

Novel application of membrane distillation for acid and water recovery from mining waste waters

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Abstract

Spent acid solutions from mining operations are costly to neutralise and present environmental issues when disposing. Therefore innovative low cost solutions are needed to overcome the high cost of neutralization and recover sulphuric acid otherwise lost. This paper describes initial laboratory results from the novel application of the low-energy direct contact membrane distillation (DCMD) process for the recovery of water and acid from acidic waste solutions generated in the mining industry. 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 H₂SO₄ (B) 0.5 M H₂SO₄ + 0.2 M NaCl (C) 0.5 M H₂SO₄ + 0.2 M Na₂SO₄ + 0.2 M NaCl. In all tests the temperature of the feed solution was kept at 60 °C. The test work showed that fluxes remained reasonably stable, within the range of 20 and 31kg/m²/h for all experiments. The final concentration of H₂SO₄ in sample solution A increased on the concentrate side of the DCMD system from 40 g/L (0.4M) to 245 g/L (2.45M) while sample solutions B and C increased from 45g/L to 240 g/L (2.4M) and from 55g/L to 295 g/L (2.95M), respectively. In all the experiments, the sulphate separation efficiency was over 99.9% and overall water recovery exceeded 80%. DCMD is clearly viable for high recovery of high quality water from spent acid solutions, but the effect of chloride passing into the permeate as HCl needs to be considered.

Keywords: direct contact membrane distillation, sulphuric acid recovery and mining acidic waste solutions

Introduction

Mining is a large industrial water use that is growing fast, and uses water in remote areas where it is often 'self supplied' and more scarce. Water is needed at the mine site to meet operational requirements such as dust suppression, mineral processing, coal washing and hydrometallurgical extraction. For these applications, water is generally extracted from surface water bodies and ground water aquifers or is a by-product of mine dewatering processes. At some stage of the mining operation, water is unwanted and has no value to the operation. At modern mine sites, these waste streams are collected and discharged to settling ponds and tailings dams. Many ores contain sulphide minerals such as pyrite (FeS₂) [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. The acid generation process is accelerated when bacteria are present. The production of waste acidic solutions is a universal problem, and the most testing environmental issue facing the industry today. Until recently, however, the acidic waste solutions have been mostly subjected to neutralization without any proper treatment. The conventional neutralization treatment has issues associated with it such as formation of large quantities of precipitate, unacceptable cost of alkali used, and sludge disposal, which consequently increases the whole cost of the applied process. The best method to treat these kinds of acidic waste solutions is to reuse it, however, the concentration of the acid and metals are often too low to recover economically. Furthermore, concentrating dilute acidic solutions through evaporation is energy intensive and coupled with a high cost for the anticorrosive materials required for heating dilute acidic solution. 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]. After concentration of the solution, solvent extraction can be applied to selectively recover the sulphuric acid and valuable metals. The focus of this work is on the MD component of this process.

MD is an emerging thermally driven membrane process which may overcome some limitations of other membrane technologies. In MD processes, a microporous hydrophobic membrane is used to separate two aqueous solutions at different temperatures, and selective mass transfer occurs. This process takes place at atmospheric pressure and a temperature which may be much lower than the boiling point. The hydrophobicity of the membrane prevents the transport of liquid across the pores of the partition while water vapour can be transported from the warm side, condensing at the cold surface. It has been demonstrated that salt concentration in the feed has relatively little effect on mass flux of MD processes with comparison to RO processes [6], indicating that MD can effectively deal with high concentration of brine. It has 100% theoretical rejection of non volatile components and can utilize low grade heat sources [3-5]. MD processes have several configurations which are as follows: (1) direct contact membrane distillation (DCMD), (2) air gap membrane distillation (AGMD), (3) sweeping gas membrane distillation (SGMD), and (4) vacuum membrane distillation (VMD). Among these configurations, DCMD, is the most widely used because it is convenient to set up, consumes relatively low energy, and gives high water flux [2-4]. MD has potential applications in many areas of scientific and industrial interest, yielding highly purified permeate and separating contaminants from liquid solutions. MD has been applied in the laboratory scale and found applicable in a large number of areas including sulphuric acid concentration, separation of non-volatile components and treatment of waste water for removal of heavy metals [2-4]. The aim of this study is to assess opportunity for MD to recover acids and fresh water from acidic mining waste solutions using synthetically prepared acidic solutions.

