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TECHNOLOGY FOR THE TREATMENT OF STEEL-PLANT DUSTS

by

Nicholas A. Barcza and Lloyd R. Nelson

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# TECHNOLOGY FOR TREATMENT OF STEEL-PLANT DUSTS

N.A. Barcza and L.R. Nelson

Mintek, Private Bag X3015, Randburg, 2125, South Africa

## INTRODUCTION

The production of carbon steels and alloy steels (including stainless steels) generally involves the use of a proportion of recycled scrap steel, depending on its availability and cost. The characteristics of these scrap steels vary considerably according to their origins. Scrap sourced from redundant products usually contains a wide variety of elements, including zinc, lead, cadmium, nickel, and chromium.

Melting processes such as the electric arc furnace (EAF) and converter processes such as the basic oxygen furnace (BOF) and argon-oxygen decarburization (AOD) generate about 2 per cent of the product mass as fine dust or fume. Much of this material is extremely fine ( $<10\ \mu\text{m}$ ), since it is formed primarily by the oxidation of metallic vapours. Some physical entrainment of fine feed material (10 to  $200\ \mu\text{m}$ ) such as fluxing agents (e.g. lime) occurs too. The primary constituent of the fume is, however, iron oxide which is not a hazardous problem in itself. The environmental difficulties arise from the content of certain heavy metals or elements that are classified as hazardous by a number of countries, in particular the USA. These specifically include lead, cadmium, nickel, and chromium<sup>1</sup>. Very strict legislation has been, and is being, imposed to address the environmental concerns regarding the contamination of water by these elements by run-off or infiltration into the water table from dumps and landfill sites. The USA has taken the lead in this regard. The regulations of the Environmental Protection Agency (EPA) designate EAF dusts as hazardous waste material K061. Disposal of these materials in landfill sites is now illegal, and the disposal of any wastes generated from the treatment of EAF dust is dependent on delisting the wastes as non-hazardous. Obtaining permission for delisting is often a time-consuming and expensive procedure. Regulations vary from state to state, but the direct coupling of the dust-treatment plant with dust-collection equipment in a totally enclosed manner could exempt the steel producer from some of the regulatory standards.

The problem of hazardous dusts has generated an opportunity for vendors of technology and equipment to find appropriate solutions. Although a number of well established processes have been used to recover zinc, lead, and alloying components such as chromium, nickel, manganese, and molybdenum for many years, not all of these approaches fully meet the strict

EPA requirements. Some of these processes can be, and are being, adapted and new methods such as plasma-arc technology, have emerged during the past decade.

Environmental, economic and performance criteria will decide which of these processes will be acceptable, since in most instances site-specific considerations will have a major influence. The key factors are the quantity and nature of dust arisings, disposal costs, legislation, transportation considerations, energy costs (e.g. fuel-based versus electrically-based processes), product quality and value, and the availability of, and support for, technology implementation.

The world-wide production of EAF steel-plant dust probably amounts to more than 5 Mt/a and if other sources are taken into account the total could be four to five times this amount. A large proportion of these dusts are not, as yet, necessarily being treated by the most environmentally friendly and economically favourable processes. An amazing number and diversity of potential solutions have been proposed, and some have been developed and commercialized. Evaluation of the many options is a complex task yet consideration of the theoretical and practical aspects of the processes does go a long way towards indicating the best option for a given application.

## PROCESS OPTIONS

Four general categories of process options exist: chemical treatment, recycling, thermal (non-electrical), and thermal (electrical). The choice of process is primarily controlled by the type of dust to be processed. The following four broad categories of dust exist:

### Carbon-steel dusts

Low-zinc dust (<15 per cent Zn)

High-zinc dust (>15 per cent Zn)

### Alloy-steel dusts

Low-zinc (<15 per cent Zn)

High zinc (>15 per cent Zn)

Low-zinc carbon-steel dusts represent the least valuable category, and their treatment is generally dictated by environmental rather than economic considerations. Chemical treatment and recycling are appropriate processing options for such dusts.

The other three dust categories are more challenging technically and economically. Although the chemical treatment of high-zinc carbon-steel dusts may be technically feasible, thermal treatment appears to present a more promising option. Furthermore, in the USA, EPA legislation requires dusts containing more than 15 per cent zinc to be treated by a thermal route.

The alloy-steel dusts can be treated by chemical techniques if the zinc content is less than 15 per cent. However, thermal treatment for the economic recovery of the valuable alloying elements (particularly nickel, chromium, and molybdenum) is a preferable option. The

emphasis in this review is on the thermal treatment of high-zinc carbon-steel dusts and low- and high-zinc alloy-steel dusts. Selection of this approach is motivated by both environmental and economic considerations.

## THEORETICAL CONSIDERATIONS

The theoretical assessment has been limited to thermal processes involving liquid slag and metal phases, which are applicable to the treatment of the carbon-steel (high-zinc), alloy-steel (low-zinc) and alloy-steel (high-zinc) categories of steel-plant dusts (Table 1). The PYROSIM computer program<sup>2</sup> has been used to calculate ideal equilibrium simulations of 'typical' such dusts, and to predict their various product and process characteristics (Table 2), thus providing the primary criteria for evaluation.

### Carbon-steel (High-zinc) Dust

Thermodynamic simulations of the effect of incremental additions of fixed carbon on the treatment of a 'typical' high-zinc carbon-steel dust indicate two distinct potential operating regimes (Fig. 1), selective reduction of ZnO, or total reduction of ZnO and FeO.

Since the activity coefficients of all species have been taken as being unity, but in reality will deviate from ideality, these 'ideal' simulations do not always predict the exact results, but should give a realistic picture. In selective reduction, control of the fixed-carbon addition is critical to reduce and volatilize the ZnO, PbO, and CdO contents while leaving iron oxide unreduced in the slag phase. The zinc-rich product gases are amenable to further processing, preferably to yield metallic zinc (and lead) in a zinc condenser connected directly after the furnace. The iron-oxide-rich slag, which is aggressive towards refractories, is potentially recyclable to primary iron-making operations, since the ZnO, PbO, CdO, alkali metals and halide species are substantially reduced.

The maximum concentration of zinc in the vapour phase (about 50 per cent) occurs at a fixed-carbon addition of 5 per cent of the dust (by mass). The residual ZnO content in the slag is 7.5 per cent; this ZnO, together with the other heavy-metal species, could cause these slags to exceed their maximum allowable leachable limits. The low  $p_{\text{CO}}/p_{\text{CO}_2}$  ratio of 0.8 would result in some reoxidation of the zinc and a lower zinc recovery in the gas phase, probably offsetting the benefit of the relatively low energy consumption of 0.71 MWh per tonne of dust (Table 2).

If the objective is the direct condensation of metallic zinc, operation under slightly more reducing conditions (10 per cent fixed-carbon addition) is expected to enhance recoveries by lowering the losses of zinc to the slag phase (a slag containing 0.3 per cent ZnO is predicted),

and ensuring a more reducing atmosphere with a ( $p_{\text{CO}}/p_{\text{CO}_2}$  ratio of 14)(Table 2). A greater theoretical energy requirement (0.84 MWh per tonne of dust) results from the partial reduction of iron oxide to iron.

Iron oxide is totally reduced at a fixed-carbon addition in excess of 15 per cent. The minimum predicted theoretical energy requirement is 1.16 MWh per tonne of dust (Table 2). The recovery of zinc in a condenser is adversely affected by the lower concentration (39 per cent) of zinc in the off-gases (Table 2), and because of the fuming of manganese, silicon, magnesium, and iron species from the melt. These species form heterogeneous condensation sites, which promote the deleterious formation of dross within the condenser. Further possible disadvantages of total reduction are the higher cost of electrical energy, and contamination by tramp elements (particularly sulphur and phosphorus) of the metal.

### **Alloy-steel (Low-zinc) Dust**

The thermal processing of low-zinc alloy-steel dusts probably does not warrant the direct condensation of metallic zinc from the furnace off-gases. The vapour products and gases are best combusted, and the ZnO, PbO, and CdO fume collected and sold to a dedicated zinc producer as a raw material. The results of ideal equilibrium simulations predict substantially the total recovery of the valuable alloying elements (except manganese) to the metal, and a theoretical energy requirement of 1.22 MWh per tonne of dust (Table 2).

### **Alloy-steel (High-zinc) Dust**

The thermal treatment of high-zinc (up to 30 per cent ZnO in some instances) alloy-steel dusts poses a tremendous processing challenge. An innocuous, disposable slag must be produced, the recovery of alloying elements to a valuable Ni-Cr-Mo-Mn-Fe alloy maximized, and consideration given to the recovery of a valuable zinc product by direct condensation of the furnace off-gases. The selection of the optimum process parameters and metallurgical conditions that are necessary to meet the technical and economic requirements is complicated by conflicting issues.

