Zinc recovery from the water-jacket furnace flue dusts by leaching using the electrowinning return solution.

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Abstract

The Zinc containing dusts from the copper matte smelting in water-jacket furnaces at the Lubumbashi Plants whose composition is given in Table 1 are leachable in aqueous sulphuric acid solution. Leaching the dusts using a 100 g/l solution of sulphuric acid does not produce the required 85 g/l zinc minimum level in the solution submitted to the electrolysis. Return solution from the zinc electrolysis containing 100 g/l H\textsubscript{2}SO\textsubscript{4}, 35 g/l Zn\textsuperscript{++}, 10 g/l Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} as leaching agent yields a 55 g/l zinc solution. The electrolysis of the purified solution is controlled by an electrons transfer regime.
This observation was confirmed by the constant cathode overpotential and the negligible effect of the flow rate on the overall electrolysis cell potential.

Optimum conditions for the zinc electrolysis in a SEC-C.C.S type cell were determined.

**Keywords**

Zinc, dusts, recovery, electrowinning return solution, SEC-C.C.S. cell.

1. **Introduction**

The copper matte smelting in water-jacket furnaces in Lubumbashi plants yields three separated phases consisting of a matte, a slag and the dusts. The copper sulphide and the noble metals, i.e. gold and silver, are collected in the matte phase which is further processed in a Pierce-Smith converter. The slag phase is formed and its composition optimised to collect the oxide phases. The third phase from the water-jacket furnace, the dusts, naturally collected all the volatile compounds at the operating temperature of the furnace, at about 1250°C. The dusts also contain particles resulting from the wear of the agglomerated concentrate and other additives fed at the top of the furnace mouth and drawn out of the furnace by the ascending air current. Air is blown at the bottom of the furnace crucible to burn the combustible coal and to oxidise part of the iron sulphide contained in the concentrate. The size of the mechanically generated dusts ranges from 10 to 500 μm. Copper found in the dusts is hence drawn. There is also the chemically generated dusts due to the volatilisation and oxidation of low-melting temperature metals i.e. Zn, Pb, Cd, Cd, etc. Their particle size ranges from 0.5 to 2 μm. Chemical dusts particles are zinc, lead, cadmium and germanium rich.

Analysis shows that the chemical dusts formed in the water-jacket furnace contain 10 wt% Cu, 17 wt% Zn and 35 wt% Pb. These are very high metal contents
comparatively to the acceptable limits for an economical extraction from ores and concentrates. Such fine dusts with high level in heavy metals will also constitute environmental hazardous if stored as landfill in open areas, where they come into contact with the air and the rain.

Most metallurgical plants recycle the dusts from furnaces at some points of the process or separately treat them in a different section.

Zinc recovery from some industrial wastes and dusts has attracted great interest from researchers as this enables removing heavy metals from potentially hazardous materials stored as landfill. It also adds to the profitability to the metallurgy process as Zinc metal can be obtained as by-product with commercial value.

Zeydabadi et al. [1] have extracted Zinc from blast furnace flue dust containing 2.5% ZnO using sulphuric acid at low concentration followed by a purification process. They have used LIX 622 and LIX 984 cationic exchangers for liquid-liquid solvent extraction and obtained electrolyte containing 60 g/l Zn.

Gouvea and Morais [2] recently undertook a study on the recovery of zinc from industrial residues containing 30 wt% Zn and 26 wt% Cd. The authors optimized the delicate parameters for the cadmium cementation on zinc as 2h reaction time, temperature 50°C, pH 1.5 and 20% excess metallic zinc.

The influence of accompanying minerals on the selectivity of zinc extraction was analysed by T.J. Harvey and W.T. Yen [3]. The authors demonstrated the selectivity dependence of the mineralogy of the concentrate and its intimate relation to the presence of both galena and pyrite.

Comparative study of bioleaching and chemical leaching of zinc concentrates and industrial wastes also attracted the attention of many researchers [4, 5, 6].
A systematic investigation in the integration of bioleaching and chemical leaching as a cost-effective process to treat zinc sulphides was proposed by Adelso D. De Souza and his co-workers [7].

