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Effect of Chloride Electrolyte Additive on the Quality of Electrorefined Copper Cathode

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Abstract

Sodium chloride (NaCl) is used in electrorefining as an electrolyte additive for refinement of copper grains and reduction of cathode impurities such as Ag and Sb. This is done by precipitating them out of solution as metallic chloride crystals. In this study a laboratory scale electrorefining circuit was used for the electrodeposition of copper in the presence of Bone glue, thiourea, Avitone and NaCl as electrolyte additives. The effect of NaCl on physical and chemical quality of cathode deposits was studied to achieve the optimum chloride concentration in the electrolyte. Cathode chemical composition was analysed using Spark Analysis for Traces (SAFT) machine and cathode morphology analysed using Optical Microscope (OM). Anode slime elemental composition was analysed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). It was found that chloride concentration in electrolyte affect the cathode deposit physical appearance and chemical quality and also plays a major role in making the composition of anode slime. Ag in cathode was found to be lower between chloride concentrations of 0.02g/l and 0.025g/l whereas Sb in cathode was lower at concentrations lower than 0.025g/l. Chloride concentration of 0.02g/l produced smoother and compact cathode deposits which were free from pits and nodules. At higher chloride concentration cathode deposits developed a pit-like appearance on the surface and grew nodules next to the pits.

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1. Introduction

Electrorefineries around the world are constantly trying to maximise their cathode production in order to keep up with the increasing demand for copper products, which is worsened by the global technology advancement and infrastructure development [1, 2]. Attempts to capitalise on cathode production are unfortunately, in most cases, accompanied by unsatisfactory physical and chemical quality cathode production resulting from the increasingly complex and low grade ores with high concentrations of impurities [3, 4]. In the copper electrorefining process

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impurities present in the anode often report to cathode at concentrations higher than those allowed by cathode quality standards [5, 2]. These impurities are more detrimental in the rod casting stage as they cause the rod to fail as a result of increased brittleness and centerline porosity among other defects [6]. This is why it is very important to avoid anode slime entrapment and co-deposition of impurities in the cathode during the electrorefining process.

During anodic dissolution, at the positive terminal of the circuit, elements more noble than copper do not dissolve but are instead liberated from the anode as anode slime. These particles settle in the electrolyte under gravity and particles that are lighter will settle more slowly than heavier ones. Some particles can be transported and incorporated in the cathode as slime entrapment, which is a major potential source of impurities [7]. Impurities that dissolve in the electrolyte also tend to report to the cathode under abnormal operating conditions such as operating at current higher or lower than desired. These impurities have to be kept low in the electrolyte and this is done by constantly bleeding off a portion of the electrolyte and topping up with new electrolyte. Some impurities like Ag and Sb are precipitated out of solution as metallic chlorides and collected at the bottom of the cell as anode slime through the dosing chloride as one of the electrolyte additives [8, 3].

The use of electrolyte additives as grain refining and levelling agents in the electrolyte is primarily deployed to correct the problem of rough, uneven and dendritic cathode deposits. These levelling and grain refining agents work hand in hand with each other to promote deposition of dense, smooth and pure copper. The most common levelling agent used is bone glue which consists of large protein molecules forming large cations in the electrolyte. The principal grain refining agents are thiourea and chloride, added as HCl or NaCl into the electrolyte. Avitone, a petroleum liquid, is also used together with thiourea as a grain refiner [8].

Chloride ion, added as NaCl or HCl is believed to be a grain refining agent when added together with thiourea and Avitone. Knuutila et al. (1987:1) [9] explained that the grain refining action of chloride ions and thiourea with the help of Avitone is such that they may form Cu-Cl-thiourea cations, which electrodeposit on the cathode surface where they form nucleation sites for new copper crystals. All electrolyte additives require proper optimisation since there are a lot of factors that may hinder the efficiency of their surface enhancement.