Ideal equilibrium thermodynamic simulations provide a preliminary indication of the optimum processing conditions that are most likely to result in these three objectives being achieved simultaneously. Clearly, in order to render the slag innocuous for disposal its heavy-metals content, particularly of leachable lead, cadmium, nickel and chromium species, must be minimized. Whereas lead, chromium, and nickel are readily reduced from their oxides, fixed-carbon additions in excess of 20 per cent are predicted necessary to strip the chromium oxide content of the slag to acceptable levels (Fig. 2).

At a fixed-carbon addition of 21.3 per cent and a predicted theoretical energy requirement of 1.33 MWh per tonne of dust, substantially all of the nickel, iron, and chromium units are predicted to be recovered to the metal phase, but only 84.4 per cent of the manganese reports to the metal (Fig. 3). If larger additions of fixed-carbon (i.e. more than 21.3 per cent) are made to improve metal recoveries, a solid phase consisting of carbon (and possibly traces of  $\text{CaC}_2$ ) is predicted to exist under equilibrium conditions (Fig. 3).

If the direct condensation of zinc from the off-gases is to be attempted, fixed-carbon additions of less than 17.5 per cent would be desirable, since above this level the vaporizing-fuming of manganese, magnesium, silicon, and iron is predicted to become significant (Fig. 4).

Undesirable consequences of this are impaired condenser efficiency, and a predicted increase in the theoretical energy requirement.

### **Process Control Considerations**

#### **Bath temperature:**

The required addition of fixed carbon in the feed, and an appropriate operating temperature (around 1500 to 1550°C), are of fundamental importance in achieving the necessary control over the process. The process temperature is controlled by the feed-to-power ratio in electrically-based thermal systems. Increases in the temperature of operation have the positive effect of driving the reduction of alloy metal oxides substantially towards completion. However, the predicted theoretical energy requirement per tonne of dust is increased (from 1.28 MWh at 1450°C to 1.61 MWh at 1775°C for a fixed-carbon addition of 25 per cent), and vaporizing-fuming, especially of magnesium, manganese, and silicon<sup>3</sup>, becomes significant (Fig. 5). Furthermore, significant amounts of  $\text{CaC}_2$  (melting point 2300°C) can form, especially during operation at temperatures higher than 1650°C.

#### **Slag chemistry:**

In most instances the dusts produce self-fluxing slags, which possess suitable physico-chemical characteristics (liquidus temperatures less than 1450°C and viscosities less than 5 P at 1500°C) for furnace operation. Additions of flux such as silica or lime can be made where the lime-to-silica ratio of the product slag deviates significantly from about unity, but at the expense of increased process energy requirements. Flux additions can also be made to alter the activities of individual species contained within the slag phase, and hence to optimize the distribution of certain species. It may be feasible to limit the problem of the vaporization of sodium and possibly potassium to some degree (Fig. 4) by control of the slag basicity.

## DISCUSSION OF PROCESS OPTIONS

Table 3 summarizes most of the important alternative processes for the treatment of steel-plant dusts. The alternatives have been classified into non-thermal processes (chemical-, hydrometallurgical-, and recycle-based) and thermal processes (fuel-based, and electrically-based). Plasma-arc processes fall under this latter category.

### Chemical and Hydrometallurgical Treatment

A chemical pretreatment process to remove zinc, lead, and other heavy metals from scrap prior to melting in the EAF has been developed by Metals Recovery Industries (MRI) and is practised at a de-zincing plant treating 70 t/d in Hamilton, Ontario. A 400 t/d plant is now under construction at a major steel producer in North America.

Hydrometallurgical treatment of secondary fume (produced from, for example, the Waelz rotary-kiln process) to electrowin the zinc is one of the areas of chemical treatment following a thermal treatment process.

The zinc industry has used the so-called jarosite process for more than twenty years to process iron-containing zinc ferrite. Lixiviants such as NaOH, HCl, and H<sub>2</sub>SO<sub>4</sub> as well as organic lixiviants, have been used to test the treatment of steel-plant dusts. The leach residues are in some instances disposable, or they can be processed for the recovery of iron units. The NaOH process has been developed to a commercial scale to recover zinc as the primary product and lead and cadmium as by-products, and is in commercial operation for EAF dust treatment at St.-Florentin in France.

The Super Detox Process developed by Bethlehem Steel is based on chemical stabilization rather than the recovery of zinc. It is appropriate for certain dusts containing less than 15 per cent zinc, since the toxic components can be stabilized with aluminosilicates, lime, and other additives. The heavy metals are physically bound in the calcium aluminosilicate matrix. Testwork showed that about 98 per cent of the material met the required EPA toxicity-characteristic leaching procedure, although it can take up to 30 days to become fully stabilized.

Steel-plant dust from Northwestern Steel and Wire in Sterling, Illinois, is processed by the Super Detox process on an own-and-operate basis by Conversion Systems Inc. (CSI). Delisting of the dust being treated by this process is awaited.

Roanoke Technical Treatment & Services Inc. (RTT&S) has developed a chemical stabilization process to treat low-zinc EAF dust using chemicals and cement. Roanoke Electric Steel in Roanoke, Virginia, has achieved the EPA delisting of its dust based on

this chemical process, which is totally enclosed from the baghouse to the discharge for landfill. RTT&S is prepared to licence its process to steelmakers on the basis of a fixed fee per tonne of meltshop production.

### **Recycling Processes**

Many steel-plant operators have implemented processes to recycle their dust arisings and return them directly to the unit operations from which they arose, or in some cases to other processes. Dereco Inc. of Cleveland, Ohio have developed a briquetting process that has been employed at J&L Speciality Products Corp. in Midland, Pennsylvania. The briquettes consist of stainless-steel dust, and the ratio of briquettes to product metal is about 0.1. Since the dusts contain nickel, only nickel grades of stainless steel are produced from briquetted dust feed. The zinc concentration progressively builds up in the baghouse dust and once a level of 30 to 35 per cent is reached the recycle loop is purged. High recoveries are reported for most elements. Thyssen in Germany use the Lurgi-Thyssen Steel Gas process to recycle hot briquettes to both the Linz Donawitz (LD) converter and the EAF. Process Calx Inc. of Birmingham, Alabama, is promoting a briquetted product called Calx-Briq, a lime-based flux for steelmaking that incorporates EAF dust. The ingredients include bauxite, dolomitic limestone fines, and iron ore fines. The green briquettes are fired in a lime kiln, and serve as a replacement for pebble lime in steel meltshops. Testwork was carried out at IMIS in Salbillo, Mexico, during mid-1989 and further tests are being carried out in the USA.

Pelletizing is often used to agglomerate dust prior to recycling. Nippon Steel in Japan use cold-bonded pellets with a cement binder. They are recycled to the LD (BOF) converter. Krupp use a pelletized recycle feed to a commercial EAF in Siegen, and to a KHD sintering strand on a trial basis in Rheinhausen.

The recycling of fine dust without agglomeration has been tested on a full industrial scale by Klöckner Stahl GmbH at their Georgsmarienhütte works. The fine dust is injected with lime and fine carbonaceous materials via the tuyere into the combined oxygen steelmaking process (KMS process). Iron is recovered in the steel bath, and zinc, lead, and cadmium are concentrated in the fume. Some of the fume is recycled directly to the KMS process.

### **Fuel-based Thermal Processes**

The Waelz Kiln, which dates from 1923, is one of the oldest established zinc-recovery processes. It was developed for treating low-grade zinc ores, but has been adapted to handle a feed consisting entirely of EAF dust. Dust treatment plants have been operating in Germany since 1973. The most recent plant is that of Horsehead Resources Development Co. Inc. (HRD) in the USA, which was installed in 1986, and treats 410 t of dust per day.



The mild-steel dust is blended with coke breeze or other reducing agents, and limestone and is fed to the rotary kiln. The metal oxides are reduced and the volatile metals such as zinc are reoxidized in the kiln atmosphere. The oxides are recovered in baghouse filters; the zinc content of the product is between 50 and 55 per cent. Iron is not recovered but the FeO-containing residue can be disposed of. High-alloy dusts are probably unsuitable as feed, since the residual chromium level would be too high, necessitating further treatment or highly reducing conditions. Several rotary-kiln-based plants are in operation in Japan (Table 3). These operations are frequently differentiated by the widely varying reduction temperatures employed, and degrees of product metallization achieved.

The Inmetco process at Ellwood City, Pennsylvania, uses a rotary hearth furnace (RHF) instead of a kiln to treat stainless steel dusts from the EAF and AOD processes. Green composite pellets containing a reducing agent are fed directly into the RHF, which operates at about 1250°C. Zinc and lead oxides are collected in the exhaust, and the pellets, which are highly metallized are transferred to a submerged-arc melting furnace to recover the alloying elements and iron.

