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# The recovery of metallic cadmium from the cadmium containing residue in a electrolytic zinc plant

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**Abstract:** This report presents a process for recovery and purification of metallic cadmium from a residue of the purification process for zinc sulphate solution in Thai Nguyen electrolytic zinc plant. The cadmium containing residue was digested by sulfuric acid of 140 g/l at a temperature of $70^0$C for 4h, the obtained solution will be purified for removal of some impurities such as iron, copper, etc. The purified solution with concentration 50 g/l of Cd, 120 g/l of sulphuric acid and 0.1 g/l of gelatin as an additive will be subjected to an electrolysis process with current density of 50 $A/m^2$ for recovery of metallic cadmium. The temperature of electrolyte is lower $40^0$C. Overall recovery of cadmium is 90%, purity of the obtained metalic cadmium is up to 99.0%.

**Keywords:** *cadimium, electrowinning cadmium,…*

## I. INTRODUCTION

Metallic cadmium has various technological applications such as in nickel–cadmium and silver–cadmium storage batteries, functional alloys and coatings [1]. Cadmium is used for the synthesis of chalcogenide compounds and the production of semiconductor intermetallics and also in control rods in nuclear power plants [2].

Cadmium does not form separate deposits, but is an element associated with zinc and complex ores. Therefore, cadmium production technologies are developing in step with methods for production of zinc and lead. Almost all cadmium producing installations are part of zinc and lead producing facilities [3].

The main starting materials for cadmium are byproducts of zinc and lead metallurgical processes (copper–cadmium cakes, dusts left after lead blast smelting, etc.). Cadmium can be extracted from these materials either by the pyrometallurgical (fractional distillation) or hydrometallurgical method or using a combination of these methods. The most widespread technique is the hydrometallurgical method, which consists of the following operations: oxidation of cadmium; leaching; cleaning of the solution and precipitation of the cadmium sponge; oxidation of the sponge, its repeated dissolution and cleaning of the solution; electrowinning; smelting of cathodic cadmium [3, 4].

Recovery of cadmium by hydrometallurgy combined with electrolysis is commonly used for the recovery of cadmium in the process of purifying zinc sulfate solution in a electrolytic zinc plant [1,2,4]. This method has advantages of simple equipment, low chemiacls consumption (using sulfuric acid as a byproduct of zinc metal production) and

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high purity of metallic cadmium product (up to 99%).

The process of producing cadmium by hydrometallurgy method combined with electrolysis can be discribed as follows:

*Cadmium dissolution:* cadmium in the cadmium containing residue is transferred to solution by using dilute sulphuric acid

$$Cd + H_2SO_4 \longrightarrow CdSO_4 + H_2\uparrow \quad (1)$$

Other metallic impurities are dissolved in the solution according to the reaction

$$Me + H_2SO_4 \longrightarrow MeSO_4 + H_2\uparrow \quad (2)$$

*Purification of cadmium sulphate solution:* Adjust the pH of the obtained solution to remove iron, aluminum by hydrolysis. Other impurities such as Cu can be removed by cementation using Cd powder:

$$Me^{2+} + Cd \longrightarrow Me + Cd^{2+}$$

*Electrolysis of cadmium sulphate solution to obtain metallic cadmium:*

Cathode reaction:

$$Cd^{2+} + 2e^- \rightarrow Cd\downarrow$$
$$E_o = -0.4V \quad (3)$$

Anode reaction:

$$20H^- - 2e^- \rightarrow H_20 + {}^1/_20_2\uparrow$$
$$E_0 = 1.23V \quad (4)$$

Generally, electrolysis reaction of cadmium sulfate solution can be discribed as follows:

$$CdS0_4 + H_20 \longrightarrow Cd\downarrow + H_2S0_4 + {}^1/_20_2\uparrow - Q \quad (5)$$

During the electrolysis of an aqueous solution of cadmium sulphate, metals more electropositive than cadmium (e.g. Cu) will plate at the cathode in addition to cadmium, while zinc will not plate at the cathode due to more electronegative ($E_o$ = -0.76V) than cadmium So the presence of zinc in the solution has no significant effect on the quality of cadmium obtained. Cadmium metal produced by this method has a high purity (Cd > 99%).

## II. EXPERIMENTALS

### A. Preparation of cadmium sulphate solution

Cadmium residues composition is mainly Zn 13%; Fe 0.85%; Pb 0.25% and other impurities such as Al, Ni, Cu, with very small amounts. The residue will be dissolved by sulphuric acid. Cadmium, zinc and some other metallic impurities will be together dissolved by sulphuric acid. The removal of Al and Fe from the solution is easier by using hydrolysis method, by adjusting pH of the solution to pH 5.2 - 5.4, Al and Fe precipitate as $Al(OH)_3$ and $Fe(OH)_3$ then will be removed from the solution. Ni and Cu can be removed by cementation method. Zn will remain in the solution. The optimum conditions for cadmium dissolution are as follows:

- Solid/liquid ratio: 1/5.
- Concentration of sulfuric acid 140 g / l.
- Temperature: 70$^0$C.
- Time of digestion: 4h.

