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Economic and environmentally beneficial treatment of slags in DC arc furnaces

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Slags have been produced as by-products from pyrometallurgical processes for thousands of years, and have generally been regarded as waste. Many of these slags are no longer seen as residues merely to be discarded, but as potential economic sources of metals, or as useful by-products in their own right.

Slag cleaning can enhance the recovery of valuable metals in existing pyrometallurgical processes, or can produce economic value from recycling old slag dumps. For example, a process has been developed and implemented industrially for recovering cobalt from copper smelting slag in a DC arc furnace.

The relatively non-leachable behaviour of glassy slags allows them to be used as a very safe means of disposal of metallurgical waste streams, including many that are classified as hazardous. The high temperatures, reducing conditions, and good mixing that can be achieved in a DC arc furnace enable the effective functioning of this environmentally beneficial means of disposal. Lead blast furnace slag can be rendered safe for disposal by treating it using the Enviroplas process, which strips most of the hazardous lead from the slag (and traps the rest in an insoluble glassy slag) and recovers economic quantities of zinc by absorbing (in a lead splash condenser) the zinc vapour that is fumed off in the furnace. Another example can be seen in the recovery of a chromium- and nickel-containing alloy from stainless steel plant dust, while producing a disposable residual slag.

The examples presented here illustrate that it is possible to develop processes that are both economic and environmentally beneficial.

Keywords: DC arc furnace, plasma, slag cleaning, cobalt recovery, zinc fuming, Enviroplas, jigging, re-melting fines, environmental, economic

Introduction

A common feature shared by all pyrometallurgical smelting processes is the production of slag. Slag is usually a by-product of metal production, although there are processes (such as ilmenite smelting, for example) where the slag is the principal product. Most slags contain a significant amount of heavy metals, the release of which can cause environmental problems. However, the recovery of these metals may make it economic to clean the slags to the point where they are not only safe for disposal, but where they may be able to be used as products in their own right. This is sometimes a viable alternative to the conventional method of slag disposal by dumping, which occupies land unproductively, sometimes causes water pollution, and can be seen as a waste of resources.

Slags in history

Smelting history goes back at least 6 000 years to the copper smelters of the Timna valley near Eilat in Israel. Copper is the world's oldest metal and was used more than 5 000 years ago for water plumbing in the Pyramid of Cheops in Egypt. The Egyptians obtained their copper from Israel and from Cyprus.

Throughout the second millennium BC, copper was produced in Cyprus by extracting it from copper sulphide ores. The ancient Cypriots pioneered pyrometallurgical processing of copper, using the surrounding forest to supply energy for the process, and adding fluxing materials from areas close to the mines. Later, tin was found in the Iberian Peninsula, and it was possible to produce a copper-tin alloy (bronze), which was used in the manufacture of tools, implements, weapons, and ornaments. A comparison between the chemical composition of typical massive sulphide ores and ancient slag from Cyprus clearly suggests that in the smelting process the metallurgists mixed the ore with silica and manganese-bearing rocks (probably umber) to lower the melting point and regulate the viscosity of the melt, making it easier to separate the metal from the slag. The smelting of copper sulphide ores in Cyprus lasted for more that 3 500 years and produced more than 200 000 tons of copper metal. Many slag heaps remain to this day, and more than two millions tons of slag were found in the Skouriotissa area alone.

For a long time, slag was seen as a waste product fit only for dumping, but alternative applications were already in place hundreds of years ago.[1] As early as 1589, cannon balls were cast from iron slag in Germany. Slag was

Table I
Estimated annual world production of selected large-tonnage slags, millions of metric tons per annum

Type of slag	Annual world production
Iron and steel slags	300 million tons
Nickel slags (FeNi + sulphide)	15 million tons
Copper slags	14 million tons (7 to 35)
Ferrochromium slags	4.4 million tons
Ferromanganese slags (FeMn + SiMn)	[19 Mt of Mn]
Lead and Zinc slags	[9 Mt of Zn; 3 Mt of new Pb]
PGM slag	2.4 million tons
Titania slag	2.4 million tons

commonly used as ship ballast in the 1600s. Records indicate that cast-iron slag stones were used for masonry work in Europe in the 18th century. Roads made from slag were first built in England in 1813 (although, in Roman times, metal slag was already used as a road-base material). As early as 1880, blast furnace slag and steel slag were used as a phosphatic fertilizer. By the 1880s, blocks cast of slag were in general use for street paving in both Europe and the United States. San Juan in Puerto Rico has a long history of slag-paved streets. For a long time, the principal use of slag in the USA was as track ballast for the nation's railroads. Slag was also used in the building of military roads during World War I.

Worldwide slag production

Table I presents an estimate of annual world production of selected large-tonnage slags. (Note that aluminium salt slag is not included here, as the focus of this paper is on silicate slags containing metal oxides.) The estimates are done on the basis either of published figures, or by taking current metal production figures and multiplying them by a factor to take into account the expected approximate slag to metal ratio. The figures should be regarded only as rough approximations in many cases, but should serve to indicate the magnitude of the problem or opportunity to treat slags differently.

Types of slag

Slags, except for iron-making blast furnace slag, usually contain a quantity of valuable metals. Metals can be recovered from many of these.[2] Typical analyses of some common types of slag are shown in Table II.

Ferrous slags are no longer regarded as waste, and are among the most voluminous of recycled materials. Additionally, entrained metal, particularly in steel slag, is routinely recovered during slag processing for return to the furnaces.

Iron-making slag

Iron and steel slags, used mostly as construction aggregate, have comparable or even better properties than their competitive materials for a range of applications. The metals in iron and steel slags are tightly bound to the slag matrix and are not readily leached, and there are few environmental concerns regarding their application.

Blast furnace slag contains little metal, and recovery of metal (even iron) from it is usually not important. About 220–370 kg of slag is produced per ton of iron. Blast furnace slag was used as early as 1880 as a phosphatic fertilizer. Today, blast furnace and steel slag have found a wide application in areas such as cement production, road construction, civil engineering work, fertilizer production, landfill daily cover, and soil reclamation. Iron blast furnace slags are classified according to their method of cooling.

(i) *Air cooled:* molten slag is poured into pits in layers, allowed to solidify, and cooled either by ambient air or by water addition after solidification, then crushed and screened. It is used as a general aggregate in base, concrete, asphalt applications, rail ballast, roofing, shingle coating, glassmaking, and rock-wool raw material.
(ii) *Expanded or lightweight:* molten slag is poured rapidly into sloping pits, moist on the bottom to allow steam penetration while still viscous, causing many small voids. Concrete blocks are made from this material.
(iii) *Granulated:* the flow of molten slag is rapidly cooled by a high velocity mixing with water jets in a ratio of one part slag to 6–10 parts of water by mass. This is ground and used as a cement replacement in concrete making, or as an ingredient in making a blended cement. It may also be used as a lightweight fill and as a sand replacement in concrete.
(iv) *Pelletized:* this is a variation of granulating in which less water is used, with violent impelling of the viscous, but rapidly cooling slag through the air. Applications are similar to granulated slag. It may also be used in some lightweight concrete applications or products.

