Using a Direct-Current Arc Furnace to Recover Cobalt from Slags

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Cobalt can be recovered from a variety of slags by treatment with a carbonaceous reducing agent in a direct-current arc furnace at around 1,500°C. The principal materials suitable for treatment using this technology are primary smelter slags, which typically originate from the processing of sulfide concentrates. The technology has been tested using copper, nickel-copper, and lead smelting slags. In all cases studied, cobalt is recovered as a valuable by-product to help improve overall plant profitability. Pilot-plant tests have demonstrated a cobalt recovery of more than 80 percent at power levels up to 600 kW. Very high recoveries of other valuable elements, such as nickel and copper, have also been achieved.

INTRODUCTION

Slags produced by nonferrous smelters usually contain significant quantities of valuable metals, such as cobalt, nickel, copper, or zinc, present both in an entrained metallic or sulfide form and a dissolved oxidized form. These slags can emanate either from furnaces (e.g., six-in-line, reverberatory, flash, or blast) or converters; they may be internal recycle streams or final waste products. Large quantities of valuable metals are present in the huge dumps that have built up over many years of operation at various smelters. Slags are sometimes treated by slow cooling, milling, and flotation. This approach is satisfactory when the metals in the slag are in either the sulfide or metallic form, but is not suitable for the recovery of oxidized metals. Cobalt and zinc, in particular, and nickel, to a lesser extent, are found in an oxidized form, and for these slags, treatment in an electric furnace operated under reducing conditions is necessary. Conventional sla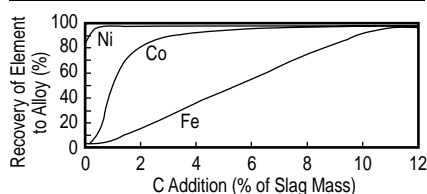g-cleaning furnaces (typically alternating-current [a.c.] immersed electrode) rely largely on a gravity-settling mechanism, whereby the entrained sulfide and metallic droplets are simultaneously collected. Sometimes, a quantity of matte is added to the slag to enhance the coalescence of entrained matte droplets. However, conditions are not usually sufficiently reducing to recover much of the cobalt; cobalt recoveries may be as low as 20 percent. The most effective means for the recovery of metals involves the addition of a reductant (such as carbon) to capture some of the metals present in an oxidized form. Processes have previously been described in which carbothermic reduction has been carried out in electric furnaces.[1–3]

The aim of a slag-cleaning process is to maximize the recovery of valuable metals (e.g., cobalt, nickel, or copper) in an alloy with the lowest possible iron content. The amount of metallic iron produced should be kept to a minimum, as the more iron present in the resulting matte or alloy, the greater the cost of the subsequent hydrometallurgical separation of the valuable metals and the resulting disposal of the iron residues. Because of the similarities in the reduction behavior of cobalt and iron, some loss of cobalt is inevitable while separating the iron from the nickel and copper.

Mintek has been working on the recovery of cobalt[4] and the associated valuable metals from slags since 1988, using direct current (d.c.)-arc furnace technology for the selective carbothermic reduction of the oxides of cobalt, nickel, copper, and zinc (where present), while retaining the maximum possible quantity of iron as oxide in the slag.

Ni-Cu SLAG CLEANING

Many nickel-copper smelters employ a slag-cleaning process whereby the concentrates are fed to a furnace that produces a matte (for further treatment) and a slag (which is stockpiled). The furnace matte is treated in a converter (often a Peirce-Smith) to remove most of the remaining iron and sulfur. This resulting white matte or alloy is then treated hydrometallurgically. The converter slag is often recycled to the furnace. Because of the highly oxidizing conditions in the converter, much of the cobalt is oxidized. The turbulent conditions cause entrainment of valuable met-
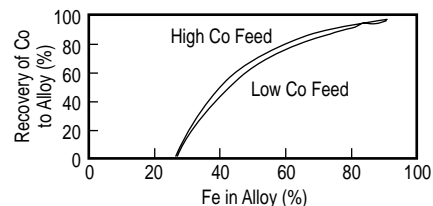

Figure 2. The recovery of cobalt to the alloy as a function of the amount of iron present in the alloy at two levels of cobalt (1.0% and 0.2%) in the example slag fed to the slag-cleaning furnace.

als as well.

