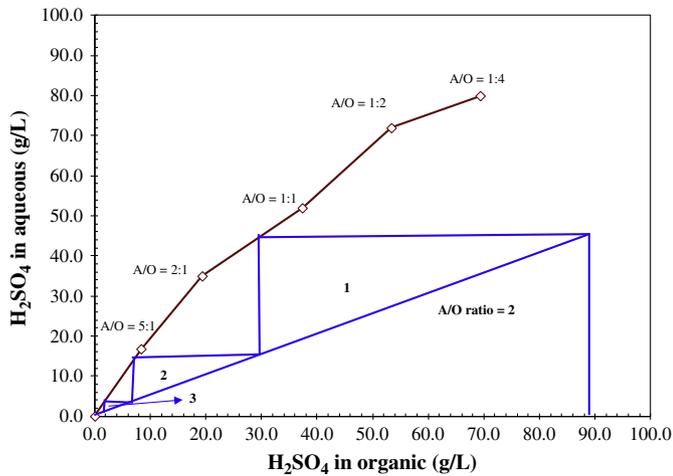


Fig. 5. Acid stripping distribution isotherm and McCabe–Thiele diagram with the TEHA system at operating A/O ratio of 2.

optimised organic system with an operating O/A ratio of 2 (Fig. 4). It was found that three extraction stages are required to decrease the acid concentration from 209 g/L in the feed to a few g/L in the raffinate with the acid concentration in the loaded organic solution of 95 g/L.

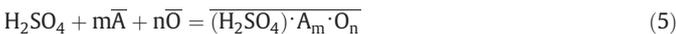
### 3.3.5. Acid stripping distribution isotherms and McCabe–Thiele diagram

The optimised TEHA organic system was loaded and the pre-loaded organic system was contacted with water at different A/O ratios and 60 °C to obtain stripping distribution isotherm. From the stripping distribution isotherm, McCabe–Thiele diagram for acid stripping at an A/O ratio of 2 was constructed (Fig. 5). It is shown that three stripping stages are required to remove more than 98% of the acid from the loaded organic solution with about 2 g/L acid left in the stripped organic solution and 45 g/L acid in the loaded strip liquor.

### 3.4. Slope analysis

Slope analysis is a useful tool to determine the stoichiometry of the coordination complex and therefore, the mechanism of the reaction. It has been shown in previous tests (Table 5) that when octanol was used as the modifier or diluent, the extraction of acid increased with the increase in octanol concentration. Therefore, it is possible that octanol also takes part in the extraction reaction. Although this phenomenon was observed by a number of researchers (Eyal and Baniel, 1991; Eyal et al., 1991; Gottlieb et al., 2000a; Haghshenas et al., 2009), the possible participation of octanol in the reaction to form part of the acid–organic complex has not been studied theoretically.

If TEHA and octanol both take part in the acid extraction reaction, the reaction could be:



where the top bars denote organic phases,  $\bar{A}$  the free TEHA and  $\bar{O}$  the free octanol in the system and  $m$  and  $n$  are digital numbers.

$K_{ex}$ , the reaction equilibrium constant, can be expressed as:

$$K_{ex} = \frac{[\overline{H_2SO_4 \cdot A_m \cdot O_n}]}{[H_2SO_4] \cdot [\bar{A}]^m \cdot [\bar{O}]^n} = \frac{D}{[\bar{A}]^m \cdot [\bar{O}]^n} \quad (6)$$

And therefore,

$$\log(K_{ex}) = \log(D) - m\log[\bar{A}] - n\log[\bar{O}] \quad (7)$$

Table 8  
Different concentration of TEHA and Octanol used for slope analysis.

Slope analysis	TEHA (%)	Shellsol A150 (%)	Octanol (%)
For TEHA	50	10	40
	45	15	40
	40	20	40
	35	25	40
For octanol	50	10	40
	50	15	35
	50	20	30
	50	25	25

where  $D$  is the distribution coefficient of the acid between the organic and aqueous phases. Eq. (7) can be re-written as Eq. (8):

$$\log(D) = \log(K_{ex}) + m\log([\bar{A}]) + n\log([\bar{O}]) \quad (8)$$

$K_{ex}$  is a constant at a fixed temperature. Let  $[\bar{O}]$  be constant, the plot of  $\log(D)$  against  $\log([\bar{A}])$  should give a straight line with a slope of  $m$  as shown in Eq. (9):

$$\log(D) = B + m\log([\bar{A}]) \quad (9)$$

where  $B$  is a constant.

