Department of Materials Science and Engineering

Alkaline leaching of iron and steelmaking dust

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Aalto University

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Abstract

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Abstract

Steel production generates significant quantities of dust and sludge in blast furnaces (BF), basic oxygen furnaces (BOF), and electric arc furnaces (EAF). These dusts contain toxic elements, such as heavy metals, and are thus classified as harmful waste making the disposal of them expensive. In addition, direct recycling of dust back to steel production is hindered due to the presence of zinc.

In this literature survey the alkaline leaching of zinc from iron and steelmaking dusts is reviewed. The characteristics of EAF, BOF and BF dust and their processing based on caustic soda (NaOH) leaching is described. Also some methods, e.g. pre-treatments, to enhance leaching are introduced.

Dusts from iron and steel production consist mainly of ferrous oxides. In addition, they contain zinc, lead and cadmium oxides as well as minor amount of many other elements. The zinc content in EAF dust can run up 30 %, when it is usually lower in BOF and BF dusts, around 1-3 % and 1.5 %, respectively. Zinc is present mainly as zinc oxide, ZnO (50-80 %), and rest is as zinc ferrite, ZnFe2O4. The dusts are very fine (usually < 0.01 mm) and have tendency to agglomerate.

Metal extraction from the dusts is difficult due to their complex composition and finding a suitable process is complicated as each dust is unique. The advantage of caustic soda leaching is its selectiveness in leaching zinc compared to iron compounds. Thus a relatively clean and iron-free solution is obtained and the complicated iron removal processes is avoided. Some facilities using NaOH leaching have been constructed for dissolving zinc from the steelmaking dusts, but they have been closed as inefficient and expensive.

For the optimal leaching conditions 6-10 M NaOH solution, liquid to solid ratio of around 10, and temperature of 80 – 95 °C has been presented. Zinc recoveries of 80-85 % can be reached but part of zinc is not dissolved and recovered. ZnO dissolves easily in caustic soda, but ZnFe2O4 is highly stable compound and is the major obstruction in the hydrometallurgical extraction of zinc. Pressure leaching, and microwave or ultrasound assisted leaching has not improved significantly zinc recovery. For breaking the zinc ferrite structure, pyrometallurgical processes, such as roasting, can be used prior to leaching. By roasting with caustic soda prior to alkaline leaching zinc ferrites can be decomposed and leaching of zinc could be improved.

Keywords BF dust, BOF dust, EAF dust, NaOH leaching, zinc recovery

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Tiivistelmä

Teräksen valmistuksessa syntyy huomattavia määriä pölyjä ja liejuja masuunissa (BF), konvertterissa (BOF) sekä valokaariuunissa (EAF). Nämä pölyt sisältävät haitallisia aineita, kuten raskasmetalleja, ja ne on siten luokiteltu haitalliseksi jätteeksi, mikä tekee niiden sijoittamisen kaatopaikalle kalliiksi. Lisäksi pölyjen sinkkipitoisuus estää niiden kierrättämisen suoraan takaisin teräksen valmistusprosessiin.

Tässä kirjallisuuskatsauksessa on tarkasteltu sinkin emäksistä liuottamista raudan ja teräksen valmistuksessa syntyvistä pölyistä. Masuuni-, konvertteri- ja valokaariuunipölyjen ominaisuuksia sekä niiden liuottamista natriumhydroksidilla (NaOH) on kuvattu. Myös jotain menetelmiä sinkin liuotuksen parantamiseksi, kuten erilaisia esikäsittelyjä, on esitelty.

Raudan ja teräksen valmistuksen pölyt koostuvat pääosin raudan oksideista. Lisäksi ne sisältävät sinkin ja lyijyn oksideja sekä pieniä määriä monia muita ainesosia. EAF pölyn sinkkipitoisuus voi olla jopa 30 %, kun se on yleensä alhaisempi BOF ja BF pölyissä, noin 1-3 % ja 1,5 %. Sinkki on pölyissä pääosin oksidina, ZnO (50-80 %), ja ferriittinä, ZnFe2O4. Pölyt ovat erittäin hienojakoisia (yleensä < 0,01 mm) ja ovat taipuvaisia agglomeroitumaan.

Metallien erottaminen pölyistä on hankalaa johtuen niiden kompleksisesta koostumuksesta ja sopivan prosessin löytäminen on vaikeaa sillä jokainen pöly on omanlaisensa. Emäksellä liuottamisen etu on, että sinkki liukenee selektiivisesti verrattuna raudan yhdisteisiin ja siten saadaan raudaton ja suhteellisen puhdas liuos, ja vältytään monimutkaiselta prosessilta raudan poistamiseksi. NaOH liuotukseen perustuvia laitoksia on perustettu ennenkin sinkin poistamiseen teräksen valmistuksen pölyistä, mutta ne on suljettu tehottomina ja liian kalliina.

Optimaalisiksi liuotusolosuhteiksi kirjallisuudesta saadaan väkevyydeltään 6-10 M NaOH liuos, neste-kiinteä suhteeksi n. 10 ja lämpötilaksi 80-95 °C. Sinkin saanti on ollut tällöin 80-85 % mutta osa sinkistä ei ole liuennut ja jäänyt ottamatta talteen. ZnO liukenee helposti natriumhydroksidilla mutta ZnFe2O4 on erittäin stabiili yhdiste ja tärkein este sinkin erottamisessa pölyistä hydrometallurgisin menetelmin. Paineliuotus sekä mikroaaltojen tai ultraäänen käyttö liuotuksen apuna ei ole parantanut merkittävästi sinkin saantia. Pyrometallurgisia prosesseja, kuten pasutusta, voidaan käyttää ennen liuotusta sinkkiferriittien hajottamiseen. Ennen emäsliuotusta tehty pasutus natriumhydroksidin kanssa hajottaa sinkkiferriitit ja sinkin liukeneminen saadaan parannettua.

Avainsanat masuunipöly, konvertteripöly, valokaariuunipöly, NaOH liuotus, sinkin talteenotto

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CONTENT

1. Introduction

Iron and steel production generates significant quantities of various solid wastes in form of dusts and sludge, and the amounts of these wastes are yearly increasing. Their disposal or possible re-use has been a serious concern for iron and steel industry.

