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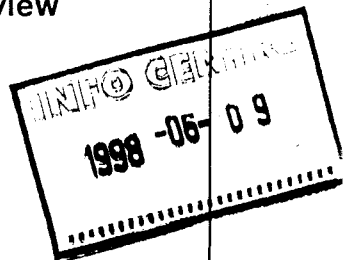
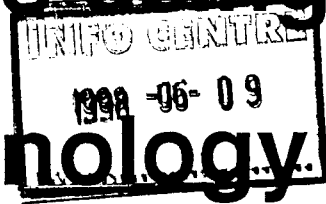*Mintek's 3.2 MVA DC-arc furnace in operation (Page 3)*

Recovery of Cobalt, Nickel and Copper from Slags using DC-Arc Furnace Technology

The treatment of cobalt containing slags has been the subject of interest in countries such as Zambia and the Republic of Congo for many years. Over past few years, this interest has grown as fear of supply disruptions and prices have increased. Today, a number of processes have been developed for treating the various slags available. In our October 1997 issue of Cobalt News, we briefly outlined a technique used in Russia which operates in parallel to the normal smelter operation. This month we are looking at a method developed by Mintek which appears very promising for treating a wide range of cobalt containing copper and/or nickel slags.

Slags produced by non-ferrous smelters usually contain significant quantities of valuable metals, such as cobalt, nickel, and copper, present both in an entrained metallic or sulphide form, and in a dissolved oxidised form. These slags can emanate from furnaces, converters or huge dumps that have built up over many years of operation of nickel and copper 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 sulphide or the metallic form, but is not suitable for the recovery of oxidised metals. Cobalt in particular, and nickel to a lesser extent, are found in an oxidised form, and for these slags, treatment in an electric furnace operated under reducing conditions is necessary.

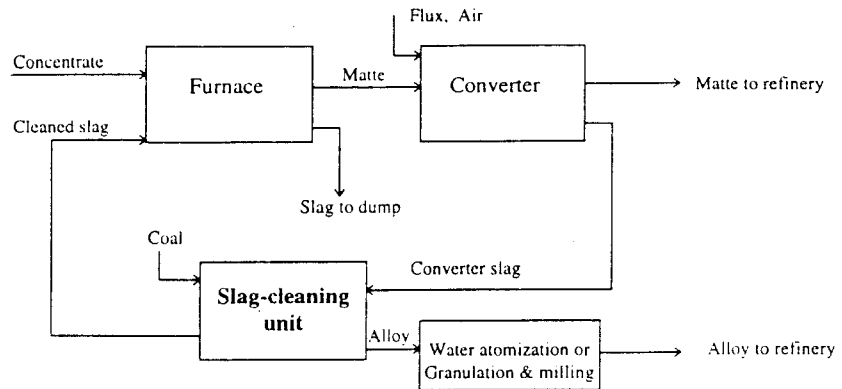Conventional slag cleaning furnaces rely largely on a gravity settling mechanism, whereby the entrained sulphide and metallic droplets are simultaneously collected. Sometimes, a quantity of matte is added to the slag to enhance the coalescence of entrained matte droplets. However, conditions are not usually sufficiently reducing to recover much of the cobalt. Cobalt recoveries may be as low as 20 per cent. 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 oxidised form.

The aim of a slag cleaning process is to maximise the recovery of valuable metals (such as Co, Ni and Cu) 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 behaviour 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 and the associated valuable metals, from slags, since 1988, using DC-arc furnace technology to effect 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.

