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Recovery of Copper from Strong Chloride-based Solution

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Abstract: Strong chloride-based copper solutions were investigated for copper recovery by using aluminium scraps. From the recovery process, the reaction rate is consistently to be first order to cupric ion. The activation energy for the process calculated from the Arrhenius plot indicates a chemical controlled process. The immersion of aluminium scraps into prepared cupric and cuprous solutions created a clean and depressed aluminium surface morphology. It is found that cuprous solution cements higher purity of copper than cupric solution. The aluminium scrap surface area also contributes to the purity of cemented copper. For a sample of copper bearing spent etching bath containing 131.6 g L^{-1} copper, more than 99% copper was recovered with 94.4% purity.

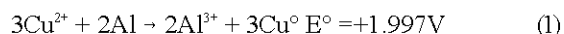
Key words: Copper recovery, aluminium, chloride, cementation

INTRODUCTION

The cementation or metal displacement reaction is an electrochemical process by which a more noble metal ion is precipitated from solution by a metal higher in the electromotive series. Several hydrometallurgical processes have been developed for the separation of metals from their spent solution. The electrolytic extraction process has been used in the precipitation and purification of metal. Although the electrolytic recovery of metal from dilute solutions is of considerable importance, there are a number of objections to electro-winning as a means of copper recovery from solution. Its operating, investment and energy costs are rather high. In addition, the acid streams formed at the anodes reduce quality of the products obtained^[1].

Cementation is still an important reaction in hydrometallurgical processing. It is very fast and probably controlled by the rate at which the ions diffuse to and from the metal surface. It is a quick and cost saving method to recover copper from a variety of leach solutions^[2-4]. Won *et al.*^[5] and Tadeusz *et al.*^[6] reported on the recovery of copper from such solutions by using iron scrap. The kinetic of copper deposition from a low concentration solution onto zinc was described by Strickland and Lawson^[7]. Masse and Piron^[8] studied the cementation of copper from an alkaline solution in their simulation work.

Cementation of copper onto aluminium^[9,10] has been studied extensively in relation to their solution composition. Its process kinetics^[11-15] indicated the reaction to be first order in nature. The overall reaction can be expressed as Eq. 1. The utilization of aluminium scraps in the cementation process would help to solve the ecological problem in waste-littering. In addition, it is an economical usage of aluminium waste compared to the cost of energy in reclaiming aluminium metal^[16-19].



Annamalai and Murr^[9] reported that the present of chloride could leach away aluminium oxide surface. A minimum of 25 mg L^{-1} chloride was required to provide effective active surface area but the aluminium surface became porous at higher chloride concentration. In the present investigation, an attempt has been made to evaluate the cementation behaviour of copper in strong chloride media by using aluminium scrap. An effort is also made to associate some critical solution factors in the recovery process.

MATERIALS AND METHODS

Materials: All experimental solutions were prepared from analytical grade chemicals and distilled water. Cuprous chloride stock solution was prepared by dissolving exact amount of pure copper bar in 0.05 M cupric chloride,

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prepared in 3.00 M sodium chloride under nitrogen atmosphere^[20,21]. The aluminium scrap specimens were taken from a 3 mm thick and 19 mm width bar, supplied by a local aluminium scraps collecting company. These pieces having surface area of 266, 570, 760 and 1140 mm² were used after slight polishing with a 600-grit sand paper. The specimens were then cleaned with ethanol followed by a cold-water rinse before use.

Experimental methods: In the copper recovery experiment, 100 mL of copper chloride solution was used in a custom-built 250 mL conical glass, installed with water condenser and purged with nitrogen. The solution was decanted into the vessel which was then immersed in a constant temperature bath. The pH of the solution was adjusted to desired value before introducing aluminium scrap specimen. The vessel was de-oxygenated throughout the experiment with high purity nitrogen gas.

Solution samples were taken at different time intervals for cupric and cuprous concentrations analysis using UV-vis (Hitachi, U-2000) and Atomic Absorption Spectroscopy (AAS) (GBC 902) in combination^[22]. Suspended copper powder and excess aluminium scraps were collected at the end of experiments. They were rinsed with distilled water followed by ethanol before drying in electric oven at 105°C.