Common practice has been dumping of the dust to the landfill close to mills, but nowadays in most industrial countries iron and steelmaking dust are considered as harmful waste as they contain toxic elements such as heavy metals. Thus, they must be stored in special landfill areas, which make the disposal expensive. On the other hand, iron and steelmaking dusts usually contain some useful resources such as iron, calcium, zinc, lead etc., which can be recovered and reused in a judicious manner [1]. In case of disposal the valuable metals are lost.

From both of economic and environmental point of view it is desirable to recover the valuables and utilize these wastes. However, direct recycling of dust back to steel production is not possible because they often contain metals and compounds that can harm the primary processes if the materials are not pre-treated [2].

The element that causes the most problems is zinc, which vaporizes easily and condenses to steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite. The use of galvanized steel scrap in steel production has been increasing, which has led to the increase of zinc content in the dusts and this trend will likely continue. Nevertheless, these flue dusts can not be reused in zinc smelters as the zinc content is too low and they contain high amounts of impurities.

Because some of these dusts can not be recycled directly or used as landfill, it is necessary to consider the recovery of valuable elements from them and to obtain residue that can be reused or safely disposed-off without affecting the environment [2]. A number of pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steelmaking dusts in primary operations [3,4]. Yet, there are still problems associated with treating these materials and none of the developed processes have been entirely satisfying [5].

Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. However, they are gradually been replaced by hydrometallurgical processes [6]. The major drawbacks with pyrometallurgical processes are high energy consumption and a need of relatively large tonnage of dust to be economically competitive.

There is an impetus for developing hydrometallurgical processes as they can fit on small-scale and an on-site process could be possible. Hydrometallurgical processes on a small scale are regarded as more environmentally suitable and economical for treating materials having relatively low zinc content. Also these processes can provide a good selectivity in metal separation and flexibility in end products. [5-7]

The choice between the processing routes depends strongly on the dust characteristic. Therefore detailed characterization is important, including particle size and the number of valuable elements and mineralogical phases. Dusts containing many elements make metal extraction complex and difficult. In addition, each dust is unique, which makes finding a suitable treatment process even more complicated.

The main target in the dust treatment is the removal of zinc so that iron containing material can be recycled and zinc recovered. Among the hydrometallurgical methods, the advantage in alkaline leaching is the selective solubility of zinc compared to iron compounds and thus relatively clean and iron-free solution is obtained and the complicated iron removal processes is avoided. Therefore, leaching with alkaline is the most promising method of the leaching processes. However, the major obstruction in the hydrometallurgical extraction of zinc is the presence of zinc ferrite ($ZnFe_2O_4$) in the dust, which is a very stable compound.

In this literature review the different techniques for alkaline leaching of zinc from carbon steelmaking dusts are reviewed, including the already commercialized processes and the processes, which are at research or pilot stage. Some general aspects considering metals separation capability, wastes and possibility to treat varying dusts will be discussed. Also the characterization and utilization of various flue dusts have been summarized. The objective of this study is to explore the technical and economic possibilities of increasing the leaching efficiency of zinc and lead from dust using alkaline medium.

2. Dust formation in iron and steel industry

During the steel production different types of dusts are emitted and the composition of these varies widely depending on the source of generation [1]. Basically, the steel production is based on two basic routes (Figure 1) [8]:

1) steel is made from raw materials including iron ore, limestone and coke along with recycled steel by the blast furnace (BF) and basic oxygen furnace (BOF) route, and
2) steel is made from recycled steel via the electric arc furnace (EAF) method.

Various dusts, such as sintering dust, blast furnace dust, basic oxygen furnace dust, electric arc furnace dust, and mill scale are formed in the processes of these two steel production routes. Steel production in EAFs accounts for about 31% of the world's annual steel production [9].

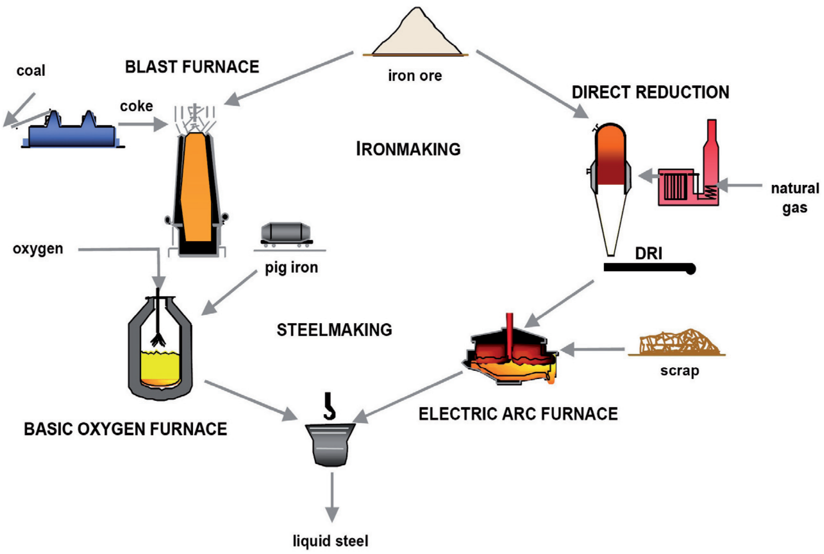


Figure 1. Steelmaking routes [10].

Steel industry generates every day significant quantities of dust, sludge and slag as waste material or byproduct (Figure 2). They usually contain considerable amounts of valuable metals and reuse of those is very much essential not only for conserving metals and minerals resources but also for protecting the environment [1]. It has estimated that the dust emission in the steel industry range between 1 to 2 % of ton of steel produced. Worldwide around 7.5 Mt of flue dust is generated annually [11].

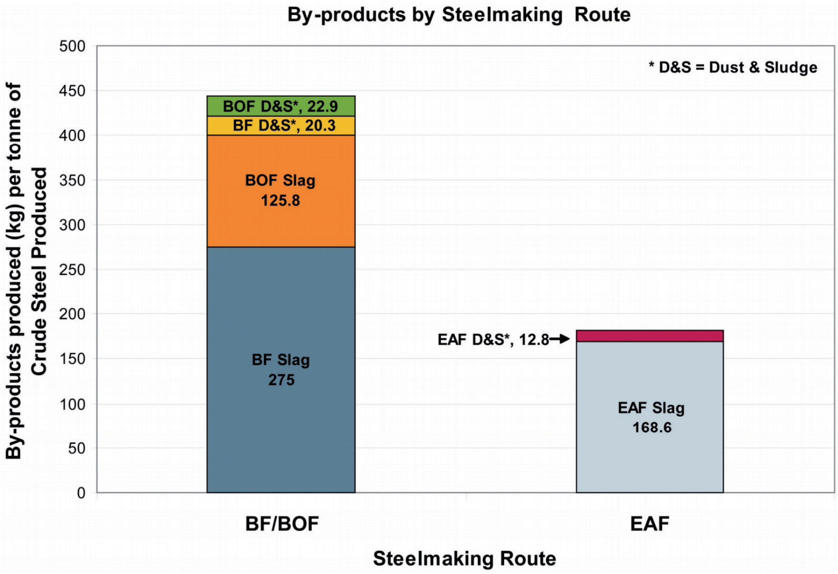


Figure 2. By-products formed in steelmaking routes [12].

