Regeneration of sulfuric acid from electrolyte waste of the copper - smelting plant using solvent extraction

P.B. Gromov, A.G. Kasikov, E.A. Shchelokova*, A.M. Petrova

I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Centre RAS, 26a Akademgorodok, 184209, Apatity, Murmansk region, Russia

ABSTRACT

Quantitative data have been obtained on the distribution of sulfuric acid in ROH - H_2SO_4 - H_2O systems in a broad acid concentration range for aliphatic alcohols of the ROH (R = C_8-C_{10}) homologous series. Alcohols had different structures. A correlation has been established between the extractive ability of the alcohols and the acid concentration, alcohol structure, temperature, time of phase contact, and phase volume ratios. The data obtained on the alcohol solubility in aqueous H_2SO_4 solutions allowed us to estimate the extragent loss in practical hydrometallurgical applications. Optimal conditions have been determined for the process of sulfuric acid recovery and purification from copper electrolyte waste. The conditions have been tested in continuous mode at a cascade of laboratory extractors.

1. Introduction

One of the kinds of sulfuric copper-nickel wastes is copper electrolyte waste. It requires regular regeneration to remove accumulating nickel and iron from solution. Normally the process involves de-coppering, electro-extraction or neutralization. However, the conventional industrial methods of the acid processing no longer meet the requirements for disposal of waste solutions and waste reduction. Returning of copper electrolytes or first-processed products to copper-nickel processes to replace sulfuric acid is the most effective recovery. A part of the sulfuric acid can be recovered via extraction, ion exchange, liquid membranes, sorption, electrocoagulation, emulsion liquid membranes, biological processes or electrodialysis [Agrawal and Sahu, 2009; Benvenuti et al., 2014; Kumar et al., 2012; Calero et al., 2014; Ivonin et al., 2000]. Taking into account the facts that sorption is effective in extraction of small substance quantities and takes longer time for phase contact whereas dialysis is used for processing of small volumes of solutions, it is the solvent extraction technique that is preferable for extracting the sulfuric acid from highly concentrated solutions. Extractants including tributyl phosphate (TBP), phosphine oxides, aliphatic alcohols, aliphatic amines and various mixtures of organic reagents have been tested and applied to recover sulfuric acid using solvent extraction [Kesieme et al., 2013; Qifeng et al., 2016; Fatmehsari et al., 2009; Agrawal et al., 2016; Kasikov et al., 2004; Viljoen et al., 2008; Prochazka et al., 2003; Gottliebsen et al., 2000a; Gottliebsen et al., 2000b; Sklokin et al., 2003; Kasikov, 2012; Voogt et al., 2009;

Agrawal et al., 2016; Cheng et al., 2016].

When the H_2SO_4 content is 300 g L^{-1} an effective extragent is TBP and its analogues. However, it is limited in application due to high solubility and proclivity to decompose in acid solutions. Compared to TBP, aliphatic alcohols are stable to decomposition. They also have a lower solubility. But the alcohols can extract the sulfuric acid at concentrations higher than 350–400 g L^{-1}. The high-molecular tertiary amines extract the sulfuric acid in a broad concentration range but they are highly viscous and cannot be used in pure form. Therefore they are usually applied as 20–40% solutions for extracting the acid from fairly diluted solutions. The resulting re-extracts contain rather diluted acid which limits their application. The depth of sulfuric acid extraction from solution increases and fairly concentrated stripped products are obtained in mixtures of tertiary amines and aliphatic alcohols/ketones. However, work [Kasikov and Bagrova, 2016] shows that substituting of the inert dilutant for aliphatic alcohols in mixtures with tertiary amine considerably increases the stripped products' viscosity in case of cobalt extraction.

