Pilot tests on Bismuth and Antimony removal from electrolyte at Atlantic Copper refinery.

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Abstract

The control of the concentration of minor impurities (As, Sb, Bi) in electrolyte has been a major challenge for Atlantic Copper in recent times. This paper describes recent studies and technologies evaluated at the Atlantic Copper Refinery that focus on the removal of Antimony and Bismuth. It is known that Antimony and Bismuth concentrations in electrolyte have to be kept within an optimum operating range in order to prevent the occurrence of different cathode nodulation phenomena. Various pilot tests have been carried out to remove Antimony and Bismuth from electrolyte by ion exchange or adsorption on Activated Carbon. Another important factor of this project was to minimize the usage of regeneration acid, as this is a major cost factor in the process with ionic exchange resins, as well as active carbon consumption.

1. Introduction

Arsenic, Antimony and Bismuth are often considered as a group whose influence on the copper electro-refining process has already been studied in depth due to the fact that, depending on operating parameters such as anode and electrolyte compositions, they report electrolyte and anode slimes. When Arsenic, Antimony and Bismuth enter the electrolyte, they undergo different reactions, depending on their respective concentrations and the presence and concentrations of other elements [1]-[2]-[3].

In prior research work carried out at Atlantic Copper [4], the behaviour of the electrolyte was studied in order to determine the optimal working conditions to prevent these undesirable phenomena from occurring and hence avoiding problems related to copper cathode quality. One of the main conclusions was that the As/(Sb+Bi) ratio should be kept within a 20-35 value range to prevent the
occurrence of floating slimes (lower value) and precipitation of arsenates from bulk electrolyte (higher value).

This is achieved by controlling these impurities in the anodes and by their extraction in the liberator cells, in which Sb and Bi are removed together with As.

The anode composition determines that it might be necessary to remove Sb and Bi, but not As, from the electrolyte, and for this reason a research project aimed at developing a process which specifically removes these elements from the electrolyte has been carried out. This project also contains a review of the various technologies of selective Sb/Bi removal from electrolyte, and the most widely-used technologies for selective Sb and Bi extraction are:

(A) Ion exchange (IX) resins: The use of these resins was developed and introduced at industrial scale by Japanese copper refineries (Saganoseki, Hitachi, Tamano) at the end of the 20th century. Since then, this process has been adopted by other refineries such as Montreal and tested in other refineries. [5], [7]-[10],[12]-[14],[19].

(B) Molecular recognition technology (MRT): This technology is mainly used for Bi removal in some refineries [6], [11].

(C) Active carbon adsorption: This process is being adopted at industrial scale in Onsan for Sb/Bi removal and tested in many other refineries. [16]-[18].

Molecular recognition technology was discarded for study purposes because it only removes Bi.

Technologies A and C were tested at Atlantic Copper at bench scale:

- Chelating resins, which simultaneously remove Sb and Bi from electrolyte, using a hydrochloric acid solution (HCl) to regenerate the resins were tested at lab scale at Atlantic Copper. As a result of the promising results, a pilot plant was put into operation at the copper refinery in order to confirm resin performance and HCl consumption figures
- Different active carbons were tested at lab scale to evaluate their Sb and Bi adsorption capacity.

This paper describes the results of these studies, which were the basis of a preliminary design of an industrial plant.

2. Experimental results

2.2 Ion exchange (IX) resins

Preliminary laboratory tests were carried out using Lewatit TP 260 resin supplied by Lanxess GmbH. This resin was selected because of its high affinity for Sb^{3+/5+}, Bi^{3+} and Fe^{3+}, whereas Cu and Ni are not removed in a high acid background. Hydrochloric acid in various concentrations was used for elution.
The main conclusions of these tests were:

- Capacities for Bi and Sb removal of around 10 g/l resin were recorded.
- Due to the fact that the AC electrolyte contains almost no ferric ion, no poisoning of the resin was observed. Nevertheless, after doping the electrolyte with ferric ion, the resin still showed good capacity for Bi and Sb, although it was already saturated with ferric ion. Regeneration with 30 % HCl could only remove about 25 % of this ion. But a second run showed that during loading, the iron concentration in the effluent was higher as in the feed, suggesting that Sb and Bi have a greater affinity to the resin, or better kinetics, and are able to replace the ferric on the resin.
- The regeneration procedure showed that Sb needs a higher concentration of HCl for its removal, as does Bi. Therefore 2 BV** of 15 % HCl should be sufficient to regenerate the resin entirely.