Flowsheets for slag cleaning

Many non-ferrous smelters employ a process whereby the concentrates are fed to a furnace which produces a matte (for further treatment) and a slag (which is dumped). The furnace matte is treated in a converter (often of the Peirce-Smith type) to remove most of the remaining iron and sulphur. This resulting 'white matte' or alloy is then treated hydrometallurgically. The converter slag is usually recycled to the furnace. Because of the highly oxidising conditions in the converter, much of the cobalt is oxi-
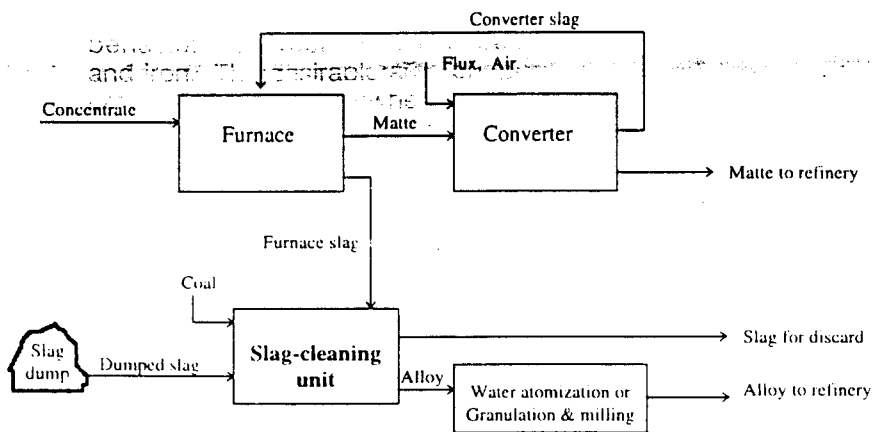

Fig. 1 - Flowsheet for cleaning of converter slag

Fig. 2 - Flowsheet for cleaning of furnace slag (also applicable to the cleaning of flash-furnace slag, without a converter present)

ents present in the slag. Figure 3 illustrates the differences in reducing behaviour between nickel, cobalt and iron. 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. Note that, in actual practice, there is less than 100 per cent carbon utilisation, and the carbon addition would need to be somewhat higher than that shown here, because of burn-off of some of the reductant.

The equilibrium behaviour shown in Figure 3 is not very sensitive to temperature and curves plotted for temperatures 100°C colder or hotter are virtually indistinguishable from those presented. Clearly, the temperature has effects other than on the chemical thermodynamics of the system. It has been reported that a 100°C increase in temperature may decrease the cobalt and nickel solubility in slag by as much as three times, at a constant partial pressure of oxygen and at a temperature around 1300°C.

dised. The turbulent conditions cause entrainment of valuable metals as well. Of all the streams in a flowsheet of this sort, the converter slag is richest in cobalt. As shown in Figure 1, 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 can be dumped (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 currently being produced. This option is shown in Figure 2. It is, of course, also possible to use a hybrid of these approached.

A wide range of slags are amenable to slag cleaning. These slags differ according to the ores which have been processed, as well as according to the type of process, and whether the slags have arisen from furnaces or from converters. Most of the slags of interest are rich in iron oxide and silica, and many have a bulk com-

position approximating that of fayalite. Fortunately, similar principles apply to the treatment of all of these slags, although the actual results will differ according to the composition of the slag.
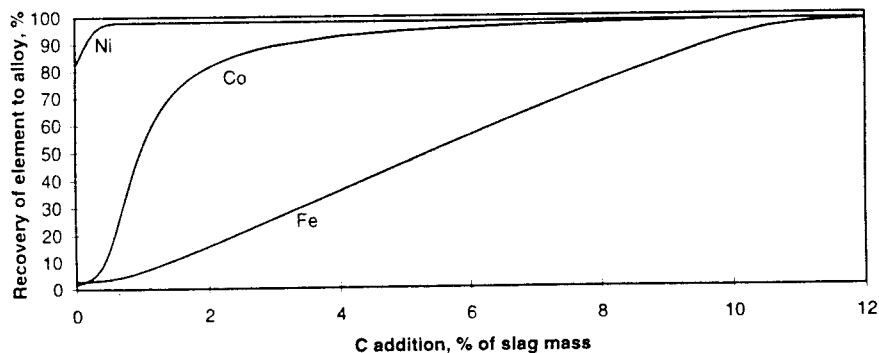

Fig. 3 - Recovery of elements to the alloy, as a function of the quantity of carbon added, at 1500°C

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 constitu-
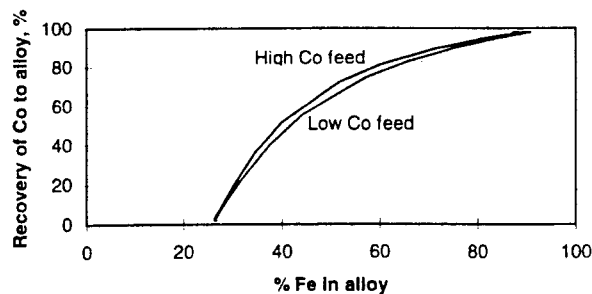

