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Title: PLASMA-ARC TREATMENT OF STEEL-PLANT DUST AND ZINC-CONTAINING SLAG - THEORETICAL AND PRACTICAL CONSIDERATIONS

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PLASMA-ARC TREATMENT OF STEEL-PLANT DUST AND ZINC-CONTAINING SLAG - THEORETICAL AND PRACTICAL CONSIDERATIONS

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1. INTRODUCTION AND BACKGROUND

The use of a proportion of recycled mild- and stainless-steel scrap in the electric arc furnace (EAF), basic oxygen furnace (BOF), and the operation of the argon-oxygen decarburization (AOD) furnace results in iron-oxide-rich baghouse dusts containing oxides of zinc, lead, cadmium, nickel, chromium, and manganese. Several of these metals are classified as hazardous in countries such as the USA, and strict legislation to control the disposal and treatment of steel-plant dusts has been, or is being, introduced in many countries. Four broad categories of steel-plant dusts exist: low-zinc carbon-steel dusts, high-zinc carbon-steel dusts, low-zinc alloy-steel dusts, and high-zinc alloy-steel dusts. Lead blast-furnace slags are also under consideration in terms of their disposal.

Mintek has primarily addressed the more economically interesting dusts, namely high-zinc carbon-steel dusts, and high- and low-zinc alloy-steel dusts. The recovery of zinc, lead and other valuable elements from lead-smelter slags has also been studied using Mintek's d.c. transferred plasma-arc process. This technology was initially developed for the smelting of high-carbon ferrochromium from chromium ore and the melting of ferrochromium metal fines. A 40 MVA (30 MW) commercial plant has been in operation at Middelburg Steel & Alloys for the past three years.

Opportunities and needs for treating steel-plant dusts have been identified in Europe and elsewhere. The merits of localized processing as opposed to centralized plants is a matter of economics, technology, logistics, and preference. The d.c. plasma route is very flexible, and lends itself ideally to both small-scale 2 to 3 MW local plants and 7 to 15 MW larger-scale centralized facilities. The d.c. plasma process is not only flexible in terms of scale, but also with regard to the type of feed material and products that can be processed. Disposable slag can be produced from virtually all types of zinc-containing solid wastes from the metallurgical industry. The products that are generated in the plasma-arc process are usually a metal and a non-toxic slag, which are tapped from the furnace in the liquid form, and a zinc-containing vapour. The metal is composed mainly of iron and alloying elements such as chromium, nickel, and manganese. The most troublesome constituents in steel-plant dusts and lead-smelter slags are alkalis and, in particular, halides, since they interfere with the condensing of zinc vapour. These species are contained in the high-temperature off-gases, and the design of the condensation process and the equipment has to take this into account.

To date only pilot-plant work has been carried out at Mintek, up to about the 800 kW level, in which the vapours have been combusted to a zinc-oxide fume and collected in a bag filter. Analysis of the fume and gas has indicated that zinc condensation is possible, but that the recovery and grade of the zinc product will be lower than for primary zinc-production processes. The scope for improving these aspects is under evaluation by Mintek. Many practical issues have to be considered in the design and operation of the process; i.e. feed handling, feed recipe, furnace atmosphere, and the removal of products, in particular the metal vapour or fume. Control of post-combustion of the vapour above the bath can, for example, reduce the electrical energy consumption by about 20 per cent. The off-gas ducting design is critical, and depends on whether the vapour is to be condensed or combusted.

A two-stage process to separate the chromium-alloy-producing step from the zinc-removal stage is proposed as an appropriate means of addressing the treatment of zinc-containing alloy-steel dusts.

2. MINTEK'S PLASMA-ARC PILOT-PLANT EQUIPMENT

Mintek's plasma-arc pilot-plant equipment consists of four furnaces which can be operated at power levels between 30 kW and 1 MW. The equipment has been described in detail elsewhere[1,2]. The furnaces employ direct current, and are operated with a single graphite electrode as the cathode and the molten bath as the anode. The molten pool of process material forms an integral part of the electrical circuit, and the furnaces can therefore be classified as d.c. transferred plasma-arc furnaces. The three smaller furnaces are rated at 50, 100, and 200 kVA, and their internal diameters range from 0.2 to 0.5 m. A schematic diagram of the 200 kVA furnace is shown in Figure 1. Processing capacities for raw materials are between 5 and 100 kg/h. The 50 and 100 kVA furnaces can be made gas-tight, and this arrangement has been successfully employed for the extraction, vaporization, and condensation of magnesium. When required, nitrogen or argon are normally used as the plasma gas, at flowrates between 5 and 20 *l*/min. The plasma gas is supplied via the central hole in the graphite cathode. The raw materials can also be fed through the electrode, although this is not practised on the 50 and 100 kVA furnaces because of the relatively small diameter of the electrode and hole (50 mm and 5 to 10 mm respectively) on these facilities. The feed systems consist of weigh hoppers (mounted on load cells for accurate control of the feed rate), vibratory feeders, and feed pipes connected to either the central hole in the electrode or to feed ports situated in the roof of the furnace. The gas-cleaning equipment consists mainly of combustion chambers and bag filters.

