

# Dechlorination from Sulphate Aqueous Solutions of Zinc Electrolysis by Electrochemical Method

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**Abstract:** To remove chlorine from zinc electrolysis solutions, the electrochemical method was carried out in this research. Copper electrodes with a purity of 99.99% were employed as the anode and cathode. In addition, the effect of applied potential, agitation rate, and reaction temperature on the efficiency of chlorine removal was investigated and dechlorination mechanism was explored. Scanning electron microscopy (SEM) was used to observe the evolution of the chlorine species on the anode surface. Based on the obtained results, the efficiency of dechlorination from electrolysis solution with a  $\text{Cl}^-$  concentration of  $295 \text{ mg.L}^{-1}$  in constant values of  $\text{pH} = 5$  and reaction time of 4 h and under optimal applied potential of 0.8 V, agitation rate of 200 rpm, and the reaction temperature of  $25^\circ\text{C}$  turned out to be 42.6%.

**Key words:** Zinc electrolysis, dechlorination, electrochemical method, effective parameter.

## Introduction

The chloride ion is one of the important impurities of hydrometallurgical zinc production industry that enters zinc sulphate leaching solution and then electrolysis section through two procedures of water impurity (low concentration) and the plant feed. The unauthorized concentration of chlorine causes many and sometimes irreparable problems in various stages of this process.

The authorized concentration of chlorine in electrolysis solution of zinc production companies is  $100 \text{ mg.L}^{-1}$  (Wu et al., 2013). This is the ideal and appropriate value for zinc hydrometallurgy process. Zinc electrowinning process can be also implemented with higher chlorine concentrations ( $500 \text{ mg.L}^{-1}$ ), but it is difficult and sometimes very harmful.

In addition, zinc electrolysis efficiency also decreases. High concentration of chlorine in the initial feed also

forces some industrialists to separate raw feed and chlorinated feed, despite its high grade of zinc.

In general, chlorine causes a lot of problems in the final stage of zinc production process, i.e. electrolysis stage. One of the most important problems of chlorine in zinc electrowinning halls is severe corrosion of lead anodes. Furthermore, during the electrolysis process, chlorine gas is produced by doing some chemical reactions, which contaminates the work environment and endangers the health of staff (Bodson et al., 1997).

Some other problems of chlorine in zinc electrolysis section are increase of lead content in electrolyte due to anode corrosion and reduction of the grade of cathode zinc (Wu et al., 2013), lack of proper adhesion on the cathode surface and the possibility of re-separation of zinc from the cathode and re-enter into the electrolyte solution (Jang-sop et al., 2012), lack of proper separation of zinc sheet from the surface of the cathode at the time of zinc sheet separation (Nusen et al., 2012),

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### Abbreviations

Rpm: Round per minute

LDHs: Layered double hydroxides

rough surface of the anode due to corrosion and subsequently, increase in energy consumption, corrosion of cathode and dissolution of deposited zinc from the cathode surface and reduction of current efficiency (Liu et al., 2015).

Various dechlorination methods have been attempted each with strengths and weaknesses. One of these methods is chlorine precipitation using silver that was proposed by Swinkels et al. (1980), in which chlorine is deposited as AgCl(s) salt. This method has significant efficiency, but it seems not to be economically practical. This is because a great amount of silver used in this process is lost.

Another method is chlorine precipitation using copper that was proposed by Bodson (1997) and its main disadvantage is the loss of significant amount of zinc and copper during the process and needs for continuing controlling of temperature and pH.

Another disadvantage of this method is producing CuCl residues during this process which is still hazardous for the environment. Recently microwave metallurgy is used for dechlorination of CuCl residues. (Shuai-dan et al., 2014).

Ion exchange method is also used for dechlorination. In this method, ZnAl – NO<sub>3</sub> LDHs has been used as the ion exchanger and it helps to remove chloride ion from the aqueous system but one of the main disadvantages of this method is high zinc loss during the process (LV et al., 2009). Another experimental investigation is photochemical oxidation of chloride ion by ozone O<sub>3</sub> in acid aqueous solution where there is an interaction between ozone and chloride ion under ultraviolet illumination. The final products of this reaction are chlorine Cl<sub>2</sub> and chlorate ClO<sub>3</sub><sup>-</sup>. Despite the high efficiency of chloride removing, producing chlorate ion and chlorine gas emission had their environmental impacts (Levanov et al., 2015).