Purification of the leaching liquor is the critical step of the hydrometallurgy of zinc as the electrolysis is rendered inefficient by even low content of some impurities in the electrolyte. The case of recovering zinc from wastes disposed off as landfill is of interest as the starting materials contain zinc in lower contents comparatively to iron and other electropositive metals. Different leaching processes, cementation and liquid-liquid solvent extraction have been suggested and efforts are currently intensified in optimising the recovery of zinc from concentrates and industrial wastes [8, 9, 10, 11].

The present work suggests a hydrometallurgical process for the zinc recovery from the above mentioned dusts using the return solution from the zinc electrowinning as lixiviant. The leaching, purification by precipitation and by solvent extraction, the zinc electrowinning are optimised in laboratory scale.

2. Experimental procedures

The chemical composition of the dusts from the water-jacket furnace is presented in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Ge</th>
<th>MgO</th>
<th>SiO2</th>
<th>S</th>
<th>CaO</th>
<th>Cd</th>
<th>Co</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>17</td>
<td>10</td>
<td>35</td>
<td>0.14</td>
<td>3.85</td>
<td>3.2</td>
<td>7</td>
<td>6.8</td>
<td>0.89</td>
<td>0.24</td>
<td>2</td>
</tr>
</tbody>
</table>

The hydrometallurgy route is foreseen as possible treatment process for the zinc extraction from these dusts considering the low sulphur content.
2.1. **Leaching**

Acid leaching in a slightly oxidizing atmosphere was considered.

The typical reaction is symbolised by Equation (1).

\[ MO + H_2SO_4 \rightarrow MSO_4 + H_2O \]  

(1)

M may represent Zn as well as Cu, Fe, Cd, Co or Ge. The leaching solution will therefore contain ions whose reduction potentials are higher than the Zn\(^{2+}/\text{Zn}\). Elimination of those ions (Cu\(^{2+}\), Fe\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\) and Ge\(^{2+}\)) from the leaching solutions is necessary before electrolysis or cementation of zinc.

Sulphuric acid solution at 100g/l was used to dissolve zinc from the dusts. The acid solution was heated up to 55°C and vigorously stirred at 900 rpm. Dusts were introduced into the solution containing reactor in the ratio 100g dusts for 700ml acid solution. 7.2g Fe\(_2\)(SO\(_4\))\(_3\) were also added to make the medium slightly oxidizing. The leaching process took 2h, and the leaching mixture filtered was analysed by Atomic Absorption Spectrometry.

2.2. **Purification**

The zinc electrolyte should be free of Cu\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\), Ge\(^{2+}\) and Sb\(^{3+}\) ions as these will deposited first and hence reduce the current efficiency during the electrowinning and deteriorate the properties and zinc metal. Those impurities make brittle the zinc galvanising shell.

The highest acceptable concentrations of impurities in zinc electrolyte are given in
Table 2: Admissible concentrations of impurities in the zinc electrolysis [1, 12]

<table>
<thead>
<tr>
<th>Element</th>
<th>[mg/l]</th>
<th>Element</th>
<th>[mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn^{++}</td>
<td>350</td>
<td>Co^{++}</td>
<td>1</td>
</tr>
<tr>
<td>Fe^{++}</td>
<td>80</td>
<td>Ni^{++}</td>
<td>1</td>
</tr>
<tr>
<td>Cd^{++}</td>
<td>12</td>
<td>Ge^{++}</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cu^{++}</td>
<td>10</td>
<td>Cl^{-}</td>
<td>50</td>
</tr>
<tr>
<td>As^{+++}</td>
<td>1</td>
<td>F^{-}</td>
<td>50</td>
</tr>
<tr>
<td>Sb^{+++}</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The overpotential for the H$_2$ formation on cobalt metal electrode is lower than the one for the deposition of zinc metal on the same electrode. This means that zinc electro-deposition will be rendered very difficult if Co$^{++}$ ions are present in higher concentration than an equilibrium limit that may be estimated by the Nernst equation.

$$E = E_0 + \frac{RT}{nF} \log [M^{++}]$$  \hspace{1cm} (2)

Where E is the actual reduction potential of the couple M$^{++}$/M, $E_0$ is the standard potential of the couple in a molar ion concentration at 298K, R is the universal gas constant, T the temperature of the electrolyte, n is the number of electrons exchanged per ion, F the Faraday’s number and [M$^{++}$] the molar concentration of the ion in the electrolyte.

