

CHAPTER TWO

LITERATURE REVIEW

2.1 NATURE OF ELECTRIC ARC FURNACE DUSTS

Electric arc furnace (EAF) dust is formed during the steel recycling process. In the EAF steelmaking process the temperatures reach 1600 °C or higher and virtually all of the volatile elements in the charge, such as zinc, lead, and cadmium enter the gas phase. Also, the high temperatures in the EAF cause small amounts of iron, chromium, manganese, and nickel to be transported into the gas phase. As the metal vapours exit the furnace, they are oxidised and cooled. The condensed particles and other particulate matter are collected in the baghouse (McCrea and Pickles, 1995). The off-gas is cleaned by a variety of methods to prevent dust being discharged into the atmosphere and to enable trouble free recovery of the calorific content of the off-gas. Dust compositions vary from one furnace to another and depend on the characteristics of the charge. Table 2.1 lists partial composition of EAF dust generated in many countries. The table shows that dust composition vary widely.

Table 2.1: Partial EAF Dust Composition.

Component (Mass percent)						Dust source	Reference
Fe	Zn	Pb	Cd	Ca	Cl		
20.10	32.30	2.88	0.04	1.38	6.80	Japan	Itoh and Azakami, 1994
16.55	27.80	3.22	0.07	11.50	4.05	Co-Steel Lasco, Canada	Donald and Pickles, 1995
22.90	23.40	5.00	0.15	4.00	5.00	Azma Electric Steel Mill, Spain	Lopez <i>et al.</i> , 1991
28.20	18.40	2.15	N/A	N/A	N/A	Koppel Steel Corporation, U.S.A.	Bodger and Kneller, 1997
33.60	23.40	2.96	0.09	4.23	2.85	Canada	Zabett, 1997

Table 2.2: Chemical Composition of Some Typical Carbon and Stainless Steelmaking Dusts (McCrea and Pickles, 1995)

Element	Carbon Steelmaking Dusts (wt %)	Stainless Steelmaking Dusts (wt %)
Fe	24.9-46.9	22.2-35.9
Zn	11.12-26.9	1.77-6.22
Pb	1.09-3.81	0.23-0.78
Cd	0.03-0.15	0.008-1.79
Cr	0.06-0.58	2.01-10.1
Ni	0.01-0.12	0.15-3.34
Mo	< 0.02-4.6	0.37-1.48
Mn	0.77-2.93	2.36-4.59
Mg	0.77-2.93	1.70-4.74
Cu	0.06-2.32	0.09-1.26
Ca	1.85-10.0	1.76-6.93
Si	1.35-2.49	1.36-4.83
Cl	0.51-2.36	0.47-1.17
F	0.01-0.88	1.36-4.83
K	0.06-0.88	0.80-5.07
Na	0.29-2.31	0.47-4.60

The chemical composition of some typical carbon steelmaking dusts compares with stainless steelmaking dusts are shown in Table 2.2 (McCrea and Pickles, 1995). It is quiet clear from this table that the dusts which were produced from different charge types gave different in composition ranges. The iron content of all dusts are very high. The zinc content varies widely, from 11.12-26.9% in carbon steelmaking dusts, probably due to the different types and amounts of scrap steel and the use of galvanised scrap added to the EAF. The stainless steelmaking dust contains high concentrations of chromium and nickel due to the scrap contains stainless steel. The calcium content of all dusts is relatively high. This can be attributed to the charging of lime in the steelmaking process in EAF.

Previous researchers have employed reflected light microscopy (RLM), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and x-ray diffraction (XRD) analysis to examine the EAF dust. These results indicated that EAF dusts were very fine grained. The dust particles varied greatly in size from 1 to more than 300 microns, but most particles were in the range 1 to 6 microns. Some particles were less than 0.1 micron, while others were significantly larger with diameter over 800 micron

(Badger and Kneller, 1997). The particles were predominantly spherical in shape, but some were cenospheres (spheres with gas holes), while others were more angular particles.

X-ray diffraction analysis of 32 samples of EAF dusts identified that the dominant phases were the iron spinels: magnetite (Fe_3O_4) and zinc ferrite ($\text{ZnO}\cdot\text{Fe}_2\text{O}_3$). The majority of the iron was in the form of magnetite (Hagni *et al.*, 1991), while some results were presented as hematite (Zunkel, 1995) because of the different sources of dusts. Magnetite was one of the most abundant particles in the EAF dusts and typically occurred as spheres. SEM-EDS analysis indicated that many grains had composition that were solid solutions between zinc ferrite and magnetite. The minor elements lead, cadmium were in the oxide form. The halides were presented as ZnCl_2 , PbCl_2 and CaCl_2 in either simple or complex form (Zunkel, 1995).

2.2 EAF DUST TREATMENT METHODS

Methods for the treatment of steelworks dusts can be divided into two main categories: recycling methods, and methods for recovering iron and/or zinc. Recycling involves returning dusts to the steelmaking process, though not necessarily to the furnace from which it was obtained. No separation of zinc from iron is performed. The second category includes methods in which iron and zinc are separated to some extent and one or both of these metals are recovered for later use.

2.2.1 Recycling Methods

Recycling of dusts to electric arc furnaces (EAFs) poses few of the problems inherent with recycling to blast furnaces. EAFs have shorter shafts and the high-temperature off-gas is quickly removed from the furnace. This prevents any reoxidised zinc returning to the bath via condensation on the burden. This characteristic of EAF steelmaking concentrates zinc and other volatile heavy metals in the fume efficiently and allows

EAFs to operate with high scrap loading. Due to this high heavy metal content, the disposal of EAF dust in land-fill sites is illegal in the U.S.A. (Kaltenhauser, 1986).

One way to increase the zinc content of the EAF dust is to return all or part of it to the furnace from which it was generated. The most common method in the practice of returning dust to the furnace is to charge "greenballing" (unfired) pellets of dust. Other plants prefer to charge briquettes of dust or to inject dust directly into the melt (Morris *et al.*, 1985).

In processes developed by Pellet Technology Corporation (Goksel and Provis, 1977), self-fluxing, self-reducing, hardened pellets were produced from many types of iron-bearing waste materials. Wastes such as fume dusts, ore fines and mill-scale were blended with coke and binding agents, lime, silica and water, then aged and pelletised. Green pellets were screened and dried before being heated under steam in an autoclave for one to two hours at about 200 °C. This procedure produced hardened pellets with sufficient strength to be used as blast furnace feed. A rotary kiln was used to heat hardened pellets; rapid reduction rates were found and metallic iron was formed (Weiss *et al.*, 1986). Much of the zinc was reduced, volatilised and captured in the fume and this two stage process, therefore, was not a simple recycling process. Other small and large scale trials were conducted in cupolas where hardened pellets were smelted at 1450 °C to yield molten iron and a zinc-rich fume (Goksel and Provis, 1977).

Harris (1980) described the semi-commercial Agglomert process that has been used to agglomerate a large variety of waste oxidic fines at raised temperatures. Preheated fines were heated to between 870 and 980 °C in a fluid-bed and then briquetted. Republic Steel Corp. in the U.S.A. conducted a one month blast furnace trial using Agglomert briquettes as 20% of the feed and claimed to obtain satisfactory results although no data was given.

2.2.2 Methods for Recovery Zinc and/or Iron

(I) Pyrometallurgical Processes

a) Zinc Oxide Production

Urger (1986) described Waelz-based methods that have been used to treat zinc oxide-enriched EAF dust. The Waelz kiln process was first commercialized in Upper Silesia Germany, in 1923. Berzelius Metallhütten GmbH has been operating on 100% EAF dust since 1977. In their practice for treating enriched EAF dust in Waelz kilns (Figure 2.1), coal was added to the charge to complete zinc oxide reduction. Temperatures of the gas stream in the oxidation zone exceeded 1300 °C. The fume collected typically contained 52-58% zinc which was in the form of zinc oxide. A clinker rich in metallic iron was produced but was dumped or used in road construction. Energetically and economically it was expensive as substantial amounts of fuel and reductant were required because of the endothermic nature of carbonaceous reduction of iron oxide.

