Using Ausmelt Technology for the Recovery of Cobalt from Smelter Slags

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The occurrence of cobalt with copper and nickel and the propensity for this material to report mainly to the final-process discard slag has provided a substantial resource in both current arisings and stockpiles in many copper and nickel smelting operations. Ausmelt has undertaken investigations for the recovery of cobalt from smelter slags using top-submerged lancing technology. These tests, conducted at both the laboratory and pilot-plant scales, have provided good evidence of the application of this proven technology to the recovery of cobalt from these sources.

INTRODUCTION

Ausmelt top-submerged lancing technology for the reduction of base metals from slags, typically copper, nickel, and, to a lesser extent, cobalt, currently encompasses a broad range of materials and is established in 11 commercial plants (Table I). A description of the technology and its development has been reviewed previously;[1] the full range of process conditions covered by the technology is shown in Figure 1.[2]

The relative ease with which the lance facilitates a strongly reducing process environment via a reduction in the lance fuel/air ratio and the use of reductant coal suggested a standard approach to the reduction of cobalt from slag. Early studies undertaken by Ausmelt examined cobalt recovery as an additional element when investigating copper and nickel matte production.[3] Since 1995, several studies have specifically targeted cobalt and examined methods for extracting cobalt from a variety of material sources. These studies on laboratory and pilot-plant scales produced end products ranging from low- to high-grade cobalt-containing matte and alloy.

PROCESS DEVELOPMENT

Customary source materials for cobalt are copper and nickel discard slags, including slags from reverberatory and electric furnaces, as well as Peirce-Smith converters. Typical slags from these sources are given in Table II. These materials represent both current production streams and stockpiles; some of these stockpiles are significant, ranging to the hundreds of thousands of tonnes. This is reflected in the range of plant sizes studied (200,000–500,000 t/y) in conjunction with the pilot-plant testwork.

A direct reduction of cobalt from typical nonferrous smelter slags requires a strongly

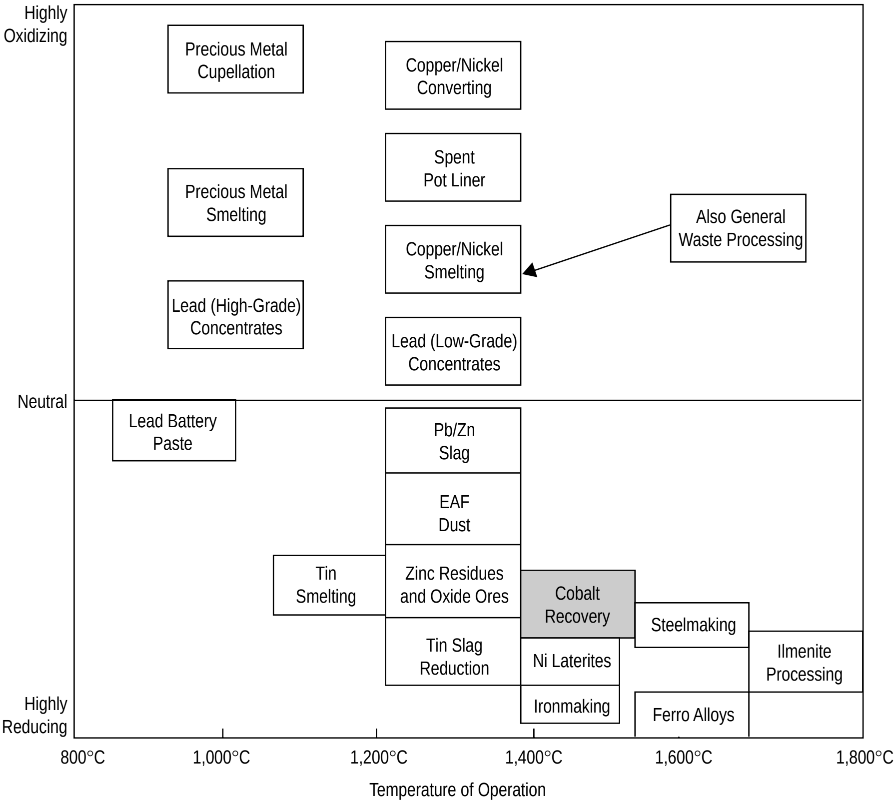

Figure 1. Processes used or under development that use Ausmelt technology as categorized by the range of conditions employed.