2. Experimental Procedure

A lab scale electrodeposition cell was constructed using a DC rectifier, dosing pump, hot plate magnetic stirrer, glass beakers, pipettes, plastic pipes and a plastic electrorefining cell with a bottom inlet pipe and a top outlet pipe simulating the industrial electrorefining cell. The electrorefining set up had 5 anodes and four cathodes connected in the Walker Parallel set up. Anodes used in the experiment are cast from fire refined copper and the cathode is cut from industrial copper starter sheet with copper contents of 99.5% and 99.9% respectively. The electrolyte used has the same compositions as that used in industrial practice as shown on Table 1.

Table 1: Analysis of electrolyte

Element	Composition
Copper	47g/l
Sulphuric acid	222g/l
Nickel	5.2g/l
Chloride	0.18g/l
Iron	712ppm

The electrolyte temperature was set at 70°C with the flow rate at 3.6l/min and inter-electrode spacing of 3cm simulating those used in an industrial set up. Electrolyte additives were also added at concentrations similar to those used at industrial electrorefining with NaCl varied as shown on Table 2. Current and voltage were set at 8.0A and 1.2V respectively which gives a current density of 275A/m² as is used in the industrial electrorefining process.

Table 2: Concentrations of electrolyte additives during the experimental process

Experiment no.	NaCl (mg/l)	Glue (mg/l)	Thiourea (mg/l)	Avitone (mg/l)
1	0.00128	1.37	0.68	0.57
2	0.00256	1.37	0.68	0.57
3	0.00512	1.37	0.68	0.57
4	0.00896	1.37	0.68	0.57
5	0.02176	1.37	0.68	0.57

The electrorefining process was run for 2 hours per experiment before removing cathodes for elemental analysis using SAFT analysis machine and surface morphology examination through an Optical microscope. Anode slimes were collected at the bottom of the cell and analysed through CIP-OM machine to find the elements liberated from the anodes and those that are precipitated from electrolyte at the end of every experiment.

3. Results and discussion

3.1. Surface Morphology

Copper deposition was successfully attained on all five experiments where the effect of Chloride concentration on cathode surface was studied using Optical Microscope. Figure 1 show smooth surface of cathode produced on experiment 2. Copper grains are fine and free of nodules and dendrites at chlorides concentration of 0.02g/l. Microscopic images on figure 2(A) show scattered pits on cathode from experiment 5, which will potentially serve as weak points for deterioration of cathode during operating conditions. Figure 2(B) show nodules which have initiated next to the pits which suggest that pits also serve as nuclear areas for nodular growth which in turn may entrap other solid impurity particles.

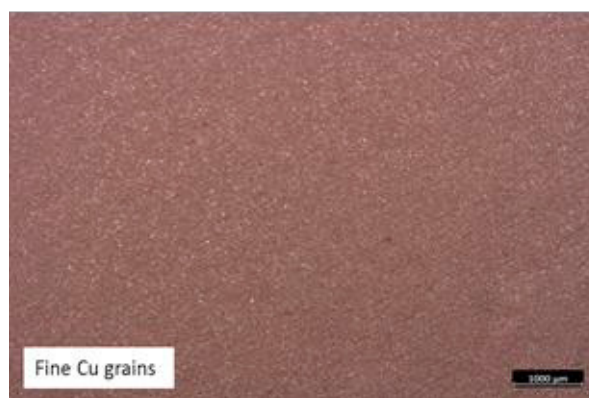


Figure 1: Optical Microscope image of cathode from experiment 2.

