

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### **Emerging pyrometallurgical processes for zinc and lead recovery from zinc-bearing waste materials**

G. Assis (geninea@pyro.mintek.ac.za)

*Pyrometallurgy Division, Mintek, Private Bag X3015, Randburg, 2194, South Africa*

#### **ABSTRACT**

Zinc and lead can be recovered economically from some hazardous waste residues, dusts, and slags by various pyrometallurgical processes, rendering these materials into a form that is safe for disposal. A number of these processes are reviewed, with particular reference to Mintek's developments in this field.

Since 1990, Mintek has been researching the extraction of lead and zinc from a variety of zinc-bearing wastes using a combination of DC arc furnace technology and an Imperial Smelting Process lead-splash condenser. Mintek's Enviroplas process was first demonstrated during 1994/1995 on a 5.6 MVA pilot plant at Mintek. This plant has processed over 1000 t of feed material, either liquid or solid lead blast furnace slag, and electric arc furnace dusts, since it first 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.

**KEYWORDS:** Zinc; Lead; DC arc furnace; Slag; EAF dust; Fuming; Hazardous wastes; Enviroplas; Ausmelt; AllMet; Kawasaki; IBDR-ZIPP; Environmental regulations; Emerging technologies.

**Zinc and Lead Processing Symposium,  
The Metallurgical Society of CIM, Calgary, Canada, August 1998**

**MINTEK PAPER NUMBER 8423**

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### INTRODUCTION

The increase in the utilization of galvanised scrap in electric arc furnace (EAF) steel production has led to an increase in the amount of hazardous metals present in steel plant wastes. In 1997, worldwide production of EAF steel-plant dust amounted to approximately 3.5 Mt/a (Japan's production of EAF dust was 500 000 t (1); North America produced 730 000 t (2), with Western Europe also producing roughly the same amount), with the total amount of waste produced by steel producers probably being four to five times this amount.

In 1988, EAF dust was classified under the United States Resource and Recovery Act (RCRA) as a "hazardous waste" by the Environmental Protection Agency (EPA). EAF dust was designated as hazardous waste K061 ("Emission control dust/sludge from the primary production of steel in electric furnaces" (3)) as it failed the EPA's Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) test for cadmium, lead and hexavalent chromium (3). In 1993, the EPA passed regulations requiring that EAF dust be treated thermally or chemically to remove or stabilize leachable toxic metals, and specified that dusts with a zinc content above 15 % had to be treated in a high-temperature metal-recovery (HTMR) process. For dust containing less than 15 % zinc, stabilization prior to disposal was permitted so long as the stabilized product met the same TCLP test requirements as the slags and residues produced by HTMR methods. At this stage, EAF dust could also be sold as a source of zinc to the fertilizer industry (4).

In July 1995, however, the EPA ruled that stabilization and subsequent disposal in conventional landfills is permissible for all EAF dusts, regardless of zinc content, as long as the stabilized product meets the requirements for all 14 elements of the TCLP leachate standards. To date, only the Super Detox stabilization treatment by EnviroSource has been approved by the EPA as conforming to these stringent requirements (3). However, the stabilization process fails to recover any valuable constituents and increases the volume of the waste going into landfill sites (5). In general, EAF dust disposal and treatment costs in the USA lie between \$125 and \$200/t (excluding transport costs of approximately 10 % of the treatment cost per ton) (2).

Other steel plant wastes, although not being explicitly listed as hazardous wastes by the EPA, still need to conform to the TCLP requirements to enable them to be landfilled.

The United States is not the only country to have imposed strict regulations on the disposal of steel plant wastes. Japanese, Canadian, and European steel mills are also subject to similar regulations regarding these wastes (6).

Furthermore, three highly influential bodies have come to the fore in the last ten years in developing precedents for the development and implementation of international standards regarding hazardous wastes, with particular reference to the definition of

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

“hazardous waste” and the prevention of transfrontier movements of these wastes. The work performed by the Organisation for Economic Co-operation and Development (OECD) in the 1980's contributed significantly to the creation of relevant European Community directives in this regard. It also 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 developments at the Basel Convention radically changed the basis of international trade in secondary materials from January 1998. The Convention instituted a *de-facto* ban on the trade of certain secondary materials that it classified as hazardous during the Fourth Meeting of the Conference of Parties in Kuching, Malaysia (23 – 28 February 1998). Primarily, the ban seeks to prohibit the transboundary movements of these materials between developed and developing countries. The ban thus not only limits trade in these materials but also, possibly inadvertently, prevents the shipment of materials from producers to research institutions such as Mintek. This obviously restricts the capability of these institutions to fulfill their obligations to the International Community in this regard.

The legislation of these international and national regulations, and the prospect of more stringent regulations being proposed in the future, raises the electric steel producers' concern that landfilled EAF dust holds a future liability. The on-site treatment of steel plant wastes, and the recovery of zinc, iron, and other commercial materials from these wastes to offset treatment costs is thus becoming increasingly attractive. Further, direct coupling of the treatment or recovery plant to the waste-collection equipment in a totally enclosed manner could exempt the steel producer from some regulatory standards.

The problem of hazardous wastes has produced an opportunity for vendors of technology and equipment to find appropriate solutions. Although a number of well-established processes are currently being used to recover zinc, lead, and alloying components such as chromium, nickel, manganese, and molybdenum, not all of these processes currently meet the new legislative requirements, nor are they all economically viable. Some of these existing processes can and are being adapted, and new methods are being developed.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### COMMERCIAL PROCESSES FOR STEEL PLANT WASTE TREATMENT

#### Slag disposal

Slags from blast furnaces, EAF's and basic oxygen furnaces (BOF) are all saleable by-products. Typically, on-site contractors handle the slag by:

- Cooling and crushing the material
- Separating out the metallic portions for recycling
- Selling or landfilling the remainder.

