COBALT RECOVERY FROM SOUTHERN AFRICAN COPPER SMELTERS

*R. T. Jones and C. Pawlik

Mintek
200 Malibongwe Drive, Private Bag X3015, Randburg, 2125, South Africa
*(*Corresponding author: rtjones@global.co.za)*

ABSTRACT

Cobalt occurs together with copper in the southern African copper belt, and a large portion of this cobalt ends up in copper smelting slags, mostly dissolved in oxide form. It is possible to achieve high recoveries of cobalt by reductive smelting of the copper slags, using some form of carbon as a reducing agent in an electric furnace. For example, a 40 MW DC arc furnace was operated at Chambishi Metals in Zambia from 2001 to 2008, and demonstrated cobalt recoveries of around 80% from slag to an iron-rich alloy containing copper and cobalt. The alloy was atomized prior to leaching. With the recent increase in demand for cobalt (and the resulting high metal prices), there has been increasing interest in this process route. There is also an alternative hydrometallurgical process for recovering the valuable metals from the slag. The choice between these process options requires a trade-off between capital and operating cost and environmental acceptability. This paper examines the potential for cobalt recovery from slags, and outlines various process options.

KEYWORDS

Africa, Cobalt, Copper, Furnace, Hydrometallurgy, Pyrometallurgy, Recovery, Slag, Smelter

INTRODUCTION

Cobalt has had a number of important uses in society since antiquity, and its principal use has changed dramatically over time. Since at least 2250 BC, cobalt-based pigments (cobalt blue) have been widely used to colour manufactured goods such as glass and pottery. Later, cobalt became known for its magnetic and wear-resistant properties and high-strength alloys, and most of the cobalt produced was consumed in the production of cobalt-based superalloys. The greatest recent growth in cobalt demand is due to it being essential to the rechargeable lithium-ion batteries used in consumer electronic devices and increasingly to drive electric vehicles.

Cobalt is usually produced as a by-product of copper or nickel. The copper belt in the Democratic Republic of the Congo (DRC) and Zambia supplies most of the world's cobalt production. In 2018, the DRC was expected to produce 90 000 tons of the world total of 140 000 tons of cobalt (Shedd, 2019). This paper focuses on the southern African copper industry, and specifically the cobalt that is able to be produced as a co-product from this.

A BRIEF HISTORY OF SOUTHERN AFRICAN COPPER SMELTING

Copper deposits in South Africa have been documented since at least 1685, when the Cape governor, Simon van der Stel, 'discovered' the 'Copper Mountain' at Springbok. South Africa's first public commercial mining company (imaginatively called the 'South African Mining Company') was established in Cape Town in 1846, to exploit the rich copper resources that were believed to exist in Namaqualand.

The first large-scale mine was sunk in 1852. Industrial-scale smelting began in South Africa in the 1850s or 1860s when copper was produced by the O'okiep Copper Company in cupola furnaces, and the partially smelted copper matte was exported to South Wales for further refining. The O'okiep Copper Company was floated on the New York stock exchange during the 1940s, and in the 1960s, O'okiep Copper Company paid the highest dividend ever on the NYSE for that period. Messina Copper Mine was producing a high-grade matte by 1914. Copper smelting started in the Zambian copper belt in 1931, with two reverberatory furnaces and two Peirce-Smith converters at Nkana. In 1966, Palabora Mining Company started smelting copper in a coal-fired reverberatory furnace and three Peirce-Smith converters. There are currently seven primary copper smelters and a secondary smelter in southern Africa (Jones & Mackey, 2015), as listed in Table 1. It should be noted that 40% of South Africa's copper production is a by-product of the platinum group metal (PGM) industry, and those smelters are not listed here.

