

2 Bioleaching of a Cobalt-Containing Pyrite in Stirred Reactors: a Case Study from Laboratory Scale to Industrial Application

DOMINIQUE HENRI ROGER MORIN, PATRICK D'HUGUES

2.1 Introduction

The Kilembe sulfide deposit in the district of Kasese (located 420 km west of Kampala, Uganda), which was mined for 26 years (1956–1982), produced 16 million tons of copper ore and a cobalt-rich pyrite concentrate that had been stockpiled at the Kasese railway terminal, 12 km downhill from Kilembe Mine. The amount of concentrate available on site was approximately 900,000 t and contained approximately 80% pyrite and 1.38% cobalt, (an estimated cobalt metal reserve of some 11,300 t). Most of the cobalt is disseminated in ionic form within the pyrite lattice.

Heavy rainfalls dispersed the pyrite concentrate in large trails over several kilometers downhill from the stockpile, causing the release of sulfuric acid and heavy metals and consequently the deterioration of the environment in this area (Fig. 2.1).

The “Kasese project” started in the BRGM facilities at Orléans in 1988 with the first laboratory-scale testwork. The objective was to demonstrate that the recovery of cobalt from Kasese pyrite using (bio)hydrometallurgy was technically and economically feasible. In 1992, the Kasese Cobalt Company (KCC) was created to establish the techno-economic viability of the project, and then to find investors for the industrial project. Ten years after the first tests in the BRGM laboratory, in 1998, the project became a reality with the inoculation of the bioleach tanks on-site.

Step by step, the study of the applicability of bioleaching to recover cobalt from the cobaltiferous pyrite concentrate passed all the required feasibility studies. From the beginning, a large number of positive features appeared to give the project a real chance to succeed:

- The pyrite concentrate did not require any mining investment.
- Water was potentially abundant at the Kasese site.
- Limestone is abundant as it is a major component of the subsurface of the Rift Valley near the site.
- The region is served by reasonable infrastructure, including electricity supply.
- There was a strong political motivation to eradicate the environmental black spot represented by the stockpile at the border of a natural reserve



Fig. 2.1. Aerial view of the pyrite concentrate stockpile before the implementation of the bioleaching plant. In the background, devegetated areas downhill from the stockpile due to pyrite run-off

(Elizabeth National Park) that contaminated several square kilometers of land and a lake (Lake George).

- The site topology below the stockpile is characterized by a gentle slope, appropriate for the hydraulic transport of the slurries and solutions.
- There was virtually no activity on the land around the site.
- Natural biodegradation of the pyrite could be observed on-site, and was confirmed by initial laboratory tests.

Notwithstanding the aforementioned points, the feasibility of the project could only be established after a long series of amenability assays and optimization works, the main results of which are described in this chapter. This involved demonstrating the “bioleach-ability” of the pyrite concentrate, and that cobalt could be efficiently solubilized using an acceptable level of energy consumption. This result was obtained after optimizing the operating conditions of bioleaching and by determining specific design criteria for the

equipment and the power requirement. A major and unique specificity of the process used in the KCC plant is the management of the pregnant solution to extract four metals, cobalt, zinc, copper and nickel, after the removal of iron. Only cobalt is recovered in economic quantities, the other metals having marginal grades in the concentrate. This makes a quite complex hydrometallurgical flowsheet that has, however, been shown to be efficient, robust and flexible.

Beyond the description of the case study, this chapter highlights the spin-offs of the optimization work required to ensure a viable application of the bioleaching technique to the cobaltiferous pyrite of Kasese for the benefit of the development of biohydrometallurgy in general.

2.2 Feasibility and Pilot-Scale Studies

2.2.1 Characteristics of the Pyrite Concentrate

The stockpiled cobaltiferous pyrite is a flotation concentrate, the typical composition of which is shown in Table 2.1. The cobalt is mainly disseminated in pyrite in an unidentified form, but is also present in very small amounts as siegenite $[(\text{Co},\text{Ni})_3\text{S}_4]$ and in a pentlandite $[(\text{Ni},\text{Fe},\text{Co})_9\text{S}_8]$ – bravoite $[(\text{Fe},\text{Ni},\text{Co})\text{S}_2]$ association. Microprobe analysis showed that the cobalt present is in ionic form in the pyrite crystal lattice with an average grade of 1.7% and, in this connection, it was observed that the dissolution of cobalt was strictly proportional to the decomposition of pyrite up to at least 85% pyrite degradation. The gangue minerals are mostly quartz, silicates and neogene gypsum; there is no significant amount of carbonates present. The particle size distribution of the concentrate is such that more than 95% of the particles by weight are less than 150 μm in size with 80% of particles (P80) smaller than 90 μm . The average specific gravity of the concentrate is about 4,000 kg m^{-3} .

2.2.2 Bioleaching of the Cobaltiferous Pyrite

Cobalt sulfides are known to be leachable under bacterial activity and cobalt in solution can reach concentrations as high as 30 g L^{-1} (Torma 1988). The

Table 2.1. Average composition of Kasese pyrite flotation concentrate limestone

Fe (%)	Sulfide (%)	Sulfate-S (%)	Sulfur (%)	Co (%)	Ni (%)	Cu (g t^{-1})	Zn (g t^{-1})	Pb (g t^{-1})
38.3	40.9	0.73	0.3	1.38	0.12	2 005	167	24
Cd (g t^{-1})	As (g t^{-1})	Sn (g t^{-1})	Sb (g t^{-1})	Mn (%)	Al (%)	Si (%)	Ti (%)	Ca (%)
<2	303	<10	<10	0.03	1.16	3.5	0.05	1.4

solubilization of cobalt from pure cobaltite, or CoS, or from other sulfide minerals has been reported elsewhere (Thompson et al. 1993). In the case where cobalt is finely disseminated in a sulfide matrix, like pyrite, the bioleach processing is quite similar to the bioleaching of a refractory gold ore (Chap. 1), with the aim being to oxidize and dissolve the pyrite in order to release the metal (in gold processing the metal is exposed but remains in the mineral and is solubilized by cyanide).