A schematic diagram of the 1 MW plasma-arc pilot-plant equipment is shown in Figure 2. The furnace consists of a refractory-lined cylindrical shell, a conical roof, and a small flat roof positioned on top of the conical roof. The furnace has an internal diameter of 1.3 m and an internal height of 1.75 m (distance from hearth to roof). The hearth and sidewalls of the furnace are lined with refractories such as magnesia ramming material and chrome-magnesia bricks. The furnace is equipped with water spray-cooling to the sidewalls. The conical and flat roofs are usually lined with an alumina castable, and are also water cooled. The flat roof contains three feed ports and the central entry port for the graphite cathode (125 mm diameter, 70 mm hole diameter). The off-gas port is located in the conical roof. The return electrode consists of several steel rods, built into the refractories, and connected at their lower ends to a steel plate which, via radially extending arms, is linked to the furnace shell and further to the anode cable. The feed system consists of six 0.9 m^3 hoppers mounted on load cells and fitted with independently controlled vibratory feeders. The feed can be distributed around the electrode (feeding through the feed ports in the flat roof), or may be supplied via the central hole in the electrode, or any suitable combination of side and central feeding can be used. The gas-cleaning system consists of a water-cooled off-gas pipe, a refractory-lined combustion chamber, water-cooled ducting, a 'forced-draft' gas cooler, a reverse-pulse bag filter, a fan and a stack. The furnace is operated at power levels between 500 kW and 1 MW (typically 600 kW, 2500 A, 240 V) with feed rates of 0.2 to 1 t/h. The amount of raw materials required for testwork to establish process data for scaling up to commercial operations lies in the range of 20 to 50 t. The furnace is operated on a 24-hour per day basis for periods of at least 5 days.

3. APPLICATION OF MINTEK'S PLASMA-ARC PILOT-PLANT EQUIPMENT FOR THE SMELTING OF ZINC OXIDE CONTAINING SOLID WASTES FROM THE METALLURGICAL INDUSTRY

3.1. Fuming of Lead-smelter Slag

The suitability of the Mintek 1 MW plasma-arc furnace for the smelting and fuming of lead-smelter slag has been successfully demonstrated. About 80 t of granulated lead blast-furnace slag, containing 14 per cent ZnO and 2,8 per cent PbO, were smelted at feed rates of over 800 kg/h and energy inputs up to 800 kW (3000 A, 270 V). The furnace shell was lined with chrome-magnesite bricks, while an alumina castable was used for the lining of the roof. The average temperature of the tapped slag was around 1500°C. Charcoal was used as the reducing agent. The charcoal-to-slag ratio in the feed was chosen to selectively reduce the zinc and lead oxides, while leaving the iron oxide in the smelted slag. The lead-blast furnace slag and charcoal were fed continuously through three feed ports, equispaced around the central electrode. Zinc and lead vapours, and carbon monoxide, were burnt at the off-gas port of the furnace, and the mixed oxide of zinc and lead was collected in a bag filter. High extraction levels (more than 95 per cent extraction from the slag) of zinc and lead were achieved. Almost all the extracted zinc and lead reported to the vapour phase and fume in the bag filter. Only about 0.1 per cent of the zinc input and approximately 1 per cent of the lead input passed into a metal phase which accumulated in the hearth of the furnace. The fumes produced contained about 80 per cent ZnO and 15 per cent PbO. The impurities in the fumes were relatively low. The fumes contained approximately 0.5 per cent FeO, 0.6 per cent SiO_2, 0.4 per cent CaO, 0.2 per cent MgO, and 0.2 per cent Al_2O_3. The composition of the siliceous slags (residual slags) produced was typically as follows: 35 per cent SiO_2, 26 per cent CaO, 20 per cent FeO, 8 per cent MgO, 5 per cent Al_2O_3, 0.7 per cent ZnO, and less than 0.2 per cent PbO.

3.2. Smelting of EAF Dust

Small-scale testwork was conducted on the smelting of EAF dust (high-zinc carbon-steel dust) in the 50 kVA plasma-arc furnace. In total 10 batch tests on about 10 kg EAF dust each were carried out. The Fe_2O_3, ZnO, and PbO levels of the EAF dust were 32.0, 30.6, and 4.2 per cent respectively. The average particle size of the dust was around 1 µm. The dust was pelletized and fed to the furnace together with anthracite and silica flux. The anthracite addition was such as to selectively reduce the zinc and lead oxides, leaving the iron oxide behind in the smelted slag. Silica was added to the feed to achieve a slag with an acceptably low liquidus and a basicity ratio ($CaO + MgO/SiO_2$ mass ratio) of about unity. The volatilized zinc and lead were subsequently burnt, and the mixed oxide was collected in a bag filter. The furnace was operated at a power level of 30 to 40 kW, and at a temperature of about 1500°C. The zinc and lead were almost completely extracted from the EAF dust and recovered as an oxidic fume. Both the levels of zinc and lead oxide in the slags produced were below 0.2 per cent. Standard leach tests were carried out on these slags, and they were found to be disposable according to EPA regulations. The fumes produced contained about 72 per cent ZnO, 8 per cent PbO, 3 per cent FeO, 1.3 per cent SiO_2, and 0.4 per cent MgO.

