Recovery of cobalt from slag in a DC arc furnace at Chambishi, Zambia

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Synopsis

The 20 Mt reverberatory furnace slag dump at Nkana in Zambia contains a substantial quantity of cobalt. A 40 MW DC arc furnace has been built at Chambishi for the purpose of recovering cobalt from the slag. The technology was jointly developed by Mintek and Anglovaal Mining Ltd (Avmin), and the furnace was designed by Bateman Titaco.

Testwork at the 150–250 kW scale was conducted at AVRL, and larger scale piloting was conducted at Mintek (in partnership with Avmin) in a 3 MW DC arc furnace. Approximately 840 tons of Nkana dump slag (ranging from 0.66% Co) was processed at power levels around 1-2 MW. Good overall cobalt extraction was achieved, and approximately 100 tons of cobalt-bearing alloy was produced (containing 5 to 14% Co). This testwork demonstrated that the Nkana dump slag could be processed in a DC arc furnace of suitable design, to produce a cobalt-bearing alloy suitable for further hydrometallurgical processing.

Bateman Titaco were contracted to design and build the furnace, and the design team contained representatives from Avmin and Mintek. The project was conceived as a fast-track exercise, and many activities had to be run in parallel. Notable features of the furnace include an ABB power supply, a Concast conductive hearth, the refractory design, and copper cooling in the sidewalls.

Power to the furnace was switched on during January 2001.

Introduction

Cobalt has been in use since at least 2250 BC, when the Persians used it to colour glass. It was not until 1735, however, that Swedish scientist G. Brandt first isolated metallic cobalt, and it was not until 1780 that it was recognized as an element. Today, cobalt is used mainly in high-temperature steel alloys, magnetic alloys and hard-facing alloys resistant to abrasion. Jet engines in current 747 aircraft are estimated to contain 180 kg of cobalt apiece.

Identified world cobalt resources are about 11 million metric tons. The vast majority of these resources are nickel-bearing laterite deposits, with most of the rest occurring in nickel-copper sulphide deposits hosted in mafic and ultramafic rocks in Australia, Canada, and Russia, as well as in sedimentary copper deposits in the Democratic Republic of the Congo (DRC) and Zambia. In addition, it is estimated that there are between 2.5 and 10 million tons of hypothetical and speculative cobalt resources in deep-sea manganese nodules and crusts on the ocean floor.

Worldwide production of cobalt is currently over 30 kt/a (compared to world nickel production of around 700 kt/a). Demand is expected to rise along with production of superalloys (increasing at perhaps 7% per annum) used for jet engines and gas turbines, as well as catalysts for oil refining (about 4% per annum), and especially rechargeable batteries (growing about 40% per annum). Cobalt supply is expected to continue to increase over the next few years, primarily from new nickel mines, where cobalt is produced as a by-product.

For many years, cobalt production was dominated by Zaire (now the DRC). At its peak in 1986, state-owned Gecamines produced 14.5 kt/a of cobalt. However, as a result of the conflict in that country, production dropped to below 5 kt/a by 1993.

In recent years, there has been a great deal of interest expressed in the recovery of cobalt (often together with nickel and copper) from a variety of slags. A process to carry this out, using a DC arc furnace, has been under development at Mintek since 1988, and has successfully been demonstrated at pilot scale[1]. The process involves the selective carbothermic reduction of the oxides of cobalt, nickel, and copper, while retaining the maximum possible quantity of iron as oxide in the slag. Early pilot-plant testwork[1] at Mintek demonstrated recoveries of 98% for nickel and over 80% for cobalt, at power levels of up to 600 kW.

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Figure 1—DC arc furnace building at Chambishi

More recently, attention has been focused on the Nkana slag dump on the Zambian Copperbelt. More than six decades of copper mining and smelting at the site near Kitwe, 250 km north of Lusaka, have left behind about 20 million tons of slag grading between 0.3 and 2.6% cobalt. This dump, covering a square kilometre to a depth of about 30 m, is probably the world's largest cobalt resource that is situated above ground. Many attempts have been made over the years to recover cobalt from this dump, and much research has been carried out in this field. Anglovaal Mining Limited (Avmin) of South Africa purchased the reverberatory furnace slag dump at the Nkana smelter and the Chambishi Roast Leach Electrowinning (RLE) plant in 1998 for US $50 million. 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.