2.2.3 Inoculation and Microbial Populations

The original culture used to inoculate the first amenability tests of the KCC project originated from acid mine drainage waters sampled by BRGM. In order to adapt the inoculum to the cobaltiferous pyrite, the microorganisms were subcultured several times on this substrate. Originally, Collinet-Latil and Morin (1990) isolated strains of *Acidithiobacillus ferrooxidans* and *At. thiooxidans* from this population. During the first continuous bioleaching testworks, *Leptospirillum*-like bacteria, associated with the rod-shaped bacterial population, were identified (Battaglia et al. 1994b; Battaglia-Brunet et al. 1998).

Since 2000, single-strand conformation polymorphism (SSCP; Chap. 12) has been used to investigate and compare the diversity of the bacterial culture in different operating conditions. This includes at laboratory and industrial scales, in batch and continuous modes, and in air-lift reactors and mechanically agitated reactors (Battaglia-Brunet et al. 2002; d'Hugues et al. 2003; Foucher et al. 2003). The predominant organisms (five strains out of seven) were studied using 16S ribosomal RNA gene sequencing. The results revealed the presence of bacteria affiliated to the genus *Leptospirillum* (two different strains), *At. thiooxidans*, and also an *At. caldus* like organism and a *Sulfobacillus thermosulfidooxidans* like organism. Whichever operating conditions were used, organisms related to *Leptospirillum* spp. (probably *L. ferriphilum*) and an *At. thiooxidans* like organism were always present, within a community of two to six different bacterial species. The occurrences of *At. caldus* like and *S. thermosulfidooxidans* like bacteria were more variable (d'Hugues et al. 2003). Attempts were made to determine the proportions that were attached to solid particles or freely suspended in the medium using a combination of PCR-SSCP and microscopic techniques (Battaglia-Brunet et al. 2002; d'Hugues et al. 2003; Foucher et al. 2003). In the liquid phase, *At. thiooxidans* like bacteria were dominant during the early phase of batch, but were later supplanted by *Leptospirillum*-like bacteria. *Leptospirillum* spp. were always in the majority on the solids. The growth of *S. thermosulfidooxidans* like bacteria seemed to be favored by less intensive agitation-aeration operating conditions. In laboratory batch tests with pyrite, *At. thiooxidans* like bacteria were always present in significant numbers at the beginning of the tests; however, *Leptospirillum* spp. always appeared as the major contributor to

bioleaching, especially at industrial scale in continuous conditions. The predominance of *Leptospirillum* organisms over both *At. thiooxidans* and *At. caldus* has been observed in other industrial cultures (Rawlings et al. 1999). *Leptospirillum* spp. have been found by other authors to be the major solid colonizer on pyrite, whereas sulfur-oxidizing *Acidithiobacillus*-like organisms are less represented on the solids fraction (Norris et al. 1988). From these various observations, it was assumed that pyrite dissolution mainly resulted from oxidation by ferric iron located at the interface between the pyrite surface and the attached *Leptospirillum* organisms. The critical role of *Leptospirillum* spp. would be the subsequent reoxidation of ferrous iron produced during pyrite oxidation. The development of *At. thiooxidans* or *At. caldus* would be of less direct importance to the overall bioleaching efficiency.

From the tests carried out on the KCC industrial operation, it was shown that the industrial population was mainly composed of microorganisms that were also present in laboratory-scale cultures growing on the same concentrate; however, it was not determined whether the main industrial strains were indigenous to the Kasese concentrate or originated from the inoculum used at laboratory scale. Appropriate studies of the biodiversity in the Kasese stockpile and in the Kilembe deposit where the pyrite was extracted might be a valuable contribution to the understanding of the role of microbial ecology in the development of new mineral technologies (Johnson 2001). Even though the first tests using different molecular biology approaches led to quite promising, reproducible and coherent results, the work to be carried out on the ecology of iron-oxidizers and sulfur-oxidizers remains considerable. Future studies will have to be cross-checked using different techniques and will have to go beyond merely identifying the microorganisms present, and focus also on the microbial population dynamics of these bioleach systems.

2.2.4 Optimizing the Efficiency of Bioleaching

Preliminary tests showed that the cobaltiferous pyrite could be satisfactorily bioleached to release cobalt in solution (Morin et al. 1993). Extensive studies on the influence of some key operating parameters were carried out in batch tests using 200-mL air-lift tubes (Battaglia et al. 1994a), such as pH, influence of dissolved iron and cobalt, nutrient medium optimization, solids concentration, particle size distribution, inoculum size and temperature. The resulting optimized operating conditions found were:

- Optimum growth temperature: 35°C with thermotolerance up to 46°C
- Solids concentration: 10–15% (by weight)
- Particle size: all particles ground to smaller than 63 µm
- pH in the tanks: between 1.3 and 2.0

In addition, the bioleaching population displayed relatively high tolerance to soluble ferric iron (more than 35 g L⁻¹) and cobalt (more than 5 g L⁻¹). The basic nutrient medium was initially adapted for bioleaching arsenopyrite

concentrate, using a modified 9K medium. This 0Km medium (9K without iron, "m" indicating modification of the basal salts) has the following composition: $(\text{NH}_4)_2\text{SO}_4$, 3.7 g L⁻¹; H_3PO_4 , 0.8 g L⁻¹; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.52 g L⁻¹; KOH, 0.48 g L⁻¹. The same medium was tested on the cobaltiferous pyrite using different nutrient concentrations. The best bioleaching rate was obtained when using the classic concentrations of the 0Km medium. Therefore, it seems that the substrate characteristic (pyrite vs. arsenopyrite) did not influence the optimal nutrient requirements of the bacterial population.