In all the above-mentioned methods, chlorine is removed from the solution as deposition. Therefore, a costly filtration operation is required for dechlorination, which greatly causes these methods not to be economically feasible. The electrochemical method is so useful and attractive due to its simplicity, low operational costs, and lack of need to the costly filtration process. Electrochemistry has various uses in industries. One of its main applications is metal production through

electro- winning method and removal of impurities from waters and waste waters (Fernandes, 2016).

In recent years, the use of electrochemical methods to remove chlorine impurities from concrete (Gerardo et al., 2000; Orellan et al., 2004; Huang et al., 2014; Liu et al., 2016), cast iron Artefacts (Liu et al., 2008), and waste water (Mustafa, 2014) has been investigated. However, the use of this method for dechlorination of electrolysis solutions in zinc processing companies has not been studied. According to the dechlorination from sulphate solutions of electrolysis unit by electrochemical method along with the investigation of the amount of applied potential, agitation rate, and reaction temperature have been studied.

### Materials and Methods

A simulated zinc electrolysis sulphate aqueous solution was prepared and used in all experiments. Sulphuric acid H<sub>2</sub>SO<sub>4</sub> and sodium hydroxide NaOH were used to regulate pH and silver nitrate AgNO<sub>3</sub> and potassium dichromate K<sub>2</sub>CrO<sub>4</sub> were used to determine chlorine concentration through Mohr method.

All these materials were made in Merck Company, Germany. Water distilled twice by American SDL 12L device made in OES Co. was used to wash the electrodes.

### Solution Analysis

The initial chlorine concentration of the initial solution was determined using Mohr titrimetric analysis. Then, to determine the amount of copper and zinc in the solution, atomic absorption spectrometer was applied. In Mohr analysis, 10 ml of the sample was first poured into an Erlen and five drops of potassium chromate were then added. Titration process was done using silver nitrate AgNO<sub>3</sub>. When the colour of the solution is changed to yellow, titration operation is stopped and the volume of silver nitrate consumed is recorded. To ensure the test results and reduce errors, this operation was repeated three times and the average was obtained. To determine the chlorine concentration in mg.L<sup>-1</sup>, the following formula was used:

$$\text{Cl (\%)} = \frac{V \times M \times 35.5 \times 1000}{10} \quad (1)$$

where  $V$  is the volume of consumed silver nitrate in ml, and  $M$  is the molar mass of silver nitrate.

Based on the obtained results, the contents of simulated zinc sulfate aqueous solution were Zn<sup>2+</sup> 65 g.L<sup>-1</sup>, Cu<sup>2+</sup> 1 g.L<sup>-1</sup>, H<sub>2</sub>SO<sub>4</sub> 120 g.L<sup>-1</sup> and chloride ion concentration 295 mg.L<sup>-1</sup>.

### Electrochemical Dechlorination

To carry out each experiment, 500 ml of the electrolyte solution containing chlorine was poured into a beaker with 600 ml capacity. The pH was measured using pH meter device, Mettler-Toledo GmbH, MP230 made in Switzerland. Copper sheets as electrodes with a purity of 99.99% and with a 22 cm<sup>2</sup> surface area as anode and cathode electrodes were washed and cleaned using distilled water to remove surface contaminants before starting the experiments. Submerged area of each electrode was measured and was equal to 9 cm<sup>2</sup>. Electrodes were connected to positive and negative poles of the power supply using interface wire. Potentiometer device, model Leybold Didactic GMBH, with a D.C. current and a power of 300 V and 50 A made in Germany was used to apply different potentials to the solution.

Digital multimeter device (DT-9205A) was also used to measure and record potential applied on the solution. Digital multimeter was connected to a power supply and then the beaker containing the solution was placed on a magnetic stirrer. Heating and stirring were done using a magnetic stirrer, model C-MAG HS 10, made in IKA Germany. The fully insulating foam was also used to keep the distance of electrodes (a constant distant of 1.5 cm) and prevent their interaction during agitation. Figure 1 shows an image of assembled system used in the electrochemical experiment.

To investigate the effect of applied potential on dechlorination, various values of potential in a range of 0.2 to 2.5 V (an error of  $\pm 0.15$ ) were tested. After determining the optimal value of potential, the effect of temperature and agitation rate on dechlorination efficiency has also been studied. after electrochemical dechlorination, the surface morphology of the copper anode was observed by SEM (Semini SEM300, ZEISS Co., Germany).

