Pyrometallurgical Pre-Treatment of EAF Dust at Reduced Pressure*

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ABSTRACT

Electric Arc Furnace (EAF) dust is a hazardous material, which has to be treated for its content of leachable heavy metals. In metal recovery processes, such as plasma furnace, the gas, which contains metal vapors, is led from hot cyclone to a splash condenser. Dross formation on the surface of zinc bath as well as the surface of droplets made by splasher, often impairs condenser performance. Besides, the content of lead and iron in zinc alloy substantially degrades the final product. A pre-treatment of the EAF dust is suggested to resolve this problem by removing more volatile species, which include alkali halides, lead oxide and cadmium content, from the EAF dust. The process involves evaporation of volatile species at about 900°C in a virtually closed system under reduced pressure and condensation of the vapors at a lower temperature.

1. INTRODUCTION

In excess of 600,000 tons of dust are generated annually in carbon steel electric arc furnace (EAF) shops in the United States and Canada. This is equal to about 2% of the steel produced. EAF dust is rated as a hazardous material due to its content of leachable heavy metals, i.e. Pb, Zn, Cd and Cr. Therefore, it must be treated before disposal to meet certain environmental regulations.

There is a number of different processes to treat EAF dust, which includes low temperature chemical stabilization, high temperature vitrification, hydrometallurgical recovery of metals, and pyrometallurgical zinc oxide and zinc metal recovery [1].

In high temperature metal recovery processes such as plasma arc furnace [2], dust is mixed with reductant and fluxes, and heated in the fuming reactor. Reduced zinc and lead are vaporized in the reactor along with the other volatile species leaving a metallic and/or oxide residue substantially free of heavy metals. These fumes generated in the reactor are led through hot cyclone to a splash condenser. The splasher mechanically makes droplets to provide surface for condensation of the zinc and lead vapors. The problem which arises in these processes is the formation of dross, which is made of condensed alkali halides, re-oxidized metal oxides and carried over dust, in the condenser. Dross forms a viscous layer on the top of zinc bath and covers the surface of droplets generated by splasher. This hinders contact between zinc vapor and droplets or zinc bath and often impairs condenser performance. Furthermore, zinc product has a low quality due to its content of lead and iron.

In some countries EAF dust is washed before metal recovery process and therefore by removal of alkali halides the problem of dross formation is not encountered. However, beside the potential water contamination of wet processes, it is not viable for the inland plants. Therefore, it is important to find other solution with the least risk of further environmental problem.

The present work consists of both theoretical analysis and laboratory experimentation. In principle, the process is similar to that of distillation with the major differences of high temperature and reduced pressure.

2. THERMODYNAMICAL COMPUTATIONS

Chemical composition of a typical EAF dust is given in table 1. Major part of EAF dust, 60-80%, is composed of iron, zinc and calcium oxides. The rest includes compounds of lead, magnesium, manganese, sodium, potassium, aluminum, silicon, cadmium, etc. Potassium and sodium are mostly in the form of chlorides, while the other compounds are mostly in the form of oxides. During the process of heating, a partial melting of EAF dust starts at temperatures as low as 350°C. Partial melting of dust continues as the temperature rises and the evaporation of volatile species becomes significant at about 900°C. At temperatures between 850°C to 900°C, when the content of chlorides and lead oxide and other minor volatile species evaporate, the remaining liquid solidifies as its melting temperature changes to higher values.

