Journal of Advanced Chemical Engineering
ISSN: 2090-4568

DOI: 10.4172/2090-4568.1000156

Research Article Open Access

Optimization of Industrial Copper Electro Winning Solutions

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Abstract

Laboratory testing using industrial electro winning solutions was performed to determine the best Faradic cell efficiency for copper cathode recovery. The variables tested were solution flow rate, recycle ratio, reagent addition combinations of guar and thiourea, and addition amount of acid mist suppressant CAL FAX DBA-70. The ideal flow rate was determined to be 37.85 liter/min. Additionally, the ideal recycle ratio was determined to be 10:1. The reagent addition scheme from testing which showed the highest efficiency was with 680 g/tonne guar of cathode copper won and with 135 g/tonne thiourea of cathode copper won. These values for reagent addition only reflect the best efficiency and should not be assumed to be the best reagent concentration for copper purity. The amount of foaming agent that showed the best efficiency was the test with 2 ppm of foaming agent. Again this amount of reagent is based on efficiency and should not be taken as the amount of reagent that does the best acid mist suppression. Additional proprietary surface characterization work indicates these additives may have enhanced the cathodic reduction surface morphology of some noble minor impurities. Subsequently, these operating parameters were introduced into the plant operation and proved successful after their implementation.

Keywords: Faradic cell efficiency; Copper electro winning; Foaming agent; Electro winning solution

Background

Copper electro winning has become a dominant technology for the production of marketable high grade copper cathode products. The literature is robust with applications, optimizations, additives and developments in this field [1-15].

Tests of forty hours duration and at room temperature were performed for this project using samples of actual industrial electro winning solutions. These industrial solutions were comprised of 60 g/L Cu plus 65 g/L Ni, 3 g/L Fe, and 30 g/L free sulfuric acid. Other confidential minor impurities were also present including some solubilized precious metals. The testing apparatus utilizing stainless steel anodes and cathodes is illustrated in Figures 1 and 2.

The testing regime was carried out in four parts and is as follows

Variable feed rate tests: Tests were performed with feed rates of 18.93, 37.85 and 56.78 liter/min, respectively. In subsequent testing a fixed ratio of recycled solution was used. This ratio was defined as 10 volumes of solution recycled from an external overflow catch tank per volume of contained electrolytic cell solution.

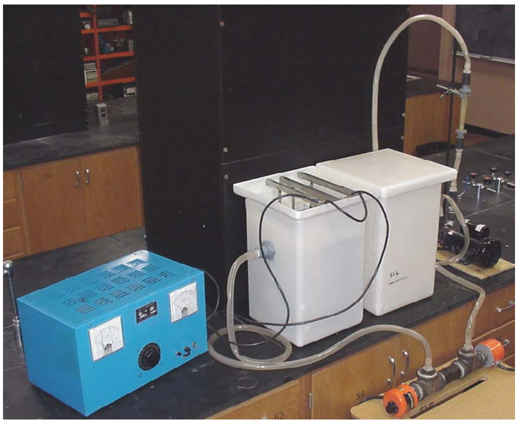

Figure 1: Electro wining test equipment set up.

Recycle ratio tests: Tests were performed with a variety of recycle ratios of new electro winning solution to recycled electro winning solution. Recycle ratios of 2.5:1, 7.5:1, and 15:1 were used at a feed rate of 37.85 liter/min. Note this also allowed the 10:1 recycle ratio test at 37.85 liter/min from part 1 to be compared to the recycle ratios in part 2.

Reagent addition concentration tests: Tests were then performed using a recycle ratio of 10:1 and feed rate of 37.85 liter/min with various combinations of reagents added. Reagent addition schemes consisted of all of the various combinations of 136 g/tonne guar, 450 g/tonne guar or 680 g/tonne guar along with 45 g/tonne thiourea, 135 g/tonne thiourea, or 450 g/tonne thiourea.

