

# Plasma processing of dusts and residues

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**Abstract:** The use of plasma furnaces for the recycling of metal scrap, of metallurgical residues and of fly-ashes from municipal solid waste (MSW) and sewage sludge (SS) incineration is reviewed. Aluminium dross, titanium scrap, spent automotive catalysts and stainless steelmaking dust are examples of current plasma melting applications. Wherever possible, hollow graphite electrodes tend to replace water-cooled metal torches. This trend also holds for plasma processing of MSW and SS incineration residues. In comparative pilot tests with these residues carried out with transferred-arc metal plasma torches and with graphite electrodes, respectively, no difference in processing behavior was observed. Under oxidizing conditions in the furnaces and in the off-gas systems, any de novo synthesis of dioxins was avoided and a vitrified slag, a small off-gas volume and a secondary fly-ash mainly containing volatile chlorides and sulfates were obtained.

## 1. Introduction

Thermal plasmas find increasing attention in materials processing for their high energy densities, low gas flow rates, ease of installation, and free choice of chemical potentials. Drawbacks are the costs for torches, electrodes, and power supplies, for plasma gases and electric energy. Industrial applications of thermal plasmas therefore depend on the balance between plasma-specific benefits and costs. This balance may change with time and location and cause plasma processes to emerge and disappear again.

## 2. Scrap recycling

### Steel

In materials recycling, thermal plasmas are used very successfully in steelmaking from scrap in the electric arc furnace (EAF): In 1993, 223 mio t of steel were produced in EAFs worldwide representing 31% of the total world production of crude steel (1). However, metallurgists speak of plasma furnaces only in the case of intentionally gas-stabilized electric arcs. Since EAFs are normally not operated with gas-stabilized arcs, they are not called plasma but arc furnaces. Occasionally, this arbitrary definition may give rise to confusion.

### Titanium

For the recovery of titanium scrap, plasma melting processes have become well established (2). Apparently, the operation of an argon plasma system at atmospheric pressure is economically feasible when it competes with a high vacuum system.

### Aluminium

The treatment of aluminium dross and scrap in plasma-heated rotary furnaces has been developed in order to replace the conventional rotary salt furnace process with its problems concerning the salt cake disposal (3,4). Presently, Alcan is operating two plasma rotary furnaces with an annual capacity of 14,000 t of dross in its Guillaume-Tremblay Works in Jonquièrre, Québec. The non-transferred plasma torch of the Westinghouse type is run with air. The dross is charged without preparation, and at the end of the batch operation the products are cooled down to 400°C under Ar atmosphere to keep  $Al_2O_3$  and AlN formation low. The Al recovery is 80 to 90% with respect to metallic Al input. A second plasma rotary furnace plant was built by Plasma Processing Corporation in Ravenswood, West Virginia, with an annual capacity of 40,000 t of Al dross. PEC plasma torches with non-transferred arcs are operated with oxygen. By using pure oxygen, the AlN content decreases while the highly exothermic  $Al_2O_3$  formation is promoted thus lowering the electric power demand.