After the screening, the most critical operating parameters in batch cultures were further investigated in more detail in continuous operations with agitated tank reactors at laboratory (80 L), pilot (4 m³) and semi-industrial (65 m³) scales (Morin et al. 1995; d'Hugues et al. 1997). It was found that the mineral oxidation rate was at least 30% faster in continuous mode than in batch conditions, showing the importance of running continuous bioleaching tests when the objective is to evaluate performances with a view to application at an industrial scale.

The following operating conditions were investigated in detail:

- Solids concentration
- Residence time
- Oxygen and carbon dioxide: gas-liquid transfers, consumption and limiting concentrations in solution
- Nutrient concentrations
- Recycling of cobalt solutions

The solids concentration for the operation constitutes one of the most critical parameters of the bioleaching process in terms of impact on the size of the equipment. Since the industrial bioleach plant was planned to operate at a pulp density of 20% solids, several factors, such as oxygen requirement, nutrient availability, physical effect of mechanical shearing and turbulence on the bacterial cells generated by agitation, were suspected to limit the bioleaching efficiency at such a high solids concentration. A test was carried out at 20% solids in a continuous laboratory-scale unit composed of four stirred reactors arranged in a cascade (d'Hugues et al. 1997). The gas balance method was used in order to follow O₂ and CO₂ consumption throughout the experiment. Using on-line gas analyzers, it was possible to simultaneously monitor the physiological behavior of the microorganisms and the pyrite oxidation kinetics. The best pyrite oxidation kinetics obtained was 80% cobalt extraction in 4.5-days' residence time. It was later demonstrated that even more efficient kinetics could be achieved at 20% solids, and that the minimum residence time before washing out the reactors was 1 day.

The dissolved oxygen concentration below which oxygen availability was limiting was 1.2 mg L⁻¹. This limiting dissolved oxygen concentration was slightly greater than the values stated in the literature at that time (Pinches et al. 1988; Chapman et al. 1993) and was generally in the range 0.1–1.1 mg L⁻¹. The oxygen requirement for pyrite oxidation was estimated to be on average

0.89 kg of O₂ per kilogram of pyrite oxidized (11% below the theoretical value resulting from the stoichiometry of reaction of 1 kg kg⁻¹ to produce sulfur as sulfate and iron as ferric iron).

In the absence of oxygen limiting conditions, the role of the bacteria in the oxidation of the pyritic substrate did not seem to be directly related to their growth. Similar observations had already been made by various researchers (Nagpal et al. 1993; Mandl 1984). However, the quantity of biomass formed in the first steps of bioleaching influenced the overall efficiency of cobalt recovery.

Carbon dioxide uptake rate measurements also allowed it to be demonstrated that high agitation rates could affect bacterial productivity. More than high shearing effects induced by the agitation system, the excessive hydrodynamic turbulence caused by aeration and agitation was suspected to be the main physiological stress factor for the microbial population. It was suspected, as already observed in similar cases (Bailey and Hansford 1993), that the mechanical and hydrodynamic forces limited bacterial productivity by inhibiting bacterial contact with the solid substrate.

Preliminary laboratory- and pilot-scale studies carried out at 10% solids indicated that reagent-grade chemical compounds (orthophosphoric acid and ammonium sulfate) could be successfully replaced by fertilizer-grade chemicals such as diammonium phosphate and urea, which would be, in economic terms, more suitable for industrial-scale bioleaching; however, as limiting phenomena were expected at higher solids concentration, the test of replacing urea by ammonium was also carried at 20% solids (Fig. 2.2).

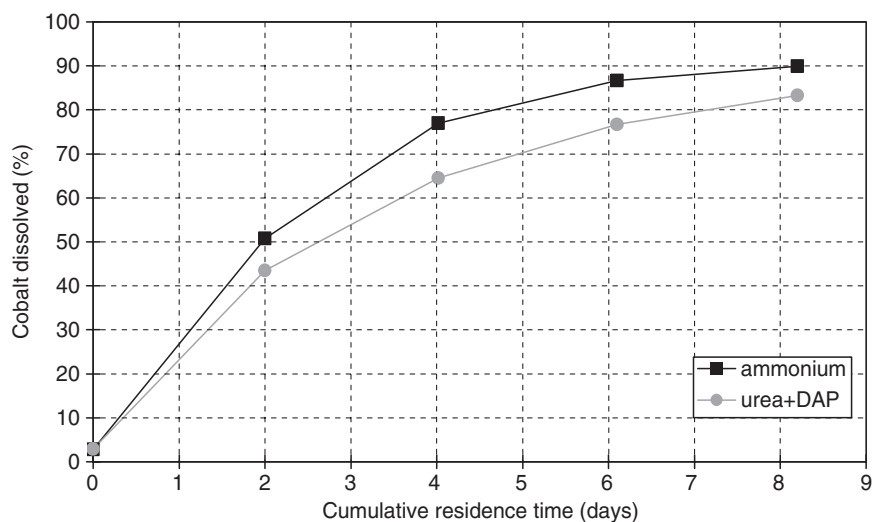


Fig. 2.2. Influence of the nitrogen source on the kinetics of cobalt dissolution. DAP diammonium phosphate

When nitrogen was provided as ammonium, improvements in bacterial growth and pyrite oxidation were observed (d'Hugues et al. 1997). These results were correlated with a more efficient attachment of the bacteria to the solid substrate, and also to an increase in the formation of iron precipitates. It was concluded that the use of ammonium rather than urea improved the bioleaching efficiency by favoring bacterial attachment to the solid substrate.

Other authors have also reported a positive influence of precipitates on the oxidation of ores, for example, Southam and Beveridge (1993) showed that bacterial cells were cemented to mineral surfaces by iron precipitates. This phenomenon could play an important role in sulfide mineral oxidation by creating an acidic oxidative microenvironment which would favor chemical and biological substrate degradation.

The influence of variations of solution composition as a result of bioleaching on pyrite degradation was also evaluated. It was shown, for example, that the dissolved cobalt concentration had only a limited inhibitory effect at more than 5 g L⁻¹. This tolerance of the bioleaching microorganisms to high concentrations of soluble cobalt was essential for the industrial application as it meant that pregnant bioleach solution could be recycled to the feed after iron removal to upgrade the concentration of cobalt in solution and consequently minimize water consumption.