Of all the streams in a flowsheet of this sort, the converter slag is richest in cobalt. It is possible to divert this liquid stream of converter slag for slag cleaning, allowing most of the valuable metals to be reclaimed. The impoverished slag can still be recycled to the furnace (with fairly minimal disruption to the existing process and with the benefit of reduced quantities of magnetite, which otherwise builds up in the furnace), or it can be disposed of (breaking the recycle entirely, necessitating some changes to the operation of the furnace).

A second possibility is to leave the converter slag recycle stream alone and focus on the treatment of the furnace slag, which is the point at which the waste materials finally leave the process. It is also possible to treat material from existing slag dumps at the same time, as the dumped material is usually similar to the furnace slag that is currently being produced. It is, of course, also possible to use a hybrid of these approaches.

Process Chemistry

A wide range of slags are amenable to slag cleaning. These slags differ according to the ores from which they arise, the type of process used, and from which part of the process they originate (e.g., furnaces or converters). Most of the slags of interest are rich in iron oxide and silica. Fortunately, similar principles apply to the treatment of all of these slags, although the actual results will differ according to the individual slag composition.

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

Figure 1. The recovery of elements to the alloy as a function of the quantity of carbon added at 1,500°C.

able degree of separation to take place during smelting; the intention is to separate the valuable nonferrous metals from the iron and the gangue constituents present in the slag. Figure 1 illustrates the differences in reducing behavior between nickel, cobalt, and iron for a typical nickel-copper slag.[4] 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. In actual practice, there is less than 100 percent carbon utilization, and the carbon addition would need to be somewhat higher than that shown here, because of burn-off of some of the reductant.

The most striking feature of this separation process is the variation of cobalt recovery according to the iron content in the alloy. An example of this behavior is shown in Figure 2. It can be seen that the recovery of cobalt (in percentage terms) is highest (albeit, not by very much) in the slag with the highest initial cobalt content. This is in-line with experimental findings[2,5] that recoveries are dependent on initial slag composition, with higher grades leading to better recoveries. If we accept the evidence presented elsewhere[5] that metallic iron is the effective (intermediary) reductant in the process, it may be more correct to say that the recovery of valuable metals is related to a combined function of the iron and nonferrous metal contents of the initial slag.

The calculations for Figures 1 and 2 were carried out using Mintek's Pyrosim computer software[6] for the calculation of steady-state mass and energy balances for pyrometallurgical processes. These simulations were based on the assumption of chemical equilibrium between gas, slag, and alloy. An operating temperature of 1,500–1,550°C has been selected for the process, in accordance with that used for a similar process.[2] This temperature ensures that the alloy remains molten, as melting temperatures in the range of 1,300–1,420°C have previously been reported for similar materials.[2] This is one of the important determinants of a suitable operating temperature for the furnace.
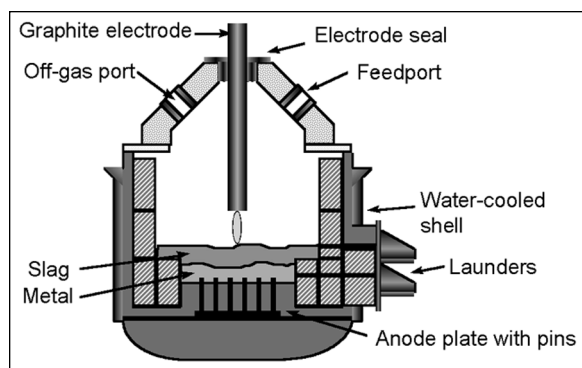
Figure 3. A schematic of a d.c. transferred plasma-arc furnace.