To consolidate the good results from the lab scale tests, a pilot plant was run for four months in the copper refinery. The plant was supplied and operated by Kurion Technologies Ltd (now called Belmar Technologies Ltd, UK).

The pilot plant operation was aimed at evaluating the following issues:

i) To confirm the behavior of the resins at industrial scale:
   - TP260 Lewatit cationic Exchange resin for Sb and Bi removed from the Atlantic Copper electrolyte: Operation and design parameter optimization at industrial scale.
   - MP62 Lewatit® anionic Exchange resin for dirty HCl recovery: Evaluation of this resin developed by Lanxess GmbH (?), and aimed at minimizing HCl consumption.

ii) Determination of design and operating data to estimate the investment and cost operation of an industrial plant.

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*If no ferric ion is present in the feed.

**BV: Bed Volume
Figure 1 shows a flow sheet of the pilot plant:

The plant was operated as a worker/polisher configuration with two columns in series. The electrolyte was loaded at 5 – 6 BV into the top of the first worker column (called “worker”) where it passes through the resin bed, and then from the bottom of this column it is transferred to the top of the second polisher column (called “polisher”).

When the resin of the first column is exhausted, the second column becomes the new “worker” column while the first column is being regenerated. When the regenerating step is finished, the first column again becomes the “polisher” column until the second column is exhausted. This cycle repeats continuously.

Before regenerating, a water blanket was pumped through the resin in order to recover the void electrolyte.

HCl (15%) was used for TP 260 resin regeneration. The acid was pumped through the resin into a spent acid tank from where it was sent to the column used for acid recycling loaded with the MP 62 Lewatit anionic Exchange resin. Bi/Sb chloro-complexes were held back from the resin through ion exchange, and the cleaned acid was used again for the regeneration of the Bi/Sb pilot plant. The loaded resin was then regenerated using 2 BV 3 M sulfuric acid. The eluate from the MP 62 resins was pumped to the waste water system.
Figure 2 shows a diagram with both processes integrated:

![Diagram of pilot plant process]

Figure 2. Scheme of pilot plant process

A total of 53 cycles were done during the 4-month period, and the most relevant results are:

A. Bi/Sb removal by TP260 Lewite resin

At the beginning of the tests, removal efficiencies were above 90% for Bi and Sb. After 15 cycles the removal efficiency dropped to an average of 70%, as shown in Figure 3. This was due to solids precipitation during a regeneration step, when the electrolyte was rinsed out with water. When this precipitation happens inside the resin bed, the capacity of the resin suffers due to bad diffusion during the loading cycle.

![Graph of total retention with precipitation]

Figure 3: Lewatit TP 260 Sb, Bi and Fe removal capacities
The following adjustments were made to avoid precipitation and to enforce regeneration efficiency:

- All eluting acid was pumped to the dirty acid tank (previously, the final fraction of this stream was pumped back to the fresh acid tank).
- Instead of water, sulfuric acid was used to displace the electrolyte in the column before regeneration.
- The concentration of the acid was monitored to ensure a concentration of between 15 – 20 % HCl
- Counter-flow regeneration was done to loosen the resin bed.
- The pause steps between regeneration were prolonged.

All these measures led to increased capacity and, as a consequence, removal efficiency, as depicted in Figure 4:

![Total Retention (without precipitation)](image)

The Bi and Sb removal efficiency rose to 90 % again and it was concluded that the following process parameters were important for successful regeneration:

- Time: the longer the regeneration time, the better the elution
- Concentration of HCl: the higher the HCl concentration, the more efficient the elution.
- Temperature: higher temperature, better elution.
- Water: water can cause precipitation on the resin when it is loaded, and has to be replaced by sulfuric acid.

TP 260 resin showed good Sb and Bi retention capacity, as shown in Figure 5. After 50 cycles, the resin capacity was still within the same range as at the beginning. The final combined capacity was 10-14 g/l resin.
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**B. Dirty HCl recycling with the MP 62 Lewatit anionic**

MP 62, a weak alkaline anionic resin, is capable of removing the Bi/Sb-chloro-complexes from HCl solutions and can be regenerated with sulfuric acid, which is readily available at the Atlantic Copper plant.