Table I. Ausmelt Commercial Plants

Client	Location	Feed Rate (t/y)	Feed
Rio Tinto Zimbabwe	Eiffel Flats, Zimbabwe	7,500	Cu/Ni residue
Korea Zinc Company Ltd.	Onsan, Korea	90,000	Pb/Zn slag
Anglo American Corporation	Bindura, Zimbabwe	12,000	Cu residue
Korea Zinc Company Ltd.	Onsan, Korea	120,000	Zn residue
Mitsui Mining and Smelting Company	Hachinohe, Japan	100,000	Zn/Pb slag
Funsur/Minsur SA	Pisco, Peru	30,000	Sn concentrates
Hindustan Copper Ltd.	Ghatsila, India	72	Anode slimes
Metaleurop	Nordenham, Germany	122,000	Pb materials
Gold Fields of South Africa	Tsumeb, Namibia	120,000	Pb materials
CNIEC	Zhong Tiao Shan, China	200,000	Cu concentrates
Alcoa of Australia	Portland, Australia	12,000	Spent pot lining

reducing slag potential and an operating temperature of 1,350–1,500°C. Such conditions can be readily achieved in the Ausmelt furnace, although the issue of containment at elevated temperatures has clear implications for commercial process applications.

This issue fostered two approaches: the production of a matte phase by the addition of a sulfidizing agent at lower temperature (1,300°C to 1,350°C) and the production of an alloy/matte phase at higher temperatures (1,400°C to 1,500°C). The matte-production approach would typically produce a low-grade cobalt product; upgrading or treatment would then follow via existing processes.

Recent developments in the use of external cooling devices offer the promise of long-term containment integrity in high-temperature systems. This would facilitate the production of sulfur-deficient alloy as an alternative route with no requirement for a sulfidizing agent, no requirement for a convert upgrade/slag reduction step, and capital and operating cost implications.

Most tests conducted at Ausmelt have been at the pilot-plant scale (100 kg/h), with peripheral studies conducted at the laboratory scale (500 g). The pilot-plant investigations focused on the production of cobalt-containing matte, generally of low grade (Table III). The trials conducted on the electric-furnace slag were aimed at a matte of specific composition for processing in existing commercial operations to recover the contained cobalt.

The pilot work investigated and demonstrated the applicability of Ausmelt technology to produce matte containing up to 8% cobalt and 10–20% sulfur, along with discardable slags containing less than 0.1% cobalt and 0.1% copper. In a two-stage operation subsequent to reduction, converting or upgrading of the matte produces a combined alloy/matte product containing 15–20% cobalt.

FACTORS INFLUENCING COBALT RECOVERY

During the studies, certain parameters were examined to determine their influence on the composition and recovery of cobalt to the end products: reduction rates, the use of sulfidizing agents, fluxing and slag chemistry, and distribution ratios.

Reduction Rates

The reduction of cobalt from the typical levels of the source materials to less than 0.1% requires strongly reducing conditions. Under these conditions, cobalt, copper, nickel, and iron are also reduced from the slag. The major reactions occurring during the reduction stage are

$$CoO_{(slag)} + Fe_{(matte/alloy)} = Co_{(matte/alloy)} + FeO_{(slag)}$$

$$CoO_{(slag)} + FeS_{(matte/alloy)} = CoS_{(matte/alloy)} + FeO_{(slag)}$$

$$NiO_{(slag)} + FeS_{(matte/alloy)} = NiS_{(matte/alloy)} + FeO_{(slag)}$$

$$2CuO_{(slag)} + FeS_{(matte/alloy)} = Cu_2S_{(matte/alloy)} + FeO_{(slag)} + 1/2\ O_{2(gas)}$$

$$FeO_{(slag)} + C_{(solid)} = Fe_{(alloy)} + CO_{(gas)}$$

$$CO_{(gas)} + 1/2O_{2(gas)} = CO_{2(gas)}$$

As the feed materials contain insufficient sulfur to form the relevant sulfides, metallic cobalt and iron are formed and a matte/alloy product results. It was generally found that with a high iron content in the alloy, high recoveries of cobalt from the slag were obtained.

As expected, all trials showed that the reduction rate of cobalt and other metals from the slag decreased as the metal content in the slag decreased. Typically, a 50 minute reduction period under strongly reducing conditions (30 kg/h reductant coal) was

Table II. Typical Cobalt Source Materials

Source	Co	Cu	Ni	Fe	S	SiO_2	Al_2O_3	CaO	MgO
Reverberatory (1)	0.8	1.1	30*	25.3	0.7	43.1	6.7	7.1	2.3
Reverberatory (2)	0.2	0.6	0.1	32.0	0.5	35.0	3.0	9.0	5.0
Converter	0.5	2.0	0.3	50.0	0.5	28.0	0.5	0.5	0.3
Electric Furnace	0.2	0.1	0.3	31.6	0.8	41.4	1.7	1.1	11.7

* Denotes ppm value.

adequate to leave low levels of metal in the slag.