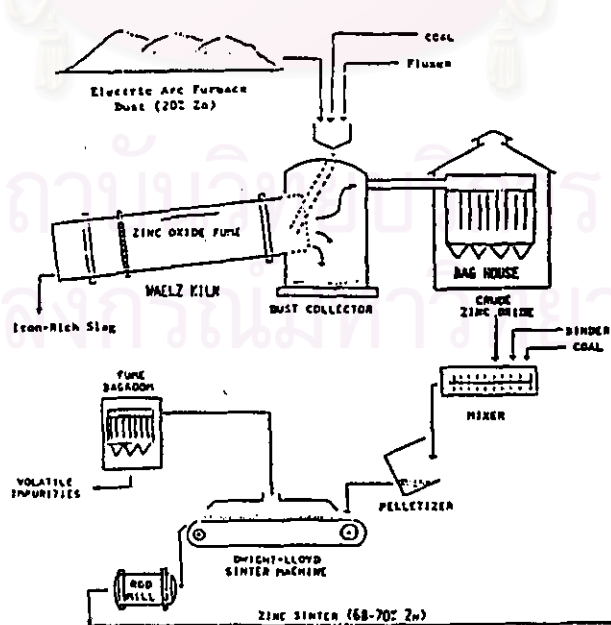


Figure 2.1: Waelz kiln operation (Urger, 1986).

The INMETCO process was developed by INCO in the mid 1970's (Pargeter and Lehmkuehler, 1986). The most significant step in the process was the thermal reduction of metal oxides by carbon in a rotary hearth furnace (RHF), see Figure 2.2 . Since 1980 extensive laboratory and plant scale work has established the RHF reduction process as a suitable method for producing direct reduced iron (DRI), for recovering of zinc from EAF dusts and for treating stainless steelmaking wastes. In a commercial plant operating in the U.S.A., crushed coal and ground swarf and mill-scale were pelletised with EAF dust and water then charged to a rotary hearth furnace heated by auxiliary burners. A temperature of 1300 °C ensures rapid and nearly complete metal oxide reduction. Discharged hot pellets were charged to an EAF where final reduction and melting yields a pig iron alloy. Over 99% of lead and zinc was captured in the baghouse in oxide form.

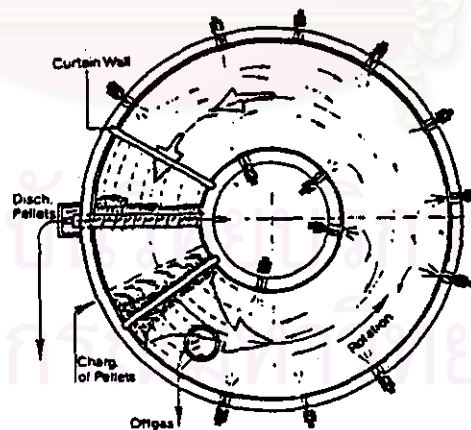


Figure 2.2: Schematic of INMETCO rotary hearth furnace
(Pargeter and Lehmkuehler, 1986).

In a small scale process under development at the University of Wollongong, New South Wales, Australia, an EAF was used to smelt pellets containing EAF dusts, other steelwork wastes, hazardous organic wastes and sewage (Worner, 1992). Between one half and one third of the dust to be smelted was added to sewage to aid the settling of solids. Lime was added to neutralise pathogens and to act as a flux during smelting. After most of the water was removed, the remaining dust and waste was added to the sewage and the mixture was air or oven dried. Pellets were dropped into a furnace which was operated at temperatures between 1450 and 1500 °C. Carbon and hydrogen from the wastes rapidly reduced iron oxides and a carbon-saturated iron melt was formed. Slag and metal flowed counter-currently to each other and were continuously tapped from opposite ends of the furnace. The final slag contained between 0.2 and 0.5% iron and the metal was essentially free of zinc, lead, cadmium and copper. Zinc was recovered as zinc oxide from the fume. It was proposed that oxygen and additional lime would be injected tangentially into the slag near the melt out-flow region to aid the counter-current flow of slag. It was proposed to achieve post-combustion of smelter off-gas by injecting oxygen tangentially into the slag. The angle of injection would aid the counter-current flow of slag. Due to the high concentration of phosphates in the sewage, additional lime would be added to increase dephosphorisation of the metal. Pre-reduction of pellets using smelter gases was proposed but little information on this step has been published.

Floyd *et al.* (1993) invented the Ausmelt process concept. This small plant was designed to process 50,000 ton/annum of EAF dust in a two stage process. EAF dusts and silica sand were pugged with water and fed continuously with lump coal into an Ausmelt furnace for smelting. No pre-treatment of the feed was required except that if fine dry feed was used, some agglomeration by water was necessary to prevent entrainment in the off gases. Fuel oil, dry fine coal, natural gas or liquefied petroleum gas could be used as fuel. The design smelting temperature was 1300°C. Zinc in the feed materials was reduced to metal vapour and re-oxidised in the furnace chamber with afterburner air supplied by the Ausmelt lance. Lead, silver, arsenic, cadmium, chlorine, fluorine and some potassium and sodium also vaporised and left the furnace in the gas stream. The furnace gases were passed to the gas handling train and cooled to 180 °C by evaporative cooling. The cooled gases were filtered in a baghouse and discharged to the atmosphere.

A first slag, containing typically 4.5% Zn, 0.4% Pb and 25 ppm Ag, was transferred continuously from the first furnace via a launder into the second Ausmelt furnace for further zinc fuming from slag. The second furnace was operated at 1350 °C. No oxygen enrichment of the combustion air to the second furnace was required and 98.7% of the zinc was recovered in the form of zinc oxide.

Misao and Mizuta (1978) have patented a dust treatment process which involved blowing fine iron making dust with nitrogen into a molten pig iron bath inside a stirred, sealed pot. In trials, 82.0% of the zinc was recovered in a bag filter as zinc oxide.

In a similar process (Arbed, 1980) iron, zinc and lead were recovered from blast furnace, BOF, EAF dust and sludge wastes. Ground and dried wastes were blown into the bottom of a molten iron bath along with basic fluxing agents, solid carbonaceous reductant and fuel. Lead was recovered as metal below the liquid iron phase, zinc was captured in the fume as zinc oxide and iron from the wastes entered the iron bath.

b) Metallic Zinc Production

Litz (1991) reported on a pilot plant run of the Elkem process in April, 1987. EAF dust, pelletised with coke and flux, was fed to an air tight, "Multi Purpose" electric arc furnace. The charge was heated to 1400 °C, reducing and volatilising the zinc plus some lead. The volatiles were condensed using a lead-splash condenser. The condenser off-gas was cooled and any dust was collected by a dust collector and recycled to the arc furnace. The Elkem Sealed Electric Furnace Process was installed on a commercial scale at Laclede Steel in the U.S.A. but was never successfully commissioned due to major technical problems (Zunkel and Schmitt, 1995).

The Plasmadust process was developed by SKF Steel in Sweden and used as a commercial plant to recover iron and zinc from EAF, BOF and blast furnace dusts (Eriksson, 1985). An electric arc generator was used to heat a CO/H₂ gas mixture and the dust. Powdered flux and coal were injected through tuyeres into a coke filled shaft furnace (Figure 2.3). A temperature of about 2500 °C was reached in the raceway

adjoining the tuyeres and this resulted in rapid melting and reduction of FeO and ZnO. The presence of excess coke produced a strongly reducing off-gas which prevented the re-oxidation of zinc in the vapour phase. For dusts of high zinc and lead levels, a zinc condensing unit was used to recover the metals. The off-gas was cleaned and used for generating heat or electricity. Liquid iron was tapped from the hearth along with the slag. When stainless steelmaking dust was charged, chromium, nickel and molybdenum were recovered in the metallic iron phase. Presently, only stainless steelmaking dusts have been treated by this process. The treatment of EAF dust was discontinued for technical and economic reasons (Kola, 1990).