The resin was in good condition up to the 8th regeneration cycle when problems with solids precipitation inside the resin occurred. Some adjustments were made to avoid the precipitation and enforce regeneration efficiency but it was not possible to recover it.

A new start with a fresh resin was done and after 6 regenerations the resin was still in good condition. Table 1 shows the results:

**Table 1. MP 62 Lewatit: Percentage removed in each regeneration.**

<table>
<thead>
<tr>
<th>% removed</th>
<th>Fe</th>
<th>Bi</th>
<th>Sb</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Regen.</td>
<td>20</td>
<td>98.07</td>
<td>98.90</td>
<td>16.95</td>
</tr>
<tr>
<td>2nd Regen.</td>
<td>25.35</td>
<td>98.98</td>
<td>87.57</td>
<td>9.19</td>
</tr>
<tr>
<td>3rd Regen.</td>
<td>93.17</td>
<td>97.36</td>
<td>91.95</td>
<td>11.67</td>
</tr>
<tr>
<td>4th Regen.</td>
<td>87.83</td>
<td>94.79</td>
<td>89.77</td>
<td>-14.50</td>
</tr>
<tr>
<td>5th Regen.</td>
<td>72.27</td>
<td>91.93</td>
<td>92.20</td>
<td>14.60</td>
</tr>
<tr>
<td>6th Regen.</td>
<td>75.38</td>
<td>88.72</td>
<td>94.41</td>
<td>3.62</td>
</tr>
</tbody>
</table>

From the results it was possible to conclude:

- No poisoning of the resins by ferric ion was observed.
- Both resins tested (TP 260 and MP 62) showed good behaviour:
  - TP 260: The pilot plant test trials showed that a **resin retention capacity** of over 80% could be achieved. The combined capacity for Bi/Sb was 12 g/l resin. (8-10 g/L resin for Sb and 4-6 g/L resin for Bi) after 50 cycles.
• MP 62 was able to recover a HCl for use in the TP 260 regeneration. Nevertheless more tests are necessary to consolidate the results.

• TP 260 regeneration procedure and HCl consumption were optimized in order to minimize costs. But, it was found that one third of the HCl used was lost in each regeneration of the TP 260 resin. The two main sources of this loss of hydrochloric acid are:
  o Own lossage or acid decomposition in the regeneration of the resin.
  o Mixing with other fluids during the process (water, sulfuric acid)

• Hydrochloric acid intake was determined for a complete cycle, including the recycling of the MP62 resin with sulphuric acid. The following process consumption parameters would be the basis for a commercial plant:
  Chemical consumptions per regeneration cycle:
  HCl (18%) consumption: 1.5 BV (without HCl recycling)
  HCl (18%) consumption: 0.3 BV (with HCl recycling)
  H$_2$SO$_4$ (38%) consumption: 0.2 BV (without HCl recycling)
  H$_2$SO$_4$ (38%) consumption: 0.8 BV (with HCl recycling).
  Water: 5 BV

2.3 Active Carbon (AC) laboratory studies

2.3.1 Description
The study focused on the use of activated carbon (pulverised and granular) as adsorbent to remove Sb from electrolyte in the copper electro-refining process, in order to compare this technique with the ion exchange resin adsorption process.
Two studies were performed at laboratory scale. First, batch test were carried out to determine the adsorption capacity of different activated carbons. One test consisted of several activated carbons tested at laboratory scale in discontinuous experiments, after which the best one was selected.
In a second study, a columns test was carried out with that active carbon, in order to find the proper operating conditions for maximizing the adsorption capacity of Sb removal. The tests were made at laboratory scale using small columns working continuously until the activated carbon was exhausted. This experimental procedure enabled us to determine the breakthrough curve, and as a consequence, the active carbon consumption and column design parameters could be estimated more accurately.
2.3.2 Results

- Batch Studies: determining the adsorption isotherms

Firstly, the load capacities of five activated carbons (3 pulverized and 2 granular) were studied by contact between electrolyte and adsorbent for 24 hours (to ensure equilibrium) inside the stirring reactors; the temperature was controlled (50°C) with a thermostatic bath.