Foaming reagent concentration tests: These tests were performed

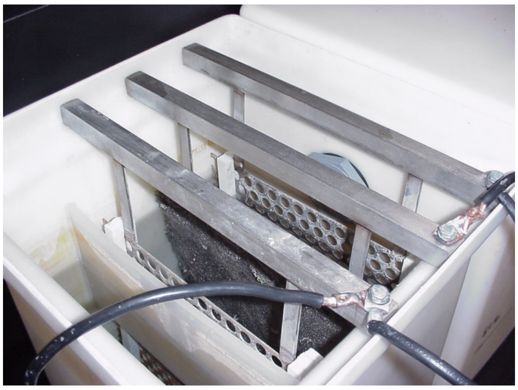

Figure 2: Electro wining test cell.

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Received July 29, 2016; **Accepted** August 03, 2016; **Published** October 04, 2017

Citation: Corby Anderson G (2017) Optimization of Industrial Copper Electro Winning Solutions. J Adv Chem Eng 7: 156. doi: 10.4172/2090-4568.1000156

using 37.85 litre/min, 10:1 recycle ratio, 680 g/tonne guar, and 135 g/tonne thiourea with various concentration of foaming agent added. The amounts of foaming agent used were 2 ppm, 10 ppm, and 50 ppm.

Efficiency Calculations

The cathodic copper efficiency for each test was calculated by two methods. The first based the efficiency on the weight of copper plated out on the cathodes compared to the calculated amount of copper based on the Faradic current efficiency. The efficiency for this case was calculated by the following equation:

$$\frac{\text{Weight of actual plated copper}}{\text{Weight of theoretical plated copper}} \times 100$$

The second method of calculating current efficiency is based on solution assays. The amount of copper left in solution versus the amount of copper in the head solutions is compared to the theoretical amount of copper left in solution based on the Faraday current efficiency versus the head solution. The efficiency is calculated by the following equation:

$$\frac{\text{Amount of copper in head} - \text{Amount of copper in sample}}{\text{Amount of copper in head} - \text{Theoretical amount of copper in sample}} \times 100$$

The solution assays were done by titration for copper and free acid. Additionally, the final solutions were also analyzed by ICP for copper.

Variable feed rates

Three tests were performed with variable feed rates and a fixed recycle ratio of 10:1 and no reagents added. The first had a feed rate of 18.93 liter/min and showed an efficiency of 83.1% based on solution analysis. The copper from this test plated out as a powder that gathered in the bottom of the electro winning cell. This powdered copper sludge forms due to the low throughput of solution. The second test, performed at 37.85 liter/min, had an efficiency of 85% based on solution assay. The copper in this test plated out smoothly onto the cathodes as is desirable. The third test, performed at 56.78 litre/min, had an efficiency of 78% based on solutions. The copper in this test also plated out smoothly onto the cathodes. The flow rate of 37.85 liter/min from the second test was chosen for the flow rate for the remaining tests.

Recycle ratio

Three tests were performed using various recycle ratios. However, due to the same flow and reagent conditions present in test 2 of the variable feed rate tests, it was also compared to the recycle ratio tests to determine optimum recycle ratio. All of the recycle ratio tests used a flow of 37.85 liter/min with no reagents added. The first test using a recycle ratio of 2.5 to 1 had a solution based current efficiency of 66%. The second test using a recycle ratio of 7.5 to 1 had a solution based current efficiency of 60%. The third test using a recycle ratio of 15 to 1 had a solution based efficiency of 54%. When compared to the efficiency of the 10 to 1 recycle ration (85%) it was determined that the 10 to 1 recycle ratio was the optimum ratio. Likely this is an optimal level for effective mass transfer in conjunction with the related multi metal ionic composition.

Reagent addition concentration

The reagent addition concentration test work was comprised of nine tests. All of the tests used a recycle ratio of 10:1 and a feed rate of 37.85 litre/min. The various reagent additions for each test as well as the efficiency based on solution assay are presented in Table 1.

As Table 1 shows, the best efficiency at about 100% based on solution assays is reached with 680 g/tonne guar and 135 g/tonne thiourea. The cathode weight calculated current efficiencies also mirrored this result. In addition the copper cathode deposits were smooth and adherent. Subsequent proprietary work was done to examine the surface morphology of these deposits. This combination of reagents was thus chosen as the standard condition for the remaining tests. Subsequent proprietary testing of copper purity for the different reagent combinations did confirm that this combination is the most effective; as the reagents added are done so to produce a better copper product. In addition, the further proprietary cathode surface studies indicated that the effective reduction of minor noble impurities may have caused the noted efficiency enhancements.