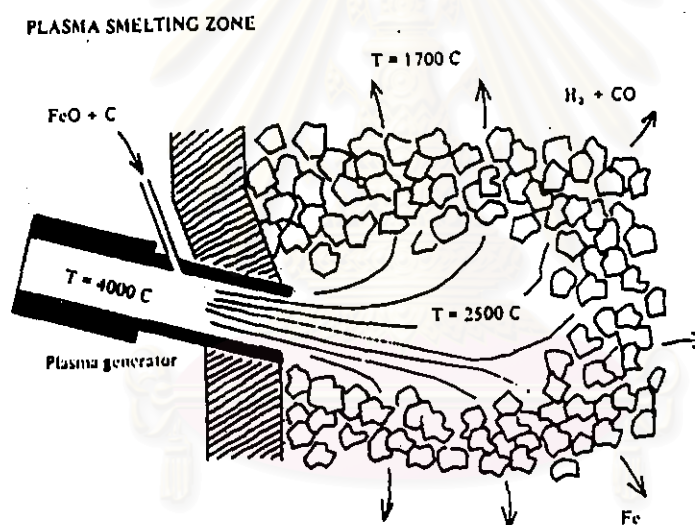


Figure 2.3: Schematic view of the Plasma Smelting reaction zone (Eriksson, 1985).

The Hi-Plas furnace developed by Davy McKee (Naden *et al.*, 1987) produced a liquid iron alloy and zinc metal from EAF dusts. The furnace (Figure 2.4) was heated by an electric arc struck between a cathode gun and the molten pool of reactants which was in contact with an anode at the base of the furnace. Dry dust, flux and excess coke were injected tangentially into a reaction sleeve surrounding the arc at the top of the furnace. The reactants were heated by radiation and convection as they fell into the hearth, where

reduction occurred. Molten metal was tapped from the hearth and liquid zinc was condensed from the off-gas in a zinc splash condenser. Dust entrainment in the off-gas stream was minimised by melting the reactants before they entered the main body of the furnace. Dust emission had to be minimised to enable the condenser to operate at maximum efficiency. The Hi-Plas technology was developed to treat EAF dust (Stockham and Ayars, 1990) and although it would be able to treat blast furnace and BOF dusts, the researchers indicated that the low zinc levels (less than 10 to 15% ZnO with high Cr, Ni, Mo, Mn) in these materials would make this option uneconomic.

- I - DC Transferred arc
- II - The plasma gun
- III - The reaction sleeve or cyclone reactor
- IV - The molten pool of reactants
- V - A number of points
- VI - The anode in the bottom of the furnace

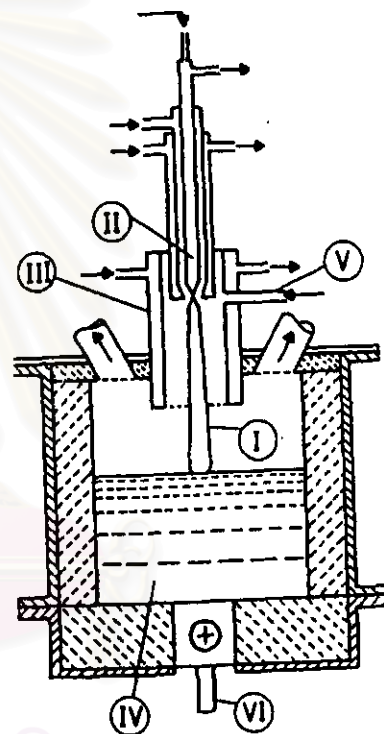


Figure 2.4: Davy Hi-Plas furnace design (Stockham and Ayars, 1990).

Liquid iron, zinc, lead and slag were produced in a 1 MW extended arc flash reactor operated by Tibur Howden of Canada (Alcock *et al.*, 1986). An intense, controlled plasma was generated by injecting Ar, N₂ or CO (or mixtures of all of them) through electrodes into a closed furnace. Agglomerated EAF dust, flux and coal was dropped through the plasma and smelting reactions occurred in the hearth of the furnace. Liquid pig iron and slag were tapped and off-gases were cleaned in a cyclone before zinc and

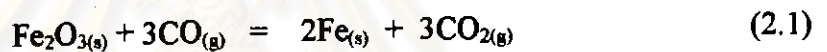
lead were condensed out as metals. Injection of free dust directly into the plasma to eliminate the need for agglomeration was proposed by Alcock *et al.* (1986). Dusts originating from EAFs, BOFs, open hearths and blast furnaces, and from vacuum oxygen decarburisation processes have been treated in a smaller extended arc flash reactor (Pickles *et al.*, 1977). Various ferroalloys were produced depending on the waste smelted, and metal recovery was generally above 89%. When EAF dust was treated, the final level of zinc in the metal phase was less than 20 ppm, down from an initial level of 25.3% in the charge.

A molten ferroalloy was also produced in the treatment of various wastes and fines in the Tetronics plasma furnace (Cowx and Roddis, 1986). The furnace was equipped with a plasma torch which was struck from a water-cooled cathode to a molten slag bath. The torch could be rotated to distribute the energy more evenly and aid bath mixing. Argon was injected to stabilise the plasma arc column. In plant trials, stainless steelmaking dust, dust generated in an argon-oxygen decarburisation vessel and anthracite were fed into a furnace by the way of a conveyor and screw. A positive pressure in the furnace maintained reducing conditions by excluding air ingress and nearly complete metal oxide reduction resulted. Zinc and lead were recovered in the fume as metallic form, a non-hazardous slag was produced and a molten ferroalloy containing nickel, chromium and molybdenum was tapped from the furnace.

Lopez *et al.* (1991) stressed that one disadvantage of the treatment of EAF dusts was the small particle size which as a rule was less than 15 microns. An initial pelletising process was carried out to form micro-pellets which consisted of EAF dust, coke, limestone and bentonite. Pellet production was carried out in a pelletising disc. The final size of the pellets ranged from 3 to 4 millimeters. The pellets thus obtained were dried at a temperature of 180°C for a time which depended on the type of furnace used. The process was applied to some dusts from the Azma (Madrid) Electric Steel Mill. When the pellets were dried they were charged into a retort furnace where they were treated at a temperature of 1020 °C for 2 and a half hours. The gases produced were condensed at 600 °C in order to recover 98.15% Zn. The products obtained in the first stage of the process were : 99.9% rich condensed metallic zinc and lead and iron-enriched reduced pellets. The reduced pellets were heated at a higher temperature for iron melting,

between 1350-1400 °C for 2 hours. Three products were obtained : metallic iron, silver-rich metallic lead and slag. The products could be removed separately from the molten bath as a result of their different densities. This process has only been carried out at the laboratory scale.

Azakami (1985) has presented a new method to recover zinc by the iron-reduction distillation process. The principle of this process consisted of two stages of reduction using a mixture of hematite and zinc oxide at 1:1 molar ratio as a starting material. In the first stage, hematite was preferentially reduced by carbon monoxide to metallic iron at 700-800 °C in highly reducing atmosphere (p_{CO_2}/p_{CO} ratio = 0.1) and zinc oxide was kept unchanged. In the second stage, the temperature was higher (900-1100 °C) and zinc oxide was reduced by metallic iron. The zinc vapour was cooled and recovered as molten zinc. The basic reaction in the first stage was shown as follows:



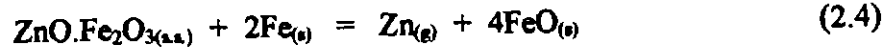
The basic reaction in the second reduction stage was:



$$\Delta G^\circ = 196,010 - 133.59T \text{ (J/mol)} \quad (2.3)$$

The second reduction stage was carried out at 900-1100°C and preferably under vacuum of 10^{-5} atmosphere for fast elimination of zinc vapour from the system. It was found that the reaction of zinc oxide with iron was promoted by increasing temperature, increasing iron to zinc oxide molar ratio and decreasing briquette size (l/d ratio less than one). Further work was carried by Itoh and Azakami (1994) who found that in EAF dust treatment by this process, cadmium evaporated completely at the beginning of first reduction stage while lead and copper remained with the iron and zinc oxide at the end of the first reduction stage. The process produced high purity zinc and a recovery of 97.0% was attained.