The detrimental effect of the couple Fe$^{+++}$/Fe$^{++}$ on the current efficiency is worth known.
Iron was removed from the electrolyte by precipitation using a saturated lime solution at pH 3.4. 1.5 l of filtrate was treated with saturated lime solution. The pH of the solution was continuously monitored.

The ions Cu$^{2+}$ and Ge$^{2+}$ were removed from the filtrate by solvent extraction using 10% volume LIX 64N in solution in ESCAID 100. This mixture constitutes the organic phase (OP). The regenerating aqueous solution consisted of 100 g/l H$_2$SO$_4$. The ratio of (organic phase OP) / (aqueous phase AP) used is 1:1. The filtrate obtained after precipitation (AP) was mixed to the identical volume of the organic phase, and stirred for five minutes. The mixture was left for twenty minutes decantation and separation between AP and OP. The operation was repeated and the [Cu$^{2+}$] and [Ge$^{2+}$] of the aqueous phase were measured after 6, 12, 18 and 21 extraction cycles. The stirring speed was fixed at 1200 rpm.

Cobalt was eliminated from the electrolyte by cementation using zinc powder, in presence of antimony in acid solution at temperature comprised between 72 and 82°C. Products formed during cobalt cementation on zinc in zinc sulphate electrolytes and the optimal conditions of formation are presented in details in the work by Oluf Bøckman and Terje Østvold [13]. They performed their experiments at temperatures comprised between 71 and 73°C, at about pH 5. Previous work [13, 14], observed that Antimony can act as catalyst of cementation of Co$^{2+}$ by zinc powder. Antimony was added to the solution in three different concentrations, i.e. 15 mg/l, 20 mg/l and 25 mg/l. Three samples of solution were taken at 40 minutes interval up to 120 minutes to monitor the remaining [Co$^{2+}$].

Part of the cadmium is removed during this step.

Cadmium was eliminated from the electrolyte following a two-step cementation at room temperature using zinc powder. The two-step cementation is aimed to
reducing the contact time between the precipitate and the solution to avoid re-
dissolution of the Cd cements.

Cementation at room temperature aimed to finalise the cadmium removal partially
done during the previous step. Samples were taken, filtrated and analysed at 40
minutes interval to monitor the $[\text{Cd}^{2+}]$.

2.3. **Electrowinning**

Zinc is one of the latest metals deposited by electrolysis process because of its
negative reduction potential. The electrolysis was conducted in acid solution with
a Pb-1%Ag anode and Al cathode. Millazo [12] reported that in neutral solution
zinc deposited on cathodes is not compact. Millazo also recommends the zinc
electrolysis be conducted under high current density, typically higher than 3
A/dm$^2$. He also suggested that chloride ions in the electrolyte solution may react
with the PbO$_2$ and dissolve the passivating layer on the anode, leading to the
pollution of the cathode metal by Pb. Fluoride ions may dissolve the protective
film of Al$_2$O$_3$ that prevents zinc from allying with the Al cathode. Hence these
two ions must be kept at low concentration in the electrolyte.

It is well known that zinc deposition on cathode is rendered possible due to the
high overpotential for the hydrogen formation by reduction of H$^+$ on the
aluminium metal [15].

Combined effect of impurities in the electrolyte is detrimental on the electrolysis
current efficiency and the electrocrystallisation of zinc [16, 17, 18, 19].

Tripathy et al. [18] and, Ivanov and Stefanov [19] have explicitly shown the
detrimental effect of Sb(III) when present even at trace levels in the zinc
electrolyte.
Vett and Holtan [in 12] observed that the zinc electrolysis current efficiency was 0.903 for a solution of ZnSO$_4$ containing 0.003g/l Co$^{++}$. The efficiency was 0.917 for a solution of ZnSO$_4$ containing 0.005g/l Sb$^{+++}$. However, in a solution containing the two ions at the above concentrations the zinc electrolysis current efficiency dropped to 0.76.