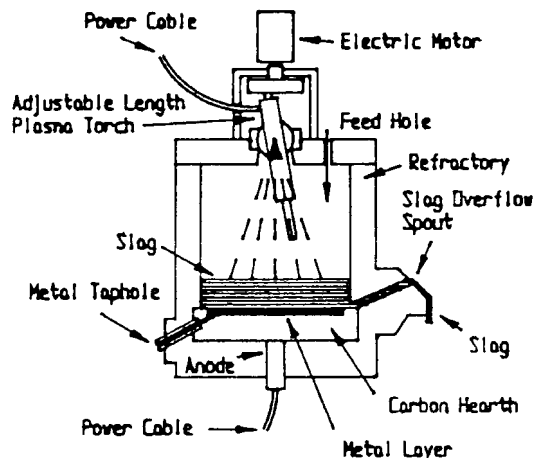
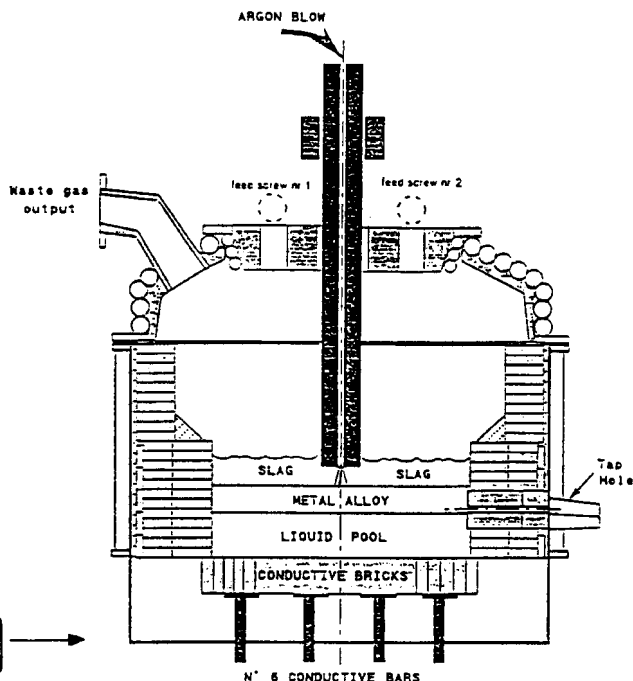


Fig. 1 Plasma furnace for the recovery of platinumoids from spent automotive catalysts (5).

Fig. 2 7 MW furnace for the recovery of stainless steelmaking dust at Terni (11).



Consequently, a rotary salt-free furnace has recently been taken into operation at Voerde, Germany, which is equipped with an oxy-fuel burner instead of a plasma torch. Apparently, the use of plasma torches in the case of Al dross processing is dependent on the local energy cost relations.

### Platinoids

For the recovery of platinoids from spent automotive catalysts a plasma melting furnace has been in operation since 1984 at Multimetco, Anniston, AL (USA) with a feedrate of  $> 1$  t/h and a recovery rate of  $> 98\%$  of Pt, Pd and Rh. The catalysts are crushed, blended with lime and other additives, a molten calcium aluminate slag produced and the platinoids collected in a liquid carbon-saturated iron layer at the bottom. A DC cathode plasma torch (Tetronics) is installed through the roof, the anode being placed into the furnace hearth made of carbon, Fig. 1 (5,6).

### Steel scrap fines

With the aim of reducing the gas flow rate in a cupola furnace so that low-cost fine scrap like borings and turnings could be charged without excessive dusting, the 45 t/h cupola furnace at the foundry in Defiance, Ohio, was equipped with 6 plasma torches to superheat the blast. The cupola was commissioned in 1989 (7,8). At Sept-Fons in France, a 20 t/h cupola was retrofitted with a plasma torch for blast superheating which permitted to feed the cupola with steel scrap instead of pig iron (9).

## 3. Processing of steelmaking dust

### Chromium steel

The Scandust plant at Landskrona, Sweden, was built in 1984 and has successfully been operating as a smelter for non-agglomerated stainless steelmaking dust. The coke-filled shaft furnace is equipped with 3 plasma torches of 4 MW each. A typical production figure is 35,000 t dust/year (10).

In 1992, a plasma-arc furnace was installed at Terni, Italy, to process 20,000 t/year of dusts and slurries arising from the two electric arc furnaces and the AOD vessel operating at Terni. The dust processing furnace, Fig. 2, is equipped with one hollow graphite electrode (cathode). Argon or nitrogen is blown through the hole in the graphite electrode to stabilize the arc. The dust is charged through two holes in the roof by means of 2 screw feeders together with 270 kg of coal and 60 kg of lime per t of dust. The alloy produced contains typically 11% Cr, 2.5% Ni and 5% C, while the volatile metals (Zn, Pb, Cd) are recovered as dry dust rich enough in ZnO to be traded, and the slag (380 kg/t alloy) is dumped. The single graphite electrode furnace is designed for 7 MW and 20 kA. The diameters of the hollow electrode are 300 and 15 mm. During commissioning, it was found most important to keep the feeding rate and the electric power in adequate balance (11).