Donald and Pickles (1995) reported that iron can participate in the reduction of zinc ferrite. Reduction of zinc ferrite by iron proceeded according to the following reaction:



It was found that the reaction of solid zinc ferrite with iron was promoted by increasing temperature from 850 to 1100°C, increasing iron to zinc ferrite molar ratio from 1:1 to 3:1, decreasing zinc ferrite particle size, and for briquettes with aspect ratio (l/d) less than one. Addition of lime (CaO) and sodium chloride also promoted the reaction. Lime additions caused the formation of the highly stable calcium ferrite product, which lowered the activity of the iron oxide product, and decreased FeO activity. Sodium chloride promoted the reaction by causing cracking in the product layer. The reaction involved an initial stage in which the reaction was chemically controlled. Once a product layer had formed around the outer surface of the briquette then the reaction was controlled by the diffusion of zinc gas away from the reaction interface. Further work was carried by Donald and Pickles (1996) who stated that iron could also participate in reduction of zinc oxide. The reduction of zinc oxide by iron according to the reaction:



was studied using a thermogravimetric technique. Briquettes of zinc oxide powder and electrolytic iron were reacted in the temperature range of 800 to 1150°C in an argon atmosphere. First, a thermodynamic analysis was performed using the Facility of the Analysis of Chemical Thermodynamic (F*A*C*T) computational system, and then the effect of experimental variables on the reaction kinetics was determined. These variables included argon gas flow rate, reaction temperature, reagent particle size, iron to zinc oxide ratio, aspect ratio of the briquette, briquetting pressure and alkali and alkaline earth additions. It was found that initially the reaction was chemically controlled with an activation energy of 230 kJ/mol. Additions, such as sodium chloride and calcium fluoride, promoted the reaction, and the activation energies were 172.5 and 188.7 kJ/mol, respectively. Once a product had formed, the reaction was limited by the diffusion of zinc gas away from the reaction interface. The experimental data were fitted to a parabolic rate law, and the parabolic rate constant was found to be

$$k_p = -2.47 + 0.0021 T \text{ (K)} \quad (2.5)$$

c) Other Forms of Zinc Production

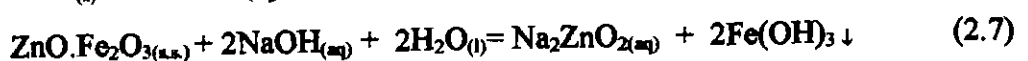
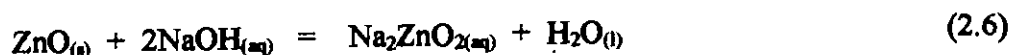
Hay (1992) stated that the Yawata steelworks in Japan has employed a chlorination process to treat every type of dust generated at the plant. Dusts in dried or slurried form and oily sludges were roasted using entrained oil and carbon as the heat sources. The residue was then wetted, mixed with CaCl_2 and pyrite cinder, dried and charged to an inclined rotary kiln. Fuel was burnt at the end of the kiln and the counter-current gas flow remove volatile metal chlorides as they formed. Over 90% of zinc, lead, copper, sulfur and potassium and 60% of sodium were removed from the pellets in this way and the final oxidised iron pellets were fed to the blast furnace. A secondary dechlorination step might be helpful in lowering the iron chloride level before using the oxidised pellets.

(II) Hydrometallurgical Processes

According to Piret and Muller (1992), hydrometallurgical treatment processes are only viable when almost all zinc is present as zinc oxide and metallic zinc. The presence of $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$, ZnS and Zn_2SiO_4 requires stronger acid or alkali leach or reducing conditions. These conditions result in a loss of selectivity with respect to the separation of zinc from iron, necessitating additional treatment steps to ensure adequate separation or recovery.

a) Cebedeau Process

Frenay *et al.* (1986) reported results of pilot plant trials on the treatment of EAF dust by the Cebedeau process. Dust used in the trials averaged 21.2% Zn, of which one third was present as $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$. The Cebedeau process leaches zinc oxide with NaOH and the important reactions are:



Up to 70% of zinc was removed when dust was treated with 240 g NaOH/l for 90 minutes at 95 °C. When the ferrite fraction was leached separately with 450 g NaOH/l for 240 minutes at 95 °C and the zincite (ZnO) fraction leached as before, zinc recovery was between 80 to 85%. After leaching, the solution was centrifuged and the solid, ferruginous residue dumped. Zinc powder was added to the solution to recover lead and copper. Zinc was recovered by electrolysis. This process was implemented at a plant in France. However, due to the inefficiency of the plant, processing was discontinued (Geutskens, 1990).

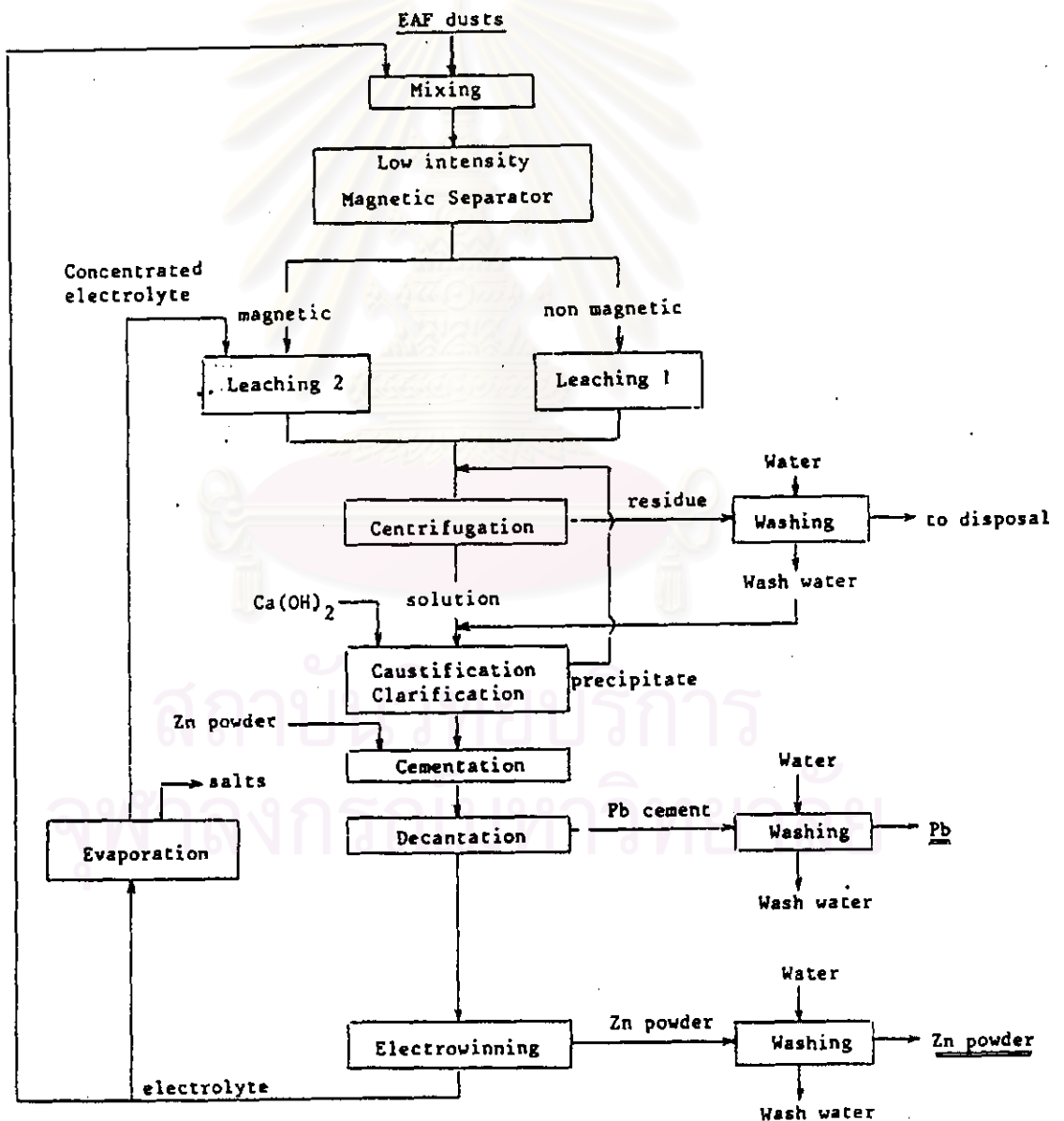


Figure 2.5: Schematic of Cebedeau process (Frenay *et al.*, 1986).

b) The UBC-Chaparral Process

Dreisinger *et al.* (1990) described the UBC-Chaparral process that was developed to treat EAF dust. In a complex, multi-step operation, chloride was removed first by washing with water and lime. Free lime had then to be removed otherwise the efficiency of subsequent steps was impaired. Acetic acid was used to selectively leach lime and then zinc powder was added to precipitate lead and cadmium. Leaching with sulphuric acid then precipitated gypsum and regenerated acetic acid. Finally zinc was leached with NH_3 and CO_2 and a mixed $\text{Zn}(\text{OH})_2/\text{ZnCO}_3$ material was precipitated after treatment with steam. Only 55% of Zn and Pb was recovered and further steps may be necessary to render all waste products non-toxic. The authors claimed that the zinc, lead and cadmium products may be of value to nonferrous metal producers. No iron was recovered.