Table 2 contains the acceptable concentration limits of impurities for good zinc electrolysis. Zinc electrolysis is made possible by the high overpotential of hydrogen formation on the cathode. Everything should be set up to have that overpotential as high as possible, i.e. the temperature of the electrolyte should not be higher than 35°C, and the electrolyte must be quasi pure. Additions of inhibitors such as colloids are necessary, and the current density must be high, ~4 A/dm$^2$. The high current density however has a detrimental effect on the quality of the deposition as it leads to the formation of fine loose zinc particles. Diverse techniques such as the forced circulation of the electrolyte in SEC-C.C.S. cells, and the Periodic Short Circuiting (PSC) method have been shown leading to good quality of the metal deposited on the cathode and to a good efficiency of the zinc electrolysis.

Metallurgical challenges surrounding the zinc electrowinning make it a passionate subject of research in extractive metallurgy of non-ferrous metals.

Electrowinning from ammoniacal, alkaline, nitrate chloride, sulphate, acid solution are continuously being investigated [16, 17, 18, 19, 20, 21, 22, 23].

The present work aims to determining the optimal conditions for the complete cycle of extracting zinc from the water-jacket furnace dusts.
3. Results and discussion

3.1. Leaching

Leaching using a 100 g/l H₂SO₄ yielded solutions containing only 20 g/l zinc, which is low for the electrowinning.

Leaching using the return solution from the zinc electrolysis cells in the Kolwezi Zinc Plant (UZK) containing up to 35 g/l zinc was than envisaged.

The composition of the return solution from the electrowinning cells that was used as lixiviant in this work is presented in Table 3.

Table 3: Composition of the lixiviant (return solution from the zinc electrowinning)

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn²⁺</th>
<th>Cu²⁺</th>
<th>Cd²⁺</th>
<th>Fe²⁺</th>
<th>Fe³⁺</th>
<th>Co²⁺</th>
<th>Cl⁻</th>
<th>Mn²⁺</th>
<th>Ni²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration [g/l]</td>
<td>33 - 35</td>
<td>0.00013</td>
<td>0.00072</td>
<td>0.025</td>
<td>0.025</td>
<td>0.00057</td>
<td>0.017</td>
<td>0.0033</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

The composition of the solution hence obtained after leaching is given in Table 4.

Table 4: Chemical composition of the solution after leaching and filtration

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn²⁺</th>
<th>Cu²⁺</th>
<th>Cd²⁺</th>
<th>Co²⁺</th>
<th>Fe (total)</th>
<th>Ge²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[g/l]</td>
<td>55.7</td>
<td>8.89</td>
<td>1.14</td>
<td>0.26</td>
<td>1.65</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The amount of zinc hence dissolved is equal to: m = (55.7 – 35) g/l x 700 ml

= 14.49 g

The total amount of zinc introduced in the leaching reactor is M = 17% x 100g

= 17 g
The zinc leaching efficiency in the above condition is $\eta_{\text{leaching}} = \frac{14.49}{17} = 85\%$

3.2. **Purification**

Most hydrometallurgical Zinc plants remove iron from leaching liquor by precipitating ammonium jarosite $\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ at a controlled pH and temperature [24, 25].

The iron content dropped to 21 mg/l at a pH value of 3.4 when introducing the saturated lime solution into the leaching solution. This iron content being lower than the acceptable limit of 80 mg/l, precipitation was assumed complete.

The results of copper and germanium elimination by solvent extraction are presented in Table 5.

Table 5: Evolution of [Cu$^{++}$] and [Ge$^{++}$] in mg/l in the purified solution during solvent extraction

<table>
<thead>
<tr>
<th>Elements</th>
<th>Number of operations</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{++}$</td>
<td></td>
<td>2120</td>
<td>1080</td>
<td>247</td>
<td>123</td>
</tr>
<tr>
<td>Ge$^{++}$</td>
<td></td>
<td>51</td>
<td>10</td>
<td>5</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The purification by solvent extraction was considered finished after 21 operations despite having [Cu$^{++}$] higher than the admissible limit as [Ge$^{++}$] dropped already below the acceptable limit at 1 mg/l. The exceeding copper will help for the solubilisation of the Antimony during the cementation of cobalt by the zinc powder.