The overall management of the project was handled by Kvaerner, with Dowding Reynard & Associates 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.

Chambishi Metals plc (owned 90% by Avmin, with ZCCM holding the remainder) recently commenced the commissioning of its new slag processing facility. Avmin have constructed a new wing at the Chambishi cobalt refinery, and the smelter and leach plants are expected to ramp up to full production during 2002. The new treatment facility will blend, smelt, leach, and electrowin cobalt and copper from Nkana slag. The additional section is expected to add about 3.6–4.1 kt/a of cobalt, and 2.7–4.5 kt/a of copper to Chambishi's output. The expanded plant will have the capacity to process around 7 kt/a of cobalt, and 15 kt/a of copper. The 20 Mt of cobalt-rich slag from Nkana will pass through the new plant prior to being refined into cobalt and copper cathodes in the existing plant. The life of the slag treatment plant is expected to exceed 30 years.

All told, Avmin expect to have invested US $185 million in Chambishi (including the slag treatment facility as well as other improvements) by the time commercial production begins.

Theoretical background to the smelting process

Mineralogical studies have shown that cobalt is present as CoO in copper reverberatory furnace slag. Copper in the slag is mainly attributed 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 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 a DC arc furnace.

When carbon is added to the slag, the various metallic elements reduce to different extents, at a given level of carbon addition. 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.

This process needs to operate at a temperature above the liquidus temperature of the alloy containing the Co, Cu, and Fe. Of these elements, Fe has the highest melting point of around 1540°C. For present purposes, let us assume an operating temperature somewhere between 1500 and 1600°C.

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

$$CoO + Fe = Co + FeO \qquad [1]$$

At equilibrium, the degree of separation between Co and Fe can be indicated by the equilibrium constant, K, which is strictly a function of temperature only. Over the temperature range of interest, K has a value of approximately 30.

$$K = \frac{a_{Co} \cdot a_{FeO}}{a_{CoO} \cdot a_{Fe}} \qquad [2]$$

The activities a may be expressed in terms of activity coefficients γ and mole fractions x.

$$K = \frac{\gamma_{Co}\chi_{Co} \cdot \gamma_{FeO}\chi_{FeO}}{\gamma_{CoO}\chi_{CoO} \cdot \gamma_{Fe}\chi_{Fe}} \qquad [3]$$

In the interests of simplicity, we may lump together the ratio of the activity coefficients of these four chemical species in solution. Individual activity coefficients may be obtained from the literature. Holzheid et al.[2] obtained values for γ_{FeO}

of 1.70 ± 0.22, and for γ_{CoO} of 1.51 ± 0.28. Teague[3] indicates that the activity coefficient of Co in fayalitic slags is 0.92. The data reported[4] for the activity coefficient for Fe in fayalitic slags varies widely between 0.3 and 0.6.

$$\text{Define} \quad \gamma = \frac{\gamma_{CoO} \cdot \gamma_{Fe}}{\gamma_{Co} \cdot \gamma_{FeO}} \tag{4}$$

If we make the reasonable assumption that γ is not a strong function of composition, then we may derive a simple expression to show the relationship between the recovery of Co to the alloy and the recovery of Fe to the alloy.

From Equations [3] and [4]:

$$K\gamma = \frac{\chi_{Co} \cdot \chi_{FeO}}{\chi_{CoO} \cdot \chi_{Fe}} \tag{5}$$

Expressed in terms of numbers of moles:

$$K\gamma = \frac{n_{Co} \cdot n_{FeO}}{n_{CoO} \cdot n_{Fe}} \tag{6}$$

Note that the above equation may also be expressed in terms of mass percentages, simply by taking into account a conversion factor to allow for the ratios of the molecular masses.

$$K\gamma = 0.988 \left(\frac{\%Co \cdot \%FeO}{\%CoO \cdot \%Fe} \right) \tag{7}$$

If the amounts of cobalt and iron initially present in the feed are denoted by a superscript zero, the following mass balance equations may be written.