At British Steel Sheffield works, a 3 MW DC arc furnace is in operation for stainless dust processing. It is equipped with a solid graphite electrode, i.e. no plasma-stabilizing gas is added (12).

At the Chiba works of Kawasaki Steel, a pilot 1.5 MW DC plasma arc furnace has been operated with stainless steelmaking dust fed through the hollow graphite electrode by means of  $N_2$  carrier gas. The Cr and Ni yields were higher than those achieved by blowing the dust into the top and bottom blown converter without prior agglomeration (13).

### Ferronickel

Based on the existing experiences with hollow-electrode DC arc furnaces for stainless dusts and for the production of ferrochromium from chromite fines (14), the Greek ferronickel producer LARCO, on the basis of an experimental study, came to the conclusion that the most feasible concept for recycling of their dusts and sludges (1.2% Ni, 8 to 10% C; 230,000 t/year) was a large DC electric furnace with dust feeding through the hollow central graphite electrode (15). At present, the largest furnace operating as a smelter for fines is the 40 MVA FeCr furnace at Krugersdorp, South Africa, with a production rate of 6.3 t FeCr/h (14), Fig. 3.

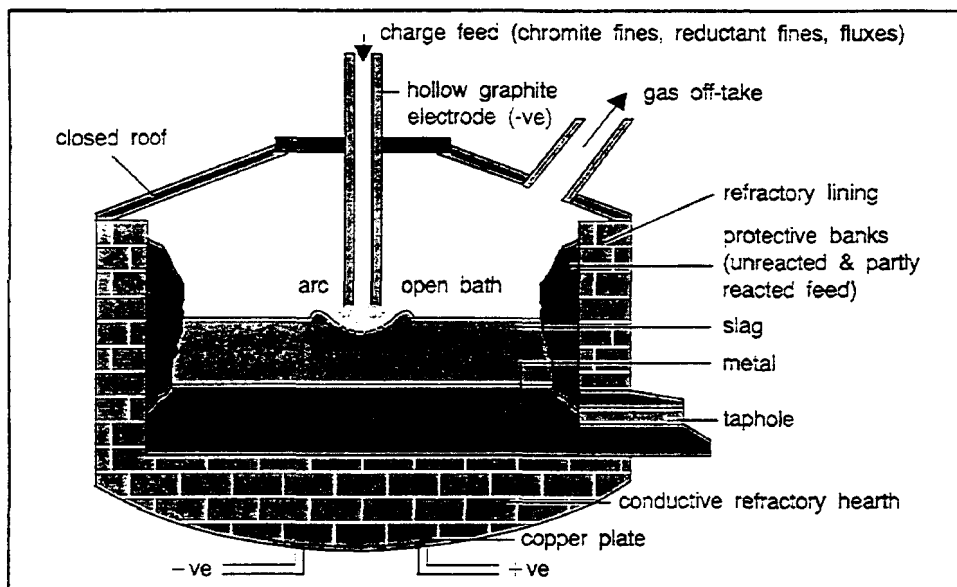


Fig. 3 40 MVA DC plasma furnace for ferrochromium production from chromite fines at Krugersdorp, South Africa (14).

### EAF steel

Plasma furnaces have also been considered for processing normal EAF dusts containing relatively high amounts of zinc (16), which has to be separated before recycling the residue back into the steelmaking process. Therefore, the treatment consists of evaporating the zinc under reducing conditions and producing a ZnO-rich flue dust which can be traded to the zinc industry. Since ZnO is more easily reduced than  $Cr_2O_3$ , the high temperatures required in stainless dust recycling are not really needed here. Consequently, non-electric processes, like the rotary kiln, the rotating hearth or the circulating fluidized bed may be more adequate and economic methods than plasma smelting.

## 4. Processing of solid residues from waste incineration

### Aims of plasma processing

Thermal plasmas have been taken into consideration for the processing of solid residues from municipal solid waste and sewage sludge incineration plants. The aim is to produce an inert vitrified slag to be used as road- or land-fill, a secondary fly-ash containing the volatile salts and oxides to be further treated and re-used, and a small gas volume that can readily be cleaned. A number of pilot investigations have recently been carried out (5, 17-22), and first industrial furnaces started operating in Japan. In some cases metallic plasma torches are used (18,21,22), in others graphite electrodes are preferred (5,19,20).