Methods

The flow diagram of the experimental rig is shown in Figure 1. In this test, the membranes used were flat sheet PTFE supported on polypropylene scrim backing.

The membranes had an active area of 0.0169 m², pore size of 0.45 μm and were supplied by Ningbo Chanqi, China. The flow rate into the module hot and cold sides were 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. Conductivity was measured using a conductivity meter in the permeate tank. A cartridge filter was used to capture scaling and salt precipitations at the highest temperature point in the hot cycle before entering the MD module. The water flux (F_w) was estimated based on Equation 1. The chloride content in the feed and permeate was determined by titration using silver nitrate (standardized with sodium chloride) and potassium chromate as an indicator. Inductively coupled plasma (ICP) was used to measure the concentration of sodium present in the feed and permeate. The sulphate concentration in the feed and permeate were measured spectrophotometrically using Hach Method 8051 (based upon USEPA Method 375.4 for wastewater. This effectively uses a barium reagent to precipitate barium sulphate and measure the resultant turbidity of the sample. The concentration of the cation and anion (SO₄²⁻, Na⁺ and Cl⁻) presented in the feed and permeate were recorded and discussed in section 3.

$$F_w = \frac{\text{Mass of permeate}}{\text{Effective membrane area} \times \text{operating time}} \quad (\text{kg/m}^2/\text{hr}) \quad [1]$$

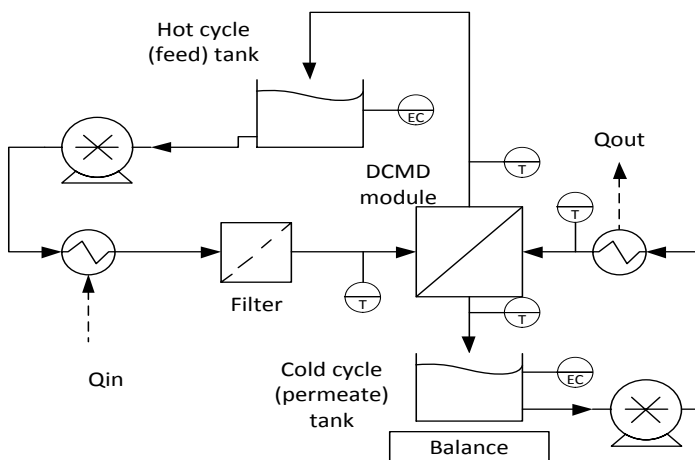


Figure 1 DCMD Experimental flow diagram

Results and discussion

Figure 2 shows the effect of flux over time. The variation of flux due to acid concentration and the presence of inorganic salts in the feed are also shown in the Figures 2 and are summarized in Tables 1 and 2 for three different synthetic solutions (A) 0.5 M H₂SO₄ (B) 0.5 M H₂SO₄ + 0.2 M NaCl (C) 0.5 M H₂SO₄ + 0.2 M

$\text{Na}_2\text{SO}_4 + 0.2 \text{ M NaCl}$. Membranes exhibited high salt rejections (>99.9%) demonstrated by low crossover of sodium as shown in Table 2. Fluxes remained reasonably stable, within the range of 20 and 31 kg/m²/h for all experiments. This is expected since the vapour pressure is not dependent on the salinity and eliminates the salinity effect seen in other desalination methods such as reverse osmosis [6]. The sulphuric acid concentration was found to be increasing over time in the feed tank for test solutions A, B and C. The final concentration of H_2SO_4 in sample solution A, increased on the concentrate side of the DCMD system from 40 g/L (0.4M) to 245 g/L (2.45M) while sample solutions B and C increased from 45g/L to 240 g/L (2.4M) and from 55g/L to 295 g/L (2.95M), respectively. Tomaszewska and Mientka [3] reported similar experimental results when concentrating a sulphuric acid solution from initial concentration of 50g/m³ to 150g/m³. Also, Tomaszewska (2000) [2] reported concentrating sulphuric acid solution obtained after apatite phosphogypsum extraction from an initial concentration of 16% H_2SO_4 to 40%.

