# THE TREATMENT OF METALLURGICAL WASTES USING THE ENVIROPLAS PROCESS

by

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#### **ABSTRACT**

DC plasma-arc technology using a hollow graphite electrode (cathode) has been successfully implemented in the primary metallurgical industry in South Africa up to the 30 MW scale. Mintek has applied its expertise base, established over the past fifteen years, to testing the treatment of metallurgical wastes such as carbon- and stainless-steel plant dusts, lead- and zinc-containing slags, and residues from the base-metal industry. Favourable results have been achieved, and disposable products were produced. The evaluation of numerous wastes indicates that recovery of zinc as metal gives the best economic return from these sources. Direct recovery via a splash condenser or electrolytic zinc extraction from fume are the two preferred alternatives under review. In both instances dehalogenation is an important issue, but can be achieved by suitable treatment processes.

The Enviroplas technology provides a flexible, commercially viable approach to the treatment of a wide variety of wastes. Mintek, together with its associate Pyromet CC, are installing a plasma-arc pilot-plant facility with both an ISP lead-splash condenser of about 5 t/d condensed zinc capacity and a combustion chamber to burn zinc vapour to zinc oxide. This will demonstrate the suitability of the Enviroplas technology for treating specific metallurgical wastes, so that customized industrial plants can be engineered based on large-scale testwork.

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#### Introduction

Mintek began research and development work into evaluating the potential advantages of plasmaarc technology for pyrometallurgical applications during the 1970s. The applications considered included the smelting of metal fines arising from the steel and ferro-alloy industries, and the smelting of fine ores used in the above industries (1). At that time, environmental regulations were not as strict as they are today. However the ability of plasma-arc furnaces to handle fine feed and achieve high recoveries with low residual levels of reducible metal oxides in the slag phase was recognised. The design of such furnaces allows them to be well sealed, which favours the capture and control of emissions.

Limited commercial success was achieved in the use of plasma arc technology during the 1980s although noteworthy technical developments were made on a pilot-plant scale. Several plants based on plasma-arc technology were closed during the economic recession in the 1990s. However, the 40 MVA (30 MW) dc transferred plasma-arc furnace used for ferrochrome production at Palmiet Ferrochrome (formally MS&A) near Johannesburg in South Africa has remained commercially viable even when compared with the best conventional submerged-arc furnaces during these recessionary times.

Mintek developed the technology for the ferrochrome process used at this plant, and from this experience has been able to turn its attention to the treatment of carbon- and stainless-steel dusts, and lead- and zinc-containing slags and residues from the base-metal industry. All of these can contain environmentally hazardous heavy metals that can leach into the water table if not properly disposed of (2). Even when disposed of in landfill sites or chemically stabilized, they carry an ongoing liability in some countries such as the USA.

Open-bath de transferred plasma-arc furnaces have been used in several environmental installations, as shown in Table I. Several further plants are under investigation for the treatment of EAF dusts and lead slags. Non-electrical based processes and conventional electrical furnaces have been extensively used for the treatment of environmental waste materials and have been reviewed elsewhere (3,4).

The use of a hollow graphite cathode instead of a water-cooled plasma torch has found increasing favour in metallurgical plants treating both primary raw materials and secondary arisings. The advantages include safety, convenience, economics, reliability, and high current capability. The ability to feed through a hollow graphite cathode offers specific advantages when treating very fine dusts, since carry-over is limited. The feed materials are absorbed directly into the liquid bath beneath the electrode. The Enviroplas TM process has been developed on this basis, although provision to feed through the furnace roof or via a weir (if liquid slag is to be charged) is made under some circumstances. Pilot-plant testwork carried out at Mintek over the past eight years to treat EAF dusts from carbon- and alloy-steel plant operations, lead blast-furnace slags, and zinc-containing residues has shown that disposable slags meeting EPA requirements can be produced (5,6). Zinc-enriched fume has been produced by combusting furnace vapours in a combustion chamber and filtering the off-gases in a bag-filter plant. The economics of treating such materials shows that zinc metal condensation is favoured when the zinc content of the feed material is more than about 20%, and where more than 10 kt/a of material is available. Zinc recovery and purity are critical considerations, and zinc splash condensers have apparently not been very successful when used to recover metal from EAF dusts. A lead splash condenser offers potentially greater efficiency, and Mintek has decided to install a demonstration-scale plant to prove the linking of a dc arc furnace with an ISP lead splash condenser (7). The plant is due for commissioning and test campaigns by mid-1994. Pyromet CC is constructing most of the plant.

## TABLE I. LIST OF INSTALLATIONS SIMILAR TO ENVIROPLAS

#### 1. DC TRANSFERRED ARC SMELTING PROCESSES

| DATE | COMPANY   | LOCATION             | PROCESS  | PRODUCT   | CAPACITY<br>kt | DUST/FEED<br>TYPES                                      |
|------|---|----------------------|--|---|----------------|---|
| 1989 | (14)<br>Avesta<br>St Steel                      | Sheffield<br>UK      | Modified TRD<br>dc plasma arc<br>with fume<br>combustion                                 | Crude<br>ferroalloy<br>Zn enriched<br>fume by<br>product        | 8              | St Steel<br>Millscale                                   |
| 1989 | (15,16)<br>Florida<br>Steel                     | Jackson<br>TN USA    | Modified TRD<br>dc plasma<br>arc/Zn splash<br>condenser                                  | Crude Zn<br>metal   | .7             | Carbon  |
| 1989 | IMS (15,16)<br>Nucor-<br>Yamato                 | Blythville<br>AR USA | (As above)   | Crude Zn<br>metal   | 11             | Carbon Steel  |
| 1989 | IMS (17)<br>Kawasaki<br>Steel                   | Chiba Works<br>Japan | Similar to Mintek's dc arc furnace with hollow graphite cathode                          | Crude<br>ferroalloy<br>and dust                                 | 3              | St Steel  |
| 1992 | Multiserv(18) Ilserv (Plasminox <sup>TM</sup> ) | Terni<br>Italy       | Modified TRD<br>de plasma are<br>furnace with<br>fume<br>combustion                      | Crude ferroalloy Zn enriched fume by product                    | 24             | St Steel Sludge Millscale                               |
| 1994 | (7)<br>Mintek<br>(Enviroplas™)                  | Randburg<br>RSA      | Premelter/ Hollow graphite electrode feed with lead splash condenser/ combustion chamber | Ferroalloy<br>Zinc metal<br>or fume                             | 10             | St Steel & alloy<br>steels<br>Carbon Steel<br>LBFS, LZR |
|      |   | 2. NON TRAN          | SFERRED ARCS   | MELTING PR  | OCESS          |   |
| 1984 | (19)<br>Scandust<br>(SKF and<br>BUS)            | Landskrone<br>Sweden | SKF (Scanarc)<br>shaft furnace<br>with arc heater<br>tuyeres                             | Crude<br>ferroalloy<br>and Zn<br>enriched<br>fume<br>by product | 45             | St Steel and alloy steels                               |