The addition of CO₂ (at 1% of the volume of air) injected in the series of continuous stirred bioreactors improved microbial growth, though 2% CO₂ did not bring further improvement. This effect of CO₂ was only observed under optimal conditions of oxygen supply, indicating that control of the kinetics by CO₂ transfer only occurred when the mineral oxidation was no longer limited by the transfer of O₂. In terms of operability, the combination of the effects of the dissolved CO₂, excess acidity and high ferric iron concentration justified having a continuous addition of limestone to the bioleach tanks. As described later, the control of pH in the tanks by limestone addition was a critical operating parameter in the full-scale operation.

Some main operating parameters to be also determined for the engineering of the industrial plant were the power consumption required for dispersing air (to promote oxygen transfer), and the elimination of excess heat. In 1-m³ reactors it was demonstrated that the agitation system could ensure an oxygen transfer efficiency up to 40%. Together with oxygen transfer, power consumption and heat transfer were studied and optimized in a 65-m³ tank equipped with the same agitation system as the laboratory-scale unit. The BROGIM agitation system was designed in a collaborative project between Robin Industries (France, now Milton Roy Mixing) and BRGM (Bouquet and Morin 2005). The agitation system was designed so that the air at the bottom of the tanks is dispersed by a disk turbine, whereas the pumping effect in the tank is ensured by one propeller (or two propellers) placed above the turbine. The pilot testwork in the 65-m³ tank confirmed the efficiency of the agitation system to disperse air and provided data required to scale up the system to industrial size.

2.2.5 Solution Treatment and Cobalt Recovery

2.2.5.1 Neutralization of the Bioleach Slurry

As a result of pyrite oxidation, iron and sulfate were the main chemical species in the bioleach liquor. The first step of the treatment process involved neutralizing the solution at a pH close to 3 (Fig. 2.3). Adding a limestone slurry caused the iron(III) to precipitate as jarosites and ferric hydroxide, accompanied by the formation of gypsum.

The solids were then separated from the liquid by thickening and filtration, using a nonionic or cationic flocculant. The filterability, evaluated by means of a 0.5-m² pilot belt filter, was in the range 0.32–0.48 t (dry weight) solids h⁻¹ m⁻². The efficiency and the stability of the filtration could only be ensured if gypsum crystals reached a significant size (more than approximately 100 µm). This was readily achieved by recycling a fraction of the neutralized slurry to the feed of the neutralization stage, thereby seeding with gypsum crystals and improving crystal growth. The recycling of neutralized slurry facilitated minimizing the size of the equipment required for neutralization and filtration at the industrial-scale operation.

A typical solid residue composition is shown in Table 2.2. The cobalt and sulfur contents in the residue (0.1 and 2.4%, respectively) were actually lower

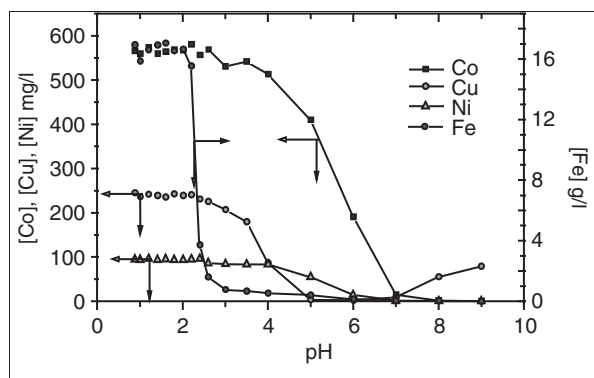


Fig. 2.3. Solubilities of Co, Cu, Ni and Fe versus pH in a typical bioleach solution neutralized with lime slurry

Table 2.2. Composition of the solids residue obtained after neutralizing the bioleach pulp with the substances listed

Co (%)	Fe (%)	Cu (g t ⁻¹)	Ni (g t ⁻¹)	Sulfate-S (%)	S total (%)	Sulfide (%)	CO ₃ (%)	C _{org} (%)	Si (%)	Ca (%)	Moisture (% H ₂ O)
0.1	13.2	470	145	13.9	16.4	2.4	0.1	0.15	1.7	13.6	29.5

after recycling of the unleached pyrite as described in Sect. 2.3.4; gypsum represented about 60% of the solids by weight. Limestone consumption was about 1.1 t per tonne of oxidized pyrite concentrate. Beside the calcium carbonate grade (94% on average), a critical characteristic of the limestone was its magnesium content, as this element was likely to build up along with the water recycling and consequently to interfere with the purification treatment and the extraction of the valuable metals. Moreover, it is costly to eradicate magnesium from the final effluent. It was established that its grade had to be less than 2% to minimize its impact on the process performance.

In order to minimize the volume of organic phases involved in the solvent extraction stages of the hydrometallurgical plant, the pregnant solution from the filtration stage was recycled to the bioleach section, thereby increasing the cobalt concentration to approximately 5 g L^{-1} , the apparent threshold of inhibition for the bacterial activity. A very small amount of cobalt was lost during filtration owing to coprecipitation. However, acid washing of the filter cake resulted in a recovery of more than 99% cobalt in solution in the pilot-scale operation, and this was also confirmed at the industrial scale.

2.2.5.2 Removal of Iron from the Pregnant Solution

The primary solution coming out of the belt filter had the average composition shown in Table 2.3. The final iron-removal step aimed (1) to oxidize the ferrous iron present (approximately 0.5 g L^{-1}) to ferric iron and (2) to complete the precipitation of iron as hydroxide and jarosites in order to achieve a final concentration in the liquor of less than $1\text{--}5 \text{ mg L}^{-1} \text{ Fe}$. This treatment was required to avoid iron contamination and deleterious precipitation of ferric compounds during the further purification and extraction stages. Both air and hydrogen peroxide were used for the oxidation of the ferrous iron. For neutralization, the pH was adjusted to 4 by the addition of limestone; no detectable cobalt losses were observed during this step.