$$n_{Co} = n_{Co}^0 + n_{CoO}^0 - n_{CoO} \tag{8a}$$

$$n_{Fe} = n_{Fe}^0 + n_{FeO}^0 - n_{FeO} \tag{8b}$$

Recoveries R_{Co} and R_{Fe} may be defined as follows:

$$R_{Co} \equiv \frac{n_{Co}}{n_{Co}^0 + n_{CoO}^0} \tag{9a}$$

$$R_{Fe} \equiv \frac{n_{Fe}}{n_{Fe}^0 + n_{FeO}^0} \tag{9b}$$

Combining Equations [8] and [9]:

$$n_{CoO} = \left(1 - R_{Co}\right)\left(n_{Co}^0 + n_{CoO}^0\right) \tag{10a}$$

$$n_{FeO} = \left(1 - R_{Fe}\right)\left(n_{Fe}^0 + n_{FeO}^0\right) \tag{10b}$$

Substituting Equations [9] (re-arranged) and [10] into [6] gives:

$$K\gamma = \frac{R_{Co}\left(n_{Co}^0 + n_{CoO}^0\right) \cdot \left(1 - R_{Fe}\right)\left(n_{Fe}^0 + n_{FeO}^0\right)}{\left(1 - R_{Co}\right)\left(n_{Co}^0 + n_{CoO}^0\right) \cdot R_{Fe}\left(n_{Fe}^0 + n_{FeO}^0\right)} \tag{11}$$

This can be simplified to:

$$K\gamma = \frac{R_{Co}\left(1 - R_{Fe}\right)}{R_{Fe}\left(1 - R_{Co}\right)} \tag{12}$$

This can be re-arranged to give:
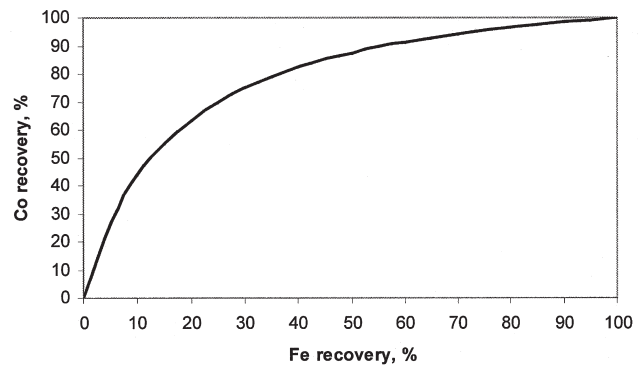

Figure 2—Relationship between Fe recovery and Co recovery to the alloy

$$R_{Co} = \frac{K\gamma \cdot R_{Fe}}{1 - \left(1 - K\gamma\right)R_{Fe}} \tag{13}$$

It is certainly possible to calculate a value for $K\gamma$ from published theoretical data, 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 actual plant data to the model. Values of $K\gamma$ may be found by fitting experimental data to Equation [13]. For illustrative purposes, the curve in Figure 2 shows a value of $K\gamma = 7$. It may be possible to modify the shape of the curve, to some degree, by changing the composition of the molten slag in the furnace to favour the activity coefficients of CoO and Fe over those of Co and FeO.

Development of the process at Mintek and at AVRL

Smelting testwork was carried out in DC arc furnaces at Anglovaal Research Laboratories (AVRL) and at Mintek. In addition, some small-scale laboratory tests were carried out at Mintek to investigate some of the more fundamental aspects of the process. A wide variety of test conditions (including the addition of many slag modifiers) were investigated at AVRL at a scale of 150—250 kW. In support of the design of the commercial installation, Mintek and Avmin conducted collaborative testwork, up to October 1999, at the 1 to 2 MW scale, in which approximately 840 tons of Nkana dump slag (ranging from 0.66% Co) was successfully processed in a 3 MW DC arc furnace. Good overall cobalt extraction was achieved during the tests, and approximately 100 tons of cobalt-bearing alloy was produced (containing 5 to 14% Co). Various refractories were tested in the smelting campaigns. The testwork demonstrated that Nkana dump slag can be successfully processed in a DC arc furnace of suitable design, to produce a cobalt-bearing alloy amenable to further hydrometallurgical processing.