## Applications of Enviroplas

Lead blast-furnace slags (LBFS) contain between 10 and 14% ZnO and 2 to 3% PbO, and ISF furnaces produce slags with slightly lower levels. These slags are becoming increasingly unacceptable environmentally in several countries, since the heavy metals are potentially leachable into ground water. Mintek carried out testwork at power levels of up to 800 kW on LBFS to recover lead and zinc and produce a slag with low levels of zinc and lead. The vapour was combusted to produce an enriched fume suitable for electrolytic zinc recovery after dehalogenation. Testwork has also been carried out to determine the rate of zinc extraction from LBFS as a function of temperature and rate of reductant addition. The fuming rate of zinc was about 50 kg/m²/h in the

dc arc furnace at 800 kW. This compares favourably with submerged fuming on a 2 MW scale of only 20 kg/m²/h (Table II) (8). The slags produced fully met EPA leach test criteria. Mintek and Pyromet CC are collaborating with clients in the USA and Europe to evaluate the applications of Enviroplas to LBF and ISF slag treatment, and to scale-up the technology to industrial operations.

TABLE II. A COMPARISON BETWEEN SUBMERGED ARC AND DC ARC FUMING OF LEAD SLAGS

| PARAMETER                     | SUBMERGED ARC SLAG (8)  | DC PLASMA ARC                            |
|-------------------------------|-------------------------|--|
| Fuming furnace power, MW      | 2.2                     | 0.8                                      |
| Total energy, kWh/t           | 650 (hot slag feed)     | 1030 (cold slag feed)<br>400 (hot feed)* |
| Zinc fumed, kWh/t             | 4810 (total Zn. 1 pass) | 3920 (hot feed)*                         |
| PWG zinc produced, kWh/t      | 6500                    | -  |
| Input slag analyses           | 18% Zn, 4.2%Pb          | 10.9%Zn, 2.6%Pb                          |
| Discard slag analyses         | 6%Zn, 0.2%Pb            | 0.8%Zn, 0.2%Pb                           |
| Zn fumed, %                   | 75                      | 94                                       |
| Zn fuming rate, kg/m²/h       | 20                      | 50                                       |
| Temperature, °C               | 1310                    | 1480                                     |
| Power flux, MW/m <sup>2</sup> | 0.1                     | 0.5                                      |

<sup>\*</sup> Calculated

Carbon and alloy-steel dusts have been treated successfully in pilot-plant tests at power levels of up to 800 kW. Micropellets containing reductant and flux were successfully smelted. Dust of about 1  $\mu$ m was also successfully fed direct into the dc arc furnace via the hollow graphite cathode. Slags fully meeting EPA criteria were produced, and high levels of zinc and lead extraction were readily achieved. A zinc-rich fume was collected, and is being evaluated for electrolytic zinc production. Condensation of zinc will be studied on Mintek's new pilot-plant facility to demonstrate the zinc collection efficiency and zinc purity. A typical process flow sheet for EAF dust treatment is shown in Figure 1.

Other applications for the Enviroplas process include treating ferro-alloy dusts produced from the smelting of high-carbon and low-carbon ferrochromium and ferromanganese alloys. Such dusts are best co-smelted with reject alloy fines from such plants to produce a clean metal and a disposable slag. This approach makes the treatment economically attractive.

Electrolytic zinc plants produce a residue rich in iron oxide (hematite, goethite, or jarosite containing heavy metals) that is environmentally unacceptable in many countries. Chemical treatment methods to recover these residual heavy metals have not been economically successful to date. An alternative approach under investigation is the extraction of zinc from the lead–zinc residue (LZR) produced after the first-stage neutral leach in the electrolytic zinc circuit (4). The residue is calcined and fed into the dc arc furnace via the hollow cathode, together with flux and reducing agent, e.g. coke. This produces a disposable slag and either a zinc-enriched fume that can be recycled to the leaching circuit or condensed direct in a splash condenser. The disadvantage of the latter option is the lower grade of zinc metal produced (PWG) compared with electrolytic zinc (SHG or HG). However, given the failure of other approaches and the possibility of upgrading PWG to HG or even SHG, this might be a viable longer term commercial option, particularly for primary zinc deposits that contain high levels of manganese, such as Gamsberg in South Africa.

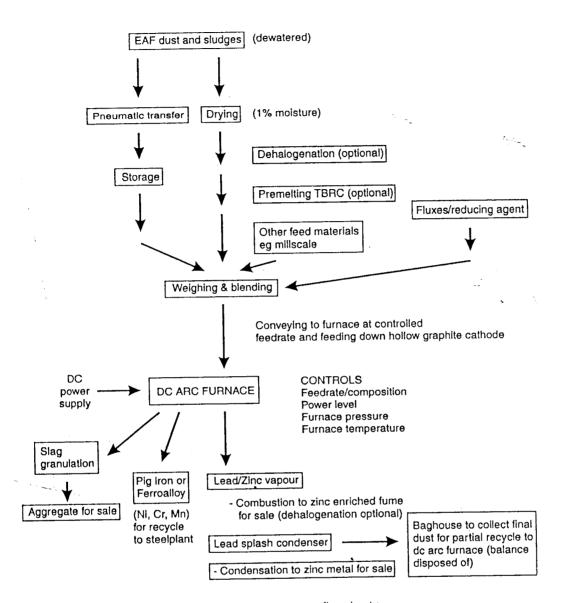


Figure 1. Enviroplas process flowsheet

Zinc-containing residues and drosses are produced in the secondary zinc and brass industries, and from hot-dip galvanizing of steel, and are suitable for treatment by the Enviroplas process. Only limited test work has been carried out to date, but the results are encouraging. Typical materials that can be treated using Enviroplas are shown in Table III.

