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ORIGINAL ARTICLE

Recovery of alumina and some heavy metals from sulfate liquor

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Abstract The gibbsite bearing shale occurrence in the Paleozoic sedimentary sequence of SW Sinai, Egypt, was found to be associated with several metal values. From sulfate liquor prepared by proper leaching, the recovery of these metal values has been studied. Alumina was first separated in the form of potash alum followed by Cu-selective extraction by hydroxyoxime LIX-973N solvent. Then U recovery using an anionic exchange resin Amberlite IRA-400 was achieved. For the associated heavy metal Zn, it was subsequently extracted using di-2-ethylhexyl phosphoric acid. The relevant factors affecting the extraction process were adequately studied.

1. Introduction

After studying the proper leaching conditions of Abu Zeneima metalliferous gibbsite ore material in a previous work (El Hazek et al., 2008), a proper sulfate leach liquor of the contained metal values (Al, Cu, Zn, U, Co and Ni) has been prepared for studying their recovery in the present work. There are indeed several recovery procedures that can be applied, and the choice of the convenient procedure for each metal value would actually depend upon its concentration, the associated recoverable metal values, presence of other impurities such as iron besides the nature of the pregnant liquor. Taking these factors into consideration, it was found convenient to first recover Al from the acidic medium through potash alum crystallization. This has been performed by adding KOH which would be converted into K_2SO_4 by partial neutralization of the present acid. Starting by alum manufacture is greatly advantageous, as the density and acidity of the working leach liquor would be reduced. On the other hand, the concentration of the studied metal values will in turn be increased during alum preparation due to the required evaporation.

On the other hand, while the ion exchange procedure was found quite suitable for U due to its relatively low concentration, solvent extraction would be the preferable procedure for the studied heavy metals. Accordingly, the extractant LIX-973N would be used for Cu recovery whereas D_2EHPA would be used for Zn recovery. It is worth mentioning herein that either of these solvents can also be used for Co and Ni extraction at proper working conditions. The relevant studied extraction

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and stripping factors of both Cu and Zn such as pH, concentration of the extracting and the stripping reagents as well as the contact time and the O/A ratio have been properly studied.

Several works have indeed been performed upon Abu Zeneima mineralized ore material for the recovery of the different contained metal values. Ritcey Ritcey (1991) has studied Cu recovery using LIX-973N and U by a tertiary amine from their sulfate liquor. Amer (1993) has also applied the ion exchange technique for U using Amberlite IRA-400 anion exchange resin. Mahdy (1995) has presented a number of flowsheets for the recovery of U, Cu and Mn using different methods such as precipitation, crystallization besides using the organic solvents LIX-64N and TBP as well as the anion exchange resin. On the other hand, Amer (1997) and Amer et al. (2000) have also studied Cu and U recovery from sulfate liquor. In addition, Abdel Fattah (2003) has studied the leaching and recovery of Al, Cu, Zn and U from acidic sulfate liquor as well as from caustic soda liquor. In this work, Al, Cu and Zn were recovered by crystallization and solvent extraction techniques while for U the Amberlite IRA-400 anion exchange resin has been used.

2. Experimental

2.1. Material and reagents

To study the applicability of the above-mentioned procedures in the present work for Al, U, Cu and Zn recovery, a suitable leach liquor of the working metal values of Abu Zeneima gibbsite ore was first prepared using mostly the studied optimum leaching conditions (400 g/L acid, S/L ratio of 1/3 at 80 °C for 4 h). Analysis of the leach liquor obtained under these conditions indicated the following assay: Al 28.2 g/L, Zn 4.725 g/L, Cu 400 ppm and U 75 ppm while Co and Ni assay amounted to 150 and 165 ppm respectively.

The reagents used involve the specific Cu Chelating extractant LIX-973N belonging to the hydroxyoximes (product of M/S. Cognis) while the acidic extractant D_2EHPA belongs to the organophosphorus compounds and (product of Merric Co.) was used for Zn extraction. Both solvents were diluted in local kerosene produced by Misr Petroleum Co. For U recovery, Amberlite IRA-400 anion exchange resin (product of Rohm and Haas Co., USA) has been used.

2.2. Extraction and stripping procedures

Extraction and stripping tests were performed in separatory funnels where the prepared organic phase and the aqueous leach liquor on the loaded organic and the stripping solution were shaken for a proper time. The two phases after equilibration were then allowed to separate and an aliquot sample of the aqueous phase was analyzed for its metal content while that in the organic phase was obtained by a difference.

2.3. Analytical procedures

For the analysis of Al, Cu and Zn, the atomic absorption technique was adopted using a Unicam atomic absorption spectrophotometer model 969 flame type, auto gas box at wavelengths 309.30, 222.60 and 307.70 nm respectively (Weltz and Sperling, 1999). On the other hand, for U determination, an oxidimetric titration method against ammonium metavanadate was used in the presence of diphenylamine sulfonate indicator. Prior to titration, proper reduction of U was performed using ammonium ferrous sulfate (Mahmoud et al., 2003).

3. Results and discussion

3.1. Alum crystallization

Potash alum is preferred than sodium alum for Al recovery in the present work as alum. This is due to the fact that the latter is extremely difficult to purify and is much more soluble than the former (www.google.com). On the other hand, from the solubilities of K_2SO_4, $Al_2(SO_4)_3{\cdot}9H_2O$ and potash alum in water as a function of temperature, it is evident that the solubility of all the three compounds increases with an increase in temperature. At high temperatures (> 70 °C), potash alum is the most soluble among the three salts, while K_2SO_4 is the least soluble which will thus be the first to precipitate from solution. On the other hand, at low temperatures (< 46 °C), alum is the least soluble of the three salts and will be the first to precipitate.

For potash alum preparation in the present work, 2 L of the prepared leach liquor assaying 28.2 g/L Al was mixed with about 0.5 L containing 116 g of KOH. This solution was then slowly evaporated until 1 L at a temperature not exceeding 45 °C. To ensure separation of the least soluble alum, the evaporated solution was left overnight and the obtained alum was filtered and properly washed with methanol, dried and weighed. From the obtained weight of 660 g, a crystallization efficiency of about 70% has been obtained (calculated after taking in consideration that potash alum solubility at 4 °C is 39 g alum/L). Leaving the solution to further cooling after 24 h, further alum crystallization has been occurred.

3.2. Copper recovery

The volume of the 2 L working pregnant liquor after alum crystallization has been decreased to 1 L due to evaporation and therefore the concentration of all the dissolved metal values has been doubled. The Cu content of the latter has thus been increased to 800 ppm and its pH was found to attain 0.5.

3.2.1. Copper extraction

3.2.1.1. Effect of aqueous phase pH. The effect of pH on Cu extraction with LIX-973N was carried out in the range from 0.2 to 2.0 as indicated by Calligaro et al. (1983) using NaOH or H_2SO_4 solution. The working extraction conditions involved 1/1 as organic/aqueous ratio, 5% solvent concentration in kerosene as a diluent and a shaking time of 5 min. It was observed from the obtained results plotted in Fig. 1, that Cu extraction does not greatly depend on the pH of the aqueous phase in the tested range (0.2–2.0). At pH 1, the Cu extraction efficiency attained 98.2% ($D = 55$). The latter could be considered as an optimum value in a manner to avoid increasing the pH and in turn possible interference from iron and/or its precipitation. The remaining Cu at this pH can be recovered by variation of other conditions.

3.2.1.2. Effect of LIX-973N concentration. The effect of LIX-973N concentration on Cu extraction efficiency has been