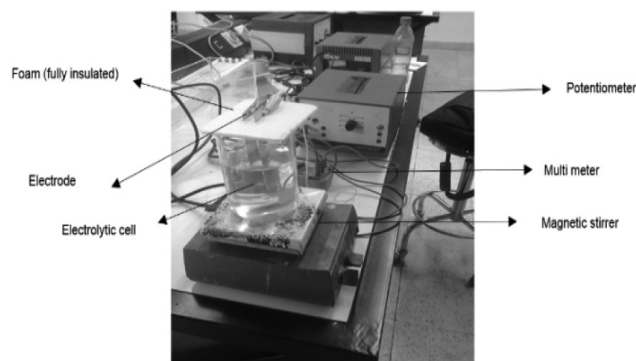


Figure 1: System assembled to carry out electrochemical experiments.

In the end of each test, electrodes were removed from the solution and the sample was filtered. Then, 30 ml of it was kept in a specific container for chlorimetry analysis. For the next experiments, the beaker was again washed with distilled water and new electrodes with the same dimensions and characteristics were replaced.

## Result and Discussion

### The Effect of Applied Potential

Figure 2 shows the effect of the potential applied on dechlorination efficiency. According to this figure, by increasing potential from 0.2 to 0.8 V under fixed chloride concentration of 295 mg.L<sup>-1</sup>, dechlorination efficiency increases from 12.7% to 42.6%. Greater increase of potential up to 2.5 V leads to the reduction of dechlorination to about 17%.

According to Figure 3, by applying an external potential between the anode and cathode, the electron is discharged from the copper anode and transferred to the cathode and subsequently, copper ion was released in the solution (anode has a positive charge and cathode has a negative charge).

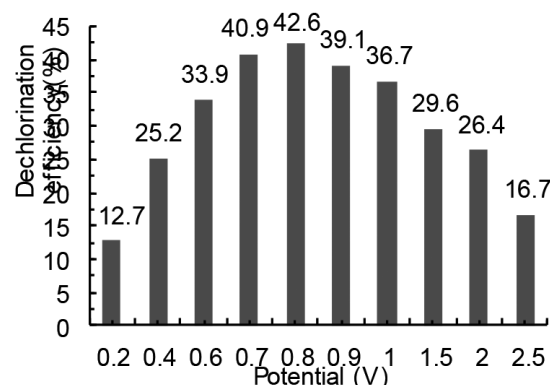


Figure 2: The effect of applied potential on dechlorination efficiency.

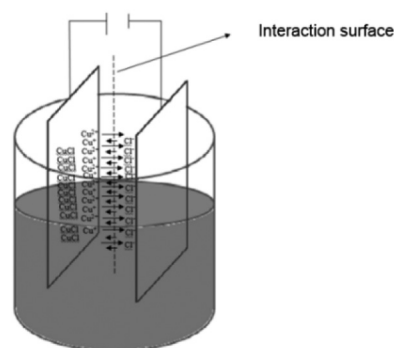
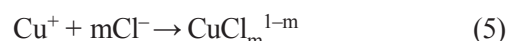
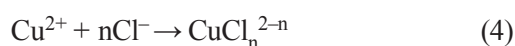
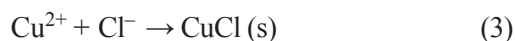


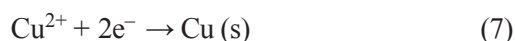
Figure 3: Dechlorination mechanism by electrochemical method.

Copper oxide and  $\text{Cu}^+$  and  $\text{Cu}^{+2}$  ions are produced and accumulated near the surface of the anode. Because of the electric field, ions of copper are distributed toward the cathode (-). This is while chlorine ions that are negatively charged move toward the anode (+) and these ions meet in an interaction area and the following reactions occur:



As it can be seen, there are different forms of  $\text{Cl}^-$  complex  $\text{CuCl(s)}$ ,  $\text{CuCl}_n^{2-n}$ ,  $\text{CuCl}_m^{1-m}$  in  $\text{Cu} - \text{Cl}^- - \text{H}_2\text{O}$  system. However, interactions that lead to dechlorination from solution are those that form solid  $\text{CuCl(s)}$  complex (first and second interactions). This complex is deposited on the anode surface after the formation and subsequently, the concentration of chlorine in the solution is reduced. Other forms of chlorine complexes with copper are solution and are not effective in decreasing the chlorine concentration. Another issue is that some of the copper ions pass through the interaction area and are reduced by getting electrons from the cathode and deposit on the cathode surface.