The main raw materials in iron and steel plants are iron oxide ore (containing hematite, Fe_2O_3, and magnetite, Fe_3O_4) and steel scrap. The use of scrap in BOF and EAF brings other elements into furnaces and they end up into dust. Under the conditions of steel production some metals such as zinc, cadmium and lead evaporate and pass nearly all to the dust and sludge and very low amount remains in the steel and slag. As soon as metal fumes are out from the furnace, temperature decreases and metal fumes oxidize and condense. Iron is also vaporized due to high temperature and turbulence in the furnace. In addition, lime and silicon are charged in the furnace and these elements end up in the collected dust as well [4].

The recycling cycle of steel is well established for the steel industry. The recycling of steel scrap has obvious economic and resource conservational benefits. The electric arc furnaces can use 100 % steel scrap as raw material in steel production. However, the major challenge in this is to maintain the quality of steel products and to minimize contamination of other metals. For the last decades the EAF’s share of total steel output has been increasing. This trend will likely continue in the future and has to some extent created an ever-increasing environmental issue. [8]

Dusts from iron and steel production consist mainly of ferrous oxides. In addition, they contain zinc, lead and cadmium oxides as well as minor amount of other elements. The iron industry has traditionally sintered fines in integrated operations and part of the dust is again charged into the furnace. Nevertheless, the reuse is limited because dusts and sludge often contain metals and compounds that can harm the primary processes if the materials are not pre-treated. A direct re-use of them will lead to accumulation of those elements in charge materials and decrease steel quality. In addition, the adoption of pelleting has made sintering of dusts uneconomic [6].

The steelmaking dusts are rich in zinc and lead. The main source of zinc is galvanized steel sheet scrap and use of them in steel production has been increasing, which has led to the increase of zinc content in the dusts and this trend will likely continue. Any zinc-bearing scrap included in the charge will result in discharge mainly of zinc oxide in the flue dust. The BOF process uses minimum 25 % scrap whereas EAF technology uses virtually 100 % recycled steel [8] and the dust from EAF can run up to 30 % of zinc. The amount of zinc is usually lower in BOF and BF dusts containing around 1 – 3 % and 1.5 % of zinc, respectively [6].

Zinc is the element that causes the most problem in treating flue dusts and also hinders the direct recycling of dust back into steelmaking furnaces. The presence of zinc in steelmaking process leads to many harmful effects such as the decrease in the steel quality. Zinc vaporizes easily and condenses to steel production fumes ending up to flue dust or sludge. When vaporized zinc is carried out from the furnace with other gaseous reaction products from the steel production, zinc compounds can be formed such as zincite (ZnO) and zinc ferrite ($ZnFe_2O_4$), which is also known as franklinite. The zinc ferrite is formed when zincite particles are in contact with iron at elevated temperatures under oxidizing conditions.

Composition of flue dusts is extremely variable and depends on the type of steel being made, and the nature and quantity of used scrap, and alloy additions. Fe in dust is mostly in Fe_3O_4 phase, 50 – 80 % of zinc is present as ZnO, rest balanced mainly as compound with Fe in a mixed zinc-iron ferrite spinel. Individual particles in the dust are mostly less than 1 μm, though agglomeration is prevalent causing poor recoveries by physical separation methods. [13]

Disposal, recycling or recovery of these dust emissions has been a major concern for the metal industry. Due to increasing environmental regulations, landfilling has become expensive and recycling is limited due to accumulation of impurities (heavy metals, alkali and halides). Alternative processes are thus necessary.

The chemical and mineralogical analyses are important for defining the most appropriate recycling strategy. The choice between pyrometallurgical or hydrometallurgical processing routes is strongly dependent on the dust characteristics. These include particle size, the amount of valuable elements and mineralogical phases. These characteristics may indicate the amount of leachable constituents. [14]

Three types of dust, BF, BOF and EAF, emitted in the iron and steel industry are shortly described below. The emphasis has been on the EAF dust.

2.1 Blast furnace dust

Blast furnace (BF) flue dust is a solid waste material from the iron making process consisting of a mixture of oxides. The main solid components in the flue dust are Fe, C, SiO_2, Al_2O_3, CaO and MgO [15]. The BF dusts are usually rich in carbon (40 – 50 %) and iron (20 – 30 %). The zinc (1.5 %) and lead levels are generally low since only minor amounts of these elements are permitted to enter into the iron making process. Beside of those there are other oxide elements in lesser amounts. An example of BF dust with some characteristics is presented in Table 1. [1,6,8,16]

Part of the blast furnace dust can be readily recycled trough the sinter plants. Sintering is a major method of recycling and recovering iron-bearing waste oxides and secondary materials such as BF dusts. Nevertheless, traditional sintering capacity is not expected to increase in the future. Despite that sintering can replace iron pellets and add stability to BF operation, the environmental concerns and high capital and operating costs have lead to a decline in traditional sinter plants. [15]

The adoption of pellet sintering in remote locations has made sintering of dusts uneconomic to recycle iron blast furnace dust to the pellet plant. This has led to land filling practice as the small tonnage and low value of units do not justify installing a large agglomeration plant [6]. At steelmaking operations without sintering plants, BF dust is also sometimes mixed with other by-product residues, briquetted, and recycled into the blast furnace. Other ways to handle the dust and sludge are stockpiling or sale. [15]

Table 1. Physical and chemical properties of a typical BF flue dust sample [1].