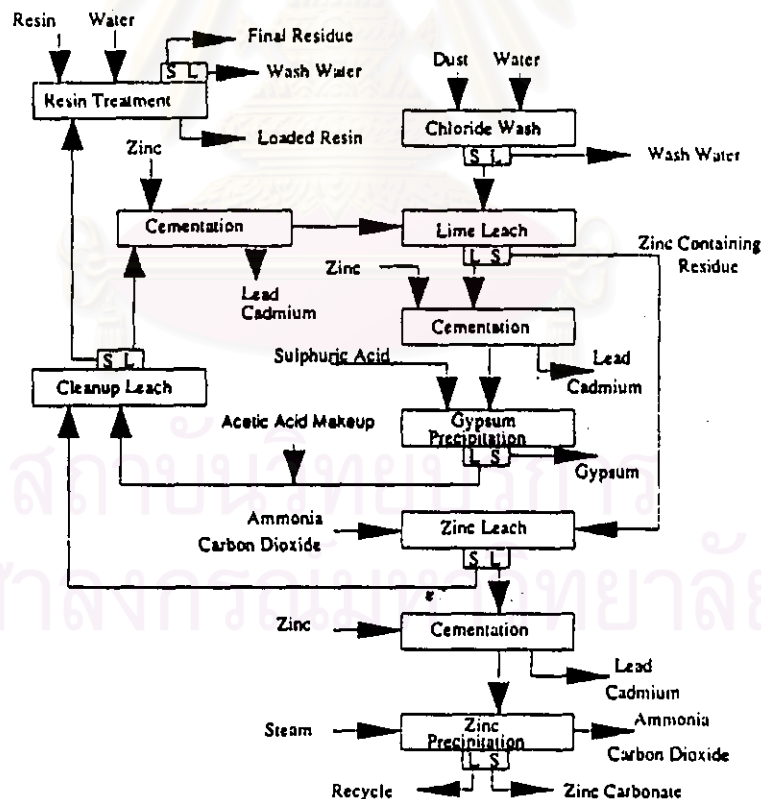
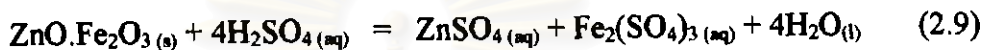
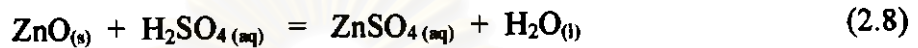


Figure 2.6: The generalised flowsheet for the UBC-Chaparral process (Dreisinger *et al.*, 1990).

c) Acidic Leaching

Cruells *et al.* (1992) found that it was possible to beneficiate the EAF dusts by leaching the non-magnetic fraction with sulphuric acid at low acid concentration (0.1-2.0 M). The samples were magnetically concentrated with a permanent laboratory magnet of low intensity to obtain two different fractions: magnetic fraction 52% and non-magnetic fraction 48% by weight. The main leaching reactions are:

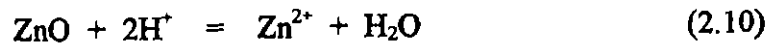


In laboratory scale, the effect of the solid:liquid (dust:solution) ratio was also studied under the following conditions: stirring rate 1000 min^{-1} , sulphuric acid concentration 2.0 M, temperature $30 \text{ }^\circ\text{C}$, 24 hours and pulp ratio (S:L) between 1:5 and 1:20. The best selectivity for the process of leaching EAF dusts took place with a sulphuric acid concentration of 1M within 3 hours, with a solid:liquid ratio of 1:10, at the temperature of $30 \text{ }^\circ\text{C}$. Zinc recovery was about 80%. Zinc ferrite was not preferentially leached by dilute sulphuric. Therefore, 20% of zinc was still in the form of zinc ferrite.

d) ZINCEX Process

Di'az *et al.* (1995) introduced the ZINCEX process. The MODIFIED ZINCEX PROCESS (MZP) was a new hydrometallurgical process for the production of zinc from secondary zinc sources. It was based on a modification and simplification of the original ZINCEX process, developed and designed by TECNICAS REUNIDAS, S.A. who built two industrial plants of capacity 8,000 and 11,500 ton/annum Zn in 1975 and 1980. Both have been successfully working recovering zinc from pyrite cinders leach liquors and others sources. The MZP used two of the main stages of the former process : electrowinning and, with small variations, the cationic solvent extraction cycle. The MZP has been developed and operated for several secondary materials at the pilot scale by TECNICAS REUNIDAS, S.A. together with other Spanish companies (ALOURA, S.A. and QUIMITECNICA, S.A.) and the support of the Commission of the European Communities within the Raw Materials and Recycling program. The

process incorporates novel steps to adapt to the treatment of zinc secondary materials. Zinc secondary material was leached with dilute sulphuric acid (Equation 2.10) at around 40 °C. A solution bearing the zinc with some impurities and the zinc leaching residue were produced.



Zinc leaching efficiency for EAF dust was 70-91%, which depended on the insoluble zinc ferrite content. For high zinc ferrite content, the zinc recovery was low.

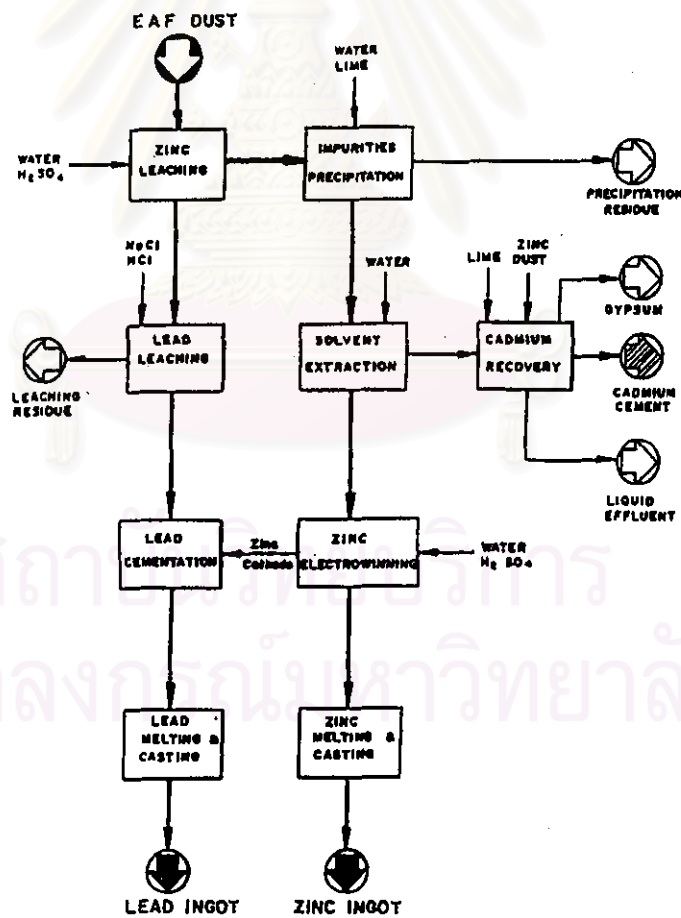
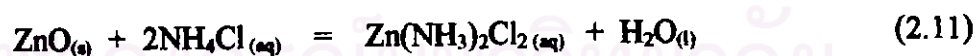


Figure 2.7: Schematic of Modified ZINCEX process (Di'az *et al.*, 1995).

e) EZINEX Process

Olper (1995) described the EZINEX process, an acronym derived from “Engitec Zinc Extraction”, was developed by Engitec Impianti SpA of Milan Italy. The basis of the process is metallic zinc recovery performed by a hydrometallurgical system. Research was started on a laboratory scale where various zinc containing materials from different sources-EAF dust from steel works, Waeltz oxides, oxides from converters, zinc ashes were tested. In August 1993, a pilot plant capable of treating 500 tons of EAF dust per year was erected and operated at a major Italian steel mill belonging to the Pittini Group. The plant, Ferriere Nord, is located near Udine, Italy. The pilot plant’s treatment capacity was designed to allow for an accurate scale-up to a commercial plant. Specifically, a full industrial size and capacity cell performed the electrolysis process. Research was conducted during an 8-month (20 days/month operating schedule) period where enough data were accumulated to test the process with EAF dusts of varying compositions and Waeltz oxides. The results allowed Engitec to determine the optimal operating conditions and the appropriate construction materials for EZINEX, and to define and produce samples of all products and by-products. Specifically, Engitec verified the quality of the electrolytically deposited zinc, which reached, under optimised conditions, a high purity level.