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* An application for a US patent has been made by W-K. Lu and A. Zabett

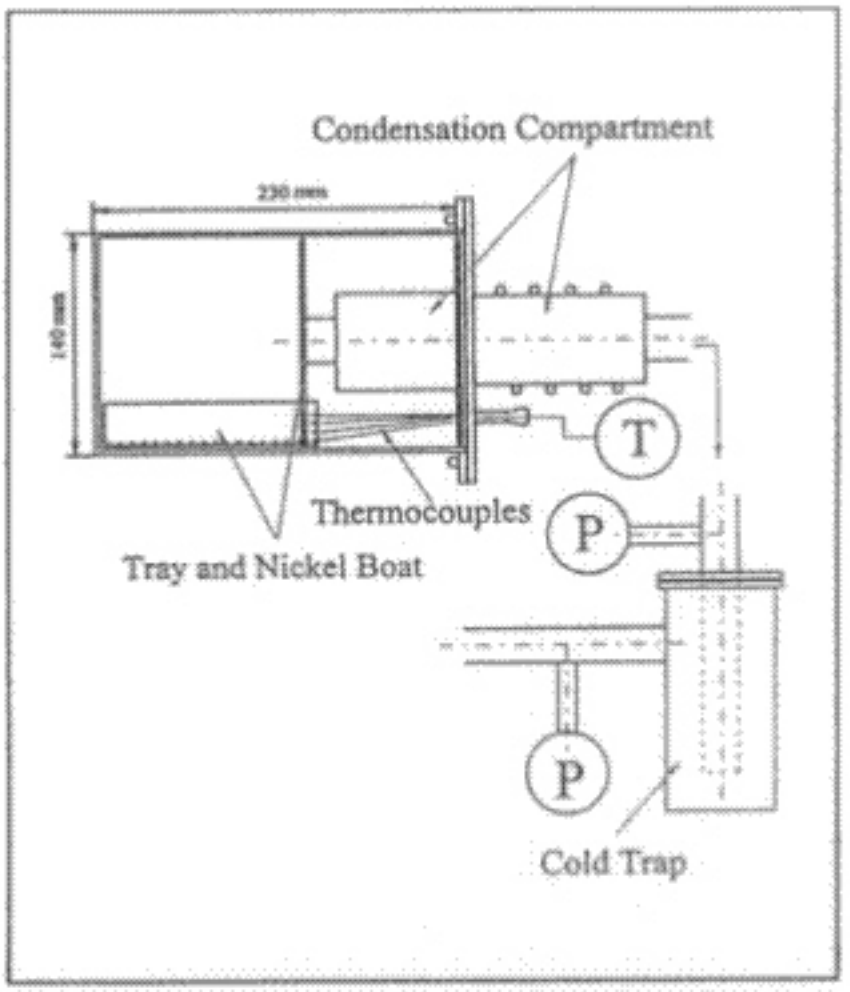

Fig. 2. Experiment setup with rectangular reaction chamber.

protection of vacuum pump. The temperature of the dust at different height inside the dust bed and the pressure of the system at a location close to cold section are recorded during the experiment.

The second apparatus is a rotary reaction chamber designed to accelerate heat transfer to dust by exposing colder dust to hot walls of the reaction chamber by rotating it and therefore benefiting more from direct radiation and conduction from hot chamber walls. The cylindrical reaction chamber is made of stainless steel and inside the chamber is nickel plated to prevent reaction between the chamber wall and zinc oxide. A stopper, see figure 3, is used to keep the dust in the hot zone and also to prevent excess heat radiation to the cold section. Air jet is used instead of water for cooling the cold zone. The chamber is held by two bearings. A DC motor with variable speed is connected to the chamber by a chain drive. All experiments were run at a speed of 1 rpm. The rest of the setup is