The density of air-cooled blast furnace slag is in the range of 1120–1360 kg/m^3; expanded blast furnace slag coarse aggregate is in the range of 560–880 kg/m^3; and the fine aggregate is in the range of 800–1120 kg/m^3.

Applications of iron blast furnace slag include: road base aggregate (40%), asphaltic or bituminous concrete aggregate (38%), fill (10%), concrete masonry units, concrete paving, rail ballast, roofing systems, speciality, and structural concrete. Blast-furnace slag has a typical selling price in the USA of about $5 per ton.

Steel-making slag

Steel furnace slags emanate from a range of sources. Differences in slags from the various process units are due more to raw materials and desired final steel chemistry than

Table II
Typical analysis (mass %) of some common types of slag

	Al_2O_3	CaO	Co	Cr	Cu	Fe_{Total}	MgO	Ni	P	S	SiO_2
Blast furnace slag	6–12	38		-		<1	10		-	1	36
Steel slag	15–29	30–50		-		7–10	3–10		1–3	-	10–18
Charge chrome slag	24	7		8–12		3.1	29		-	-	28
Stainless steel slag	2–9	45–48		3–4		3–7	3–7		-	-	26–32
Ni flash furnace slag	0–6	0–2.5	0.1–0.6	-	0.2	36–45	2.5–8	0.3–4	-	0.2–1.3	27–40

to the process itself. Open-hearth slag from reverberatory furnaces is produced where molten iron, ore, and scrap are refined with limestone as a flux for a long period, with fuel and air injection to heat and burn out carbon. The process is slow and obsolete, but many old slag disposal areas contain this slag. Basic Oxygen Furnaces (BOF, BOP, or LD) have scrap and molten iron charged along with chemical lime to remove silica. Refining of the carbon level is done by injected oxygen. Electric Arc Furnaces (EAFs) use AC or DC electric arcs to melt scrap (or metallized ore, or both), along with chemical lime (either calcitic, or calcitic plus dolomitic).

Steel furnace slag typically contains approximately 40% calcia, 10% magnesia, up to 30% iron oxide, and a few per cent manganese oxide. These are beneficial components in ironmaking. In an integrated steel mill, the steel slag can be fed into a blast furnace in limited quantities along with limestone, ore, or pellets and scrap, with coke for fuel and chemical reduction.

How much steel slag can be recycled depends on the phosphorus content of the steel furnace slag. Phosphorus accumulates in the molten iron product of the blast furnace and then returns in the steel furnace slag from the steel furnace. The phosphorus steadily increases in percentage until the system must be purged by stopping the recycle.

Another direct recycle is the direct return to the BOF steel furnace where the lime actually required (for reaction when the molten iron being charged is low in silicon) does not create adequate slag cover in the furnace. Similarly, steel slag can be recycled directly to the EAF where there is not as much lime required for impurity removal as in the BOF, but more slag cover is required than the lesser lime amount would contribute.[3]

The characteristic steel slag is relatively high in iron, and in calcium reacted with other impurities to form mineral compounds that are heavy, dense, hard, abrasion resistant, and dark coloured. Where furnaces have short residence times, and if there is excess lime addition, there may be unreacted lime, which requires ageing before slag use in some applications. It can take six months for the slag to 'cure', i.e. for the lime content to hydrate and for the calcium silicate to expand. The curing makes the slag amenable for use in road construction and as a cement admixture.

Entrained steel in slag is a valuable commodity. It is common for independent processors to recover the steel and sell it to the steel mill at prices below those of scrap. The output of molten slag is about 10 to 15 per cent of the mass of steel produced. Entrained steel can make up as much as 50 per cent of the slag. Reprocessing the slag can reduce the steel content to as low as 5 per cent.[4] By applying mineral processing technologies such as crushing, milling, classification, and magnetic separation, it is possible to produce steel scrap and iron concentrate (with Fe > 55%) from steel slag.

Chaparral Steel, Texas, previously cooled and crushed their steel slag before selling it to the road construction industry. More recently, they have developed their CemStar process[5] that adds slag to the raw material mix that is fed to the rotary kiln of an adjacent cement plant producing Type I Portland cement. A slag magnetic separation process allows lower grade metallics to be recovered and recycled back to the furnace. The lower-grade iron slag is fed into the cement plant kilns, serving as a substitute for limestone. This by-product-to-resource conversion thus conserves natural resources while reducing energy requirements 10–15%. CO_2 emissions are reduced because less limestone is used, and less fuel needs to be combusted. Furthermore, the value of the slag is increased 20 times, relative to its road construction value.

Charter Steel in Saukville, Wisconsin uses a DC electric arc furnace for steelmaking. Near to this plant, there is a processing plant that processes the steel slag for use on railroads.

Applications of steel slag include: road base aggregate (39%), asphaltic or bituminous concrete aggregate (15%), fill (19%), rail ballast, and speciality uses.

Stainless steel slag

Stainless steel slag contains a significant quantity of chromium and a certain amount of nickel. Since stainless steel slag can release a noticeable amount of Cr as high as 1 ppm in solution formed by rainwater, it may cause environmental concerns. It is desirable to treat stainless steel slag prior to its application or even landfilling. Recovery of Cr and Ni from stainless steel slag is not only very important for the environment, but makes good economic sense too.

Ferro-alloy slag

Ferro-alloy slag includes by-products from FeMn, SiMn, and FeCr production. Much attention has been focused on slags containing chromium. Charge chrome slag can contain around 8–12% Cr. Like stainless steel slag, it can also release Cr into water and it may be harmful to the environment. Magnetic separation has been used to recover Cr from this slag on a test scale. Gravity separation has been effectively used to separate Cr from this slag on an industrial scale in India and South Africa. After separating out the entrained metal, the resulting slag can be used as concrete aggregate. FeCr slag from Tornio in Finland is used as building and road construction material.

Vanadium slag

Vanadium-bearing slags are used as an intermediate feed material in the vanadium industry. Over two-thirds of worldwide vanadium production is derived from by-product or co-product sources, and mining capacity has only a swing role.

Non-ferrous slag

Among the non-ferrous slags, copper slag has been subjected to the most extensive research work, with a history of over 100 years. By using flotation, leaching, or roasting, it is possible to recover Cu, Co, and Ni from copper slag. This paper examines an alternative pyrometallurgical metal recovery process based on the open-bath carbothermic reduction of metal oxides (such as cobalt, nickel, and copper) in the presence of a silicate slag.

Lead-containing slags, such as lead blast furnace slags, are classified as hazardous, and there can be substantial benefits in processing these further.

Other examples of metal recovery from non-ferrous slags are the recovery of Nb and Ta (as well as Au and Ag) from tin slag.

Salt slag

Salt slag is used in the secondary aluminium industry, and much effort has been expended on its treatment due to its serious effect on the environment. (This material is outside the scope of this paper.)