2.2.5.3 Zinc Removal

Despite the low content of zinc in solution, a zinc solvent extraction unit was required to avoid poisoning of the downstream cobalt extraction. The zinc extraction used a mixture of 5% di(2-ethylhexyl)phosphoric acid (D2EHPA) diluted in kerosene. The optimal operating parameters were established by means of continuous bench-scale testwork that demonstrated the efficiency of

Table 2.3. Typical average composition (mg L^{-1}) of the primary biosolution from the belt filter

Co	Cu	Ni	Fe	Zn	Mg	Sn	Sb	Pb	Cd	Al	Mn
4,663	313	406	3,000	46	900	<0.1	4	3.6	2.7	90	12.4

a typical three-stage treatment: extraction/scrubbing (to remove the traces of cobalt extracted by the solvent)/stripping. As was expected, zinc was removed from the aqueous feed below 1 mg L^{-1} and was recovered completely in the stripped liquor. Good recovery of the small amount of cobalt loaded or carried along with the D2EHPA was obtained by scrubbing with a dilute sulfuric acid solution. All scrubbed organic-phase analyses have shown that the cobalt concentration in the solvent, before stripping, was below 1 mg L^{-1} . Nickel was not extracted, but copper (and manganese) was slightly extracted and partially scrubbed. About 1.9% of the feed copper was lost in the stripping solution. Owing to the low level of iron in the feed solution, the balance for this metal was difficult to assess. Iron was extracted and appeared to be stripped. Organic-phase analysis showed the presence of an iron-circulating load, but the fact that no build-up was observed indicated that an acceptable equilibrium could be reached. All lead was extracted and stripped but with time, and owing to recycling of the stripping phase, precipitation of lead sulfate was observed. Only 20% of the feed aluminum was extracted, despite the half-extraction pH (pH value at which the extracted metal is distributed in equal quantities in the aqueous and organic phases) for this metal being in the range 1–2. This was explained by the fact that aluminum loading was kinetically inhibited.

2.2.5.4 *Copper Removal*

A number of processes such as cementation and sulfidization were considered for the removal of copper, but it was concluded that these were inadequate and/or too expensive. Solvent extraction by LIX 622 combined with electrowinning was tested, but although this gives a satisfactory metallurgical solution, the investment payback was too low for the metal production involved. Finally, it was decided to precipitate copper hydroxide by neutralizing the zinc raffinate with limestone and sodium hydroxide. A two-step precipitation was designed in order to minimize cobalt loss. In the first step the zinc raffinate (pH 2.5) is neutralized in a series of three tanks by addition of limestone in the first two tanks and of caustic soda in the last one. After thickening, the overflow is routed to the second stage, whereas the underflow is filtered on a filter press. The solid residue is collected and sold as a by-product. In the second stage, the pH of the solution is increased to 7 using sodium hydroxide. After thickening and clarification, the liquor is sent to the cobalt solvent extraction. Since coprecipitation of cobalt begins to be significant at this pH, the thickened underflow is recycled back to the process in order to release the solids that have been precipitated.

2.2.5.5 *Cobalt Solvent Extraction and Electrowinning*

Final hydrometallurgical purification of the cobalt and electrowinning were first studied using laboratory-scale equipment to determine the general

operating parameters. These parameters were then tested in a continuous circuit to optimize (1) the solvent extraction at pilot scale (10 L h⁻¹ of aqueous solution) and (2) the cobalt electrolysis in a 2-m³ cell, with 1-m² electrodes.

CYANEX 272 (dissolved in kerosene at 15% v/v) was selected for extracting and purifying the cobalt from the decopperized leachate. The cobalt extraction yield was around 99%, leaving a raffinate with less than 5 mg L⁻¹ cobalt. The pH in the mixer-settlers used for loading was adjusted continuously by addition of caustic soda containing 140 g L⁻¹ NaOH. Nickel, magnesium and calcium are rejected from the solvent during scrubbing. The scrub solution was prepared from strong electrolyte after (1) dilution in order to achieve a cobalt concentration of about 10 g L⁻¹ and (2) adjustment to pH 3 by addition of NaOH.

Results from the laboratory and pilot tests of electrowinning led to the following basic design characteristics:

- Temperature: 70–75°C
- Spent electrolyte: 40 g L⁻¹ Co, 10–13 g L⁻¹ H₂SO₄
- Strong electrolyte: 45 g L⁻¹ Co, 2 g L⁻¹ H₂SO₄

The reactions involved are as follows:

- Cathodic reactions:
 $\text{Co}^{2+} + 2e^- \rightarrow \text{Co metal}$
 $2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{g})$
- Anodic reaction:
 $\text{H}_2\text{O} \rightarrow 0.5\text{O}_2(\text{g}) + 2\text{H}^+ + 2e^-$

Cathode: SS 316L

Cell voltage: 5 V

Current efficiency: 60–70%

Anode: Pb–Sb alloy

Current density: 300 A m⁻²

Pulling cycle: 4–5 days

With the earlier electrowinning tests, performed at laboratory scale and without final iron removal or zinc solvent extraction, the chemical grade of the cobalt deposit was 99.73% Co. At the industrial scale, the efficiency of the purification stages results in a cobalt grade often in excess of 99.9%.

2.3 Full-Scale Operation: the Kasese Plant

Construction of the full-scale bioleaching operation began in 1998 and was completed in 1999. Bioleach tanks at the KCC plant are shown in Fig. 2.4.

2.3.1 General Description of the Process Flowsheet

A simplified block diagram of the process flowsheet is shown in Fig. 2.5.