Test		Guar Concentration	Thiourea Concentration	Efficiency
Letter	Number	grams/tonne Cu won	grams/ton Cu won	%
A	1	135	45	87%
A	2	135	135	78%
A	3	135	450	81%
B	1	450	45	94%
B	2	450	135	81%
B	3	450	450	95%
C	1	680	45	86%
C	2	680	135	101%
C	3	680	450	97%

Table 1: Reagent Additions and Efficiencies for Reagent Addition Concentration Tests.

Foaming agent concentrations

Three tests were performed using various amounts of CAL FAX DBA-70. This is a mist suppressant used in copper electro winning. Previous industrial experience had shown that mist suppressants can be effectively used in conjunction with copper solvent extraction circuits [16]. All three of these tests had similar calculated current efficiencies based on the copper cathode weight plated out. In this case, the solution based calculated efficiencies, showed a wide range from 101% to 91% efficiency. The test done with 50 ppm foaming agent had the longest lasting foam during experimentation. The test with 2 ppm foaming agent did not have any foam present in the electro winning cell; however, a small amount of foam was present in the recirculation tank. The 2 ppm foaming agent test also had the highest solution based efficiency calculated at 101%. The efficiency based on the plated copper would suggest that the quality of the copper be used to determine which amount of foaming agent would be ideal. Further proprietary work was done in this area and indicated that the reduction of minor noble impurities in an enhanced cathode surface morphology may have been influenced by the foaming agent and other reagent additions.

Summary

Laboratory testing using industrial electro winning solution was performed to determine the best cell efficiency. The variables tested were solution flow rate, recycle ratio, reagent addition combinations of Guar and Thiourea, and addition amount of acid mist suppressant CAL FAX DBA-70. A summary is shown above in Table 2. The ideal flow rate was determined to be 37.85 litre/min. Additionally, the ideal recycle ratio was determined to be 10:1. The reagent addition scheme from testing which showed the highest efficiency was 750 g guar/tonne copper won and 150 g thiourea/tonne copper won. In addition, the values for reagent addition only reflect the best efficiency and should not be assumed to be the best reagent concentration for copper purity. The amount of foaming agent that showed the best efficiency was the

Test #	Test Conditions	Copper Won	Solution
		Efficiency	Efficiency
1	Flow 5 gpm	85%	83%
2	Flow 10 gpm	87%	85%
3	Flow 15 gpm	78%	78%
4	Recycle 2.5:1	69%	66%
5	Recycle 7.5:1	57%	60%
6	Recycle 15:1	48%	54%
3A1	See Table 1	78%	87%
3A2	See Table 1	63%	78%
3A3	See Table 1	66%	81%
3B1	See Table 1	77%	94%
3B2	See Table 1	70%	81%
3B3	See Table 1	79%	95%
3C1	See Table 1	71%	86%
3C2	See Table 1	86%	101%
3C3	See Table 1	88%	97%
A	Foam 2 ppm	87%	101%
B	Foam 10 ppm	88%	94%
C	Foam 50 ppm	88%	91%

Table 2: Summary of Cu Electro winning Optimization Testing.

test with 2 ppm of foaming agent. Again this amount of reagent is based on efficiency and should not be taken as the amount of reagent that does the most acid mist suppression. It is likely that the role of some key minor noble solution impurities and their enhanced cathodic reduction surface morphology was influenced by all of these additives causing the higher efficiencies. However, this additional confirmatory surface analysis data is client privileged. Subsequently, these operating parameters were introduced into the industrial plant and proved to be successful in the operation.

Acknowledgements

This paper was first published in the proceedings of the XXVIII International Mineral Processing Congress, ISBN: 978-1-926872-29-2. Copyright of International Mineral Processing Congress papers will be held by the authors and not the organizing society/body.

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