Table 1. Southern African copper smelters

Smelter	Location	Technology	Production Capacity, kt/a
Kansanshi	Solwezi, Zambia	IsaSmelt	400
KCM (Konkola Copper Mines)	Nchanga, Chingola, Zambia	Flash	310
Chambishi (China Nonferrous Metal Mining Group)	Chambishi, Zambia	IsaSmelt	250
Mopani	Mufulira, Zambia	IsaSmelt	230
Palabora	Phalaborwa, South Africa	Reverb	160
Dundee Precious Metals	Tsumeb, Namibia	Ausmelt	45
Rubamin	Likasi, DRC		20
Copalcor	Germiston, South Africa	Induction (Secondary)	5
			1420

The southern African copper belt (spanning Zambia and the Democratic Republic of the Congo) produced over two million metric tons of copper in 2018, representing about 10% of world supply. As can be seen in Table 2, the production of primary copper from southern Africa is exceeded only by Chile and Peru.

Table 2. World mine production of copper in 2018 (Flanagan, 2019)

Country / Region	Mine production, kt/a	%
Chile	5800	28
Peru	2400	12
DRC + Zambia	2070	10
China	1600	8
USA	1200	6
Australia	950	5
Indonesia	780	4
Mexico	760	4
Russia	710	3
Other	4400	21
TOTAL (rounded)	21000	100

PYROMETALLURGICAL RECOVERY OF COBALT FROM COPPER SLAGS

Copper smelting slags are complex materials comprising oxides, sulfides, silicates, and glassy amorphous materials. They can contain appreciable amounts of valuable metals such as copper, cobalt, and zinc, as well as iron. Mineralogical studies have shown that cobalt is present as CoO in copper reverberatory furnace slag. Copper in the slag is attributed mainly to the presence of copper-rich sulphides. The cobalt oxide, and, to a lesser extent, the copper oxide associated with the silicate/oxide phases, is reduced by Fe from the alloy to form metallic Co (and Cu), resulting in the formation of FeO in the slag.

The CoO in the slag is associated primarily with Fe_2SiO_4, and analysis by scanning electron microscopy showed some Fe_2SiO_4 particles with no detectable Co or Cu, thus demonstrating that it is, in principle, possible to remove essentially all the Co and Cu from this phase.

Because the cobalt is present in the slag in oxidized form, recoveries would be very low if conventional slag cleaning (typically using an AC slag resistance furnace) was used, as this relies largely on a gravity settling mechanism, whereby entrained sulphide and metallic droplets are simultaneously collected. Other conventional recovery techniques, such as slow cooling of the slag, followed by milling and flotation, are also inappropriate for the recovery of oxidized metals dissolved in slag. Conditions need to be sufficiently reducing to recover a significant fraction of the cobalt present. These conditions can be achieved very effectively by means of the addition of a reductant (such as carbon) to an electric furnace.

This process needs to operate at a temperature above the liquidus temperature of the alloy containing the Co, Cu, and Fe, requiring an operating temperature somewhere between 1500 and 1600°C. This is substantially above the liquidus temperature of the principally fayalitic slag, around 1150°C.

When carbon is added to the slag, the various metallic elements reduce to different extents, at a given level of carbon addition, governed by their relative thermodynamic stabilities. This behaviour allows a reasonable degree of separation to take place during smelting. The intention in this part of the process is to separate the valuable non-ferrous metals from the iron and the gangue constituents present in the slag. The desirable area of operation is clearly somewhere in the region where the recovery of cobalt is high, and the recovery of iron to the alloy is still reasonably low.

The interchange between Co and Fe can be seen by studying the liquid-liquid reaction between the oxides in the slag and the metals in the alloy:

$$CoO + Fe = Co + FeO \tag{1}$$

A recovery equation was derived (Jones, Geldenhuys, & Reynolds, 2009) to express the recovery of cobalt to the alloy, R_{Co}, in terms of the recovery of iron, R_{Fe}, the equilibrium constant K (strictly a function of temperature only), and the ratio of the activity coefficients γ. This equation is shown, together with its graphical representation, in Figure 1. Over the temperature range of interest (between 1500 and 1600°C), K has a value of approximately 30. It is possible to calculate a value for $K\gamma$ from published theoretical data for individual activity coefficients (if these are available for the particular system and conditions of interest), but this would only apply strictly to a perfect equilibrium system. It may be more useful to use the form of the theoretically derived equation, and to fit the model to actual plant data. Values of $K\gamma$ may be found by fitting the equation to experimental data. For illustrative purposes, the curve in Figure 1 shows a value of $K\gamma = 14$.
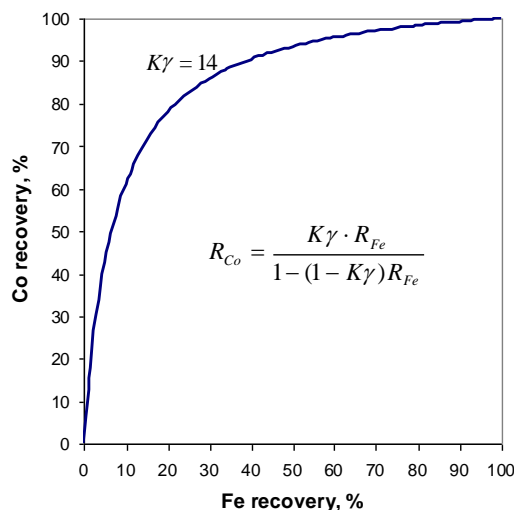
Figure 1. Relationship between Co recovery and Fe recovery to the alloy

The Kγ recovery equation produces curves of the correct functional form that are applicable across the whole range of different extents of reduction. Kγ for a particular metal has a characteristic value that depends on the temperature of operation, and to some degree on the composition of the slag and metal system under consideration (as this affects the individual activity coefficients). Process design calculations can be carried out with confidence, knowing that there is good theoretical justification for the form of the equation, and that the single parameter Kγ is based on experimental work. The equation clarifies the dependency of the recovery of the valuable metals on the recovery of iron in the furnace, and this allows a furnace operator to control the smelting process more easily and to target the correct degree of reduction.

The iron-rich alloy can be atomized prior to leaching, as it is very hard to crush. There are two principal options for the downstream treatment of the atomized alloy. One option involves an oxygen-sparged atmospheric tank leach at about 90°C with an iron concentration of ~60g/l. A second option utilises pressure leaching (for faster kinetics) at a lower iron concentration, precipitating hematite (lowering the requirement for a neutralizing agent). The choice between these process options requires a trade-off between capital cost and environmental acceptability.

Chambishi Metals

More than six decades of copper mining and smelting at the Nkana smelter site near Kitwe, 250 km north of Lusaka, Zambia, left behind about 20 million tons of fayalitic slag grading between 0.3 and 2.6% cobalt, with an average of approximately 0.75% Co and 1.2% Cu. The Nkana slag dump, covering a square kilometre to a depth of about 30 m, formed probably the world's largest cobalt resource that is situated above ground. Anglovaal Mining Limited (Avmin) of South Africa purchased the reverberatory furnace slag dump at the Nkana smelter from Zambia Consolidated Copper Mines (ZCCM), and the Chambishi Roast Leach Electrowinning (RLE) plant in 1998. In July 1999, plans were announced to expand the Chambishi RLE plant to incorporate a US $100 million smelter facility to process the slag, increasing the Chambishi production by 4 kt/a of cobalt and 3.5 kt/a of copper. Avmin's intentions were to install a crushing and screening plant for the slag, a suitably sized DC furnace, an atomizing facility; and to upgrade the existing cobalt refinery situated at Chambishi (about 30 km from Nkana) and produce a variety of cobalt and copper products.

The overall management of the project was handled by Kvaerner, with Dowding Reynard & Associates (DRA) providing the equipment for material handling and feed preparation circuits for the solid dump slag, Bateman Titaco providing the DC arc furnace, Atomising Systems (through Bateman IST) supplying the water atomizer, and Hatch providing the leaching equipment.

Description of the pyrometallurgical aspects of the process are provided by Jones, Denton, Reynolds, Parker, and Van Tonder (2002), Nelson et al. (2004), as well as Barnes and Jones (2011). The development of the novel pressure leach process is described by Munnik et al. (2003).