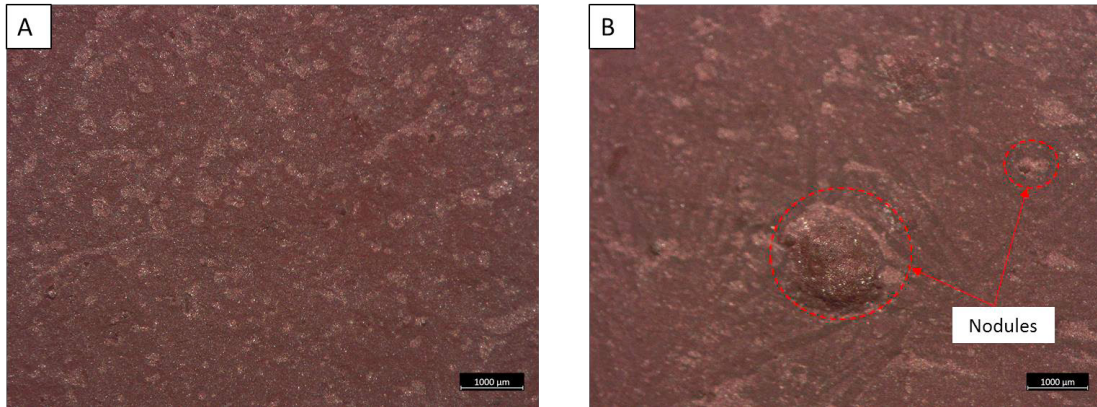


Figure 2: Optical Microscope image of cathode from experiment 5 with pits (A) and nodules (B).

1.2. Cathode chemical quality

Figure 3(A) and (B) shows Ag and Sb concentration in cathode respectively versus chloride concentrations. It can be seen that Ag is higher both on the lowest and highest chloride concentration which is experiment 1 and 5 respectively while on the other hand Sb is higher at the highest chloride concentration on experiment 5. The lowest Ag in cathode is produced on experiment 2 and 3 whereas the lowest Sb in cathode is produced on experiment 1 and 4.

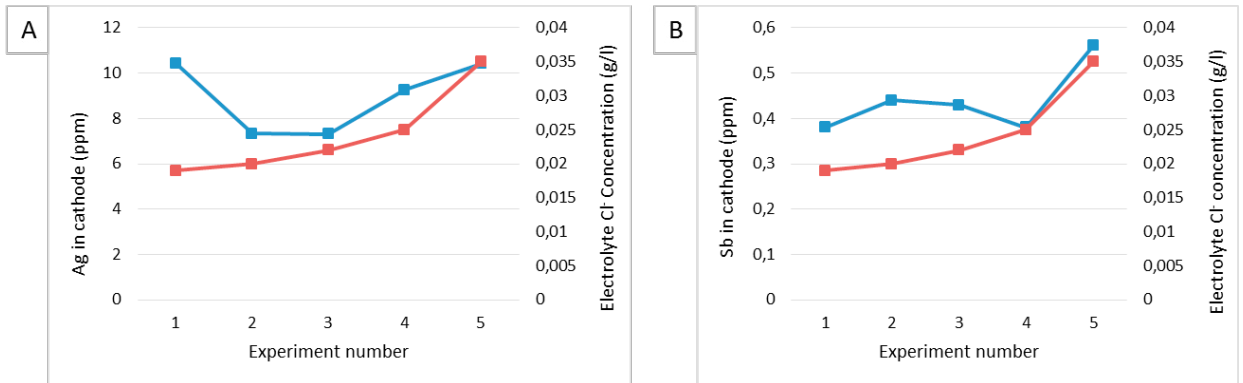


Figure 3: Analysis results of (A) Ag in cathode versus chloride in electrolyte and (B) Sb in cathode versus chloride in electrolyte.

1.3. Anode slime chemical analysis

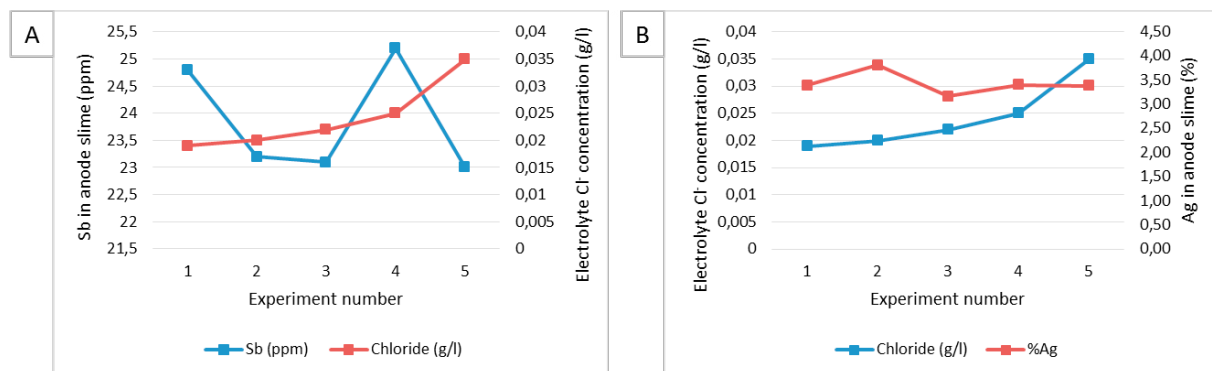


Figure 4: Analysis results of (A) Sb in anode slime versus chloride in electrolyte and (B) Ag in anode slime versus chloride in electrolyte.