The following reactions take place in the cathode:



According to the above reactions, some amount of copper released from the anode is like to be discharged and deposited on the cathode surface and the hydrogen ions spewing from solution as gas (Wu et al., 2013).

According to Figure 2, it can be seen that by increasing the potential to 0.8 volts, dechlorination efficiency increases and then decreases. Under the potential of 0.8 volts, the reactions for the formation of  $\text{CuCl (s)}$  are carried out more and better and concentration of chlorine in the solution is reduced. In potentials of higher than 0.8 volts,  $\text{CuCl}_n^{2-n}$  and  $\text{CuCl}_m^{1-m}$  complexes are formed that do not affect the reduction of chlorine concentration in the solution (which is due to low stability).

Based on the results and observations, in potentials higher than 1 V, the copper anode was heavily corroded and with the passage of time, the colour of the solution became light blue and in higher potentials, it became dark blue that was due to the increased copper ions

in solution as well as the formation of  $\text{CuCl}_n^{2-n}$  and  $\text{CuCl}_m^{1-m}$  complexes. In Figure 4, an image of solution under experiment has been shown. In potential of 1.5 volts and after a retention time of two hours, the colour of solution completely changed into blue.

To prove the above claim and determine the concentration of copper in solution, the sample was analyzed (atomic absorption). Copper concentration was  $145.71 \text{ mg.L}^{-1}$ . Figure 5 shows an image of the anode (in the potential of 1.5 volts) that is high corroded after the experiment, which indicates that the potential increase causes anode to participate in reaction more rapidly. Another point was that with the increase of potential, the amount of deposit at the electrodes (especially cathode) was increased, which indicates that electrodes attract more impurities under high potentials.

### The Effect of Agitation Rate

According to Figure 6, by increasing agitation rate up to 200 rpm, dechlorination efficiency is also substantially increased. However, in the absence of agitation, dechlorination efficiency is low and turns out to be



Figure 4: The colour of solution before (left) and after (right) experiment.

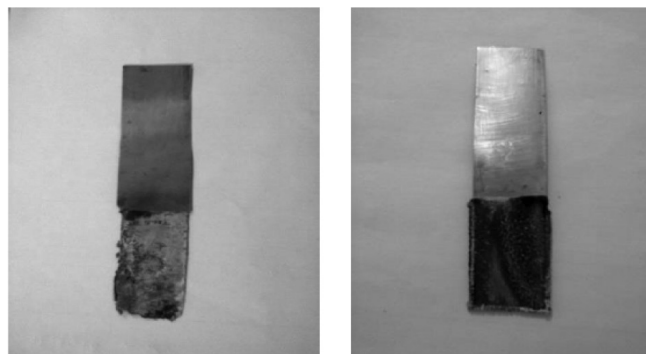
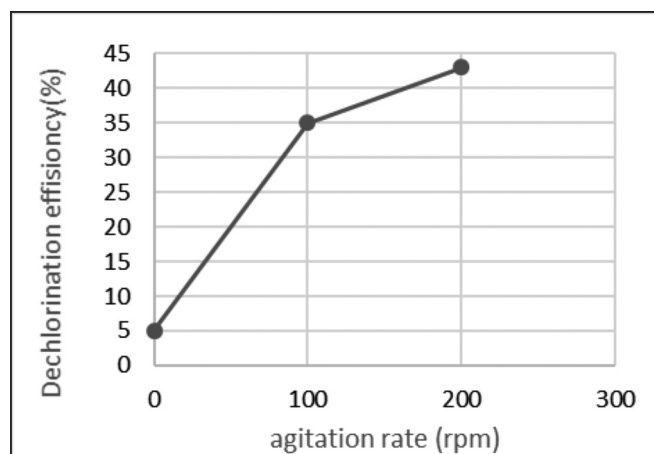


Figure 5: High corrosion of anode (left) and increased impurity (right) under high potentials.





**Figure 6: The effect of agitation rate on dechlorination efficiency.**

only 5.2%. Copper is easily oxidized in the absence of agitation and in an electric field and copper ions accumulate near the anode. This phenomenon causes the surface of the anode to be ineffective, and also reduces the number of copper ions in the electrolyte; subsequently,  $\text{CuCl (s)}$  formation is reduced and dechlorination efficiency is also reduced.