Despite the fact that in some cases the extraction properties of aliphatic alcohols are inferior to traditional industrial extraction systems including N- and P-containing extractants, the alcohols have several advantages. According to their physical-chemical properties the high-molecular monohydric aliphatic alcohols, acting as organic solvents, refer to organic substances with a large molecular mass and a high boiling point. The alcohols poorly dissolve in water and even worse in water-salt solutions. The alcohols also have medium values of dielectric

permeability and viscosity [Ritcey and Ashbrook, 1984].

In this work, in addition to investigation of sulfuric acid extraction by aliphatic alcohols, were studied the density and viscosity of alcohols extracts of saturated sulfuric acid, solubility of alcohols in aqueous sulfuric acid solution and conditions of sulfuric acid separation from aqueous media by solvent extraction method. The aim of this study was to reveal the possibility of utilizing this extragent class during recovery of sulfuric acid from the mother liquor. The mother liquor forms in the copper-nickel vitriol process at the Norilsk Nickel MMC (Russia). The task was to obtain 80–85% sulfuric acid solutions containing not more than 10% co-extracted impurities from concentrated solutions (650–700 g L^{-1}) and to produce a regenerated acid containing less than $8 \cdot 10^{-2}$ wt% of organic impurities.

2. Starting materials and experimental methods

2.1. Reagent and solutions

The monoatomic aliphatic alcohols: 1-octanol (Merck), 2-ethylhexanol-1 (Russia), 1-nonanol (Merck), 1-decanol (Russia) and mixture alcohol C_8-C_{10} (1-octanol (vol. 45%)) - 1-decanol (vol. 55%) (China) used in this study. The sulfuric acid involved had less than 10^{-6} wt% impurities. The copper electrolyte waste of the copper-nickel process was provided by Norilsk Nickel MMC (Russia) and contained the following main components, g·L^{-1}: Ni 18.4, Cu 7.2, Fe 1.4 and H_2SO_4 650.0.

2.2. Apparatus and procedure

All the extraction and stripping tests were carried out in a 200 ml two-necked glass flask. A mechanical stirrer and a thermometer were fitted into its openings. The flask was heated using a water bath which controlled the temperature within ± 2°C. In each experiment a volume ratio of an organic phase and a sulfuric acid were added to the flask and preheated to required temperatures. The two phases were mechanically mixed at a set of stirring speeds for certain period of time. After the contact the mixture was transferred to a separating funnel and settled at the contact temperature for certain period of time before phase separation. The aqueous phase was additionally filtered through a dense paper filter (green band) to remove mechanically captured traces of the organic phase.

Acid content was determined volumetrically using 0.1 M NaOH solution in presence of phenolphthalein indicator with an error of ± 0.2 g L^{-1}. The concentration of sulfuric acid in the organic phase was calculated due to material balance by the Eq. (1):

$$C(H_2SO_4)_O = \frac{A_{init} \cdot C(H_2SO_4)_{init} - A_{raf} \cdot C(H_2SO_4)_{raf}}{O_{extr}} \quad (1)$$

where $C(H_2SO_4)_O$ is the concentration of the sulfuric acid in the organic phase (g·L^{-1}); $C(H_2SO_4)_{init}$ and $C(H_2SO_4)_{raf}$ are concentrations of the sulfuric acid in the aqueous phase before and after extraction step (g·L^{-1}); A_{init} and A_{raf} are volumes of the aqueous phase before and after extraction step (L).

The distribution ratio D was taken as the ratio between the concentration of sulfuric acid in the organic phase and concentration of sulfuric acid in the aqueous phase. The extraction percentage of sulfuric acid, E (%), was calculated according to the following formula:

$$E = \frac{O_{extr} \cdot C(H_2SO_4)_O}{O_{extr} \cdot C(H_2SO_4)_O + A_{raf} \cdot C(H_2SO_4)_{raf}} \cdot 100 \quad (2)$$

The amount of aliphatic alcohols in the equilibrium aqueous phase was determined by gas chromatography-mass spectrometry with a Shimadzu GSMS-QP 2010 device (measurement error ± 0.001 g L^{-1}).