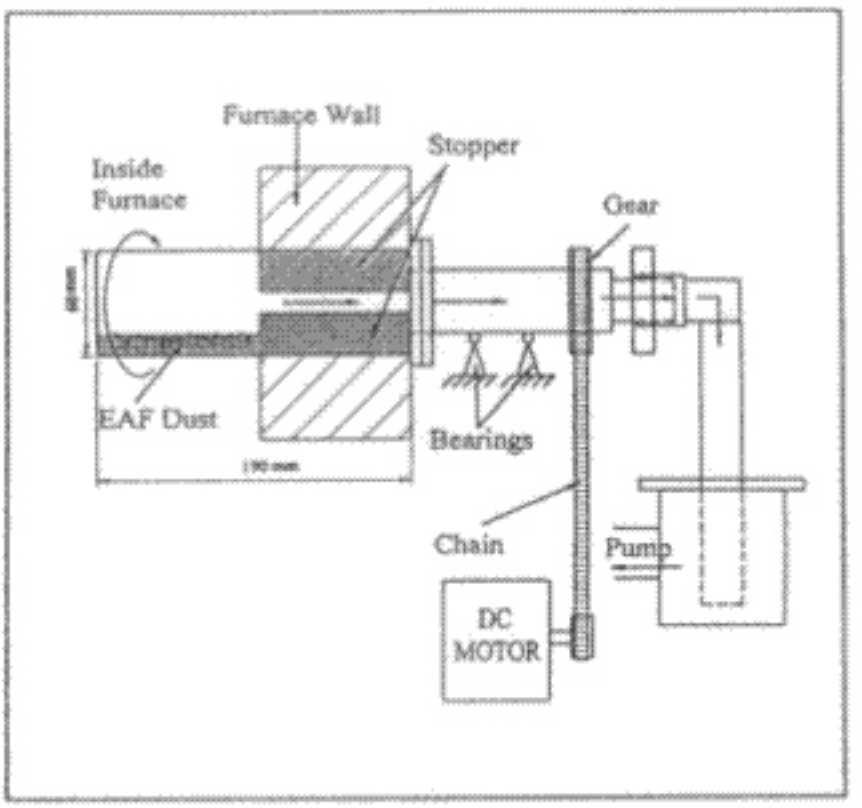

Fig. 3. Experimental setup with rotary reaction chamber.

similar to the first apparatus.

The third apparatus is a stationary cylindrical stainless steel chamber. The reaction chamber is identical to the one used in rotary apparatus but is not rotating during the experiments. This apparatus is used for the comparison purposes to identify the effect of rotation in the rotary chamber.

In all experiments a muffle furnace is used for heating the reaction chamber. The furnace is preheated to experiment temperature and the reaction chamber is inserted in the furnace at the beginning of experiment and withdrawn at the end. Experiment duration is from the time that reaction chamber is placed inside the furnace until the chamber is withdrawn from the furnace. This includes the heating time for the assembly itself, which is longer in the case of rectangular chamber due its larger mass. Most experiments were run at a furnace temperature of 1100°C. For this furnace temperature, the heating time of the reaction chamber itself to about 1000°C is approximately 2 minutes for the cylindrical chamber and 25 minutes for the rectangular chamber. Total time for separation of over 90% of alkali halides and lead oxide at furnace temperature

Table 1. Chemical composition (%wt) of EAF dust and the residues after treatment at a furnace temperature of 1100°C.

	Duration	Fe	Zn	Pb	Na	K	Cd	Cl	Ca	Mn	Mg
EAF dust as is	N/A	33.6	23.4	2.96	1.36	0.83	0.09	2.85	4.23	2.73	1.92
Stationary Chamber	12 min.	34.8	24.9	0.54	0.49	0.16	<0.04	<0.2	4.55	3.13	2.17
Rotary Chamber	7 min.	34.0	23.0	0.18	0.41	0.05	0.01	0.13	4.95	N/A	N/A

of 1100°C is about 7 minutes in rotary chamber, 12 minutes in stationary cylindrical chamber and 30 minutes in the rectangular chamber

In the rectangular apparatus, 100 grams of EAF dust was treated each time. Samples for chemical analysis were taken from different heights of the dust bed after each experiment. In rotary and stationary cylindrical chambers, 25 grams of EAF dust was treated each time. Chemical analysis of the samples was carried out using an ICAP spectrometer, JEOL 9000.

4. RESULTS AND DISCUSSION

4.1 Mass and heat transfer

Physical changes in the system include steps of evaporation, mass transfer in gaseous phase and condensation. In the first apparatus with rectangular reaction chamber heat transfer to dust includes the following steps,

i. heat radiation from reaction chamber walls to top surface of the dust bed
ii. heat radiation and conduction from reaction chamber walls to tray and from tray to nickel boat
iii. heat radiation and conduction from nickel boat to dust
iv. heat radiation, conduction and convection inside the dust bed.