Fig. 4 - Recovery of Co to the alloy, as a function of the amount of Fe present in the alloy, at two levels of Co (1.0% and 0.2%) in the slag fed to the slag-cleaning furnace
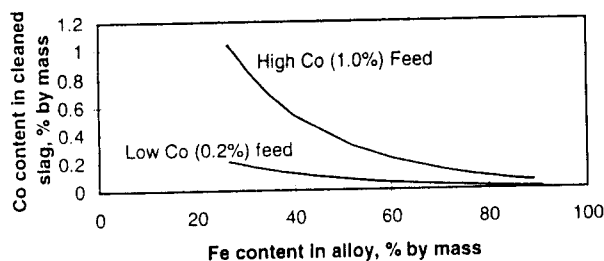
Fig. 5 - Residual Co content in cleaned slag as a function of the Fe content in
the alloy

However, the solubility is even more strongly affected by the reducing nature of conditions in the furnace (i.e. the partial pressure of oxygen in the system). The most striking feature of this separation process is the variation of cobalt recovery according to the iron content in the alloy. This behaviour is shown in Figure 4. It can be seen that the recovery of cobalt (in percentage terms) is highest (albeit not by very much) in the case of the slag with the highest initial cobalt content. This is in line with experimental findings that recoveries are dependent on initial slag composition, with higher grades leading to better recoveries. If we accept the evidence presented elsewhere that metallic Fe 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 non-ferrous metal contents of the initial slag.

However, as shown in Figure 5, the residual cobalt content in the cleaned slag, as a function of the iron content of the alloy, is very sensitive to the initial cobalt content.

DESCRIPTION OF A DC-ARC FURNACE

The DC-arc furnace has a single electrode positioned above the molten bath; the molten metal in the furnace forms part (the anode) of the electrical circuit. The furnace comprises a refractory-lined cylindrical steel shell, and a water-cooled roof line with an alumina refractory. The outer side walls of the furnace are spray-cooled with water to protect the refractories and to promote the formation of a freeze lining within the vessel. The roof contains the central entry port for the graphite electrode and up to three equi-spaced side feed ports. 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 which, via radially extending arms, is linked to the furnace shell and further to the anode cable. A schematic diagram of this arrangement is shown in Figure 6.

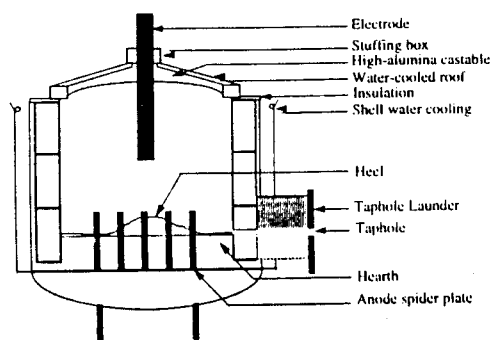Molten slag may be fed directly to the 5.6 MVA furnace from a pre-melting furnace. The solid-feed system for the 3.2 MVA furnace comprises a batching plant and a final controlled feeding system. The batching plant consists of feed hoppers mounted on load cells, vibratory feeders positioned under the hopper, and enclosed belt conveyer, a bucket elevator, and pneumatically actuated flap valve to direct the feed to one of two final feed hoppers. The final feeding system is made up of separate centre and side feeding arrangements. The centre feeder uses a screw feeder discharging into a telescopic pipe attached to the hollow graphite electrode. The side feeders are vibratory, and discharge into feed chutes.

The gas-cleaning system consists of a water-cooled off-gas pipe, a refractory-lined combustion chamber, water-cooled ducting, a forced-draft gas cooler, a reverse-pulse bag filter, a fan, and a stack. The condensed fume and dust, which accumulates in the lower conical section of the bag plant, is discharged via a rotary valve into a collecting drum. This dust would, of course, be recycled back to the furnace in an industrial situation.