Recently testwork has been carried out on the 1 MW pilot-plant on the smelting of alloy-steel dusts (high- and low-zinc). The steel-plant dusts were charged to the furnace, without prior agglomeration, via the central hole of the graphite cathode. The off-gases were burnt and collected in a bag filter. High extraction levels of zinc, chromium and nickel were achieved. A disposable slag, a ferro-alloy rich in chromium and nickel, and a zinc-oxide fume were produced.

4. POTENTIAL OF PLASMA-ARC TECHNOLOGY FOR THE EXTRACTION OF METAL VALUES FROM ZINC OXIDE CONTAINING FEED STOCKS

Fuel-air-based processes, such as the Waelz process, have been established to treat steel-plant dusts. Zinc and lead are volatilized, re-oxidized and recovered in a bag plant. The partial pressure of oxygen above the process material is high, and large amounts of fuel are employed. This makes it difficult to control the reduction process, which is especially important when selective reduction, i.e. the reduction of only specific metal oxides in the feedstock, is required. The large volumes of off-gas, accompanied by extensive carry-over of uncondensable species, and the high CO_2 levels in the off-gases of these processes are also disadvantageous in case the direct recovery of metallic zinc in a splash condenser should be practised. Because the partial pressure of oxygen is high, the chromium oxide in alloy-steel dusts cannot be effectively reduced. Iron oxide can be metallized to a large degree but a further smelting, in an electric-arc furnace for example is necessary to produce a pig iron or ferro-alloy.

Plasma-arc technologies exist, and new ones are emerging, for processing zinc- and lead-bearing steelworks dusts (e.g. the Tetronics, SKF, Davy, Mannesmann-Demag, and the Mintek Enviroplas processes). All these processes operate on the principle of reducing the zinc and lead oxides in the dust at high temperatures (above 1500°C), vaporizing the zinc and lead, and then either re-oxidizing the vapours to a crude mixed oxide or condensing them in an ISP-type splash condenser. Chromium oxide present in the dusts can also be readily reduced, together with oxides of metals such as iron and nickel, and the metals are recovered from the furnace in the liquid form. This is not the case for fuel-air processes.

In the Mintek Enviroplas system the feed can be charged to the furnace, without prior agglomeration, via the central hole of the graphite electrode. The liquid bath in the arc-attachment area is moved in a downward direction by electromagnetic forces at the high current fluxes prevailing in industrial-scale plasma-arc systems. Fine steel-plant dusts (usually 100 per cent smaller then 10 μm) are rapidly absorbed in the molten slag bath, minimizing elutriation or carry-over of feed to the gas phase. High reaction rates and efficient fuming of zinc metal can be achieved. The vaporization of unwanted species in the arc-attachment zone can be controlled to a large degree, since the supply of cold feed under the electrode lowers the bath temperature in this area. Steel-plant dusts are variable in composition, and the required size of operation can vary over a wide range for different steel producers and processors of dust. In this regard, the Enviroplas system is extremely flexible, as any type of steelworks dust can be treated, and both small-scale (2 to 3 MW or 10 000 to 20 000 t of steel-plant dust per year) and large-scale plants (7 to 15 MW or 30 000 to 70 000 t of steel-plant dust per year) can be accommodated.

5. THEORETICAL CONSIDERATIONS

Ideal equilibrium calculations have been performed using the Mintek PYROSIM computer program[3], to simulate the thermal treatment of steel-plant dusts. The chemical analyses of the 'typical' carbon-steel and alloy-steel dusts, used in the calculations are shown in Figures 3 and 4. The simulations were conducted at a fixed temperature (1550°C) and pressure (1 atm).

The results of the simulation for high-zinc carbon-steel dust are given in Figures 3 and 5. Most of the zinc is removed from the slag at a carbon addition of 7.5 per cent (of the steel-plant dust feed). Very little iron is theoretically produced at this carbon addition, as most of the iron is retained as iron oxide in the slag. At a carbon addition of 15 per cent almost all the iron is extracted from the slag, but the theoretical energy requirement increases from about 0.8 (at 7.5 per cent carbon addition) to 1.1 MWh per ton of steel-plant dust processed. The CO-to-CO_2 mass ratio in the off-gas also increases from about 5 to 400 when the carbon addition is raised from 7.5 to 15 per cent. This is advantageous when metallic zinc is condensed from the gas phase, due to less re-oxidation of the zinc. However, the larger gas volumes at higher carbon additions are associated with increased carry-over of feed.