The reduction of metallic iron, which was evident when cobalt levels in the slag fell below 0.2%, is shown in Figure 2. This dilutes the cobalt level in the product and raises the liquidus temperature of the product material. If operation at lower temperatures is desired, then consideration must be given to providing sufficient sulfur to allow a purely matte phase to form.

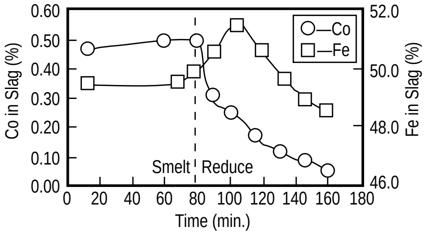

Figure 2. The reduction of cobalt and iron from slag.

Sulfidizing Agents

The addition of a sulfidizing agent such as pyrite was found to

- Act as a collector phase to promote removal of the base metals from the slag.
- Decrease the liquidus temperature of the final cobalt-containing product.
- Allow the collecting phase volume to be increased in cases where the expected metal yields are low. This provides sufficient volume of matte/alloy product to allow separation from the slag.
- Benefit applications where a matte product is desirable for further treatment in existing plant flowsheets.

Pyrite-addition rates of up to 20% of slag material were typical. While this is a significant proportion of the feed, it was found that decreasing this rate resulted in more difficult separations of matte from slag and higher operating temperatures due to the higher quantity of alloy with a high melting temperature.

Gypsum was also tested as a sulfidizing agent, with a view to achieving an improved sulfidizing efficiency over pyrite, which is substantially reduced by the loss of latent sulfur. Gypsum, however, proved generally unsuitable in facilitating the production of a matte phase.

Fluxing and Slag Chemistry

The separation of the cobalt-containing product from slag was found to improve with the addition of limestone through the improvement of the slag fluidity when operating between 1,300°C and 1,400°C. Temperatures below 1,350°C were targeted in order to minimize refractory wear. In cases where the slag chemistry is compatible with the refractory materials, operation at higher temperatures removes the need for fluxing. Fluxing-addition rates of between 9–14 wt.% were found to be adequate for the materials tested.

Distribution Ratio

The distribution of cobalt and iron between slag and matte is determined by the exchange equilibrium of the two reactions

$$\mathrm{CoO_{(slag)} + FeS_{(matte/alloy)} = CoS_{(matte/alloy)} + FeO_{(slag)}}$$

$$\mathrm{CoO_{(slag)} + Fe_{(matte/alloy)} = Co_{(matte/alloy)} + FeO_{(slag)}}$$

The extent of the reactions is dependent on bath conditions with respect to either oxidizing (converting) or reducing operations. The amount of sulfur in the matte is also a factor in the equilibrium.

Sorokin et al.[4] presents the distribution of cobalt between matte and slag in terms of mass percent as the distribution ratio C as per

$$C = \frac{\%\mathrm{Co_{(matte)}} \times \%\mathrm{Fe_{(slag)}}}{\%\mathrm{Co_{(slag)}} \times \%\mathrm{Fe_{(matte)}}}$$

For the trials investigated, the results generally indicate a linear relationship, however, several sets of data suggest that other factors and, possibly, nonequilibrium conditions existed during the trials. This was especially the case when highly reducing conditions produced low iron in the slag and allowed the formation of a greater proportion of metallic iron in the matte/alloy.

COBALT LOSSES TO SLAG AND RECOVERIES

Two effects cause losses of cobalt and other metals to the slag. The first is the concentration of cobalt dissolved in slag as oxide and sulfide. That concentration maximum is set by the equilibrium between the slag and another cobalt-containing phase, such as matte or alloy. The second effect is the physical entrainment of matte or alloy in the slag. In the absence of sufficient sulfur to allow the reduced metals to form a matte, the re-

