Use of sulphur dioxide as reducing agent in cobalt leaching at Shituru hydrometallurgical plant

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Synopsis

Copper oxide ores deposits in the Katanga province of the Democratic Republic of Congo (DRC) contain at variable level cobalt oxide minerals. In contrast to copper oxide minerals which readily dissolve in the sulphuric acid solution, the cobalt oxide bearing is difficult to dissolve, especially if cobalt is present in the third oxidation state (Co$_2$O$_3$). This species become soluble after reduction of Co$^{3+}$ to Co$^{2+}$. In practice, the use of reducing agent is therefore necessary in order to transform the insoluble minerals into soluble cobalt sulphate species. The following reducing agents are currently used at the Shituru plant: ferrous ions, which are present in leach solutions, pulverised copper or sodium meta bisulphite (MBS).

Due to the high consumption of reducing agents (0.8 t MBS/t of solubilized Co; 1.2 t Cu/t-Co), cobalt production is expensive. The use of sulphur dioxide as reducing agent was then investigated in order to reduce operating cost. This reagent also presents the advantage of sulphuric acid production during the leaching process. It has been added in the leaching vessel (tank).

From the laboratory and industrial tests, selective leaching of cobalt (78%) has been performed. The cobalt leaching kinetic depend on sulphur dioxide dosage. Dissolution of copper, iron and manganese remained very low. No emanation of SO$_2$ gas was observed during the process.

Introduction

Cobalt oxide minerals, which are present in copper oxide ores in Gécamines concession, are leached in sulphuric acid solution with more than 90% efficiency. If present in the third oxidation state (abundance of superior oxide Co$_2$O$_3$), reduction of Co$^{3+}$ to Co$^{2+}$ is necessary in order to dissolve it. The common reducing agents used at the Shituru Hydrometallurgical Plant are:

➤ Ferrous ions which are present in solution as result of ore leaching and other from acid leach of iron scrap
➤ Copper powder
➤ Sodium metabisulphite (Na$_2$S$_2$O$_5$).

In order to increase cobalt production, it has been recommended to proceed to a direct leaching of cobalt rich oxide ores without previous concentration. In this case, however, the high dosages of copper powder and sodium metabisulphite, which were necessary, also induced an increase in operating cost. Consumption of these reagents averaged 0.8 (metric) ton of Na$_2$S$_2$O$_5$ and 1.2 ton of copper powder per ton of dissolved cobalt, representing approximately 47% of the total operating cost per ton of cobalt metal produced.

Many reducing reagent has been proposed to leach cobalt III from oxide ores. The sulphur dioxide seems to be the most used in the cobalt and manganese leaching plant (1-3).

Laboratory test works have been performed at Gécamines Metallurgical Research Department to investigate the use of sulphur dioxide as reducing agent during the leaching of copper and cobalt ores. Thereafter, plant trials have been conducted at Shituru. Interesting results have been achieved and it has been demonstrated that sulphur dioxide represents an economical alternative as reducing agent, which can replace both Na$_2$S$_2$O$_5$ and copper powder.

This paper reports the possibility of sulphur dioxide use at Shituru plant and its impact on the copper-cobalt flow sheet of the plant.

Laboratory test work

Experimental procedure

Laboratory test works were performed at 40°C and pH 4.05. The ore (density of 2.77 kg/dm$^3$), assaying 4.02% Cu, 1.72% Co, 5.09% Fe... was finely ground to 80%—200 mesh (74 µm) and mixed with spent electrolyte from the Shituru plant which contained copper 14.69 g/l, cobalt 8.79 g/l and

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| Table I  
Variation of pH and redox potential (Ag/AgCl) as function of sulphur dioxide injection time |
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<tbody>
<tr>
<td>Time min</td>
<td>Temperature °C</td>
<td>pH</td>
<td>Redox potential mV</td>
</tr>
<tr>
<td>0</td>
<td>40</td>
<td>4.05</td>
<td>325</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>2.68</td>
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<td>192</td>
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<tr>
<td>180</td>
<td>40</td>
<td>1.98</td>
<td>198</td>
</tr>
</tbody>
</table>

Iron 1 mg/l to form a pulp of density 1.6 kg/l. A volume of 1000 ml of the pulp was used in each test. Gas, 20% SO₂ in air, was blown in the pulp at 100 l/h through a perforated agitation disc. The test was performed in a period of 3 h without further pH regulation. Samples of liquid and solid were taken and analysed by atomic absorption spectrometry.