When a typical high-zinc alloy-steel dust is smelted at 1550°C, a carbon addition of 20 per cent is predicted to be necessary to extract most of the chromium from the slag formed during the process. The theoretical energy requirement is about 1.3 MWh per ton of steel dust at 20 per cent carbon addition (Figure 6). Significantly more energy is required for the smelting of a typical high-zinc alloy-steel dust than is needed for a high-zinc carbon-steel dust. Also, the level of CO in the off-gas is much higher when high-zinc alloy-steel dust is processed (67 per cent versus 31 per cent), because the iron oxide in the dust has to be extracted as well to achieve satisfactory recoveries of chromium and manganese to the metal.

When high-zinc alloy-steel dust is smelted with a carbon addition of 20 per cent, direct condensation of zinc from the gas phase could be a problem due to the high volumes of gas and excessive carry-over of feed. Also, at this high carbon addition the level of fuming of manganese, magnesium, silicon, and iron is predicted to become significant[4].

Mintek therefore carried out a theoretical study on the smelting of high-zinc alloy-steel dust in a two-stage process. The principle of this two-stage process is shown in Figure 7 and Table 1. The Mintek PYROSIM program[3] was used to calculate the values in Table 1. The chemical analyses of high-zinc alloy-steel dust, used for the calculations, are given in Figure 4.

In the first stage, the zinc oxide, the nickel oxide, and some of the iron oxide are selectively reduced. A gas rich in zinc and a valuable nickel-containing alloy are produced. Slag produced in the first unit is transferred in the liquid form to the second stage, where more strongly reducing conditions are achieved by the further addition of carbon, yielding a disposable slag and a chromium alloy.

It is envisaged that the impurity levels, derived from the carry-over of dust and fuming, in the off-gas stream of the first unit will be greatly reduced in comparison with a single-stage process. Dust entrainment should be lower because of the decreased gas volume (less CO), and partial reduction will depress the fuming of species such as magnesium, manganese, and silicon. The direct condensation of zinc vapour produced in the first stage may therefore become a viable processing option.

6. CONCLUSIONS

Testwork at power levels in the range 30 kW to 800 kW on the Mintek plasma-arc pilot-plant equipment has demonstrated that this technology is most suitable for the treatment of steel-plant dust and zinc-containing slag to recover valuable by-products such as a zinc-oxide fume, a ferro-alloy containing chromium and nickel, and a disposable slag. The plasma-arc technology developed by Mintek has been extensively tested at power levels between 500 kW and 1 MW, and has been successfully implemented at a scale of 40 MVA by Middelburg Steel & Alloys for the production of ferrochromium.

7. ACKNOWLEDGEMENTS

This paper is published by permission of Mintek. The contribution made by Mr M.D. Boyd of Mintek in performing the equilibrium calculations is gratefully acknowledged.

8. REFERENCES

1. N.A. BARCZA, T.R. CURR, G.M. DENTON, and D.A. HAYMAN. Mintek's role in the development of plasma-arc technology based on a graphite cathode. *ISPC-9*, Sep. 1989.

2. D.A. HAYMAN. Mintek's new plasma furnace. *SAIMM Colloquium on Ferrous Pyrometallurgy*. South Africa, Apr. 1989.

3. R.T. JONES. *Proceedings : APCOM '87*, Johannesburg, SAIMM, 1987. vol. 2, pp. 265-279.

4. N.A. BARCZA, and L.R. NELSON. Technology for the treatment of steel-plant dusts. *World Steel*, vol. 1, no. 1, Nov. 1990 (in press).

Table 1

Predicted effect of carbon addition on process variables associated with the treatment of high-zinc alloy-steel dust in a two-stage process

Stage 1					Stage 2				
C addition* %	Zn recovery %	Alloy mass† kg	Ni %	Energy† MWh/(t dust)	C addition* %	Alloy mass kg	Cr %	Mn %	Energy† MWh/(t dust)
5.0	92.6	22.9	85.8	0.651	15.4	451.0	22.8	7.6	0.654
7.5	99.1	82.0	24.0	0.765	13.3	389.0	26.4	8.7	0.576
10.0	99.7	191.8	10.2	0.867	10.1	273.4	37.4	12.2	0.464
12.5	99.9	171.1	6.8	0.976	7.2	288.4	56.8	18.0	0.354

* Carbon addition as a percentage of steel-plant dust input
† Alloy mass and energy per 1 t of steel-plant dust input