The large-scale testwork was set up in such a way that it would mimic the mode of operation of the industrial-scale furnace. Approximately 10% more Fe reduction was required in the large-scale testwork to achieve Co recoveries similar to those achieved in the medium-scale tests. The differences in mode of operation between the medium-scale and large-scale tests were highlighted as the probable cause for the higher recoveries of cobalt (relative to that of iron) achieved in the

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medium-scale testwork. The medium-scale testwork was conducted by continuously feeding mixtures of dump slag, reductant, and fluxes to an initial molten metal bath containing small quantities of slag, such that the power and feed input were balanced in order to achieve the desired operating temperature. After a preset quantity of feed, or period of time, was reached, the feed was stopped, the power reduced, and the furnace tilted in order to remove the product slag and metal. The majority of the product slag was retrieved from the furnace, and a set quantity of metal was allowed to remain in the furnace for the commencement of the next cycle.

The following principles have been well established.

➤ Cobalt and iron recovery increases with increased carbon addition.
➤ Cobalt is preferentially reduced over iron. The reduction of cobalt is favoured above that of iron, especially under less reducing conditions. Highly reducing conditions lead to increased reduction of iron without a significant benefit in terms of cobalt recovery.
➤ The effect of temperature in the range 1450 to 1700°C has only a slight effect on the recovery of cobalt relative to that of iron. Temperature has a negligible effect on the solubility of cobalt in the slag.
➤ The recovery of cobalt relative to that of iron increases with an increased Co/Fe ratio in the dump slag.
➤ Changing of the slag chemistry through the addition of certain fluxes affects the recovery of cobalt from the slag. However, it was found that the slag chemistry had a lesser effect on the recovery than did the redox conditions. In general, it was found that fluxing was beneficial only under less reducing conditions, and that its effect decreased with increased reduction.
➤ An increase in the CaO content of the slag significantly increases the recovery of cobalt to the metal alloy. The effect of CaO is significantly more pronounced under less reducing conditions. Under very reducing conditions, the effect of CaO becomes negligible. At lower reductant additions, fluxing with CaO also increases the recovery of cobalt preferentially to that of iron.

Process description of Chambishi operation

The 20 Mt Nkana slag dump has an average cobalt content of 0.76%, although there is quite a variation in grade, according to the location in the dump. The slag is reclaimed from the Nkana dump, then road-transported across the approximately 30 km from Kitwe to Chambishi.

Upon arrival at Chambishi, the slag is deposited, according to its grade, in a number of stockpiles close to the plant. In order to blend the feed slag, material is loaded from each stockpile and fed into a primary screening plant prior to being processed in the feed preparation plant[5]. The slag crushing circuit reduces the run-of-mine slag to a product in which 80% passes 15 mm size. The slag then passes to a 1200 ton capacity surge silo from which it is fed at a rate of 60 t/h into a fluidized-bed drier, fuelled by diesel or furnace off-gas. The bone-dry slag is discharged onto a heat-resistant sacrificial conveyor which feeds the dry slag storage silo. An automatic sampler provides samples for moisture analysis and size distribution.

Slag is taken from the silo, by conveyor, to the blending plant where fluxes such as burnt lime (about 6%), coal as a reductant, and small quantities of other materials such as rutile are added. The blended feed is weighed before being fed to the furnace. As the furnace requires a specific ratio of slag, lime/rutile, and coal, the mix is conveyed in batches to eight furnace feed-bins, with the various materials being deposited in a single 'sandwich' layer on the conveyor belt.

Aside from the contained cobalt and copper, the feed slag contains an average of about 20% total Fe, 43% SiO_2, 8% Al_2O_3, 8% CaO, 3% MgO, 3% K_2O, and 0.6% S.

The flowrate of the slag and flux mixture, and the addition of coal at the correct ratio (about 4% of the mass of the slag) are maintained by the control system. The dump slag, fluxes, and reductant are fed by gravity through eight feed ports in the roof of the furnace. (There are sixteen feed ports available, with eight in use and eight blanked off.)

The average slag tapping temperature is around 1500°C. Molten slag is tapped from the furnace into 60 ton slag pots, which are carried by slag haulers to the nearby new dump where they are emptied out.

The alloy is tapped into ladles that are transported by crane to a ladle-heating station where the temperature of the alloy is elevated to about 1650°C, using a plasma torch. The superheated molten alloy is then lip poured into a pre-heated tundish feeding a water atomizer (rated at 500 kg/min).