Recovery of cobalt from slag by a pyrometallurgical process had not been practised previously, and the project was pioneering in many respects. The project, named COSAC (Cobalt from slag and copper by product) was fast-tracked to take advantage of the high cobalt price that was current at the time. The project was designed to incorporate the following aspects:
- To continue to operate the existing Chambishi cobalt and sulfuric acid plant while improving cobalt plant recoveries and production and upgrading and de-bottlenecking various portions of the plant
- To install material handling and crushing and screening facilities at the Nkana dump
- To implement cobalt production from slag by means of a DC furnace smelting of 700 000 tons per annum of dried slag, followed by atomization of the alloy produced
- Installation of a leach plant to solubilise the atomized alloy, and integrate the leach plant into the existing refinery
- To dispose of the barren slag from the furnace on a new slag dump at Chambishi.

The dump had been extensively sampled, and 'mining' of the dump followed a rigorous plan to ensure a consistent feed grade to the metallurgical plant. This was necessary because of the extremely wide variation in the quality of the dump slag, varying from a small tonnage of high grade (> 6% Co) converter slag dating back to the early years of operation (predating cobalt recovery circuits in the beneficiation plants) to the more recently produced low-grade 0.3% Co reverb slags. Crushed slag was transported by road to the Chambishi site where it was dried prior to smelting.

As already mentioned, the project was pioneering in many aspects:
- The very high degree of slag superheat (> 400ºC) necessary to ensure tapping of the molten Fe-Co-Cu-S alloy placed very high demands on the furnace cooling system
- Side feeding of a DC furnace (as opposed to hollow-electrode feeding) was novel
- The atomization process selected for the molten alloy, necessitated by its toughness, which made it almost un-millable, also provided its own set of challenges
- The leach circuit design was novel and untested prior to this project.

The selection of a DC arc furnace was initially controversial, yet the project team believed the reasons for selecting DC over AC were compelling:
- Given the known variability of slag feed composition, the DC furnace was able to handle wide variations
- The power input from a DC arc furnace is not constrained by slag conductivity
- The DC open-bath configuration could handle fines without operational issues
- The DC furnace was able to utilise high-volatile coal as a reductant, if required
- The DC furnace had a lower electrode consumption
- The DC furnace provided better control on iron reduction, and decoupled any requirement for the slag to have specific electrical properties.

This process saw the first industrial implementation of solid (non-hollow) electrodes for a DC arc furnace. Previously, both chromite smelting and ilmenite smelting applications used hollow graphite cathodes through which the feed materials were introduced into the furnace. It also pioneered the successful use of side feeding of the DC furnace, and clearly demonstrated that radiation from the arc did not result in instantaneous destruction of the upper sidewalls – a surprisingly common misconception prior to this installation.

The cobalt-from-slag DC arc furnace at Chambishi Metals closed down at the end of 2008, as a result of high operating costs and an expectation of low cobalt prices in the future.

STL

The Big Hill in Lubumbashi in the Democratic Republic of Congo (DRC) consists of about 14 million metric tons of granulated slag, largely iron silicate, issued from the pyrometallurgical processing of copper ores produced at the time by the smelting plants of Gecamines in Lubumbashi. Depending on the composition of ores treated at different times, the Big Hill consists of layers of rich slag (rich in cobalt but relatively poor in zinc) and layers of poor slag (poor in cobalt but rich in zinc). A slag processing plant called 'Societe pour le Traitement du Terril de Lubumbashi' (STL)", is located beside the Big Hill. The rich slag, containing an average of 2.1% Co and 1.4% Cu, is expected to be depleted by 2021 when the process will need to start treating the poor slag. STL produces a rich cobalt alloy and zinc oxide dust from the rich slag.

The slag treatment process comprises drying of slag and coke in a rotary kiln, and carbothermic reductive smelting of slag in a 36 MW submerged arc furnace. The 'white alloy' (Fe-Cu-Co), rich in cobalt and relatively poor in copper, is granulated under a water spray, as is the waste slag. The smelting reduction is accompanied by fuming of volatile metals and oxides, which are recovered as a zinc-rich metal oxide powder after de-dusting the gas from the electric furnace. STL processes roughly 260 000 metric tons per year of rich slag.