Let  $[\bar{A}]$  be constant, the plot of  $\log(D)$  against  $\log([\bar{O}])$  should give a straight line with a slope of  $n$  as shown in Eq. (10):

$$\log(D) = C + n\log([\bar{O}]) \quad (10)$$

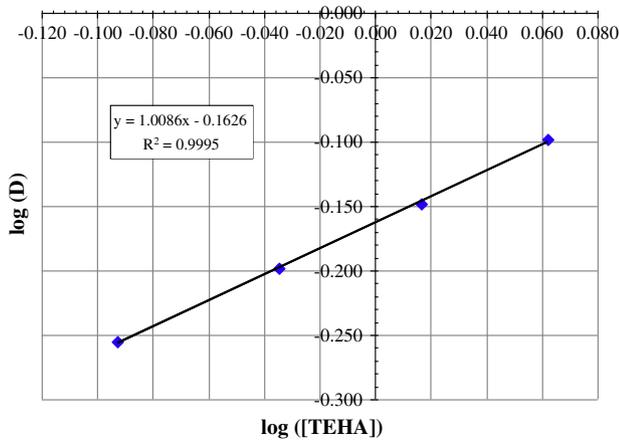
where  $C$  is a constant.

To determine the role of TEHA in the acid extraction, the octanol concentration was fixed at 40% while the percentage of the diluent Shellsol A150 varied to meet the changes of the TEHA concentration (Table 8). To determine the role of octanol in the acid extraction, the TEHA concentration was fixed at 50% while the percentage of the diluent Shellsol A150 varied to meet the changes of the octanol concentration (Table 8). To keep the free TEHA concentration or  $[\bar{A}]$  and free octanol concentration or  $[\bar{O}]$  relatively constant so that minimum TEHA and octanol were involved in the complexing reaction with the acid and their initial concentrations can be used in Eqs. (9) and (10) with minimum error, the acid concentration in the feed solution was only 14 g/L for slope analysis with TEHA and 11 g/L for slope analysis with octanol.

The TEHA concentrations and the distribution coefficients with different TEHA concentrations are shown in Table 9. In the plot of  $\log(D)$  against  $\log([\bar{A}])$  (Fig. 6), it was found that a straight line formed with the slope value of  $m$  being very close to 1, indicating that one TEHA molecule reacts with one acid molecule. This is in agreement with that reported by other researchers such as Agrawal et al. (2008).

Table 9  
Initial TEHA concentrations and distribution coefficients of acid with different TEHA concentrations.

$[\bar{A}]$ (%)	$[\bar{A}]$ (M)	$\log([\bar{A}])$	Acid in raffinate (g/L)	Acid in organic (g/L)	Distribution coefficient $D$	$\log(D)$
50	1.154	0.062	7.79	6.21	0.80	−0.098
45	1.039	0.016	8.18	5.82	0.71	−0.148
40	0.923	−0.035	8.57	5.43	0.63	−0.198
35	0.808	−0.093	9.00	5.00	0.56	−0.255



**Fig. 6.** A plot of log(D) vs. log( $\bar{A}$ ) with varying TEHA concentrations and fixed octanol concentration of 40% at an O/A ratio of 1 and 22 °C.