The dust and the spent electrolyte based on ammonium and alkali chloride, with a zinc content of 10-15 g/l, was mixed in a proper ratio (no details given) in the leaching reactor, at temperature of 70-80°C for one hour. The main leaching reaction is :



Other metals like copper, cadmium, nickel, and silver reacted in the same mechanism, while lead went into solution by the strong complexing action of the chloride ions. The iron oxides, the zinc ferrite and silica were not dissolved during this step. During the leaching, the alkali chlorides were solubilised, increasing the chloride load of the solution.

The first commercial plant was located at the FERRIERE NORD Italy site and had a nominal treatment capacity of 10,000 tons per year. Start-up was commenced on September, 1995. No further details have been published since.

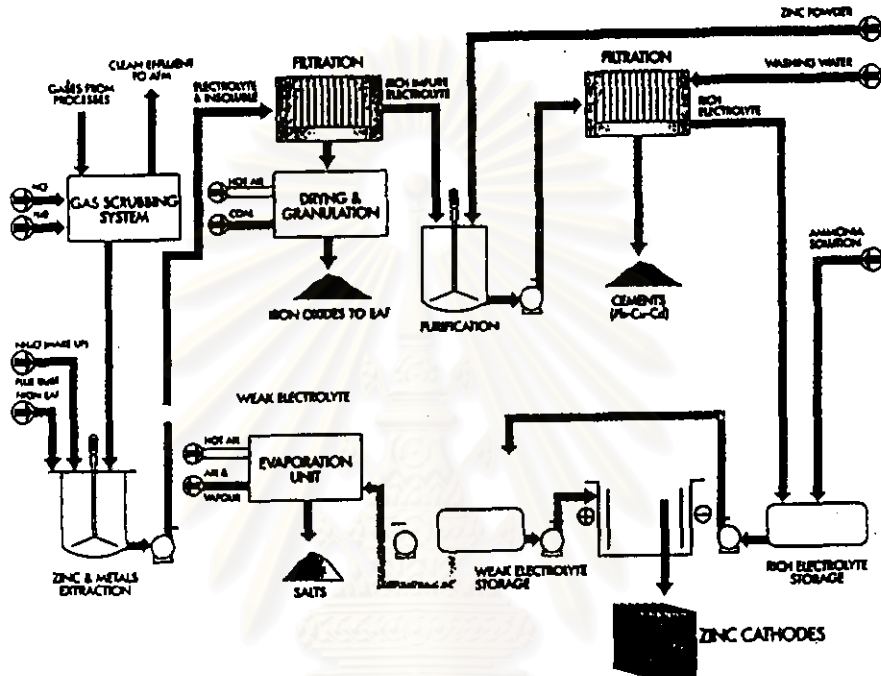


Figure 2.8: Schematic of EZINEX process (Olper, 1995).

2.3 PROCESS EVALUATION

An acceptable EAF dust treatment process needs to fulfill the following requirements:

- 1) have low capital and operating costs,
- 2) generate a minimum of residue which must be non-hazardous by present and future standards,

- 3) be able to treat a wide variety of EAF dust compositions with minimal preparation and
- 4) be capable of treating small amounts of EAF dusts (approximately 60,000 tons per year for EAF dust generated in Thailand) thereby avoiding the costs and liabilities associated with transporting the dusts and be able to recover the zinc, iron and alloying values.

A summary of EAF dust treatment processes are shown in Table 2.3 and 2.4 .

In the pyrometallurgical treatment processes, high temperatures are used, and the recovery of zinc product was quite high. Zinc is the contained metal value usually considered for recovery, with iron second. Some hazardous elements such as lead, cadmium, and some alkaline compounds were removed from EAF dust after processing. Some iron bearing products that have a high percentage of iron can be treated in ironmaking or steelmaking processes. The Waelz and INMETCO processes have been operated at the commercial scale but both processes produce zinc oxide. Since there is carbon monoxide and carbon dioxide present in the carbothermic reduction process, volatile zinc fume is reoxidized to be zinc oxide product. On the other hand, zinc oxide product has to be processed to obtain metallic zinc which is more usable. The Elkem and Plasma processes were supposed to operate at the commercial scale but both of them have been shut down due to technical and economic reasons (high temperature operating at 2500 °C for the Plasma process).

Hydrometallurgical treatment processes use leaching methods as the main extraction process. The processes operate between 30 to 95 °C with low capital and operating cost but require large amounts of chemical reagent for treating liquid waste which were in the form of acid or alkaline solutions. The highest percent zinc recovery that was presented in the summary was 90%, but most were about 60-80%. Only the EZINEX process had iron oxide as an iron bearing product.

The iron-reduction distillation process involves the recovery metallic zinc and low operation temperatures. In this process, zinc recovery is high and iron can be recovered by ironmaking or steelmaking processes.

Table 2.3: EAF Dust Pyrometallurgical Treatment Process Summary.

PROCESS	PROCESSING	OPERATING TEMPERATURE (°C)	REDUCTANT	FORM OF ZINC IN THE FEED DUST	% RECOVERY	ZINC BEARING PRODUCT	IRON RECYCLE, IRON BEARING PRODUCT	OTHER PRODUCT	SCALE	REFERENCES
Waelz	Agglomeration	1300	coal	N/A	N/A	ZnO	No	Clinker rich in metallic iron	Commercial	Urger, 1986
INMETCO	Pelletising	1300	crush coal	N/A	99% Zn and Pb	ZnO	Yes-pig iron	N/A	Commercial	Pargeter and Lehmkuochler, 1986
Elkem	Pelletising	1400	coke	N/A	N/A	Zn metal	No	Fe slag	Pilot Commercial-never complete	Litz, 1991 Zunkel and Schmitt, 1995
Bath Smelting :- Ausmelt :- Japanese Patent 53,046,406	Agglomeration, Pelletising	1450-1500	carbon	N/A	N/A	ZnO	Yes-iron oxide	Pb, Cd and Cu metal, Fe residue	Small	Worner, 1992
	Agglomeration	1300-1350	lump coal	ZnO	98.7% Zn	ZnO	Yes-reduced iron	Fe slag / residue	Small	Floyd <i>et al.</i> , 1993
	Fine ironmaking dust with nitrogen	N/A	N/A	N/A	82.0% Zn	ZnO	N/A	N/A	N/A	Misao and Mizuta, 1978
Plasma :- Hi-Plas	Agglomeration	2500	coal, coke	N/A	N/A	Zn metal	Yes-pig iron	Fe slag	Commercial-discontinued	Eriksson, 1985 Kola, 1990
	Agglomeration	1600	coke	ZnO	89% Zn	Zn metal	Yes-pig iron	Fe slag	Pilot	Naden <i>et al.</i> , 1987 Stockham and Ayars, 1990 Pickles <i>et al.</i> , 1977 Alcock <i>et al.</i> , 1986 Cowx and Roddis, 1986
Reduced Pellet	Pelletising	1020	coke	ZnO, ZnO.Fe ₂ O ₃	98.15% Zn	Zn metal	Yes-iron metal	Silver-rich metallic lead / slag	Laboratory	Lopez <i>et al.</i> , 1991
Iron-Reduction distillation	Pelletising	900-1100	Fe	ZnO, ZnO.Fe ₂ O ₃	97.0% Zn	High purity Zn metal	Yes-iron oxide	Cd metal / PbO, CuO	Laboratory	Azakami, 1985 Itoh and Azakami, 1994 Donald and Pickles, 1995 Donald and Pickles, 1996
Chloridised Roasting	Pelletising	N/A	CaCl ₂	N/A	90% Zn	ZnCl ₂	N/A	Pb, Cu, S, K and Na	N/A	Hay, 1992

Table 2.4: EAF Dust Hydrometallurgical Treatment Process Summary.