Constituents	Sample I (%)	Sample II (%)
Carbon	29.90	33.62
Fe_2O_3	51.10	49.50
SiO_2	6.31	8.30
Al_2O_3	5.12	2.54
CaO	4.90	1.96
MgO	0.88	1.33
Pb	0.024	0.019
Zn	0.042	0.028
MnO	0.58	0.02
K_2O	1.22	0.154
Na_2O	0.47	0.07
Fe(T)	35.7	34.62
Bulk density (g/cm^3)	1.42	1.32
Specific gravity (g/cm^3)	2.59	2.56
Porosity (%)	45.17	48.53

A direct use of the dusts would decrease the agglomeration costs and energy as they substitute pellets or briquettes. However, BF dusts can contain elements that can cause operational difficulties if the dust is recycled directly without pre-treatment [16]. Substances, such as Na, K, Zn, Pb, Cd, S, cyanides, oils, etc., can be present in BF dust and hamper the reuse of dust to the sintering plant. Alkalis lower down the softening and melting temperature of iron and sinters in blast furnace performance and they can accumulate. In addition, zinc causes problems by forming a circuit in the furnace, which results in extra coke consumption. Also the condensation of zinc in cooler region of blast furnace cause serious problems. Dusts with high Zn, Pb and alkali contents have hitherto been almost entirely dumped [1].

2.2 Basic oxygen furnace dust

Basic oxygen furnaces (BOFs) produce steel from molten iron (from the BF) and ferrous scrap metal [8]. Around 1 – 2 % of the raw materials fed into furnace are converted into dust during the steelmaking process. It is estimated that about 4.3 Mt of flue dust is generated annually in the world in basic oxygen process. The dust is generally collected as sludge by scrubbing in a wet gas cleaning plant [11].

The BOF dust is an iron rich by-product, which contains calcium oxides in its different forms [11]. BOF dust also contains varying amounts of zinc, lead and other metals. The primary source of these metals is the scrap used in the steelmaking process [15]. Zinc content is higher than in BF dusts due to used scrap in BOF and it varies depending on the quality of the scrap. The zinc content is usually from 1 % to 4.0 % [6,17].

2.2.1 Recycling possibilities

Iron and steel plants are typically land-disposing the collected BOF dusts and sludge. Some companies are recycling these directly to steelmaking with other wastes from steel plant. The BOF fumes are mixed and agglomerated with other iron oxide materials such as mill scale [15]. The waste oxides have a cooling effect in a BOF and use of them can save scrap and/or lump ore [18].

If the zinc content is sufficiently low the BOF dust is recycled to the blast furnace via sintering plant [15]. However, the zinc content is usually high enough to prevent the direct recycling of the BOF dust. At the same time the Zn content is too low to economically justify further processing of zinc recovery [6]. Though zinc accumulates in the BOF dust, the content is usually around 2 % in the BOF dust. If recycling is installed, it can be increased to 25 %. Even then the dusts should be concentrated if they are wanted to be utilized in the zinc industry [18].

Also, if the dust is recycled directly into iron and steelmaking process it increases operating costs and rises the build-up of impurities in the melt [11,19]. The presence of zinc in the feed materials of a blast furnace can cause serious damage to blast furnace refractories, which will shorten the life of a blast furnace. The zinc content of the fume, slag or steel can increase substantially unless a bleed stream is provided to keep the zinc build-up at manageable levels. Zinc build-up has not occurred in facilities using this recycling practice [15].

The concerns related to BOF dust are the cost of landfilling and difficulties in recycling the dust. Recovery of iron is an attractive option only if the zinc content can be reduced to acceptable level and it can be done economically. It has suggested that the zinc content of BOF dust should be reduced to below 0.4 % (wt-%) in order to be recycled in the iron- or steelmaking process [17]. Numbers of processes have been studied to remove zinc from BOF dust and some of these processes may be viable in the future [15].

2.2.2 Chemical composition

The chemical composition of BOF dust varies depending on the alloying elements and the used scrap. The composition can vary even from heat to heat. BOF dust is very rich in iron consisting in range of 55 - 73 % of iron. It also contains calcium oxides, around 5 – 9 %, in its different forms [11]. BOF dust can also contain some harmful species such heavy metals (Cd, Cr, Pb, Mn, Ni) [15]. In Table 2 are represented examples of chemical composition of the BOF dust and sludge from various references. Only elements that occurred with more than 1 % are collected into the table.

The BOF dust contains mainly iron oxide, iron ferrite, calcium (magnesium) oxide, calcium (magnesium) carbonate, and also some other metal oxides. Iron is present in different phases mainly as FeO, Fe_2O_3 and Fe_3O_4. Besides iron compounds, often following phases, CaO, $Ca(Mg)CO_3$, $FeAl_2O_4$, FeNi, $FeCr_2S_4$, and $FeTiO_3$, as well occur in the dust. Zinc is usually present as zincate (ZnO) and as ferrite ($ZnFe_2O_4$) [11]. L.-M. Wu [11] found that 74 % of zinc was in the form of ZnO and 26 % was present as zinc ferrite.

Table 2. Reported chemical composition of BOF dust and sludge in various references [1,11,17,20,21].

	BOF dust		BOF sludge			
Element	(%) [11]	(wt-%) [20]	(wt-%) [21]	(wt-%) [17]	(wt-%) [20]	(%) [1]
Fe	55.7	30 - 85	47.67	54 - 70	54 - 70	61 - 64
Ca	8.54	-	6.8	-	-	-
CaO	-	8 - 21	-	-	3 - 11	9 - 11
Mg	1.66	-	0.55	-	-	-
Zn	0.197	< 0.2	2.74	0.9-3	1.4 - 3.2	-
Pb	0.099	< 0.04	0.18	0.1 - 1	0.2 - 1.0	-
Cl^-	-	-	7.09	-	-	-
SiO_2	-	-	-	-	-	0.71 - 1.97
C	-	1.4	-	-	0.7	-

2.2.3 Particle size and morphology

The BOF dust consists mainly of very fine-grained spherical particles. The spherical particles are believed to have formed by volatilization and condensation mechanism [11]. The particle sizes are ranging from less than 5 µm to as large as 1 mm and as spherical formations in diameter from 3 to 100 µm. Some large particles are observed to be agglomerates of smaller dust particles [17]. L.-M. Wu [11] found that more than 80 % of the dust was finer than 2.0 µm and about 57 % was even finer than 1.0 µm. The finest particles had an average size of ~200 nm.

There are two types of particles in the dust [11]:

1) A rim of iron oxide and a solid core of metallic iron
2) Porous iron oxide and/or slag particles.