TABLE III. TYPICAL COMPOSTIONS OF FEED MATERIALS THAT CAN BE TREATED BY THE ENVIROPLAS PROCESS, % BY MASS

|                                      |                                |                                       | Iron Ste   | eel & St. Ste | eel Industry      | Lead      | d/Zinc Industry |  |  |
|--------------------------------------|--------------------------------|---------------------------------------|------------|---------------|-------------------|-----------|-----------------|--|--|
| Comp                                 | onents                         | Carbon<br>EAFD                        |            | Alloy<br>EAFD |                   |           | Lead Slags      |  |  |
|                                      |                                |                                       | Low Zinc   | Н             | igh Zinc          | BF Slag   | ISF Slag        |  |  |
| Fe                                   | <sub>2</sub> 0 <sub>3</sub>    | 40                                    | 45         |               | 35                | 35        | 40              |  |  |
| M                                    | Mn0                            |                                       | 5          |               | 3                 |           | 3.6             |  |  |
| Cr                                   | Cr <sub>2</sub> 0 <sub>3</sub> |                                       | 14         |               | 12                | -         | -               |  |  |
| N                                    | i0                             | 0.2                                   | 8          |               | 2                 | -         |                 |  |  |
| Zı                                   | 10                             | 30                                    | 2          |               | 25                | 14        | 7               |  |  |
| Pt                                   | 0                              | 2                                     | 0.5        | 1             |                   | 4         | 1               |  |  |
| Ca                                   | 10                             | 5                                     | 5          |               | 6                 | 10        | 25              |  |  |
| Mg                                   | g0                             | 3                                     | 4          |               | 1                 | 5         | 1               |  |  |
| Al                                   |                                | 2                                     | 0.5        |               | 0.1               | 5         | 5               |  |  |
| Si                                   | ),                             | 8                                     | 5          |               | 5                 | 20        | 2               |  |  |
| Cart                                 | Carbon 1 0.5 0.5               |                                       | •          | -             |                   |           |                 |  |  |
| A                                    | 3                              | <100ppm                               | -          |               | -                 |           | 0.1             |  |  |
| Cu                                   |                                | 0.2                                   | -          | -             |                   | 0.2       | 0.4             |  |  |
| S                                    |                                | 0.5                                   | -          | -             |                   | 2.0       | 2.8             |  |  |
| Cd                                   |                                | 0.03                                  | •          |               | •                 | 55ppm     | <5ppm           |  |  |
| <del></del>                          | Na <sub>2</sub> 0              |                                       | 1.5        |               | 1.5               | 1.3       | 0.5             |  |  |
| K <sub>2</sub> (                     |                                | 1                                     | 0.5        |               | 0.5               | 0.9       | 0.3             |  |  |
| C-                                   |                                | 2.5                                   | 1.5        | 1.5           |                   | 0.1       | -               |  |  |
| F                                    |                                | 0.5                                   | 0.5        | 0.5           |                   | 0.02      | _               |  |  |
|                                      |                                | · · · · · · · · · · · · · · · · · · · | Zinc & Bra | ss Industrie  | s                 |           |                 |  |  |
| Components                           | Top<br>Dross                   | Spelter                               | Zinc Ash   | Brass<br>Ash  | Copper<br>furnace | Zinc Lead | ch Residue      |  |  |
|                                      |                                |                                       |            | Asii          | dusts             | Neutral   | Jarosite        |  |  |
| Zn (Zn0)                             | 95                             | 95                                    | 70         | 50            | 45                | (25)      | (5)             |  |  |
| Pb (Pb0)                             | 0.1                            | 3                                     | 2          | 2             | 10                | (5)       | (5)             |  |  |
| As                                   | -                              | -                                     | -          | 0.1           |                   | 0.75      | -               |  |  |
| Cu                                   | •                              | 0.03                                  | 0.2        | 30            | 4                 | •         | -               |  |  |
| Cd                                   | 0.1                            | 0.02                                  | 0.02       | 0.05          |                   | 0.2       |                 |  |  |
| Fe (Fe0)                             | 2                              | 5                                     | 2          | 1             | -                 | (45)      | (40)            |  |  |
| Mn                                   | -                              | -                                     | 0.03       | 0.1           |                   | -         | -               |  |  |
| Al (Al <sub>2</sub> 0 <sub>3</sub> ) | 2                              | 0.02                                  | 0.2        | 1             |                   | (1)       | -               |  |  |
| Cl-                                  | -                              | -                                     | 2          | 0.2           | 4 .               | -         | •               |  |  |
| S                                    | -                              | -                                     | •          | -             |                   | 15        | 10              |  |  |

The Enviroplas process can also be used for the vitrification of lower zinc containing EAF dusts from carbon-steel, alloy-steel and ferro-alloy plants and fly ash residues. The ceramic materials that are produced can be used in the building industry in instances where the recovery of zinc metal or alloys is uneconomic. The cost of the additional fluxing agents and energy required is similar to that for the reductant and energy for zinc or alloy extraction, but the total product of vitrified slag is potentially saleable, largely offsetting the production costs. The slag composition has to be carefully selected to ensure that the product meets EPA leach test criteria. The Enviroplas process avoids the use of costly molybdenum electrodes and the low-power-flux operation as practised in the conventional glass industry.

#### **Technical Considerations**

The carbothermic reactions taking place in the plasma-arc furnace are assumed to occur at the interface of the molten slag and carbon, and can be presented in the general form:

$$MO + C \iff M + CO$$
 (1)  
 $MO + CO \iff M + CO_2$  (2)  
 $CO_2 + C \iff 2CO$  (3)

Since CO<sub>2</sub> is unstable in the presence of carbon at normal reaction temperatures, the basic stoichiometry can be calculated from the first of the equations. In the case of zinc-containing waste materials, reactions of iron or FeO with ZnO have been described for slag fuming processes(9). For example:

$$ZnO + 2FeO \iff Zn + Fe_2O_3$$
 (4)  
 $Fe_2O_3 + CO \iff 2FeO + CO_2$  (5)

An experimental investigation is planned to study the mechanism of zinc reduction in the plasmaarc furnace. The extent to which metallic iron is produced depends on temperature and the amount of carbon available.