The St Joe Flame Reactor, which has been in operation as a 20kt/a demonstration plant since 1983 at Monaca, in Pennsylvania, treats a variety of waste materials. Dry feed is injected into a reducing high-temperature flame produced by combusting fine coal that is injected into a water-cooled burner. Oxygen enrichment is used to produce a high-temperature flame, between 1500 and 1800°C. The volatile metals are oxidized, and are recovered in a baghouse. The slag, which contains the iron as oxide, is suitable for cement aggregate since it passes the EPA leaching test. Cobalt, nickel, and copper can be reduced, but the oxygen potential is too high for the reduction of chromium oxide. HRD has had a recent proposal to TAMCO, Etiwanda, California, accepted for a 40 t/d EAF dust-treatment plant.

The zinc-rich fume must be further processed to recover the valuable metallic elements. The fume is relatively high in iron oxide, alkalis, and chlorides. These elements, together with lead, are removed prior to treatment in an electrothermic process, a variation of which is also used in Japan by Ryoho Recycle Company. At the St Joe zinc plant, a novel 'U-tube' zinc condenser is used.

### **Electrically-based Thermal Processes**

The electrically-based thermal processes allow sealed reactor design, high energy-density operation at low oxygen potentials, reduced gas volumes, and suitably high off-gas temperatures. These features afford the following major process advantages:

- the potential to condense valuable metals directly from the furnace off-gases, and

- the potential to substantially strip the slag phase of chromium oxide and other alloying elements, and so maximize their recovery to a valuable alloy phase.

The Elkem multi-purpose furnace (EMPF) technology will be applied industrially for the first time at the Laclade Steel in Alton, Illinois, for the treatment of EAF dust (110 t/d). The process requires a dried agglomerated feed, which is prepared by blending dried EAF dust, carbonaceous reductant, and silica flux together with a water-free binder, followed by briquetting and extensive screening. In this way, the presence of water vapour and dust in the furnace off-gases are minimized.

The briquettes are fed to a totally sealed three-phase slag-resistance furnace. Selective carbothermic reduction of the zinc oxide is carried out in the furnace but, consistent with the simulations (Fig. 1), some reduction of iron oxide to metallic iron is claimed necessary to maximize the recovery of zinc to the vapour phase. The aggressive fayalite-type slag produced by this reaction is contained by a non-consumable freeze-lining, achieved with a hot-media thermal oil-cooling system. The metallic zinc product is condensed from the furnace gases in an Imperial Smelting Process (ISP) zinc splash condenser connected after the furnace.

### **Plasma-arc Processes**

Numerous plasma-arc processes have been proposed for the commercial treatment of steel-plant dusts, owing to a number of perceived processing advantages (Table 4).

#### **Three-phase, a.c. plasma-arc systems**

The Mannesman-Demag dust-treatment system is based on 3-phase a.c. plasma technology developed by Krupp. Trials conducted on the 30 t/d pilot-plant facility have been primarily aimed at the thermal destruction of organic pollutants contained in filter dusts derived from waste incineration plants, but the treatment of EAF dusts is planned for the future. The main features of the furnace are three water-cooled a.c. plasma torches, which serve as the energy source by forming a 'star-point' on the melt. This eliminates the need for the bottom anodic connection required by most d.c. plasma systems, but could aggravate the condensation of zinc vapour onto the torches (the 'cold finger' effect), and introduces the potential hazards associated with the use of water-cooled torches in a hot, corrosive metallic vapour. Further processing of the fume recovered from the off-gases to yield the valuable metal fractions is required.

The Tibur-Howden Process uses a similar a.c. system, but employs three inclined graphite electrodes, which generate a gas-stabilized plasma arc. Preliminary trials have been

conducted on a 1 MW pilot-plant facility which employed briquettes made from dust, coal, and flux, so as to minimize the carry-over of dust to the ISP zinc splash condenser, which was connected to the furnace-gas offtake. A cyclone operated at 900°C was connected between the furnace and the condenser to remove particles, but the low-temperature reoxidation of the zinc vapours is a potential problem with this approach. The latest available information indicates that this process may not be being actively pursued.

### **Transferred plasma-arc systems**

Davy has carried out preliminary testwork on the plasma treatment of EAF dust in a 1 MW pilot-plant at Stockton, England. The facility consists of a Hi-plas plasma-arc furnace connected to an ISP splash condenser. The furnace has the advantage of being able to handle EAF dust fines directly by means of pneumatic injection of the raw-materials mix into a water-cooled sleeve reactor, which surrounds the plasma torch. Radiation from the plasma-arc melts these materials, which then drip into the molten anode bath. Electrical power is supplied to the furnace by means of a water-cooled d.c. plasma-arc torch. In the context of EAF dust treatment, the presence of both a water-cooled torch and a water-cooled sleeve reactor could pose a potential hazard, owing to the 'cold finger' effect and stray arcing.

Sealing of the furnace is simplified by the presence of a single plasma torch cathode, and the use of electrical energy ensures that the highly reducing conditions necessary to minimize the reoxidation of zinc in the condenser are maintained. However, Davy state that their process requires both 20 Nm<sup>3</sup> of pneumatic conveying gas and 4 Nm<sup>3</sup> of argon plasma gas per tonne of dust, which could result in an undesirable lowering of the partial pressure of zinc in the condenser, which would reduce the efficiency of condensation. The carry-over of dust would aggravate this problem.

Tetronics Research and Development (TRD) initially developed commercial steel-plant dust-treatment processes using a 1.4 MW extended-precessing plasma-arc pilot plant. The furnace employs a single water-cooled plasma torch, inclined at angles of up to 15° from the vertical, and precessing at speeds of up to 1500 r/min (typically 30 r/min). The advantage of this arrangement is that it provides an enlarged arc-attachment area. The pilot-plant test facility has been operated using all three broad categories of steel-plant dusts, and both the combustion of the off-gases to produce ZnO, and direct condensation of metallic vapours in an ISP zinc splash condenser, have been successfully demonstrated.

A commercial plasma furnace for the treatment of 22 t/d of alloy-steel (low-zinc) dust has been operational at BSC's Sheffield works since 1989. The operation yields an innocuous slag, a saleable ZnO-rich fume produced by combustion of the furnace off-gases, and a valuable Ni-Cr-Mo-Fe-alloy which is recycled to the stainless-steel works.

Two commercial TRD plasma facilities for the treatment of carbon-steel dusts have also been installed by International Mill Services (IMS) in the USA. The first 20 t/d plant was installed at Florida Steel (Jackson, Tennessee) in 1989, and the second 30 t/d plant at Nucor-Yamata Steel (Blytheville, Arkansas), also during 1989. In both of the processes selective carbothermic reduction of the dusts is carried out, with the key objective of producing an innocuous slag, and to recover valuable condensed metal species (particularly zinc) directly from the furnace off-gases.

Initial difficulties were experienced in achieving recoveries of metallic zinc in the condenser much greater than 70 per cent, but with increasing operating experience a zinc recovery of around 85 per cent in the condenser is expected. A secondary difficulty was encountered with the use of water-cooled plasma torches in the hot corrosive furnace environment, which resulted in an explosion. This persuaded TRD to recommend the substitution of the plasma torch by a single graphite electrode, based on some of the known advantages of this simpler arrangement (Table 5).

Kawasaki Steel Corporation (KSC) has treated stainless-steel dusts in a 1.5 MW d.c. arc furnace in an effort to recover the valuable chromium and nickel alloy units that they contain. The trials were conducted at KSC's Chiba Works in a 1.5 MW d.c. furnace, and the use of a single d.c. graphite electrode was claimed to yield a low electrode consumption. The dusts were blended with an addition of 10 per cent coke (by mass) to enhance their transport characteristics, and were directly injected, without any prior agglomeration, down a hollow graphite electrode into the molten anode bath. A nitrogen carrier-gas flowrate of 20 Nm<sup>3</sup> per tonne of dust was employed, and dust entrainment was kept to an absolute minimum by feeding the dusts into the hottest region of the melt.

The recoveries of chromium and nickel to the metal (83.4 and 93.8 per cent respectively) was promoted by the low partial pressure of oxygen that could be maintained in the sealed d.c. arc furnace. The only known application of this pilot plant to date is the treatment of stainless-steel dusts.

Mintek has recently applied its d.c. transferred plasma-arc technology, which uses a hollow graphite cathode, to the treatment of zinc-containing materials, including carbon- and alloy-steel dusts (Enviroplas Process). Testwork has been carried out on a 1MW pilot-plant, and high zinc recoveries to the gas phase (more than 98 per cent extraction) and low levels of chromium in the slag were achieved. The pilot plant is not currently equipped with a condenser, so the off-gases are combusted and the fume is collected in a baghouse. Analyses of the fume, indicate that, with the gas composition (i.e. CO/CO<sub>2</sub> ratio), and the off-gas temperature achieved, a suitably adapted zinc splash condenser should give good zinc recoveries (probably greater than 80 per cent).