In our previous work [5], we demonstrated experimentally on groundwater concentrated by reverse osmosis that water flux in the MD process is not significantly dependent on the feed water salinity up to 361,000 mg/L total dissolved solids (TDS), which is almost ten times the salinity of typical seawater [8]. Cath et al., [6], reported similar results where the feed water salinity of 76,000 mg/L were treated using MD. Importantly, unlike reverse osmosis, MD offers complete rejection of non-volatile constituents in the feed solution while maintaining this flux. In reverse osmosis, higher recovery and concentration of species can lead to greater transport of ions through the membrane at the same time as osmotic pressure increases from the salt concentration increase due to the pressure requirements to recover water. Almost almost 100% rejection of ions and dissolved non-volatile compounds during MD can lead to easier and more simplified treatment. In the case of mining wastewater that can be high in colloidal compounds, and particularly in ferrous compounds our previous work [5] has shown that MD is particularly well suited to simply modifications to improve performance that are not possible in RO applications. This work included the addition of a simple cartridge filter in the MD setup at the point when the temperature of the stream was at its greatest. This means that materials with the potential to precipitate at high temperature from the groundwater brine studied were easily separated before entering the main unit. This in turn led to a significant reduction in fouling/scaling of the MD membrane and significantly enhanced the performance of the system. Replacement of the cartridge filter was far less labour intensive than any cleaning requirements for the membrane. While this is similar to providing microfiltration or ultrafiltration pre-treatment to RO in order to remove colloidal matter, it is more effective in collecting potential scale compounds as they will often form or start to form outside the MD unit due to the temperature increase where in RO they form near to membrane due to significant concentration polarisation.

It is important to note, that while non-volatile compounds are virtually completely retained by the MD technique, volatile compounds such as HCl can pass through the membrane to the permeate. Tomaszewska et al., [7], reported HCl recovery from a pickling solution containing salts of Cu, Fe, Zn and Mg. It was reported that

the amount of salt in the feed solution increased more than two folds from 160,000 mg/L to 360,000 mg/L, while the HCl flux increases as the concentration of salts and acid increases from 200 mol/m²/day up to 870 mol/m²/day. The author also presented another pickling solution taken from an electroplating plant containing mainly ferrous chloride (23,000 mg/L) and hydrochloric acid (127,000 mg/L), salt rejection of above 99% was achieved using MD, and salt concentration increased from about 3.5 times from 23,000 mg/L to 78,000 Fe mg/L. Similarly in this MD experiment, it was found that water and HCl vapour were transported across the membrane in solution B and C, whereas H₂SO₄ was retained for the all experiments. The pH of the permeate in solution A was found to be ~ 7, and no acid was detected in the permeate tank, whereas 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⁻ 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. In all the experiments, the sulphate separation efficiency was over 99.9% [Table 3]. These results imply that sulphuric acid can be easily recovered or concentrated by the MD process; however some transfer of HCl must be accepted where chlorides are also present. This is not necessarily a problem for the technique as recovery of sulphuric acid is probably the greatest concern. There is also the potential benefit of capturing a relatively pure but dilute HCl stream for use in some processing applications.