Operating factors that can influence reaction rates include operating temperature, slag composition and viscosity, reductant entrainment in the slag, and degree of agitation. In the case of zinc fuming processes, a fine reductant may be advantageous to provide a greater slag-reductant surface area for the reduction of ferric ions. However, with decreasing sizing, there is an increasing tendency for reductant fines to be swept from the furnace with the off-gas.

Before metallurgical wastes are treated in a plasma-arc furnace, the question of pre-treatment must be addressed. Apart from any drying or agglomeration treatment that may be required, a critical issue at present is the dehalogenation of carbon-steel dusts, from which zinc is to be recovered in a condenser. Extensive problems have been experienced in various attempts to commercialize such processes. Accretion effects in off-gas systems and dross formation resulting from the carry-over of halides and alkalis have led to operational problems. Mintek is currently conducting testwork to evaluate the available options. Cognisance has been given to the very variable nature of steel-plant dusts in order to avoid the development of a process that is sample-specific. Two treatment options are currently under investigation.

## Roasting of Pelletized Dust

Batch treatment of dust pellets in an oxy-propane-fired rotating reverberatory furnace has shown the following trends.

| Element                 | Cl   | F    | Na   | K    | Cd  |
|-------------------------|------|------|------|------|-----|
| Average removal: mass % | 92.5 | 53.0 | 43.2 | 63.6 | >95 |

The moderate extent of removal for fluorine is not considered to be too serious since experience of fuming operations has shown that a good proportion of this element reports to the final discard slag. The effective removal of cadmium is very significant with respect to the quality of zinc that may be subsequently recovered. Lead removal may exceed 80% during roasting, but zinc losses were shown to be minimal.

#### Pre-melting of Dust

This option would allow for the possibility of transferring dehalogenated molten EAF dust as slag to a fuming furnace. Alternatively, a two-stage batch process may be operated in cycles of melting, reducing, and tapping, using one furnace with alternative gas offtakes. Preliminary trials of melting down in a 100 kVA plasma-arc furnace followed by immediate tapping gave the following results.

| Element                 | Cl   | F    | Na   | K    | Cd  |
|-------------------------|------|------|------|------|-----|
| Average removal: mass % | 93.6 | 39.0 | 29.8 | 53.3 | >95 |

The potential for zinc loss by volatilization is much greater with this option, due to a variable carbon content in the dust and higher temperatures compared to roasting.

Future testwork will address the handling of material evolved during thermal dehalogenation. This product will be high in halides and alkalis, and will contain lead, zinc, and cadmium. Hydrometallurgical treatment may provide a supplementary yield of these metals, but the question of halide disposal would remain. Suggested treatments include the removal of fluorides with lime, leaving a final disposable product of crude brine.

Following techno-economic evaluation, the preferred process option can be demonstrated using the new pilot-plant facilities. This scale of demonstration would require minimal scale-up to the commercial requirements of an individual mini-mill operator, to treat about 10 to 15 kt/a.

During the past five years Mintek has gained considerable experience in the processing of steel-plant dusts and lead/zinc-containing slags with testwork up to the 0.8 MW scale. Alloy-steel dust has been processed with feed rates of about 250 kg/h at a power level of 500 kW. Alloys were produced with 6 to 8% nickel and 20 to 24% chromium, with a non-leachable discard slag containing about 3.0% Cr<sub>2</sub>O<sub>3</sub>. Reduction was carried out at around 1550 °C, and losses for the water-cooled furnace shell were about 250 kW. Lead/zinc-containing slags have been fumed at feed rates of about 780 kg/h and power levels of up to 800 kW. Zinc was fumed from the slag bath at about 50 kg/m<sup>2</sup>/h, with an average tapping temperature of 1480 °C. Testwork has shown that disposable slags can be produced from waste materials containing lead and zinc. Some typical results are shown in Table IV.

Extensive use is made of the Mintek PYROSIM(10) computer program to simulate the processing of metallurgical waste materials. This program performs ideal equilibrium calculations based on the minimization of the free energy of multi-component/multi-phase systems. Simulations are conducted at selected temperatures and levels of reductant addition. Processes can be broken

down into stages to determine, for example, the energy saved by feeding molten zinc-containing slag from a lead blast furnace directly to a plasma-arc furnace for fuming. Figures 2 to 4, derived from PYROSIM simulations illustrate some aspects to be considered when designing a zinc fuming process. With varying proportions of reductant, calculations were performed over a range of temperatures for a theoretical material containing reducible zinc, lead and iron. The material contained 2.5% PbO, 12.5% ZnO, and 35.0% FeO with the balance made up of refractory oxides.

TABLE IV. TYPICAL RESULTS FOR THE ENVIROPLAS PROCESS

| COMPONENTS                     | TYPICA | AL DISCARI % by mass | SLAGS | TYPIC ( | AL FUME, %<br>COMBUSTE | FUME, % by mass<br>MBUSTED) |  |  |
|--------------------------------|--------|----------------------|-------|---------|------------------------|-----------------------------|--|--|
|                                | EA     |                      | FD    |         | EAFD                   |                             |  |  |
|                                | LBFS   | CARBON               | ALLOY | LBFS    | CARBON                 | ALLOY                       |  |  |
| Fe0                            | 20     | 60                   | 5     | 0.5     | 3                      | -                           |  |  |
| SiO <sub>2</sub>               | 35     | 15                   | 40    | 0.6     | 1                      | 8                           |  |  |
| Ca0                            | 20     | 10                   | 15    | 0.4     | -                      | -                           |  |  |
| Mg0                            | 5      | 2                    | 15    | 0.2     | 0.4                    | 8                           |  |  |
| Al <sub>2</sub> 0 <sub>3</sub> | 1      | 5                    | 10    | 0.2     | -                      | _                           |  |  |
| Zn0                            | 1      | 1                    | 0.02  | 80      | 70                     | 55                          |  |  |
| Pb0                            | 0.2    | 0.2                  | -     | 15      | 8                      | 3                           |  |  |
| $Cr_2O_3$                      | -      | -                    | 3     | -       | -                      |                             |  |  |
| NiO                            | -      | -                    | 0.2   | -       | -                      | _                           |  |  |
| Zn recovery, %                 | >95    | >90                  | >95   | -       | -                      | -                           |  |  |
| Ni Rec., %                     | -      | -                    | >98   |         | _                      |                             |  |  |
| Cr Rec., %                     | -      | -                    | >95   | -       | -                      | -                           |  |  |