Incineration slag or residue

The residue from the incineration of municipal waste, especially the fly ash portion, has a high concentration of heavy metals and dioxins. It needs special treatment, such as vitrification by re-melting, or extraction using acid or other solvents.

Types of product

After entrained metals have been recovered from slag, and once the chemical composition has been altered to safe levels, it is possible for slag to be put to many uses, and for it to be sold in many different forms.

Glass

In order to achieve the correct chemical balance in the production of glass, sources of lime, silica, and alumina are used to supplement the other fluxes and colourants that may be added. Bottle makers can use blast furnace slag as a partial source of all three. Aggressive magnetic upgrading to remove iron permits slag to be used in both clear glass and coloured glass products. It is of special importance that the melting point of all ingredients be relatively low, and corundum contamination from the iron-making process must be minimized.

Mineral and glass wool

Blast furnace slag has many of the mineral ingredients of mineral wool and is a principal raw material for its manufacture. Some other minerals are blended with coarse slag, together with coke as a fuel source, and melted in a cupola furnace, by forcing in air to burn the coke. The liquid is then metered out through a restricted opening over high speed rotating cylinders that throw it into the air, forming fibres that solidify and fall onto a pile or a moving conveyor to form a blanket. This fibrous product, either in bulk form or blanket, is an absolutely non-flammable inert insulation with high heat resistance, and is also commonly used in pressed ceiling tiles. The total amount of glass and blast furnace slag used to make new fibreglass and slag wool insulation in the USA reached nearly 1 million tons in 2002. Fibreglass insulation now accounts for the second-highest usage volume of post-consumer glass.

Masonry units

Expanded blast furnace slag has a cellular structure that confers on it many desirable properties. Slag concrete masonry units have low drying shrinkages, and are light grey to white in colour. Concrete masonry units made with blast furnace slag aggregates have low thermal conductivities. The slag units have better insulating properties and fire resistance than do many of the other aggregates. Slag concrete masonry units have a great effect on both sound absorption and the reduction in sound transmission through walls.

Roofing systems

Blast furnace slag is a preferred product for use in built-up roofing systems where aggregate is used to protect and preserve the roofing bitumen from the effects of the weather. Blast furnace slag provides greater bonding with the roofing bitumen than conventional aggregates. Durability of blast furnace slag is excellent: it performs well in freezing and thawing and sulphate soundness tests. Blast furnace slag's lightweight, high reflectivity, better insulation value, and higher fire resistance are all advantages in built-up roofing systems.

Blasting grit

Slag of small particle sizes can be used for sandblasting applications, although care should be taken to avoid the use of slags containing potentially harmful elements, as fine dust can easily be inhaled in this sort of working environment.

Rail ballast

Coarse aggregate sizes of air-cooled blast furnace slag and of steel furnace slag are used as rail ballast for all types of railroad tracks, from industrial sidings to high-speed main lines. The screenings or fine aggregate sizes of slag are used below the ballast as sub-ballast to prevent intrusion of sub-grade soils into the ballast sections. Slag provides better drainage because of its high void space, its cleanliness, and its high resistance to degradation. Slag's rough, angular shape provides an interlocking stable roadbed. Its sharp corners and rough, pitted surfaces grip the ties firmly and prevent shifting of the track on curves. Slags have high resistance to wear and abrasion, minimizing degradation from heavy traffic. Slags are highly resistant to change by wetting and drying, freezing and thawing, extreme changes in temperature, and chemical attacks.

Slag cement

The cement industry, with an annual worldwide production of around 1.5 billion tons, is one of the largest users of high-grade limestone, coal, electricity, and other minerals. Each ton of cement requires 1.3 tons of limestone, 0.2 tons of coal and around 100 kWh of electricity. Worldwide, cement production is estimated to account for more than 1.6 billion tons of CO_2, or around 8% of total CO_2 emissions from all human activities.[6] This estimate was based on the following figures from 1993: cement production at 1.25 billion tons, CO_2 emissions at 1.25 tons per ton of cement, and global CO_2 emissions of 20 billion tons.

Cement makes up about 12% of the average residential-grade concrete. A typical concrete mix contains (by mass) 12% Portland cement, 34% sand, 48% crushed stone, and 6% water. Substitution of cement ingredients, or cement, or aggregate is environmentally beneficial.

Concrete aggregate

The quality of structural and paving concrete is an important factor in any construction project. The coarse aggregate constitutes a major portion of the concrete, and careful selection of the aggregate is vital to ensure the best results. Blast furnace slag is often used when maximum durability, higher strength, hardness of aggregate, fire-resistance, better insulation, and lighter weight are required. The shape and texture of blast furnace slag promotes excellent bonding with cement mortar. Blast furnace slag's density and absorption are different from most conventional concrete aggregates and should be taken into account in mix designs. Deleterious particles in blast furnace slag are less than 1%. Durability of blast furnace slag is excellent: it performs well in freezing and thawing, and sulphate soundness tests. Blast furnace slag is non-reactive in a high alkali environment, such as concrete and soils. Fire resistance ratings of blast furnace slag concrete are higher than other normal and lightweight concretes.

The potential size of the market for concrete aggregate is enormous relative to the amount of slag produced in all metallurgical processes. Using figures already presented in this paper, it can be calculated that the total production of all slags worldwide is approximately 6 per cent of the amount of crushed stone needed for concrete aggregate. Although this is not a very high value application, it would often be preferable to make constructive use of slag otherwise destined for dumping (at least for those slags that are non-hazardous and have appropriate structural and chemical properties).

Aggregate base

The base course of a road is a layer that needs to be able to provide stable support for the surface layers. A base course can be made up of compacted aggregate, asphalt, or concrete. 100% crushed slag aggregate has been tested and proven as a superior base course material over time, with no other base course material offering so many proven advantages as slag. The density of blast furnace slag is approximately 2.0 t/m^3, and that of steel furnace slag is approximately 2.6 t/m^3. Conventional aggregates in the same product size are 2.1 to 2.3 t/m^3. Slag bases have proven to be long wearing and to require minimum maintenance, and are completely stable under all possible moisture conditions. Slag aggregate bases drain better than most conventional aggregates of similar size grading. Depth of base is reduced with slag aggregate because of its high strength.

Embankment and backfill material

Slag is well suited for use as a structural fill material for the construction of highway embankments or the filling of other large areas.

Topsoil additive

An unusual product made by WayLite[7] of Bethlehem, Pennsylvania, is topsoil made from forging sands, leaf mulch (for bulk), and slag (to correct the pH). Seeds were found to germinate 50 per cent faster in this topsoil than in regular topsoil.

Smelting in a DC arc furnace

A particularly effective way of recovering metals and rendering slags fit for further use is by means of the extreme conditions that can be facilitated by an ultra-high-temperature plasma arc. Mintek has been using DC transferred plasma-arc furnaces for many metallurgical applications since the late 1970s.[8] These furnaces employ direct current, and use a graphite electrode as the cathode, and the molten metal bath in the furnace as the anode. The molten pool of process material forms an integral part of the electrical circuit. The furnace vessel consists of a refractory-lined cylindrical steel shell with a conical roof. These furnaces have been well described previously.[8] The remainder of this paper will focus on various metal-recovery applications using DC arc furnaces.