Crushed and sized blast furnace slag can be used in concrete production, as a substitute for rocks and gravel, and as an aggregate in road construction. Almost all the blast furnace slag produced in the USA is re-used. The slag has an average selling price of \$5/t (6).

Slag from EAF's and BOF's generally cannot be used as a road aggregate because the material expands (largely due to its free lime content (7)), leading to premature road failure. However, manufacturers are able to sell their slag, at an average price of \$3/t (6), for use in other aggregate applications (e.g. as a cement additive). However, approximately half of the slag produced in the USA is landfilled.

In 1991, Canada's Ministry of Transportation placed a moratorium preventing the use of steel slags in road construction. Since then, Dofasco has developed a new method for processing steel slags that results in an aggregate material that does not expand, facilitating its use in road construction. The material has been successfully tested in six locations. Dofasco is also selling steel-slag fines for use in aggregates for industrial construction applications such as warehouses and parking lots (6).

#### EAF dust disposal

The alternatives presently available to steel producers to manage EAF dusts include:

- Shipping to an off-site processor
- Processing on-site by themselves or by a contractor
- Selling the dust to an exempt market such as the fertilizer industry
- Stabilizing and disposing of the dust
- Vitrifying and selling the vitrified product.

These alternatives are, however, becoming increasingly restrictive and expensive because of the limited number of domestic off-site processors, the limited success of emerging technologies, the vulnerability of exempt markets, and the marketability of stabilized and vitrified products. Although the "stabilize and dispose" option appears to have become increasingly available, the legality of this option is still not clear (8).

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### Metal recovery processes from EAF dusts

The most commonly practised and oldest commercial process is the Waelz kiln. The zinc-enriched fume from the kiln is usually further treated by thermal processes (e.g. the ZCA electrothermic process or the Imperial Smelting Furnace). Although many variants of the Waelz kiln-type of process are under development, none of these produce saleable Prime Western (PW) grade zinc metal directly. A process that is able to recover zinc metal and produce a disposable slag should thus have an economic advantage in that it may reduce the cost of dust treatment.

At least nine methods for managing EAF dust from carbon steel scrap melting are currently practised commercially. These are summarized in Table I.

Table I - Commercial processes for EAF dust treatment (8, 9,10,11)

Process	Type	Zn-bearing product	Fe-bearing product	Other products
Waelz Kiln (2 stage)	Pyro	Zinc oxide	Iron oxide / metallized iron	PbCl <sub>2</sub> / CdCl <sub>2</sub> fume
Waelz Kiln (1 stage)	Pyro	Zinc oxide	Iron oxide / metallized iron	-
Flame reactor	Pyro	Zinc oxide	Slag	-
ISF tuyere injection	Pyro	Zinc metal	Slag	-
Laclede Steel	Pyro	Zinc metal	Slag	-
MF/Electrothermic	Pyro	Zinc oxide	Slag /residue	-
EZINEX	Hydro	Zinc metal	Iron oxide	Salt mixture
Super Detox	Stabilization	-	-	Stabilized dust
IRC	Vitrification	-	-	Glassy granules

### **Alternative methods**

Perhaps the most obvious solution is removal of the zinc from the galvanized steel scrap before it is melted in the furnace. The dust would then, in theory, contain fewer hazardous substances. A number of technologies have been evaluated, including preheating, heat treatment and hot screening, heating and vacuum volatilization, and chemical dezincing. The latter appears most promising at present.

To minimize EAF dust treatment and disposal, some steel producers are modifying their furnace operations or employing commercially available technologies to decrease the amount of dust generated. A favoured minimization approach involves collecting and recycling the dust back to the furnace using fluxes and reductants to increase the zinc content from the typical single pass level of 15 – 25 % to 40 – 45 %.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

This approach decreases tonnage-based shipping and tipping fees associated with material treatment, as well as increasing steel-making process yields. The dust can be injected back into the EAF directly, or it can be agglomerated using the Dereco briquetting (8), or a similar technique, to enhance its incorporation into the melt.

With the approved delisting of EAF dust by the EPA, the Super Detox stabilization process developed by Bethlehem Steel Corporation, and now marketed by EnviroSource, has come to the fore. This process involves mixing EAF dust with aluminosilicates, lime and other additives. The heavy metals are chemically treated until they obtain their least soluble states through precipitation and oxidation/reduction, followed by physically being bound in the aluminosilicate matrix. The material solidifies to become concrete-like, is fairly impermeable and can be disposed of in non-hazardous landfills. Super Detox is commercially practised at Bethlehem Steel Corporation's plants in Johnstown and Steelton, Pennsylvania, and at Conversion Systems', Inc. plant at Northwestern Steel and Wire in Sterling, Illinois (3). Regional plants are also in operation in Ohio and Idaho (12).

A number of vitrification processes are also in commercial operation. For more than two years, the dust generated at Nucor's plant in Hickman, Arkansas has been recycled at Inorganic Recycling Corporation's (IRC) vitrification facility at Nucor-Arkansas (2, 12). The only recycled product is a glass/ceramic material in which solid materials are embedded very tightly in a glass base. The material is primarily sold as roofing granules for shingles, although it may also be used as a loose grain abrasive for sand blasting. Problems have, however, occurred in the vitrification industry with regard to the safe use of vitrification products, particularly as sandblasting media. Some vitrification products are easily blasted to dust if used in this application. The dust may be inhaled by operators, overexposing them to lead and cadmium (6). In general, most vitrification products can, however, be safely used as roofing granules or as ceramic glazes.