DIRECT-CURRENT ARC FURNACE TECHNOLOGY

A d.c. arc furnace can be used to reduce the feed slag (introduced as a molten stream of currently arising slag, a solid stockpiled material, or a combination of the two), using a low-cost reducing agent, such as coke or coal. The principal product from this stage is an iron-rich alloy containing most of the incoming cobalt, nickel, and copper. In the case of zinc-containing slags, the furnace off-gas contains zinc vapor that can be processed in a lead-splash condenser. The slag from the d.c. arc furnace can safely be disposed of or, possibly, sold.

Direct-current arc furnaces are widely used for scrap melting in the steel industry. They have also been used industrially for smelting applications in the areas of ferrochromium production and ilmenite smelting; these processes were developed and piloted by Mintek.[7]

The d.c. arc furnace has a single graphite electrode positioned above the molten bath; the molten metal in the furnace contacts the anode of the electrical circuit. The furnace comprises a refractory-lined cylindrical steel shell and a water-cooled roof lined with an alumina refractory. The outer sidewalls of the furnace are cooled to protect the refractory and promote the formation of a freeze lining within the vessel. The roof contains the central entry port for the graphite electrode (either solid or hollow for center-feeding) and any additional feed ports that may be required. The return electrode, or anode, consists of multiple steel rods built into the hearth refractories and connected at their lower end to a steel plate that, via radially extending arms, is linked to the furnace shell and the anode cable. A schematic diagram of this arrangement is shown in Figure 3.

The inherent stability of a d.c. arc offers the potential for improved operational control. A d.c. arc furnace operates under open-arc conditions with the electrode positioned above the bath. This results in a significant amount of energy being dissipated in the arc (and then transferred to the bath), rather than having to rely only on the resistive heating of the slag in order to supply energy to the furnace bath. This renders the energy supply nearly independent of slag composition, which allows the slag chemistry to be optimized for the best recovery of valuable metals (instead of for the required electrical characteristics).

As the current flowing in a d.c. arc furnace has to travel through the entire depth of the liquid
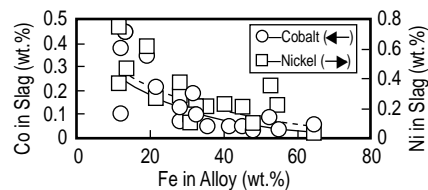
Figure 4. Results of 100 kVA and 200 kVA tests on nickel-copper converter slag.

bath (as opposed to merely between the electrodes of an a.c. furnace), the temperature distribution is more likely to be relatively even. The bath of a d.c. arc furnace is usually fairly well mixed, which is important for coalescence and settling. Some other slag-cleaning furnaces[8] have had to resort to mechanical stirrers to ensure adequate mixing in the molten bath. Furthermore, it is possible to achieve a specified power input, almost without regard to the temperature of the slag. This is in marked contrast to the case of an a.c. furnace, where as the slag gets hotter, the conductivity increases, thereby limiting the amount of energy that can be dissipated in the slag by the mechanism of resistive heating. This fact limits the temperature that can be obtained in a submerged-electrode or slag-resistance a.c. furnace.

Among the other benefits of using a d.c. arc furnace, d.c. power supplies reduce the problems of harmonics and flicker associated with a.c. power supplies. The simple configuration of the furnace also makes it structurally simpler and easier to maintain. There is improved gas sealing, as there is only a single electrode. The electrode consumption is significantly less than that of submerged-electrode furnaces. A list of the benefits can be found elsewhere.[4]

Because of the extremely aggressive nature of the superheated slag, the sidewalls must be surrounded by water-cooled panels, as is also required for other industrial slag-cleaning processes.[8] A controlled freeze lining minimizes slag erosion of the refractory lining.