Water atomization, involving the 'smashing' of a stream of molten alloy with a high-pressure stream of water, is used to directly produce fine particles of the cobalt-rich iron alloy (otherwise virtually unbreakable) with a mean diameter of less than 100 µm. The alloy particles are pumped as a slurry to the downstream leach plant.

DC arc furnace

The DC arc furnace has a single electrode positioned above the molten bath. The single solid graphite cathode, 60 cm in diameter, is maintained in a central position in the furnace, at the correct height, according to the desired voltage and current settings. The molten alloy in the furnace forms part (the anode) of the electrical circuit. The furnace comprises a refractory-lined cylindrical steel shell, and a water-cooled refractory-lined roof (with twelve panels). The outer side-walls of the furnace are water-cooled, to protect the refractories, and to promote the formation of a freeze lining within the vessel. The portion of the side-walls in contact with the superheated molten slag is lined with thermally conductive refractories, and is copper cooled (with Fuchs-designed panels). The roof contains the central entry port for the graphite electrode and 16 feed ports equally distributed around the electrode. The Concast hearth comprises magnesite-carbon bricks overlaid by a layer of steel-clad bricks (to make them electrically conductive). The hearth is in contact with the molten alloy, and is also connected further to the anode busbars.

The furnace has two slag tapholes (only one of which is used at a time) and two metal tapholes. The slag and metal tapholes are on opposite sides of the furnace. Two Paul

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Wurth drills and mud guns for opening and closing the taphole are mounted on sliding rails so that they can be used at either taphole.

The furnace has an outside diameter of 11 m, and an inside diameter at the slag level of 9.26 m. The freeboard above the level of the molten slag varies between 3.3 to 4 m, depending on the contents of the furnace. The slag depth is usually kept to about 80 cm, and the metal depth is about 40 to 70 cm at the outer edge of the bath. The heel is 40 cm thick at the edges; and 118 cm thick at the centre of the dished bottom.

The ABB power supply (2 x 40 kA and 1200 V, output of 40 MW) is based on thyristor-controlled rectifiers. A prominent feature of the power supply is its particularly high voltage specification, to accommodate the highly resistive molten slag that leads to high voltage operation.

The design and construction of the furnace was done as a fast-track project, with many activities being carried out in parallel in order to save time. Communication was facilitated, during the design phase, by regular meetings of the furnace design team to discuss and agree on the various aspects of the design. The team comprised representatives from Avmin, AVRL, Mintek, and Bateman Titaco. A co-operation agreement between Mintek and Avmin to commercialize the technology was established. AVRL were responsible for the overall process; and Bateman Titaco were responsible for the detailed engineering.

Commissioning

Commissioning of the feed preparation plant commenced in October 2000. The US $1 million 40 MW DC furnace transformer was delivered in mid-October. The drying circuits were commissioned in December, and the blending circuit early in January[5]. Power was switched on to the furnace on 24 January 2001. After warm-up, slag was tapped for the first time on 3 February. On 5 February 2001, the plant poured its first alloy from the new furnace. After commissioning the atomizing system, the leach plant received its first alloy by late April 2001. The leach plant is the final section of the new plant, from where material is passed into Chambishi Metals' existing, but now expanded, cobalt refinery.

During the first three months of operation, the furnace has shown itself to be extremely forgiving, and has tolerated relatively wide swings in both feed recipe and operating temperature, albeit at reduced power levels.

A water-pipe leak on the outside of the furnace was discovered on 5 May, and hydration of some of the refractory bricks led to a furnace shut-down for inspection. The assessment is that no structural damage exists, but re-lining of the furnace refractories will be required. The team at the plant is in the process of implementing this plan of action. The effect is that Chambishi Metals' cobalt metal from slag is now expected during the third quarter of 2001, while ramp-up to full production should be achieved in 2002. Avmin's toll-refining facility at Chambishi continues to function normally.

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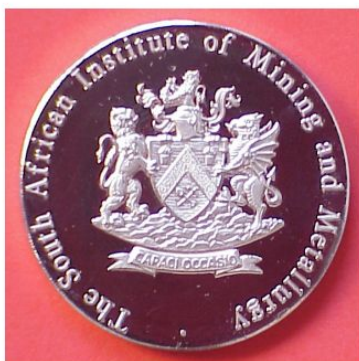
This paper was awarded a silver medal by the South African Institute of Mining and Metallurgy in 2002