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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 (ΔH) was −13.2 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 H_2SO_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 $\overline{(H_2SO_4)AO_2}$.

The optimised TEHA system was used to extracted 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.

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; Gottliebsen 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; Gottliebsen 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 H_2SO_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 Cyanex923, 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 (Titrando 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_2SO_4 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 Gottliebsen 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 striping

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_2SO_4

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