## EMERGING TECHNOLOGIES

The problem of hazardous zinc-bearing wastes has produced an opportunity for research engineers to find more appropriate solutions than those industrially practised at present. Well-established processes seem to leave much to be desired in terms of both economic return and meeting legislative requirements. However, it would appear that some of the emerging pyrometallurgical technologies may provide a better solution to the problem. These technologies involve production of either zinc metal or zinc oxide.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### ZINC METAL-PRODUCING PROCESSES

#### Enviroplas

Mintek has conducted a number of extensive campaigns on their 5.6 MVA multi-purpose demonstration-scale pilot plant to test their ENVIROPLAS™ process, which directly produces zinc metal from various zinc-bearing wastes. The process is based on the carbothermic and metallothermic reduction of metal oxides in the waste material (e.g. NiO, Cr<sub>2</sub>O<sub>3</sub>, ZnO) at temperatures from 1400 to 1600 °C, in a DC arc furnace. The opportunities for implementation of the Enviroplas technology have been grouped into three areas:

- ENVIRODUST for EAF dusts
- ENVIROSLAG for Imperial Smelting Process slags and Lead Blast Furnace (LBF) slags
- ENVIRORES for zinc/lead calcine leach residues (either neutral or final leach)

There are many common features among these different materials, especially regarding the fuming and condensation considerations. However, the pretreatment required is very different for each material. LBF slags may be fed in liquid form, possibly via a holding furnace. EAF dust needs to be dehalogenated, agglomerated and dried prior to being fed directly as a solid into the fuming furnace. The zinc calcine leach residues are roasted or premelted to selectively adjust the composition before liquid transfer to the fuming furnace (See Figure 1).

Testwork is continuing on the 5.6 MVA pilot plant at Mintek, with three major campaigns having been conducted during the last twelve months alone. Steady progress towards the first commercial plant installation continues to be made.

#### Description of demonstration plant

The pilot plant has been described in detail elsewhere (13). The general equipment arrangement comprises two DC arc furnaces served by a 5.6 MVA power supply, a raw-material feed system, an Imperial Smelting Process (ISP) lead-splash condenser, a combustion chamber, and a gas cleaning system. The DC arc furnaces are fully controlled using a PLC, with a PC-based Supervisory Control and Data Acquisition system providing a console for configuring operational parameters, feed management, alarm annunciation, and data logging.

#### Pilot plant test results for LBF slag

During the first four smelting campaigns in 1994/1995, a total of 1000 t of LBF slag was processed (13, 14). A typical analysis of the LBF slag is given in Table II. Metallurgical coke was used as a reductant.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

Zinc oxide contents in slags tapped from the fuming furnace of between 1.5 – 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 with US EPA regulations. About 20 t of zinc metal were tapped from the ISP condenser, and the weighted average composition met PW grade specifications.

Table II - Typical LBF slag analysis (14)

Compound	Mass percentage, %
SiO <sub>2</sub>	25
CaO	20
ZnO	14
PbO	3
FeO	25

About 850 kg of residual slag, 50 kg of zinc metal, 45 kg of condenser dross and 10 kg of fume were produced per ton of LBF slag. The condenser dross contained about 60 % lead and 16 % zinc (mostly oxide, some metallic), but a better dressing 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 to 180 kg/h were obtained, which corresponded to zinc volatilization fluxes of 40 – 60 kg zinc/hm<sup>2</sup> (based on a hearth area of the fuming furnace of 3 m<sup>2</sup>).

The net electrical energy requirements, based on total energy consumption levels per ton of LBF slag and on measured energy losses, were 330 and 190 kWh/t of LBF slag for the premelter and fuming furnace, respectively. Thermal efficiencies of both furnaces at this scale of operation were approximately 60 %. The optimal premelter operating temperature was found to be 1300 °C, while the tapping temperatures of the fuming furnace were around 1450 °C.

Another campaign was run on the 5.6 MVA facility using only the fuming furnace in September 1997. A typical analysis of the LBF slag is given in Table III. Metallurgical coke was again used as the reductant.

The average amount of zinc oxide in the slag tapped from the furnace was 6 %, although 1.1 % was achieved. The lead oxide contents of the residual slags was 0.07 % at lowest and 0.23 % on average. An overall zinc recovery to the fume of 77 % was achieved. Zinc volatilization fluxes of 44 – 192 kg zinc/hm<sup>2</sup> (based on a hearth area of the fuming furnace of 1.3 m<sup>2</sup>) 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.



## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

Table III - Typical LBF slag analysis

Compound	Mass percentage, %
SiO <sub>2</sub>	20
CaO	15
ZnO	20
PbO	4
FeO	30

### Pilot plant test results for EAF dust

Non-dehalogenated EAF dust was initially treated in the plant with the lead-splash condenser by-passed (15). The slag tapping temperatures for this testwork were found to be between 1450 and 1530 °C, with the slag containing 0.6 % zinc oxide and 0.05 % lead oxide. The zinc extraction was found to be 98 %, with the fume produced containing 70.3 % zinc oxide, 5.9 % lead oxide, 3.1% Fe<sub>2</sub>O<sub>3</sub>, 4.2 % Cl, 1.2 % F, 2.2 % Na, 3.4 % K, and smaller percentages of SiO<sub>2</sub>, CaO, and MgO. Preliminary leach tests were conducted on the fume, revealing the following removal levels via the wash water: 92 % Cl, 70 % F, 95 % Na, and 95 % K. Zinc and lead extractions were insignificant.

It was feared that high levels of halogens, especially chlorine, may interfere with the condenser operation by facilitating the excessive formation of dross. The dust was therefore dehalogenated (reducing the chlorine level from 2 % to 0.2 %) and then calcined (dried in a rotary kiln at 500 – 600 °C) before being fed to the furnace for the next campaign.

During this campaign a zinc fuming rate of 150 – 200 kg/h was obtained at operating temperatures between 1450 and 1500 °C. The slags tapped from the furnace contained an average of 1.6 % zinc oxide, resulting in 96 % zinc extraction. The slags conformed with US EPA regulations, and the condensed zinc generally met PW grade specifications. The condenser efficiency, however, was low and inconsistent (28 – 68 %).