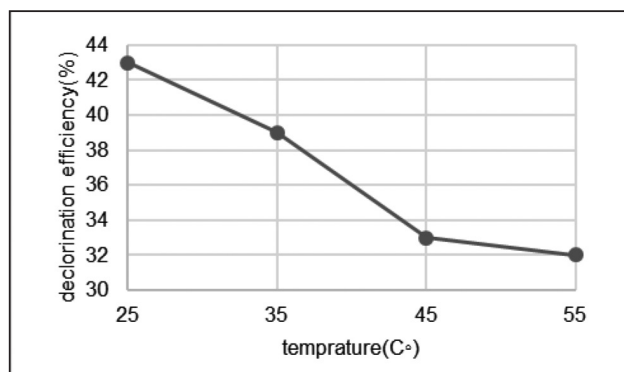
In contrast, by creating agitation, mass transfer is accelerated. Copper ions quickly leave the anode surface and do more and better chemical interactions with chlorine ions that are accumulated close to the anode (because of the electric field and the opposite charge); therefore, the resulting interactions are done more completely,  $\text{CuCl (s)}$  complex is formed, and dechlorination efficiency is increased.

### The Effect of Reaction Temperature

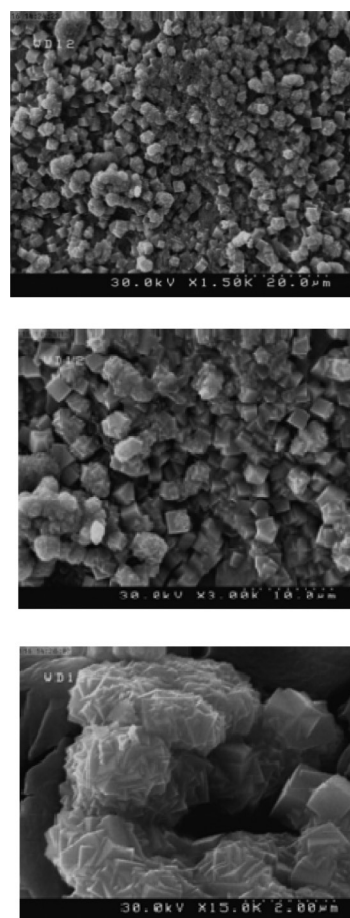
Temperature is an important factor in many chemical reactions. With the increase of temperature, the (kinetic) rate of chemical reactions usually increases. However, as in Figure 7, increasing temperature from 25°C to 55°C, dechlorination efficiency has declined. This is because the electrochemical dechlorination process is mainly controlled by charge transfer step rather than the chemical reaction. In other words, with increasing temperature, the kinetics of reactions of the solution complex formation is increased and opportunities for solid  $\text{CuCl(s)}$  formation are reduced.

### Investigating the Anode Surface by SEM after Electrochemical Dechlorination

To observe species deposited on the anode surface, scanning electron microscopy (SEM) was used with different magnifications. Based on Figure 8, anode surface is completely covered with different species



**Figure 7: The effect of reaction temperature of dechlorination efficiency.**



**Figure 8: SEM images of the anode surface (different magnifications).**

and there is no empty space. Due to the difference in shapes of electron micrographs, it can be concluded that the anode surface is not just covered with copper and chlorine ions, but other (anion) impurities are absorbed to the anode during the reaction and have deposited on it. One of the anions that are likely to be attracted to the copper anode ( $\text{S}^{2-}$ ) is sulphur that requires more research.

## Conclusions

1. Dechlorination by electrochemical method depends on parameters of applied potential, reaction temperature, and agitation rate.
2. Potential applied to the electrodes is the most important parameter in determining the chemical reactions in solution. Therefore, finding the optimum potential is the first step for dechlorination by electrochemical method. With the gradual increase of the potential from 0.2 to 0.8 V, the removal efficiency is also substantially increased. However, in potentials of higher than 0.8 volts, removal efficiency has a declining slope.
3. Results showed that with increasing agitation rate and decreasing reaction temperature, the removal efficiency of chlorine increases.
4. Based on SEM, anode surface is completely covered with different species and there is no free space. In addition, the anode surface is not just covered by copper and chlorine ions, but other (anion) impurities are absorbed to the anode during the reaction and have deposited on it.
5. The highest removal efficiency turned out to be 45.9% at a potential of 0.8 volts, agitation rate of 200 rpm, and the reaction temperature of 25°C.
6. Electrochemical method is a simple, easy, low-cost method with a relatively acceptable performance for reduction of chlorine concentration that can be implemented in zinc production industry.

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