Testwork at Mintek has confirmed many of the theoretical considerations presented earlier in the paper. For example, additions of excess fixed carbon have resulted in the build-up of a solid carbonaceous phase on top of the slag, and some  $\text{CaC}_2$  has been formed with CaO-rich slags during operation at high temperatures (greater than  $1600^\circ\text{C}$ ). The flexibility of the open-bath process used, combined with the better temperature control afforded by the hollow-electrode-feed and power-control systems, has facilitated achieving the necessarily different operating conditions to treat a wide variety of dusts very effectively. Low dust levels and high temperatures in the off-gases should favour good condenser efficiency.

The scale-up of the equipment and process should not present any difficulties, since a 40MVA ferrochromium-production furnace based on this technology has been in operation at the Krugersdorp Works of Middelburg Steel and Alloys since 1988. A zinc splash condenser is expected to be effective up to about the 5MW scale. A lead splash condenser would have to be used at higher operating levels, since larger-scale zinc splash condensers (more than 2000  $\text{Nm}^3/\text{h}$ ) have not as yet been implemented.

### **Non-transferred plasma-arc processes**

The Plasmadust process developed by SKF Plasma Technologies AB employs a low shaft coke-filled furnace, usually fitted with three non-transferred plasma-arc heaters (rated at 6MW each) in the base of the furnace. A commercial plant in Sweden (Scandust) has been in operation since 1984, treating at first carbon-steel dusts, and more recently stainless-steel dusts (200 t/d).

The feed, which consists of fine coal and fluxes, is injected into the reactor close to the arc-heaters, together with recycled gases. Superheated gas ( $3000$  to  $5000^\circ\text{C}$ ) from these arc-heaters drives the reduction reactions in the lower part of the coke-filled shaft.

Gases generated at the tuyere level pass up the coke-filled shaft and enter a hot cyclone, where solids are removed before they enter a metal-condensation system at temperatures between  $1050$  and  $1200^\circ\text{C}$ . Three parallel zinc splash condensers were initially employed for condensation of the metallic vapours arising from the treatment of carbon-steel dusts, but difficulties were experienced with the distribution of hot gases between these condensers. Furthermore, problems were experienced with the formation of hard zinc and dross, the latter probably as a result of the reoxidation of zinc at the reduced temperatures (as low as  $1050^\circ\text{C}$ ).

To improve the zinc recovery, SKF designed and developed a lead-spray zinc condenser in which the zinc condenses into a spray of lead droplets, to replace the zinc splash condensers. The attendant physical driving forces for the condensation and dissolution of up to 2.5 per cent zinc into a lead droplet, where the activity of zinc is substantially less than unity, are far

more conducive to efficient zinc recovery in the product gases typical of the SKF operation (only 6 to 10 per cent zinc and 1100°C). However, despite the installation of the lead-spray zinc condenser, the treatment of carbon-steel (high-zinc) dusts was terminated in favour of the treatment of alloy-steel (low-zinc) dusts. In the processing of these alloy-steel dusts, the low zinc content of the furnace off-gases (less than 6 per cent zinc) does not justify condensation of the metallic species, which are treated in a venturi scrubber and collected in a ZnO-rich thickener sludge, which is sold as feed material to a primary zinc producer.

Hot metal and an innocuous and disposable slag are tapped from the base of the furnace. When carbon-steel dusts are treated, the coke-filled shaft results in the almost total reduction of the iron oxide. In the case of alloy-steel (low-zinc) dusts, valuable Ni-Cr-Mo-alloyed iron is readily recovered.

The Plasmadust process is best suited to a large scale of operation. The relatively high capital costs of the process makes it applicable to regional dust-treatment operations.

The Westinghouse Plasma Cupola and MKR Flash Direct Reduction processes are two further non-transferred plasma-arc systems for dust treatment that are under development.

## **SUMMARY AND CONCLUSIONS**

The treatment of dust arisings depends on the nature of the dust, environmental, technical and economic considerations. Four broad categories of dust have been defined, and various processing options have been reviewed. High-zinc and alloy-steel dusts are of primary environmental concern and potential economic interest. An overview of theoretical factors affecting their processing has therefore been given, with particular reference to thermal smelting processes using electrical energy.

Simulations clearly show that each specific dust type should be processed with the appropriate additions of fixed carbon and flux, and the appropriate temperature, to achieve the maximum recovery of zinc into and from the vapour phase. When alloying elements such as nickel, chromium, molybdenum, and manganese are present, the recovery of zinc has to be related to the conditions necessary to achieve the required reduction levels of these elements to meet both environmental and economic considerations. Each process application must, therefore, be evaluated on its own merit.

Although many different unit operations and processes have been developed new industrial plants will have to take environmental issues into account to a far greater extent than before. This is bound to influence the selection of the appropriate technology very profoundly in the future.

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Table 1: Classification of steel-plant dusts on the basis of chemical analysis (in percentage by mass)

Species	Carbon-steel dust (high-zinc)		Alloy-steel dust (low-zinc)		Alloy-steel dust (high-zinc)	
	Range	Typical	Range	Typical	Range	Typical
ZnO	15 - 45	32.5	1 - 15	2.5	15 - 30	18.5
PbO	< 5	3.0	0 - 2	0.5	< 5	2.0
Fe <sub>2</sub> O <sub>3</sub>	30 - 60	40.0	30 - 60	43.0	30 - 60	41.0
Cr <sub>2</sub> O <sub>3</sub>	< 1	0.5	10 - 25	19.0	10 - 20	15.0
NiO	< 1	0.2	2 - 10	6.0	2 - 6	2.5
MnO	< 7	3.0	2 - 10	5.0	2 - 10	5.0
MoO <sub>3</sub>	< 0.5	-	< 2.5	-	< 2.5	-
CaO	2 - 30	5.5	2 - 12	7.5	2 - 12	5.0
SiO <sub>2</sub>	2 - 8	8.0	2 - 17	7.0	2 - 12	5.0
MgO	< 8	1.0	2 - 10	4.5	< 10	1.5
Al <sub>2</sub> O <sub>3</sub>	< 2	1.0	< 2	0.5	< 2	0.5
Na <sub>2</sub> O	< 7	2.0	< 10	1.5	< 10	1.5
K <sub>2</sub> O	< 2	1.0	< 2	0.5	< 2	0.5
Cl <sup>-</sup>	< 4	1.5	< 4	1.5	< 4	1.5
F <sup>-</sup>	< 2	0.5	< 3	0.5	< 3	0.5

Note: 'Typical' analyses were used in the ideal equilibrium simulations.

Table 2: Predicted overall mass and energy balances for various thermal processing options (Basis: 1 t dust; temperature 1550°C; pressure 0.85atm)

Parameter	Carbon-steel dust (high-zinc)		Alloy-steel dust (low-zinc)	Alloy-steel dust (high-zinc)
	Selective Reduction	Total Reduction		
<b>Input</b>				
Fixed-carbon addition, %	5 - 10	15	21.1	21.3
<b>Theoretical energy requirement, MWh/(t of dust)</b>	0.71 - 0.95	1.16	1.22	1.33
<b>Products</b>				
Gas, kg	433	563	455	614
Slag, kg	615	434	197	117
Solids*, kg	0	0	11	10
Metal, kg	2	104	290	472
<b>Predicted Analyses</b>				
Gas: Zn, %	51.7	46.4	39.0	4.4
Pb, %	6.4	5.0	4.2	1.0
P <sub>co</sub> /P <sub>co2</sub>	0.8	14	4 x 10 <sup>2</sup>	2 x 10 <sup>4</sup>
Slag: ZnO, %	7.5	0.3	0.006	0.0
Cr <sub>2</sub> O <sub>3</sub> , %	0.8	1.1	0.1	0.0
FeO, %	58.8	52.7	0.0	0.0
Metal: Ni, %	n.a	n.a	0.5	8.7
Cr, %	n.a	n.a	1.1	24.0
Mn, %	n.a	n.a	1.1	6.2
C, %	n.a	n.a	0.9	5.5
Si, %	n.a	n.a	0.0	0.2

Notes: \* Stable solid carbon (and CaC<sub>2</sub>) phase predicted at equilibrium  
n.a. Not applicable  
All percentage analyses are quoted on the basis of mass



Table 3: List of process options available for the treatment of steel plant dusts

