



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

by M.D. Mwema*, M. Mpofo†, and K. Kafumbila†

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 bearings are difficult to dissolve, especially if cobalt is present in the third oxidation state (Co_2O_3). This species become soluble after reduction of Co^{+3} in 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_2O_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 ($\text{Na}_2\text{S}_2\text{O}_5$).

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 $\text{Na}_2\text{S}_2\text{O}_5$ 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 $\text{Na}_2\text{S}_2\text{O}_5$ 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

* Gécamines Metallurgical Strategies Direction, Likasi, Democratic Republic of Congo.

† Gécamines Metallurgical Research Department, Likasi, Democratic Republic of Congo.

© The South African Institute of Mining and Metallurgy, 2002. SA ISSN 0038-223X/3.00 + 0.00. This paper was first presented at the SAIMM Conference: Copper cobalt nickel and zinc recovery, 16-18 July 2001.

Use of sulphur dioxide as reducing agent in cobalt leaching

Table I

Variation of pH and redox potential (Ag/AgCl) as function of sulphur dioxide injection time

Time min	Temperature °C	pH	Redox potential mV
0	40	4.05	325
30	40	2.68	232
60	40	2.65	189
90	40	2.53	173
120	40	2.37	159
150	40	2.07	192
180	40	1.98	198

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

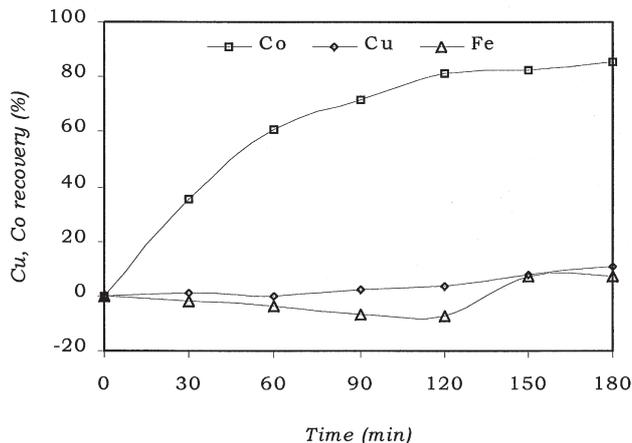


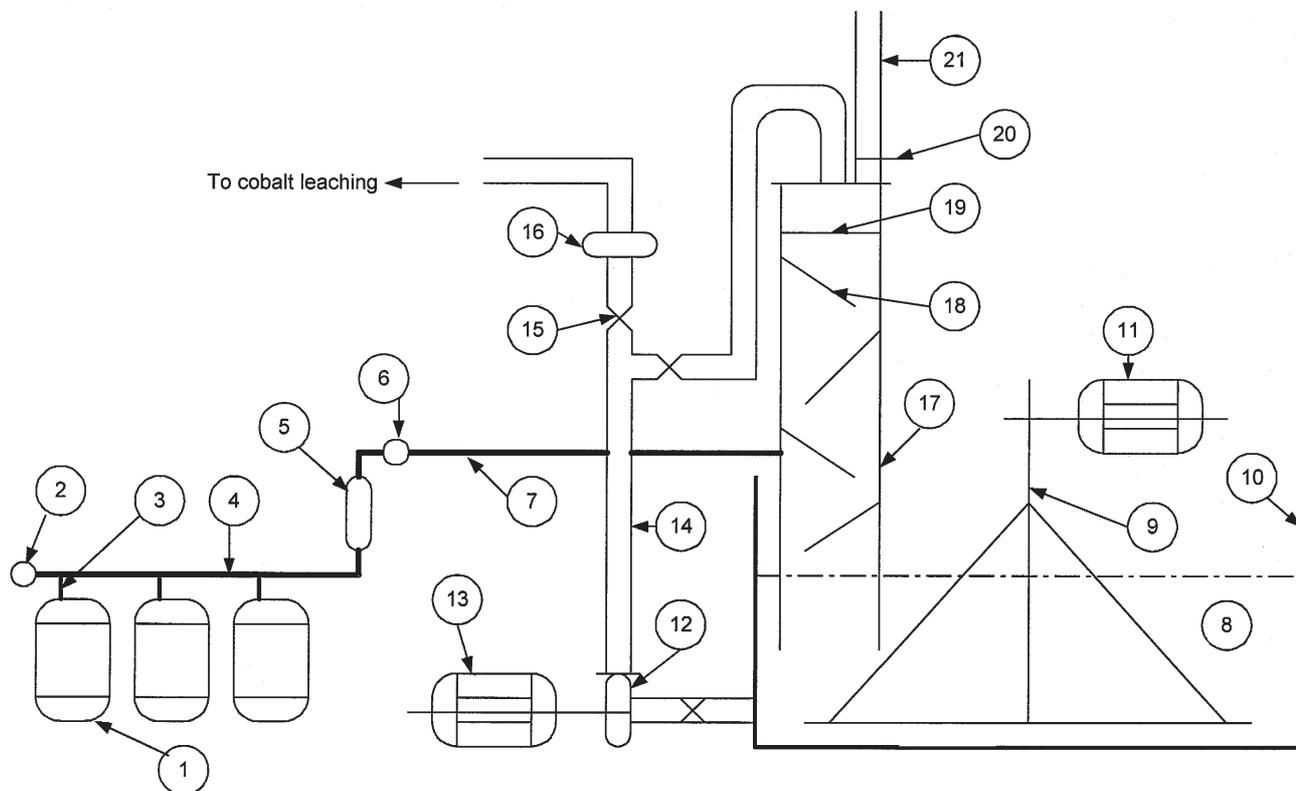
Figure 1—Copper and cobalt leaching recovery as function of time (laboratory test)

