

The Enviroplas Process for the Recovery of Zinc, Chromium and Nickel from Steel-Plant Dust

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1. INTRODUCTION

The treatment of electric arc-furnace and converter dusts has received considerable attention over the past ten years, as new and changing environmental legislation has been introduced. The most commonly practised commercial process is the Waelz kiln which is operated in the United States of America by Horsehead¹. The resulting clinker consists of low grade pre-reduced iron units that can in principle be recycled to the arc furnace. However, the zinc-enriched fume from the Waelz kiln is unsuitable for direct use in a conventional electrolytic zinc plant, but can be treated as such by a thermal process (e.g. electrothermal - ZCA or an ISF plant). Many variants of the abovementioned Waelz kiln type of process are under development (e.g. using rotary hearth furnaces). However none of these produce saleable PW grade zinc metal directly. A process that is able to recover zinc metal and produce a disposable slag would have a potential economic advantage that should reduce the cost of EAF dust treatment and minimise the potential longer term liability inherent in most non-thermal processes.

Mintek, an international R&D and technology transfer organisation based in South Africa and serving the mining, mineral,

metallurgical and related industries has successfully developed d.c. plasma-arc furnaces for various applications. These include ferro-alloy and ilmenite smelting, as well as metal recovery from base metal slags. However, EAF dust treatment proved to be a rather difficult challenge due to its very fine and chemically complex nature. A number of campaigns were carried out at Mintek in a d.c. arc pilot plant furnace linked to an ISP lead-splash condenser. The results, especially in terms of low zinc recovery, were somewhat disappointing in three of the four campaigns carried out to date. This was in spite of considerable attention being given to feed preparation (dehalogenation, drying, calcining, etc).

It was decided to agglomerate the EAF dust to reduce the postulated reaction between the CO product gas and zinc or iron oxides in the dust, which produces zinc, partly reduced iron oxide, and CO₂. This CO₂ in turn reacts with the zinc to produce zinc oxide at the lower temperatures present in the condenser. The successful and conclusive results of this pretreatment approach (dehalogenation and agglomeration of the EAF dust) are given in this paper. Previous work on the treatment of alloy-steel dust and on the production of zinc oxide from EAF dust is also described briefly.

2. PILOT PLANT DESCRIPTION

A schematic diagram of the pilot plant is presented in Fig. 1, and a picture of the furnace is shown in Fig. 2. The pilot plant has been described in detail in an earlier paper². The basic equipment comprised a 5.6 MVA power supply, a feed system, a d.c. plasma-arc furnace, an ISP lead-splash condenser, a combustion chamber and a gas-cleaning system. The d.c. arc furnace consisted of a refractory-lined cylindrical shell, a conical roof and a small flat roof positioned on top of the conical roof. The conical roof contained the off-gas and feed port, while the central entry port for the graphite electrode was located in the flat roof. The furnace internal and external diameters were 2m and 2.5m respectively.

The refractory lining consisted of chrome-magnesite bricks. The outer shell was equipped with water spray-cooling, while the

conical roof was cooled using water-cooled panels. The conical and flat roofs were lined with alumina castable.