An in-depth assessment of the results of these three smelting campaigns, during which about 200 t of EAF dust was processed, was carried out to identify the causes of the low zinc condensing efficiency. The very fine dust particles and equipment problems were singled out as having affected the condenser performance most severely.

During the final campaign, 50 t of dehalogenated and calcined dust was melted without the addition of a reducing agent, cast in tapping trays, then crushed and screened to obtain 2 – 8 mm agglomerate. The agglomerated dust was smelted under the same operating conditions as those employed for the fine dust. A partial analysis of the agglomerated EAF dust is given in Table IV. The reductant used was metallurgical coke.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

Table IV - Partial analysis of agglomerated EAF dust (15)

Compound	Mass percentage, %
ZnO	22.6
PbO	1.4
Fe <sub>2</sub> O <sub>3</sub>	51.5

The levels of zinc oxide and lead oxide in the residual slags tapped from the fuming furnace were below 1 and 0.1 %, respectively. The zinc metal tapped from the ISP condenser met PW grade specifications. About 658 kg of residual slag, 60 kg of furnace metal, 148 kg of zinc metal, 93 kg of condenser dross, and 7 kg of fume were produced per ton of EAF dust. A zinc extraction in the furnace of 96.7 % and a zinc condensation efficiency of 82.9 % were achieved on a zero-recycle basis. The net specific energy requirements, based on the total energy consumption in kWh/t of EAF dust and on energy losses, was 950 kWh/t of agglomerated dust. The thermal efficiency of the furnace was approximately 79 %, with an average tapping temperature of 1480 °C.

### **The AllMet process**

AllMet's system combines a modified version of a rotary hearth furnace direct-reduced-iron (DRI) process with Tetronics-process plasma technology to process waste oxide by-products with no secondary waste generation. The technology can process mill scale, BOF dust, EAF dust, oily waste-water sludges, grindings and scarfings.

Nucor-Yamato Steel Co. is currently building a steel-plant waste recycling plant at Blytheville, Arkansas. The plant has a maximum capacity of 110 000 t/a but will initially only process the Blytheville, Arkansas mill's 80 000 t/a output of EAF dust, mill scale and sludges. The rotary hearth furnace capacity will range from 100 – 110 000 t, with the intention being to process 44 000 t of mill scale and 36 000 t of EAF dust annually. The process will produce 50 – 60 000 t of direct-reduced-iron (DRI), which will be sold to a mini-mill. The possibility of utilising the extra production capacity by bringing in mill scale from the Hickman plant is also under consideration. Construction and cold plant commissioning was completed by Itam Techint Italmimpianti Inc. in February 1998. Hot commissioning was underway at the time of going to print, and the plant was expected to be fully operational by May 1998 (16).

Nucor-Yamato currently disposes of its dust at a cost of over \$150/t but significantly less than \$200/t (6). It is hoped that the AllMet process will cost the plant less than \$140/t. This cost does not take into account the money the mini-mill will save on disposing of mill scale and sludge.

AllMet also has a letter of intent for construction of another large plant for an as yet undisclosed US-based integrated steel maker (16).

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

### Description of the AllMet process

An in-depth process description is given by Pargeter (17). EAF dust, mill-scale fines and sludges, and an above-stoichiometric amount of coke fines are blended and pelletized to between 0.762 and 1.524 mm in diameter (17). The green pellets are placed on the hearth of an INMETCO rotary hearth furnace in a two to three pellet-high layer. Here they are carburized and metallized, and exit the hearth as high-carbon DRI. To enable energy retention (5), the pellets are hot-charged (1100 °C) back to an electric furnace via refractory-lined containers, or to a BOF hot-metal charging ladle. The DRI pellets contain 75 – 85 % iron, with 90 % metallization and about 5 % carbon.

The zinc oxide and salt particulate (primarily NaCl and KCl) from the rotary hearth furnace offgas are collected in a baghouse and become the feed for the Tetronics DC furnace. At this stage, the baghouse dust consists of approximately 70 % zinc, so it can now be more cost effectively smelted in a plasma furnace than dust with a lower zinc content. The dust is mixed with carbon fines and fed to the furnace, where the zinc oxide is rapidly reduced and zinc metal is volatilized. The furnace offgas is thus rich in zinc and carbon monoxide, but it also contains cadmium, lead and salt vapours. All of the constituents of this stream, except for the carbon monoxide, are condensed out in a zinc splash condenser containing a molten zinc and salt bath. The carbon monoxide-rich stream is fed back to the rotary hearth furnace where it is combusted. The molten lead and zinc are tapped separately and cast for resale. The salt is tapped and quenched, brine is bled off, and the salt is recovered by evaporation using a spray drum dryer heated by the process offgas.

The PW grade zinc metal product is projected to be of a high enough quality to be sold to the hot dip galvanizing market. The lead will be sold as scrap grade lead to the secondary lead market, and the salt mixture will be sold as a flux to the aluminium industry.

## ZINC OXIDE-PRODUCING PROCESSES

### **The Ausmelt process**

This bath-smelting technique is based on the Sirosmelt top-submerged lance process developed by Dr John Floyd with the Australian Commonwealth Scientific and Industrial Research Council (CSIRO), and commercialized by Ausmelt of Australia (18).

The Ausmelt technology may be used to recover lead via the direct smelting of concentrates, lead softener slags, lead sulphate, copper dross flue dusts, QSL slags, and ISF slags. Zinc may be fumed from sulphide concentrates and from oxide or carbonate concentrates. Zinc plant leach residues and EAF dust can also be treated using Ausmelt technology (19).

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

The Ausmelt process is not currently in commercial use for the processing of EAF dust, but the pilot plant at the Colorado School of Mines Institute in Denver, Colorado is capable of processing approximately 10 t of dust/day (20). Design studies have been completed for major smelting projects, which were on hold in 1995 due to low zinc prices.