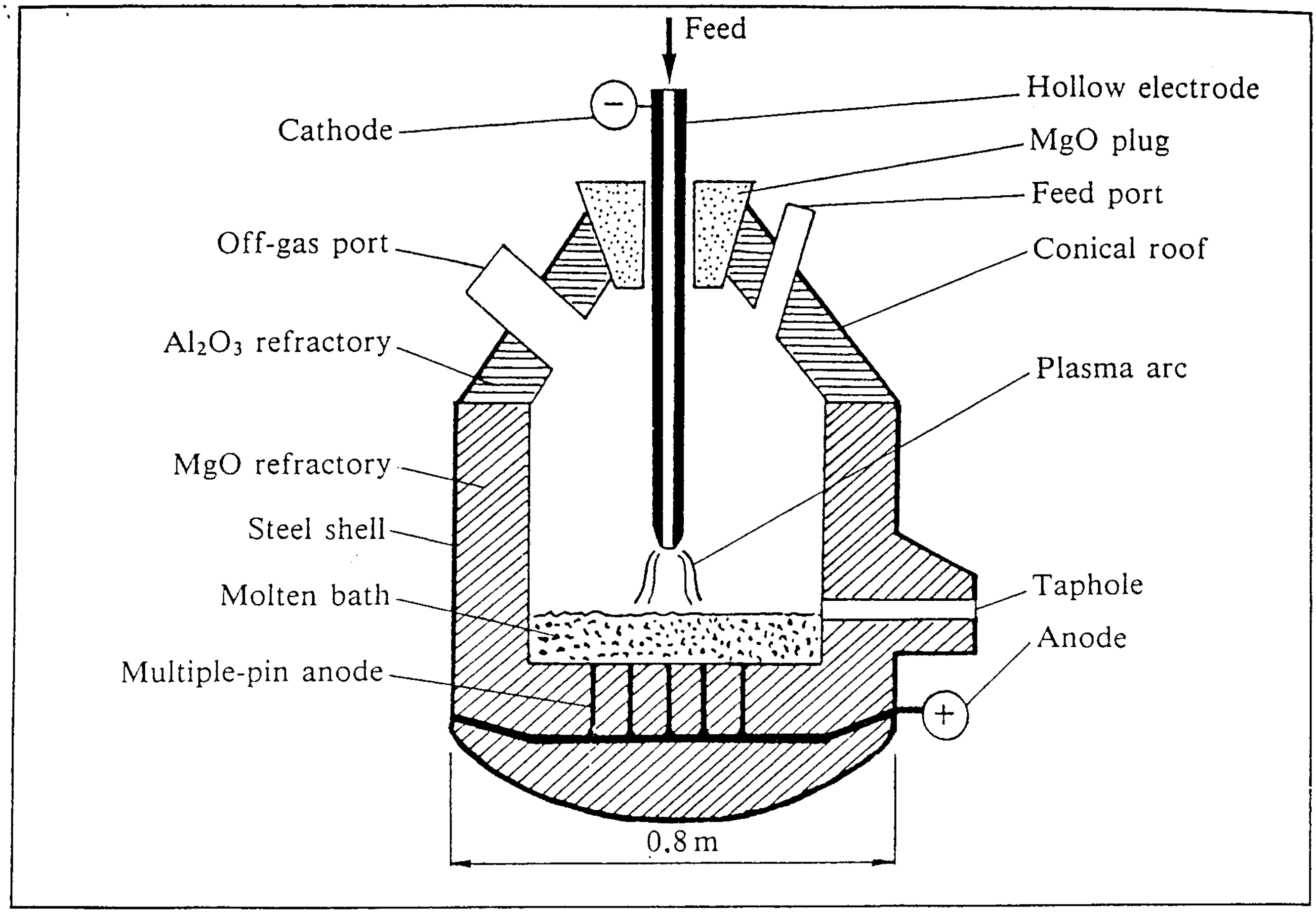

Figure 1. Schematic diagram of the Mintek 200 kVA plasma-arc furnace

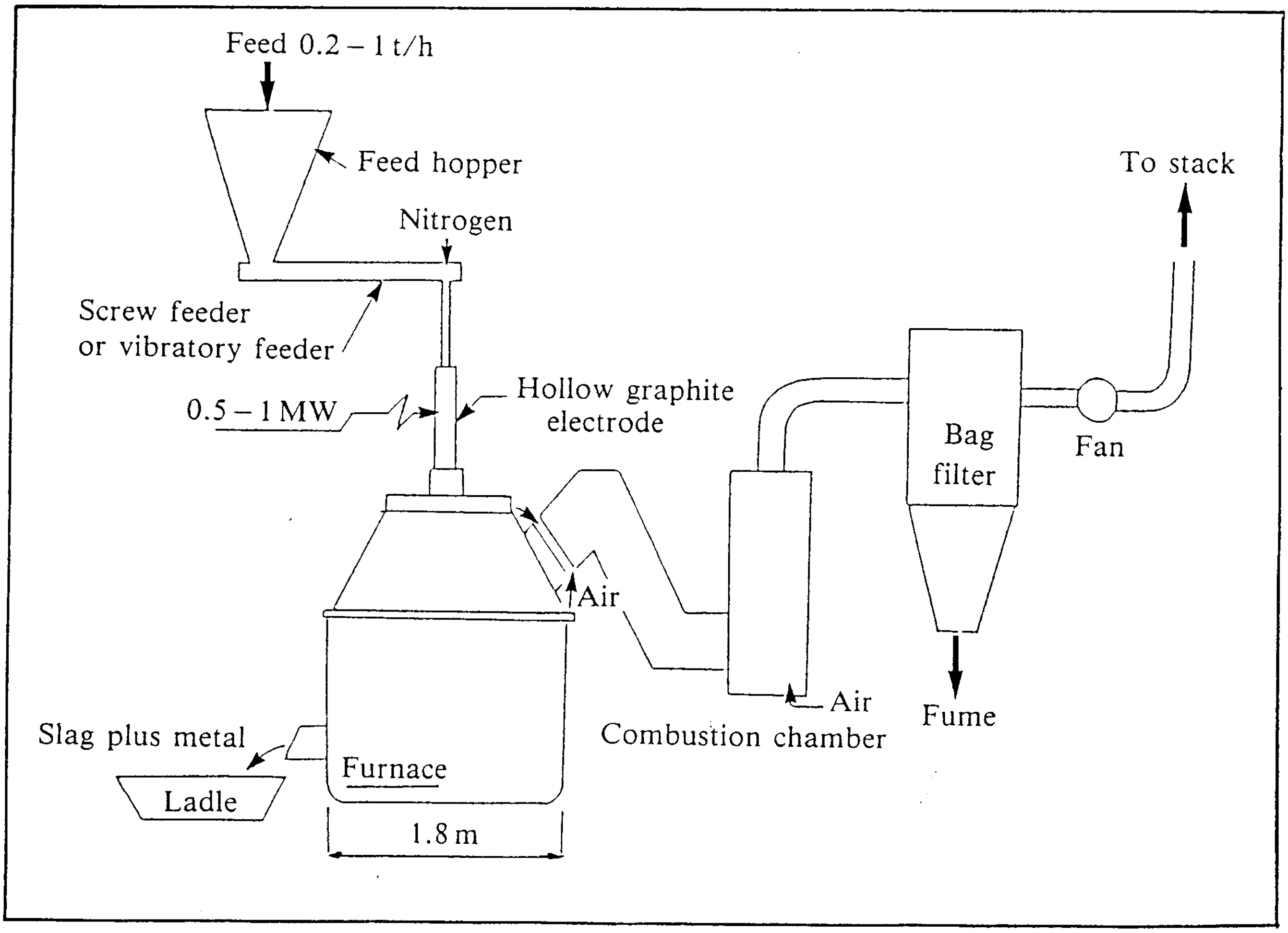

Figure 2. Schematic diagram of the Mintek 1 MW plasma-arc furnace