### Destruction of dioxins and furans

In view of the requirement to destroy all dioxins and furans in the thermal process and to prevent any de novo synthesis during off-gas cooling, the proper choice of the oxygen potentials in and downstream the furnace plays an important role. From equilibrium considerations, the re-formation of dioxins is expected to occur at temperatures below 500°C and at relatively low oxygen potentials (23), Fig. 4. Therefore, the off-gases should be quenched rapidly in the temperature range between 600 and 200°C in an atmosphere containing an excess of air, and the dust entrained with the off-gas should not contain any coal or soot particles which might locally create reducing conditions.

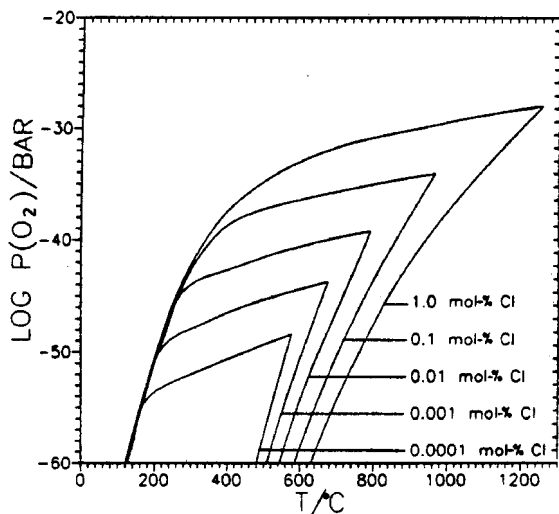


Fig. 4 Calculated regions in which the partial pressure of 2,3,7,8-TCDD reaches 0.1 ng/m<sup>3</sup> for a C/H mole ratio of 2/1 and Cl contents from 0.0001 to 1.0 mol-% in the system (23).

### Metal torches versus graphite electrodes: pilot melting tests

In the melting furnace itself, a reducing atmosphere may be desirable to produce a liquid metal phase of the heavy metal oxides contained in the feed mix, but it will more likely be preferable to obtain only liquid slag which includes the non-volatile heavy metal oxides in a non-leachable form. In that case the melting process will take place in an oxidizing atmosphere. The use of graphite electrodes may therefore be limited by the environmental and product requirements. With this question in mind, results recently obtained in this laboratory (LTH) from pilot processing tests with dusts and ashes from municipal solid waste (MSW) and from sewage sludge (SS) incineration with metallic plasma torches are compared with tests carried out in a DC arc furnace with a hollow graphite electrode in similar scale in another laboratory (IME) of RWTH Aachen (20). The LTH equipment described in (21) was operated with 2 argon-stabilized tungsten-electrode plasma torches at 250-350 kW, Fig. 5.

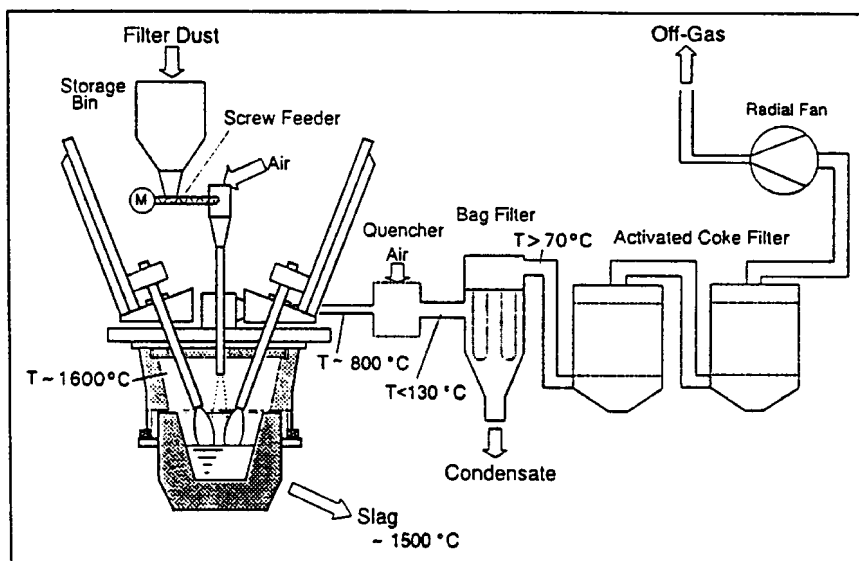


Fig. 5 Pilot plasma furnace at LTH (RWTH Aachen) with two metal plasma torches for AC operation, with dust feeding and flue-gas cleaning system (21).