An initial test was performed with an electrolyte/activated carbon ratio of 10 ($V_{\text{elec}}/M_{\text{AC}} = 10$ L electrolyte/kg activated carbon), measuring Sb concentration in electrolyte after contact with carbon and equilibrium solutions. The results are shown in Table 2.

<table>
<thead>
<tr>
<th>Eluate (CA-P-BM8)-pulverized</th>
<th>112.5</th>
<th>74.9</th>
<th>3.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluate (CA-P-N35)-pulverized</td>
<td>96.5</td>
<td>78.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Eluate (CA-P-N52)-pulverized</td>
<td>81</td>
<td>79.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Eluate (CA-G-CG1100)-granular</td>
<td>83</td>
<td>72.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Eluate (CA-G-MG1050-AW)-granular</td>
<td>94.7</td>
<td>68.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

After that, a new study of the adsorption capacity of the best activated carbon was carried out by contact between the same AC amount and different $V_{\text{elec}}/M_{\text{AC}}$ ratios until equilibrium, using the equipment described above. In this case, the same electrolyte amount was placed in each reactor together with different AC amounts ($V_{\text{elec}}/M_{\text{AC}} = 50$, 100 and 500). All results are shown in Table 3.

<table>
<thead>
<tr>
<th>V.elec/MAC</th>
<th>Sb Content</th>
<th>Sb Retention</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>L electrolyte/kg AC</td>
<td>mg Sb/L</td>
<td>%</td>
<td>g Sb/kg ads</td>
</tr>
<tr>
<td>Eluate (CA-P-N52)-pulverized</td>
<td>10</td>
<td>81</td>
<td>79.7</td>
</tr>
<tr>
<td>Eluate (CA-P-N52)-pulverized</td>
<td>50</td>
<td>155.5</td>
<td>61</td>
</tr>
<tr>
<td>Eluate (CA-P-N52)-pulverized</td>
<td>100</td>
<td>166.4</td>
<td>58.3</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Eluate (CA-P-N52)-pulverized</th>
<th>500</th>
<th>202.8</th>
<th>32.6</th>
<th>49.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluate (CA-G-CG1100)-granular</td>
<td>10</td>
<td>83</td>
<td>72.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Eluate (CA-G-CG1100)-granular</td>
<td>100</td>
<td>170</td>
<td>43.5</td>
<td>13.1</td>
</tr>
<tr>
<td>Eluate (CA-G-CG1100)-granular</td>
<td>500</td>
<td>225.2</td>
<td>25.1</td>
<td>37.8</td>
</tr>
<tr>
<td>Eluate (CA-G-MG1050-AW)-granular</td>
<td>10</td>
<td>94.7</td>
<td>68.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Eluate (CA-G-MG1050-AW)-granular</td>
<td>100</td>
<td>175.3</td>
<td>42</td>
<td>12.7</td>
</tr>
<tr>
<td>Eluate (CA-G-MG1050-AW)-granular</td>
<td>500</td>
<td>214.5</td>
<td>29.1</td>
<td>44</td>
</tr>
</tbody>
</table>

The pulverised and granular AC studied achieved similar adsorption yields (68.7 – 80.9%) under related experimental conditions.

Results showed that the lower the $V_{ELEC}/M_{AC}$ ratio, the higher the Sb adsorption, but not the experimental loading capacity.

In the related equilibrium studies carried out, pulverized AC showed slightly better extraction yields and higher load capacity than granular ones (best yield: 79.7%; highest capacity: 49.1 g Sb/kg adsorbent).[14].

In the end, CA-G-CG1100 was selected for best availability of supplier and cost criteria.

- **Second study: Column tests (determination of breakthrough curves):**

This study focused on testing the Active Carbon CA-G-CG1100 until exhaustion with electrolyte of around 300 mg/L of Sb content. Tests were carried out in glass columns (2 and 3 cm in diameter). A slight vacuum was applied by a pump that allows the electrolyte to pass through the column. The electrolyte is kept at a constant temperature (55°C), and adsorption equipment (column, AC plus lines) operate at room temperature. Figure 6 shows the experimental equipment.

