INDIRECT ELECTRO-OXIDATION PROCESS FOR LEACHING OF MOLYBDENITE CONCENTRATE BY HYPOCHLORITE: A MODIFIED APPROACH

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ABSTRACT

The leaching of low-grade molybdenite concentrate by hypochlorite, generated in situ by the modified approach has been investigated. The electrolysis of the pulp is conducted in the presence of calcium chloride, in order that quantitative precipitation of calcium sulfate and calcium molybdate is facilitated, as dissolution progresses. Therefore, at all times during electro-oxidation, the brine composition remains unaltered. The brine solution does not leave the electrolysis circuit and is recirculated without any purification. The solids, after filtration, containing calcium molybdate, calcium sulfate and unreacted gangue are leached with recycled Mo solution at ambient temperature to build molybdenum concentration, leaving behind calcium sulfate and gangue.

Introduction

Low grade molybdenite concentrates recovered from porphyry copper ores, contain copper sulfides in various amounts. Selective dissolution of molybdenum values has been achieved by sodium hypochlorite generated externally or electrolytically generated in situ. The pilot plant was operated at an optimum pH between 5.5 and 7.0, in order to minimize copper dissolution, so that, formation of insoluble copper molybdate leading to molybdenum loss, could be lowered. Warren and Mounsey (1983) found an optimum pH of 9.0 in solutions containing carbonate. At higher pH, as against 5.5 and 7, copper molybdate is unstable and copper forms oxide or hydroxide.

The salient features of the USBM process are as follows: at the start of the electro-oxidation process, the brine solution essentially consists of Na⁺, Cl⁻, and CO₃²⁻ besides OH⁻ as the major species. As dissolution progresses, the solution chemistry becomes increasingly complex with the entry of chlorites, chlorates, molybdate, sulfate and copper ions, when pH of the slurry is maintained between 5.5 and 7.0. Build up of some of the species, is known to lead to the catalytic decomposition of hypochlorite to chlorate, that does not participate in the dissolution process. The leach liquor, containing low molybdenum values and a host of ionic species, is subjected to purification wherein molybdenum is transferred to a recovery stage.
Chemistry of the Electro-Oxidation Process

The electrolysis of brine, in alkaline media, followed by the oxidation of molybdenite can be represented as electrode reactions:

\[ 2 \text{Cl}^- \rightarrow \text{Cl}_2(g) + 2 \text{e}^- \quad \text{(anode)} \quad (1) \]
\[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2(\text{cathode}) \quad (2) \]

Solution reactions:

\[ \text{Cl}_2(g) \rightleftharpoons \text{Cl}_2(aq) \quad (3) \]
\[ \text{Cl}_2(aq) + 2\text{OH}^- \rightleftharpoons \text{ClO}^- + 2\text{Cl}^- + \text{H}_2\text{O} \quad (4) \]

Hypochlorite consumption reaction:

\[ \text{MoS}_2 + 9 \text{ClO}^- + 6 \text{OH}^- \rightarrow \text{MoO}_4^{2-} + 9 \text{Cl}^- + 2 \text{SO}_4^{2-} + 3 \text{H}_2\text{O} \quad (5) \]

Chlorate formation reaction:

\[ 3 \text{ClO}^- \rightleftharpoons 2 \text{ClO}_3^- + \text{Cl}^- \quad (6) \]

chlorate is also formed electrochemically by the reaction at anode [Barr et al, 1979]:

\[ 6 \text{OCl}^- + 3\text{H}_2\text{O} \rightleftharpoons 2\text{ClO}_3^- + 4\text{Cl}^- + 6 \text{H}^+ + 3/2 \text{O}_2 + 6 \text{e}^- \quad (7) \]

The total chlorate production is the sum of reactions (6) and (7). The stability domain of \( \text{ClO}_3^- \), in the presence of chloride, covers the domains of \( \text{HOCl} \) and \( \text{ClO}^- \). The transformation of \( \text{ClO}^- \) to chlorate is catalyzed by the presence of transition metal compounds, such as nickel and copper hydroxides. Solution pH is maintained at an optimum value of 6 to 8 by periodic additions of Na\(_2\)CO\(_3\). During prolonged electro-oxidation, the chlorate concentration continues to build up, as do Cu\(^{2+}\), CO\(_3\)^{2-} and SO\(_4\)^{2-}, reducing the availability of free chloride. At pulp densities of around 2-3% solids, reported in the literature, the molybdenum concentration in the electrolyte is expected to be low, even after extended duration of electro-oxidation. Circulating large volume of lean solutions through the purification stage, for recovery of molybdenum values, reduces throughput.