The majority of the particles in the BOF dusts consist of the spheres with a solid core [11]. The agglomerated particles formed of smaller ones had somewhat porous surface [17].

A zinc-rich thin layer has found to be present at the surface of the particles. The morphology of the particles (about 40 μm) showed a metallic iron core inside the particle and a slightly agglomerated ferrous oxide layer, and also a formation of agglomerated fine particles of zinc ferrite as an external coating (Figure 3). Iron was distributed equally within the particle as the dominant species in various forms. [17]

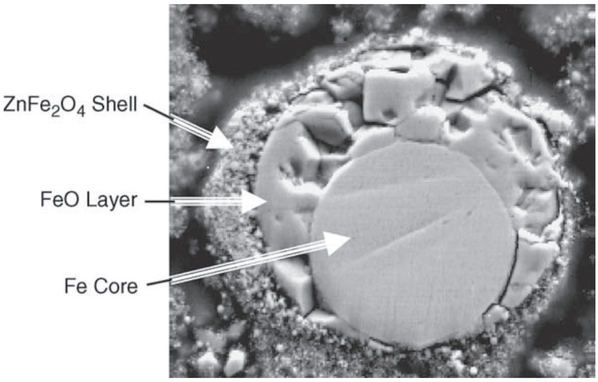


Figure 3. A spherical particle from BOF sludge [17].

2.3 Electric arc furnace dust

The particulate matter that is removed from emissions of electric arc furnace in dry system is called electric arc furnace dust (EAFD). It is reported that around 10 to 25 kilograms of dust is generated per ton of steel produced in EAF [5,6,9,14,22]. This is approximately 1 – 2 % of the charge [23]. Dust formation and some operations in EAF are represented in Figure 4. Dust formation is strongly linked to the process, which can be divided into five steps: furnace charging, smelting, refining, slag foaming, and casting. During the steelmaking process the temperature can reach ≥ 1600 °C in which metals, such as Fe, Zn, Cd and Pb, are volatilized and entered to the vapor phase. Dust is generated when vapor is cooled and collected [4,7,22].

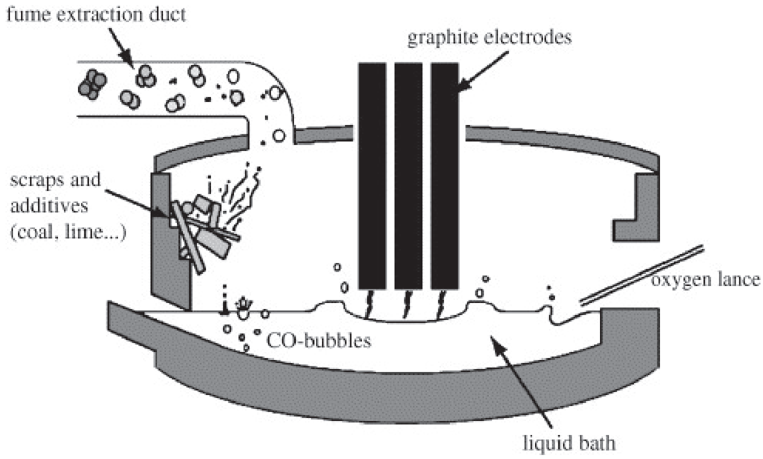


Figure 4. Dust formation in the EAF [22].

The composition of EAFD varies considerably and is dependent on the composition of charge, the type steel being made, and the operating conditions and procedures [6,24]. Because in steel manufacturing with EAF 100 % of the raw material can be steel scrap, the EAF dust can contain high amount of non-ferrous metals and the composition differs from BOF and BF dusts [8].

When galvanized scrap is used in the EAF, most of the zinc from the steel scrap ends up in the flue dust. This is because of zinc vapor pressure is higher than iron vapor pressure at steelmaking temperature and also due to very low solubility of zinc in molten steel and slag [25]. The concentration of zinc can reach as high as 40 % in the dust, but is usually between in 11 - 27 % [3,19]. Also lead and cadmium with trace amount of chromium and arsenic are found in the EAF dust. Therefore EAF dust fails in toxicity tests and is classified as hazardous waste K061 by US Environmental Protection Agency (EPA). [5,6,8,14,15]

Recycling of steel scrap has resource conservation and economic benefits associated with EAF steelmaking [6]. Steel production by EAF has been increasing and this trend is expected to continue in the future [26]. As a result, growing quantities of EAF flue dust will be generated and more zinc will be available to recover. Annually, the world generation of EAF dust is estimated to be around 3.7 million tons. An estimation of the steel recycling alternatives is necessary due to the great amount of generated dust. [25]

2.3.1 Recycling of EAFD

In the old days most of the EAF dust was landfilled as treating of the dust was not economic [26]. Common practice for disposal has been landfilling near the plants [27]. Another common option has been to stockpile the EAF. However, both of these have become non-viable as the sites available for stockpiling or landfilling are steadily depleted [6]. In addition, with these options the valuable metal values are lost.

Before the EAF dust was not processed further because EAF operators consider further treatment to be uneconomical and legally unnecessary [27]. The more stringent environmental regulations have been put into effect and the situation has changed as the EAF dusts have been classified to hazardous waste in most industrialized countries [5,6].

Since the use of scrap as raw material the EAF dust contains higher amounts of non-ferrous metals. Thus the direct recycling of the dust back to the EAF unit is difficult because of possible operating problems. Also the EAF dusts are extremely fine and difficult to handle. Nonetheless, recycling achieves lower net dust production and reduces overall disposal costs, but does not result in a net reduction or disposal of heavy metals. A new recycled dust with a higher zinc and lead content can be obtained and iron may be partially recovered. [2]

The content of valuable metals (lead and zinc) and the need to reduce imports will certainly encourage the utilization of this waste [27]. Treatments of these dusts are limited today to its stabilizing and to storage as dump place or to recovery of metals. In case of stabilization and land filling the potential of recovering zinc and other metals is lost. New technologies are still emerging in this field [6]. Now part of the dust is put in regulated dumps awaiting technical developments [26].

Zinc, due to its relatively large amount present, is the most valuable component in EAF dust [14]. The research and processing the EAFD from carbon steelmaking commonly aims mainly to recover zinc (and lead). The use of galvanized steel scrap has increased the zinc content in the EAF dust and thus increasing the interest on recovery of zinc from these dusts. Also the fact that zinc has been used progressively in the galvanizing process of the carbon steel has increased its price [25]. Nowadays still about 60 % of EAF dust is used as landfill (Figure 5), which means an annual of even 800,000 t loss of zinc [28].