The octanol concentrations and the distribution coefficients with different octanol concentrations are shown in Table 10. In the plot of log(D) against log( $\bar{O}$ ) (Fig. 7), it was found that a straight line formed with the slope value of n being very close to 2, indicating that two octanol molecules reacts with one acid molecule. This clearly demonstrates that octanol does participate in the formation of acid-organic complexes and promote the extraction of acid. A test was conducted with 100% octanol and it was found that no acid was extracted, indicating that octanol acts as a synergist to improve the acid extraction by TEHA. When the organic solution consists of both TEHA and octanol, the reaction can be expressed as:



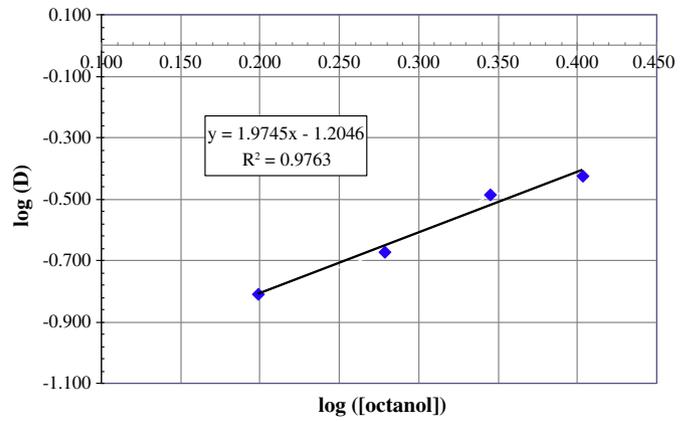
### 3.5. Acid extraction in the presence of metals

Extraction test was conducted using the optimised TEHA organic system and a feed solution containing 200 g/L H<sub>2</sub>SO<sub>4</sub> and small amount of metals including Fe, Ni, Zn, Co and Cu at an O/A ratio of 2 and 22 °C (Table 11). This solution mimicked a process solution from a copper smelting plant after concentration by 10 times using MD. It was shown that very small amounts of metals including 71 mg/L Fe, 13 mg/L Cu, 8 mg/L Zn, 1 mg/L Ni and Co were co-extracted by the organic solution. The metals in a sulphate solution are present in cation ions and should not be extracted by amines such as TEHA. Therefore, most probably, the metals were entrained in the organic solution and a scrub or washing stage using water at a high O/A ratio should remove most or all of the metals from the organic solution if pure acid product solution is required.

To verify that the metals were entrained, the loaded organic solution was scrubbed with water at an O/A ratio of 10 and 22 °C (Table 12). The acid concentration dropped from 85.1 g/L in the loaded organic solution to 81.6 g/L in the scrubbed organic solution, indicating that only 3.5 g/L acid was scrubbed with a scrubbing efficiency of 4.1%. The scrubbing efficiencies of metals are in the range of 97–100% in a single contact,

**Table 10**  
Distribution coefficients of acid with different octanol concentrations.

$\bar{O}$ (%)	$\bar{O}$ (M)	log( $\bar{O}$ )	Acid in raffinate (g/L)	Acid in organic (g/L)	Distribution coefficient D	log(D)
40	2.531	0.403	7.97	2.98	0.37	-0.427
35	2.215	0.345	8.25	2.70	0.33	-0.485
30	1.899	0.278	9.04	1.91	0.21	-0.675
25	1.582	0.199	9.48	1.47	0.16	-0.809



**Fig. 7.** A plot of Log(D) vs. log([octanol]) with varying octanol concentrations and fixed TEHA concentration of 50% at an O/A ratio of 1 and 22 °C.

suggesting that the metals were entrained and two scrubbing stages could be used to scrub all metals.

### 3.6. Development of a conceptual process flowsheet

A conceptual flowsheet to recover water, acid and metal values from acidic waste or process solutions is shown in Fig. 8. In arid areas, recovering water is very important. The fresh water recovered by MD can be also used for scrubbing the entrained metals and stripping the extracted acid. The sulphuric acid concentration in the loaded strip liquor is usually lower than that in the feed. Therefore, a second MD is necessary to further increase the acid concentrate up to 10 M H<sub>2</sub>SO<sub>4</sub> (Zhang, 2004).

## 4. Conclusions

Three extractants for the recovery of sulphuric acid from acidic waste solutions were tested including TEHA, Alamine 336 and Cyanex 923. Amongst the three extractants, TEHA performed best in terms of acid extraction and stripping. Therefore, the TEHA system was selected for optimisation.