Calculations of the heat and mass transfer show that heat transfer inside the dust bed is most likely the rate-controlling step (iv). The experimental study of heat transfer inside the bed with the use of rectangular reaction chamber confirms that the heat transfer inside the dust bed is the slowest step in the separation process. When the coldest location inside the dust bed reaches to about 900°C the separation process is almost completed.

A numerical program has been developed for the study of heat transfer inside the dust bed [3]. With the use of this program, it has been shown that for the stationary cylindrical chamber and at the laboratory conditions, it takes approximately 12 minutes for the center of dust bed to reach to 900°C. This time is equal to the treatment time of EAF dust in this apparatus.

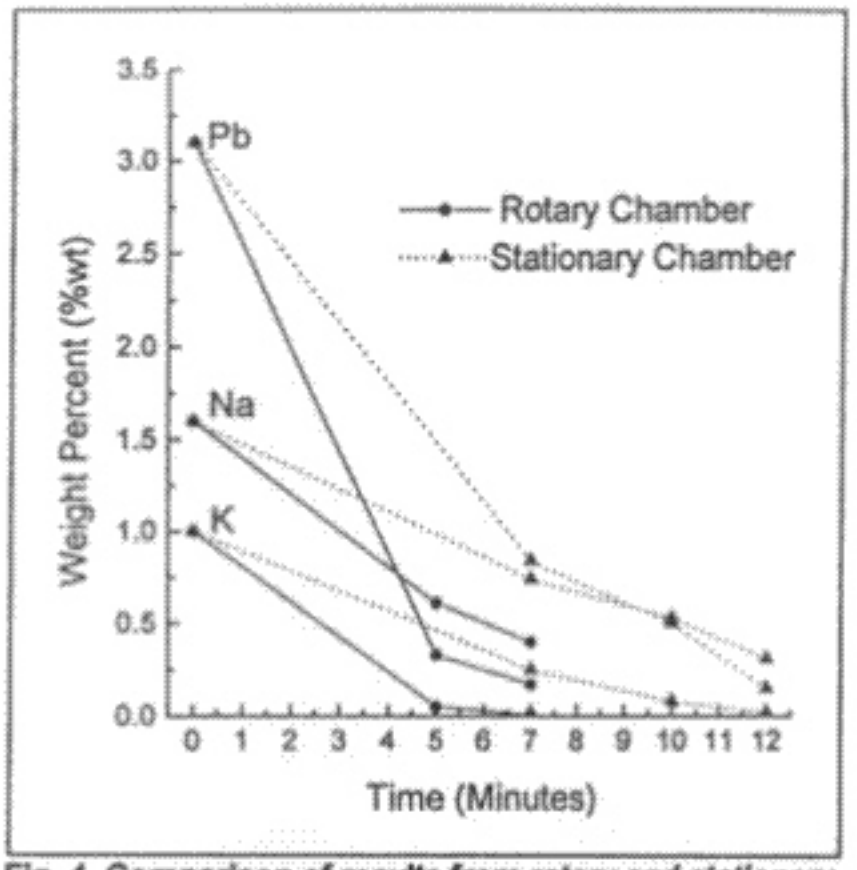

Fig. 4. Comparison of results from rotary and stationary cylindrical reaction chamber.

The rotary chamber, which was designed to accelerate the heat transfer to dust, decreased the treatment time significantly. A comparison of the results from this apparatus with those from stationary cylindrical chamber is given in figure 4. In order to remove about 95% of alkali halides and lead oxide, the total treatment time including heating-up time is decreased from about 12 minutes for stationary cylindrical chamber to about 7 minutes for the rotary chamber. Based on these results also the heat transfer inside the dust bed appears to be the rate-controlling step.

