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Recovery of molybdenum from copper leach solutions by solvent extraction

ABSTRACT

Solvent extraction (SX) of Mo from acidic solutions has been used in some limited applications. However there is little documentation on Mo recovery from copper SX aqueous streams. The low content of Mo in these streams, and also the relatively high concentration of other metals/anions (Fe, Al, Cu, SO_4, etc.), increases the difficulties of processing these solutions. This work describes a new process capable of purifying and concentrating Mo by solvent extraction from industrial copper leach solutions. The solvent extraction process uses a modified phosphinic acid reagent (Cyanex®600). The reagent is highly selective for molybdenum over common impurities found in copper SX aqueous streams such as Cu, Al and Fe, and exhibits fast extraction and stripping kinetics. Molybdenum stripping was achieved by using ammonia/ammonium carbonate mixtures and high stripping efficiency was obtained. Piloting results using real feed solutions confirm the ability to purify Mo from dilute acid solutions, concentrating the metal more than one thousand times. High quality of ammonium molybdate hydrates and molybdenum oxide hydrate crystals were obtained as final products.

INTRODUCTION

Molybdenum occurs in nature most commonly as molybdenite (MoS_2). It can be found in porphyry deposits) that contain primarily molybdenite (about 59% of the global reserves and copper porphyries (about 39% of the overall molybdenum reserves) **[1]**. Oxidic ores can also be found although they are not as common. With the growing demand for molybdenum applications and the limited resources, it has become paramount to increase supply by improving recovery efficiency in current mining operations and/or utilizing and processing recycled materials.

Traditionally, molybdenum is recovered from molybdenite using flotation and roasting which is a very costly and time intensive route. Also, recovery via flotation is relatively low yield and the extraction processes are sub-optimal. In addition, the environmental fingerprints of this technology are significantly high.

Solvent extraction (SX) is a well-established technology that can be extremely selective toward a specific target metal. The use of SX for molybdenum recovery has been limited for two reasons: the metal has to be present as an oxidised aqueous ionic species and conventional extractants have significant performance drawbacks. Pressure oxidation leaching of molybdenite can be used to oxidize and solubilise molybdenum in aqueous media and the process has some significant advantages over the traditional roasting method **[2]**. Examples of additional sources that are not currently utilised for molybdenum recovery are the aqueous streams from copper SX operations. Cruz and Regahezza reported that up to several hundred ppm of molybdenum is found in the different aqueous streams involved in the sulphuric acid extraction of copper **[3]**. Traditionally this molybdenum has not been recovered although it is already mined, solubilised, and exists as extractable oxidised species. Although present in significant lower concentrations than copper, the molybdenum value is high and could bring additional revenue to the copper producers **[4]**. Smelter dusts and slags from copper smelters are other untapped sources of molybdenum **[5]**. These materials require an oxidising leaching step to solubilise the value metals prior to solvent extraction. Other sources of molybdenum include, spent catalyst, recycled alloys, scrubbing solutions from the roasters, etc.

This article describes a process for molybdenum extraction and concentration from a copper plant SX raffinate solution using a modified phosphinic acid-based extractant, Cyanex 600.

Molybdenum aqueous chemistry

Molybdenum chemistry is complex and depends on a variety of factors such as pH, metal concentration, and oxidation state. In strongly basic conditions, molybdenum exists primarily as tetrahedral MoO_4^{2-} while at pH less than 6, isopolymolybdates such as $Mo_7O_{24}^{6-}$and $Mo_8O_{26}^{4-}$ are dominant. Under strongly acidic conditions, cationic molybdenyl, MoO_2^{2+}, becomes the predominant species. Some of the molybdenum equilibrium reactions can be written as shown in **Equations (1)–(3) [6,7]**.