EXPERIMENTAL WORK ON THE SLAG-CLEANING PROCESS

The experimental work on the slag-cleaning process began on the laboratory scale, and was extended to the pilot scale on Mintek's d.c. transferred plasma-arc furnaces.[4,7,9] In addition to numerous 100 kVA (60 kW) supporting batch tests, five campaigns (50–100 hours each) have been carried out at the 200 kVA (150 kW) scale, and a campaign (treating about 20 tonnes of slag) has also been undertaken on the 3.2 MVA (600 kW) furnace. The treatment of more than 1,000 tonnes of cobalt-bearing lead blast-furnace slag has been demonstrated (for zinc fuming) in Mintek's 5.6 MVA (1–3 MW) furnace facility at up to 2 t/h in a sealed furnace linked to a lead splash condenser.[9]

NICKEL SMELTER SLAGS

Nickel-Copper Converter Slag A

Using converter slag from a nickel-copper plant, tests were carried out in 1990 on a 100 kVA furnace operated at 30 kW and on a 200 kVA furnace operated at 85 kW with low additions of reductant (in order to minimize the reduction of iron). The slag contained 47% Fe, 3.5% Ni, 3% Cu, 3% S, and 0.45% Co.

The tests examined four different methods of operation in an attempt to optimize the selective reduction of the slag. These methods included smelting of composite pellets of milled slag and graphite, adding selected quantities of crushed coal to already molten slag, cofeeding crushed cold slag and coal, and pneumatically injecting pulverized coal into the molten slag.

In the 100 kVA furnace, the produced alloy typically comprised 48% Fe, 16% Ni, 14% S, 14% Cu, and 1.7% Co. In the 200 kVA furnace, an alloy of 44% Fe, 22% Ni, 15% Cu, 10% S, and 2% Co was produced. At this level of reduction, 91% of the iron was retained in the slag phase, while only 50% of the cobalt, 63% of the copper, and 83% of the nickel were recovered to the alloy. The injection of pulverized coal greatly improved the reduction and the recovery of nickel and cobalt oxides from the slag.

The results of these tests are shown in Figure 4, where the scatter of results needs to be seen in the context of the various methods employed. Under good conditions, at 7% carbon addition in the 100 kVA furnace, calculated recoveries of 97% Ni, 81% Co, and 78% Cu were obtained, while retaining 80% of the iron in the slag.

Nickel-Copper Converter Slag B

This slag was generated in a plant utilizing a conventional six-in-line furnace and Peirce-Smith converter configuration. The bulk slag contained 49% Fe, 30% SiO_2, 3.6% Ni, 1.25% Co, and 1.0% Cu. During testwork carried out in
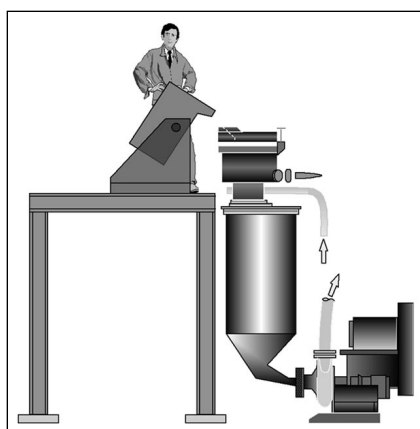

Figure 5. Small-scale water atomization of the alloy (courtesy of Atomising Systems, Sheffield).

1993, the 200 kVA furnace was operated at power levels of 100–170 kW and tapping temperatures of 1,400–1,500°C. The produced alloys comprised 35–50% Fe, 25–35% Ni, 8–10% S, 5.5–8.5% Cu, and 0.5–5.5% Co. From the starting level of 1.25% cobalt in the feed slag, it was possible to produce a discard slag with typical values of 0.22–0.29% cobalt, with a few points well below these levels.

The most abundant phase present in the solid converter slag is Fe_2SiO_4 (olivine), followed by Fe_3O_4 (magnetite spinel). The cobalt is associated primarily with the olivine; whereas the nickel is distributed between the olivine and the spinel. Copper was present only in entrained sulfides. The analysis of highly reduced slags has shown that it is possible to remove virtually all of the cobalt and nickel from the olivine in the slag.