4.2 Chemical analysis and degree of separation

Table 1 shows the chemical analysis of an EAF dust and that of the residues after treatment in cylindrical reaction chambers both in stationary and rotating

Table 2. Chemical composition of EAF dust and the residues after treatment in the rotary reaction chamber at a furnace temperature of 1100°C (%wt).

Experiment duration	Fe	Zn	Pb	Na	K	Cd	Ca	Mn	Mg
EAF dust as is	30.2	18.5	1.79	1.10	0.58	0.07	11.1	2.11	1.26
Residue after 4 minutes	32.1	19.5	0.41	0.54	0.24	0.04	16.3	2.61	1.28
Residue after 6 minutes	34.1	21.0	0.19	0.22	0.06	0.03	15.6	2.38	1.19
Residue after 8 minutes	36.2	19.7	0.16	0.18	0.06	0.03	14.4	2.37	1.14

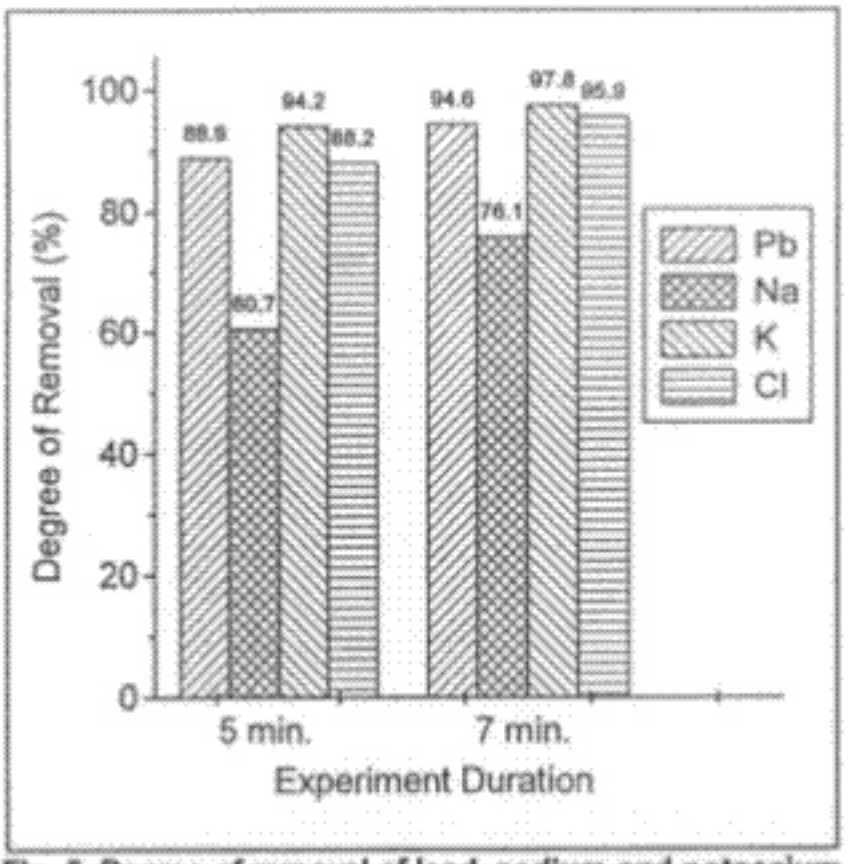

Fig. 5. Degree of removal of lead, sodium and potassium from EAF dust after 7 minute treatment at furnace temperature of 1100°C.

conditions. Figure 5 shows the degree of removal for the volatile species from EAF dust. It can be seen that alkali halides and lead oxide are substantially removed from EAF-dust. It should be noted that the remaining portion of sodium is in the form of oxide.

Table 2 contains the chemical composition of EAF dust from another steelmaking shop. The results of experiments carried out in the rotary chamber for different lengths of time and at a furnace temperature of 1100°C are given in this table.

Comparable results may be obtained at lower temperatures but longer treatment time. Experiments have been carried out successfully using the rotary chamber at a furnace temperatures of 950°C for a total time of 10 minutes. In these experiments the maximum temperature of the walls inside the chamber was recorded to be 915°C. These observations confirm that a dust temperature of approximately 900°C is enough for the separation process.