Cobalt recovery from slag

Mintek has worked on the recovery of cobalt from slags in a DC arc furnace since 1988. 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 at Mintek demonstrated recoveries of 98% for nickel and over 80% for cobalt, at power levels of up to 600 kW.[9,10]

In the mid to late 1990s, attention was focused on a particular slag dump that is probably the world's largest cobalt resource that is situated above ground, namely 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 covers a square kilometre to a depth of about 30 m. 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.

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 essentially all the Co and Cu from this phase.

Because the cobalt is present in the slag in oxidized form, recoveries would be very low if conventional slag cleaning (typically using an AC slag resistance furnace) were 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:

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

An expression has been derived[11] for the recovery of cobalt to the alloy, R_{Co}, in terms of the recovery of iron, R_{Fe}, the equilibrium constant K, and the ratio of the activity coefficients γ.

$$R_{Co} = \frac{K\gamma \cdot R_{Fe}}{1-(1-K\gamma)R_{Fe}} \quad [2]$$

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 [2]. For illustrative purposes, Figure 1 shows the function for 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

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 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.

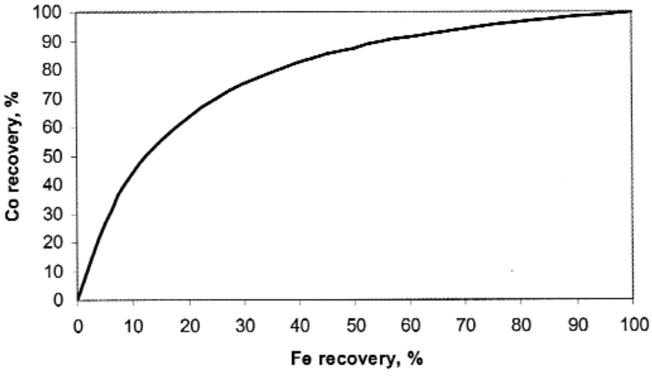

Figure 1. Relationship between Fe recovery and Co recovery to the alloy

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 additional cobalt recovery.
- The effect of temperature in the range 1450 to 1700ºC 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 the Chambishi operation[11]

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. 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 that 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.

The average slag tapping temperature is around 1500ºC. 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 1650ºC. The superheated molten alloy is then lip poured into a pre-heated tundish feeding a water atomizer (rated at 500 kg/min). Here, sufficiently small particles of alloy are produced, and pumped as a slurry to the downstream leach plant.

Water atomization of alloys

Cobalt-rich iron alloys are virtually unbreakable, which poses a problem of providing suitably sized material to the downstream leaching 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. The use of water atomization eliminates the need for the addition of sulphur, thereby simplifying subsequent stages of separation.

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 flowrates. This technology is commonly used in the powder metallurgy industry, and appears to be very cost effective when compared to the option of granulation and milling. 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. The application of water atomization (by Atomising Systems Ltd, of Sheffield, UK) to large industrial-scale production of an intermediate alloy was implemented for the first time at Chambishi, and this technology is now regarded as commercially proven. 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.

The unit consists of a refractory-lined tundish, an atomizing chamber, a high-pressure 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.

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

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 side-walls of the furnace are water-cooled, using copper coolers, 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 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 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.

Commissioning

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. After a number of commissioning or operating problems in the early stages of the plant's existence, the plant is now reported to be running very well.

Recovery of nickel from slags

At some nickel-copper smelters, slag cleaning is practised primarily using settling of the matte from the slag. Other base metal smelters simply stockpile their furnace slag. One industrial example that can be mentioned is the production of copper and nickel at Harjavalta in Finland.[12] Copper smelting in Harjavalta produces 250 000 tons of slag per

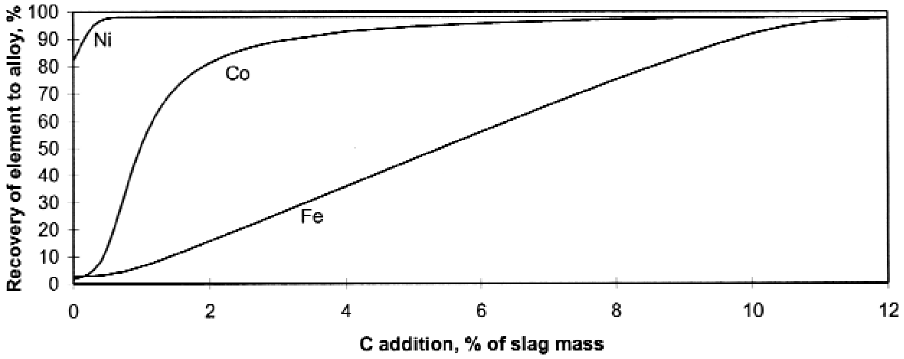

Figure 2. Recovery of the elements to the alloy from a hypothetical slag, as a function of the quantity of carbon added, at 1500°C

year. This is first reprocessed (using flotation) to recover the remaining copper. Next the slag is stored in land basins and, at last, it is covered with soil. Copper slag has also been used to build noise barriers and in the asphalt paving of the Harjavalta industrial site. Harjavalta's nickel slag is processed and granulated. Approximately one-half of the annual slag amount of 100 000 tons is used in sandblasting and in roofing-felt manufacture. The rest is piled in heaps and landscaped. Off-gas cleaning and other process stages produce a total of 5 300 tons of various precipitates in a year. These are stored in basins lined with plastic. The condition of the plastic lining is monitored to prevent drainage to groundwater.

Mintek contends that there is a real advantage to using a DC arc furnace under reducing conditions to recover almost all of the nickel and vastly more cobalt than is achieved currently at many plants. Linked to the work Mintek has done on the recovery of cobalt from slags has been the recovery of valuable base metals from nickel slags.

As shown in Figure 2, nickel is reduced very readily, far more so than cobalt and iron. This indicates that a very high recovery of nickel can be expected from a slag-cleaning process operating under reducing conditions.

Nickel-copper converter slag 'A'– 100 kVA and 200 kVA

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), at low additions of reductant (in order to minimize the reduction of iron). The feed slag had a composition of Co: 0.45%; Cu: 3%; Fe_{Total}: 47%; Ni: 3.5%; and S: 3%. These 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, co-feeding crushed cold slag and coal, and pneumatic injection of pulverized coal into the molten slag. On the 100 kVA furnace, the alloy produced typically comprised Co: 1.7%; Cu: 14%; Fe: 48%; Ni: 16%; and S: 14%. On the 200 kVA furnace, an alloy of Co: 2%; Cu: 15%; Fe: 44%; Ni: 22%; and S: 10% 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. It was found that injection of pulverized coal greatly improved the reduction, and hence the recovery, of nickel and cobalt oxides from the slag. Under good conditions, at 7% carbon addition, on the 100 kVA furnace, calculated recoveries of Co: 81%; Cu: 78%; and Ni: 97% were obtained, while retaining 80% of the iron in the slag.