Under these conditions, cadmium recovery is up to 90%; The obtained cadmium sulphate solution contains: Cd 80 g/L, Zn 20 g/L, the impurities such as Fe, Cu, Al, Ni are of trace amount.

### B. Cadmium electrolysis

The feed electrolyte was prepared as discribed above. The cadmium Electrolysis was studied with the experimental conditions are as follows: The cathode current density 35-60 A/m$^2$; Concentration of in electrolyte feed 30-70 g/l of cadmium, 90-150 g/l of free $H_2SO_4$; Temperature of the electrolyte: 25-60 $^0$C and gelatin concentration: 0 to 0.3 g/l.

Bench scale electrolysis was carried out in a cell of inert plastic construction with working volmes of 800 ml, using lead alloy

(Pb/Ca/Sn) anodes. Aluminum alloy (HS1A) was used for the cathode. The cathode current density was 35- 60A/$m^2$. Operating current was calculated assuming a current efficiency of 80%. Cell voltage was approximately 2.4V in all tests. The temperature during the tests ranged from 25 to 60°C.

Power to the cell was provided by a constant current DC rectifier supply.

Electrolyte was fed continuous in to the cell, and allowed to overflow to maintain a set cathode immersion level and the cell was operated for 4h in batch mode to bring the cell contents to the spent electrolyte conditions for continuous mode.

At the end of that time, the cathode was removed, weighed and cleaned. The plated cadmium was dried to determined the weigh and the actual current efficiency and with that information, the flow of electrolyte for the continuous cycle was corrected.

The current efficiency was calculated by using Faraday law of electrolysis. Faraday's laws can be summarized by

$$m = \left(\frac{It}{F}\right)\left(\frac{M}{z}\right)$$

$$H = m_r / m$$

where:

- $m$ is the mass of the substance (theoretically) liberated at an electrode in grams
- $m_r$ is the practically obtained mass of the substance at an electrode.
- $I$ is the constant current of electrolysis
- $F = 96485$ C $mol^{-1}$ is the Faraday constant
- $M$ is the molar mass of the substance ;
- $z$ is the valency number of ions of the substance (electrons transferred per ion);
- $t$ is the total time the constant current was applied;
- *H is the* current efficiency .

For cadmium electrolysis, M=112.41g; z=2.

The plated cadmium at the cathode will be analyzed by ICP-MS to determine the contents of cadmium and other impurity elements.

## III. RESULTS AND DISCUSSION

### A. Effects of organic additives

The effect of an organic additive gelatin on the electrolysis of cadmium from acidic sulfate solutions are studied.

*Experimental conditions:*

- Current density 50 A/$m^2$.
- Cadmium concentration in the electrolyte: 50 g/l.
- The concentration of free $H_2SO_4$ : 90 g/l.
- Temperature of electrolyte: 35 $^0$C.

Experimental results are presented in Figure 1.

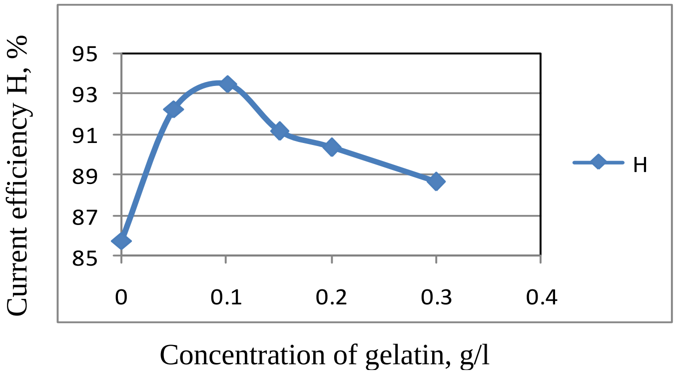

**Fig.1:** Effect of the concentration of gelatin to the current efficiency

It is observed that addition of gelatin increases the current efficiency and decreases the energy consumption. Gelatin when present in the solution polarizes the cathode causing the electroreduction of cadmium at more negative potentials. The presence of gelatin affects the degree of crystallinity of the electrodeposits indicating that the deposits are also more ductile. Scanning electron micrographs of cadmium deposits obtained in the presence of magnafloc show that compact deposits are formed with an instantaneous nucleation and growth mechanism. It is evident that the presence of gelatin decreases the number of grains and increases the sizes of the crystallites.