A. Recent commercial non-thermal processes

Process name and reference	Technology owner	Process/comments	Location/end-user	Production capacity	Date
1. <u>Chemical</u> 1.1. CEBEDEAU Process <sup>4</sup>	CEBEDEAU, Liege, Belgium, and S.E.R.H., St.-Florentin, France	Caustic-soda leaching / electrowinning. Dust mixed with spent electrolyte for leaching. Pb and Cu recovered by Zn cementation. Remaining caustic solution electrolysed for Zn	S.E.R.H. St.-Florentin, France	35 t/d	Mar. 1986
1.2. Super Detox Process <sup>5</sup>	Conversion Systems Inc. (CSI), Horsham PA, USA	Chemical stabilization of low-Zn baghouse dust with aluminum-silicates, lime and other additions to render disposable as landfill	North Western Steel & Wire Sterling IL, USA.	120-150 t/d	Apr. 1989
1.3. Roanoke Process <sup>5</sup>	Roanoke Technical Treatment & Services Inc. Roanoke VA, USA	Chemical stabilization of low-Zn dust with chemicals and cement to render disposable	Roanoke Electric Steel Roanoke VA, USA	12 - 20 t/d	Nov. 1989
2. <u>Recycle</u> 2.1 Dereco Inc. Process <sup>5</sup>	Dereco Inc. Cleveland OH, USA	Briquetting and recycling to EAF and AOD. ZnO level builds up to 30-35%. The system is purged and treated for dusts elsewhere	J & L Speciality Products Corp., Midland PA, USA	10 t/d	Sep. 1987
2.2 Process Calx <sup>5</sup> ,	Process Calx Inc. Birmingham AL, USA	Lime flux for EAF and BOF dusts. Based on briquettes (fired) using EAF dust as an ingredient. Others fluxes include dolo-lime, dolomite, limestone, iron-ore fines to replace pebble lime	Demonstration at IMIS Salttillo, Mexico	Demonstration only	Jul. 1989

Table 3: (continued)

## B. Fuel-based thermal processes

Process name and reference	Technology owner	Process/comments	Location/end-user	Production capacity	Date
3. Kilns 3.1 Inmetco-Rotary Hearth Furnace/Submerged-Arc Furnace (SAF) <sup>4,6</sup>	INMETCO/Mannesmann Demag AG, Ellwood City PA, USA Duisburg, Germany	Dust is reduced by pelletizing with carbon and heating in a rotary kiln by fuel-fired heaters. Secondary dust is processed to recover Zn. Hot sponge is melted in SAF. Used for steel and alloy dusts	Ellwood City PA, USA Design stage only - Germany	50 t/d 900 t/d (proposed)	1978 Possibly 1991/92
3.2 Zia Technology Inc. Process <sup>5,7</sup> (ZTI)	Zia Technology Inc. & Air Products and Chemicals Inc Caldwell TX/Allento PA, Tega Clay SC, USA	Inclined Rotary Reduction kiln System (IRRS) with oxygas-fired burner. Dust pelletized with coal and binder. Secondary dust (75% ZnO) processed in a vertical retort and Zn splash condenser. Fe/slag pellet (85% metallized)	Chaparral Steel, Midlothian TX, USA ZIT own and operate Caldwell TX, USA	150 t/d	End 1990
3.3 Waelz-kiln/ HRD Process <sup>4</sup>	Horsehead (HRD), Palmerton PA, USA	Conventional dust-treatment process developed in 1920s. ZnO fume from kiln smelted to recover Zn. Low temperature (<1200°C), strongly reducing (< BUS), limestone-fluxed. 90% metallization	Palmerton PA, USA Calumet City IL, USA Rockwood TN, USA	410 t/d 200 t/d 150 t/d	1980
3.4 Waelz-kiln/ BUS Process <sup>4,8,9</sup>	Berzelius Umwelt-Service (BUS), Duisberg, Germany	Pelletized dust, excess reductant, and silica mixture fed to kiln. Reduced Zn and Pb vapours are then reoxidized, for treatment in an ISF to yield metallic Zn and Pb. Waste slag from the kiln is harmless, and used in road-building or landfilled. 90% metallization achieved	BUS, Duisberg Works, Germany Cia Industrial Asua-Brandio Bilboa, Spain BUS / Metaleurop Lille, France	150 t/d 180 t/d 190-220 t/d	1973 mid-1987 mid-1992
3.5 KSC Process <sup>4</sup>	Kawasaki Steel Corp. (KSC) Japan	Pellets containing less reductant fed to grate preheater (800°C) and then rotary-kiln operation. Low Zn (<25 %Zn) dust in exhaust gases sent to Zn producers. Metallized pellet product (80-90%) not necessarily rendered disposable	Chiba Works, Japan Mizushima, Japan Chiba Works, Japan	200 t/d 670 t/d 1000 t/d	1968 1973 1977

Table 3: (continued)

## B. Fuel-based thermal processes (continued)

Process name and reference	Technology owner	Process/comments	Location/end-user	Production capacity	Date
<b>Kilns (continued)</b> 3.6 NSC Process <sup>4</sup>	Nippon Steel Corp. (NSC) Japan	Pellets with understoichiometric carbon addition fed to preheater (500°C) and rotary kiln. Metallized pellet product not necessarily rendered disposable	Muroran Works, Japan	400 t/d	1971
3.7 HTR Process <sup>4</sup>	Himeji Tekko Refine (HTR) Co. Nippon Kokan K.K. (NKK). Toshin Steel Co., Ltd. Japan	Selective reduction of pellets by feeding to preheater and rotary kiln (1400°C). Energy also supplied by kerosene burner. Metallized pellet product not necessarily rendered disposable	Fukuyama Works (NKK) Japan	1000 t/d	1974
3.8 Sumitomo Dust Reduction <sub>0</sub> (SDR) Process <sup>7,10</sup>	Sumitomo Metal Mining Co. Ltd., Japan	Pellets with understoichiometric carbon addition fed to preheater (200°C) and rotary kiln. ZnO product recycled to ISF. Metallized pellet product (90-95%) not necessarily rendered disposable	Wakajama, Japan Shisaka Works, Japan	670 t/d 140 t/d	1975 Aug. 1977
3.9 Sumitomo Prereduction Method (SPM) <sup>4</sup>	Sumitomo Metal Mining Co. Ltd., Japan	Feed not pelletized to produce a zinc-free material suitable for recycle via sinter plant. 80-95% metallization	Kashima, Japan	600 t/d	1975
<b>4. In flight</b> St Joe (Horsehead) Flame Reactor <sup>4,5</sup>	Horsehead Resources Development Co. Inc. (HRD) Palmerton PA, USA	Flash smelting process using oxygen-enriched fuel (gas) with dust pneumatically injected into a water-cooled reactor. Iron-rich slag and post-combusted fume (crude ZnO) are produced. ZnO treated by smelting at Zinc Corp. of America (ZCA)	Pilot Plant in Monaco PA, USA (CMP/ERPI tested process) TAMCO project proposal. Etiwanda CA, USA - owned and operated by HRD. Contract in s/w USA under consideration.	55 t/d 30-40 t/d (proposed)	mid 1991 Not finalized Not finalized

Table 3: (continued)

