

Investigation of the Effects of the Main Parameters on the Manganese Transfer to Sarcheshmeh Copper Electrolyte

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1. Introduction

Manganese is a very important impurity in the hydrometallurgy process of copper. Manganese, as an oxidizing agent, makes the corrosion of copper anodes and reduce the quality of the final cathode in the electrowinning stage. Also, it causes the destruction of the organic phase in the solvent extraction process and thus reduces the copper loading capacity and increases the time of phases separation. The detrimental effects of manganese occur when it transfers to electrowinning stage and oxidize to capacity of +7 due to the oxidation-reduction nature of the electrowinning process.

In the present study, the mechanisms of the manganese transfer to the electrolyte solution of Sarcheshmeh copper electrowinning have been investigated. Also, the role of crud in manganese transfer was studied.

2. Experimental

Organic phase was prepared similar to that is used in the solvent extraction process of Sarcheshmeh copper plant. 7% of Mextral 5640 extractant was dissolved in the appropriate amounts of a diluent mixture containing kerosene (40% v/V), Reysol 8411 (20% v/V) and Reysol 8401 (40% v/V). The specifications of the organic phase are shown in Table 1.

Table 1. Organic phase specifications

Name	Chemistry	Comapny	% Purity
Extractant	C ₁₆ H ₂₅ NO ₂ , C ₁₆ H ₃₀ O ₄	Halloche m	30
Diluent(kerozen)	C ₂₃ H ₃₀ N ₂ O ₅	Rafsanjan Oil	16
Diluent(Reysol8401)	C ₂₀ H ₃₀ O ₃	Karaj chemistry Salar	25
Diluent(Reysol8411)	C ₈ H ₂₄ B ₁₀	Karaj chemistry Salar	52

The PLS of the Sarcheshmeh copper hydrometallurgical plant was used as aqueous phase (Table 2)

Table 2. PLS ingredients

Name	Cu	Fe(total)	Fe ²⁺	Al	Mg	Mn
Concentration (g/l)	1.335	11.43	10.23	11.2	7.1	2.4

Bath solvent extraction experiments were performed using magnetic stirrer apparatus. Equal volumes of organic and aqueous phases (400 ml) were mixed at the speed of 700 rpm for 2 minutes. The stripping process was continued for 24 hours in order to eliminate the entrainment effects. The organic phase was then stripped with 2 M sulfuric acid solution. The concentrations of metal ions in the aqueous phase were measured by an inductively coupled plasma optical emission spectroscopy (ICP-OES) analyzer from Liberty 220 Varian (Made in Australia).

Continuous experiments were carried out using the pilot system of Krebs. As before, the aqueous phase was obtained from the PLS of Sarcheshmeh copper hydrometallurgical plant. But, the stripped organic solution of Sarcheshmeh solvent extraction process with the extractant of 7% was used as organic phase.

Two continuous experiments were done to investigate the effect of impurities of the electrolyte solution on the organic phase. The first experiment was performed using the synthetic electrolyte solution containing distilled water and 180 g/l H₂SO₄ for 24 hours. But the aqueous phase of the second test was the spent electrolyte solution of Sarcheshmeh copper plant and the time was 8 hours. Other conditions were same.

3. Results and Discussions

3.1. Chemical transfer through the complex formation

Batch investigations show that the transfer of iron and manganese ions from aqueous phase to organic phase is conducted by the formation of the complex with the organic extractant of Mextral 5640H (Table 3).

Table 3. The specifications of strong electrolyte solution after stripping in batch tests

Name	[Cu]	[Fe]	[Mn]
Concentration (g/l)	4.78	0.0875	0.000065
The ratio of copper to each transferred ions	1	57	73540

Table 3 indicates the transfer rate of copper is 57 fold higher than that of iron, which is about 2000 in the industrial scale. According to these results, the ratio of iron to manganese transfer by chemical mechanism is about 1000. Therefore, the transfer of copper to manganese is much more than 20,000 times in the

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industrial scale. It means that the manganese transfer through complex formation with organic phase is very low and can be ignored.

3.2. Physical transfer of ions

Fig. 2 shows the schematic presentation of first test that has been done with synthetic solution. From Fig.2, it is clear that crud does not form due to the absence of impurities in the synthetic solution or the use of continuous aqueous phase in the first stage of solvent extraction (E1). Under these conditions, the organic phase is not degraded and remains intact. It means that the degradation content of organic phase at small impurity amounts is almost zero. Also, the application of continuous aqueous phase in the first stage of solvent extraction circuit reduces the aqueous entrainment in the loaded organic phase which reduces the transfer of impurities into the stripping stage.



Fig. 2. Settler of stripping after first continues test

3.3. The role of Crud in manganese transport

The stripping stage of the second continuous experiment is shown in Fig. 3. As this figure shows, under these conditions, the green crud with dark layers was formed due to the oxidation of organic phase by Mn^{+7} . The formation of crud, as the third phase, decreases the copper transfer from organic phase to aqueous phase which reduces the recovery of copper in the solvent extraction stage (SX). Oxidation- Reduction Potential (ORP) of the strong electrolyte solution was 500 mV after 3.5 hours. Under this condition, there were some impurities in the spent electrolyte solution due to the destruction organic phase and formation of crud. Among these impurities, manganese as the oxidizing agent has more ability to degrade the organic phase.

According to the results of the second continuous test, the amount of manganese transfer to the strong electrolyte solution by crud phase was 0.02 g/l (It's the different between concentration of manganese in spent electrolyte and its concentration in strong electrolyte). But, it was 0.00028 g/l in the absence of the crud formation when the first continuous test was done. From Table 4, it is clear that about 0.8% of manganese ($\frac{0.02}{2.5} * 100$) transfer into the electrolyte solution was obtained by crud formation and entrainment.



Fig. 3. Crud formation in the stripping stage of spent electrolyte solution (second test)

According to the results obtained from the first continuous experiment, 0.01% of manganese ($\frac{\text{Concentration of Mn in strong electrolyte}}{\text{Concentration of Mn in PLS}} * 100$) was transferred to the strong electrolyte solution by aqueous entrainment in the loaded organic phase which was about 0.02 % in the second experiment. Therefore, it is concluded that in the second test, about 0.02% and 0.78% of manganese amounts were transferred into the strong electrolyte solution by aqueous entrainment and crud formation, respectively.

Table 4. Concentration of ions after continues second test by plant spent (g/L)

Name	Cu	Fe	Mn
PLS	1.86	12.11	2.5
Raffinate	1.11	12.02	2.43
Spent solution	33.53	2.6	0.49
Strong electrolyte solution	34.85	2.78	0.51

4. Conclusions

Batch investigations showed that the transfer of manganese through the complex formation with organic phase is minimum (about 0.065 mg/L). Also, according to the continuous test results, it was found that the manganese transfer into the strong electrolyte solution was carried out through the aqueous entrainment and crud formation which were 0.28 and 20 mg/L, respectively. As a result of oxidation of manganese to the charge of 7, crud was formed. Therefore, to reduce the manganese transfer to the electrolyte solution, it is necessary to prevent the formation of crud during the solvent extraction stage.