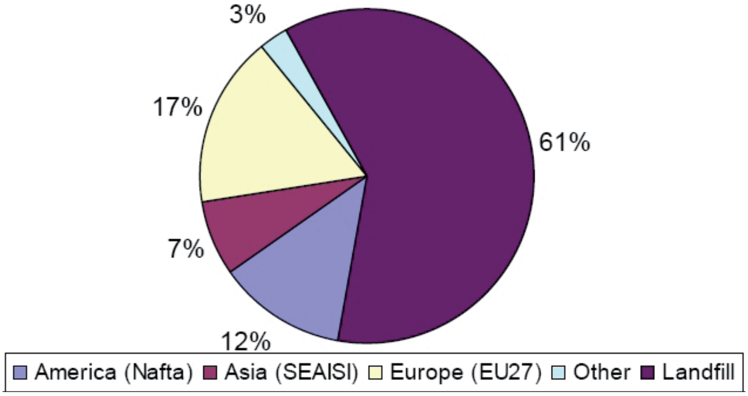


Figure 5. EAFD recycling in the world [28].

Industry is aware of the potential for further recovery of zinc and is increasing the treating of these materials. Even though a large part of EAFD is landfilled, substantial quantities of these dusts are upgraded and then used as feedstock for the production of primary zinc [26]. EAF dust is one of the main recycling resources of zinc. The recycling of zinc is an important issue because the natural resources of zinc are not believed to be adequate to maintain its future sustainable development. About 30 % of world's supply comes from recycled zinc. [29]

Standards exist for the acceptable treatment and disposal of EAF dusts and their treatment residuals. Nevertheless the high cost of treatment and disposal continue to present challenges for more cost-efficient means of treatment and recovery [15]. Attractiveness of resource recovery from dust may depend to large extent on the economics of the alternative of disposal. In both cases, in disposal or processing, it is though extremely hard and difficult to handle these dusts unless they are first pelletized [30].

2.3.2 Chemical composition of EAFD

Since the EAF dust is physically, chemically and mineralogically very complex material, it is difficult to characterize. As mentioned before, their chemical composition varies considerably and is dependent on the grade/composition of utilized scrap and furnace additives, on the operation conditions and procedures, and the type of steel being produced [9,15]. Also the degree of returned dust back to the process affects the chemical composition [24]. Even a minor change in the operating procedures from heat-to-heat could result in a variation in the composition of the dust [9]. Because of the wide range of composition in EAFD it is necessary to make accurate and precise analysis of each individual case in order to optimize any recycling or recovery.

Anyway, some general trends with the composition of EAFD can be noted. Usually, EAF dust contains iron and other metallic oxides from alloying metals in the scrap [15]. The major element is iron and its content varies from 16 to 44 wt-% [31] and the average iron concentration is around 30-wt% with the carbon steel EAFD [32].

Zinc compounds are the other main components observed in the dust and their concentration can vary between 2 – 40 % [3,24,25,27,31]. In addition, the EAF dust also contains smaller amounts of lead, manganese, calcium, sodium and potassium as well as trace amounts of other elements, such as cadmium, chromium, nickel, copper, magnesium, silicon and chlorine [5,6,9,14,27]. The amounts of Zn, Pb, Cu, Cr and Cd in the EAFD are on the rise, as the quantity of scrap coming from the automotive industry is used with an ever-increasing ratio [3].

The dusts from carbon steelmaking are all rich in zinc and lead, whereas the dusts from stainless steelmaking are relatively low in these [9]. The zinc contents in EAF dust from stainless steel production are between is 1 – 7 % [24,25]. However, stainless steel dusts are richer in alloying elements such as chromium, nickel, manganese etc. and contain important amount of nickel and chromium [9,31].

In Table 3 are represented examples of the chemical compositions of EAF dust from various references. The generally prevailing elements in EAF dust vary in concentrations of Fe 10-47%, Zn 2-46%, Pb 0.4-15.14%, Cr 0.06-11%, Cd 0.01-0.30%, Mn 1-5%, Cu <3%, Si 1-5%, Ca 1-25%, Mg 1-12%, Al 0.1-1.5%, C 0.11-2.36%, S 1.5-2.5%, Na 0.5-4%, K 0.35-2.3%, Cl (0.01-4%) and F (0.01-0.9%) [3-5,7,14,19,24,33-36].

Table 3. Reported chemical composition of EAF dust in various references (wt-%) [3,5,7,14,19,33-36].

Component									
	[3]	[34]	[19]	[7]	[33]	[5]	[35]	[14]	[36]
Zn	33	29	11.12-26.9	24.8	19.4	31.2	13.6	12.20	20.5
Fe	26	25	24.9-46.9	32	24.8	18.3	29.8	37.08	21
Pb	3.05	4	1.09-3.81	1.84	4.5	1.02	0.69	1.72	4
SiO_2	3.15	3	-	-	1.4	3.41	-	-	0.4
Cu	0.24	0.3	0.06-2.32	0.02	-	-	-	0.17	0.38
Cd	0.049	0.07	0.03-0.15	0.03	-	-	0.02	0.01	0.18
Cr	0.24	-	0.06-0.58	-	-	0.19	0.09	0.22	0.19
Al	0.6	-	-	-	-	0.68	-	0.41	0.6
Mn	1.83	3	2.46-4.60	3.31	-	2.2	-	-	2.25
Ca	2.9	-	1.85-10.0	4.08	-	15.6	-	-	12.5
Na	1.03	-	0.29-2.31	-	-	3.8	-	-	1
K	0.85	-	0.06-1.12	-	-	0.67	-	-	0.68
Sn	0.024	-	-	-	-	-	-	-	-
Sb	0.06	-	-	-	-	-	-	-	-
Cl	0.011	4	0.51-2.36	-	-	-	-	-	3.8
F	0.073	-	0.01-0.88	-	-	-	-	-	-

2.3.3 Mineralogical composition of EAFD

The EAF dust is a mixture of metal oxides, silicates and sulfates [24]. Dust is formed from vaporized and oxidized metals and elements from liquid metal and slag. Most of the constituents in the dust are in oxide form because the exhaust gas-line of the furnace is oxidizing. However, also chlorides, sulfides, silicate and sulfates occur in minor concentrations. In

Table 4 are shown the typical mineralogical forms of elements occurring in average in the EAF dust.