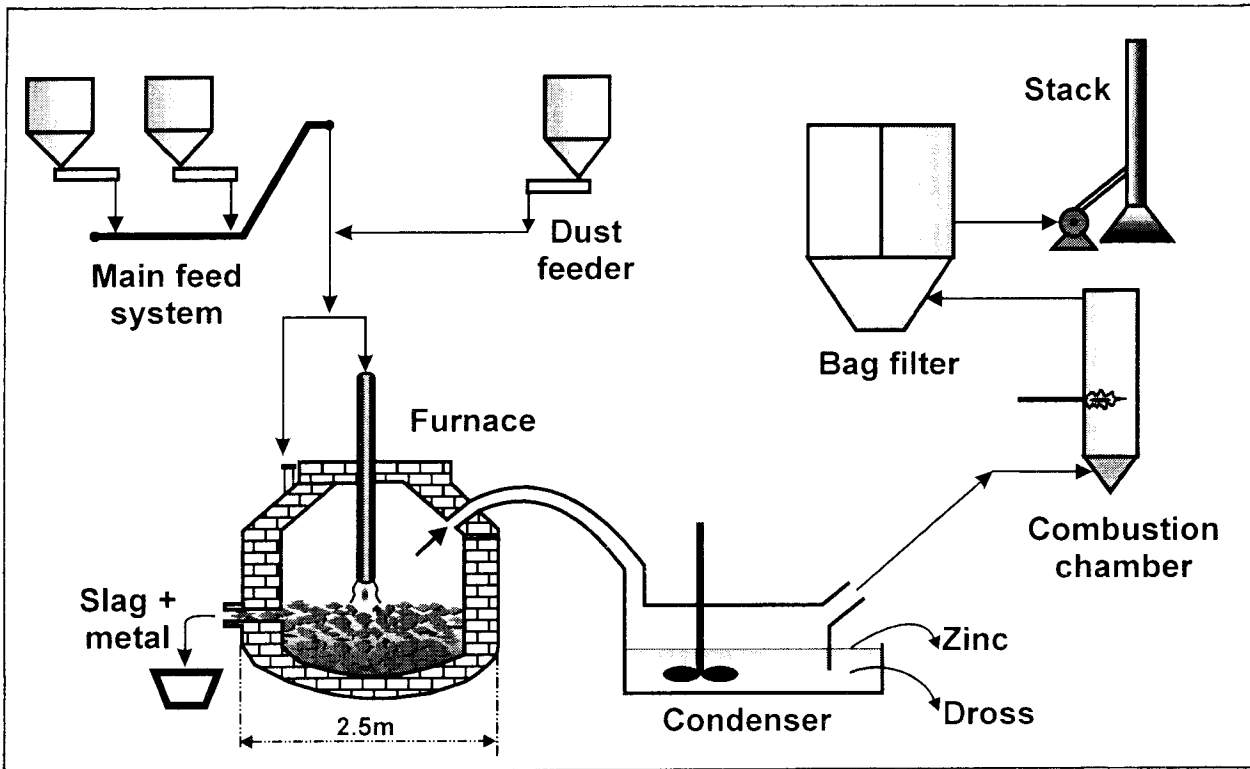


Figure 1 Schematic diagram of the pilot plant

The furnace was operated with a single graphite cathode employing direct current, and the molten bath was part of the return electrode or anode. The return electrode consisted further of numerous steel rods embedded into the hearth refractories and linked to the anode cable. The feed system comprised a conventional feed arrangement (feed bins on load cells, conveyor belts and screw feeders) and a dedicated dust feeder. The dust feeder consisted of a 1.5m³ hopper equipped with a bin activator in its conical section, and a screw feeder that could deliver the EAF dust either via the roof port or through the hollow electrode at up to 2t/h.

The furnace was connected to the lead-splash condenser via a short refractory-lined duct. The condenser assembly consisted of a condenser body with a single rotor, a lead-circulation pump, a cooling launder with immersible water-cooling pins, and a zinc-separation bath. The condenser body was essentially a steel box, about 2m wide, 4m long and 2m high lined with refractory

bricks. The condenser contained approximately 22t (metric ton, 1000kg) of lead and was designed to condense up to 350kg of zinc per hour.

The off-gas system behind the condenser comprised a refractory-lined combustion chamber, water-cooled ducting, a gas cooler, a reverse-pulse bag filter, a fan and a stack. The designed gas flowrate of the bag filter was 27 000Nm³/h.

The power supply consisted of two transformers and two rectifiers, capable of delivering 10kA to the furnace. The pilot plant was fully controlled using a PC-based SCADA system (supervisory control and data acquisition) which provided a console for the configuration of the operating parameters, recipe management, alarm annunciation and data logging. Manual and semi-automatic operation were also available.