Large-scale testwork on converter slag was conducted during 1994 on a 3.2 MVA d.c. arc furnace operating at a power level of 600 kW. The sequential feeding of reductant was used as the preferred mode of feeding. Operating temperatures were in the region of 1,300–1,600°C, and neither the temperature of the bath before the reduction period nor the tapping temperature seemed to have a pronounced effect on the cobalt recovery.

The average electrode consumption during the campaign was 2.6 kg/MWh, while the dust loss was low—1% of the mass of the feed. The alloy produced comprised 56.9% Fe, 26.4% Ni, 7.8% Co, 3.8% Cu, and 2.1% S. The cobalt levels achieved in the discard slag were between 0.15–0.33%.

A coal addition of 9% was required to achieve cobalt recoveries of at least 80%. Increasing the coal addition beyond this level did not significantly increase the recovery of cobalt. Increasing the batch mass of slag from 500 kg to 1,000 kg and increasing the reduction period by 75% resulted in increases in cobalt recovery from 71% to 86% and from 70% to 82% for coal additions of 9% and 11%, respectively. The main factor affecting cobalt recovery appears to be the time allowed for the reduction to take place. At this scale of operation, a duration of two hours was required to achieve cobalt recoveries greater than 80%.

Nickel-Copper Furnace and Converter Slag

During 1995, a campaign was undertaken on the 200 kVA furnace with the intention of combining furnace slag with the converter slag previously treated. When treating furnace slag containing 0.22% cobalt on its own, the maximum cobalt recovery that could be obtained was 66%, with a cobalt value of 0.08% in the discard slag. As in previous testwork, the cobalt in the discard slag when treating converter slag on its own was still in the region of 0.22%. However, by com-
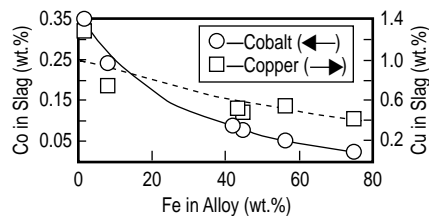

Figure 6. Results of a 100 kVA test on copper-converter slag.

bining increasing amounts of furnace slag with converter slag, values approaching 0.08% cobalt in the discard slag could still be achieved. This resulted in cobalt recoveries approaching 90%, while the average recovery was in the region of 85%.

Water Atomization of Alloys

Cobalt-rich iron alloys are unusually hard and tough, which poses the problem of providing suitably sized material to the downstream leaching units. It is common practice in a number of slag-cleaning processes to add sulfur (in the form of pyrite, concentrate, or matte) to the alloy in order to make it sufficiently brittle to be able to be successfully milled after granulation. Apart from the inconvenience and expense of having to add this material to the furnace, this sulfur needs to be removed during subsequent hydrometallurgical processing. The use of water atomization eliminates the need for the addition of sulfur, thereby simplifying subsequent separation stages.

Water atomization, involving the smashing of a stream of molten alloy with a high-pressure stream of water, can directly produce fine particles of alloy with a mean diameter of less than 100 µm (even as small as 40 µm). The particle size distribution of the powder is controlled by a combination of the metal temperature and the metal and water flow rates. This technology is commonly used in the powder-metallurgy industry. The design of the atomizing system is simplified by not having any tight constraints on the range of particle sizes and shapes of the particles. Small-scale experiments have been carried out successfully on 5 kg batches of alloy produced at Mintek.

This technology is commercially available up to the industrial scale (from companies such as Atomising Systems Ltd.[10] of Sheffield, United Kingdom) and appears to be very cost-effective when compared to the option of granulation and milling. This step introduces another level of flexibility into the process; one can now optimize the metallurgy to maximize recovery of the valuable metals without needing to be too concerned with the physical properties of the alloy.