4.3 Low iron content dust

In addition to steel making EAF dust, some low iron content dust have also been treated in this separation process. Table 3 shows the chemical composition of a

Table 3. Chemical composition (%wt) of a secondary incinerator dust and the processed products after a total treatment time of 6 minutes inside a furnace at 1100°C.

	Before Treatment	After Treatment	Condensed Phase
Mass	25 gram	8.3 gram	~15 gram
Zn	27.1	75.1	3.45
Fe	1.13	2.33	0.52
Pb	7.37	0.16	7.23
Na	14.4	2.72	17.5
K	16.1	0.48	20.3
Sn	0.22	0.69	<0.01
Cl	27	0.87	50.3
Pb/Zn	27.2%	0.21%	---

secondary dust generated in a resistant electric furnace, which is used for treatment of incinerator dust and bottom ash. The experimental results with the use of rotary chamber are included in table 3. The Pb/Zn ratio has decreased from 0.27 to 0.0021.

5. SUMMARY

- Thermodynamical computations of reactions following an equilibrium path show that separation of alkali halides and lead oxide from the remaining compounds in EAF dust is feasible. This has been confirmed experimentally in an open system at atmospheric pressure but a very large volume of carrier gas is required.

- Laboratory experiments have shown that under reduced pressure of the order of one torr in a virtually closed system the removal of volatile species from EAF dust is fast and can be achieved with a dust temperature as low as 900°C.

- The most likely rate-controlling step in the removal of volatile species from dust is the heat transfer inside the dust bed. This slow step can be improved by accelerating the heat transfer with the use of a rotary chamber.

- Other hazardous dusts, such as secondary incinerator dust, containing volatile species such as alkali halides and lead oxide can also be treated in this process.

ACKNOWLEDGEMENT

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2. Plasma furnace treatment of EAF dust, CMP Report No. 88-2, The EPRI Centre for Materials Production, Carnegie Mellon Research Institute, 1988.
3. A. Zabett, "A study of removal of alkali halides and lead oxide from EAF dust", Ph.D. thesis, McMaster University, to be submitted in 1998.

APPENDIX

A.1. Typical EQUILIB input data file.

```
(gram) 34Fe + 24Zn + 3.1Pb + 2.4Mn +
(gram) 1.6Na+ 1K + 4.6Ca + 1Mg +
(gram) 1Al + 0.5Si + 2.7Cl + 0.1F +
(gram) 2O2 =
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A.2. Typical result from EQUILIB output file.

```
10138.   litre (   50.541          vol% NaCl
                +  24.351          vol% KCl
                +  9.4160          vol% Pb
                +  4.9203          vol% Zn
                +  4.7896          vol% PbO
                +  2.8729          vol% NaF
                +  1.2823          vol% KF
                + ...

          ( 1000.00 C,0.10000E-02 atm, gas_ideal)

+  1.7635   gram
                (  24.843      wt.% (Na2O)(SiO2)
                +  12.962          wt.% Ca2SiO4
                +  12.105          wt.% Na6Si2O7
                +  8.8502          wt.% Pb
                +  7.3053          wt.% ZnO
                +  5.6357          wt.% MnO
                +  5.0654          wt.% FeO
                + ...

          ( 1000.00 C,0.10000E-02 atm, liquid)

+  35.755   gram Fe3O4
   ( 1000.00 C,0.10000E-02 atm, S2, a= 1.0000   )

+  29.354   gram ZnO
   ( 1000.00 C,0.10000E-02 atm, S1, a= 1.0000   )

+  12.998   gram Ca2Fe2O5
   ( 1000.00 C,0.10000E-02 atm, S1, a= 1.0000   )

+  5.5334   gram (MnO)(Fe2O3)
   ( 1000.00 C,0.10000E-02 atm, S1, a= 1.0000   )

          + ...
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