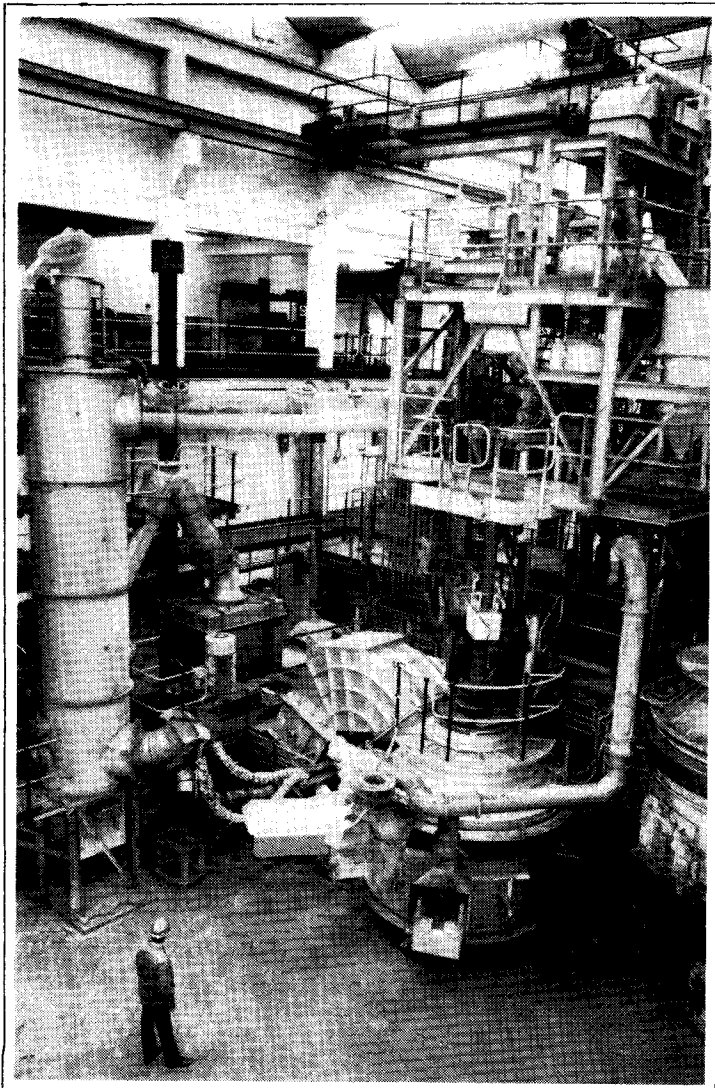


Figure 2 Photograph of the pilot plant

3. TREATMENT OF ALLOY-STEEL DUST

The suitability of the Enviroplas process for the smelting of alloy-steel dust and the co-melting of swarf was successfully demonstrated at the Mintek pilot plant. The detailed results of the testwork are described elsewhere³. The ISP lead-splash condenser (shown in Fig. 1) was by-passed, i.e. the off-gas was routed from the d.c. arc furnace directly to the combustion chamber. Alloy-steel dust (from a stainless-steel operation), metallurgical coke and some silica flux were employed during the main part of the campaign. The coke consumption was about 250kg per 1000kg dust. The furnace was typically operated at 1.1MW (7.3kA and 150V) on a 24-hour per day basis. Feed was supplied at a constant rate (about 750kg/h

dust) via the feed port in the roof, and molten slag and metal were tapped every 2 to 3 hours. Tapping temperatures between 1500 and 1650°C were measured with an optical pyrometer. The dust contained:

- 13.6 per cent Cr_2O_3
- 2.9 per cent NiO
- 5.6 per cent MnO
- 44.1 per cent Fe_2O_3

The ZnO level was relatively high, at 9.7 per cent from mild steel scrap used in the charge to the stainless steel EAF. The crude ferroalloy product contained about 17 per cent chromium, 4 per cent nickel, 4 per cent manganese and 1 per cent molybdenum. Typical slag analyses were as follows:

- 36 per cent SiO_2
- 23 per cent CaO
- 20 per cent MgO
- 1.4 per cent Cr_2O_3
- 1.0 per cent FeO
- 0.03 per cent NiO
- 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 recoveries of chromium, nickel and molybdenum were about 95, 96 and 94 per cent respectively. The energy consumption was 2.27 MWh/t dust. Taking the theoretical energy requirement (1.4 MWh/t dust) into account, this indicates a thermal efficiency of the furnace of 62 per cent. 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 anticipated that a 10MW operation, capable of processing about 50 000t/a of dust, would have a thermal efficiency of about 85 per cent.

4. PRODUCTION OF ZINC OXIDE FROM EAF DUST

A total of 17t raw (non-dehalogenated) dust was delivered from the dedicated dust feeder to the d.c. arc furnace. As in the case of the treatment of alloy-steel dust, the lead-splash condenser was by-passed and the zinc vapour was burnt to a crude zinc oxide. The

average analysis of the EAF dust was as follows:

- 20.8 per cent ZnO
- 2.1 per cent PbO
- 38.6 per cent Fe₂O₃
- 5.0 per cent SiO₂
- 8.3 per cent CaO
- 3.2 per cent MgO
- 1.2 per cent Al₂O₃
- 6.1 per cent C
- 1.4 per cent Cl

Metallurgical coke with a fixed carbon content of 80.5 per cent was used in the proportion of about 40kg per ton of EAF dust. A relatively low coke addition was required because the raw dust contained 6.1 per cent carbon. The addition of coke was designed to extract more than 95 per cent of the zinc while minimising the reduction of iron oxide (selective reduction). The furnace was operated at power levels of 630 to 650kW, and at feedrates of dust of about 500kg/h. The rate of heat losses from the furnace was 200 to 210kW (i.e. measured losses through water-cooled shell and roof plus an extra 50kW for losses via the non-water-cooled bottom of the furnace). Slag tapping temperatures were between 1450 and 1530°C. The average composition of the slag produced was as follows:

- 0.6 per cent ZnO
- 0.05 per cent PbO
- 53.2 per cent FeO
- 11.5 per cent SiO₂
- 16.5 per cent CaO
- 6.7 per cent MgO
- 3.4 per cent Al₂O₃

The zinc extraction from the slag was 98 per cent. About 50kg metal was tapped from the furnace per ton of EAF dust feed. It analysed 97.6 per cent Fe, 0.6 per cent Cu and 0.8 per cent S. The fumes produced contained on average 70.3 per cent ZnO, 5.9 per cent PbO, 3.1 per cent Fe₂O₃, 4.2 per cent Cl, 1.2 per cent F, 2.2 per cent Na, 3.4 per cent K and smaller percentages of SiO₂, CaO and MgO. Preliminary leaching tests were carried out where this zinc-oxide rich fume was subjected to a water-washing treatment in order to produce a cleaner, dehalogenated fume. The initial tests revealed the following removal levels via the wash water: 92 per cent Cl, 70 per cent F,

95 per cent Na, and 98 per cent K. Zinc and lead extractions were insignificant (below 1 per cent).

5. PRODUCTION OF PW GRADE ZINC FROM EAF DUST

Since July 1995, four EAF dust smelting campaigns have been carried out on the pilot plant to demonstrate the production of PW grade zinc directly from EAF dust. In total about 300t of dust, containing 20 to 25 per cent zinc oxide, was processed through the plant. The dust was dehalogenated before being fed to the d.c. arc furnace. It is known that high levels of halogens, especially chlorine, interfere with the proper operation of the condenser by forming large amounts of dross. During aqueous dehalogenation (washing with water), the chlorine level in the dust was reduced from about 2 per cent to 0.2 per cent. The dehalogenated dust was then dried in a rotary kiln at 300°C to reduce its water content to below 1 per cent. During the first smelting campaign it was established that the relatively high levels of moisture in the dust (0.3 to 1 per cent H₂O) resulted in the generation of excessive amounts of sticky dross (so-called toothpaste dross) in the condenser, and consequently very poor zinc recoveries from the condenser. The remaining dehalogenated dust was further dried ('calcined') in a rotary kiln at 500 to 600°C to reduce its water content to below 0.1 per cent. This dust was smelted at a feedrate of 1t/h using 95kg of coke reducing agent per ton of dust. The operating power was about 1.3MW and the zinc fuming rate was between 150 and 200kg/h, at operating temperatures of 1450 to 1500°C.

Zinc oxide levels of 1 to 2 per cent were achieved in the slags tapped from the furnace, which corresponds to zinc extraction efficiencies of 95 to 98 per cent. The slags were submitted for TCLP leaching tests, and were found to conform with US EPA disposal regulations, while the zinc tapped from the lead-splash condenser met PW grade specifications in most cases. However, the efficiency of zinc condensation was

relatively low and inconsistent (28 to 68 per cent condensing efficiency). The highest efficiency of zinc condensation (about 70 per cent) was obtained during a relatively short period of steady-state uninterrupted operation of about 24 hours, during which 25t of dehalogenated and calcined dust was processed. The dust contained:

- 24.6 per cent ZnO
- 2.3 per cent PbO
- 44.7 per cent Fe₂O₃
- 4.4 per cent SiO₂
- 7.7 per cent CaO
- 3.8 per cent MgO
- 1.0 per cent Al₂O₃
- 3.3 per cent MnO

The tapped slag contained on average 1.6 per cent ZnO and the zinc extraction was about 96 per cent. Zinc extraction and zinc condensing efficiency were calculated as follows:

$$\%Zn \text{ extraction} = \frac{Zn \text{ in feed} - Zn \text{ in slag}}{Zn \text{ in feed}} \times 100$$

$$\%Zn \text{ condensing efficiency} = \frac{Zn \text{ in condensed metal}}{Zn \text{ in vapour}} \times 100$$

Zn in vapour being defined as:
Zn in feed - Zn in slag.

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

Appropriate equipment changes were implemented to improve the availability of the pilot plant. About 50t of the dehalogenated and calcined dust that was left over after the third smelting campaign was melted without the addition of a reducing agent, cast in tapping trays, and then crushed

and screened to obtain 2 to 8mm agglomerate. The agglomerated dust was then smelted at the same operating conditions as employed for fine EAF dust. The coke addition was 90kg per ton of agglomerated dust, which was fed at a rate of 1000kg per hour. The average slag tapping temperature was 1480°C.