The first step of cementation was conducted at 72 to 82°C to remove Cobalt and part of the cadmium. The residual cobalt content and antimony content are shown Table 6.
Table 6: Evolution of the cobalt content [mg/l] and the residual antimony content [mg/l] as functions of the cementation time and of the initial antimony content as added before cementation

<table>
<thead>
<tr>
<th>Reaction time [min]</th>
<th>Initial [Sb] mg/l</th>
<th>40</th>
<th>80</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Co++] mg/l</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 mg/l</td>
<td></td>
<td>71</td>
<td>67</td>
<td>65.2</td>
</tr>
<tr>
<td></td>
<td>Residual [Sb+++] mg/l</td>
<td>3</td>
<td>0.87</td>
<td>0.31</td>
</tr>
<tr>
<td>20 mg/l</td>
<td></td>
<td>41</td>
<td>35</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Residual [Sb+++] mg/l</td>
<td>3.7</td>
<td>0.99</td>
<td>0.67</td>
</tr>
<tr>
<td>25 mg/l</td>
<td></td>
<td>29</td>
<td>11</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>Residual [Sb+++] mg/l</td>
<td>5.7</td>
<td>1.8</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>[Cu++] mg/l</td>
<td>19</td>
<td>5</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The acceptable cobalt content 1 mg/l was achieved after 120 minutes when 25 mg of antimony powder was added to the solution to purify. It is noticeable that the [Cu++] in the purified solution was lower than the 10 mg/l limit.

Part of the cadmium contained in the leaching solution was eliminated during this first step of cementation but its residual level in the solution was still very high (744 mg/l). This rendered necessary the second step of cementation at room temperature to decrease [Cd++] below 12 mg/l. The evolution of cadmium content during cementation at room temperature of the solution is shown in Table 7.

Table 7: Residual Cadmium content after cementation at room temperature
### Reaction Time

<table>
<thead>
<tr>
<th>[min]</th>
<th>0</th>
<th>40</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cd++] mg/l</td>
<td>744</td>
<td>11</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The electrolyte hence purified has the chemical composition shown in Table 8.

#### Table 8: Composition of purified solution before electrolysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn**</th>
<th>Fe (total)</th>
<th>Ge**</th>
<th>Co**</th>
<th>Cd**</th>
<th>Sb***</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M] mg/l</td>
<td>91000</td>
<td>21</td>
<td>0.47</td>
<td>0.91</td>
<td>0.81</td>
<td>0.47</td>
<td>17000</td>
</tr>
</tbody>
</table>

3.3. **Electrolysis**

The type SEC-C.C.S. electrolysis cell is a 280 ml prism made of glass. The electrolyte is introduced into the cell via a series of perforated channels that lie parallel to the base of the prism. A peristaltic pump maintains a forced circulation by injecting and sucking up the electrolyte parallel to the electrodes through the holes perforated in the channels placed at the bottom of the cell. Hence the electrolyte sweeps across the electrodes. The aluminium cathode is placed in between two anodes in Pb-1% Ag. This arrangement allows the formation of symmetric current lines in the electrolyte. The distance between anodes and cathode is 3 cm. The circuit of the fluid starts in a 2 litre container heated up to the required temperature by standing it in simmering water.

The cathodes were cut out of pure aluminium sheets and mechanically polished. The surface of the cathodes were finally stripped in 65% HNO₃, dried and weighed before the electrolysis. Stripping in nitric solution also eliminated the polishing marks.

The experimental conditions consisted of:
- 1.5 litre of the electrolyte of composition given in Table 8, were introduced to fill up the all fluid circuit (electrolysis cell, container in simmer water, connecting flexible, pump)

- Temperature was varied from 30 to 50°C
- Current density (J) was varied from 3 to 9 A/dm²
- Electrolyte flow rate was varied from 60 to 120 l/h
- The electrolysis time was 2 h for all the experiments.
- One variable was changed at a time when the others were kept constant.

The cathode polarisation curves $\eta_c = f(J)$ were obtained by systematically imposing a constant current density, J, and measuring the subsequent quasi static cathode overpotential $\eta_c$ using a reference calomel saturated electrode. Drawing of cathode polarisation curves enables the determination of working regime and the characterization of the kinetics of the electrolysis phenomenon.

The polarisation curves at 35, 40 and 45°C for three different flow rates, i.e. 60, 80 and 100 l/h are presented in Figure 1.