$$7MoO_4^{2-} + 8H^+ \leftrightarrow Mo_7O_{24}^{6-} + 4H_2O \quad (1)$$

$$Mo_7O_{24}^{6-} + 3H^+ + HMoO_4^- \leftrightarrow Mo_8O_{26}^{4-} + 2H_2O \quad \textbf{(2)}$$

$$Mo_8O_{26}^{4-} + 20H^+ \leftrightarrow 8MoO_2^{2+} + 10H_2O \quad \textbf{(3)}$$

Given the typical high acidity of raffinate solutions from Cu SX operations, the most likely molybdenum speciation is the cationic MoO_2^{2+} species. Molybdenum concentration in these types of streams can range between a few ppm to several hundred of ppm. Therefore the challenge here was to identify an extractant with both high selectivity and affinity that preferentially binds to molybdenum. Furthermore, the formulation must achieve fast kinetics and good physical properties.

RESULTS AND DISCUSSIONS

A phosphinic acid-based reagent, Cyanex 600, has been developed for molybdenum recovery from low concentration acidic feeds. A lab pilot plant scale process using the formulated product demonstrated successful extraction, stripping, and crystallisation conditions.

Extraction

Cation exchange is the proposed mechanism of molybdenum extraction by phosphinic acid. The extraction reaction is shown below, **Equation (4)**.

$$MoO_2^{2+} + 2(H_2R_2)org \rightarrow MoO_2(HR_2)2_{org} + 2H^+ \quad \textbf{(4)}$$

Cyanex 600 formulations have high affinity for molybdenum, allowing high extraction efficiency even at low pH values. The Mo extraction dependence on pH is shown in **Figure 1**.

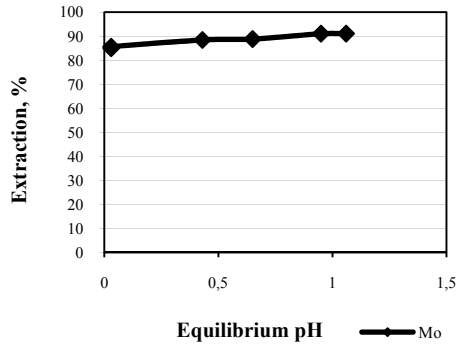

Figure 1 Molybdenum extraction percentage from a synthetic feed containing 25 ppm Mo, 1.5 g/L Cu, 3.7 g/L Fe and 6 g/L Al using 3 vol% Cyanex 600

Extraction kinetics

Kinetics are extremely important in extraction processes, especially when the target metal is present at low concentrations. **Figure 2** shows the extraction kinetics for molybdenum

from a real Cu SX raffinate ($[Mo]_{feed}$ = 90 ppm) using 10 vol% Cyanex 600. The results indicate 90% of molybdenum is extracted in 60 seconds.

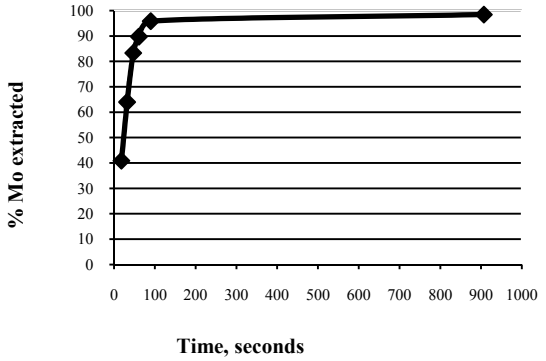

Figure 2 Mo extraction kinetics from Cu raffinate

Selectivity

Common impurities present in typical Cu SX aqueous streams include copper, aluminium, iron and zinc. **Figure 3** shows the acid dependence of iron, copper, and aluminium loading. These results indicate that only iron will be co-extracted with molybdenum. Molybdenum extraction is highly favoured over iron extraction and Mo/Fe selectivity increases dramatically at high acidities. This is due to iron extraction sharply decreasing with pH while molybdenum extraction not having a strong pH dependence.