The chemical analyses of the agglomerated EAF dust and the metallurgical coke used for the testwork are given in Tables I and II. The agglomerated dust contained:

- 22.6 per cent ZnO
- 1.4 per cent PbO
- 51.5 per cent Fe₂O₃

Typical analyses of products are shown in Tables III and IV. The levels of ZnO and PbO in the slags were below 1 and 0.1 per cent respectively. The zinc metal product conformed to PW grade specifications. Maximum levels of lead, copper, iron and cadmium in PW grade zinc are 1.4, 0.20, 0.05 and 0.02 per cent respectively.

A zinc mass balance is provided in Table V. For each ton of agglomerated dust fed to the furnace, 658kg residual slag, 60kg furnace metal, 148kg zinc metal, 93kg dross, and 7kg fume were produced. It can be derived from Table V that during the single pass operation (no recycling of drosses and fumes), the zinc extraction in the furnace and the zinc condensation efficiency were 96.7 per cent and 82.9 per cent respectively. About 80 per cent of the zinc in the feed reported to the zinc metal tapped from the condenser. The proportions of zinc that passed into the slag, dross and uncondensed fume were 3, 14 and 2 per cent respectively. The use of several condenser rotors in series, as practised industrially, should further increase the efficiency of zinc condensation, and the recycling of drosses and fumes should result in an overall zinc recovery of more than 95 per cent.

Table I : Chemical analysis of agglomerated EAF dust, mass %

ZnO	PbO	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	CuO	C	Cl
22.6	1.38	51.6	6.2	7.7	4.3	1.3	0.23	0.002	0.02

Table II : Chemical analysis of metallurgical coke, mass %

Fixed C	Ash	Volatiles	H ₂ O
78.2	18.3	3.1	0.4

Table III : Typical analysis of non-metallic products, mass %

Material	ZnO	PbO	FeO	SiO ₂	CaO	MgO	Al ₂ O ₃	CuO
Slag	0.9	0.05	54.1	12.4	12.2	6.7	3.5	0.11
Fume	66.3	9.5	2.4	1.9	1.2	0.65	0.70	0.07
Dross	33.8	47.9	2.6	1.6	1.1	0.57	0.48	0.08

Table IV : Typical analysis of metallic products, mass %

Material	Zn	Pb	Fe	Cu	Cd
Furnace metal			95.6	1.5	
Zinc	98.5	1.3	0.04	0.04	0.03

Table V : Zinc mass balance

Material	Mass, kg	Zn Content, %	Zn Content, kg
EAF dust input	40 108	18.1	7 274
Zinc metal*	5 940	98.1	5 830
Slag	26 396	0.92	242
Dross	3 743	27.2	1 016
Fume	296	53.3	158
Furnace metal	2 387	0.0	0

* About 10 per cent of the zinc was tapped as hard metal containing about 1.5 per cent iron, however this is expected to decrease with scale up.

An energy balance was carried out for the d.c. arc furnace. The average energy input was 1200kWh per ton of agglomerated dust, at a mean tapping temperature of 1480°C. The rate of heat losses through the water-cooled parts of the furnace (shell and conical roof) was measured, and an extra 70kW was added as an estimate for the non-water-cooled flat roof and bottom of the furnace. The rate of loss of energy was on average 250kW, and the calculated specific energy requirement, based on actual kWh per ton of agglomerated dust and on energy losses was 950kWh per ton of agglomerated dust. Expressed as a percentage

of the power input, the rate of heat losses was 21 per cent, thus the furnace thermal efficiency was roughly 79 per cent.

6. FURTHER TECHNICAL DEVELOPMENTS

Some further technical developments are required for the Enviroplas process, particularly in the area of EAF dust pretreatment. It was established during pilot-plant testwork that the agglomeration of EAF dust improved the zinc recovery significantly. Due to practical constraints, it was decided to melt EAF dust

without the addition of a reducing agent, to produce agglomerated dust material and so to prove the process. Other options for agglomeration and dehalogenation, as well as the feeding of hot agglomerated dust to the d.c. arc furnace are being evaluated in order to improve the economics of the process. Once a decision has been made concerning the best process route, one more pilot plant campaign (200 to 300t dust) is required to demonstrate the process fully before the technology can be implemented.

7. TECHNO-ECONOMIC ASPECTS/MARKET CONSIDERATIONS

An evaluation of the capital and operating costs of the selected process options shown in Fig. 3, has led to the segmentation of the market for the Enviroplas process as follows:

- 10 to 20 kt/a of EAF dust - individual steel producers
- 50 to 100 kt/a of EAF dust - centralised treatment plant
- 10 to 100 kt/a of EAF dust - co-treatment plant.

