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Application of membrane distillation and solvent extraction for water and acid recovery from acidic mining waste and process solutions

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ABSTRACT

Direct contact membrane distillation (DCMD) and solvent extraction (SX) were tested in series to recover water and acid from acidic mining waste solutions. In the DCMD step with the synthetic acidic waste solution, the concentration of H_2SO_4 increased from 0.85 M in the feed solution to 4.44 M in the concentrate. Sulphate and metal separation efficiency was >99.99% and the overall water recovery exceeded 80%. After recovery of water with DCMD, the concentrated solution was then subjected to recovery of sulphuric acid using SX with an organic system consisting of 50% TEHA and 10% ShellSol A150 in octanol. Over 80% H_2SO_4 was extracted in a single contact from the waste solution containing 245 g/L H_2SO_4 and metals with various concentrations. After three stages of successive extraction, nearly 99% of acid was extracted, leaving only 2.4 g/L H_2SO_4 in the raffinate. The extracted acid was stripped readily from the loaded organic solution using water at 60 °C. After scrubbing the loaded organic solution at an O/A ratio of 10 and 22 °C, 98–100% of entrained metals were removed in a single contact with only 4.5% acid lost in the loaded scrub liquor. It was found that the phase disengagement time was in the range of 2–4 min for both extraction and stripping, indicating reasonable fast phase separation.

Introduction

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. Minerals industry is increasingly being forced both by regulatory and cost pressures to reduce the amount of liquid waste they produce. This requires a strong focus on waste reduction by recycling, regeneration and reuse. 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 neutralisation 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 neutralisation processes which could instead be recovered and reused. 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 [1]. Furthermore, recycling of acid would mean elimination of the safety problems associated with its transport to the site. H_2SO_4 is of interest because it is 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. Several other treatment methods include both active and passive treatment technologies to mitigate the problems of acid and salt accumulation in acidic process effluents. Many of these treatment techniques are commercialised while others are not standard industry practice

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and still at the exploratory stage. These includes 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) [3], bioreactor tanks (i.e. vessels that contain colonies of metal immobilising bacteria or contain sulphate reducing bacteria (SRB) causing the metal to precipitate as sulphides) [4], 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 [1,5–8]). However viable acid and water recovery on 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 best approach to deal with acidic effluents is to recover the water, the acid and the valuable metals. A combination of treatment methods such as MD and SX 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 Q4 acid, as well as valuable metals.

SX is a well-established treatment method to purify and recover metals from waste solutions [9]. It is not a method for water recycling; however, it is used in hydrometallurgical processes such as recovering of acids (H_2SO_4, HCl), precious heavy metals and treatment of metalloids present in a wastewater [9]. 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 increasingly 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 [1,7,9–11]. SX is economically viable method when both the solute concentration and waste water flowrates are high [12]. To achieve a high concentrated solute, MD maybe applied [5,8].

MD is an emerging thermally driven membrane process and can be applied to concentrate acid and recover fresh water from acidic Q5 waste solutions [13,14]. 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, consumes relatively low energy, and gives high water flux [5,15]. Thus, DCMD is commonly applied for investigations in which water is the major fluxing component such as desalination [5]. In DCMD 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 takes 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 (40–80 °C) compared to conventional distillation [5,15,16]. The MD process is capable of treating highly concentrated solutions utilising low-grade heat for water distillation. It is promising technique for minimising RO concentrate discharge [5,17]. A study of MD on RO brine by the authors [5], demonstrated that salt concentration in the feed up to 361 g/L has little effect on mass flux of MD processes with comparison to RO processes, indicating that MD can effectively deal with highly concentrated brines, and can be applied for desalination and wastewater recycling in places where waste heat, solar or geothermal sources are available [5,15]. MD has potential applications in many areas of scientific and industrial interest to obtain highly purified permeate from solutions containing contaminants. It 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 [8,18]. The combination of MD with SX however is a novel concept of value in recovering acid from metals in the brine.

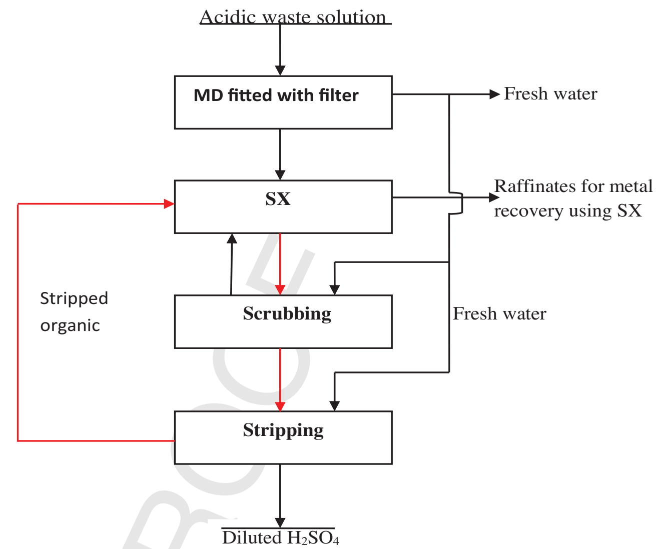

Fig. 1. A conceptual flow-sheet to recover water, sulphuric acid and metals (inorganic salts).

In this study, acid and by-product recovery from acidic mining waste solution is achieved by combining DCMD and SX. To achieve high water recovery and concentrate the acid for reuse, DCMD is applied to concentrate the waste solution for efficient acid and metal recovery using SX. A conceptual flow-sheet to recover water, sulphuric acid and metal values is shown in Fig. 1.

In Fig. 1, MD is applied to recover fresh water and concentrate sulphuric acid solution and metals from acidic mining waste solution. The concentrated acidic solution is then treated using SX to extract the acid. The fresh water recovered by MD can be also used for scrubbing the entrained metals and stripping the extracted acid. This integrated approach of acid recovering using MD and SX may be applied in industries such as mining to effectively recover of acid, valuable metals and fresh water for reuse.

The aim of this study is to assess the potential and opportunities for DCMD to concentrate H_2SO_4 and recover fresh water from process acidic solutions and also to identify how MD can work in combination with SX in the mineral processing industry for acid recovery.

Materials and methods

DCMD experiment

Experiments were conducted in DCMD mode to confirm the viability of MD to concentrate a 4 L synthetic acidic waste solution

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