## C. Electrically-based thermal processes

Process name and reference	Technology owner	Process/comments	Location/end-user	Production capacity	Date
5. <u>Shaft Furnace</u> Ryoho Recycle Co. Process <sup>10</sup>	Ryoho Recycle Co. Japan	Dusts washed, roasted with CaCl <sub>2</sub> to remove 90% of Pb and sintered. Sinter fed with coke to electro-thermic shaft furnace for Zn	Onahama plant, Ryoho Recycle Co., Japan	100 t/d	1974
6. <u>Submerged-arc furnace (SAF)</u> Elkem multipurpose furnace (EMPF) <sup>11,12</sup>	Chemical Waste Management Inc., Oak Brook IL, USA under licence to Elkem Technology a/s.	Dust briquetted and fed to SAF. Slag resistance heated. FeO-rich discard slag contained by thermal oil freezeline control. Zn splash condenser (ISP design) 2000Nm <sup>3</sup> /h, largest to date	Elkem Technology Norway Pilot-plant in Mefos, Sweden  LacLade Steel Alton IL, USA	4MW/ 50 t/d  110 t/d	1991  1991
7. <u>Plasma-Arc</u>					
3-Phase, a.c. <u>Plasma</u>					
7.1 Mannesman-Demag 3-phase a.c. Plasma Process <sup>11</sup>	Mannesman-Demag (formally Krupp), Duisberg, Germany	Dust to be fed into open slag bath under 3 a.c. water-cooled torches. Circulating flue dust, cloud cyclone collects oxides	Siegen Steelworks, Essen, Germany  Waste plant planned	30 t/d  30 t/d	Wastes since 1989  Planned
7.2 Tibur-Howden <sup>4,13</sup> Plasma Extended Arc Reactor(PEAR)	Howden Corp. Canada, Ltd. Canada Univ. of Toronto, Canada	Dust briquettes fed between 3 a.c., graphite electrodes. ISP Zn splash condenser recovers Zn	Pilot-plant, Scarborough, Ontario, Canada Present status uncertain	1MW/ 24 t/d	1986
<u>Transferred Plasma-Arc</u>					
7.3 HIPLAS Process <sup>4,13,14</sup>	Davy, Stockton, UK and Butler PA, USA Hockett Services Inc.(HMS) (owner/operator)	Single, d.c. transferred plasma-arc torch system, with pneumatic injection of feed into a sleeve reactor (torch and sleeve water-cooled). Zn condensed in ISP Zn splash condenser	Pilot-plant, Davy Research, Stockton, UK  FeMn fines, Fishermans Bend, Melbourne, Australia	1MW/ 24 t/d  5MW - not in operation	Oct. 1989  1989
7.4 Tetronics R&D Co. Ltd. (TRD) Process <sup>4,11,14</sup>	International Mill Services Inc. (IMS), Philadelphia, PA., USA Multiserv International Ltd., London, UK	Dust fed directly via feed ports in roof into open slag bath. Water-cooled d.c. torch preprocessed to rotate over bath surface. More recently, stationary gas-stabilized graphite electrode used. Selective reduction of C-steel dusts; FeO-rich discard slag, and Zn recovered in ISP Zn splash condenser. Total reduction of alloy steel dusts. Furnace gas combusted to yield ZnO fume	Pilot-plant, Faringdon, UK  British Steel Stainless plc, Sheffield, S. Yorkshire, UK  Florida Steel, Jackson TN, USA  Nucor-Yamato Steel, Blytheville AK, USA	1MW/ 10 t/d 3MW/ 22 t/d  2MW/ 20 t/d 3MW/ 30 t/d	Since 1984 July 1989  early 1989 late 1989

Table 3: (continued)

## C. Electrically-based thermal processes continued

Process name and reference	Technology owner	Process/comments	Location/end-user	Production capacity	Date
7.5 KSC Hollow Electrode Process <sup>4</sup>	Kawasaki Steel Corp. (KSC) Japan Design- ASEA Metallurgy AB	Direct gas-assisted feeding of K-BOP dusts down hollow, d.c. graphite electrode. High carrier gas flowrate (400 NI/min.)	Chiba Works, KSC, Japan	1.5MW/ 20 t/d	1990
7.6 ENVIROPLAS Process	Mintek, Randburg, RSA Pyromet cc, Johannesburg, RSA	Directly feed down a hollow, d.c. graphite electrode. At present, fume combusted to ZnO and collected in bag filter. Zn condenser system being developed. Pb splash condenser recommended for large-scale operations(> 5MW) Carbon-steel and both alloy steel dust types have been treated	Pilot-plant, Mintek, Randburg RSA Similar 40MVA ferrochromium furnace in operation at MSA, Krugersdorp, RSA.	1MW/ 10 t/d	1988
<u>Non-transferred plasma-arc</u> 7.7 PLASMA-DUST Process <sup>4</sup>	SKF SCANDUST/SCANARC Plasma Technologies AB, Hofors, Sweden	Coke-filled shaft furnace with 3 x 6MW plasma-arc generators. Dusts pneumatically injected. Both C-steel and alloy steel dusts treated. Problems with the condensation of Zn in Zn splash condenser experienced. Resolved with Pb spray condenser	Demonstration-scale, Hofors Sweden. Scandust AB, Landskrona, Sweden.	1.5MW/ 20 t/d 18MW/ 200 t/d	1980 Mar. 1984
7.8 Westinghouse Plasma Cupola Process <sup>4</sup>	Westinghouse Electric Corp. Sponsored by Electric Power Research Inst. (EPRI)	Cupola with 2MW arc heater to treat mill-scale fines and briquettes to produce pig iron. Limited tuyere injection of fines possible at present	Demonstration-scale, Westinghouse Plasma Centre, Waitz Mill, Madison, Pittsburgh PA, USA	2MW/ 27 t/d	1986
7.9 MKR Flash Direct Reduction <sup>4</sup>	MKR Inc. Costa Mesa CA, USA	Flash reduction process. Slag/metal spheres and a metallic Zn/Pb dust fraction are products	Pilot-plant, HUNOSA, Spain	400KW 3 t/d	Jun. 1986

**Table 4:** Potential advantages of transferred-arc plasma processes for the treatment of steel-plant dusts

1. Feed  
Directly accepts steel-plant dusts (-10 $\mu$ m)  
Employs cheaper carbonaceous reductant fines (e.g. coal fines)  
Employs cheaper fine fluxes (e.g. silica sand).
2. Energy  
Essentially independent of atmosphere (low  $p_{CO}/p_{CO_2}$  possible)  
Substantially independent of slag composition and physico-chemical properties, which allow optimum process metallurgical conditions to be employed.
3. Furnace flexibility  
Feedrate-to-power ratio can be controlled directly to effect process control  
Short residence times allow rapid response to variations in dust compositions  
Rapid start-up and shut-down procedures.
4. Capital and operating costs  
Relatively low  
Smaller on-site dust-processing facilities are also commercially viable  
Reduced gas volumes (higher  $p_{CO}/p_{CO_2}$ ) lower the capital required for waste-gas treatment.

**Table 5:** Advantages of graphite electrodes over plasma torches for steel-plant dust processing

1. Energy  
Improved overall energy efficiency (no water cooling)  
Far less restrictive maximum current-carrying limit.
2. Plasma gas  
Possible use of cheaper nitrogen instead of argon  
Less, or even none, required:
  - lower potential for dust entrainment
  - less dilution of condensable metal vapours.
3. Process  
Graphite consumed instead of thoriated tungsten (cathode tip), copper (water-cooled torch) and argon gas  
Elimination of 'cold finger' condensation of metallic vapours, which can lead to 'stray arcing'  
Centre-feeding down hollow electrode easily accommodated.
4. Maintenance  
Higher availability (torches require regular replacement)  
Elimination of dangers posed by water leaks  
Saving on de-ionized water circuit and associated instrumentation.