The curves in Figures 2 and 3 indicate an increasing tendency for zinc rather than iron to be produced with increasing temperature. Experimental results indicated on the plot in Figure 3 were obtained from testwork on the fuming of LBFS at the 500 kW scale of operation. LBFS intimately mixed with charcoal reductant was fed at controlled rates to a plasma-arc furnace and varying power input levels were used leading to a range of tapping temperatures. Zinc reduction at this scale approached the theoretical equilibrium levels at temperatures of 1450 °C and higher. At lower temperatures it is assumed that less favourable kinetics and slag viscosities prevailed.

Figure 4 illustrates the energy penalty resulting from operations at significantly higher temperatures and levels of reductant addition. Although reductant additions should be kept to a minimum level for reasons of process economics, the final choice of reductant level is made from a consideration of the CO:CO<sub>2</sub> ratio required to prevent back-reaction of Zn to ZnO in a process where zinc is to, be recovered in a condenser.

When considering the process variable of temperature it is important to take into account the possible influence on the quality of metal product. In the case of alloy-steel dust processing, the yield of alloy produced for recycling will be about 1% of charge mass for alloy-steel production. The dilution factor therefore will probably make the control of metal composition in the treatment furnace less critical and the process would be operated at the highest temperature commensurate with the economic recovery of chromium and nickel, and satisfactory rates of refractory erosion. However, in the case of zinc-containing wastes, it is desirable to recover saleable zinc directly from a condenser. It is likely that side reactions will occur above 1500°C, leading to the cofuming of undesirable elements such as magnesium, manganese, and silicon if they are present in the material. Iron carry-over must also be minimized to limit the formation of hard zinc in the condenser.

Process design by simulation may indicate the most energy-efficient degree of selective reduction to recover valuable metals from waste. However, the first priority has to remain the production of a disposable slag. Reduction may need to be driven beyond the optimum economic point for metal recovery to achieve this. In the case of zinc recovery from LBFS slag some reduction of iron is necessary to achieve the required low levels of zinc and lead in final discard slags. A phase-chemical study(11) of spent slag containing 0.2% lead after plasma-smelting of LBFS has revealed lead present as discrete metal droplets, droplets of metal encircled by a sulphide phase, Cu/Pb alloy droplets, as a minor constituent of a (Fe,Cu)S phase, and dissolved in the slag matrix. Quenching by high-pressure water granulation serves to prevent agglomeration of droplets, and retains a high proportion of lead compounds dissolved in the slag matrix. In this manner, leachable lead is reduced to acceptable limits.

The most important aspect in the control of the ENVIROPLAS process is the balance of power input to the furnace with the feed rate of raw material. This highlights the importance of accurately calculating the specific energy requirements for the process in order to achieve thermal equilibrium at the desired temperature. With set-points for voltage and power, power input control is achieved by automatic adjustment of the arc length. Set-points are chosen to maintain the shortest possible arc without exceeding any electrical limits imposed on the power supply. Short arcs contribute to stable operating conditions and increase the stirring effect resulting from high currents. Excessive side reactions are prevented by the introduction of feed materials at a controlled rate into the arcattachment zone to limit the temperature.

#### Mintek's Pilot-plant Facilities

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Serious consideration was given to adapting the existing 3.2 MVA furnace, which has been described elsewhere (12,13), to waste treatment with the recovery of saleable zinc and lead. The concept was rejected mainly because a furnace of this capacity, which has an operating range of 0.5 to 1 MW dc power, could barely sustain the very smallest practicable ISP splash condenser.

It was decided to opt for a larger plant, which would cater for both waste processing tests and conventional smelting operations. The main questions addressed were how best to obtain a versatile unit and to achieve 'right-sizing' without sacrificing operability. The fruits of our deliberation are described below: a schematic flowsheet is shown in Figure 5. At the time of writing, the erection phase is underway, with the feed system and one arc furnace already in position. Mechanical completion is planned for early 1994.

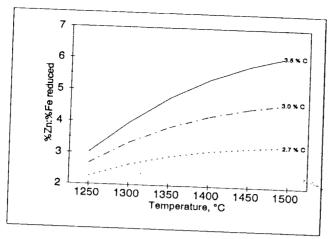


Figure 2. Selectivity of zinc reduction: ratio Zn:Fe at equilibrium

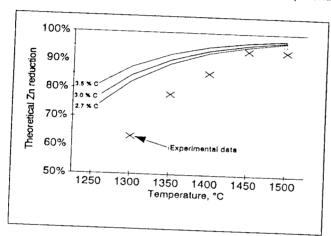


Figure 3. Selectivity of zinc reduction: percentage of Zn reduced at equilibrium

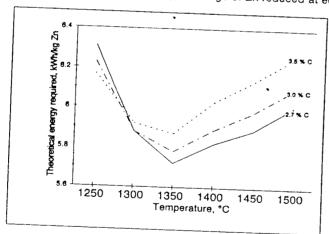


Figure 4. Variation of specific energy requirement for zinc recovery

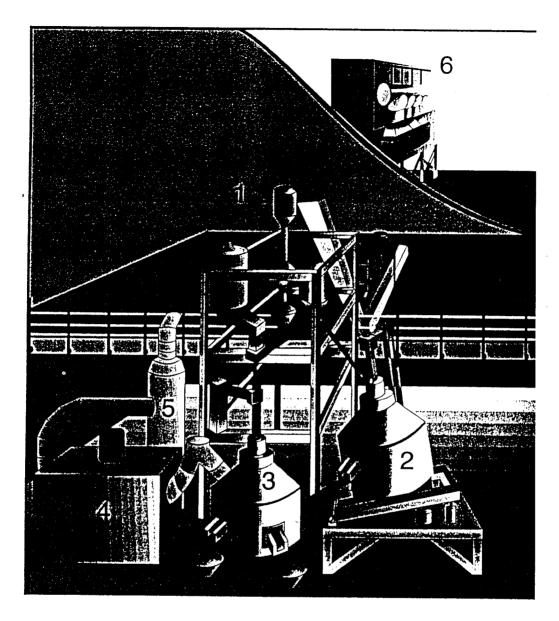


Figure 5. Schematic arrangement of the new Mintek demonstration-scale pilot plant

## Batching and Feed System (1)

For granular and lumpy materials, an improved version of the system used for the 3.2 MVA unit was designed. This comprises 8 batching bins, of varying sizes, which are mounted on load cells. Using the mass-loss principle, the various ingredients are fed to a Flexowell conveyor, chosen for its capability to operate at a high angle of incline, which then supplies an essentially homogenous mixture to the furnace feed bins.