**Table 11**  
Concentrations of metals in the feed and raffinates and their extractions.

Solution	Acid	Fe	Cu	Ni	Zn	Mg	Co
	Concentration (g/L)						
Feed	206.0	10.166	0.994	0.200	0.189	0.118	0.216
Raffinate	35.77	9.636	0.952	0.192	0.187	0.114	0.205
Loaded organic	85.12	0.071	0.013	0.001	0.008	0.000	0.001
	Extraction (%)						
	82.64	1.40	2.55	0.97	8.61	0.00	0.98

**Table 12**  
Scrubbing metals from loaded TEHA organic system.

Solution	Acid	Fe	Cu	Ni	Zn	Mg	Co
	Concentration (g/L)						
Loaded organic	85.12	0.071	0.013	0.001	0.008	0.000	0.001
Loaded scrub liquor	35.13	0.690	0.128	0.010	0.078	0.000	0.010
Scrubbed organic	81.60	0.002	0.000	0.000	0.000	0.000	0.000
	Scrubbing (%)						
	4.10	97.18	98.46	100.00	97.50	100.00	98.00

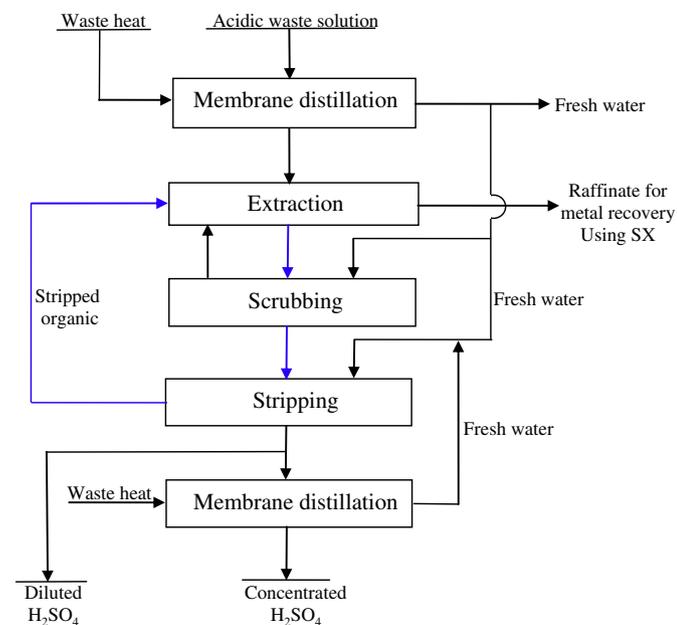


Fig. 8. A conceptual flowsheet to recover water, sulphuric acid and metal values from mining waste solutions.

A number of diluents and modifiers were tested with various TEHA concentrations. An optimum organic composition consisting of 50% TEHA, 40% octanol and 10% Shellsol A150 was determined. The acid extraction increased with the increasing extractant concentration and decreased from 82% to 72% when the temperature increased from 22 to 60 °C at an O/A ratio of 2. The change in enthalpy ( $\Delta H$ ) was found to be  $-13.2 \text{ kJ mol}^{-1}$ , indicating that the extraction reaction is exothermic in nature. As a result, the increase in temperature results in decrease in acid extraction and increase in acid stripping.

The optimised TEHA organic system was further characterised. The acid extraction reached 99% after three successive extractions with fresh organic solution. Only 2 g/l acid was left in the raffinate, indicating almost all acid can be recovered in a counter current operation. The extraction and stripping kinetics of the optimised TEHA system was fast. Within 0.5 min, 81.8% acid was extracted and the extraction reached equilibrium. Within 2 min, 75% acid was stripped and the stripping reached equilibrium. Extraction distribution isotherm and McCabe–Thiele diagram showed that three stages are required at an operating O/A ratio of 2 and 22 °C to extract 98% acid and leave ~5 g/l acid in the raffinate. Stripping distribution isotherm and McCabe–Thiele diagram showed that three stages are required at an operating A/O ratio of 2 and 60 °C to strip nearly 98% acid and leave ~2 g/l acid in the stripped organic solution. Slope analysis showed that the extracted species consists of one acid molecule, one TEHA (A) molecule and two octanol (O) molecules and can be expressed as  $(\text{H}_2\text{SO}_4)_2\text{AO}_2$ .