Disadvantages

1. Electrode sealing more difficult.
2. Graphite consumed.
3. Power off while electrode segments added.

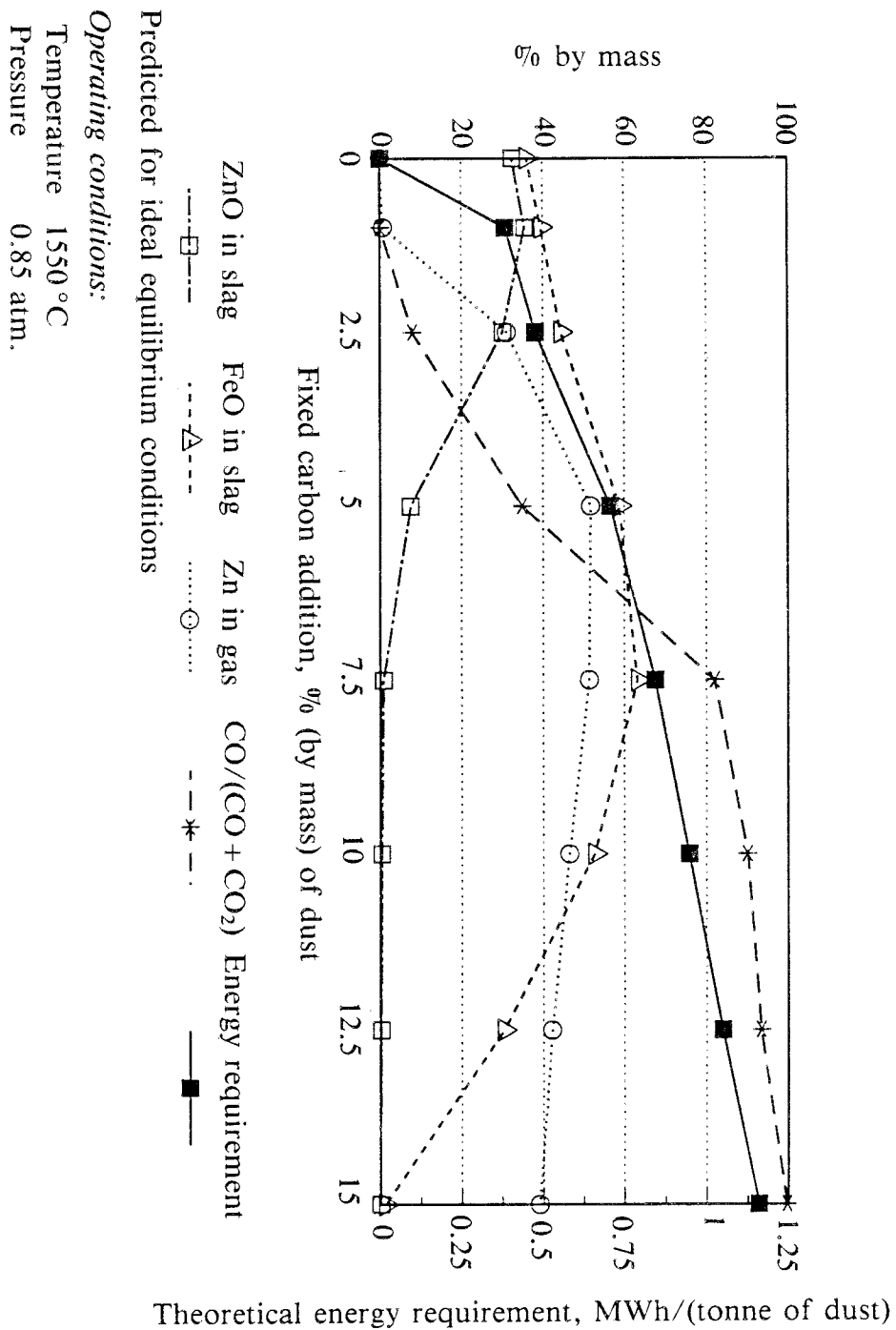


FIGURE 1. Predicted effect of fixed carbon addition on some process variables associated with the treatment of a carbon-steel (high-zinc) dust

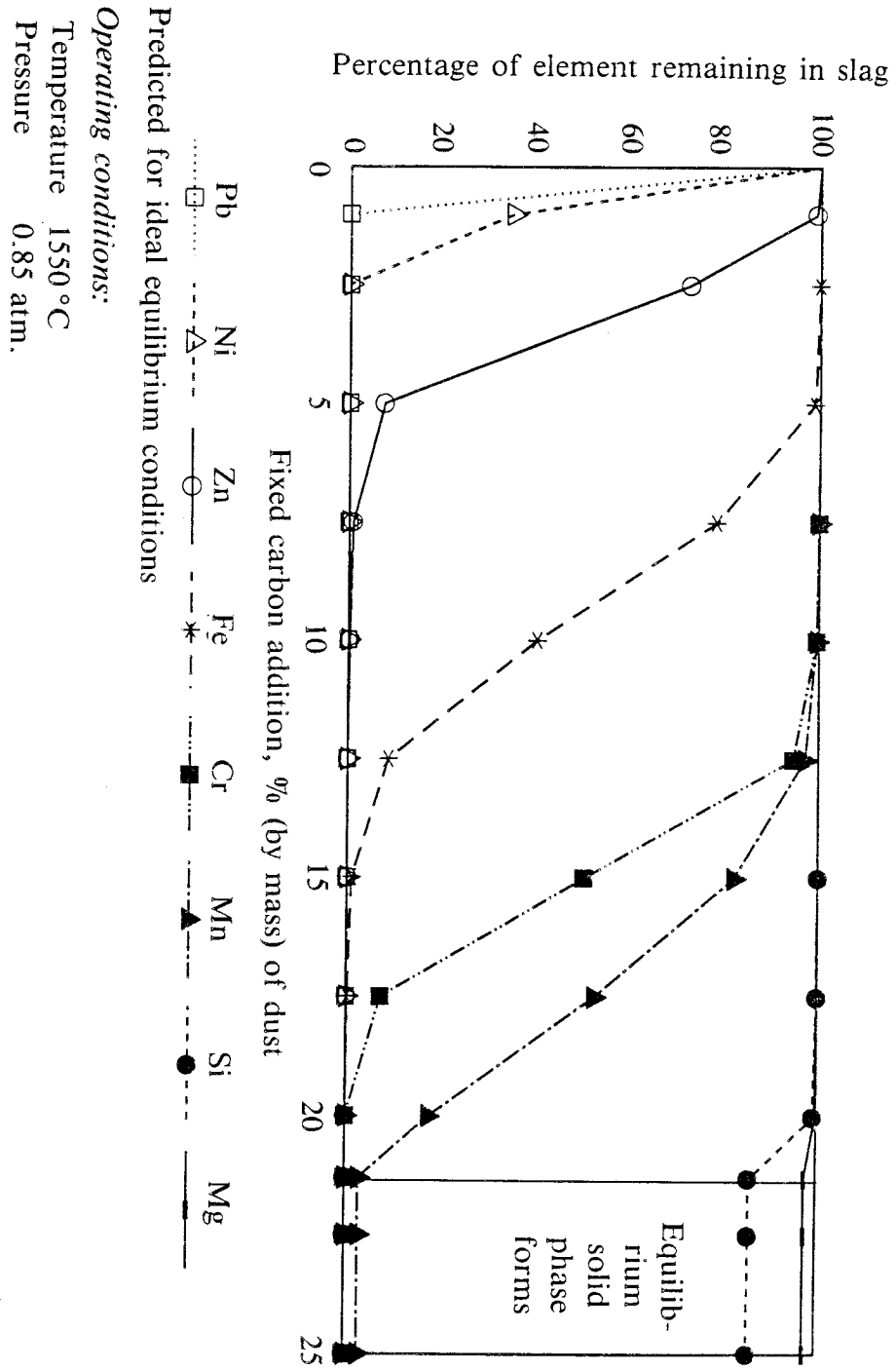


FIGURE 2. Predicted effect of fixed carbon addition of the sequence of reduction of elements from the slag phase for an alloy-steel (high-zinc) dust



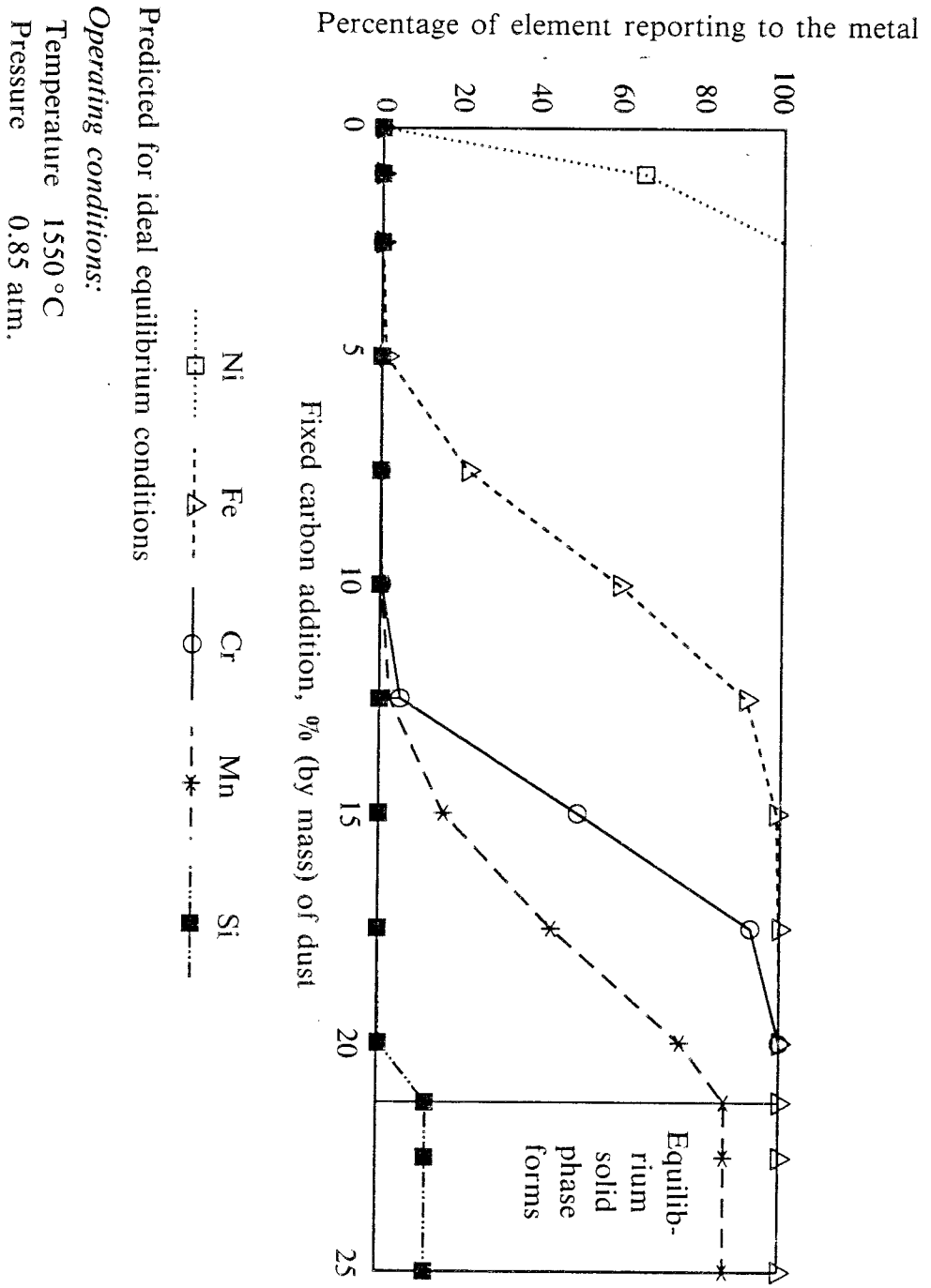


FIGURE 3. Predicted effect of fixed carbon addition on the recovery of elements to the metal phase for an alloy-steel (high-zinc) dust