Fig. 2.4. Bioleach tanks (Bioco reactors) at the Kasese Cobalt Company (KCC) plant

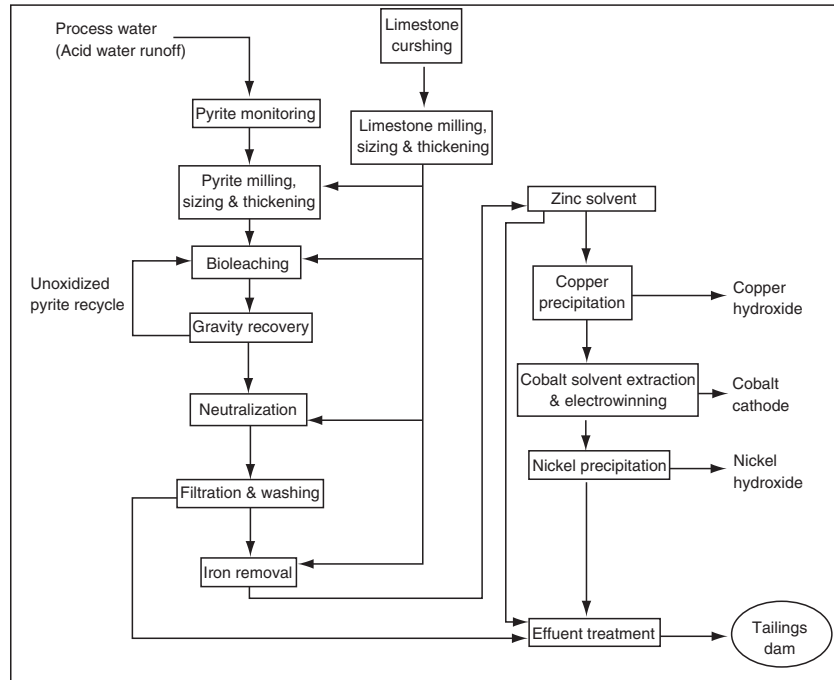


Fig. 2.5. General process flowsheet of the KCC installation

The seven main steps of the process are as follows:

1. Pyrite concentrate reclamation by hydraulic monitoring
2. Physical preparation of the pyrite concentrate and limestone
3. Bioleaching
4. Iron removal
5. Solution purification and solvent extraction
6. Cobalt electrowinning and conditioning
7. Effluent treatment and waste management

The general characteristics of these steps are outlined in the following sections and the bioleaching treatment is described in more detail.

2.3.2 Pyrite Reclamation and Physical Preparations

Pyrite concentrate is reclaimed from the stockpiles at a nominal rate of 245 t day⁻¹ using high-pressure monitor guns and is then pumped to the process plant. Reclaimed slurry is thickened and the thickened underflow is pumped to the regrind circuit, where the pyrite particle size is reduced to P80 < 35 µm (“passing 80%, i.e., size under which 80% by weight of the mineral sample is smaller than”). Reground pyrite, classified by hydrocyclones is thickened to 50% solids prior to bacterial oxidation. After recycling of a fraction of the pregnant solution from filtration of the bioleach slurry to build up cobalt and the addition of a concentrated solution of nutrients, the pulp density of the feed to the bioleach circuit is reduced to 20%.

Limestone is crushed to smaller than 90 mm at the quarry prior to transport to the plant site at Kasese, where it is subjected to secondary crushing to smaller than 9 mm by a energy impact crusher and then ball milling to 80% smaller than 44 µm. Ground limestone is stored in a tank as a slurry at 50% solids in weight and is distributed to the bioleach and neutralization circuits by means of a ring at a steady flowrate in order to avoid plugging of the pipes.

2.3.3 Bioleach Circuit

The bioleach circuit includes a primary stage with three tanks in parallel, and secondary and tertiary stages of one tank each. Theoretically, this configuration is optimized to ensure a safe retention time for the bacterial growth in the primary stage and sufficient mineral biooxidation in the later bioreactors. The design is a compromise between the following constraints: (1) to minimize the overall unit volume; (2) to minimize the number of tanks (and thus the number of mixing systems) and (3) to ensure a maximum height of slurry owing to the admissible head pressure of the blowers (about 150 kPa). Every tank [constructed of stainless steel, 304L (BS) grade] has the same total operating volume (1,380 m³), and gravity transfer through gutters ensures the bioleach slurry flows from one stage to the next.

Air is supplied to the bioleach tanks by five blowers (HV Turbo), which can feed each tank up to the equivalent value of $20,000 \text{ m}^3 \text{ h}^{-1}$ air in normal conditions (0°C , 100 kPa). The operating airflow rates in the tanks are in the range $10,000\text{--}15,000 \text{ m}^3 \text{ h}^{-1}$ in the primary-stage reactors and between $5,000$ and $10,000 \text{ m}^3 \text{ h}^{-1}$ in the secondary- and tertiary-stage reactors. Flowmeters on every air feed pipe monitor airflow rates in cubic meters per hour for normal conditions (i.e., they are converted into values at 0°C and 100 kPa and are expressed as normal cubic meters per hour). Aeration and mixing in the tanks are ensured by air injection and the BROGIM system designed according to the size of the tanks and to the oxygen transfer and mixing requirements (Fig. 2.6).

The nominal average temperature in all tanks is 42°C . Heat control is ensured by internal stainless steel cooling coils connected to a cooling tower. Each primary tank contains more than 1.5 km of coils for heat transfer. Heat transfer efficiency is an important design criterion for the mixing system. The pH is kept as constant as possible in every tank by the continuous addition of limestone slurry at a controlled rate. The nominal values are $1.4\text{--}1.5$ and $1.5\text{--}1.7$ in the primary and secondary/tertiary tanks, respectively. Limestone addition functions not only to neutralize the acidity produced by the oxidation of the sulfide compounds, but also to generate CO_2 in situ for the autotrophic mineral-oxidizing bacteria.

