

## ***ENVIRONMENTAL TREATMENT OF EAF/AOD DUSTS***

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### **1. INTRODUCTION**

During the production of carbon steel in electric-arc furnaces (EAF), or when stainless steel is produced in an EAF/AOD operation, 10 to 20 kg of flue dust is generated per ton of steel. Dusts are also produced when smelting chromite ores. These dusts, which are usually captured in a bag filter, have traditionally been dumped on landfill sites. In most countries the dumping of plant dusts is now regarded as an environmental hazard because toxic metals, such as lead, nickel, cadmium and chromium, may be leached into drinking-water supplies. Mintek is developing the Enviroplas™ process for the treatment of solid wastes from the metallurgical industry, especially plant dusts, zinc-bearing slags and residues, to produce inert slag and at the same time to recover metal values such as nickel, chromium and zinc<sup>1-5</sup>. The Enviroplas™ process is based on the carbothermic reduction of metal oxides in the waste material (e.g. NiO, Cr<sub>2</sub>O<sub>3</sub>, ZnO) at temperatures of 1400 to 1600°C, in a d.c. plasma-arc furnace. In the case when zinc-bearing EAF dust is smelted, zinc is volatilized and captured in a lead-splash condenser. During thermal treatment of dust from a stainless-steel operation (alloy-steel dust), a crude ferro-alloy containing chromium and nickel is tapped from the furnace. Dusts from smelting chromite can also be treated by the Enviroplas™ process. However, economics indicate that hydrometallurgical treatment is more appropriate, due to the low levels of valuables. In this regard, Mintek is addressing the formation, removal and long term stability of Cr(VI) contained in these dusts.

### **2. DESCRIPTION OF PILOT PLANT**

A schematic diagram of the pilot plant is shown in Figure 1. The equipment consisted of a 5,6 MVA d.c. power supply, a raw material feed system, a plasma-arc furnace, a combustion chamber, a gas cleaning system, and instrumentation for data logging and control. The plasma-arc furnace comprised a refractory-lined cylindrical shell, a conical roof, a small flat roof positioned on top of the conical roof, and a central graphite electrode. The furnace employed direct current and was operated with a single graphite electrode as the cathode and the molten bath as the anode. The furnace had an internal diameter of 2 m and a shell diameter of 2,5 m. The hearth of the furnace was lined with a chrome-magnesite ramming mix, while the side-walls were lined with chrome-magnesite bricks. Alumina castable refractory was used for the roofs. The shell was equipped with water-spray cooling, and water-cooled panels were used at the conical and flat roofs. The flat roof contained the feed port, and the off-gas port was located in the conical roof. The return electrode consisted of several steel rods, embedded into the hearth refractories and further linked to the anode cable. The dust feed system consisted of a 1,5 m<sup>3</sup> hopper, with a bin activator located in the conical section of the hopper, and a screw feeder. Coke and silica were delivered via the main feed system, which comprised eight storage bins, a conveyor belt, a final feed hopper and a screw feeder.

The furnace was fully controlled using a PC-based SCADA (Supervisory Control and Data Acquisition) system, which provided a console for the configuration of operating parameters, recipe management, alarm annunciation, and data logging. The furnace was operated at power levels of 0,7 to 1,5 MW (typically 1,1 MW, 7,3 kA and 150 V) on a 24-hour basis. Feed was supplied to the furnace at a constant rate (about 750 kg dust per hour). Molten slag and metal were tapped every 2 to 3 hours.