Korea Zinc operates Ausmelt technology for lead and zinc recovery from QSL slag (21), as well as a zinc residue smelter which treats 125 000 t of zinc residue annually (18). Both smelters are currently operational (20).

### Description of the process

The Ausmelt system for the treatment of high-zinc EAF dust utilizes two refractory lined Ausmelt furnaces (see Figure 2). EAF dust and fluxes are mixed and agglomerated to prevent dust entrainment in the offgas system. They are then fed with lump coal into the first Ausmelt furnace (described elsewhere (21, 22)). Fine coal (or natural gas or fuel oils) and combustion air (enriched to contain 40 % oxygen) are injected into the liquid slag bath in the furnace through a cooled lance. The smelting furnace is used primarily to melt the EAF dust, and operates between 1250 and 1350 °C.

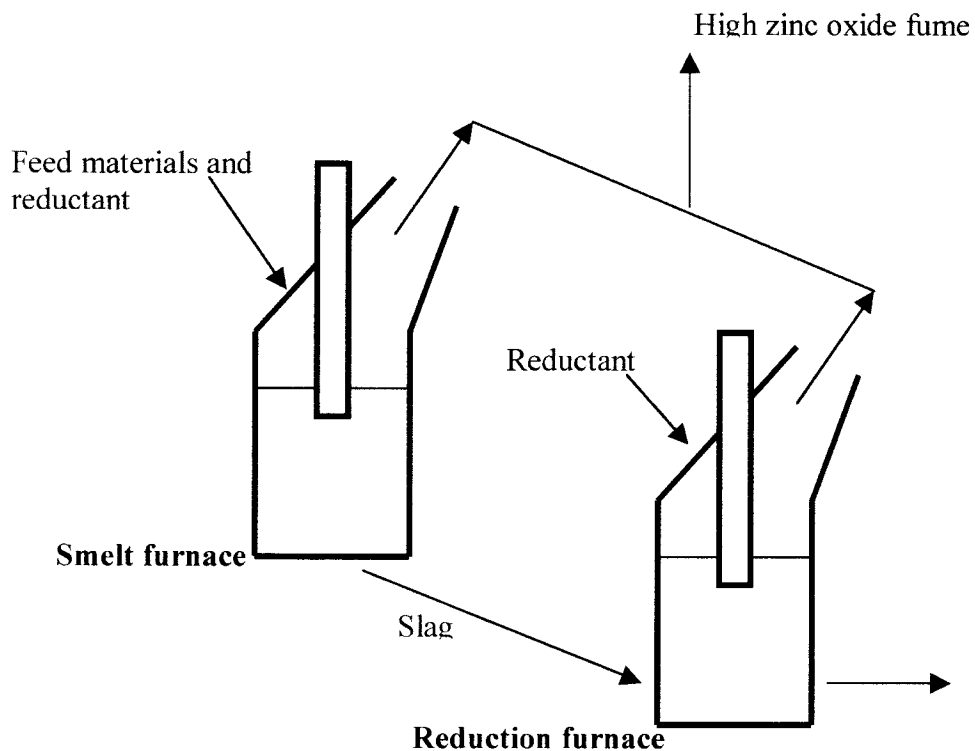


Figure 2 - The Ausmelt furnace system

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

Lump coal is added to the molten slag bath to ensure that reducing conditions are present in the bath. These conditions facilitate the formation of vaporized zinc metal, which is afterburnt to an oxide fume just above the bath. The fume, along with silver, arsenic, cadmium, halogens, and some sodium and potassium, leaves the furnace in the gas stream and is collected in the baghouse.

The smelt slag flows continuously from the smelt furnace through a launder to the reduction furnace for further zinc removal. The reduction furnace is typically operated at 1400 °C for improved metal recovery. Oxygen enrichment is not required for the reduction furnace, but reductant (usually coal), fuel, and combustion air are added. Here again, the fumed zinc, lead and cadmium are re-oxidized above the slag bath and are collected in a bag filter for sale to zinc smelters.

Obviously, the two lead-containing zinc oxide fumes (one from each furnace) are of different composition, and depending on the ultimate fume-product market, pre- or post-production dehalogenation may be required to obtain the suitable chlorine and fluorine levels. The reduced iron oxide-rich slag is tapped continuously and granulated for discard. As it conforms to the EPA TCLP tests, it can be disposed of as landfill.

Table V provides the estimated production for 90 000 t/a of EAF dust in an Ausmelt EAF dust smelter (22). The calculations were performed assuming an EAF dust composition of 20 % zinc, 2.5 % lead, 30 % iron, 4 % silica and 6 % moisture.

Table V – Estimated products for a 90 000 t/a EAF dust smelter

	Smelt stage fume	Reduction stage fume	Total recovery to fume	Discard slag
t/a	18 400	3 800	-	70 000
Zinc, %	70	>75	98	<0.5
Lead, %	10	<5	96	0.1
Iron, %	<1	<1	-	36
Chlorine, %	<2	3	85	-

### The IBDR-ZIPP and related processes

The Iron Bearing Dust Recovery – Zinc Iron Plasma Project (IBDR-ZIPP) process is the commercial application of the plasma torch-fired vertical-shaft furnace originally developed by Westinghouse and now marketed by Philip Environmental Inc. Pilot plant tests for the process (treating up to 10 t/d of EAF dust) were completed at the Westinghouse Pilot Facility outside Pittsburgh, Pennsylvania (23). The technology is able to process zinc-bearing wastes, mill scale, and other iron-bearing constituents.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

A commercial IBDR-ZIPP plant was to have been built in Hamilton, Ontario, Canada (23, 24). The plant was designed to be able to process 60 000 t of EAF dust annually, with a maximum of 75 % dust in the charge. The remainder of the charge was to contain a reasonable proportion of low-grade steel scrap to boost the iron content of the burden (6). The plant was scheduled to start operations in 1996 (25), but construction has been put on hold. Philip still intends to commercialize the IBDR-ZIPP technology (24).