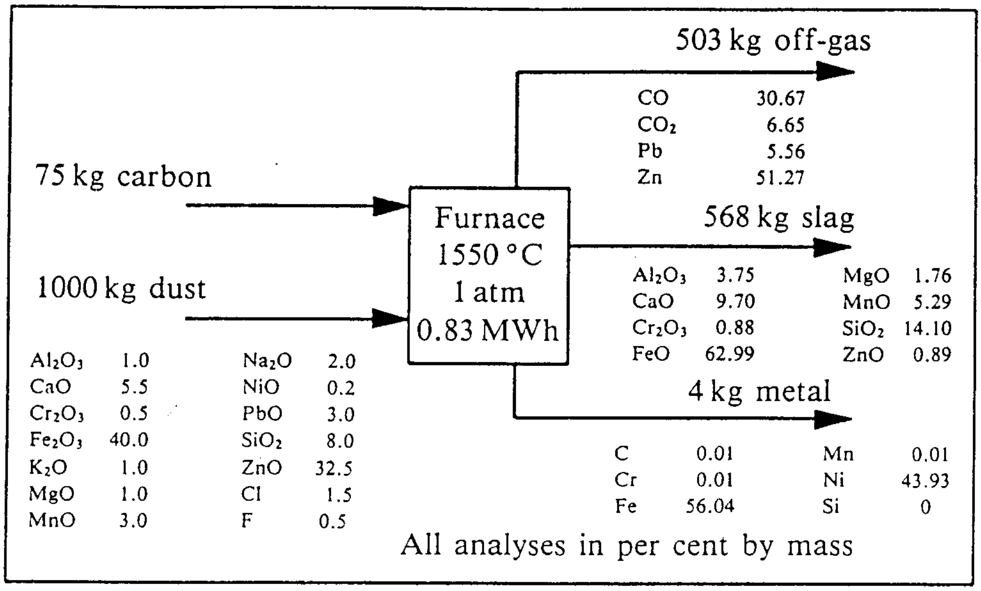

Figure 3. Predicted mass and energy balance for high-zinc carbon-steel dust

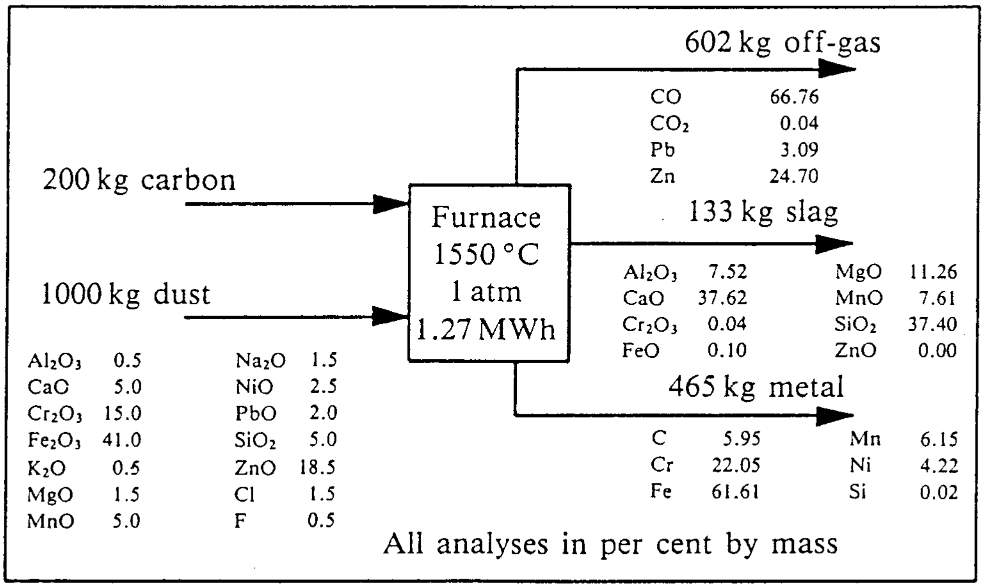

Figure 4. Predicted mass and energy