The first case applies to individual steel plants where the economies of scale dictate minimal EAF dust pretreatment, the production on-site of a disposable slag, and the sale of zinc-oxide enriched fume. Future options could be the production of electrolytic zinc using novel technology such as the Ezinex process⁴ or the use of a zinc (splash or other) condenser. However the production of only 2 to 4kt of zinc per annum limits the commercial options for zinc recovery. The steel producer would require to process his own dust or outsource the operation on site or over the fence (i.e. tolling). This option gives steel producers the benefit of a cost per ton of EAF dust of about \$150/t, compared with other typical thermal treatment costs (including transport of the dust to a central facility) of up to double this figure.

The second case applies to a central regional treatment plant where the 10 to 20 kt/a zinc production would help to carry the cost of EAF dust pretreatment, to maximise zinc recovery, and possibly the upgrading of zinc from PW grade to SHG (depending on market demand); hot dip galvanizers actually prefer PW grade. The most appropriate operator of such a central plant would be an existing zinc producer. Here an ISP lead-splash condenser producing PW grade zinc would probably be most advantageous, since the cost would be less than \$60/t EAF dust for hydro-dehalogenation or about \$20/t EAF dust for pyro-dehalogenation. However, electrowinning of zinc from zinc-enriched fume using the Ezinex process is a good alternative especially since the product is high grade zinc and there is little zinc-ferritic residue produced, unlike in the case of treating dust directly by an electrowinning route. However, the cost is almost \$100/t EAF dust.

The third case applies to existing thermal lead producers that operate blast or flash furnaces, which produce a slag that often contains over 10 per cent zinc. Such plants are probably liable to treat their slags once the current Bevill exemption expires, and could potentially increase the viability of their slag treatment operation by including EAF dust in the process flowsheet (probably by adding it to the slag holding furnace prior to liquid transfer to the d.c. arc fuming furnace). A potential profit of \$30/t EAF dust, excluding dust treatment charges, is possible for high grade zinc.

For the preliminary economic analysis of the Enviroplas process (Table VI and Fig. 4), the following assumptions were made: zinc content of dust 20%, d.c. arc furnace thermal efficiency 85%, operating availability 90% (7884 h per annum), electricity unit cost 50\$/MWh, coke breeze unit price 50\$/t. The capital charge is based on a 5-year plant amortisation. The capital costs of a distillation plant to produce SHG zinc (cases 2 and 3) were estimated at \$7.5 million. In all cases an existing infrastructure was assumed. The estimates relate to battery limits facilities with provision made for EPCM (Engineering Procurement & Construction

Management), site development and vehicles. For the operating costs, all major variable elements were identified and costed individually. Fixed costs embrace production and analytical labour, maintenance, insurance and overheads. A cost comparison of the process options is shown in Table VI. Case 1 is penalised by its smaller scale and lower product value, but the economics are helped by a generally cheaper plant and process. The centralised plant concept has some economic merit. The hydro-dehalogenation and Mintek/Ezinex processes

compare poorly with the thermal dehalogenation, but the former could be worth re-examining if a location is found where the salty wash water can be discharged to a river or the sea. This will certainly result in a significant cost saving. Undoubtedly, the best option is case 3 where economies of scale can be realised. It should be noted that cases 2A and 2B have the potential of producing PW grade zinc, thereby avoiding the distillation operation. The cost difference is significant, as can be seen from the last line of Table VI.