Nickel-copper converter slag 'B'– 200 kVA

This slag was generated in a plant utilizing a conventional six-in-line furnace and Peirce-Smith converter configuration. The composition of the bulk slag was Co: 1.25%; Cu: 1.0%; Fe_{Total}: 49%; Ni: 3.6%; and SiO_2: 30%. During testwork carried out in 1993, the furnace was operated at power levels of 100 to 170 kW, with tapping temperatures of 1400 to 1500°C. The alloys produced comprised Co: 4.5 to 5.5%; Cu: 5.5 to 8.5%; Ni: 25 to 35%; Fe: 35 to 50%; and S: 8 to 10%. 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 to 0.29% cobalt.

The most abundant phase present in the solid converter slag is Fe_2SiO_4 (olivine), followed by Fe_3O_4 (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 sulphides. 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.

Nickel-copper converter slag 'B'– 3.2 MVA

Large-scale testwork on converter slag was conducted, during 1994, on a 3.2 MVA DC arc furnace operating at a power level of 600 kW. The sequential feeding of reductant was used as the preferred mode of feeding at that time. Operating temperatures were in the region of 1300 to 1600°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, at 1% of the mass of the feed. The alloy produced comprised Co: 7.8%; Cu: 3.8%; Ni: 26.4%; Fe: 56.9%; and S: 2.1%. The cobalt levels achieved in the discard slag were between 0.15 and 0.33%.

Coal addition of 9% was required to achieve cobalt recoveries of at least 80%. Increasing the coal addition did not significantly increase the recovery of cobalt. Increasing the batch mass of slag from 500 kg to 1000 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%.

Table III

Analyses (mass %) of feed and product slags before and after slag cleaning in a DC arc furnace. 'PGM' figures are in g/t and represent the total of Pt + Pd + Rh + Au.

	Al_2O_3	CaO	Co	Cr_2O_3	Cu	FeO	MgO	Ni	S	SiO_2	PGM	Total
Feed	3.6	5.8	**0.12**	1.2	**0.20**	35.6	12.3	**0.44**	0.10	38.1	**7.0**	97.5
Product	5.0	6.8	**0.02**	2.2	**0.05**	22.7	14.9	**0.04**	0.35	45.1	**0.6**	98.1

Nickel-copper furnace and converter slag–200 kVA

During 1995, a campaign was undertaken on a 200 kVA furnace with the intention of combining furnace slag with the converter slag previously treated. When treating furnace slag containing 0.22% Co 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 combining increasing amounts of furnace slag with converter slag, values approaching 0.08% Co in the discard slag could still be achieved. This resulted in cobalt recoveries approaching 90% being attained, while the average recovery was in the region of 85%.

The fume produced was of the order of 1% of the mass of the slag fed. The electrode consumption was 2 kg/MWh.

Recovery of platinum group metals

The DC arc furnace is a key component of the ConRoast process[13] that is envisaged for the next generation of more environmentally friendly platinum group metals (PGM) smelting plants. Existing PGM smelters are based on the traditional matte smelting process where the PGMs are concentrated in a sulphidic matte phase where they are collected by base metal sulphides. The traditional matte smelting process suffers from high SO_2 emissions from furnaces and converters. The ConRoast process solves the SO_2 emission problem by dead-roasting the sulphide concentrate feed material prior to smelting in a DC arc furnace. The gases from the roaster have a steady high concentration of SO_2 coming from a well-enclosed unit that enables them to be treated effectively. Reductive smelting of the oxidized feed material is carried out in a DC arc furnace that is able to operate at sufficiently high temperatures and under reducing conditions that ensure that chromite spinel precipitation in the furnace is no longer the problem that it would be for high-chromium concentrates in a traditional matte smelter. In the ConRoast process, the PGMs are collected in an iron alloy that also contains the base metals. Testwork has demonstrated the production of slags that have a sufficiently low PGM content that they could be discarded or used for other purposes. Other feed materials that are sufficiently low in sulphur (for example, low-grade high-chromium concentrates or revert tailings) can also be fed into the DC arc furnace in place of dead-roasted sulphide concentrates, and the PGMs can be collected in an alloy.

The platinum group metals are often found together with nickel, copper, and cobalt sulphide deposits, and therefore are often found in non-ferrous slags. Even in small quantities, these can be economically significant. The PGMs follow the nickel, copper, and iron through the pyrometallurgical process, and can be extracted from the hydrometallurgical leach residues for further processing. It is to be expected that very high recoveries of PGMs would be obtained from slags containing reasonable quantities of PGMs, especially if the slag-cleaning furnace operates under significantly reducing conditions.

As part of a larger test campaign, some limited work was carried out on low-grade PGM slags, to determine whether it would be possible to effectively recover PGMs from slags even at very low concentrations. A few hundred kg of slag was processed at a feedrate of 100 kg/h, with an anthracite addition of 4% by mass. The data presented here represents three batches of slag fed to and tapped from the furnace. As can be seen from Table III, the PGMs and base metals were able to be collected very effectively in an iron alloy, leaving only very small quantities in the residual slag. A slag sample from this campaign was quenched and subjected to a toxicity characteristic leaching procedure (TCLP) test, and was found to very comfortably comply with the criteria for safe disposal of slag.

Processing of jigged ferromanganese fines

Ferromanganese is commonly produced using carbothermic reduction of manganese ore in submerged-arc furnaces. In order to maximize the recovery of manganese, it is usual to use the slag from the production of high-carbon ferromanganese in the production of silcomanganese. However, the final discarded slags from the silicomanganese furnace still contain an appreciable amount of entrained metal. A gravity method to recover entrained metallics was jointly developed by Mintek and Bateman Titaco. The APIC jigging process, which uses the action of water at high pressure, separates by density at very high yield, metallics from the remaining oxide of crushed slag. The method is cost effective as it utilizes water and has a low requirement for energy and labour. It is currently used in South Africa and elsewhere in the world. The metallic product from the jigging plant is not all recovered in saleable size fractions and grades, and requires further treatment.

A DC arc furnace is suitable for the direct processing of these metal fines without prior agglomeration, and it was therefore possible to investigate the direct production of saleable ferromanganese alloy from the re-melting or smelting of jigged metal fines.[14] The first process option involved the re-melting of high-carbon ferromanganese (HCFeMn) jigged metal fines that were close to the desired composition. Lime was added as a flux to increase the fluidity of the slag. The second process option involved smelting of HCFeMn jigged metal fines together with silicomanganese fines. The silicon in the alloy is used to reduce manganese and iron oxides from the slag portion modified with manganese ore and lime flux. The temperature is kept below 1600°C, to minimize the formation of volatile manganese and silicon monoxide vapours.