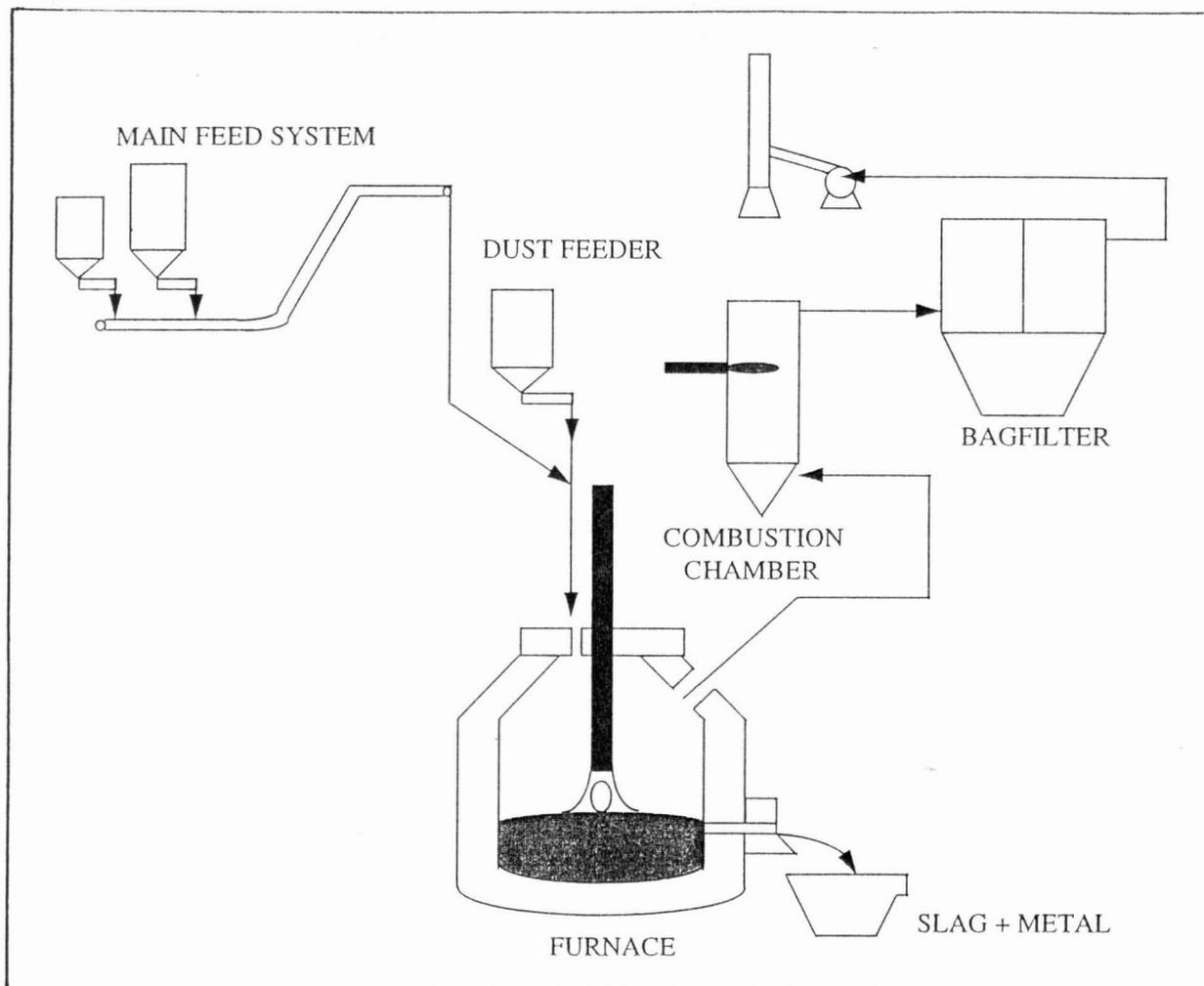


Figure 1: Schematic diagram of the pilot plant

### 3. TREATMENT OF ALLOY-STEEL DUST AND SWARF

The suitability of the Enviroplas process for the smelting of zinc-bearing alloy-steel dust was first demonstrated at Mintek in 1990, during a 5-day continuous campaign on the 500 kW scale of operation. The results of this testwork are described elsewhere<sup>2</sup>. In 1995 a 3-day campaign was carried out on the smelting of alloy-steel dust and co-melting of swarf in Mintek's 5,6 MVA plasma-arc furnace. During the main part of the campaign, dust, coke and some silica were employed, while for the last four taps, swarf (stainless steel shavings) was included in the charge. The swarf was added manually via a large access port at the beginning of each smelting/tapping operation.

#### 3.1 Feed Materials and Products

The chemical analyses of the alloy-steel dust and swarf used in the campaign are shown in Table 1. The dust contained on average 13,6 per cent  $\text{Cr}_2\text{O}_3$  and 2,9 per cent NiO. The ZnO level was relatively high at about 10 per cent. The chromium and nickel contents of the swarf were 18,1 and 8,5 per cent respectively. The coke contained about 77 per cent fixed carbon, 17 per cent ash and 4 per cent volatiles, and the silica sand had an  $\text{SiO}_2$  level of 99,2 per cent. A small quantity of silica sand was added as a flux (1 to 2 per cent by mass of the total charge) to lower the basicity ratio or the  $(\text{CaO}+\text{MgO})/\text{SiO}_2$  mass ratio from about 1,5 to 1,2. This achieved a good fluid slag at 1600°C and thus enhanced the reaction kinetics.