Table 4. Mineralogical phase distribution of major elements present in EAF [19,37].

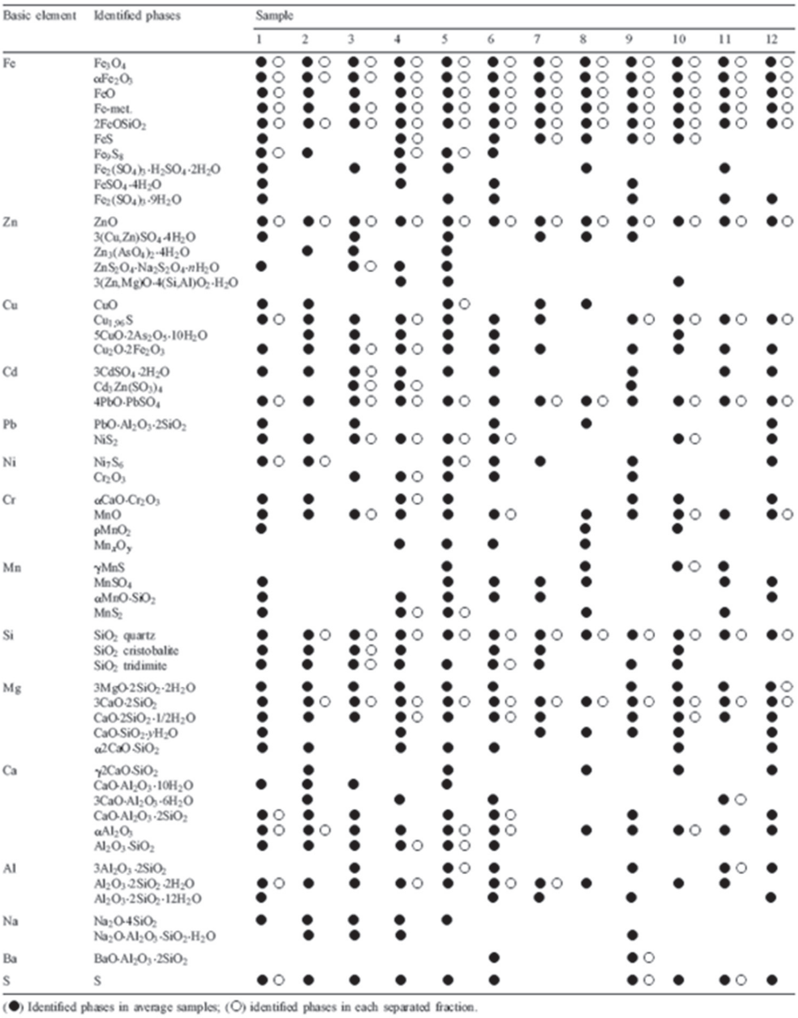
Element	Phases containing element
Fe	Fe_3O_4 is most prevalent phase. In this phase Fe cations are replaced to various degrees by Zn, Mg, Ca, Cr, Mn, etc. Some Fe occurs as a metal or as α-Fe_2O_3
Zn	50-80% as ZnO. Balance mainly associated with Fe in a mixed zinc iron ferrite spinel. Very small amounts of zinc may be as a sulphide, carbonate, silicate or aluminate
Cd	Distribution not well established, but possibly as for Zn considering the similarities in most properties of the two elements
Pb	Mostly as an oxide. $PbSO_4$, $PBCO_3$, and $PbCl_2$ are also present
Cr, Ni	Replace Fe in Fe_3O_4spinel phase. Some Cr could be as Cr_2O_3
Ca	As CaO and $CaCO_3$ mainly. The balance may occur as a fluoride, ferrite, or silicate.
Si	Mainly present as quartz.
Halides	Cl, Na, F, K, present as salts or chlorides.

Iron is occurring commonly as magnetite (Fe_3O_4) phase which makes up the matrix of the EAF dust. Its mass share can exceed of 50 % [24]. For example the following phases have been found to be present in the EAF dusts: $ZnFe_2O_4$, Fe_3O_4, $MgFe_2O_4$, $FeCr_2O_4$, Mn_3O_4, MgO, SiO_2, $Ca_{0.15}Fe_{2.85}O_4$ and ZnO [25]. With iron-bearing spinel phases ($ZnFe_2O_4$, $MgFe_2O_4$, $FeCr_2O_4$, $Ca_{0.15}Fe_{2.85}O_4$) one important property is that iron is partly replaced by cations. The cations that can replace the iron are Al^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ca^{2+} and Ge^{2+} [25].

Laurionite (PbOHCl) has been identified in the EAFD when the lead content has been high [31] but in low concentrations lead is present mainly as an oxide (PbO) [24]. Also presence of minor compound such as Zn_2SiO_4 (willemite), $CaSiO_3$ and SiO_2 have been discovered [31]. In addition, it has been found a substantial amount of salts like sylvite (KCl) and NaCl as well as some carbon (coke) in the EAF dust [38].

More detailed information of the phases identified in EAF is presented in Table 5 [24]. In all average samples and all separated fractions the following phases were identified: Fe_3O_4, Fe_2O_3, FeO, Fe (metallic), $2FeO*SiO_2$, ZnO, SiO_2 (quartz), $3CaO*2SiO_2$, $4PbO*PbSO_4$ [24].

Table 5. Phases identified in the EAF dust samples [24].