**Results and discussions**

The temperature of pulp, the pH and the redox potential were monitored as shown in Table I.

From these data, it was observed that the temperature of the pulp is not influenced by the reaction, while the pH of the pulp as well as the redox potential continuously decrease.

The results shown in Figure 1 clearly indicated that cobalt was selectively leached, while copper and iron solubilization remained at very low level. After 3 h, cobalt recovery was nearly 86%, copper 11% and iron 7%.

**Industrial test**

**Experimental**

The industrial test works conducted at the Shituru plant aimed:

![Figure 2—Schematic of the sulphur dioxide injection system to be installed at the Shituru plant](image)
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- to investigate the application of the technique of liquid SO\textsubscript{2} injection in the pulp, with respect of environmental regulations and personal security
- To find out the optimal conditions of liquid SO\textsubscript{2} absorption for maximum cobalt recovery.

The experimental device used is illustrated in the Figure 2. Liquid SO\textsubscript{2} of 99.9\% purity was stored in cylinder tanks containing 1 t SO\textsubscript{2} each at 280 KPa. From there, liquid SO\textsubscript{2} was sent through pipe 4 to the absorber column 17. The ore pulp flowed through pipe 14 to the absorber column from top to the bottom in counter current movement with the gas. From the storage tank 10, with 291 m\textsuperscript{3} capacity, the pulp was allowed by a centrifugal pump to continuously circulate at 100 m\textsuperscript{3}/h through the pipe 14, the absorber column and back to the storage tank 10. Since SO\textsubscript{2} used was liquid, the absorber column chimney remained closed during the experiment. After 12 h pulp conditioning as previously described, 30 m\textsuperscript{3}/h of the pulp stream was sent through modulating valve 15 to the cobalt leaching (cobalt leach circuit).

The ground ore (density of 2.93 kg/dm\textsuperscript{3}), assaying 3.95\% Cu, 1.11\% Co, 3.75\% Fe... was mixed with spent electrolyte from the same plant which contained copper 9.46 g/L, cobalt 8.25 g/L and iron 0.5 mg/L to form a pulp of density 1.34 kg/L. The in-plant tests were performed at 32°C and pH 4.3.

**Results and discussions**

**Variation of temperature, pH and redox potential**

In the course of experiment, it was observed that variation of temperature, pH and redox potential exhibits the same behaviour as in the laboratory test (Table I). The test was run in a period of 13 h. The pulp temperature in the storage tank remained almost unchanged at 32–33°C, while the pH varied from 4.30 to 2.06 and the redox potential from 215 to 133 mV as shown in Figure 3.

**Leaching performances**

The result of the leaching test is represented in Figure 4, which clearly indicates that a significant cobalt leaching has been achieved. Cobalt leaching was performed to an extent of approximately 80\%, while that of copper remained negligible.

**Environmental considerations**

During the plant test, it was important to check the emanation of SO\textsubscript{2} gas over the storage tank and over the leaching reactor for environmental considerations. No sulphur dioxide was detected over the storage tank during the test works. But, after 10 h of SO\textsubscript{2} absorption in the pulp and full flow (100 m\textsuperscript{3}/h) re-circulating in the storage tank, 30 m\textsuperscript{3}/h of pulp were sent to the pachucas where oxidation acidic conditions are prevailing, SO\textsubscript{2} gas was detected around and the test was stopped. This SO\textsubscript{2} emanation can be explained by the fact that the pulp was saturated in SO\textsubscript{2} gas and the more acidic conditions prevailing in the leach reactors were favourable to the SO\textsubscript{2} emission.

**Conclusions**

From the above, it has been demonstrated that substitution of conventional reducing agents used in Gécamines hydrometallurgical plants (copper powder, sodium metabisulphite) by sulphur dioxide in leaching of trivalent cobalt is possible. Selective cobalt leaching can be achieved at high recovery level. In contrast to most impurities, manganese is leached to a significant extent.

The obtained results, so far, showed that the absorption of SO\textsubscript{2} gas can be operated, with respect to environmental regulation, if SO\textsubscript{2} absorption does not reach the saturation level in the pulp.

The selective cobalt leaching which applying this method can perform induces an important modification of the copper–cobalt classical flow sheet. Instead of simultaneous dissolution of copper and cobalt, selective leaching of both species is possible. First, cobalt can be leached in reducing conditions with the use of sulphur dioxide. The second stage will be conducted under oxidation conditions to dissolve copper and rest of cobalt.
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References