The optimised TEHA system was used to extract acid from a synthetic process solution containing a number of metals. It was found that a small amount of metals were entrained. After scrubbing the loaded organic solution in a single stage at an O/A ratio of 10 and 22 °C, 97–100% of entrained metals were removed with 4% acid lost in the loaded scrub liquor. A conceptual process flowsheet has been developed to recover fresh water, acid and metals from acidic waste solutions using a combination of MD and SX.

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## **7. Application of membrane distillation and solvent extraction for water and acid recovery from waste solution (Chapter 7)**

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The aim is to study the viability of SX to selectively recover acids ( $\text{H}_2\text{SO}_4$ ) that would be pre concentrated by MD to assess the viability of the combined processes.

The paper was published in the proceeding; Mine Water Solutions in Extreme Environment Annual Conference as follows:

U.K. Kesieme, H. Aral, N. Milne, M. Duke, and C. Y. Cheng. Application of membrane distillation and solvent extraction for water and acid recovery from waste solution. Mine Water Solutions in Extreme Environment Annual Conference, Lima, Peru, Chapter 4, 424 – 433

**Declaration of co-authors enclosed**

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## 8. Conclusions and Recommendations (Chapter 8)

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This investigation demonstrates MD and SX application for acid and water recovery from mining and metallurgical operations. Spent acids are usually neutralised with lime and disposed of. Furthermore, lime neutralisation of waste acid generates solid waste which causes environmental degradation. Recycling acid from waste streams of industry is an environmentally friendly method as it generates less waste and produces more fresh water. However viable acid recovery on current technologies has not proven to be viable. The novel concept of MD and SX for water and acid recovery in mining were found to be viable technologies to achieve acid recovery from mining waste water.

MD has the capacity to desalinate RO saline concentrates to hypersaline concentrations, demonstrating its viability as a high recovery desalination technology. Importantly, these data shows that the flux is not significantly dependent on the feed water salinity. Therefore, MD can exceed the limitation of RO due to its non-reliance on overcoming osmotic pressure. An interesting feature of MD as a thermal process is the separation of the saline water heating zone (heat exchanger) from the evaporating zone (membrane). The separation has allowed the convenient placement of the filter between the zones to capture precipitating salts immediately after heating, but prior to evaporation to enhance water recovery. The key finding for this research was the MD setup including a solids filter will be useful for concentrating mine waste waters prior to SX.

Using seawater desalination as an application, the cost model for MD showed its cost sensitivities, in particular with regards to carbon pricing and economic opportunity for using MD with waste heat. The results show that cost of desalination schemes will increase by introduction of a price for carbon, but RO still remains lowest cost. However, under carbon tax, MD has the best economics when the heat source has a low cost (e.g. waste heat). Specifically compared with MED, MD has lower cost materials. Compared with RO, MD has lower reliance on electricity. This assessment has therefore guided the economically viable means of operating MD for mining wastewater treatment. The potential commercial opportunities for MD stem from its lower plant footprint and capital cost, so MD becomes economic when driven by low cost solar thermal energy or waste heat.

The viability of MD to concentrate spent acid ( $\text{H}_2\text{SO}_4$ ) showed essentially no transfer of the acid to the permeate. The concentrated  $\text{H}_2\text{SO}_4$  remaining on the feed may be selectively recovered using SX. The outcome of this testing showed that for a process is viable for concentrating waste leach solutions containing sulphuric acid, iron, aluminium, magnesium, scandium, nickel, cobalt, manganese and sulphates. For the HCl loaded leach solution, HCl was depleted in the feed and successfully captured in the permeate tank (as free acid). Therefore, MD without SX can be applied for the treatment of industrial effluents containing HCl and salts. The salts were completely retained in the feed. Therefore depending on the presence of  $\text{H}_2\text{SO}_4$  and HCl, which are acids commonly used in mineral processing and hydrometallurgical extractions, either MD or MD/SX stages can be used to recovery the acid and clean water.