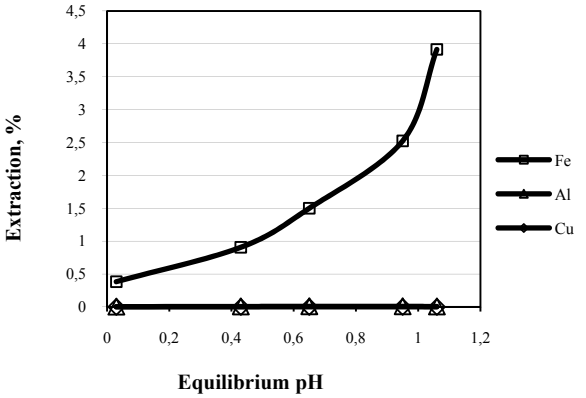

Figure 3 Fe, Al and Cu extraction percentages from a synthetic feed containing 25 ppm Mo, 1.5 g/L Cu, 3.7 g/L Fe and 6 g/L Al using 3 vol% Cyanex 600

The intrinsically high selectivity of the extractant can be complimented by designing a scrub step in the SX circuit. **Figure 4** demonstrates effective scrubbing conditions. The results show that by using 100 g/L H_2SO_4 almost quantitative iron removal can be achieved with minimal molybdenum losses.

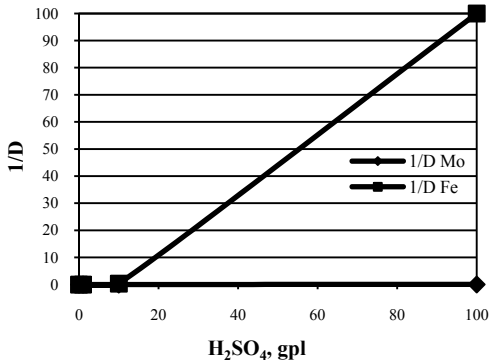

Figure 4 Scrubbing results for Mo and Fe using H_2SO_4

Stripping

Due to the strong complex between the extractant and molybdenum, acid stripping is not efficient. Molybdenum stripping involves a speciation change for molybdenum and is achieved by using a mixture of ammonia/ammonium carbonate for obtaining the best stripping efficiency and physical properties. The stripping reaction shown in **Equation (5)** is highly favourable, allowing the desired strip efficiency even for rich electrolyte containing high molybdenum concentrations.

$$MoO_2(HR_2)_{2org} + 2NH_4OH \leftrightarrow (NH_4)_2MoO_4 + 2H_2R_{2org} \quad \textbf{(5)}$$

Crystallisation

Rich electrolyte from a pilot plant run was used to generate a high quality mixture of ammonium molybdate hydrates and molybdenum oxide hydrate crystals via acidification. The major impurities found with the crystals were P, and S, while minor impurities were: As, Cu, Fe, Si, Zn, and Na. The crystal quality and purity could be improved with suitable washing of the filter cake.

Pilot plant results

In addition to extraction and stripping, an essential part of the process is molybdenum concentration. For economic crystallisation processes, the ppm levels of molybdenum in aqueous feeds must be strengthened to a rich electrolyte concentration greater than 40 g/L. This was successfully done in a continuous pilot plant run using a real Cu SX raffinate feed solution and a unique configuration. For the extract portion of the process, initially 100% of the organic was recirculated to allow molybdenum build-up in the organic phase. Once molybdenum concentration reached a pre-determined concentration, a bleed of the organic phase was sent to scrubbing/stripping steps while recirculating the rest of the organic. Scrubbing was done using acid concentrations varying between 5 and 100 g/L. Molybdenum was stripped using an ammonia/ammonium carbonate mixture. The pilot plant was run for

100 hours. Pilot plant operating conditions are indicated in **Table 1** and a schematic flowsheet is shown in **Figure 5**.