Recovery of Sb and Ag in anode slime is expressed by the anode slime elemental analysis on Figure 4(A) and (B) respectively. The highest Sb concentration in slime is found on experiment 4 whereas the highest Ag concentration is found on experiment 2. From figure 4(B) it can be seen that more Ag is precipitated at chloride concentration of 0.02g/l as also supported by lower Ag in cathode on Figure 3(A).

4. Conclusion

Concentration of chloride in electrolyte plays a significant role on the physical appearance of cathode deposits as well as their chemical composition during electrorefining. Chloride concentration of 0.02g/l produced smoother and more compact cathode deposits which were free from pits and nodules. At higher chloride concentration of 0.025g/l and above cathode deposits developed a pit-like appearance and formed nodules. Ag in cathode was higher at chloride concentrations below 0.02 and above 0.025g/l whereas Sb was higher at chloride concentration above 0.025g/l. Higher precipitation of Ag in anode slime was achieved at chloride concentration of 0.02g/l. chloride concentration of 0.02g/l was therefore chosen to be the optimum concentration due to lower impurities found in cathode and more Ag precipitated and recovered in the anode slime.

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Appendix A

Table 3: Elemental analysis of cathodes

#	Cathode																		
	Ag	As	Bi	Cd	Co	Cr	%Cu	Fe	Mn	Ni	P	Pb	S	Sb	Se	Si	Sn	Te	Zn
1	10.4	0.1	0.1	0.2	0.2	0.1	99.99	5.2	<0.1	3.1	2.8	0.5	9.6	0.4	0.4	2.9	<0.1	1.0	0.5
2	7.3	0.3	0.4	0.4	0.4	0.2	99.99	10.0	<0.1	4.7	0.3	1.6	12.0	0.4	0.3	3.3	0.3	0.2	0.6
3	7.3	0.2	0.2	0.3	0.1	0.2	99.99	0.4	<0.1	0.4	0.6	0.7	3.1	0.4	0.4	1.6	0.1	0.2	0.3
4	9.3	0.1	0.1	0.4	0.3	0.1	99.99	5.6	<0.1	2.6	0.2	<0.1	11.6	0.4	0.4	1.5	0.2	0.4	0.3
5	10.4	0.1	<0.1	0.1	<0.1	0.8	99.99	1.0	<0.1	0.2	0.5	0.1	7.7	0.6	0.2	3.8	0.2	0.9	0.5

Table 4: Elemental analysis of anode slime

Anode Slime																
#	%Ag	%Au	%Cl-	%Cu	%Ba	%Bi	Mo (ppm)	%Ni	%Pb	%Se	%Te	As (ppm)	Sb (ppm)	%Al ₂ O ₃	Pd (ppm)	Pt (ppm)
1	3.39	0.21	0.20	26.4	0.60	0.01	4.40	0.81	0.05	0.53	0.44	449.35	24.80	0.80	116.70	100.10
2	3.81	0.19	0.25	26.5	0.17	0.00	76.00	0.41	0.08	0.68	0.53	344.05	23.20		96.39	92.78
3	3.17	0.20	0.24	31.5	0.10	0.00	1.00	0.33	0.00	0.69	0.57	350.30	23.10	0.60	90.70	83.00
4	3.40	0.22	0.23	27.0	0.09	0.10	44.00	0.35	0.11	0.54	0.59	279.85	25.20	0.50	117.60	103.60
5	3.38	0.21	0.07	29.0	0.16	0.01	28.00	0.19	0.15	0.61	0.42	190.00	23.00	0.30	130.60	119.00

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