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:



1. Liquid SO₂ (1 t) 2. Manometer 3. Flexible pipe 4. Ramp 5. Flow meter 6. Valves 7. Pipe 8. Cobalt ore pulp 9. Agitation system 10. Storage tank (Capacity: 291 m³) 11. Agitator electrical motor 12. Centrifugal pump 13. Centrifugal pump motor 14. Pulp pipe 15. Modulating valves 16. Pulp flow meter 17. Sulphur dioxide absorption column 18. Tray 19. Perforated iron sheet 20. Joint 21. Chimney

Figure 2—Schematic of the sulphur dioxide injection system to be installed at the Shituru plant

Use of sulphur dioxide as reducing agent in cobalt leaching

- ▶ to investigate the application of the technique of liquid SO₂ injection in the pulp, with respect of environmental regulations and personal security
- ▶ To find out the optimal conditions of liquid SO₂ absorption for maximum cobalt recovery.

The experimental device used is illustrated in the Figure 2. Liquid SO₂ of 99.9% purity was stored in cylinder tanks 1 containing 1 t SO₂ each at 280 KPa. From there, liquid SO₂ 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 291m³ capacity, the pulp was allowed by a centrifugal pump to continuously circulate at 100 m³/h through the pipe 14, the absorber column and back to the storage tank 10. Since SO₂ used was liquid, the absorber column chimney remained closed during the experiment. After 12 h pulp conditioning as previously described, 30 m³/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/dm³), 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.

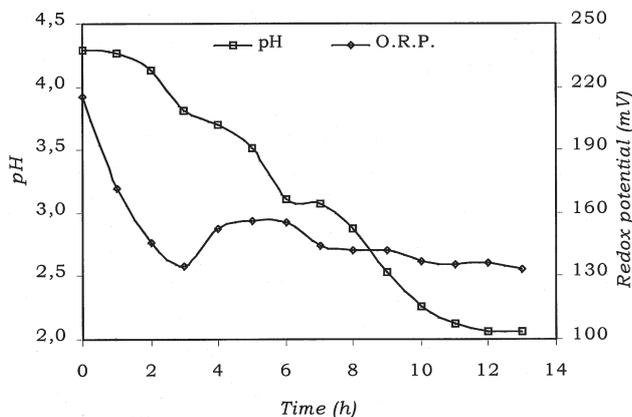


Figure 3—pH and redox potential (Ag / AgC) in leach pulp as function of time (industrial test)

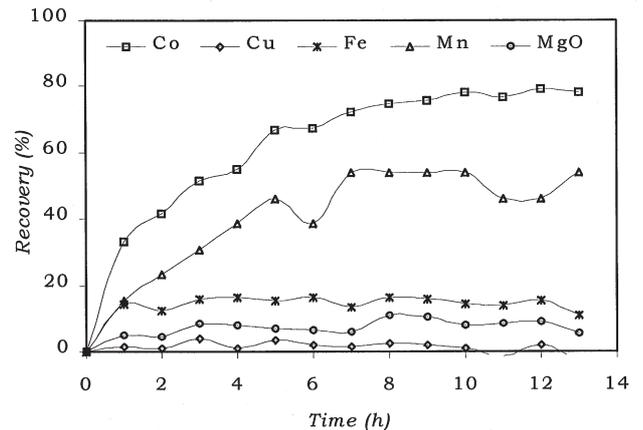


Figure 4—Leaching recovery as function of time (industrial test)

After 13 h, impurities leaching were 5.63% for MgO, 10.7% for Fe and 53.9% for Mn.

Herewith it was demonstrated that an industrial use of sulphur dioxide as reducing agent in cobalt ores leaching is feasible. This method induces selective cobalt leaching towards most impurities (copper, iron, magnesium), but manganese, which is an important impurity in cobalt electro-winning, is dissolved to a great extent.

Environmental considerations

During the plant test, it was important to check the emanation of SO₂ 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 SO₂ absorption in the pulp and full flow (100 m³/h) re-circulating in the storage tank, 30 m³/h of pulp were sent to the pachucas where oxidation acidic conditions are prevailing, SO₂ gas was detected around and the test was stopped. This SO₂ emanation can be explained by the fact that the pulp was saturated in SO₂ gas and the more acidic conditions prevailing in the leach reactors were favourable to the SO₂ 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 SO₂ gas can be operated, with respect to environmental regulation, if SO₂ 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.

Use of sulphur dioxide as reducing agent in cobalt leaching

Acknowledgements

The authors would like to express their gratitude to the management of Gécamines for permission to present this paper and the financial support. They also thank Dr Eng. K. Kongolo for valuable suggestions.

References

1. BERTINI, M. MAREZIO and DUBY, P.F. Novel leaching applications of the SO₂/O₂ system, *XXI International Mineral Processing Congress*, July 2000. Rome (Italy).
2. MILLER, JAN D. and WAN, RONG YU . Reaction kinetics for the leaching of MnO₂ by sulfur dioxide, *Hydrometallurgy*, May 1983.
3. GILL, J.B., GOODALL, D.C. and JEFFREYS, B. New leaching agents for oxides, *Hydrometallurgy*, December 1984. ◆