Table III. Typical Pilot Plant Results

Slag Source Material	Cobalt (%)	Copper (%)	Nickel (%)	Iron (%)	Sulfur (%)
Electric Furnace					
Feed	0.15–0.17	0.07–0.09	0.20–0.24		
Product	0.8–3.1	0.7–4.6	1.2–8.3	53.1–65.5	24.3–26.9
Slag	0.04–0.08	0.01–0.04	0.04–0.05	—	—
Recovery	62.5*	70.0*	72.7*	—	—
Reverberatory Furnace					
Feed	0.07–1.0	1.0–1.4	Low Levels	—	—
Product	2.4–10.5	11.6–26.8	—	39.8–58.0	9.0–25.5
Slag	0.03–1.0	0.05–0.28	—	—	—
Recovery	91.2–97.5	86.4–96.4	—	—	—
Converter					
Feed	0.47	1.6	3.8	—	—
Product	0.98–2.0	8.0–15.5	14.4–35.5	29.0–32.5	18.5–20.2
Slag	0.02–0.11	0.19–0.50	0.03–0.53	—	—
Recovery	90.4–97.1	81.4–91.2	88.4–99.4	—	—

* Denotes maximum achievable recovery based on slag used (0.15%) and a slag discard level of 0.05% Co.

sulting metal alloy has a high liquidus temperature. If such alloys are present, they will form mushy rafts of material that are mixed with the slag and are difficult to separate from the slag.

In the Fe-Co-S system at high operating temperatures, a greater quantity of metallic iron and cobalt are soluble in the matte without separation.[4] Maintaining a matte/alloy temperature higher than 1,300°C is recommended to produce a matte product with high levels of dissolved metallic iron and cobalt. It was noted that when the mixed matte/alloy product was tapped, cooling allowed the separation of the matte and alloy phases. Also, if rapid cooling or quenching of the product is achieved, the formation or separation of large quantities of alloy from the total matte/metal product will be minimized. From the trials conducted, it was generally found that for high recoveries of cobalt from low-grade slags (<0.4% cobalt), the iron content in the matte/alloy increases significantly.

A process achieving high levels of cobalt recovery by producing discard slag containing less than 0.05% cobalt, less than 0.03% copper, and less than 0.05% nickel was demonstrated consistently in the pilot trials. The product targeted for these trials was a matte/alloy with approximately 1% cobalt and cobalt recovery to matte/alloy in excess of 60%. Recoveries of 90% were obtained in processing converter slags containing up to 0.5% cobalt.

UPGRADING/CONVERTING LOW-COBALT PRODUCTS

Some additional work was conducted on the upgrading/converting of low-cobalt products. Converting at both pilot and lab scale showed that rapid oxidation of metallic iron and cobalt to slag occurred before sulfur oxidation. It was determined during laboratory tests that at least 60% of the cobalt is oxidized to slag during converting and suggested that the recovery of cobalt to a final matte product can only be achieved after a hard reduction of the final converting slag. This reduction must be controlled to achieve cobalt in the slag at levels of ~0.15%, otherwise the iron content of the matte/alloy rapidly increases below this level and dilutes the matte/alloy product. In the pilot-plant trials on converter-slag material, this resulted in the production of a metal alloy with up to 26% cobalt and a low-grade cobalt matte containing ~8% cobalt. These products separated upon slow cooling.

COMMERCIAL IMPLEMENTATION

The process route chosen for each commercial application will depend on project specifics, including the product grade/recovery relationship, downstream processing requirements, and overall project economics. In the implementation of a commercial processing unit used to produce a low-grade (~8%) cobalt-containing matte, the system would comprise a single furnace that would operate under the following specified parameters:

- The use of pyrite, concentrate, or other material as a sulfidizing agent for matte formation.
- The use of limestone as a flux to maintain slag fluidity.
- Low lance-combustion stoichiometry of 80–90%, and the use of lump coal for reducing conditions.
- An operating temperature of up to 1,400°C to allow the separation of the matte phase.

If it is desirable to upgrade this product, then a second furnace can be employed to produce a cobalt-containing product of up to ~20% cobalt. This furnace would operate in a batch mode, whereby the convert step would be followed by a slag-reduction stage to recover oxidized cobalt from the slag.

An alternative is the use of a single furnace to produce a sulfur-deficient matte/alloy product. This system would require operation at higher temperatures.

Ausmelt has investigated the use of water-cooled copper fingers in order to increase plant operating temperatures to the range of 1,400–1,500°C in normal operations. Thus, the need to add a sulfidizing agent to lower the product liquidus can be avoided. This possibility, coupled with a higher level of cobalt in the end product, allows for an alternative treatment route for the recovery of cobalt from these raw materials, which could, in turn, provide for reduced capital and operating costs via the single furnace system.

The metallized product would require granulation to facilitate further downstream processing. Based on the pilot-plant results obtained on both low (<0.1% cobalt) and high (>0.2% cobalt) grade feeds, recoveries in excess of 90% from a 1% cobalt slag feed to an 8–20% cobalt in matte product is predicted.

References

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