RESULTS AND DISCUSSION

Reaction kinetics: The reaction kinetics of copper deposition from strong chloride media were studied by using aluminium specimens comprising surface area of 266, 570 and 1140 mm². The solutions pH values were adjusted to 4.02 and experiments were conducted at 25°C room temperature. By analyzing the standard rate expression for the process, the experimental data fit reasonably and consistently with the reaction being first order to Cu²⁺ as found for most cementation reactions, reported by previous researchers. All the slopes agree well for a first order reaction as shown in Fig. 1.

Effect of temperature: Several researchers^[9,12,15] reported that the amount of copper deposit increased linearly with solution temperature in the range of 28-45°C. In this study, experiments were conducted at 25 to 64°C using aluminium scrap bar with 1140 mm² surface area. The pH value was set at 4.02. The experimental data are plotted as a graph of Log [cementation rate] versus the reciprocal of the absolute temperature. These findings are good fitted with the reported earlier that, the reaction showed first order kinetics. From the slope of Arrhenius

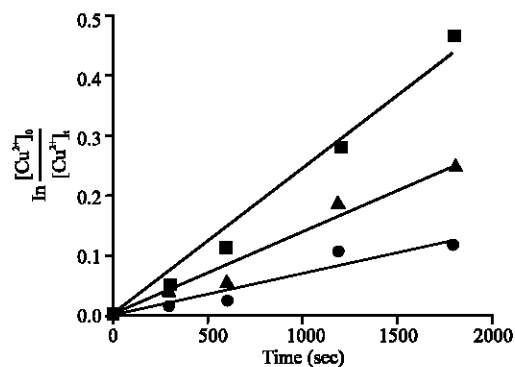


Fig. 1: Plots of cementation $\ln \frac{[Cu^{2+}]_0}{[Cu^{2+}]_t}$ versus time

Aluminium scrap surface area: (•)=266 mm², (▲)=570 mm² and (■)=1140 mm²

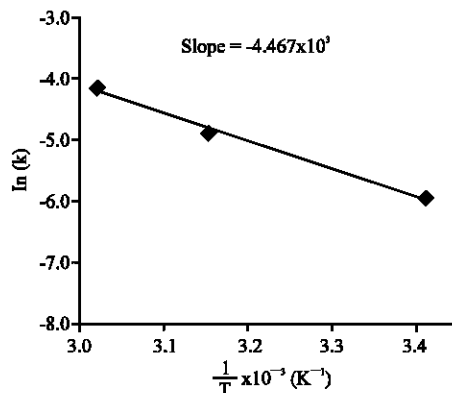


Fig. 2: Arrhenius plot of $\ln k$ versus $1/T$

plot in Fig. 2, the activation energy is calculated to be 37.12 kJ mol⁻¹. This value indicates a chemical controlled kinetic.

Effect of pH on copper recovery: Experiments were performed at various pH values as stated in Table 1 for 20 min. Constant values of the other parameters such as 25°C solution temperature and aluminium scraps bar with 1140 mm² surface area were chosen. From Table 1, the pH values do not affect significantly on the copper recovery within the chosen range. The cementation reaction in a closed experimental vessel becomes difficult to control due to the evolution of hydrogen gas^[23,24] from the dissolution of aluminium in acidic solution. Strong acid is not required for the process because chloride ions in the solution are sufficient to do the surface cleaning job besides cuprous dissolution^[25].

Table 1: Change in copper recovery efficiency according to pH value

Initial pH value	Copper recovery (%)
2.30	24.4
3.02	22.2
4.02	21.8

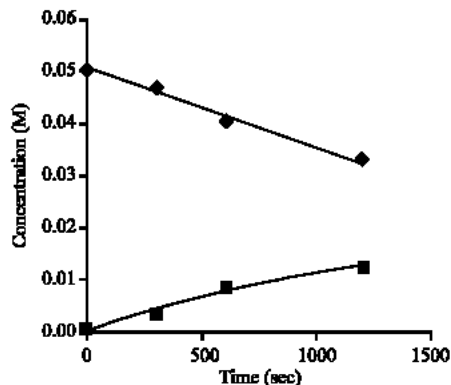
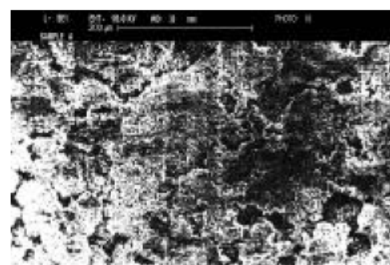