**Table 1:** Chemical analyses of alloy-steel dust and swarf, mass%

Alloy-steel dust						
Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	NiO	MnO	ZnO	PbO	MoO <sub>3</sub>
44,1	13,6	2,9	5,6	9,7	1,2	0,3

Swarf						
Fe	Cr	Ni	Mn	Mo	Si	C
68,9	18,1	8,5	1,6	0,4	0,6	0,05

The typical analyses of ferro-alloys produced during the first and second part of the campaign (i.e. for periods without and with swarf additions) are shown in Table 2. Carbon, sulphur and phosphorus contents were 5, 0,1 and 0,05 per cent respectively. Because of the relatively small amounts of crude ferro-alloy obtained per ton of steel product, no problems are anticipated with regard to contamination when the ferro-alloy is recycled to the steelmaking process. About 15 kg dust is generated per ton of stainless steel product, and approximately 0,5 kg ferro-alloy is obtained per kilogram of dust.

**Table 2:** Typical analyses of ferro-alloy products, mass %

	Fe	Cr	Ni	Mn	Mo	Si
Condition 1*	63	17	4,3	3,6	0,7	0,5
Condition 2*	62	17	5,4	2,7	0,6	0,7

\* Condition 1 : no swarf included in recipe

\* Condition 2 : swarf added in a swarf-to-dust mass ratio of 30-to-70

Typical slag analyses were as follows: 36,5 per cent SiO<sub>2</sub>, 22,6 per cent CaO, 19,7 per cent MgO, 1,4 per cent Cr<sub>2</sub>O<sub>3</sub>, 1,0 per cent FeO, 0,03 per cent NiO and 0,01 per cent ZnO. Slag samples were submitted for toxicity leaching tests and were found to conform to US EPA regulations for disposal. The average results of the TCLP (toxicity characteristic leach procedure) tests are given in Table 3.

**Table 3:** TCLP test results

	Leach analyses, ppm							
	Cr	As	Se	Ag	Cd	Ba	Hg	Pb
Average result	0,7	0,01	<0,02	<0,01	<0,01	0,5	<0,01	0,01
Specified max.	5	5	1	5	1	100	0,2	5

The fumes produced contained typically 56,1 per cent ZnO, 6,1 per cent PbO, 6,3 per cent FeO, 1,7 per cent Cr<sub>2</sub>O<sub>3</sub>, 0,5 per cent NiO and 3,4 per cent MnO. The fume was contaminated with about 2 per cent Na, 4 per cent K, 2 per cent F, 3 per cent Cl and 0,5 per cent S.

### 3.2 Mass Balances and Recoveries

About 20 t alloy-steel dust, 5 t coke, 2,2 t swarf and 270 kg silica were fed to the furnace. In total 11,4 t crude ferro-alloy, 5,4 t slag and 2,8 t baghouse fume were produced during the campaign. A typical charge consisted of 1550 kg dust, 420 kg coke and 30 kg silica. For the last four taps, when swarf was added, the charges contained about 875 kg dust, 240 kg coke, 20 kg silica and 375 kg swarf.

Recoveries for chromium, nickel and molybdenum were calculated, based on analyses and masses of dust fed and of slags and fumes produced. It was assumed that chromium, nickel and molybdenum that did not report to the slag or fume went into the ferro-alloy. This method was chosen because of the relatively large hold-up of metal in the furnace during the short smelting campaign. The recoveries of chromium, nickel and molybdenum were about 95, 96 and 94 per cent respectively. These recoveries were obtained during the last two days of the campaign, when the  $\text{Cr}_2\text{O}_3$  in the slag had stabilized between 1 and 2 per cent. During the first day of operation, i.e. during warm-up and when steady-state operation was not yet achieved, the  $\text{Cr}_2\text{O}_3$  contents of the slags were around 10 per cent, and the chromium recovery was only about 80 per cent; nickel and molybdenum recoveries were still about 95 per cent each.

### 3.3 Energy Balances

Ideal equilibrium calculations were performed at a fixed temperature of 1600°C, using the Mintek Pyrosim computer program<sup>6</sup>. The simulations provided theoretical energy requirements for the thermal treatment of alloy-steel dust and swarf. For charges without swarf (condition 1) and with swarf additions (condition 2, 30-to-70 swarf-to-dust ratio) the theoretical energy requirements are about 1,40 and 1,55 MWh per ton of dust respectively. This is equivalent to 2,8 and 1,7 MWh per ton of crude ferro-alloy product. The predicted alloy compositions are similar with respect to chromium content (about 18 per cent chromium) while the simulated nickel content of the alloy produced when swarf is added is higher than when no swarf is included in the charge (6,2 versus 4,7 per cent nickel).