Further, Philip has recently reached an agreement with ASW Holdings Plc., a large European steel manufacturer, with regard to an EAF dust recycling facility at Cardiff, UK. Philip will design, build and operate the plant at Cardiff for a period of five years, using a process developed by Metal Reduction Processing Ltd (MRP). MRP's proprietary technology uses rotary kilns to selectively recover zinc, iron and other constituents of EAF dust for re-use. While certain aspects of the MRP and IBDR-ZIPP processes will be merged during this venture, the MRP process is fundamentally different from IBDR-ZIPP in terms of technology, size, and end-products generated. The Cardiff facility, which will generate an estimated US \$5 million in annual revenue, will have an annual processing capacity of 20 000 t of EAF dust. The Cardiff facility brings to commercialization the MRP technology that ASW has been involved in for over two years (22). Plant construction was nearing completion in March 1998, with cold commissioning already underway. The plant is expected to be fully operational by mid-1998 (24).

### Description of the IBDR-ZIPP process

EAF dust is briquetted and dumped by truck, along with coke, in dump pits. From here, enclosed belt conveyers carry both materials to day bins. Scrap and flux (in the form of either sand or limestone) are also received by truck, stockpiled in a storage area and loaded into feed hoppers. Low-grade scrap steel may also be included in the feed to increase its iron oxide content. All the feed materials are deposited on weigh belt systems and "recipe" amounts are conveyed into a sealed airlock on the vertical shaft furnace.

Non-transferred arc plasma torches, each of which contains two tubular electrodes, heat the vertical shaft furnace. A process gas is injected into a high voltage arc to produce the plasma. Zinc and lead are liberated as gases, and move upwards and out of the furnace to be captured as lead and zinc oxide in a high-efficiency baghouse. Here it is recovered and conveyed to a holding silo. The oxides then pass through a zinc oxide wash and water evaporation system that produces a zinc concentrate, which is fed to a multi-stage caustic-leach electrowinning plant that produces high purity zinc metal powder. The powder is further processed in an electric furnace and poured into an ingot caster for sale to the high-grade zinc metals market. The electrowinning process also produces mixed salts and small amounts of lead. The lead is filtered out and sent to a lead processor, where saleable lead-cadmium cements are produced.

In addition to the recovery value of the zinc metal, the iron oxide in the feed is reduced to pig iron for recycle or sale. The inert slag produced in the shaft furnace

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

vitrifies the heavy metals remaining in it and consistently meets TCLP tests. Thus, the IBDR-ZIPP process generates no waste products requiring further treatment before disposal.

### **The Phoenix Environmental Ltd. process**

Phoenix Environmental Ltd (PEL) has developed an iron-oxygen reactor for the treatment of ferrous-bearing metal wastes. The technology can process metal turnings, swarf, punchings and ferrous-based metal dusts and produces, primarily, magnetite that can then be used in a variety of industrial applications. The process has been designed with a view to producing 3 – 34 t/d of magnetite (26).

Pilot plant tests for the process (treating up to 1.5 t/d of EAF dust equivalents in test runs spanning 12 to 16 hours) were completed at the PEL Research and Development Facility in Montgomery, Pennsylvania (27). The pilot plant has performed over 130 full-scale test runs on various iron-bearing constituents and has a maximum production capacity of 5 t/d of magnetite.

Pending the approval of the Ohio Environmental Protection Agency, PEL, in association with The Timken Co., plans to start building an iron-bearing waste recycling plant at Timken's Faircrest steel plant in Canton, Ohio in July 1998 (27). Cold commissioning is expected to be complete by April 1999, with production beginning between June and August 1999. The plant is expected to process 2500 t/a of EAF dust by the end of the first plant development phase. Plans to increase the plants capacity to 14 000 t/a of EAF dust by the first half of 2001 are already in place. At full capacity the plant will process all of Timken's EAF dust, swarf, pickling liquor solids and some low oxide mill scale.

### Description of the PEL process

Scheetz, et al (26), give an in-depth process description. The furnace consists of a plenum enclosure above a molten bath and a transfer cavity that lies adjacent to the molten bath. Both oxygen (introduced via a retractable lance) and feed (introduced through augers) enter the molten bath through the plenum cavity, with the exhaust gases also being removed from this area.

Due to its greater density, the ferrous-bearing feed arriving on top of the melt sinks towards the bottom of the bath. As the feed sinks, it melts and oxidizes. The oxidation reaction of iron with oxygen to magnetite is exothermic and self-sustainable (self-sustaining high temperature synthesis), maintaining a bath temperature of approximately 1540 °C. Material leaves the molten bath via a weir to enter the transfer cavity.

The transfer cavity conducts the molten oxide melt from the reactor to a discharge pot. The fully reacted melt in the transfer cavity is kept molten through the use of

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

propane burners and oxygen enriched air. The melt leaves this area under gravity feed, dropping through the operational floor. As it drops it is quenched by atomization using jets of compressed air. The reactor product is spherical magnetite, which may be further milled to powder form.

Process suitability tests for EAF dust treatment were conducted using a surrogate material (16.2 % ZnO, 2.5 % PbO, 2.1 % NaCl, 44.2 % Fe<sub>2</sub>O<sub>3</sub>, and 35 % Fe). The molten oxide bath was operated in an oxygen deficient condition to produce wustite to enhance zinc production. The zinc oxide produced above the molten bath in the plenum is collected in the offgas system. The process demonstrated an 81 – 96 % efficiency for zinc removal.