Fig. 3: Plots of cupric ions (◆) and cuprous ions (■) versus experimental time. Aluminium scraps surface area = 1140 mm², pH = 4.02 and temperature = 25°C

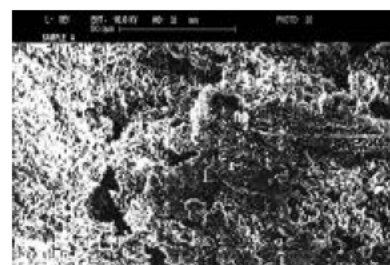
Cuprous formation: The copper cementation is generally proposed to occur in two consequent electron transfer reaction steps involving the formation of intermediate Cu⁺ [26-28]. The addition of low quantities of chlorides could modify the electrode kinetics. Gabrielli *et al.* [28] showed that deposition of copper in chloride media (less than 10⁻³ M) is mainly due to a mechanism involving CuCl formation. CuCl adsorbs onto electrode surface which partially blocks the electrode surface giving an inhibiting behaviour and causes mass transport limitation due to the diffusion of cupric ions.

The cathodic deposition of copper from cupric ions has been studied by monitoring the concentrations of both Cu²⁺ and Cu⁺ ions for 20 min (Fig. 3). Result shows that cuprous exists in the solution bath during the cementation process. It is generated from the first electron transfer process of copper cementation and cupric chloride etching processes. Strong chloride ion in the reaction bath sweeps away Cu⁺ intermediate and copper metal deposit from the aluminium surface, living a clean surface as shown in the SEM micrographs analysis later section. Evolution of hydrogen gas from clean aluminium surface due to aluminium dissolution also creates agitation effect.

Effect of cupric and cuprous cementation process on aluminium surface morphology: The immersion of aluminium scraps into a prepared cupric and cuprous solutions resulted in formation of a relatively equally

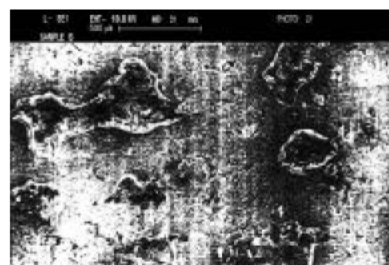


(A)

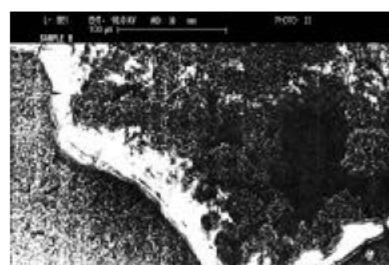


(B)

Fig. 4: SEM micrographs of the aluminium surface from cupric-aluminium system (A and B). Bath composition: pH value =4.02, aluminium surface area = 1140 mm² and temperature = 25°C



(A)



(B)

Fig. 5: SEM micrographs of the aluminium surface from cuprous-aluminium system (A and B). Bath composition: pH value =4.02, aluminium surface area = 1140 mm² and temperature = 25°C

Table 2: Cupric and cuprous effect on the copper recovery

Solution bath	Recovery efficiency (%)	Copper purity (%)
0.05 M cupric chloride	64.2	58.4
0.10 M cuprous chloride	78.3	88.9

Table 3: Characteristics of copper etching waste

Parameters	
Specific gravity	1.283 g mL ⁻¹
Total [H ⁺]	9.06% (% wt. wt. ⁻¹ as HCl)
Total [Cu]	10.26%
Total [Fe]	11 ppm

eroded and convoluted aluminium surface topography. From the scanning electron microscopy (SEM) (Leica-Cambridge S-360) in Fig. 4 to 5, dendritic copper deposit, as claimed by Annamalai and Murr^[9] is not found on the surface of aluminium substrates. Chloride ions in the solution are probably swept away reduced copper leaving a clean corroded aluminium surface. Since aluminium surface is constantly polished during the reaction, it is again believed that the reaction is chemically controlled.