Energy balances were performed for selected taps under condition 1, when the furnace was in steady-state, and for the four taps under condition 2. The actual energy consumptions for conditions 1 and 2 were 2,27 and 2,78 MWh/t dust respectively. Taking the theoretical energy requirements into account, this would indicate thermal efficiencies of the furnace of about 62 and 56 per cent respectively.

The rate of heat losses through the water-cooled parts of the furnace was measured, and an extra 20 kW was added as an estimate for the non-water-cooled bottom of the furnace. Expressed as a percentage of the power input, the rates of heat losses for conditions 1 and 2 were 41 and 39 per cent, thus the furnace thermal efficiencies based on measured heat losses were 59 and 61 per cent respectively.

From the above calculations, based on theoretical energy requirements, actual energy consumptions, and measured rate of heat losses, it appears that the thermal efficiency of the furnace was about 60 per cent. This means that approximately 60 per cent of the energy supplied to the furnace was used to drive the endothermic reduction reactions and to bring the products (ferro-alloys, slags, and gases) to the operating temperature of 1600°C. Expressed as a percentage of the power input, the rate of heat losses is expected to decrease when the process is scaled up, as experienced during other smelting processes tested at the Mintek pilot plant. It is envisaged that a 10 MW industrial plant would have a thermal efficiency of about 85 per cent.

### 3.4 Equipment Performance

In general, the equipment performed satisfactorily. The only operating problems were the relatively long interruptions when swarf was manually fed to the furnace. A dedicated feed system is required to supply this material to the furnace.

No problems were experienced with the refractories during the testwork. At the end of the campaign the furnace was used directly for another smelting trial, so no visual inspection and proper evaluation of the refractory performance could be carried out. However, from the MgO and Al<sub>2</sub>O<sub>3</sub> mass balances it appeared that little or no refractory erosion had occurred.

The arc voltage was measured as a function of the arc length, at constant power levels of about 1000 kW. The voltage gradients were 3,7 and 3,2 V/cm for conditions 1 and 2 (no swarf and swarf additions) respectively.

In order to obtain an estimation of dust carry-over into the gas stream, it was assumed that the presence of CaO in the fumes was a result of dust carry-over only. The feed entrainment calculated this way was 2,8 per cent of the dust fed to the furnace.

### 3.5 Hydrometallurgical treatment of Cr(VI)-containing dusts

Dusts obtained from ferrochromium and CLU operations, when contacted with water at 5 to 25 solids densities, have indicated the presence of leachable Cr(VI). The concentrations of Cr(VI) measured (up to 75 mg/l) were considerably higher than the permitted values (0,1 mg/l) in effluents and pose a threat to the environment. Studies are currently being conducted at Mintek to address this in different ways. An attempt is being made to determine the origin and conditions under which Cr(VI) is formed in these dusts. This would address the problem at its source, and measures could then be implemented to eliminate, avoid, or at least minimize the formation of Cr(VI). The nature of Cr(VI) in these dusts is also being studied, as this would indicate the optimum treatment option to use. Further, the removal of Cr(VI) from existing leachates by reduction with ferrous sulphate or other more cost effective options needs to be evaluated. The removal of soluble Cr(VI) from dusts is also important when considering treatment options for the long term stabilization of these dusts either by cement-based solidification, vitrification, or micro-encapsulation processes. Mintek has started to compile a database of relevant publications found in the literature on this subject, which is accessible via the Mintek library.

## 4. CONCLUSIONS AND RECOMMENDATIONS

The suitability of Mintek's 5,6 MVA plasma-arc furnace for the smelting of alloy-steel dust and the co-melting of swarf was demonstrated during a 3-day continuous campaign. About 20 t of dust and 2,2 t of swarf were treated at power levels of about 1 MW and feedrates of around 750 kg per hour. Coke was used as the reducing agent at a rate of 270 kg per ton of dust fed to the furnace. High extraction levels (about 95 per cent) of chromium and nickel were achieved. The energy consumption was 2,27 MWh per ton of dust and the thermal efficiency of the furnace was about 60 per cent. TCLP leaching tests were carried out on the slags produced, and the slags were found to be disposable according to EPA regulations. This technology is available for commercial implementation.

The hydrometallurgical treatment of Cr(VI) containing dusts should address:

- origin of Cr(VI) formation in ferrochromium baghouse dusts
- removal of Cr(VI) and optimum treatment methods in waste water and effluent
- long-term stability of treated ferrochromium solids.

## 5. REFERENCES

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