The density ρ was measured with Ostwald-Sprenge type pycnometers having a bulb volume of 10 cm^3 and an internal capillary diameter of about 1 mm. The error in the density measurements was

estimated to be within ± 0.2 g cm^{-3}.

The viscosity η of aliphatic alcohols and extracts of saturated sulfuric acid was measured at atmospheric pressure at 20 °C using a calibrated Ubbelohde suspended level viscometer (type 1831-1, Shanghai Glass Instruments Factory, China). The kinematic viscosity ν of the extracts was calculated by the Eq. (1):

$$\nu = k_1 \cdot \tau - k_2 \cdot \tau \quad (3)$$

where τ is the low flow time; k_1 and k_2 are the viscometer constants determined by the calibration fluids and the Hagen-Bach correction factor respectively. The capillary was 0.56 mm in diameter and 40 mm in length, so the correction factor k_2 could be neglected. The viscosity η was then calculated from the density ρ by the Eq. (2):

$$\eta = \nu \, \rho \quad (4)$$

The values of the viscosity and density of pure water were obtained from the literature. The error of viscosity measurements was ± 0.05 mPa s.

3. Results and discussion

3.1. Effect of contact time

The effect of contact time on extraction of sulfuric acid is shown on Fig. 1. One can see that the extent of sulfuric acid extraction varied within 19.1–20.5%. The sulfuric acid attained equilibrium in 5 min with extraction of 20.4%. This may indicate a fairly rapid H_2SO_4 extraction kinetics with 1-octanol promoted by both the reaction of forming extracted complexes and by their diffusion to the organic phase. The contact time of 5 min was chosen as an optimal condition.

3.2. The effect of initial concentration of H_2SO_4 on extraction with aliphatic alcohols

Data on the equilibrium distribution of sulfuric acid in the H_2SO_4 – ROH – H_2O extraction system over a concentration range of 100 to 1650 g L^{-1} was compiled for the model solutions (Fig. 2). The ability of alcohols to extract sulfuric acid varied depending on the hydrocarbon radical length and accessibility of the functional group. It can be evaluated in the following sequence: 1-octanol > mixture C_8-C_{10} > 1-nonanol > 1-decanol > 2-ethylhexanol-1.

Fig. 2 shows that the extraction isotherms do not feature the plateaus normally characterizing the regions of extragent saturation. This is explained by the fact that at the extraction of sulfuric acid with the studied alcohols an equilibrium volume of the organic phase increased significantly with an increase in the H_2SO_4 concentration. This gives rise to the complete mixing of the phases at higher acid concentration. The changes of equilibrium volume of the organic phase (ΔO (%) = $\left(\frac{O_{extr} - O_{init}}{O_{init}} \right) \cdot 100$, where O_{init} and O_{extr} are volumes of the
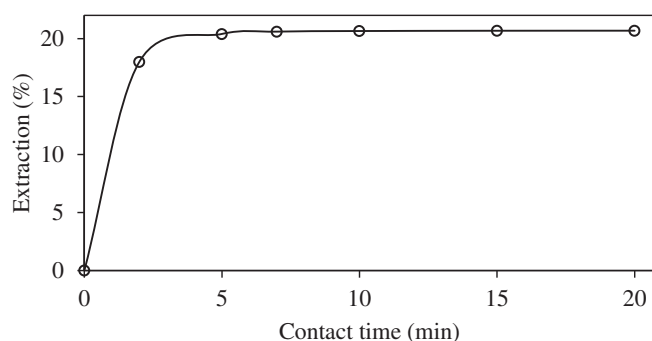

Fig. 1. Extraction percentages of sulfuric acid at different contact times. Aqueous phase: sulfuric acid solution with H_2SO_4 concentration of 600 g L^{-1}. Organic phase: 1-octanol. Conditions: O/A = 1, 20°C, separation contact time of 30 min.