PROCESS	PROCESSING	OPERATING TEMPERATURE (°C)	LEACHING AGENT	FORM OF ZINC IN THE FEED DUST	% RECOVERY	ZINC BEARING PRODUCT	IRON RECYCLE, IRON BEARING PRODUCT	OTHER PRODUCT	SCALE	REFERENCES
Cebedeau	Alkali Leaching	95	NaOH	ZnO, ZnO.Fe ₂ O ₃	80-85% Zn	Zn metal	No	Pb/Cu cement	Pilot	Frenay <i>et al.</i> , 1986 Geutskens, 1990
UBC-Chaparral	Acidic Leaching	95	H ₂ SO ₄	ZnO, ZnO.Fe ₂ O ₃ , ZnCO ₃	55-60% Zn and Pb	Zn metal	No	Pb/Cd cement	Pilot	Dreisinger <i>et al.</i> , 1990
Acidic Leaching	Acidic Leaching	30	H ₂ SO ₄	ZnO, ZnO.Fe ₂ O ₃	80% Zn	Zn metal	N/A	N/A	Laboratory	Cruells <i>et al.</i> , 1992
ZINCEX	Acidic Leaching	35-40	H ₂ SO ₄	ZnO, ZnO.Fe ₂ O ₃	70-91% Zn	Zn metal	No	Pb/Cd cement, Fe residue	Pilot	Di'az <i>et al.</i> , 1995
EZINEX	Alkali Leaching	70-80	2NH ₄ Cl ₂	ZnO	N/A	Zn metal	Yes-iron oxide	Pb/Cu cement	Commercial	Olper, 1995

N/A : The details are not available.

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2.4 DETAILED ANALYSIS OF THE IRON-REDUCTION DISTILLATION PROCESS

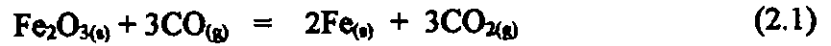
The principle of the zinc extraction process called the iron-reduction distillation process was developed by T. Azakami from Department of Metallurgy, Faculty of Engineering, Tohoku University, Sendai, Japan in 1985. Further work was also carried out by S. Itoh and T. Azakami in 1994. The iron-reduction distillation process consists of two reduction stages. The first stage is the reduction of iron oxide. The second stage is the reduction and distillation of zinc by the reduced metallic iron. In Itoh and Azakami (1994) work, experiments were carried out using reagent grade samples, industrial zinc calcine and steelmaking dust. The reagent grade sample was a mixture of iron oxide (hematite) and zinc oxide in 1:1 molar ratio. The chemical composition of the zinc calcine and steelmaking dust are shown in Table 2.5. They found by x-ray diffraction analysis that most of the zinc in the calcine existed in the form of zinc oxide but small quantities were in the form of zinc ferrite, silicate and sulfide. In the steelmaking dust, most of zinc was in the zinc oxide and zinc ferrite form. No information was provided on the source of the steelmaking dust and the concentration of the different phases present.

Table 2.5: Chemical Composition of Zinc Calcine and Steelmaking Dust, mass % (Itoh and Azakami, 1994).

Component	Zn	Fe	Pb	Cd	SiO ₂	CaO	Cl	F	C	Cu	S
Zinc calcine	60.00	8.10	1.53	0.27	2.41	0.60	trace	trace	trace	0.81	3.71
Steel dust	32.30	20.10	2.88	0.04	2.90	1.38	6.80	0.20	1.00	0.24	2.88

In Itoh and Azakami (1994) experiments, reagent grade hematite was added to the zinc calcine and steelmaking dust as an iron source, so that the ZnO/Fe₂O₃ molar ratio became unity. The addition of hematite was essential because of the low percentage of iron in the zinc calcine and steelmaking dust.

In the first stage, hematite was preferentially reduced by carbon monoxide to metallic iron at 700 - 800 °C in a highly reducing atmosphere ($p_{\text{CO}}/p_{\text{CO}_2} = 10$) while the zinc oxide was unchanged. The basic reaction in the first stage stated before in Section 2.2.2 was shown as follows :



Regarding the form of iron oxide in steelmaking dust, the authors did not mention the presence of magnetite. The iron oxides present in the steelmaking dust were not studied in this work.

Experimental results of the first reduction stage at 700 and 800 °C for calcine and steelmaking dust are shown in Figure 2.9 and are compared with those from the reagent grade samples.

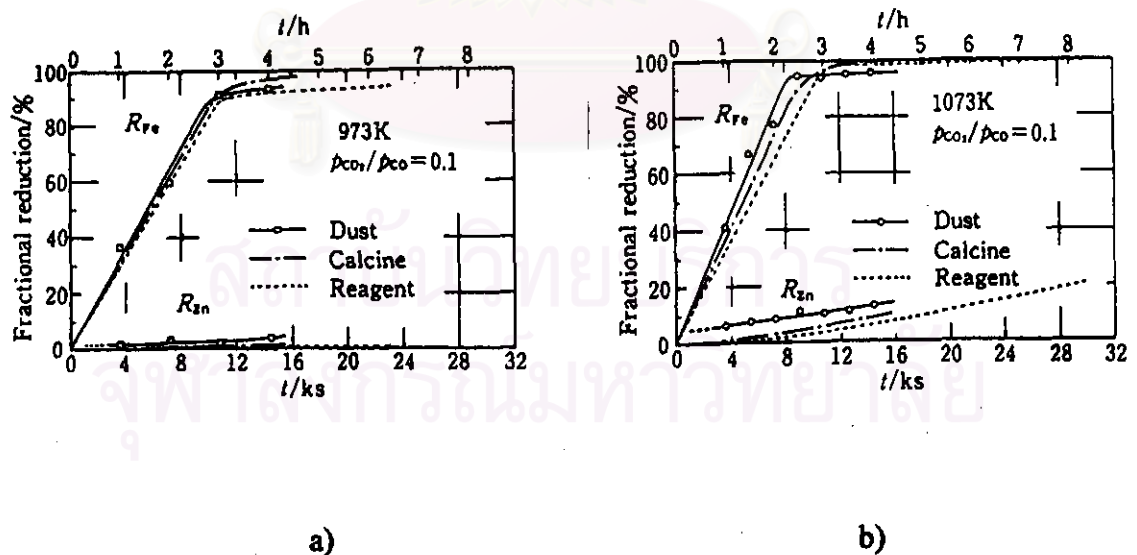


Figure 2.9: Results of the first reduction stage for steelmaking dust, zinc calcine and reagent grade samples at a) 700 °C and b) 800 °C (Itoh and Azakami, 1994).

The authors did not consider the effect of zinc ferrite reduction by carbon monoxide in this reduction stage.

Latkowska and Ptak (1987) investigated the synthetic zinc ferrite reduction by CO_2/CO gas ratio at 0.33, 1.0 and 3.0 at the temperature between 950 and 1200 °C. It was found that hematite in zinc ferrite was reduced to wustite, which was a stable reaction product, was a privileged one at every conditions. Zinc oxide appeared in the products was dependent on temperature and the reduction time. From this study, zinc ferrite reduction by carbon monoxide would be happened in the first reduction stage conditions of the iron-reduction distillation process.

The behavior of minor elements in the first reduction stage was also studied and it was found that cadmium evaporated completely at the beginning of the reduction stage while lead and copper remained with iron and zinc oxide at the end of the first reduction stage.

In the first reduction stage, the effect of gas composition and sample size were also studied. For the effect of gas composition, CO_2/CO gas ratio was used at 0.1, 0.2 and 0.3 and 700 °C. They found that smaller gas ratio gave the faster reduction rate of iron oxide but zinc oxide remained as it was in all cases. For the effect of sample size, the 2.5 and 4.5 g briquettes were reduced in CO_2/CO gas ratio of 0.1 at 700 °C. Bigger sample was slightly retarded as compared with the other.