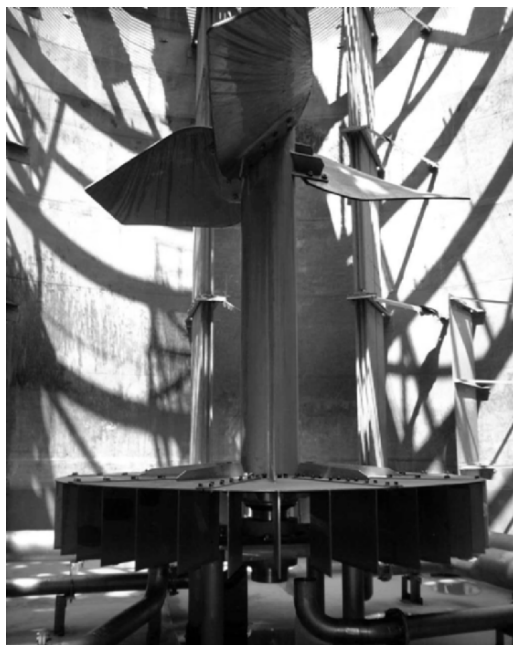


Fig. 2.6. Bottom part of the agitation system (BROGIM) in the bioleach tank

2.3.4 Recycling of Sulfide in the Bioleach Process

Very early in the study of optimization of the bioleach process, it was thought that the recycling of coarse sulfide solid particles would ensure a longer residence time of this relatively refractory fraction of the concentrate while minimizing the total residence time. Recycling that fraction of the pyrite by gravity separation, using differences in specific gravity between the different compounds, was technically conceivable as it was already used at an industrial scale in other operations, such as processing iron, tin and gold ores. In theory, such a recycling had several other advantages. A fraction of the biomass is recycled, which stabilizes the bacterial growth and the more refractory sulfides bearing copper and nickel are better dissolved, which reduces the grades of these metals in the final residue. On the other hand, improved dissolution of these metals increases their concentrations in the pregnant solution and therefore increases the operating cost of their extraction for removal from the final effluent. The recycling of refractory material may also have the drawback that, under steady-state conditions, the solids concentration in the bioleach tanks is higher than in the feed, or even constantly increases. The innovative idea of recycling the sulfide particles from a bioleach slurry to the feed of the bioleaching treatment is patented by BRGM under the name BIOGRAV.

A simulation exercise showed that pyrite recycling could significantly improve cobalt recovery, and so it was decided to implement a gravity circuit, which had, however, to be simple and low in cost. The equipment used for the recovery of the heaviest fraction of the slurry flowing out from the last bioleach tank includes a hydrocyclone aimed at removing the finest particles of iron hydroxide and a series of gravimetric spirals that produce a concentrate, which is recycled into the feed of the bioleach circuit.

2.3.5 Monitoring of the Bioleach Process Performance: Some Practical Results

Measuring O_2 and CO_2 in the off-gas flows of the tanks is a reliable method of monitoring the bioleaching performance. This method allowed taking measurements required for the determination of the optimal air flow rates. Typical results of oxygen uptake rate for a primary tank are shown in Fig. 2.7.

It appeared that an air flow rate between 11,000 and 12,000 $N\ m^3\ h^{-1}$ was the minimum value to obtain a maximum oxygen uptake rate level. The maximum oxygen uptake rate values obtained were between 1,350 and 1,400 $mg\ L^{-1}\ h^{-1}$, correlating with an oxygen transfer rate of about 1,750 $kg\ O_2\ h^{-1}$ in a primary bioleach tank and an oxygen transfer efficiency of approximately 50%. Such a high oxygen transfer efficiency value was above that originally predicted. Measurements of dissolved oxygen at the top of the bioleach tank showed that the oxygen concentration was in the range 1.5–2.0 $mg\ L^{-1}$ for

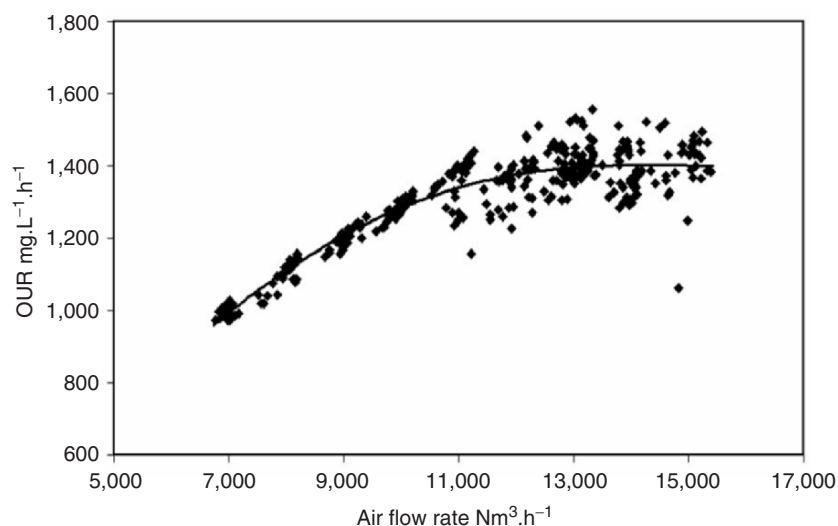


Fig. 2.7. Oxygen uptake rate (OUR) vs. air flow rate in a primary bioleach tank of the KCC plant

flow rates from 10,000 to 12,000 N m³ h⁻¹. In this range of flow rates, the oxygen concentration was above the theoretical limiting value of 1.5 mg L⁻¹.

One critical operating aspect for the aeration was the difficulty in balancing the air pressure in all the bioleach reactors. Differences in pressure load from one reactor to another frequently resulted in blower trips.

Using the gas analysis system, the CO₂ availability in the bioreactor was identified as a critical issue for the bacterial activity as it is the source of carbon for the autotrophic iron-oxidizers and sulfur-oxidizers present. In other industrial bioleach reactors, mainly dedicated to oxidation of gold-containing minerals, CO₂ is usually supplied through the dissolution of carbonates present in the concentrates. As no carbonates occur in the Kasese pyrite concentrate, the CO₂ required for optimal growth is generated by dissolution of the limestone added for pH control. Therefore, it was important that limestone addition was as constant as possible so that CO₂ could be provided to the culture continuously. This change in the limestone addition procedure helped to improve bacterial growth and consequently the bacterial density of the culture.

