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Removal/recovery of hydrochloric acid using Alamine 336, Aliquat 336, TBP and Cyanex 923

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Abstract

Solvent extraction of hydrochloric acid has been studied from solutions containing 185.42 g/L acid using Alamine 336, Aliquat 336, TBP and Cyanex 923 as extractants. Kerosene was used as the diluent. Extraction of hydrochloric acid increased with the increasing concentration of the extractants. For all the extractants studied, the species extracted into the organic phase appears to be associated with one mole of extractant. For Alamine 336, the McCabe–Thiele construction indicated the possibility of > 99.5% HCl extraction in two counter-current stages at A:O = 1:4. For Cyanex 923, the McCabe–Thiele construction indicated the quantitative extraction of HCl in four counter-current stages at the A:O = 1:5 phase ratio. The acid loaded onto Aliquat 336, TBP and Cyanex 923 could be easily stripped with water. But acid loaded onto Alamine 336 could not be stripped with water. The stripping efficiency was ~12% with dilute acid and quantitative with 1 N NaOH for acid loaded onto Alamine 336.

Keywords: Alamine 336; Aliquat 336; TBP; Cyanex 923; Extractant; Loaded organic

1. Introduction

In hydrometallurgical processes, dissolution of metals by leaching with a suitable acid or acids is quite common. Often, the leach solution is quite acidic and requires neutralization before further treatment for metal extraction. This neutralization process, besides consuming alkali adds more cations/anions to the leach liquor. These cations/anions may play a significant role during metal separating using a solvent extraction technique. So to overcome these problems, attempts can be made to recover the free acids from the leach liquor thereby avoiding neutralization.

Studies have been reported on the use of Tri-butyl phosphate (TBP) for the extraction of acid (Ritcey and Ashbrook, 1984a,b; Cox, 1992; Eyal et al., 1993). The extraction of mineral acids by Cyanex 923 (Alguacil and Lopaz, 1996) and tri-*n*-octylphosphine oxide (Petkovic et al., 1992) was investigated and reported. Cyanex 923 (Rickelton, 1993) and tris 2-(ethyl hexyl) amine (Gottlibsen et al., 2000) were also used for recovering H_2SO_4.

Although a considerable amount of work has been reported for the extraction/recovery of different acids using extractants such as TBP, Cyanex 923, tri-*n*-octylphosphine oxide and tris 2-(ethyl hexyl) amine, etc., studies concerning the removal/recovery of hydrochloric acid using different extractants and their comparison are scanty.

After leaching of a typical secondary, the leach liquor contains 185.42 g/L HCl along with different metal ions

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such as 11.8 g/L Fe, 24.8 g/L Cu, 0.23 g/L Zn, 3.8 g/L Co, 35.2 g/L Ni and 48 g/L SO_4^{--}. From this leach liquor Fe was most effectively recovered using Tri-butyl phosphate. But due to the high acidity of the leach liquor, neutralization of the liquor was necessary before the extraction of other metal ions, which requires a lot of alkali. In order to avoid neutralization steps, experiments were carried out to remove/recover HCl (185.42 g/L) using different solvents and the results obtained are reported in this paper.

2. Experimental

2.1. Reagents

The commercial solvents Alamine 336 (tri-octyl/decyl amine), Aliquat 336 $[(R_3NCH_3)^+Cl^-$, R = octyl/decyl], TBP (Tri-*n*-butyl phosphate) and Cyanex 923 (mixture of tertiary octyl and hexyl phosphine oxides) were used for the extraction of acid. These solvents were used as such without any purification. Kerosene distilled in the range, 160–220 °C, was used as the diluent. Hydrochloric acid of 185.42 g/L concentration was used and its strength was determined volumetrically by acid–base titration.

2.2. General extraction procedure

Desired volumes of the aqueous solution containing acid and the extractants were equilibrated manually in a separating funnel for 5 min (initial experiments on the effect of contact time on acid extraction indicated that 5 min is sufficient to reach equilibrium). After the phase disengagement, the aqueous phase was separated and the acid concentration was estimated volumetrically. The concentration of acid in the organic phase was calculated from the difference between the concentration in the aqueous phase before and after extraction. Also the organic phase was filtered through IPS, stripped and analysed volumetrically. While calculating the organic phase concentration, minor volume change of the organic phase was also taken into consideration.

3. Extraction of HCl using different solvents

For the extraction of HCl, Alamine 336, Aliquat 336, TBP, and Cyanex 923 were used. The initial concentration of hydrochloric acid was 185.42 g/L.

3.1. Extraction of HCl with Alamine 336

The extraction of hydrochloric acid, studied in the Alamine 336 concentration range of 10 to 100 vol.%, can be expressed in a simplified form of the general formula

$$\mathrm{H^+C1^-_{aq} + L_{org} \Leftrightarrow HC1L_{org}}, \tag{1}$$

where L = Alamine 336

The equilibrium constant, K of the reaction can be written as:

$$K = [\mathrm{HC1L}]_{\mathrm{org}}/[\mathrm{H^+C1^-}]_{\mathrm{aq}}[\mathrm{L}]_{\mathrm{org}} \tag{2}$$

or,

$$K = D/[\mathrm{L}]_{\mathrm{org}} \tag{3}$$

where $D = [\mathrm{HClL_{org}}]/[\mathrm{H^+Cl^-}]_{\mathrm{aq}}$.

$$\text{or, } \log D = \log K + \log[\mathrm{L}]_{\mathrm{org}} \tag{4}$$

The extraction studies were carried out at a 1:1 phase ratio and the results obtained were plotted in Fig. 1. From Fig. 1 it was observed that the extraction of the acid increased from 5.1 to 31.5% with increasing Alamine 336 concentration from 10 to 100 vol.%. The time taken for phase separation increased from 0.75 to 30.00 min with the increase of Alamine 336 concentration. This indicates the difficulty in phase separation at higher concentration of Alamine 336. The log D vs. log [Alamine 336] plot is a straight line with a slope of 0.958, indicating the association of one Alamine 336 molecule with the extracted species. From this plot, log K_{ex} was calculated to be −2.289.

Having decided to use undiluted Alamine 336 for HCl extraction, the extraction isotherm was obtained to find out the number of stages required at a chosen A:O ratio. The

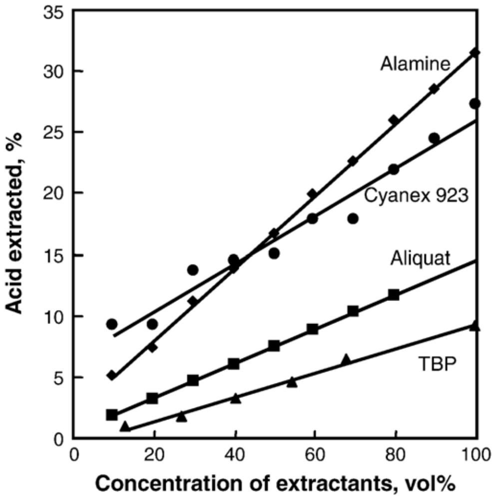

Fig. 1. Effect of extractant concentration on HCl extraction.