As shown in the illustration of a small-scale atomizing system (Figure 5), the unit consists of a refractory-lined tundish, an atomizing chamber, a high-pres-

Table I. Results of 100 kVA Tests on Copper Converter Slag

Feed	Fe in Alloy (%)	Recovery (%)		
		Cobalt	Copper	Nickel
8% Coal, Solid Slag	56	89	84	99
8–12% Coal, Molten Slag	45	84	86	99
10% Coal, Molten Slag	75	96	90	97

sure pump, and a water reservoir. Molten metal is poured into the tundish, and flows by gravity through a ceramic nozzle at the base. High-pressure (300 bar) water impinges on the metal stream, causing it to break up into small particles (typically less than 100 μm). These particles settle in a vessel below the atomizing unit, from which they can be recovered.

Downstream Hydrometallurgical Processing

The alloy produced in the reduction process can be leached with spent electrolyte from a copper or nickel electrowinning process. Mintek has developed a leaching process that solubilizes the nickel, copper, and cobalt, while rejecting the iron and any sulfur into the solid residue (by decreasing the pH appropriately). The resulting solution can be processed further to separate the cobalt, nickel, and copper from each other via conventional technology.

A direct solvent extraction process for extracting cobalt from cobalt-bearing nickel solutions has also been developed. Nickel and cobalt have been successfully electrowon from the raffinate and strip liquor, respectively.

COPPER SMELTER SLAGS
Copper Converter Slag

During 1988 and 1989, tests were carried out using a converter slag containing 52% Fe, 3.25% Cu, 0.46% Co, and 0.42% Ni. A 100 kVA furnace (operating at 20–25 kW) was used. In some tests, solid slag and coal were fed together; in others, the slag was melted first, then the coal was added. Coal (at 53% fixed carbon) additions varied between 4%, 6%, 8%, 10%, and 12% of the mass of the slag. The mode of addition of the coal and the reduction periods of the tests were also varied (around 30 minutes). The results are shown in Table I and Figure 6.

The use of fine coal (less than 1.5 mm) did not seem to have an effect on the degree of reduction. A representative composition of the alloy produced was 53% Fe, 32% Cu, 6% Co, and 6% Ni.
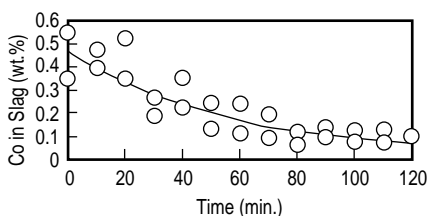

Figure 7. The kinetics of slag cleaning.

Copper Reverberatory Furnace Slag

During 1995, a campaign was conducted on Mintek's 200 kVA d.c. arc furnace to recover cobalt from copper reverberatory furnace slag (initially containing 1.3% copper and 0.77% cobalt). Alloys containing 77–78% Fe, 9–11% Cu, 6–7% Co, and 2–3% S were produced, leaving slags containing 0.08–0.16% cobalt and 0.18–0.29% copper. Coal additions of 4% of the mass of the slag fed and residence times of one to two hours gave cobalt recoveries ranging from 77–91%. Tapping temperatures of 1,490–1,560°C were attained. As shown in Figure 7, the cobalt level in the slag (and therefore the cobalt recovery) varied according to the residence time in the furnace. A retention time of two hours was required to achieve cobalt recoveries in the region of 90%.

In the case of copper reverberatory furnace slag, mineralogical studies showed that the cobalt is present as CoO. Copper in the slag is mainly attributed to the presence of copper-rich sulfides. The cobalt oxide and, to a lesser extent, the copper oxide that is associated with the silicate/oxide phases is reduced by iron from the alloy to form metallic cobalt (and copper), resulting in the formation of FeO in the slag. Given that this reaction occurs between the metal bath and the overlying slag, the exchange of cobalt and copper with iron will take place only at the slag/metal interface.

Improved recoveries of valuable metals can be achieved by allowing greater quantities of slag to come into contact with the alloy (e.g., by mild stirring) and increasing the length of the contact time between slag and metal. 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 cobalt or copper, thus demonstrating that it is, in principle, possible to remove all the cobalt and copper from this phase.