![Figure 1: (a) Tafel’s line for the electrolyte heated up to 35°C under three different flow rates (60 l/h, 80l/h, 100 l/h).](image)
The absence of the diffusion plateaus in Figure 1(a) throughout to 1(c) suggests that the electrolysis takes place under a electrons transfer regime. This is also shown by the insensibility of the cathode overpotential to changes in the electrolyte flow rate at the three temperatures.
The slopes of the Tafel’s lines and the current densities $J_0$ corresponding to zero volt overpotential at the cathode for the three electrolyte temperatures are shown in Table 10.

Table 10: Slopes and $J_0$ of the Tafel’s lines for the electrolyte at 35, 40 and 45°C.

<table>
<thead>
<tr>
<th>Electrolyte temperature</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.302</td>
<td>0.314</td>
<td>0.389</td>
</tr>
<tr>
<td>$J_0$ A/dm²</td>
<td>0.31</td>
<td>0.37</td>
<td>0.77</td>
</tr>
</tbody>
</table>

It is inferred from Figure 1 that increasing the temperature of the electrolyte lowers the cathode overpotential $\eta_c$ but increases the slope of the straight line part of the polarisation curve, hence the increase rate of the cathode overpotential, as the current density $J$ increases. The extrapolated current densities at zero volt overpotential $J_0$ also suggest that increased electrolyte temperature increases the current density limit for the transition from an ionic to an electronic conducting mode in the electrolyte.

The effects of the electrolyte temperature on the overall electrolysis potential, the cathode overpotential, the specific energy consumption and on the current efficiency were first investigated at 5 A/dm², 120l/h and 100 mg/l gelatine. The results are presented in Figure 2.
The electrolysis current efficiency dropped drastically at temperatures higher than 40°C due to a decrease of the hydrogen formation overpotential and an increase of the conductivity of the electrolyte that leads to a higher current and higher power loss along the electric wires out of the electrolysis cell. The slight decrease in the overall electrolysis potential $U_{\text{A/C}}$ and the cathode overpotential are dependent on the increased conductivity of the electrolyte at elevated temperature.

The electrolysis current efficiency decreases with the electrolyte flow rate as shown in Figure 3. This phenomenon finds its explanation in the competition between antagonist forces acting on the particulate near the cathode, i.e. the gravitational interaction and adhesion on the cathode, the drag force and mechanical erosion due to the hydraulic turbulence and the electrostatic force. Increasing the flow rate increases the drag force and the cathode erosion. This leads to a decrease of the amount of metal collected on the cathode after electrolysis. This loss is purely of mechanical origin. Particles of metal could be collected in the bottom of the cell and in the
channels. Increasing the electrolysis time would lead to complete dissolution of these zinc particulates by the sulphuric acid contained in the electrolyte.

It is also observed from Figure 3 that the electrolyte flow rate, hence the agitation does not affect $\eta_c$ and has negligible effect on the $U_{A/C}$ and on the $w$. It was noticed earlier that there was no diffusion plateaus in the cathode polarisation curves and the electrolysis kinetics was controlled by electrons transfer phenomenon.

![Figure 3: Effect of the electrolyte flow rate on the overall cell potential $U_{A/C}$, the cathode overpotential $\eta_c$, the specific energy consumption $w$ and the current efficiency $R_c$.](image)

It ressorted from this investigation that the optimum electrolyte flow rate in a SEC-C.C.S type cell is somewhere between 80 and 100 l/h.

Gelatine was added to the electrolyte to improve the structure and compacity of the cathode metal by controlling the current density on the cathode surface. Experiments conducted at 35°C, 80 l/h and 5 A/dm² have shown that introducing gelatine into the electrolyte improved the electrolysis current efficiency. This is due to the fact that gelatine favours the formation of dense and compact metal, hence less mechanical losses of zinc particulates from the
cathode. Results are illustrated in Figure 4. The structure of the metal formed on the cathode was dendritic for gelatine contents of 0 and 100 mg/l. Dendrites dissapeared at gelatine content of 200 mg/l and 400 mg/l. Gelatine helps level the cathode metal by sticking at the tips of the dendrites. This increases the local electric resistivity ahead of the dendrite and favours the growth of metal on the slack areas of the cathode. Current efficiency higher than 94% could be achieved in presence of gelatine against 90% without gelatine. Similar observation was made by A.E. Saba and A.E. Elsherief during continuous electrowinning of zinc in synthetic sulphuric acid solution [26]. The authors also found that addition of gelatine, in the range of 50 mg/l improves the quality of electrodeposited zinc. The deposit obtained becomes continuous and covers the whole electrode surface, with small grain sizes. A transition from dendritic to boulder type and the marks of dendritic growth dissapear. Copper and iron, even at low concentrations were found to decrease the current efficiency and worsen the quality of the electrodeposited zinc.