Since cadmium is very prone to dendritic deposition. The cadmium precipitate create multiple spikes, thickness of the cadmium layer are different. To overcome this drawback, a small amount of gelatin can be added as a surface-active substances into electrolyte solution. From Figure 1, it is found that the concentration of gelatin 0.1 g/l to achieve the highest current efficiency. When the gelatin concentration exceeds 0.1 g/l, the current efficiency decreases due to reducing of polarization.

## B. Effect of cadmium concentration

*Experimental conditions:*

- Current density 50 A/m$^2$.

- Cadmiumconcentration in the electrolyte solution: 30 - 80 g/l.

- The concentration of free $H_2SO_4$ : 90 g/l.

- Electrolysis temperature : 35 $^0$C.

- The concentration of gelatin: 0.1 g/l

Experimental results are presented in Figure 2.

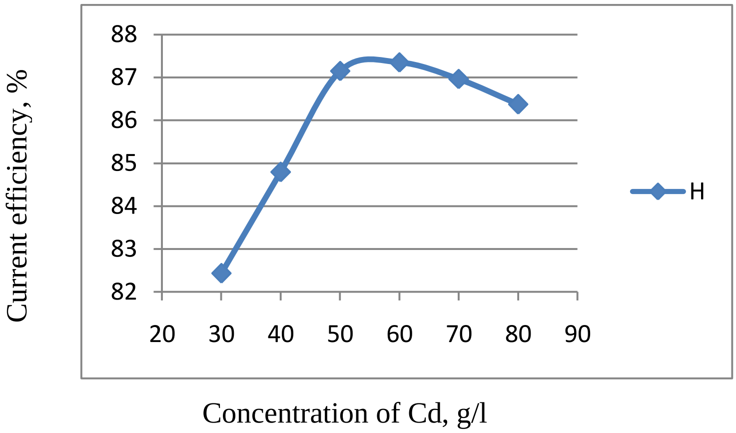

**Fig. 2.** The effect of cadmium concentration on the current efficiency

From Figure 2, we see that, when the cadmium concentration in solution increased from 30 to 60 g/l, the current efficiency increases. When cadmium concentration is higher than 70 g/l, the current efficiency does not increase but somewhat diminished.

## C. Effect of free acid concentration

*Experimental conditions:*

- Current density 50 A/m$^2$.

- Cadmiumconcentration in the electrolyte solution: 50 g/l.

- The concentration of free $H_2SO_4$ : 90 - 150 g/l.

- Electrolysis temperature : 35 $^0$C.

- The concentration of gelatin: 0.1 g/l

Experimental results are presented in Figure 3.

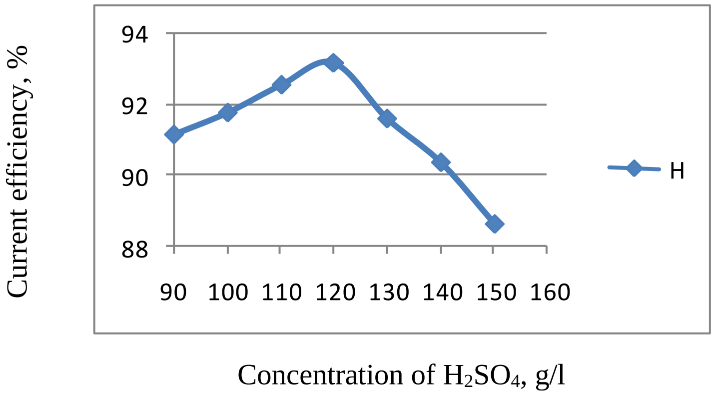

**Fig. 3.** Effect of $H_2SO_4$ concentration to current efficiency

From Figure 3, when increasing free acid concentration, the current efficiency increased. Maximum of current efficiency is reached when $H_2SO_4$ concentration is about 120 g/l. When further increasing the solution acidity, the current efficiency decreased due to the liberation of hydrogen. Hence the choice of free concentration of $H_2SO_4$ in the electrolyte solution is 120 g/l. The current efficiency reached 93.20 %.

It was determined that working with a solution in the feed of more than 30 g/L of cadmium and between 100 to 120 g/L of sulphuric acid, it was possible to obtain plated cadmium without dendritic deposition and with a higher current efficiency.