balance for high-zinc alloy-steel dust

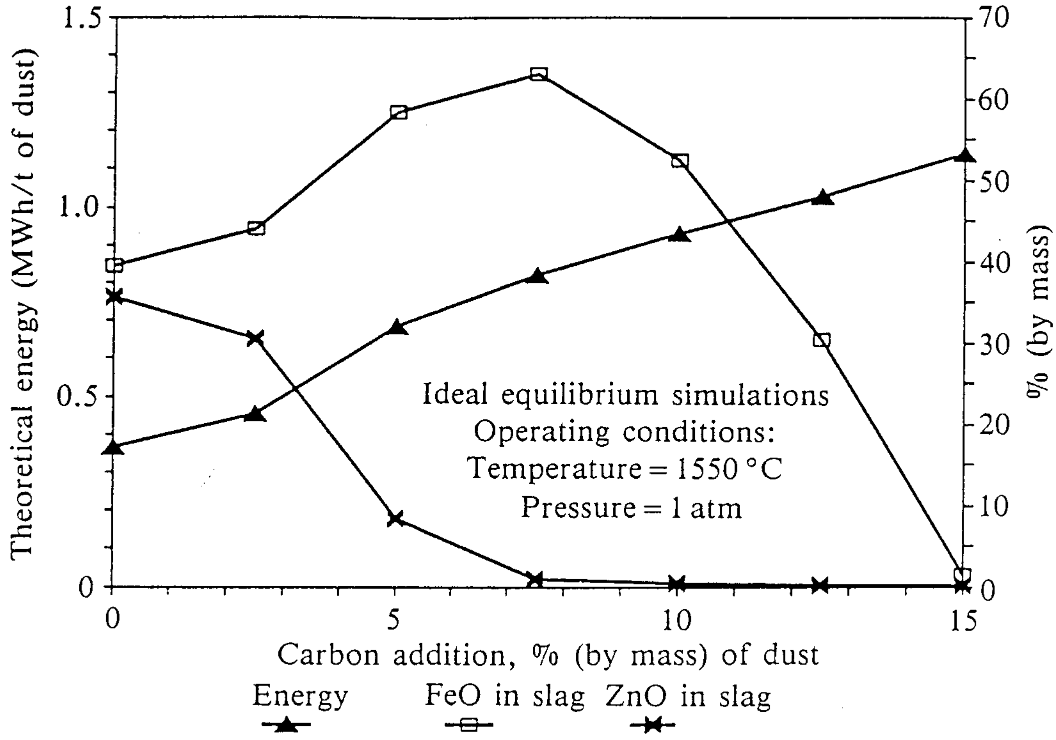

Figure 5. Predicted effect of carbon addition on energy requirement and slag composition for high-zinc carbon-steel dust