Ferromanganese alloys were produced successfully according to the ASTM specifications for high- and medium-carbon ferromanganese. The feasibility of re-melting and smelting ferromanganese jigged material in a

DC arc furnace, to produce saleable ferromanganese alloy, was proved at the 1 MW scale. The incorporation of a jigging process combined with a DC arc furnace is a feasible way of increasing the production of ferromanganese plants.

Zinc fuming from lead blast furnace slag

Since 1989, Mintek has been researching the extraction of lead and zinc from a variety of zinc-bearing wastes using DC arc furnace technology, more recently coupled with an Imperial Smelting Process (ISP) lead-splash condenser. This is known as the Enviroplas process. The Enviroplas process deals with the production of environmentally acceptable non-toxic slags, and the recovery of zinc and other valuable metals from solid wastes from the metallurgical industry.

First series of LBFS tests

The first substantial work in this field at Mintek[15] was carried out on about 80 tons of granulated lead-blast-furnace slag (LBFS), containing 14% ZnO and 2.8% PbO. This was smelted at feed rates of over 800 kg/h and power inputs up to 800 kW (3 kA, 270 V) in a 1 MW DC arc furnace. The furnace shell was lined with chrome-magnesite bricks, and an alumina castable refractory was used for the lining of the roof. The average temperature of the tapped slag was around 1500°C. Charcoal was used as the reducing agent. The charcoal-to-slag ratio in the feed was chosen to selectively reduce the zinc and lead oxides, while leaving most of the iron oxide in the smelted slag. The lead-blast-furnace slag and charcoal were fed continuously through three feed ports, equispaced around the central electrode. Zinc and lead vapour, and carbon monoxide, were burned at the off-gas port of the furnace, and the mixed oxide of zinc and lead was collected in a bag filter. High extraction levels (more than 95 per cent extraction from the slag) of zinc and lead were achieved. Almost all the extracted zinc and lead reported to the vapour phase and fume in the bag filter. Only about 0.1 per cent of the zinc input and approximately 1 per cent of the lead input passed into a metal phase that accumulated in the hearth of the furnace. The impurities in the fume were relatively low. The fume produced contained about 80% ZnO, 15% PbO, 0.5% FeO, 0.6% SiO_2, 0.4% CaO, 0.2% MgO, and 0.2% Al_2O_3. The composition of the residual siliceous slag was typically about 35% SiO_2, 26% CaO, 20% FeO, 8% MgO, 5% Al_2O_3, 0.7% ZnO, and less than 0.2% PbO.

Second series of LBFS tests

The Enviroplas process, now including an ISP lead-splash condenser, was first fully demonstrated in 1994 / 1995 on a 5.6 MVA pilot plant.[16,17] As depicted in Figures 3 and 4, the pilot plant comprises two DC arc furnaces served by a 5.6 MVA power supply, a raw-material feed system, and an ISP lead-splash condenser, a combustion chamber, and a gas cleaning system. The first furnace is used as a premelter to simulate the supply of molten slag from the lead blast furnace, and to act as a holding vessel to ensure a steady supply of molten slag to the fuming furnace.

The lead-splash condenser was a smaller version of the ISP condensers that are employed, at several plants world-wide, in combination with an Imperial Smelting Furnace (ISF) for the smelting of mixed zinc and lead sinter. The condenser assembly consisted of a condenser body with a single rotor, a lead circulation pump, a cooling launder with immersible cooling pins, and a zinc separation bath. The condenser body was basically a steel box, about 2 m wide, 4 m long and 2 m high, lined with refractory bricks. A variable-speed rotor was inserted through the cast refractory roof. The whole assembly occupied a space of approximately 5 m by 5 m. The condenser contained 21 tons of lead and was designed for a maximum zinc condensing rate of 350 kg/h.

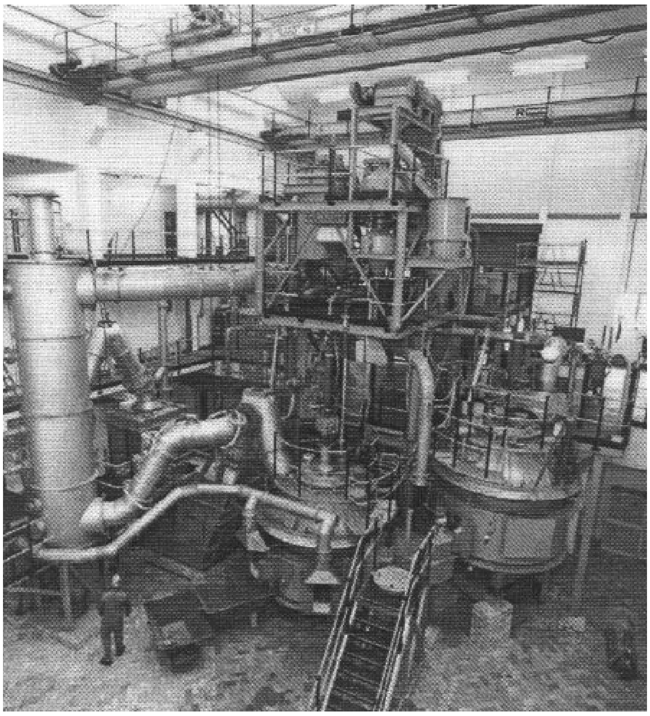

Figure 3. The 5.6 MVA Enviroplas pilot plant at Mintek, including a feed system, two DC arc furnaces (centre and right), an ISP lead-splash condenser (left background), and a combustion chamber (left foreground).

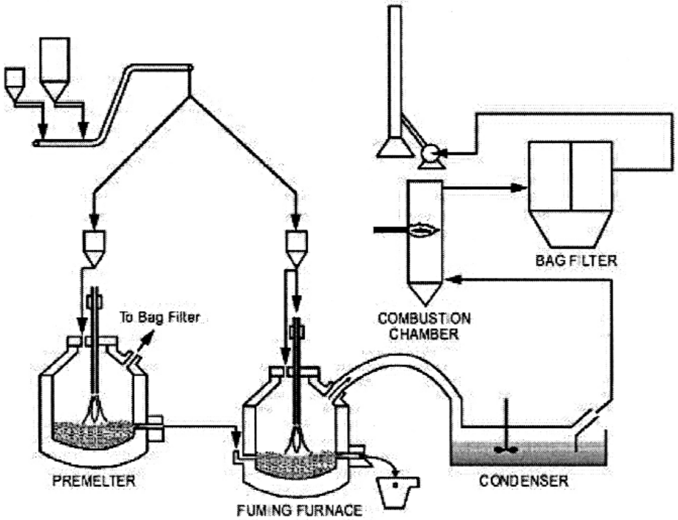

Figure 4. Schematic diagram of the Enviroplas demonstration plant.