The IME furnace (20) had a central hollow graphite electrode (cathode) dipping into the slag, and a bottom anode. The dust was fed into the furnace through the electrode hole together with some carrier gas. The power rating was 450 kW.

In both investigations, air was allowed to penetrate into the furnace to make the atmosphere oxidizing, and the off-gas was dry-quenched by large amounts of excess air. No reductant was added to the feed. Consequently, the formation of a metal phase could be avoided in the LTH test. IME reported the formation of a very small proportion of metal phase. Under similar non-reducing conditions, Ebara (Japan) melted sewage sludge residues in a 3 MW plasma furnace and obtained about 10% of metal phase (18,24). At LTH, a separate test was carried out with SS residues where a metal phase was deliberately formed by adding some carbon. In all these cases, the metal phases were mainly composed of 70 to 80% Fe, 1 to 10% Cu, 2 to 7% P and up to 1% each of Ni, Cr, Sn, Zn and C. Due to the high Cu and P contents such an alloy would not be an acceptable raw material for the steel industry. Therefore, it appears recommendable to avoid the formation of a metal phase altogether.

#### Comparison of test results

The following comparison comprises pilot test results obtained under oxidizing conditions for the melting of MSW fly-ashes and of SS grate-ashes, fly-ashes and a feed mix composed of both SS grate- and fly-ashes and spent foundry sand. In [Table 1](#), the compositions of the different feed materials are listed. [Table 2](#) contains the analyses of the slags produced, and in [Table 3](#), the compositions of the secondary fly-ashes are summarized. Results from run C have been omitted because of abnormal entrainment of fines. [Table 4](#) relates the relative amount of secondary fly-ash formed with the content of Cl and SO<sub>4</sub> in the feed material.

By comparing these results with each other, the following conclusions may be drawn: The amount of secondary fly-ash is proportional to the content of anions in the feed capable of forming volatile compounds. Consequently, these fly-ashes are mainly composed of chlorides and sulfates. The alkali salts alone represent 65 to 70% of these fly-ashes, [Table 5](#). The degrees of volatilization observed for the different feed components were very similar in all tests. The average values are summarized in [Table 6](#). It appears that in most cases the degree of volatilization is related to the tendencies of the compounds to form volatile chlorides. Typically, the volatilized components were found as condensed matter in the fly-ashes except for 5% of the chlorine and 75% of the sulfur which remained in the off-gas as HCl and SO<sub>2</sub> (20). More detailed considerations of the thermodynamics governing the evaporation and condensation processes in these multi-component systems are found in (21) and (25).

TABLE 1: Compositions of feed materials

Components wt-%-	A MSW fly-ash (LTH)	B MSW fly-ash (IME)	C SS fly-ash	D SS grate-ash	E SS residue mix
Al <sub>2</sub> O <sub>3</sub>	8.3	12.9	9.47	9.9	8.15
CaO	14.0	17.2	43.7	43.0	32.8
SiO <sub>2</sub>	17.1	27.5	15.0	22.6	35.9
MgO	1.8	2.0	1.21	1.50	1.18
TiO <sub>2</sub>	1.3	1.2	0.51	0.58	0.46
Fe <sub>2</sub> O <sub>3</sub>	2.1	4.4	5.77	6.19	5.60
Na <sub>2</sub> O	9.2	2.2	2.36	0.43	1.56
K <sub>2</sub> O	10.5	2.5	0.77	0.67	0.72
ZnO	7.1	3.8	-	-	-
PbO	1.9	0.9	0.037	0.024	0.023
P <sub>2</sub> O <sub>5</sub>	1.4	0.9	7.74	8.16	6.02
C	0.2	3.3	-	-	-
Cl	12.0	4.0	2.6	1.3	1.41
F	0.12	0.3	-	-	-
SO <sub>3</sub>	10.4	4.5	5.60	2.00	2.69