EXPERIMENTAL RESULTS

Tests have been carried out over a number of years on copper converter slags, nickel-copper converter slags, nickel-copper furnace and converter slags and copper reverbatory furnace slags using 100 kVA, 200 kVA, 3.2 MVA and 5.6 MVA DC-arc furnaces. Results of these tests show that DC-arc furnace technology has been successfully applied to the recovery of cobalt, nickel and copper from non-ferrous furnace and converter slags. Pilot-plant testwork at Mintek has demonstrated recoveries of 98% for nickel and over 80% for cobalt, at power levels of 600 kW.

The question as to why a DC-arc furnace should perform better than an AC slag resistance furnace for this type of process is explained as follows:-

1. Since DC-arc furnaces operate under open arc conditions, they do not rely on the resistivity of the slag to supply energy to the furnace bath. This renders the energy supply nearly independent of slag composition which allows slag chemistry to be optimised for the best recovery of
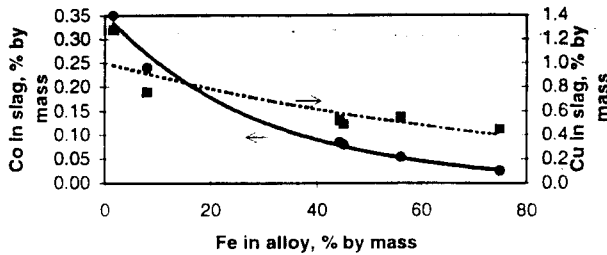

Fig. 6 - Schematic diagram of a DC transferred-arc furnace

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Fig. 7 - Results of 100 kVA test on copper converter slag

valuable metals. This also results in less erosion of the electrode.

2. Temperature distribution in the bath is likely to be more even as the current in a DC-arc furnace travels through the entire depth of the liquid bath as opposed to between electrodes of an AC furnace. This allows better control of slag viscosity and density and more efficient settling of droplets of the alloy.

3. The inherent stability of a DC-arc furnace offers the potential for improved operational control.

Upgrading of cobalt-rich iron alloys

It is possible to upgrade the alloys produced in the DC-arc process by the selective oxidation of iron. If the DC-arc furnace is run under strongly reducing conditions (to ensure the greatest possible recovery of valuable metals), the alloy will contain a large quantity of iron.

However, if this alloy is subjected to a blowing stage (using air or oxygen), much of the iron can be eliminated into a slag phase. Typically, a silica flux is added in order to combine with the resulting iron oxide to form a fayalitic slag (nominally $2FeO.SiO_2$). This blowing stage can be carried out in a converter of some kind or even in a closed furnace utilising a submerged top lance.

Tests at Mintek have been carrie out using a top-blown rotary converter (TBRC). The slag from the upgrading step would be re-cycled back to the DC-arc furnace at industrial scale, in order to recover the portion of valuable metals that have been reoxidised. It is possible to arrange conditions in the two process units such that an alloy containing only 30% iron is produced, even though a cobalt recovery of 80% is achieved.

Water atomisation of alloys

Cobalt-rich iron alloys are virtually unbreakable, which poses a problem of delivery of the alloy to the downstream process units. It is common practice in a number of slag-cleaning processes to add sulphur (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 sulphur needs to be removed during subsequent hydrometallurgical processing.

Water atomisation, 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 design of the atomising system is simplified by not having any tight constraints on the range of particle sizes and shapes of the particles.

This technology is commercially available up to industrial scale 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 optimise the metallurgy to maximise recovery of the valuable metals, without needing to be too concerned with the physical properties of the alloy.

Very little material handling is required after atomisation. A simple screen to separate oversize materials (for recycling to the DC-arc furnace) is about all that is needed. The alloy particle can be pumped as a slurry, then de-watered. Drying is not necessary, as the alloy will next be subjected to a wet process.

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 solubilises the nickel, copper and cobalt while rejecting the iron and any sulphur 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. Mintek has also developed direct solvent extraction of cobalt from cobalt-bearing nickel solutions. Nickel and cobalt have been successfully electrowon from the raffinate and strip liquor respectively.

CONCLUSION

DC-arc furnace technology has been successfully applied to the recovery of cobalt, nickel and copper from non-ferrous furnace and converter slags. Pilot-plant testwork at Mintek has demonstrated recoveries of 98% nickel and over 80% cobalt at power levels of up to 600 kW.

Mintek expects to participate in the commissioning of the first commercial units in the near future.