Copper sulfide and copper metal (with its inherent cobalt content), are immiscible with the slag, have higher densities than the slag, and are present in the slag as small entrained droplets. Settling of these droplets could be enhanced by decreasing the viscosity of the slag (either by increasing the temperature or by flux additions) and/or by increasing the settling time to allow the smaller droplets to fall.

Alloy Upgrading

Some of the alloy was upgraded by blowing with oxygen in a top-blown rotary converter (TBRC), preferentially oxidizing the iron and, thereby, concentrating the cobalt and copper in the alloy. The iron content in the alloy was lowered from 76% to 25%, with the effect that the alloy was concentrated up to 30% cobalt and 40% copper. The sulfur level in the resulting alloy was 0.8%. This means that 75% of the cobalt remained in the alloy, while 90% of the iron was removed to the slag. The slag from the TBRC would be recycled back to the d.c. arc furnace in order to prevent the blown cobalt from being lost. (It is possible to arrange conditions in the two process units such that a cobalt recovery of 80% is achieved, even though an alloy containing only around 30% iron is produced.)

LEAD SMELTER SLAGS

The Viburnum trend of southeast Missouri is mined for lead, with zinc, copper, and silver also being recovered. Although the ore contains only low concentrations of cobalt, the relatively large tonnage represents the second largest reserve of cobalt in the United States.[11] Owing to the low gangue content in the lead concentrates, a relatively small quantity of slag is produced during the primary lead smelting process. This leads to a large increase in the cobalt concentration of the lead blast furnace slag. The stockpiled lead blast furnace slag contains approximately 0.30% cobalt, which is sufficiently high to justify further investigation into optimizing the recovery of cobalt as a by-product of zinc recovery. The slag also contains 30.6% FeO, 15.3% ZnO, 11.0% CaO, 4.83% Al_2O_3, 4.6% MgO, 2.71% PbO, 2.40% S, and 0.5% CuO.[12]

The Enviroplas process[9,13] was developed to recover the zinc from zinc-rich waste materials, including lead blast furnace slag. The main goal of this process is to condense a zinc-rich gas to prime western grade zinc in a lead splash condenser. The conditions under which the zinc is fumed are sufficiently reducing to form a metallic (either alloy or matte) phase. The cobalt distribution to the alloy phase will depend on the degree of
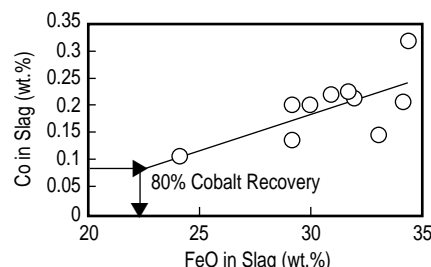

Figure 8. Cobalt in the slag versus FeO in the slag.

reduction in the fuming furnace.

The proposed process consists of three pyrometallurgical operations: a holding furnace, fuming furnace, and a lead splash condenser. A steady stream of molten slag is transferred from the holding furnace at a temperature around 1,300°C via an underflow weir to the fuming furnace (1,500°C) in which the zinc is fumed off, using coke as a reductant. The zinc-rich vapor is condensed in the lead splash condenser to recover the zinc (and any lead) fumed from the slag. Although not considered in this study, any dross and fume arising from the process are most likely to be recycled to the sinter strand of the primary lead-smelting circuit.

The process aims to recover the zinc from the slag, while simultaneously treating the material such that it passes the U.S. Environmental Protection Agency's TCLP test for toxicity characterization. Passing this test classifies the material as nonhazardous, allowing it to be disposed of cheaply (or sold).

Pilot-Scale Test Data

Test work was conducted at the 500 kW scale on a d.c. arc furnace during 1995 to quantify the evolution of zinc from lead blast furnace slag. In addition to achieving a zinc recovery of 85%, an overall cobalt recovery of 46% was achieved (even though this was not a primary objective of the test campaign). During the campaign, low cobalt values in the slag suggested that higher recoveries (comparable to those obtained in copper and nickel-copper processing using d.c. arc furnace technology) may be possible. The cobalt was recovered as a ferrocobalt alloy (4–6% cobalt).