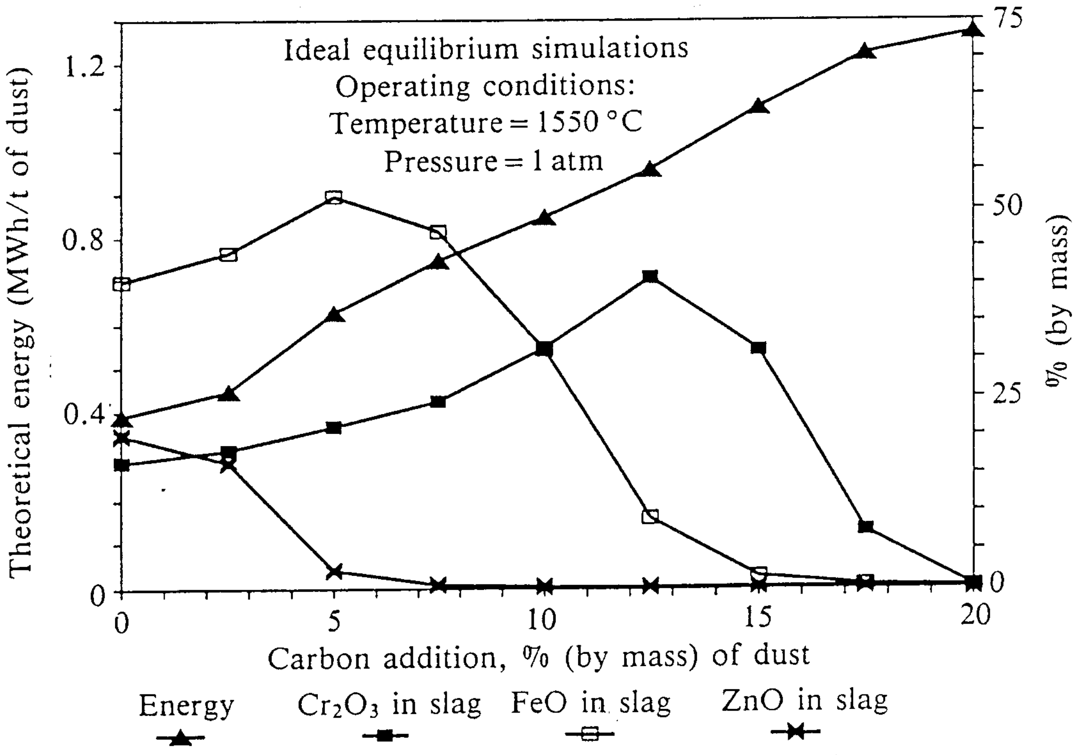

Figure 6. Predicted effect of carbon addition on energy requirement and slag composition for high-zinc alloy-steel dust

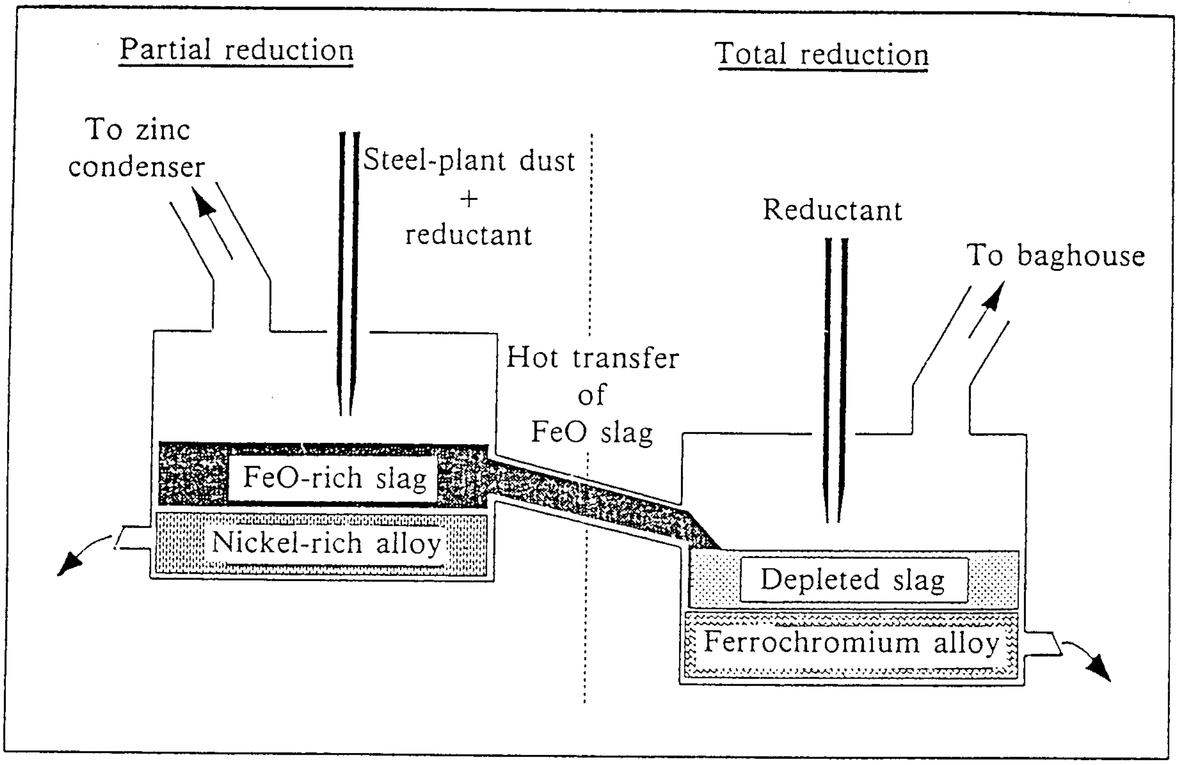

Figure 7. Proposed two-stage process for high-zinc alloy-steel dust