### **Recovery at Kawasaki Steel Corporation's Chiba works**

Kawasaki Steel Corporation of Japan is currently considering building a commercial-scale recycling furnace at its Chiba Works that would recover zinc and iron from EAF dust (26). The new process for recycling dust at stainless-steel mills is an outgrowth of Kawasaki Steel's STAR (stainless-steel advanced reactor) process.

The plant will be able to process 70 – 100 t of dust per day, and it is hoped that the plant will become operational in 1999. Currently, Kawasaki Steel's Technical Research Laboratories are operating a 10 t/d pilot plant that was built at Chiba Works two years ago.

#### Description of the process

Coke is loaded through the top of the demonstration furnace, which is 5 m tall (see Figure 3). (The commercial-scale furnace will be about 10 m high.) Oxygen is blown into the furnace through the upper and lower tuyeres, and combusts the burning coke to form two ultra-high heating zones, or raceways. The dust-injection blower, which is alongside the upper tuyere, sends the dust to the upper heating zone where it is superheated to 1650 °C and melted instantly. The molten dust filters down through the layers of burning coke and drops into the lower heating zone for compensative heating. As it travels from one raceway to the other, the molten dust, which is now molten zinc oxide, separates into zinc vapor, molten iron, and molten slag. The iron and slag sink to the bottom of the furnace and settle out so that a layer of slag tops the iron. Molten iron is then tapped through a skimmer.

Operators blow oxygen through the lower tuyere to provide additional energy to compensate for the loss of energy as the molten dust flows downward. To determine the correct amount of oxygen to inject, operators measure the temperature by analyzing the crystalline structure of the coke. During this time, the zinc gas and the exhaust gas rise in the furnace (zinc vaporizes at a much lower temperature than iron). A wet-type gas-recovery system near the furnace's top captures the zinc vapor.



## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

The crude zinc that is recovered from the dust has more than 60 % purity. It can therefore be used as a raw material for zinc smelting. The exhaust gas is recycled as fuel gas. The smelting-reduction furnace also uses low-cost undersized coke that cannot be used in blast furnaces. When the costs of the recovered zinc, molten iron, slag, and fuel gas are factored in, the new furnace reduces dust-processing costs by about 40 % compared to conventional methods. The direct production costs can be half that of current methods.

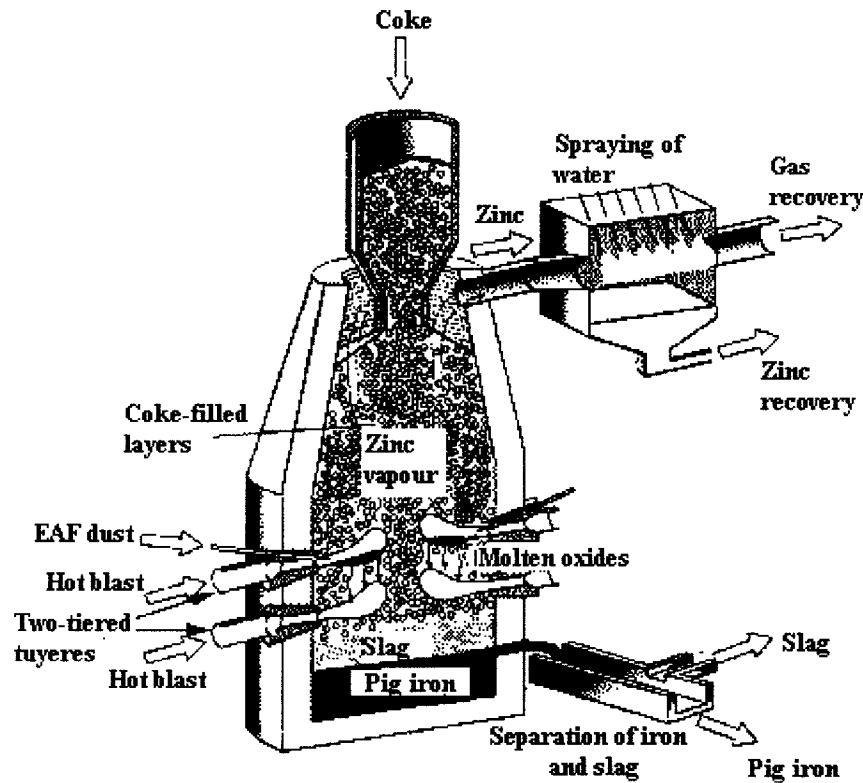


Figure 3 - Kawasaki's new dust recycling furnace

## CONCLUSIONS

Effective management of zinc-bearing wastes at a minimum cost remains a significant problem for most new and existing waste producers. Technologies to recover and recycle values from zinc-bearing wastes have come to the fore in the last two to three years, and the commercialization of a number of these technologies is now very close at

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

hand. Old process routes, as well as stabilization and disposal of, or vitrification and sale of, the wastes continue to be industrially practised. However, producing the most and highest value-added products such as commodity zinc metal, metallized iron and lead or cadmium metals, and no materials requiring disposal are clearly major focuses in the industry at present. Several of the established commercial processes are reassessing their treatment processes and developing new methods within the confines of their current processes to increase value and recyclability of their products, particularly iron-bearing products.

Also, primary electrolytic zinc producers are becoming more interested and involved in the development of technologies that can provide zinc feed to their existing plants. This interest is sparked partially by declining zinc sulphide resources and partially by plant expansions. Several electrolytic zinc producers are now co-operating with steel producers and engineering research organizations to find new or alternative supplies of low halide-containing feed materials.

Thus, cost-effective zinc-bearing waste management is fast becoming an economically driven resource recovery or recycling opportunity, although the threat of it being an environmentally driven hazardous waste management problem is always in the back of the minds of waste producers.