Fine material, such as EAF dusts, will be handled somewhat differently, and the final design will depend on the outcome of trials that are currently in progress. This part of the plant is less urgent because the first research campaign will be on a granular material such as lead blast-furnace slag. In the design of the fine feed system, due consideration will be given to the appropriate technique for dehalogenation.

One criterion applied to the feed plant is that, once steady conditions are achieved, the accuracy of batching will be  $\pm$  1–2 %.

### Furnaces (2 and 3)

Allowance has been made for two work-stations, which can accommodate different type of furnaces. One station (Item 3) will be equipped with a hollow-electrode dc arc furnace, which will probably be a permanent installation, while the second station (Item 2) will, over the years, cater for both electrical and fossil-fuel unit operations.

The permanent furnace consists of a cylindrical refractory-lined shell with a dished bottom. The side are cooled by an open film of water cascading down the outside of the shell, and the bottom of the furnace shell is air-cooled. The shell is fixed in position, and is equipped with two operational tapholes. The roof of the furnace is water-jacketed and has a refractory lining. A refractory centre section isolates the electrode from the water-cooled section of roof.

The dc power pack specified is rated at 5.6 MVA, and can supply dc current at 10 kA at a maximum voltage of 500 V. The operational envelope is wide with respect to both current and voltage. The pack, which will operate at 12 pulse, can be split into two separate 6-pulse units each having a capability of 500 V and 5 kA.

The selection of electrode voltage, current, and physical dimensions of the electrode, are chosen to achieve the following effects:

- a short arc length to limit the amount of radiant energy from the arc that impinges on the walls
- a high d.c. current, which will induce a strong flow of ionized gas under the electrode. This flow can reach a velocity of several hundred metres per second, and is expected to assist the projecting of the feed material forcefully into the slag under the electrode. By a similar mechanism, the conductive slag and metal would also be expected to move downwards from the arc zone. This would favour that cold material is rapidly mixed with the molten bath material.

The electrode control system is programmed to keep the electrode voltage and power at specified values. The same control system would also maintain a match between electric power and feed rate.

The anode consists of a large number of circular steel pins which, due to their shape, are resistant to melting over their whole length. The pins are connected to a circular hub plate, which forms the centre of a large spoked disc. The outer connecting ring of the disc provides the connection points for the return bus bars to the transformer.

For one of the initial research campaigns, which will use a lead blast-furnace slag, the process requires that the feed to the reduction furnace must be molten. Trials showed that electrical melting is the most appropriate method and the decision was made to install, in the second-work station as Item 2, another dc arc furnace to act as a pre-melter. A heated launder will be provided, and the intention is to effect a continuous feed of molten slag from the pre-melter to the fuming furnace, which will, of course, be fed with reductant.

### ISP condenser (4 and 5)

The lead splash condenser is coupled directly to the furning furnace, but a bypass facility exists. Discharge gas from the condenser or the furnace proceeds via a combustion chamber (Item 5), where carbon monoxide is combusted.

The zinc capacity of the condenser ranges from an effective low of 2 t/d up to 6 t/day (in all cases a ton refers to  $1000 \,\mathrm{kg}$ ). It will be equipped with a single rotor, which maintains the curtain of lead droplets. The depth of rotor immersion and the rotational speed can be varied over a relatively wide range.

Apart from the zinc tapping facility, this pilot-plant condenser is almost an exact copy of industrial ISP units. On an industrial scale, we expect that Prime Western Grade zinc will be produced. One aspect still to be confirmed by research is the need for the appropriate level dehalogenation of the feedstock, i.e. we still have to establish the maximum tolerable levels of halogens and alkali metals in the feedstock.

#### Gas Cleaning (6)

An existing bagfilter plant will be used to handle the minimal gas load from the pre-melter. However, the fuming-furnace gas will require different treatment, due to its high temperature and its potential for containing particulate matter. Enough dilution/cooling air will be utilized to ensure adequate gas velocities, while the main cooling load will be handled by a radiant, trombone cooler. The bag plant itself is designed for 25 000 m<sup>3</sup>/h of gas at a velocity of 0.8 m/min.

#### Controls

Apart from the ISP condenser, which will be manually operated, the plant will be automatically controlled from a PLC system which has considerable data-logging capabilities. One feature is a fairly sophisticated gas-pressure control system, which is necessary to maintain the required positive pressures in the fuming furnace and ISP condenser.

## Design of Industrial-scale Plants

Over the past three years, much thought has gone into the design of commercially sized facilities, and this knowledge, allied to the expertise derived from pilot work at Mintek and industrial experience on the part of Pyromet CC, has been put to good use in designing the pilot plant.

Indeed, the pilot plant itself could rate as an industrial unit, having a capacity of between 10 000 and 20 000 t/a of feedstock. Once this has performed successfully, we would be confident in scaling up by a factor of up to 10 times.

954

Because an industrial facility would not require the flexibility of the pilot plant, it would exhibit simpler features in certain areas, such as the furnace feed system. The furnace would be designed on very similar lines to the pilot unit, as would the lead splash condenser. Depending on capacity, the condenser may have multiple of rotors, and perhaps a slightly more elaborate zinc tapping section including a liquation stage to enable PWG grade metal to be produced directly.