### D. Effect of current density

*Experimental conditions:*

- Current density 35 - 60A/$m^2$.
- Cadmiumconcentration in the electrolyte solution: 30 - 80 g/l.
- The concentration of free $H_2SO_4$: 90 g/l.
- Electrolysis temperature : 35 $^0$C.
- The concentration of gelatin: 0.1 g/l

Experimental results are presented in Figure 4

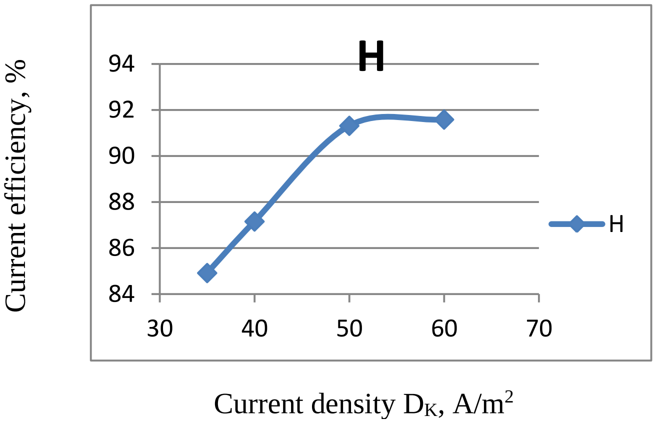

**Fig. 4.** The effect of current density

From Figure 4, when changing current density in the range of 35-50 A/$m^2$, the current efficiency increased from 84.91% to 91.31%. However, when the current density is up to 60 A/$m^2$, the current has also increased, but not significantly. Hence the choice of current density of 50 A/m2 for cadmium electrolysis process is suitable.

Smooth cathode deposits of cadmium were difficult to produce. This was attributed to the nature of the electrolyte.

Progressive improvements were however achieved and a better deposit was obtained at higher current efficiency as changes were progressively made to the electrolyte acidity;

### E. Effect of the temperature

*Experimental conditions:*

- Current density: 50 $A/m^2$.
- Cadmium concentration in the electrolyte: 50 g/l.
- The concentration of $H_2SO_4$: 120 g/l.
- The concentration of gelatin: 0.1 g/l

Experimental results are presented in Figure 5.

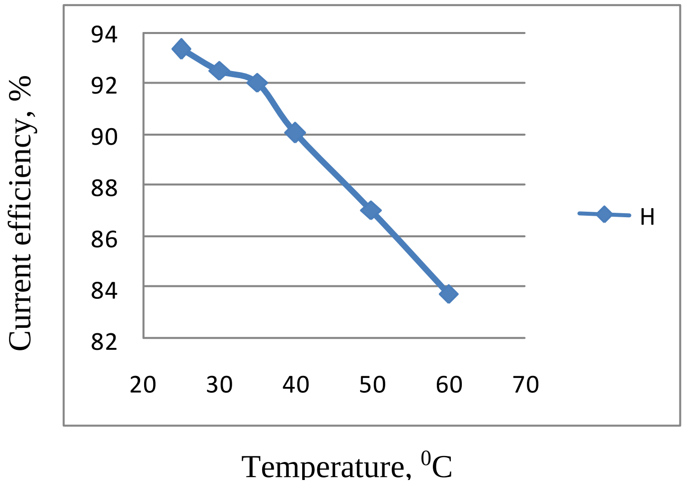

**Fig. 5.** The effect of temperature to the current efficiency

From Figure 5, when increasing the temperature of electrolyte, the current performance significantly reduced at temperatures above $40^0C$. Heating the electrolyte can increase electric conductivity, increase the liberation of gases and reduce the electric potential of electrolysis cells. But the heating increases the electrolytic dissociation of hydration ions, reduces dessired effect of surface-active substances, therefore chemical polarization can be reduced. Heating promote diffuser, convection, hydrogen liberation and leading to reducing current efficiency. Thus the electrolysis temperature should be kept lower than $40^0C$.

## III. CONCLUSIONS

Based on the experimental results carried out in this work, the optimum conditions for cadmium recovery by electrolysis are as follows:

- Current density : 50 $A/m^2$.
- Concentration of cadmium in the electrolyte: 50 g / l.
- Concentration of $H_2SO_4$ : 120 g/l.
- Temperature : < 40 $^0C$.
- Concentration of gelatin: 0.1 g/l.

In the conditions listed above, the electric current performance is 90% or higher.

## REFERENCES

1. Dinh Pham Thai, Nguyen Kim Thiet. *Theory of metallurgical processes - Electrolysis*, Viet Nam education publishing house, Ha Noi, 1997.
2. Le Xuan Khuong, Truong Ngoc Than. *Theory of metallurgical processes - hydrometallurgical*, Viet Nam education publishing house, Ha Noi, 1997.
3. Phung Viet Ngu, *Preparation of zinc*, Publisher University and vocational schools, Ha Noi, 1981.
4. Pham Xuan Kinh, Final report entitled "Study on the recovery of rare elements: Cd, In the intermediate residue of electrolytic zinc plant Company *in Song Cong – Thai Nguyen"*, 2008.
5. Mohammad Sadegh Safarzadeh[a,b], Davood Moradkhani[a, b, c], *The electrowinning of cadimi in the presence of zinc*.Hydrometallugy, Volume 105, Issues 1-2, December 2010.