HYDROMETALLURGICAL RECOVERY OF COBALT FROM COPPER SLAG

Lindblad and Dufresne (1975) proposed a hydrometallurgical process for the recovery of metal values from copper slags. The slag is ground to particles smaller than 150 μm (100 mesh), then mixed vigorously with concentrated sulfuric acid and water (typically in about a 1:1:1 ratio by mass). This mixture reacts exothermically to form a substantially dry solid material, containing the metal values of the slag in water-soluble form, without the formation of gelatinous substances from the silica in the slag. This is allowed to age or digest for a few hours. The water-soluble metal values are separated from the insoluble siliceous residue by leaching in water. This process is claimed to be superior to conventional agitated tank leaching with sulfuric acid at elevated temperatures, in that it consumes less acid, and avoids the formation of a gelatinous sludge that makes filtration excessively slow to impossible.

Experimental testwork

A sample of copper slag, with the analysis shown in Table 3, was tested at Mintek to find an alternative process to the pyrometallurgical treatment of smelting the slag to form an Fe-Cu-Co alloy (which would need to be leached to access the Co and Cu) while fuming off Zn vapour.

Table 3. Elemental analysis (mass %) of a copper slag sample

Al	Ca	Co	Cu	Fe	Mg	Mn	Si	Ti	Zn
2.95	12.4	0.48	2.18	15.2	3.04	0.18	18.1	0.21	7.54

A series of water-starved acid-contact leach tests at different curing times (up to 24 hours) was conducted based on Lindblad and Dufresne's method, to confirm the claims and potentially improve on certain operating parameters that are quoted in the patent. Test batches of 30 g were used for the tests, and the slag was ground to P80 of 75 μm. Analyses were carried out using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES).

When the curing time was increased from 1 hour to 2 hours, the Cu extraction improved from 79% to 84%, the Co extraction improved from 87% to > 99%. The Zn extraction was 97% after 1 hour of curing. No further improvement was observed when increasing the curing time further. Similar behaviour was seen with the extraction of impurities, and extractions of 90% of Al, 92% of Fe, 96% of Mg, and 20% of Si were seen. A curing time of 2 hours appeared sufficient for this material, as the value metal extraction in the subsequent water leach did not increase with increased curing time. This was significantly shorter than the 8 to 30 hours of curing time mentioned in the patent in order to attain similar recoveries.

The composition of the pregnant leach solution (PLS) emanating from the water leach, after a curing time of 2 hours, is listed in Table 4.

Table 4. Composition of pregnant leach solution (PLS) after a curing time of 2 hours (mg/L)

Al	As	Ca	Co	Cu	Fe	Mg	Mn	Si	Ti	V	Zn	S
6500	127	591	1290	3950	36000	6630	413	4870	89	57	20200	56000

The acid addition was 1000 kg per ton of slag, with a corresponding acid consumption of 650 kg/t slag (after 2 hours), and there was a mass loss of 17%. The acid consumptions were relatively low compared to agitated tank leaching which could require up to 3 to 4 times the acid used compared to the method tested here. Visual observations indicated that all samples were easily filterable by means of vacuum filtration. The solids in the slurry settled relatively easily just prior to filtration. The filtration of the material was sufficiently fast which proved that Si polymerisation was not an issue. Some Si reported to the PLS and will require removal prior to downstream processing.

A significantly shorter curing time was employed compared to that mentioned in the patent, and similar recoveries were achieved. It was also not necessary to maintain the material at elevated temperatures (75°C to 100°C) during the curing period to attain satisfactory value metal extractions. Furthermore, the use of water at ambient temperature with a reduced leaching time of 10 minutes was sufficient to reach high metal recoveries. No external energy addition to promote the leach process was required, as the process was exothermic. This leaching method proved to be suitable for the leaching of value metals from copper smelter slag, in that it reduced acid requirements, and the resulting water leach slurry had relatively unproblematic filtration characteristics.

CONCLUSIONS

Cobalt can be effectively recovered from copper smelting slags using either pyrometallurgical or hydrometallurgical processes. For a given project, there would need to be a comparison made between the cost of electrical power for smelting (for the pyrometallurgical process) versus the power used for grinding the solid slag, and the cost of the sulfuric acid (for the hydrometallurgical process). Consideration would also need to be given to the comparison of the waste products from the two alternative process options. The residual slag from the pyrometallurgical process could probably be used for road construction, whereas the residues from the hydrometallurgical process would need to be disposed safely.

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