The pilot plant is equipped with a bagfilter plant which is designed to meet the most stringent environmental requirements, and again this would most likely serve as a model for the commercial

Figures 6 and 7 show a conceptual elevation and footprint of a dedicated unit. The control room is sited to provide maximum visibility. A tapping platform is located in front of the taphole for lancing and plugging of the tap hole. Hot metal and/or slag are tapped into ladles from the furnace\_ and decanted into chill moulds for cooling; alternatively, slag can be tapped into a slag runner for collection and cooling in a lined slag pit or granulated if necessary. The slag can be disposed of

## **Economic Considerations**

From the outset, one of the key factors in the development of the Enviroplas process was 'viability'. The process, in more recent years, has been directed specifically at the treatment of environmentally hazardous materials. These materials would normally carry a premium for disposal by existing methods. In such cases the Enviroplas process is energy- and environmentally-efficient and is competitive when compared with existing disposal/treatment costs. However, the Enviroplas process was not developed just to compete with existing processes on a cost basis, but to take the viability of the process to the next stage, i.e. the successful and profitable recovery of valuable metals from the waste materials treated.

## **Examples of Operational Costs**

Two examples of the treatment cost of steel-plant dusts are shown in Tables V and VII. These examples compare carbon and steel plant dust and a typical alloy over three different plant sizes, treating 10kt, 30kt and 100kt respectively.

#### Notes

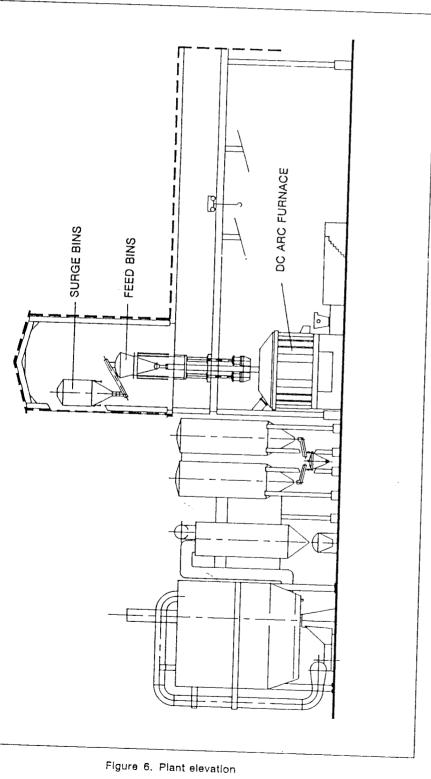
- 1. The examples ignore existing disposal costs.
- 2. Fixed and variable operating costs are based on conservative costing factors
- 3. The capital cost is for a turnkey plant, but excludes land.

## Sensitivity Factors Affecting Viability

Like any process, the Enviroplas process is sensitive to factors that impact on its economic viability, although throughout the development of the process these factors have been considered and are easily quantifiable at an early stage.

### These factors are:-

- plant throughput (eg marginal at <5000 t/a)
- zinc content (eg marginal at <15% Zn in the case of carbon-steel dusts)
- · nickel content in the case of alloy-steel dusts
- · existing disposal costs if currently low
- established and near-priced competing process
- electrical costs, which count for 35-45% of the total operating costs.



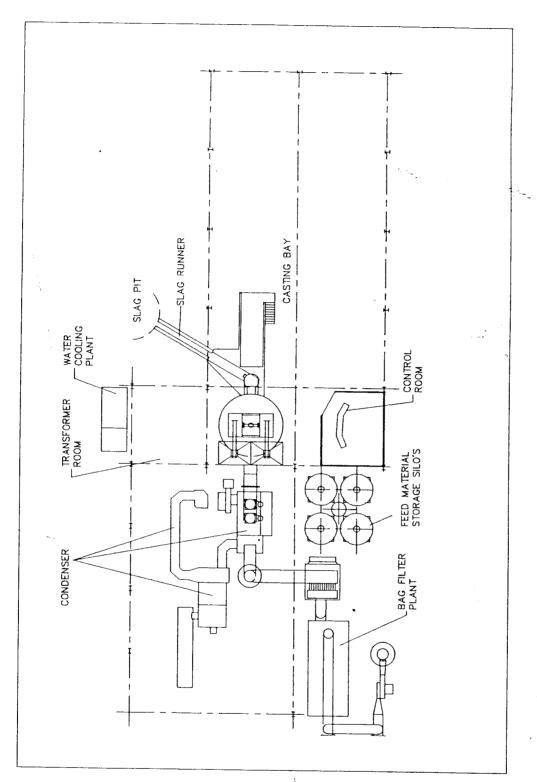


Figure 7. Plant footprint 957

TABLE V

## FINANCIAL SUMMARY - TREATMENT OF CARBON STEEL PLANT DUSTS

COUNTRY : USA DUST : DRY - ARISINGS FROM BAG FILTER PLANT

|   |                         | ,                          |                                |                |
|---|-------------------------|----------------------------|--------------------------------|----------------|
| 1.1 VARIABLE COSTS (\$'000/a)   |                         | 10 kt/a                    | 30 kt/a                        | 100 kt/a       |
| ELECTRICITY REDUCTANTS & ADDITIVES ELECTRODES CONSUMABLES                           | 509<br>84<br>116<br>100 | 1 452<br>251<br>348<br>300 | 4 584<br>837<br>1 166<br>1 000 |                |
| TOTAL VARIABLE COSTS  | TOTAL VARIABLE COSTS    |                            |                                |                |
| 1.2 FIXED COSTS (\$0'000/a)   |                         |                            |                                |                |
| OPERATING LABOUR<br>MAINTENANCE & STORES  |                         | 720<br>250                 | 880<br>500                     | 1 440<br>1 500 |
| TOTAL FIXED COSTS   |                         | 970                        | 1 380                          | 2 940          |
| 1.3 TOTAL OPERATING COSTS (\$'00  | <u>0/a)</u>             | 1 779                      | 3 731                          | 10 527         |
| COST PER TONNE DUST (Ignoring revenue from metal) (Ignoring present disposal costs) |                         | 178                        | 124                            | 105            |
| 2.1 FIXED CAPITAL (\$'000)  |                         | 5 000                      | 10000                          | 30 000         |
| 3.1 SALEABLE METALS IN DUST   | %                       |                            |                                |                |
| ZINC (t/a)  | 25                      | 2 500                      | 7 500                          | 25 000         |
| 3.2 METALS RECOVERED %  |                         |                            |                                |                |
| ZINC (t/a)  | 90                      | 2 250                      | 6 750                          | 22 500         |
| 3.3 REVENUE for ZINC METAL (\$'000/a)   |                         |                            |                                |                |
| ZINC METAL  |                         | 2 250                      | 6 750                          | 22 500         |