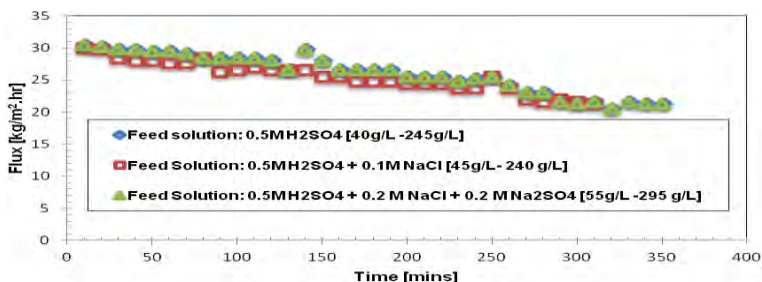


Figure 2 Flux over time during DCMD experiment and sulphate concentrations of the feed

Figure 3 shows overall volumes in the feed, permeate and the total volume (determined by the addition of feed and permeate volume) during the experiments. The initial feed solution was 5000 ml.

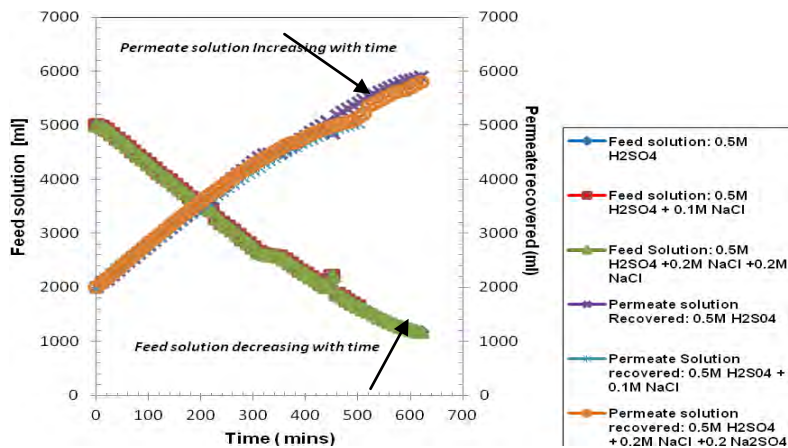


Figure 3 change in volume of the feed and permeate solution over time during DCMD experiment

In this work it was found that the permeate volume increased from the initial volume of 2000 ml to about 6000 ml in the permeate tank, and ~1000 ml was lost to dead volume (i.e. within the tubes and the MD module). The overall water recovered exceeded 80% from the initial feed solution.

Table 1 Chloride analysis

Feed composition	Initial feed Concentration [mg/L]	Initial Permeate Concentration [mg/L]	Final feed concentration [mg/L]	Final permeate concentration [mg/L]
Feed A: 0.5M H ₂ SO ₄	120	21	300	45
Feed B: 0.5M H ₂ SO ₄ + 0.1M NaCl	40000	28	19000	270
Feed C: 0.5M H ₂ SO ₄ + 0.2 NaCl + 0.2 Na ₂ SO ₄	7300	30	39000	500

This investigation demonstrates MD application for acid and fresh water recovery from mining and metallurgical operations. Mining and metallurgical processes generate effluents such as tailings water, acid mine drainage (AMD) and seepage and process acid streams, which is characterised as low pH, high acidity effluents containing sulphate, heavy metals and metalloids. MD is considered one of the possible methods to recover acid, metals and water, which is lost to neutralization. However, in comparison to conventional evaporators, MD requires more thermal energy per m³ of water processed. 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 available in various industries. In our previous work [5], we demonstrated the potential opportunity for MD especially when a low grade heat is available.