During the SX investigation, the optimized organic system consisting TEHA and ShellsolA150 in octanol performed well for the recovery of acid from acidic waste solutions. The result shows

that the system effectively extracted acid and only a small amount of metals were entrained. After 3 stages of successive extraction, nearly 99% of acid was extracted. After scrubbing the loaded organic solution in a single contact, almost all entrained metals were removed. Therefore, the TEHA organic system has the potential and can be used for recovery of  $H_2SO_4$  in mining acidic waste and process solutions after first concentrating using MD. In the case that the mining waste solution contains low concentration of acid, MD can be used to recover the water and concentrate the acid and metals. SX can be then used to selectively recover the acid and metals.

Overall, MD and SX work well together and this work has shown the viability of the two technologies for removal of clean acid and water from mining waste waters for potential reuse and environmental benefits. The work presented a useful outcome particularly for the mining and metallurgical industries that uses large amount of water to meets it operational requirement particularly for extraction of low grade ores. Water used in the extraction and operational activities can be recycled and reused. The concentrated  $H_2SO_4$  can be selectively recovered using SX, or in the case of HCl recovered by MD alone. Based on this research, the viability of MD combined with SX appears overall highly viable. Therefore future work is recommended to realise the environmental and cost benefits of implementing the technologies at a real mining site.

## 9. Future research directions (Chapter 9)

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This research has focused on an experimental study of acid and water recovery from industry spent acid streams and acidic mine wastes solutions using MD and SX and also modelling of the economic opportunities of MD and process optimization of solvents for acid recovery.

Possible implementation of MD technology in the near term would first require the resolution of a few issues. The permeate flux is relatively low compared with the recirculation rate, which has a negative impact on the electricity consumption. To be able to overcome this problem, appropriate redesign of the module that takes in account enhancing the mass transfer and increasing the membrane area per module volume (compactness) is needed. The magnitude of the permeate flux obtained in the MD process is affected significantly by the module design, the MD configuration its operating conditions, or the membrane material. Some of the important criteria are high membrane module performance (i.e. high water permeability and high salt/acid rejection), high membrane surface area to module volume ratio (i.e. high membrane packing density), low temperature and pressure drop along the membrane module, high heat transfer coefficients in both feed and permeate, high membrane liquid entry pressure (LEP) of water, good sealing and housing with good thermal and chemical resistances, and low heat transfer by conduction through the membrane material. Overall, well-designed membrane modules should provide high mass and heat transfer rates with low temperature and concentration polarization effects as well as less fouling in order to maintain high membrane permeability

With current performance, MD utilization would only be feasible in small scale application, where it could be thermally integrated with other process, or in application for treatment of special feed stock (mining waste solutions) and where other treatment process has a limited capacity in terms of treated water quality. Progress in improving MD efficiency is being made via the commercially available units, thus this issue is likely to progress positively as these more common issues with MD are resolved.

MD is an energy intensive process, so improvements in the energy efficiency of recovery are important. MD desalination of waste water relying on high thermal energy could instead be powered by an industry's own waste heat. This is a convenient position because mining industries use large amounts of water and have a lot of waste heat. However working cases of this opportunity will be strongly dependant on the specific details of each site.

In the future work, the application of MD will be addressed based on its distinctive features. For example, it may be coupled with the waste slag from mining operations as a source of thermal energy to produce freshwater from mining waste solutions and concentrate non-volatiles, such as H<sub>2</sub>SO<sub>4</sub>, heavy metal, metalloids etc., All these possibilities need further research to prove the feasibility of MD for these applications.

Membrane fouling and salt precipitation was taken in account in this current study by incorporating a filter at the highest temperature point in the cycle. The outcome presented in the current work should be supported with a theoretical model showing changes in pH and concentration as the recovery increases. Therefore a thermodynamics model developed to identify what species were likely to precipitate at different recoveries should be considered in the future work. Furthermore other methods of controlling membrane fouling need to be explored such as membrane surface modification, exploring membrane cleaning strategies and

the role of biological and chemical pre-treatments or side streams. These would advance the application of the use of the cartridge filter used in this work to control scaling and other long term fouling issues. Scaling was visually observed through the module in the current work, SEM or other evidence to support the statements of observed fouling would be useful in the future work. All the above approaches for future work would be required before implementation of a site trial.

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