The second reduction stage was carried out at 900-1100 °C and preferably under vacuum of 10^{-5} atmosphere for fast elimination of zinc vapour from the system. It was found that the reaction of zinc oxide with metallic iron was promoted by increasing temperature, increasing iron to zinc oxide molar ratio and decreasing briquette size (l/d ratio less than one). The basic reaction in the second reduction stage was :



Experimental results of second reduction stage in successive treatment of the first reduction (CO_2/CO) and second reduction (vacuum) for steelmaking dust, zinc calcine and reagent grade samples are shown in Figure 2.10 . The reaction proceeded very fast

under vacuum of 1 Pa as the temperature increased, for example, all of zinc was distilled within 20 minutes at 1100 °C.

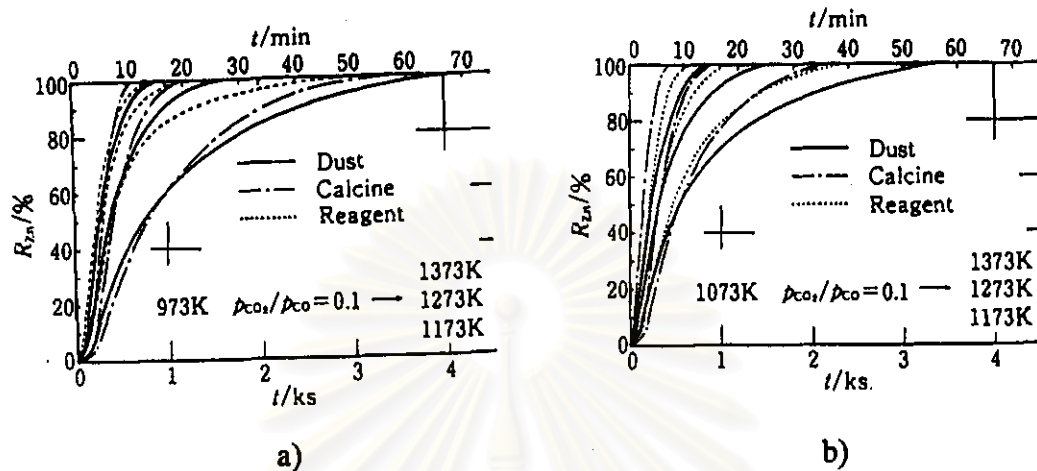


Figure 2.10: Results of the second reduction stage in successive treatment of the first and second reduction for steelmaking dust, zinc calcine and reagent grade samples at a) 700 °C and b) 800 °C for successive first reduction stage (Itoh and Azakami, 1994).

Figure 2.10 a) shows that for the steelmaking dust all of the zinc oxide was reduced and distilled at 900, 1000, and 1100 °C within 68, 26 and 15 minutes, respectively. This process used the successive briquettes reduced at 700 °C from the first stage. Figure 2.10 b) also shows that all of the zinc oxide was reduced and distilled at 900, 1000 and 1100 °C within 57, 24 and 15 minutes, respectively. This process used the successive briquettes reduced at 800 °C from the first stage. From both results at 1000 and 1100 °C of the second reduction stage the first reduction stage temperature did not have any effects on the reduction rates in the second stage. On the other hand, at 900 °C of the second reduction stage the successive briquette reduced at 800 °C from the first stage gave faster reduction rate. Two comparable lines of the reduction rates at 900 °C of the second stage with 700 and 800 °C reduction temperature of the first stage are shown in Figure 2.11 .

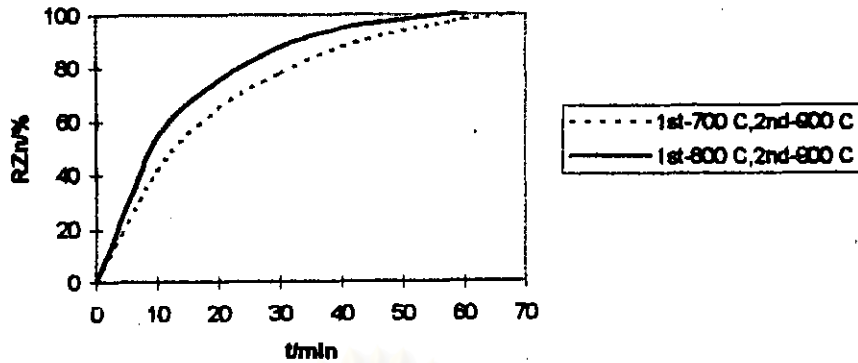


Figure 2.11: Reduction rates at 900 °C of the second stage with 700 and 800 °C reduction temperatures of the first stage for the steelmaking dust.

In the second reduction stage, application of inert gas atmosphere led to an easy industrialisation of the process for the economic reason because nitrogen is cheaper than carbon monoxide, some experiments were thus made by using nitrogen gas. Figure 2.12 shows the results of second reduction stage for the steelmaking dust both the cases of vacuum and nitrogen atmosphere. It was found that the reduction rates were very slow in nitrogen atmosphere.

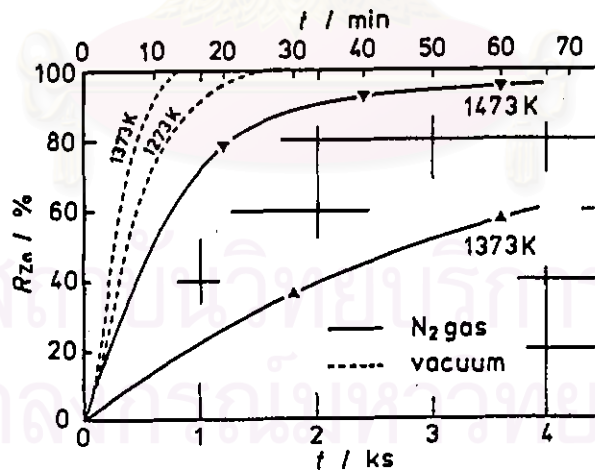


Figure 2.12: Comparison of second reduction in vacuum (broken lines) and N₂ gas stream (solid lines) for the steelmaking dust.

In this reduction stage, the authors also found that lead was volatilised with zinc vapour and then were cooled in a condenser. The cooling zinc vapour in a condenser followed

by liquation was required to separate lead. The authors did not study the behavior of sodium, potassium, chlorine and chromium elements during the second reduction stage.

From the above detailed analysis, more studies are required on the iron-reduction distillation process as follows :

- 1) Can the iron-reduction distillation process be used to treat a particular EAF dust?
- 2) What happens to the reduction of zinc ferrite by carbon monoxide in the first reduction stage?
- 3) Concerning the behavior of minor elements during the second reduction stage, does the concentration of hazardous elements be decrease?

2.5 SUMMARY

The composition of EAF dusts varies widely but zinc and iron are the two highest percentage elements from every sources of dust. The quantity of these two elements is up to 70% wt/wt of the dust. Zinc is present as zinc ferrite, while some is present as zinc oxide. The majority of the iron is in the form of hematite and magnetite, as well as the spinel zinc ferrite. The minor elements such as cadmium and lead are in the oxide form. The halides are present as sodium chloride, potassium chloride in either simple or complex form. Section 2.2 presented various methods for EAF dust treatment. Alternative processes can be classified into two major categories: recycling methods, and methods for recovery zinc and/or iron. Because zinc and iron are the two major elements in EAF dusts, the recovery of zinc and/or iron is the main consideration as well as the treatment of some hazardous elements, such as cadmium and lead.

From the evaluation of EAF dust treatment processes, the iron-reduction distillation process may be suitable for EAF dust treatment. Overall the processing route provides a number of potential advantage as follows:

- 1) a low temperature operating compared with other pyrometallurgical processes,
- 2) short operating time,
- 3) high recovery of zinc metal,
- 4) recovery of the iron values and other alloying elements,
- 5) external addition of reductant (Fe) is not required and
- 6) the amount of hazardous elements, such as cadmium and lead is reduced in the final product.

The introduction of the process would require further experimentation on particular EAF dusts. The key factors to be investigated would include :

- 1) characterisation of the specific EAF dust,
- 2) investigation of process conditions for the treatment of the particular EAF dust and
- 3) the development of a kinetic model for the reduction of the particular EAF dust.

Finally, it would be necessary to adhere to the environmental and safety regulations when handling the EAF dust, particularly in the iron-reduction distillation process.