In treating the cobalt-containing lead blast furnace slag, a residual cobalt content in the slag of about 0.08 wt.% corresponds to approximately 80% of the cobalt reporting to the iron-rich alloy.

Hydrometallurgical Treatment

The cobalt-rich alloy produced in the fuming furnace could be treated further, hydrometallurgically, to recover the cobalt and any other saleable metals. A convenient method to dispose of the iron residue would be to recycle the iron as hematite to the holding furnace (where it will leave the process as iron oxide in the discard slag from the fuming furnace). The hydrometallurgical simulations were carried out using *Aspen Plus* simulation software. The following stages are suggested (after smelting):
- Water atomization (or granulation followed by milling)
- Pressure leach in an autoclave
- Filter to remove iron as a hematite residue (hematite is returned to the holding furnace to avoid disposal problems)
- Open tank for liquid (with addition

of sodium carbonate) to precipitate basic copper sulfate
- Filter to remove basic copper-sulfate precipitate
- Drier to dry the basic copper sulfate
- Open tank to precipitate cobalt and nickel carbonate from the remaining solution
- Filter for cobalt/nickel carbonate
- Evaporator for cobalt/nickel carbonate

This process has the advantage of producing only saleable products and a disposable slag. The products would include prime western grade zinc, basic copper sulfate, cobalt/nickel carbonate crystals, and Na_2SO_4 solution.

Process Options

Based on the treatment of 37.5 tonnes per hour, or about 281,000 t/y, of hot (1,150°C) lead blast furnace slag, a comparative simulation study[14] was conducted to quantify the potential benefit of recovering cobalt as a by-product of the process. The following processing routes were compared.

In the first option, zinc is removed to 2.5% ZnO in the discard slag, and the cobalt recovery is merely a consequence of the reducing conditions needed for zinc evolution. The cobalt recovery is low at around 40% of the incoming cobalt reporting to the alloy phase. It is assumed in this case that the cobalt-rich alloy is disposed of at no cost or benefit.

In the second option, the reducing conditions in the furnace are selected (primarily by increasing the coke-feed rate) to raise the cobalt recovery to 80% (incoming cobalt reporting to the alloy). The alloy is treated hydrometallurgically to produce a saleable cobalt/nickel carbonate.

The third option describes cobalt recovery as in option two, but with a converting stage to upgrade the iron-cobalt alloy phase, with the objective of reducing the size of the autoclave needed to leach the alloy. Further simulations, not reported on here, explored the effects of blowing to an even greater degree. This resulted in a much greater recycling load and additional losses of cobalt.

Option two appears to be the most attractive option to pursue for the recovery of zinc and cobalt from lead blast furnace slag. This is mainly attributed to the higher cobalt recovery obtained by operating the furnace under strongly reducing conditions.

A sensitivity analysis of the internal rate of return of the preferred option showed that the project is fairly robust in terms of its financial response to fluctuations in capex, opex, volume, and selling price of cobalt. It is most sensitive to movements in the selling price of zinc.

The use of a separate converting stage to upgrade the cobalt-rich alloy results in a lower overall cobalt recovery owing

to the fayalite slag recycle that dilutes the cobalt in the fuming furnace slag. The main perceived advantage of a blowing unit of this nature is to reduce the quantity of iron in the iron-cobalt alloy sent for hydrometallurgical processing. The simulations of this unit were conducted without the benefit of comparative experimental data on alloys from lead blast furnace slags and should be verified experimentally. (Mintek has done some upgrading of alloys, using a top-blown rotary converter; this is reported elsewhere.[4]) In this case, the incremental cost of additional autoclave capacity was shown to be much less than the capital cost of a converter.

Cobalt recovery significantly improves the economic viability of the process (at the assumed metal prices used in this study). The additional revenue from the cobalt makes a significant difference to the overall profitability of the process.

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