Cupric solution erodes deep into aluminium surface leaving a depressed surface morphology (Fig. 4). Nevertheless, cuprous solution creates some bowl type of patterns and produces minimal slumping on the aluminium scrap surface (Fig. 5). These hemispherical pits or bowl type of patterns cover a range of effective areas with no characteristic dimension revealed. They comprise a film of non-uniform thickness which has apparently cracked during drying or upon examination in the vacuum of the scanning electron microscope. However, detail analysis on the composition was difficult to be conducted in our lab setup.

Analysis of recovered copper powder

Effect of aluminium surface area: All experiments were conducted by using aluminium scraps bar with 266, 570, 760 and 1140 mm² exposed surface areas. The solutions pH values were adjusted to 4.02 and the experiments were conducted at 25°C. The recovered copper powder was analyzed for purity after 60 min. Result shows that active aluminium scrap surface area plays an important role in controlling copper recovery efficiency and its purity, as shown in Fig. 6. Smaller surface area recovers higher purity of copper powder but has to sacrifice for slower reaction rate and low copper recovery.

Effect of cupric and cuprous cementation process: All cementation experiments were conducted at 25°C and pH 4.02. The recovery process started after aluminium scrap bar with 1140 mm² surface area was immersed into prepared copper solution. Recovered copper powder was collected after 60 min. From Table 2, cuprous ion gives better copper recovery efficiency and cements higher

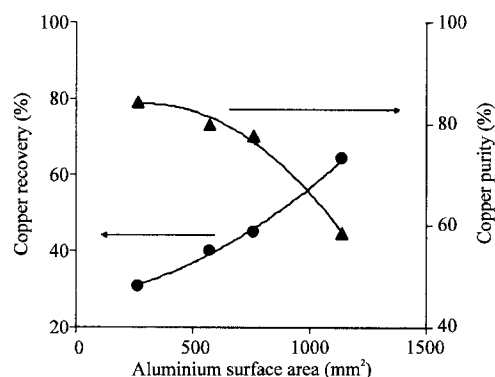


Fig. 6: Plots of copper recovery efficiency (●) and its purity (▲) versus aluminium surface area

purity copper. Therefore, all the experiments in this study were carried out in nitrogen atmosphere to avoid the oxidation of cuprous ion and strong chloride media helps to complex and dissolve cuprous intermediate for preventing sludging.

Application on industrial wastewater: A sample of spent solution was obtained from a local printed-circuit etching plant and its characteristics are given in Table 3. Carved waste aluminium cans were supplied by a local aluminium scraps collecting company.

Applying the findings obtained for the previous section, the copper recovery steps began with addition of 21 g sodium carbonate into 100 g spent solution. The pH of the solution must be greater than 1.7. Nitrogen gas was flowed into the reactor throughout the event. The cementation process started after 4.60 g of aluminium scrap was added into the de-oxygenated vessel. Suspended copper particle was filtered out from the solution after an hour of cementation. Analysis of the resulting solution indicates 99.3% copper removal and electrogravimetry analysis shows that the recovered copper is 94.4% pure.

The recovery of copper can be enhanced by applying another stage of cementation process to the treated solution, as suggested by Yiu *et al.*^[21]. In their report, recovery of copper was the main objective in stage one. Meanwhile, stage two focused on aluminium chloride production with minimal iron and copper contaminations. The remaining copper and iron was reduced to less than 1 ppm after second stage of treatment finished.

CONCLUSIONS

The copper cementation reaction in strong chloride-based media is constantly to be first order kinetics to Cu²⁺. The cementation of cupric ion occurs in two consequent

electron transfer steps involving soluble intermediate cuprous ion as proposed in previous works. In the present study, cuprous intermediate exists in the recovery pathway of copper.

Strong acid is not required in the cementation system because excess chloride ion washes out cuprous intermediate and copper metal deposits by giving a clean and depressed aluminium surface, as shown in SEM micrographs. These chloride ions help to varnish aluminium oxide layer, complex and dissolve cuprous intermediate in preventing sludging without creating problem in restraining reaction. The activation energy for the process calculated from the Arrhenius plot is found to be 37.12 kJ mol⁻¹, indicating a chemical controlled process.

Application on industrial waste shows encouraging result with more than 99.3% copper removal and acceptable 94.4% copper purity.

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