Table IV
Typical analysis of lead blast furnace slag 2, mass %

	CaO	FeO	PbO	SiO_2	ZnO
Lead blast furnace slag 2	20	25	3	25	14

Table V
Typical analysis of lead blast furnace slag 3, mass %

	CaO	FeO	PbO	SiO_2	ZnO
Lead blast furnace slag 3	15	30	4	20	20

During the first four smelting campaigns in 1994 / 1995, a total of 1000 tons of lead blast furnace slag was processed. A typical analysis of the feed slag is given in Table IV. Metallurgical coke was used as a reductant.

Granular LBFS was premelted in the first DC arc furnace (premelter) and hot slag was fed continuously from the premelter, via a transfer launder and underflow weir, into the second plasma-arc furnace (fuming furnace). Metallurgical coke was also fed to the fuming furnace through a feed port located in the roof or via the hollow electrode. The coke addition was about 30 kg per ton of LBFS. During certain periods of the smelting campaign, the premelter was switched off, the underflow was closed with refractories, and granular LBFS was fed directly to the fuming furnace. With the three units (premelter, fuming furnace, and condenser) in line, the premelter was typically operated at a power level of 650 kW (200 V, 3.25 kA), and the fuming furnace was run at about 700 kW (175 V, 4 kA). When the premelter was not used, the fuming furnace was operated at power levels of around 1.2 MW. During short periods of the campaign, the fuming furnace was run at 2.5 MW with feed rates of up to 3 t per hour.

The zinc and lead oxides contained in the slag were reduced to their metals and volatilized in the fuming furnace. Residual or ‘spent’ slag was tapped from the fuming furnace when about 2.5 t of LBFS had been fed to the premelter, i.e. at intervals of around 2 hours. Zinc was tapped once or twice a shift from the condenser, during periods when steady operation was achieved. Drosses were regularly removed from the cooling launder, as they were generated. Gases and dust passing through the condenser were burnt in the combustion chamber and further cleaned in the bagfilter. Fume was removed continuously from the bagfilter. It was the aim at the outset of the campaign to attain zinc levels in the final slags of below 1.5 per cent, to achieve zinc extraction figures of about 90 per cent.

The designed tapping temperatures of the premelter and fuming furnace were 1300 and 1450°C respectively. These temperatures were selected to minimize zinc losses in the premelter, to ensure sufficient fluidity, and to achieve a high degree of zinc extraction. Zinc oxide contents in slags tapped from the fuming furnace of between 1.5 and 2% were achieved. The lead oxide contents of the residual slags were usually below 0.2%, and all the slag samples submitted for TCLP tests were found to conform to US EPA regulations. About 20 tons of zinc metal was tapped from the ISP condenser, and the weighted average composition met Prime Western grade specifications.

About 50 kg of zinc metal, 850 kg of residual slag, 45 kg of condenser dross, and 10 kg of fume were produced per ton of lead blast furnace slag. The condenser dross contained about (mostly recoverable) 60% lead, and 16% zinc (mostly oxide, some metallic), but a better drossing procedure is expected to improve these figures. Zinc condensation efficiencies of 70–80% were attained, which were in accordance with the expected single-rotor condenser efficiencies. An overall zinc recovery of 60–70% on a zero-recycle basis was achieved. Zinc fuming rates of 120–180 kg/h were obtained, which corresponded to zinc volatilization fluxes of 40–60 kg zinc/hm^2 (based on a hearth area of the fuming furnace of 3 m^2). The net electrical energy requirements, based on total energy consumption levels per ton of lead blast furnace slag and on measured energy losses, were 300 and 190 kWh/t of LBFS for the premelter and fuming furnace respectively. Thermal efficiencies of both furnaces at this scale of operation were approximately 60%. The most suitable premelter operating temperature was found to be 1300°C, and the tapping temperatures of the fuming furnace were around 1450°C.

Third series of LBFS tests

Another campaign[18] was run on the 5.6 MVA facility using only the fuming furnace in 1997. A typical analysis of the feed slag is given in Table V.

The average amount of zinc oxide in the slag tapped from the furnace was 6%, although 1.1% was achieved. The lead oxide content of the residual slag was 0.07% at lowest, and 0.23% on average. An overall zinc recovery to the fume of 77% was achieved. Zinc volatilisation fluxes of 44–192 kg zinc/hm^2 (based on a fuming furnace hearth area of 1.3 m^2) were also obtained. The average net energy requirement (excluding losses) over the entire campaign was 0.68 MWh/t feed. The tapping temperature of the fuming furnace averaged 1356°C.

Basel Convention

The Organisation for Economic Co-operation and Development (OECD) laid the foundation for the Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, adopted in Basel on 22 March 1989 under the auspices of the United Nations Environment Program (Basel Convention). The Basel Convention radically changed the basis of international trade in secondary materials from January 1998, by instituting a *de facto* ban on the trade of materials classified as hazardous. Primarily the ban seeks to prohibit the transboundary movement of hazardous wastes between developed and developing countries. An unfortunate side effect of this ban is the prohibition of shipment of such materials from producers to research organisations such as Mintek, as South Africa is classified as a developing country despite the leading international role that Mintek has in the development of technology for economic recovery of metals and the safe disposal of hazardous wastes.

Treatment of steel-plant dusts

In most countries, the disposal of steel-plant dusts presents an environmental problem because they contain heavy metals that may be leached into the groundwater. These waste materials are costly to dispose of in approved dumping sites. Mintek’s Enviroplas technology exploits the unique ability of the open-arc DC furnace to utilize these fine feed materials directly, reducing the metal oxides and recovering the metals into an alloy phase for recycling. The recovery of valuable metal units can economically justify recycling of these materials, thereby also rendering the resulting slag safely disposable.

The use of steel scrap as a raw material in steelmaking, results in the presence of significant quantities of elements such as zinc, lead, cadmium, chromium, nickel, molybdenum, and manganese in the iron-oxide-rich baghouse dusts. Several of these elements are classified as hazardous, and there is legislation in place in many countries to govern the disposal and treatment of steel-plant dusts. Carbon-steel dust that is rich in zinc, and alloy-steel dust (that is rich in chromium or nickel, for example) contain sufficient metal that it is worth considering the economics of recovery. Disposable slag is able to be produced from the thermal plasma treatment of these materials.

The process operates on the principle of reducing the zinc and lead oxides at high temperatures (above 1500ºC), vaporizing the zinc and lead, and then either re-oxidizing the vapours to a crude mixed oxide, or condensing them in an ISP-type splash condenser. The smelting process generally produces a metal and a non-toxic slag, both tapped from the furnace in liquid form, as well as the zinc-containing vapour. The metal comprises mainly iron, along with alloying elements such as chromium, nickel, and manganese.

The most troublesome constituents in steel-plant dusts are alkalis and, in particular, halides, as they interfere with the condensing of zinc vapour. Initial pilot-plant work was carried out at Mintek at the 800 kW level in about 1990, in which the zinc vapour product was combusted to zinc oxide and was collected in a bag filter. For zinc-containing alloy-steel dusts, a two-stage process was proposed to separate the chromium-alloy-producing step from the zinc-fuming step. The first stage operates under mildly reducing conditions, such the zinc is reduced and fumed off, and the nickel and some iron is reduced to produce an iron-nickel alloy. The second stage operates under more strongly reducing conditions, allowing the chromium to be reduced to form a ferrochromium alloy.