Table 1 Pilot plant operating conditions

Configuration	4E + 1Scrub + 1 Strip + 1 acid wash
Feed solution	35 ppm Mo, 20 g/L H_2SO_4
Aqueous feed flowrate	100 ml/min
Organic flowrate	6 ml/min
Stripping flow rate	0.1 ml/min
Extraction O/A ratio	0.06:1 (1:1 including organic recycle)
Stripping O/A ratio	60:1 (1:1 including aqueous recycle)

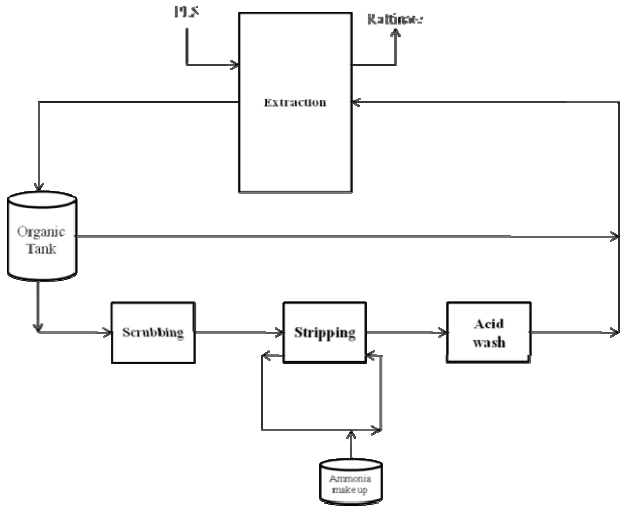

Figure 5 Pilot plant schematic flowsheet

The overall Mo extraction efficiency during the pilot plant run was 63% and the overall stripping efficiency achieved was 87%, **Figure 6**. The average molybdenum concentration in the loaded organic was 1.4 g/L, concentrating molybdenum 40-fold during the extract step.

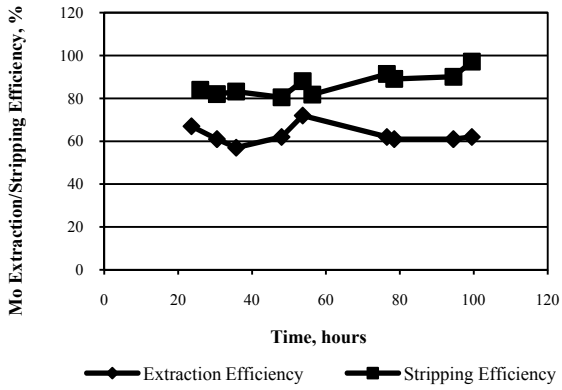

Figure 6 Mo extraction and stripping efficiency during the pilot plant run

During the stripping step, the aqueous phase was recirculated while maintaining the ammonia/ammonium carbonate level at an optimum level. In this step molybdenum was further concentrated to 56 g/L in the rich electrolyte, **Figure 7**. The combined Mo concentrating factor of the extract and strip stages was 1600-fold.

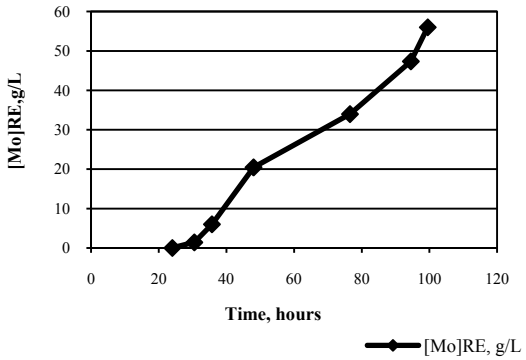

Figure 7 Molybdenum concentration in the rich electrolyte during the pilot plant run

CONCLUSION

Molybdenum was successful extracted and concentrated more than a thousand fold from feed solutions containing less than a hundred ppm Mo using a highly selective phosphinic acid based extractant, Cyanex 600, and a unique flowsheet. The process has been successfully demonstrated at the lab pilot plant scale using real feed solutions. This technology opens new venues for using SX for recovering molybdenum and other high value metals from low concentration feeds.

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