Table 2 Sodium analysis using ICP

Feed Composition	Initial feed concentration [mg/L]	Initial permeate concentration [mg/L]	Final feed concentration [mg/L]	Final Permeate concentration [mg/L]
Feed A: 0.5M H ₂ SO ₄	112	11	780	7
Feed B: 0.5M H ₂ SO ₄ + 0.1M NaCl	24100	12	92000	7
Feed C: 0.5M H ₂ SO ₄ + 0.2 NaCl + 0.2 Na ₂ SO ₄	9720	11	50000	7

Table 3 Sulphate analysis using Hach method

Feed Composition	Initial feed concentration [mg/L]	Initial permeate concentration [mg/L]	Final feed concentration [mg/L]	Final Permeate concentration [mg/L]
Feed A: 0.5M H ₂ SO ₄	40000	8	245000	2
Feed B: 0.5M H ₂ SO ₄ + 0.1M NaCl	45000	8	240000	1
Feed C: 0.5M H ₂ SO ₄ + 0.2 NaCl + 0.2 Na ₂ SO ₄	55000	7	3000000	3

Using a thermal requirement of 100 kWh/m³ and electrical requirement of 2 kWh/m³, MD became economically competitive for seawater desalination as compared to multi effect desalination (MED) and reverse osmosis (RO). The overall cost reported using MD with a low grade heat to desalinate waste water was \$0.49/m³. In our work, we used 60°C as the feed temperature, so to repeat our work on site this temperature must be freely available. However MD can operate as low as 40°C with sufficient fluxes as long as ambient temperatures are around 20°C or less (Dow et al., 2012) [9]. Low ambient temperatures in colder climates can help to drive the process as the greater temperature difference will improve efficiency in the process. Regardless, unless there are drivers from MD's unique differences (e.g. small footprint, membrane barrier benefits, corrosion resistance), MD will only be viable against competing technologies when sufficient thermal energy is available.

Conclusions

MD was shown to have the capacity to concentrate dilute sulphuric acidic solutions to a high concentration demonstrating its viability as a high recovery desalination technology;

MD can utilize a low grade heat source of 40 – 80 °C, thus a potential commercial technique to recover sulphuric acids and precious metals from mining waste water;

The removal of HCl and water vapour leaves behind a highly concentrated sulphuric acid and salts which can be recovered selectively using solvent extraction with little effort.

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References

- Lottermoser B. G., 2010. Mine waste, characterization, treatment and environmental impact. E-ISBN 978-3-642-12419-8, Third Edition, Elsevier
- Tomaszewskwa M., Mientka A., (2009). Separation of HCl from HCl – H₂SO₄ solution by membrane distillation, *Desalination* **240**: 244- 250
- Zhang J., D-Li J., Duke M., Xie Z., Gray S., (2010). Performance of asymmetric hollow fibre membrane in membrane distillation under various configurations and vacuum enhancement, *Journal of Membrane Science* **362**: 517 -528
- Tomaszewska M., (2000). Membrane distillation – Examples of applications in technology and environmental protection, *Polish Journal of Environmental Studies* **9**: 27 - 36
- Kesime U.K., Milne, N., Aral, H., Cheng, C.Y., Duke, M., 2012. Techno-economic analysis of membrane distillation technologies in the contest of carbon pricing, and opportunity for membrane distillation, Special issue of membrane distillation (Submitted), *Desalination*
- Cath, T.Y., Adam, V.D., Childress, A.E., 2004. Experimental study of desalination using direct contact membrane distillation: a new approach to flux enhancement, *Journal of Membrane Science* **228**: 5-16
- Tamaszewska, T., Gryta, M., Worawski, A.W., (2001). Recovery of hydrochloric acid from metal pickling solutions by membrane distillation, *Separation and Purification Technology* **23**: 591 -600
- Kesime U.K., Milne, N., Aral, H., Cheng, C.Y., Duke, M., 2011. Economic assessment of membrane distillation and other desalination methods in context to carbon tax. In the Preceeding of the Second Student and Early Career Researchers Symposium of Membrane society of Australia, 23rd to 25th November, 2011. Glenelg, Australia
- Dow, N., Gray, S., Li, J.D., Zhang, J., Ostarcevic, E., Liubinas, A., Atherton, P., Halliwell, D., Duke, M., (2012). Power station water recycling using membrane distillation- A Plant trial, *OzWater 12*, Sydney, Australia: Australian Water Association