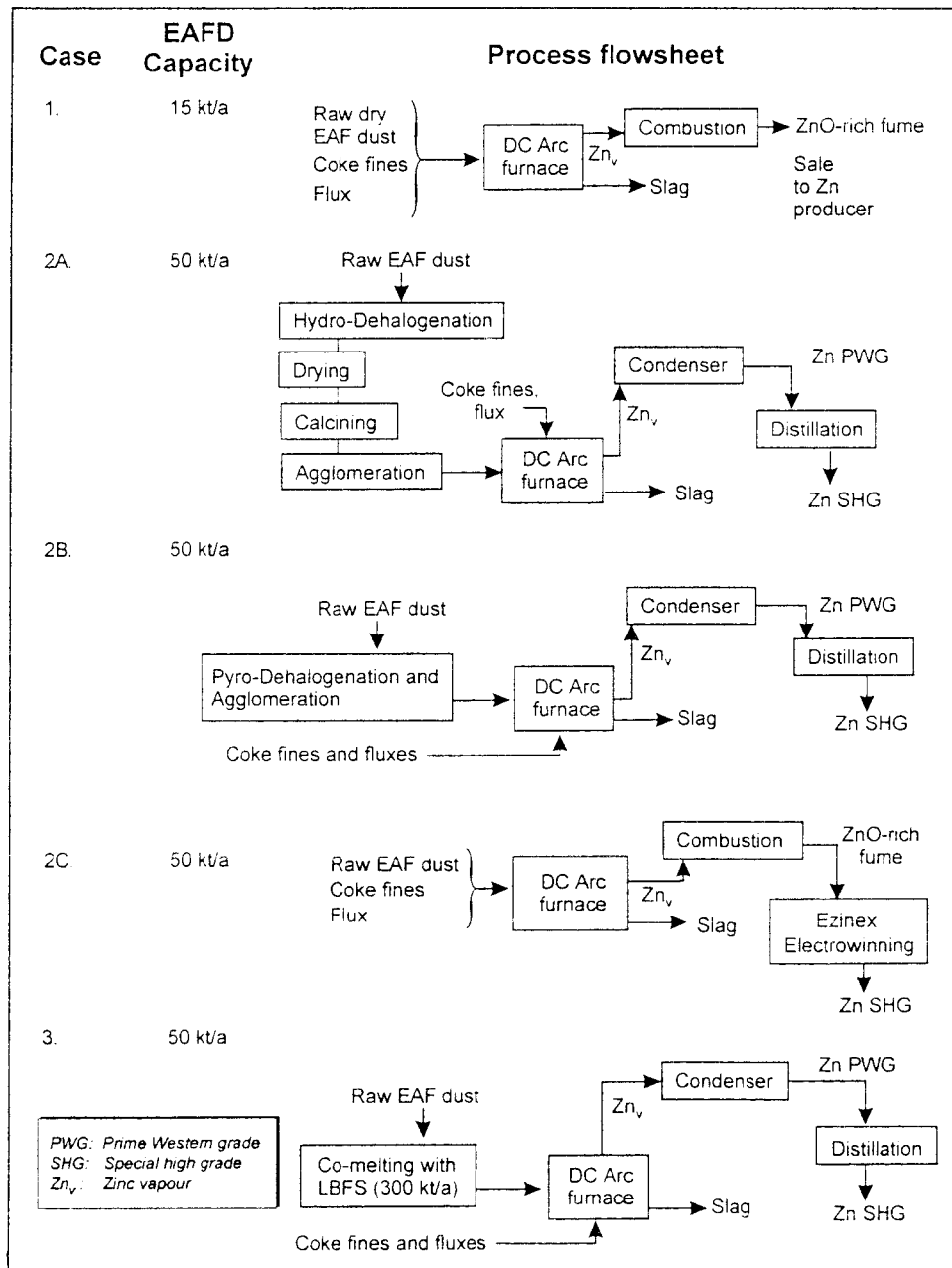


Fig.3 Process flowsheet options considered for Enviropias evaluations

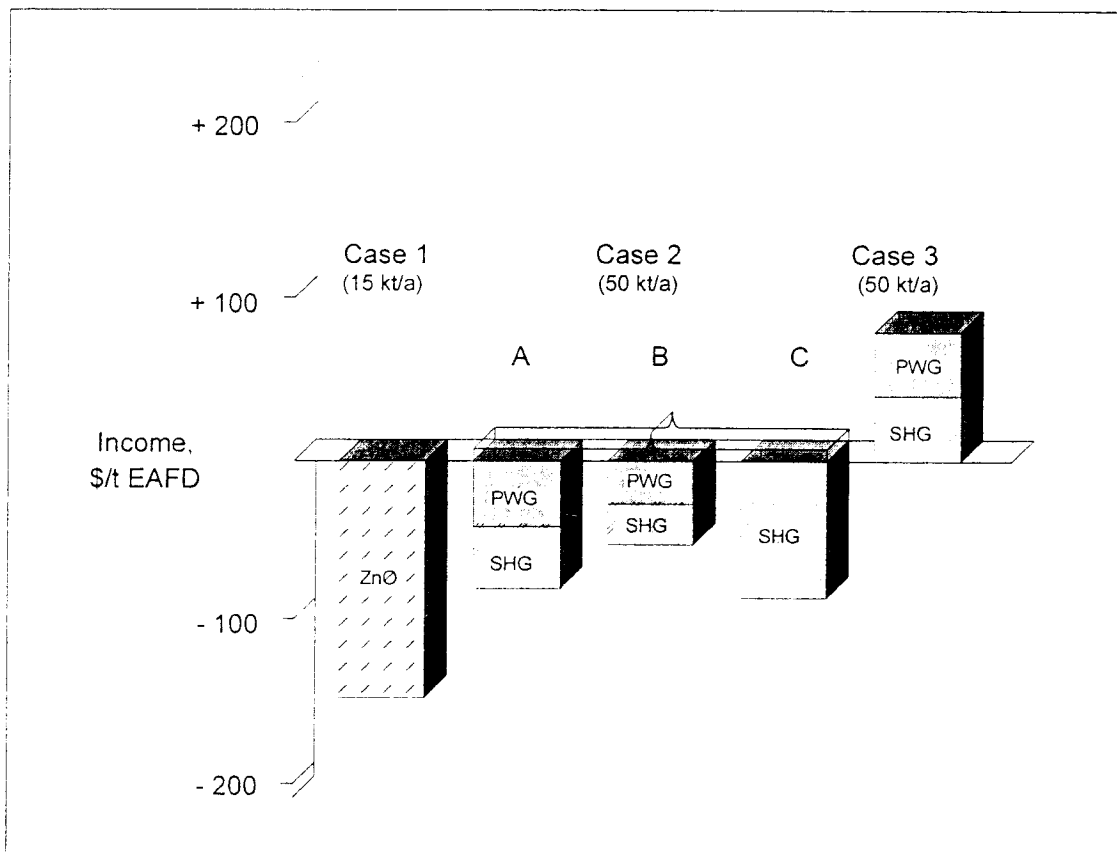


Figure 4 Financial comparison of process options

Table VI. Capital and operating costs of Enviroplas process options

PARAMETER	CENTRAL PLANT				LEAD PLANT
	MINIMILL CASE 1	CASE 2A	CASE 2B	CASE 2C	
SCENARIO	EAF dust processed in a minimill to produce a ZnO fume that is washed to remove halides	Central facility where EAF dust is hydro-dehalogenated and then agglomerated	Central facility where EAF dust is pyro-dehalogenated and agglomerated	Combined Mintek/Ezinex process to produce cathode	Incremental EAF dust addition to LBFS treatment plant (300kt/a LBFS)
EAF DUST FEED	15 kt/a	50kt/a	50kt/a	50 kt/a	50 kt/a
PRODUCT	ZnO fume	SHG Zn	SHG Zn	SHG Zn	SHG Zn
SELLING PRICE	60% of LME (\$1100t/a)	LME	LME	LME	LME
CAPEX (\$000)	6000	26400	25500	25000	12500
REVENUE (\$000/a)	1965	10850	10850	11000	10850
COSTS (\$000/a)					
- Variable	1277	5510	4495	6695	4720
- Fixed	1687	4673	4190	4053	2110
- TOTAL	2964	10183	8685	10748	6830
GROSS PROFIT (\$000/a)	-999	667	2165	252	4020
\$/t EAF DUST					
- Sales	131	217	217	220	217
- Operating	-198	-204	-174	-215	-137
- Capital	-80	-106	-102	-100	-50
- TOTAL	-147	-92	-59	-95	30
\$/t EAF DUST to PWG Zn	N/A	-56	-22	N/A	67

LBFS : Lead blast-furnace slag

N/A : not applicable

8. CONCLUSIONS

- Large scale plant work has shown that a d.c. arc furnace is able to process pretreated EAF dust to produce PW grade zinc using a lead-splash condenser. Good levels of zinc extraction (over 95%) and recovery (over 80%) have been consistently achieved provided the dust is dry, dehalogenated and agglomerated.
- The flexibility of the d.c. arc furnace permits a variety of technical and commercial options to treat EAF dust and minimise costs and environmental liabilities.
- The most appropriate approach for a stand-alone plant located at a steelwork is the treatment of raw EAF dust to produce zinc enriched fume for further treatment to recover zinc by a centralised zinc producer. The estimated cost is about \$150/t for 15kt/a EAF dust.
- The best approach for a centralised facility treating 50 to 100kt EAF dust is pyro-dehalogenation followed by PW grade zinc production where the treatment cost is only about \$20/t EAF dust.
- However, the most profitable choice would be for an existing lead producer to include EAF dust in the treatment of LBFS to recover zinc where a profit of about 60 to 70 \$/t of EAF dust could be made.

There are several lead smelters in North America that would be well placed to treat EAF dust, and testwork to co-treat dust with lead slag to recover zinc units is planned during the next year, provided the necessary interest and support are forthcoming. In the interim the alternative process options are ready to be demonstrated to prospective clients. The steel industry should encourage lead and zinc producers to implement technology such as the Enviroplas process to their mutual benefit. Mintek is ready to assist this proposed initiative.

9. ACKNOWLEDGEMENTS

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