TABLE VI FINANCIAL SUMMARY - TREATMENT OF ALLOY STEEL PLANT DUSTS

COUNTRY: USA DUST: DRY - ARISINGS FROM BAG FILTER PLANT

|   | 10 kt/a                         | 30 kt/a   | 100 kt/a  |  |
|---|---------------------------------|---|---|--|
| ELECTRICITY REDUCTANTS & ADDITIVES ELECTRODES CONSUMABLES |                                 |   | 6 429<br>1 540<br>1 160<br>1 000                      | 1  |
| TOTAL VARIABLE COSTS                                      |                                 |   |   |  |
|   |                                 |   |   |  |
|   | 720<br>250                      | 880<br>500  | 1 440<br>1 500  |  |
|   | 970                             | 1 380   | 2 940   |  |
| 00/a)   | 2 054                           | 4 526   | 13 069  |  |
|   | 205                             | 151   | 131   | \$   |
|   | 5 000                           | 10 000  | 30 000  |  |
| %   |                                 |   |   |  |
| 2.6<br>9.0<br>36.9  | 260<br>900<br>3 690             | 770<br>2 710<br>11 070  | 2 550<br>9 020<br>36 910                              |  |
| %   |                                 |   |   |  |
| 98.0<br>98.7<br>98.9                                      | 250<br>890<br>3 650             | 750<br>2 670<br>10 950  | 2 500<br>8 900<br>36 500                              |  |
| 000/a)  | 2 395                           | 7 185   | 23 950  |  |
|   | % 2.6 9.0 36.9 % 98.0 98.7 98.9 | 714<br>154<br>116<br>100<br>1 084<br>720<br>250<br>970<br>2 054<br>205<br>5 000<br>%<br>2.6<br>9.0<br>900<br>36.9<br>900<br>36.9<br>98.0<br>98.7<br>98.0<br>98.7<br>98.9<br>3 650 | 714   2 036   462   348   300   1 084   3 146   3 146 | 714 154 462 1540 1160 1000 1000 1000 1000 1000 1000 10 |

## **Future Developments**

Environmental pressures on the mining and metallurgical industries will probably continue to increase, and will spread to the developing countries, from which first-world countries are importing an ever-increasing quantity of beneficiated products. Increased amounts of scrap materials are being recycled in first-world countries to minimize importation and to address environmental issues. The composite nature of scrap generally gives rise to a variety of by-products other than the primary metal being recovered. The separation of scrap into different metal species is not feasible in many instances, and the recycling industry has to increasingly take this into account. The design of manufactured goods is now being influenced by the need to recycle, recover, or dispose of all components, but it will be at least a decade before any major influence is felt. The need to clean up existing dump sites and current arisings will therefore continue to grow.

In South Africa the availability of scrap is limited, and a high proportion of DRI is used. Most EAF dusts have therefore not posed a serious environmental problem. South Africa has only one stainless-steel producer - Columbus Stainless Steel. Serious consideration is being given to the treatment of EAF and AOD dusts from both stockpiles and current arisings. Zinc-containing drosses are produced from hot-dip galvanizing, and could be used to produce high-grade zinc feedstocks. However, testing and development work is required to ensure that PWG metal can be produced. For example, low-grade zinc secondaries could be used to produce high-grade zinc metal powders and chemicals.

The production of primary zinc from complex orebodies by fuming zinc from either roasted concentrates or primary leach residue is worthwhile pursuing, to resolve the disposal problems associated with conventional electrolytic zinc residues. Upgrading of the PWG zinc produced by direct condensation of vapour to higher grade zinc by improved reboiler and other technologies should be considered.

The Enviroplas technology offers the flexibility to treat a very wide range of environmentally hazardous materials either singly or in combinations as campaigns. The co-processing, for example of LBFS and zinc-rich EAF dusts can be considered. Disposable slags can be produced, together with valuable products that can be sold to offset treatment costs, and in some instances make profits. The demonstration of the suitability of a lead splash condenser for the Enviroplas process is eagerly awaited during 1994, so that the Enviroplas approach can be promoted to the many potential recipients of the technology.

#### Conclusions

The main advantage of the Enviroplas process are as follows.

- The process has great flexibility with regard to selection and treatment of a wide variety of feed materials; including EAF dusts and sludges, AOD alloy dusts, millscale fines, lead-blast furnace slags, and residues from electro- and hot-dip galvanizing, pickling operations, and base-metal recycling plants.
- The solid feed materials can be introduced down a hollow graphite electrode directly into the high-temperature reaction zone, so that power input and the desired reactions can be optimally controlled.
- The design of the power supply ensures the appropriate current and voltage, and hence are length, are employed to achieve efficient operation and the minimum of feed carry-over by

elutriation. Unwanted side-reactions are minimized by careful control of the feed recipe and the balance between feed rate and power input. The short arc lengths used as a result of the high currents that are attainable favour these conditions.

- The linking of lead splash condenser to an Enviroplas furnace should ensure good recoveries and qualities of lead and zinc. However, testwork is still to be carried out to demonstrate this for various feed materials. Partial pre- or post-dehalogenation is being evaluated as a means of improving the process. Pyrohydrolysis is one option under consideration(20).
- High fuming rates and extraction levels for zinc and lead, and alloying components (e.g. Ni, Cr, Mn) can be achieved at high power fluxes, which results in smaller more efficient furnaces being useable.

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# MATHEMATICAL MODELING OF IN-SITU VITRIFICATION

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#### ABSTRACT

In-situ vitrification (ISV) is a new technology used for treating radioactive, organic and inorganic contaminated soils. In this process, electricity is applied through electrodes buried in the contaminated soil to melt it and form an environmentally stable glass-like solid. The organic contaminants and volatile metals are vaporized during heating up, the non-volatile inorganic elements are dissolved and incorporated into the melt. In present full-scale operation, the ISV process can treat 4 to 6 tons of soil per hour at consumption of about 1000 kWh per ton of soil. In this study, various configurations of electrodes were examined in a mathematical model. The results may be used to optimize the ISV process.