In an effort to minimize chlorate build up, along with CO\(_3\)^{2-}, SO\(_4\)^{2-} and Cu\(^{2+}\), maintain uniform reaction rate as well as solution chemistry, addition of calcium chloride in place of sodium carbonate has been attempted. The addition of controlled amounts of calcium chloride to the brine, at the start of electrolysis, ensures the formation of calcium molybdate, calcium sulfate and copper carbonate and at all times the concentration of molybdate ions in solution is maintained around 10^{-2}M. At pH values 9-10, calcium molybdate is the stable species as indicated by the Eh-pH diagram in Fig. 1.

As a result, the temperature of the brine can be maintained at 303-308 K, in order to improve the dissolution kinetics with reduced conversion, both electrochemical as well as chemical, to chlorate. Higher temperatures affect the dissolution of chlorine gas evolved at the anode as well as the stability of hypochlorite. The schematic flowsheet of the modified electro-oxidation process is indicated in Fig. 2.
Experimental

Low-grade molybdenite concentrate from UCIL, Jaduguda, Bihar, India was used, for the electro-oxidation experiments. Analysis of the concentrate is shown in Table 1.

Experiments were conducted using two types of electrode assemblies viz., monopolar and bipolar. A schematic of the bipolar assembly is indicated in Fig. 3. The assembly consisted of four graphite electrodes, separated by perspex frames to maintain uniform gap and prevent charge jumping at the edges, with the end electrodes connected to the graphite busbars. The assembly was suspended in a 10 L glass beaker fitted with a Nylon® lid, to restrict the evolved chlorine from escaping. The lid, was provided with openings for graphite busbars, pH sensor, inlet for sodium hydroxide as well as for drawing of samples for analysis. The brine solution volume was maintained at 4.0 L, 1.2 L for monopolar cell, with 10 wt% NaCl. The slurry containing 2 wt% solids was stirred using a PTFE® coated magnetic stirrer. Known amount of CaCl₂ was added to the slurry at the beginning of each electro-oxidation experiment, with anode current density varying between 450 – 775 A/m². At all times, the pH of the slurry was maintained between 9.0 and 10.0 by frequent additions of NaOH. The solids, containing CaMoO₄ and CaSO₄, were leached with recycled Mo solution.

Results and Discussion

The results of the monopolar electrode arrangement are shown in Fig. 4. The monopolar electrode assembly consisted of concentric graphite cylinders suspended in the slurry. The dissolution was rapid, resulting in...
proportional changes in pH of the slurry. It has been reported that the rate of molybdenite oxidation was directly proportional, to the square root of the concentrations of hydroxyl and hypochlorite ions. In the present study, under reasonably constant $[\text{OH}^-]$ and current density of 775 $\text{A/m}^2$, the rate of molybdenum dissolution was linear for the duration of study.

The experiments were carried out under similar experimental conditions and the results of various electrode configurations, have been depicted in a single plot shown in Fig. 5. As the pulp density, as well as the anode current density were maintained constant for all investigations, the rate of dissolution was found to be consistent, indicating that, the formation as well as the precipitation of molybdate, sulfate and degradation of hypochlorite, if any, had little effect. The solution, after electro-oxidation, contained low amounts of sulfate and chlorate and could be recycled repeatedly without any intermediate purification. The solids were leached with recycled molybdenum solution, in order to maintain low solution volume for further purification.

The same brine solution was used for all the investigations, without the need for any purification and recycled directly from a reservoir. The objective of the exercise was to detect changes in leaching behaviour, owing to the build-up of significant amounts of chlorate and other ions, if any. The amounts of molybdenum and sulfate ions in the solution were found to be below 0.1 gpl, while the amount of chlorate was not analyzed.

**Conclusion**

Initial investigations in the use of controlled amounts of calcium chloride during leaching, proved encouraging, as the rate of molybdenite oxidation remained relatively unaffected, owing to the low build-up of molybdate and sulfate ions. Electro-oxidation was carried out at pH between 9.0 and 10.0, in order to maintain a high hydroxyl ion concentration, as the rate is reported to be directly proportional to the square root of hydroxyl and hypochlorite concentrations. Brine solution could be successfully recycled for all investigations without any purification.
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