When the bioleach reactor is affected by technical problems, the drop of pyrite oxidation leads to a “vicious cycle” of reduced CO₂ availability, as the regulation of the CO₂ level is directly related to the oxidation efficiency (acid production) through the pH regulation.

The gas analysis system has proven to be very accurate and reliable for monitoring the bacterial oxidation of the cobaltiferous pyrite. This tool was

very helpful to follow the bacterial culture and to assess the consequences of any process deviation. This system could also be used to optimize the process and evaluate the effect of any changes in the operating conditions.

2.3.6 Bioleaching Performance

Approximately 60% of the total pyrite is oxidized in the primary bioleach stage and the rest of the oxidation (20–30%) occurs in the two other stages. The other stages can be limited to one tank only, which allows the shutdown of a reactor for maintenance and the reconfiguration of the remainder to retain three primary bioreactors. The total residence time, accounting for the addition of limestone slurry and the gas hold-up, is about 6 days with the full circuit running, and the cobalt dissolution yield generally approaches 80%.

2.3.7 Processing of the Pregnant Liquor

2.3.7.1 Iron Removal

Iron is removed in two operations. The first treatment is carried out in a series of three agitated tanks of 300 m³ in series where limestone slurry is added to increase the pH of the bioleach slurry stepwise to 3. Then the neutralized slurry is filtered on a belt filter of 73 m³. The primary filtrate is pumped to the next iron removal area and the wash filtrate is used to dilute the bioreactor feed to the required density. The solid residues are repulped with raw water and transferred to the effluent treatment area.

Another neutralization of the primary filtrate to pH 5.7 removes the remaining traces of iron with the aim of achieving a final concentration of less than 1 mg L⁻¹ to prevent iron poisoning of the zinc extractant.

2.3.7.2 Solution Purification and Solvent Extraction

Zinc is extracted at pH 3 with D2EHPA diluted in high flash point kerosene. Cobalt, copper and nickel coextracted into the organic phase with the zinc are removed by scrubbing and then zinc is stripped from the scrubbed organic phase using 50 g L⁻¹ sulfuric acid. Copper is removed by neutralization in two stages from the zinc raffinate using caustic soda solution to prevent copper poisoning of the extractant in the downstream cobalt solvent extraction plant at pH 5–7. Cobalt is extracted by CYANEX 272, diluted in high flash point kerosene. Nickel coextracted onto the organic phase (with the cobalt) is scrubbed and then the cobalt from the scrubbed organic phase is stripped using 130 g L⁻¹ sulfuric acid.

Finally, the precipitation of nickel from the cobalt raffinate at pH 9–10 using caustic soda solution produces a saleable nickel hydroxide product.

2.3.7.3 Cobalt Electrowinning and Conditioning

Cobalt is recovered by electrolysis from the pure solution generated by solvent extraction (which contains 40–50 g L⁻¹ cobalt), and results in a 99.9% pure product. The cobalt cathodes are crushed, burnished and drummed for shipment.

2.3.7.4 Effluent Treatment and Waste Management

All plant effluent is treated in a single operation. This includes repulped cake from the belt filter, strip solution from zinc solvent extraction and the overflow solution from nickel precipitation. The effluent is mixed with slaked lime slurry to a pH of 9 before being hydraulically transported to the tailings dam. In the tailings dam, the final solid waste products settle and the water is pumped at a controlled rate to the Rukoki river. As a pilot-scale processing of liquid wastes, a fraction of the outflow goes to a reed bed for further polishing. Up to 10% of the effluent is treated in constructed wetlands using locally available reeds (*Phragmites mauritianus*). Results show a significant amount of heavy metals and other chemical components is retained by the reed bed (up to 90% at low flow rates).

The effluent from the wetlands has been observed to encourage vegetation growth in the 150-ha arid trail area that resulted from the earlier runoffs of pyrite before the implementation of the metal processing on the site.

2.4 Conclusion

The optimization of the bioleaching treatment in stirred tanks applied to the cobaltiferous pyrite was a remarkable opportunity to focus attention on the most critical operating parameters of this process. The feedback from the industrial operation has shown that the performances of the plant are quite consistent with the predictions. Nevertheless, the answer to the question of whether chemical engineering or microbial physiology and ecology limits the efficiency of stirred-reactor technology remains uncertain.

The feasibility study estimated the lowest cobalt price for ensuring the economic viability of the project at US \$12/lb of metal. The cobalt price was between US \$6 and US \$8/lb of cobalt when the plant was put on care-and-maintenance status in September 2002. In 2003, and more so in 2004, global demand for cobalt increased to such an extent that the price of the metal reached more than US \$20/lb and the production at Kasese could be revived. The plant was restarted within a couple of months of this decision, demonstrating the flexibility and robustness of this technology.

The KCC plant employs 250 workers, among which 96% are Ugandans. Many local contractors also benefit from this industrial activity by providing services to the plant.

After the founding step of the use of bioleaching to recover copper and uranium by heap and in situ leaching, and later the application to refractory gold concentrates in stirred tanks, the KCC plant is the first industrial installation incorporating bioleaching into a sophisticated hydrometallurgical flowsheet allowing the selective extractions of various metals. As such, in the history of biohydrometallurgy, this operation can be considered as the milestone opening an era of the complex application of bioleaching.

Acknowledgements. KCC is gratefully acknowledged for the supportive collaboration with BRGM maintained after the start-up and commissioning of the plant. The authors are quite aware that the paper describes the main features of the KCC installation without essential improvements that have been made by the operators since the commissioning. Hopefully, another paper written with the operators will show how with time the solutions to unpredictable technical issues have been found. This paper was published with the authorization and support of the Research Direction of BRGM under reference number 04001.

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