The effectiveness of additives in improving the current efficiency to above 94%, the quality of the deposited zinc metal and in developping preferred crystal orientation was also established by A. Gomes and M.I.da Silva Pereira [27], by A. Recéndiz and his co-workers [28], and by D.R. Fosnacht and T.J. O’Keefe [29]. The authors also demonstrated the effect of additives in depressing the deleterious effects of impurities.
Figure 4: Effect of the gelatine on the overall cell potential $U_{AC}$, the cathode overpotential $\eta_c$, the specific energy consumption $w$ and the current efficiency $R_c$.

The effect of the current density $J$ on the overall cell potential, the cathode overpotential, the specific energy consumption and on the current efficiency were investigated in the electrolyte maintained at 35°C, 200 mg/l gelatine and 100 l/h flow. The results are plotted in Figure 5.
Figure 5: Effect of current density on the overall cell potential $U_{A/C}$, the cathode overpotential $\eta_c$, specific energy consumption $w$ and the current efficiency $R_c$.

It is inferred from Figure 5 that increasing the electrolysis current density up to 6 A/dm$^2$ results in increased current efficiency $R_c$. This observation may be explained by the easy formation of stable nuclei due to a large number of ions discharged in the cathode. The hydrogen formation overpotential on the aluminium cathode also is high when the electrolysis current density is high, favouring the discharge of the zinc ions. Above $J = 6$ A/dm$^2$ the current efficiency drop drastically due to the Joule’s effect and the conversion of the electric energy into heat in the electrolyte proportionally to the square of the electrolysis current. The Joule’s effect in the electrolyte also leads to a temperature rise that reduces the hydrogen formation overpotential on the cathode. This effect enhances the undesired formation of hydrogen to the detriment of the zinc reduction in the cathode.

The overall electrolysis potential $U_{A/C}$ increases when $J$ increases due to the rise in electrode overpotentials and the resistivity of the electrolyte. The specific energy consumption is therefore the consequence of the above mentioned phenomenon.

4. Conclusion

The Zinc containing dusts from the copper matte smelting in water-jacket furnaces at the Lubumbashi Plants whose composition is given in Table 1 are leachable in aqueous sulphuric acid solution. Dissolved zinc may be recovered from the solution after purification and electrolysis. The metal recovery in laboratory scale and the electrolysis current efficiency are high enough to justify the extension of the experiment to the pilot scale.
Leaching the dusts using a 100 g/l solution of sulphuric acid does not produce the required 85 g/l zinc minimum level in the solution submitted to the electrolysis. Return solution from the zinc electrolysis containing 100 g/l H$_2$SO$_4$, 35 g/l Zn$^{++}$, 10 g/l Fe$_2$(SO$_4$)$_3$ as leaching agent yields a 55 g/l zinc solution. The solution obtained after purification contains 91 g/l zinc, hence acceptable for electrolysis. In these conditions, 85% of the zinc content of the dusts was dissolved after 2 hours at 55°C. Purification of the leaching solution is possible by selective elimination of iron by precipitation using a saturated lime solution at pH 3.4. Copper and germanium are removed from the electrolyte by solvent extraction using 10% LIX 64N in ESCAID 100. Finally Cobalt and cadmium levels are reduced to below the acceptable limits for the zinc electrolysis by cementation in presence of antimony at 72°C for 2 hours and at room temperature for 40 minutes.

The electrolysis of the purified solution is controlled by an electrons transfer regime. This observation was confirmed by the constant cathode overpotential and the negligible effect of the flow rate on the overall electrolysis cell potential.

Optimum conditions for the zinc electrolysis in a SEC-C.C.S type cell were determined as:

- Current density 5 to 6 A/dm$^2$
- Electrolyte temperature comprised between 35 and 40°C
- Electrolyte flow rate 80 to 100 l/h
- Gelatine level comprised between 100 and 200 mg/l

Zinc electrolysis current efficiency higher than 94% and the specific energy consumption about 3.5kWh/kg were achieved in the above conditions.

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