*Figure 6: Experimental equipment.*
Besides Sb, AC retention capacity was analyzed for other elements or compounds such as Bi and As. Three tests were performed with different operational parameters:

**Test 1. Preliminary column test:** (2 cm internal diameter column; bed height: 9.5 cm; bed volume of Active Carbon: 30 mL; flow = 14 BV/h (430 mL/h); flow rate = 1.4 m/h).

Although the pass rate is not high, yields are low (the highest is < 49%, and it decreases to < 15% at the end of the test). This seems to indicate that the Sb adsorption kinetic onto CA-CG1100 is slow. The highest capacity reached in test 1 was 23.6 g Sb/kg CA-1100. Figure 7 shows the results of this test.

![Figure 7. Sb in eluate versus time](image)

**Test 2. Kinetic process determination:** (3 cm internal diameter column; bed height: 6 cm; bed volume of Active Carbon: 42 mL) flow = 14 BV/h (430 mL/h); flow rate = 1.4 m/h)

The results enabled an exhaustive analysis of Sb adsorption kinetics onto CA-1100 (Figure 8).

![Figure 8: Active carbon adsorption kinetic test.](image)
This was a semi-batch test in which batches of electrolyte were held in the columns over different times, with the Sb content in the final effluent analyzed.

When contact time exceeds 5 minutes, yield is higher than 70%, and when the solution is in contact with AC for 30 minutes, this yield was higher than 80%. Figure 8 shows the asymptotic trend of the curve. The highest retention would be about 85%.

Attending to the Test 2 results and fitting retention higher than 70% as an initial condition, a third test was carried out keeping the solution and AC in contact for 5 minutes or more, and setting the same flow rate/bed volume ratio as that in the IX resin pilot plant tests explained in point 2.2. of this paper, for comparison purposes:

**Test 3. Removal capacity test:** The column used was the same as in Test 2, (3 cm internal diameter column; bed height: 6 cm; bed volume of Active Coal: 42 mL; flow = 6 BV/h (250 mL/h); flow rate = 0.35 m/h)

In this test, retention varies from 78.1% (after 1.5h) to 23.4% (after 27h). Retention decreases strongly in the early hours even though the AC is not exhausted. At the end of the test, the carbon is practically exhausted. The highest capacity reached (accumulated data) with CA-CG-1100 carbon was 36.6 g/kg with a 350 mg Sb/L electrolytic solution. The evolution of the Sb content in the eluate in each column is shown in Figure 9 (Tests 1 and 3).

![Figure 9: Sb in eluate versus time for Tests 1 and 3.](image)
Together with the Sb study, the AC retention capacity for Bi and As were also determined. It was found that, similar to Bi, after 9 hours less than 5% Bi in the electrolyte was retained onto the AC.

In the case of As, discontinuous test results show that more that 60% of As was retained onto the AC.

From the results it was possible to conclude:

- The pulverised and granular AC studied achieved similar adsorption yields (68.7 – 80.9%) in related experimental conditions.
- Tests with active carbon CA-CG-1100 yielded the highest capacity at 36.6 g/kg with a 350 mg Sb/L electrolytic solution. As a result, around 8.570 kg AC would be required to remove 300 kg Sb/day. This corresponds to a volume of 14.3 m$^3$. As an example, three 1.5 m internal diameter columns could be used (1.77 m$^2$ area) with a 4.5 bed height and a 2/3 filled coefficient.
- The activated carbon is not selective for Sb and Bi, because it also retains As.

3. Summary

From the results outlined in the previous sections, it can be summarized that:

- No poisoning of the Lewait TP 260 resin by ferric ion was found and this resin was chemically stable after 50 regeneration cycles.
- An average stable retention capacity of over 80% could be achieved, and the combined capacity for Bi/Sb was 12 g/l resin. (8-10 g/L resin for Sb and 4-6 g/L resin for Bi) for Lewait TP 260 resin.
- The recycling of the acid is a crucial step in the economic efficiency of the whole IX resin process. It was confirmed that MP 62 was able to recover a HCl suitable for use in TP 260 regeneration, and it was estimated that it was possible to reuse 2/3 of the total HCl consumed, but further tests to confirm these results are needed.
- The retention capacity of the Active Carbon is slightly lower than in the IX resins (maximum 78, 1% Sb retention), but it was found that activated carbon is not selective for Sb and Bi. It has a high As retention capacity and, for this reason this option was discarded from future studies.
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