## REFERENCES

1. T. Furukawa, "Recovering zinc and iron from EAF dust at Chiba Works", New Steel [online], June 1996. Available from: <http://204.243.31.49/cgi-win/csearch.exe/search.htm> (Accessed on 6 March 1998.)
2. "Recycling of EAF dust into DRI, shingles and rubber", New Steel [online], December 1997. Available from: <http://www.newsteel.com/news/nw971201.htm>
3. "Hazardous waste management system: Identification and Listing of Hazardous Waste: Final Exclusion", 40 CFR Part 261, [SW-FRL-5219-5] Reference no.: F-95-CSEF-FFFFF, Federal Register Vol. 60, No. 113, 13 June 1995, pp. 31107-31115, Environmental Protection Agency [online]. Available from: <http://www.epa.gov/fedrgstr/EPA-WASTE/1995/June/Day-13/pr-247.html>
4. "K061: A hazardous waste approved for fertilisers!", Cozinco Sales Inc [online]. Available from: <http://www.cozinco.com/k061.htm>
5. C.C. Petry, "Nucor-Yamata Steel mill to have zero waste", AMM Online [online], 25 February 1997. Available from: <http://www.amm.com/ref/hot/env225.htm>

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

6. J. Schriefer, "Reaping the value from dust and slag", New Steel [online], February 1997. Available from:  
<http://204.243.31.49/cgi-win/csearch.exe/search.htm> (Accessed on 6 March 1998.)
7. L.M. Wrona and G. Julien, "Pollution prevention in the steel industry: Toward a zero-waste plant", Iron and Steel [online]. Available from:  
<http://www.hatch.ca/expertareas/ironandsteel/services/pollutio.html>
8. A.D. Zunkel, and R.J. Schmitt, "Review of electric arc furnace dust treatment processes and environmental regulations", Electric Furnace Conference Proceedings, 1995, 147-158.
9. A.D. Zunkel, "What to do with your EAF dust", Steel Times International, Vol. 20, No. 3, July 1996, 46-50.
10. A.F.S Schoukens, F. Shaw, and E.C. Chemaly, "The Enviroplas process for the treatment of steel-plant dusts", Journal of the South African Institute of Mining and Metallurgy, Vol. 93, No.1, January 1993, 1-7.
11. R. Lee, Imperial Smelting Processes, Personal Communications, 24 & 29 April 1998.
12. A.D. Zunkel, "Electric arc furnace dust management technology: Where are we now? Where are we going?", AISE Annual Conference, Chicago, Illinois, 30 September 1996.
13. A.F.S. Schoukens, G.M. Denton and R.T. Jones, "Pilot-Plant Production of Prime Western Grade Zinc from Lead Blast-Furnace Slags using the Enviroplas Process", Proceedings of the Third International Symposium on Recycling of Metals and Engineered Materials, Point Clear, Alabama, 12 – 15 November, 1995. Publication of the Minerals, Metals and Materials Society, 1995, 857-868.
14. N.A. Barcza, D.G.C. Robertson, A.F.S. Schoukens, F. Shaw, G.M. Denton, A.W. Worcester, and D.J. Bailey, "Enviroplas Technology for the Recovery of Lead and Zinc from Lead Blast Furnace Slags", International Lead and Zinc Study Group: 6<sup>th</sup> International Conference, Madrid, Spain, June 1995.
15. A.F.S. Schoukens, M.A. Abdel-Latif, M.J. Freeman and N.A. Barcza, "The Enviroplas process for the recovery of zinc, chromium and nickel from steel-plant dust", 1996 Electric Furnace Conference Proceedings, 341-351.
16. J.K. Pargeter, AllMet, Personal Communication, 24 March 1998.

## EMERGING PROCESSES FOR ZINC AND LEAD RECOVERY

17. J.K. Pargeter, "The Missing Link: Steelmaking By-Products to Useful Raw Materials", Steel Mill Wastes and By-Products Conference, Pittsburgh, 24 – 26 June 1996.
18. Ausmelt Technology [online]. Available from:  
<http://beavis.geospace.com/ausmelt/html/technology.html>
19. Ausmelt Applications [online] Available from:  
<http://www.ausmelt.com/html/applications.html>
20. P.N. Vernon, Ausmelt South Africa, Personal Communication, 16 March 1998.
21. J.M. Floyd and W.E. Short, "Ausmelt technology for secondary zinc recovery", Sixth international recycling conference held by the International Lead and Zinc Study Group: Recycling lead and zinc into the 21 Century, Madrid, Spain, 18 – 23 June 1995, 207-218.
22. B.W. Lightfoot, W.E. Short and G.A. Guorgi, "EAF dust processing with Ausmelt technology", Zinc and Lead '95: An international symposium on the extraction and applications of zinc and lead, Sendai, Japan, 22 – 24 May 1995, 442-449.
23. B. Emeneau, Philip Environmental Inc., Personal Communication, 23 March 1998.
24. R.V. Chalfant, "Recovering zinc and iron from electric-furnace dust", New Steel [online], September 1996. Available from:  
<http://204.243.31.49/cgi-win/csearch.exe/search.htm> (Accessed on 6 March 1998.)
25. "Recycling electric arc furnace dust", Hazardous Materials Management [online], April / May 1995. Available from:  
<http://www.hazmatmag.com/library/docs/AM95/AM95023.html>
26. B.E. Scheetz, M. Vayansky, J. Cheetham and J. Workman, "The Phoenix Environmental Ltd: Iron-Oxygen Reactor Technology", 16th International Conference on Incineration and Thermal Treatment Technologies, San Francisco, California, May 1997.
27. A. Bengali, Phoenix Environmental Ltd, Personal Communication, 29 April 1998.
28. "Philip continues its consolidation program in the UK with the acquisition of two metals recycling companies and the right to a new EAF dust recycling technology", Envirobiz (International Environmental Information Network) [online], 21 August 1997. Available from: <http://www.envirobiz.com/newsdaily/970821f5.htm>