In the case of electric arc furnaces (and not for fuel-fired furnaces), conditions are sufficiently reducing that chromium oxide present in the dust can also be readily reduced, together with oxides of metals such as iron and nickel, and the metals are recovered from the furnace in liquid form. The use of electrical power is highly advantageous for these processes in comparison with the use of a fuel-fired furnace. The lower gas volumes (than would be the case where energy is provided by combustion) keep the zinc vapour at higher concentrations, and limit the carry-over of dust.

Mintek's Enviroplas process[19-22] makes provision for the feed to be charged to the furnace without prior agglomeration. Fine steel-plant dusts (usually 100 per cent smaller than 10μm) are rapidly absorbed in the molten slag bath, minimizing carry-over of feed to the gas phase. High reaction rates and efficient fuming of zinc metal can be achieved.

Enviroplas treatment of high-zinc carbon-steel dust

Initial small-scale testwork was conducted on the smelting of electric arc furnace (EAF) dust (high-zinc carbon-steel dust) in a 50 kVA DC arc furnace, operating at power levels of 30 to 40 kW, at a temperature of about 1500ºC. Ten batch tests were carried out, each on about 10 kg of EAF dust containing about 32.0% Fe_2O_3, 30.6% ZnO, and 4.2% PbO. The average particle size of the dust was around 1 μm. The dust was pelletized in this instance, and fed to the furnace together with anthracite (as reducing agent) and silica (as flux). The anthracite addition was such as to selectively reduce the zinc and lead oxides, leaving the iron oxide behind in the smelted slag. Silica was added to the feed to achieve a slag with an acceptably low liquidus temperature and a basicity ratio ([CaO+MgO] / SiO_2 mass ratio) of about unity. The zinc and lead were almost completely extracted from the EAF dust, and recovered as an oxidic fume, after being burned, and collected in a bag filter. The fume contained about 72% ZnO, 8% PbO, 3% FeO, 1.3% SiO_2, and 0.4% MgO. The levels of zinc and lead oxide in the residual slags were both below 0.2 per cent. Standard leach tests were carried out on these slags, and they were found to be disposable according to United States Environmental Protection Agency (EPA) regulations.

Enviroplas treatment of high- and low-zinc alloy-steel dust

Larger-scale testwork[20] was carried out in 1990 on a 1 MW pilot plant on the smelting of alloy-steel dusts (high- and low-zinc). Dusts from three different sources were used, with a weighted average composition of 42% Fe_2O_3; 15% Cr_2O_3; 2.7% NiO; 21% ZnO; 0.7% PbO; as well as some CaO, MgO, and SiO_2. Anthracite with a fixed carbon content of 77% was used in the proportion of 290 kg per ton of alloy-steel dust. The steel-plant dusts were charged to the furnace, without prior agglomeration, via the central hole of the graphite cathode. The furnace was operated at power levels of about 500 kW, and at feed rates of around 250 kg/h. At a designed operating temperature of 1550°C, the theoretical energy requirement was determined to be 1.39 MWh/t of alloy-steel dust. The off-gases were burned and collected in a bag filter. High extraction levels of zinc, chromium, and nickel were achieved. A disposable slag, a ferro-alloy rich in chromium and nickel, and a zinc-oxide fume were produced.

The alloy product contained an average of 66% Fe; 19% Cr; 3.4% Ni; 1.8% Si; 5.3% C; 0.06% S; and 0.04% P. Because of the relatively small quantities involved, no problems are envisaged with regard to contamination by C, S, and P, when this ferro-alloy is recycled to steelmaking furnaces. The average composition of the slags produced was 39% SiO_2; 23% CaO; 20% MgO; 3.7% Cr_2O_3; 0.09% NiO; and 0.02% ZnO. Only about 5 per cent of the chromium in the dust fed to the furnace was retained in the slag, and less than 1 per cent of the nickel and 0.1 per cent of the zinc inputs reported to the slag. The fumes produced contained on average 56% ZnO; 7.9% MgO; 8.0% SiO_2; and smaller quantities of Fe_2O_3, Cr_2O_3, and NiO. About 5 per cent each of the iron, chromium, and nickel charged to the furnace passed into the gas stream.

Enviroplas treatment of stainless steel-plant wastes

During the production of stainless steel in an electric arc furnace and converter (AOD, CLU, or VOD), between 20 and 30 kg of flue dust is generated per ton of steel. The dust, which is captured in bag filters, contains typically 2 to 4 per cent nickel in the oxide form, as well as other elements such as iron, chromium, and calcium oxides, with lesser amounts of oxides such as manganese and molybdenum. The stainless-steel rolling mill also generates a variety of solid wastes.

Large-scale (3 MW) demonstration testwork at Mintek during 2003, in which more than 1500 tons of Columbus Stainless Steel plant dust was smelted, has confirmed that about 92 per cent of the chromium and 96 per cent of the nickel can be recovered into an alloy with a composition broadly comparable to 18/8 stainless steel. The ultra-fine dust was fed to the DC arc furnace without agglomeration. The resulting slag is well within the EPA requirements for disposal at sites for non-hazardous waste. These demonstration-scale tests established the mass and energy balance data and the parameters for scale-up to commercial operation.

During 2004, the Enviroplas process will be operating on an industrial scale in a 40 MVA DC arc furnace at Mogale Alloys[23] (on the site of Samancor's Palmiet Ferrochrome plant) near Krugersdorp, South Africa. Stainless-steel-plant dust and other wastes will be smelted to form an iron-chromium-nickel alloy for recycling the valuable metals nickel and chromium to the stainless steelmaking process. Mogale Alloys plans to process about 150 000 tons of stainless-steel dust and wastes over the next three years. An agreement has been entered into with the Columbus Joint Venture for the supply of their stockpiled dust and waste materials.

Conclusions

There are environmental and economic advantages in seeing slags as a potentially useful resource rather than as waste products. In many cases, valuable metals can be recovered from slags, and the slag can be rendered inert thereby making it available as a construction material, for example.

DC arc furnace technology provides an effective means of processing slags under the appropriate conditions of high temperature and in a reducing atmosphere. This technology is already in commercial use for the recovery of cobalt from slag. A number of other potential processes are under consideration for industrial implementation.

The Enviroplas demonstration plant at Mintek has processed well over 1 000 tons of feed material, either liquid or solid lead blast furnace slag, and electric arc furnace dusts, since it became operational. Not only has the plant produced Prime Western grade zinc metal, but the final quenched slag from the process has consistently met with the United States Environmental Protection Agency Toxicity Characteristic Leaching Procedure criteria.

The recovery of metals from slags is both an environmentally responsible and an economically viable approach, as the value of the recovered metals exceeds the processing costs in a variety of cases studied in this paper.

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