MSW = municipal solid waste

SS = sewage sludge

SS residue mix = 45% SS fly-ash + 31% SS grate-ash + 24% spent foundry sand

TABLE 2: Compositions of slags

Components wt-%	A MSW fly-ash (LTH)	B MSW fly-ash (IME)	C SS fly-ash	D SS grate-ash	E SS residue mix
Al <sub>2</sub> O <sub>3</sub>	24.6	17	24.8	18.0	20.3
CaO	20.9	23	43.4	43.0	32.9
SiO <sub>2</sub>	26.8	35	14.7	21.4	32.5
MgO	2.6	5	1.34	1.44	1.32
TiO <sub>2</sub>	2.7	-	0.47	0.56	0.43
Fe <sub>2</sub> O <sub>3</sub>	4.1	11	5.24	5.81	5.06
Na <sub>2</sub> O	1.48	1.6	1.51	0.28	0.45
K <sub>2</sub> O	0.37	<1	0.07	0.08	0.12
ZnO	0.68	0.1	-	-	-
PbO	0.03	<0.1	0.004	0.005	0.003
P <sub>2</sub> O <sub>5</sub>	0.87	-	6.94	7.19	5.20
S	0.005	<0.3	0.12	0.12	0.008

TABLE 3: Compositions of secondary fly-ashes

Components wt-%	A MSW fly-ash (LTH)	B MSW fly-ash (IME)	D SS grate-ash	E SS residue mix
Na	12.2	9	10.4	18.1
K	18.9	21	17.7	9.9
Pb	4.3	5	1	1
Zn	8.6	17	-	-
Cl	31.0	31	32.3	38
SO <sub>4</sub>	7.7	9	11.1	16
P <sub>2</sub> O <sub>5</sub>	2.3	-	4.6	4.3
CaO	0.60	2.8	12.7	8.0
Al <sub>2</sub> O <sub>3</sub>	0.70	0.6	1.3	1.2
SiO <sub>2</sub>	1.0	<1	7.4	3.3
MgO	0.10	0.3	<0.05	<0.05
SnO <sub>2</sub>	1.08	-	-	-
Fe <sub>2</sub> O <sub>3</sub>	0.20	2.8	3.0	1.8

TABLE 4: Relation between secondary fly-ash formation and Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> content of feed material

	A MSW fly-ash (LTH)	B MSW fly-ash (IME)	D SS grate-ash	E SS residue mix
Cl in feed (wt%)	12.0	4.0	1.3	1.4
SO <sub>4</sub> in feed (wt%)	12.5	5.4	2.4	3.2
Relative amount of secondary fly-ash, %	30...40	10...15	3.5	5

TABLE 5: Major compounds of secondary fly-ashes

	A MSW fly-ash (LTH)	B MSW fly-ash (IME)	D SS grate-ash	E SS residue mix
Alkali chlorides and sulfates	70	67	60	65
Pb and Zn oxides	15	26	1	1
Phosphate, silicate, residual sulfate	3	1	23	24
Other oxides	12	6	16	10

TABLE 6: Volatilization degrees of the major feed components (average of tests A through E)

As, Cd, Hg	> 99%	Cl	> 98%	Si	0.5...2%
Zn	≥ 95%	P	4...60%	Ca	1%
Pb	95...99%	Cu	25...60%	Ti	< 1%
Na	40...85%	Cr	17...23%	Mg	< 1%
K	70...97%	Fe	2.5...4%	Al	< 1%
S	85...99%	Mn	2%		

No difference in processing behavior was observed with regard to the torches used. No indications were found as to a de novo synthesis of dioxins neither with graphite electrodes nor with metal torches. Apparently, both systems are applicable for an oxidizing melting process of these incineration residues. A more substantial techno-economic comparison can only be made on the basis of full-scale operational data.

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