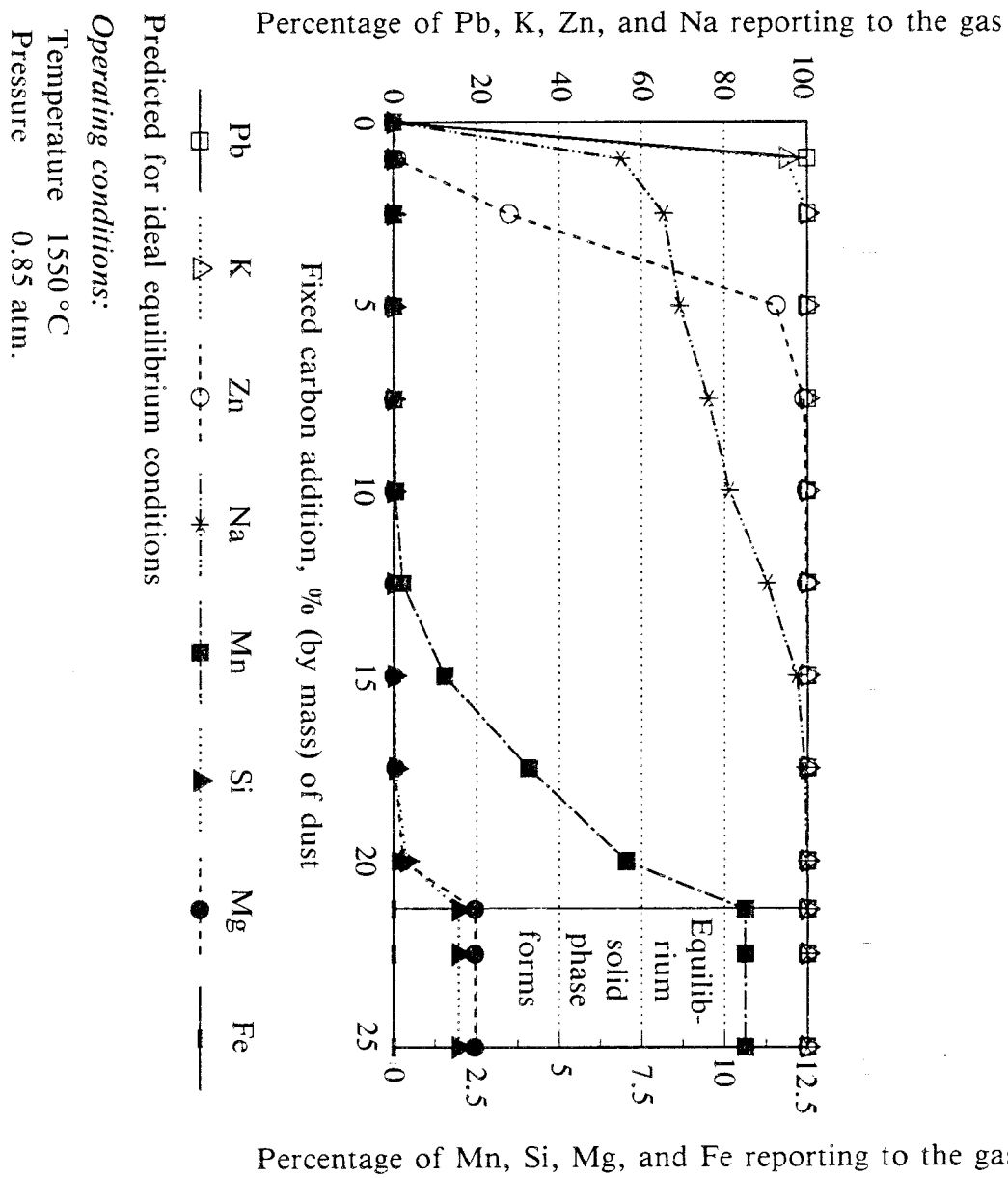


FIGURE 4. Predicted effect of fixed carbon addition on the turning of elements to the gas phase for an alloy-steel (high-zinc) dust

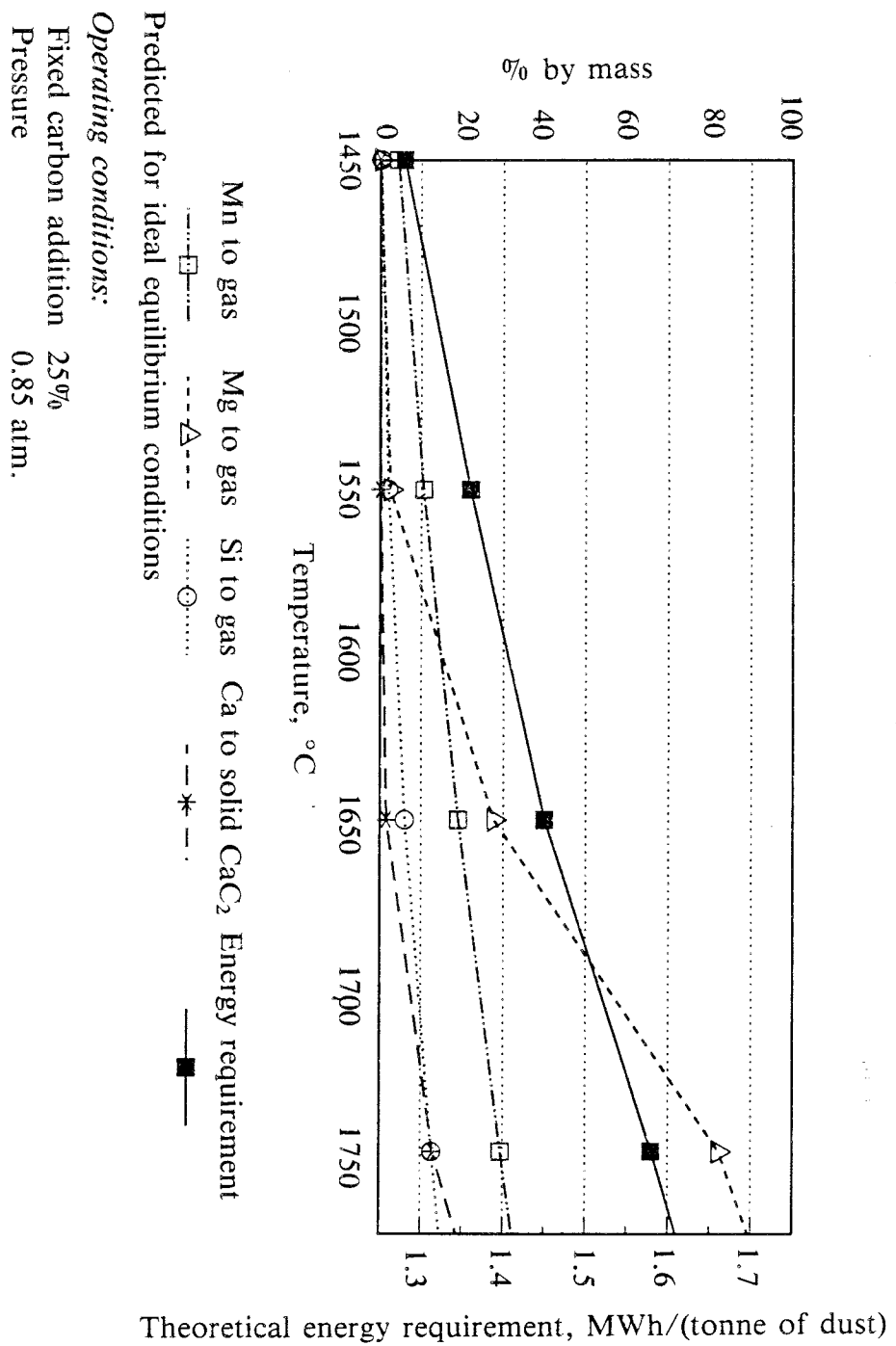


FIGURE 5. Predicted effects of temperature on the extent of undesirable side-reactions and theoretical energy requirements for an alloy-steel (high-zinc) dust