Basic element	Identified phases	Sample											
		1	2	3	4	5	6	7	8	9	10	11	12
Fe	Fe_3O_4	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	αFe_2O_3	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	FeO	● ○	●	●	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	Fe-met.	● ○	●	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	$2FeOSiO_2$	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	FeS	●			● ○		●	● ○	●	● ○	● ○		
	Fe_9S_8	● ○	●		● ○	● ○	●						
	$Fe_2(SO_4)_3 \cdot H_2SO_4 \cdot 2H_2O$	●		●	●	●			●			●	
	$FeSO_4 \cdot 4H_2O$	●			●		●			●			
	$Fe_2(SO_4)_3 \cdot 9H_2O$	●				●	●			●		●	●
Zn	ZnO	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	$3(Cu,Zn)SO_4 \cdot 4H_2O$	●		●		●		●	●	●			
	$Zn_3(AsO_4)_2 \cdot 4H_2O$		●	●		●							
	$ZnS_2O_4 \cdot Na_2S_2O_4 \cdot nH_2O$	●		● ○	●	●							
	$3(Zn,Mg)O \cdot 4(Si,Al)O_2 \cdot H_2O$				●	●					●		
Cu	CuO	●	●			● ○		●	●				
	$Cu_{1.96}S$	● ○	●	●	● ○	●	●	●		● ○	● ○	● ○	● ○
	$5CuO \cdot 2As_2O_5 \cdot 10H_2O$		●	●	●	●	●				●		
	$Cu_2O \cdot 2Fe_2O_3$	●	●	● ○	● ○	●	●	●		●	●	●	●
Cd	$3CdSO_4 \cdot 2H_2O$	●	●	● ○	●	●	●			●		●	●
	$Cd_3Zn(SO_3)_4$			● ○	● ○					●			
	$4PbO \cdot PbSO_4$	● ○	●	● ○	● ○	● ○	●	● ○	● ○	●	● ○	● ○	● ○
Pb	$PbO \cdot Al_2O_3 \cdot 2SiO_2$	●		●			●		●				●
	NiS_2	●	●	● ○	● ○	● ○	● ○				● ○		●
Ni	Ni_7S_6	● ○	● ○			● ○	●	●		●			●
	Cr_2O_3			●	● ○	●	●			●			
Cr	$\alpha CaO \cdot Cr_2O_3$	●	●		● ○	●				●	●		●
	MnO	●	●	● ○	●	●	● ○		●	●	● ○	●	● ○
	ρMnO_2	●							●		●		
	Mn_xO_y				●	●	●		●				
Mn	γMnS					●			●		● ○	●	
	$MnSO_4$	●				●	●	●	●			●	●
	$\alpha MnO \cdot SiO_2$	●			●	●	●	●					●
	MnS_2	●			● ○	● ○			●			●	
Si	SiO_2 quartz	●	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	SiO_2 cristobalite	●	●	● ○	●		●	●			●		
	SiO_2 tridimite	●	●	● ○	●	●	● ○	●		●	●		
Mg	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	●	●	●	●	●	●			●	●	●	● ○
	$3CaO \cdot 2SiO_2$	●	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○	● ○
	$CaO \cdot 2SiO_2 \cdot 1/2H_2O$	●	●	●	● ○	●	● ○	●		●	● ○	●	●
	$CaO \cdot SiO_2 \cdot yH_2O$	●			●			●	●	●	●		●
	$\alpha 2CaO \cdot SiO_2$	●	●		●	●	●				●		●
Ca	$\gamma 2CaO \cdot SiO_2$		●			●			●		●		●
	$CaO \cdot Al_2O_3 \cdot 10H_2O$	●	●	●		●							
	$3CaO \cdot Al_2O_3 \cdot 6H_2O$		●		●		●					● ○	
	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	● ○	●	●		●	● ○			●			●
	αAl_2O_3	● ○	● ○	●	●	● ○	● ○		●	●	● ○	●	●
	$Al_2O_3 \cdot SiO_2$	●	●	●	● ○	● ○	●						
Al	$3Al_2O_3 \cdot 2SiO_2$			●		● ○	●			●		● ○	●
	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	● ○	●	●	● ○	●	● ○	● ○	●		●	●	
	$Al_2O_3 \cdot 2SiO_2 \cdot 12H_2O$	●					●	●		●			●
Na	$Na_2O \cdot 4SiO_2$	●	●	●	●	●							
	$Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$		●	●	●					●			
Ba	$BaO \cdot Al_2O_3 \cdot 2SiO_2$						●			● ○			
S	S	● ○	●	●	●	●	●			● ○	●	● ○	●

(●) Identified phases in average samples; (○) identified phases in each separated fraction.

The forms of zinc present in the dust are important if recovering the zinc is considered. Zinc exists as two main compounds in the EAF dust, which are zincite (ZnO) and zinc ferrite ($ZnFe_2O_4$) [26,31,32,38]. The ratio of these depends on the type of furnace and operations, especially the dust collection systems [26].

The amount of zinc present in the zincite can vary from 30 to 70 % [31]. In some cases, it increases with the total zinc content [5,33]. More likely the amount of zincite varies with the ratio of Zn/Fe in the dust. Zincite becomes predominant form when the molar ratio Zn/Fe reaches high value and zinc ferrite is the major compound with low ratios [31]. Also some correlation with particle size has been noticed and the concentration of ZnO increased in relation to ferrite from with decreasing particle size [30].

2.3.4 Particle size distribution

In general, the EAF dust particles have predominantly an agglomerated morphology with individual fine particles forming aggregates or covering larger particles [5,6,9,25,38]. The agglomeration tendencies are most likely caused by exposure to air moisture and consequent hydration reaction. The mean particle diameter depends on this tendency [37].

The particle distribution of EAF dust is heterogeneous and the grain size of varies from 0.1 µm to around 200 µm [24,38]. Some of the particles have found to be even less than one-tenth of a micron [38]. The individual fine particles tend to be very small, generally less than 10 µm [5,19,22,25]. However, there are comparatively substantial differences in the measured particle sizes in various references. It is also reported that the most of the individuals particles are smaller than 1 µm [19,24,25], being usually less than 3 µm [23] and for the average particle size have reported to be 1.0 - 4.3 µm [6,9].

According to Machado et al. [25] around 60 % of particles had size between 0.90 µm and 4.30 µm. Lenz and Martins [38] found that approximately 90 % of the particles were smaller than 100 µm, 40 % were smaller than 10 µm and 10 % of the particles were smaller than 1.7 µm. The particle size distribution determined by Dutra et al. [14] indicated that only about 15 % of the particles are coarser than 10 µm and the median particle size (d50) is around 0.5 µm.

The shape of the individual particles in EAF dust is generally spherical [24,27,38]. Also spherical particles with wrinkled surface and elongated non-defined form have been observed. The spherical form of particles indicates that they are created in liquid conditions and they contained Fe, Zn, Pb, O, Si, Ca and spinel type metal oxides $(Fe,Zn,Mn)_3O_4$. The particles with angular shape are considered to be zincite (ZnO) [24].

The majority of zinc has found to associate with particles with a rougher surface and finer dust particles [14]. Both zinc and lead oxides tend to be present in small discrete particles or as smaller regions within a larger particle [38]. The structure of certain dust particles is represented in Figure 6 and 7 [25]. In addition to chemical composition, the morphology of the dust depends on the quality of the scrap and the mode of the operation of the EAF [14].

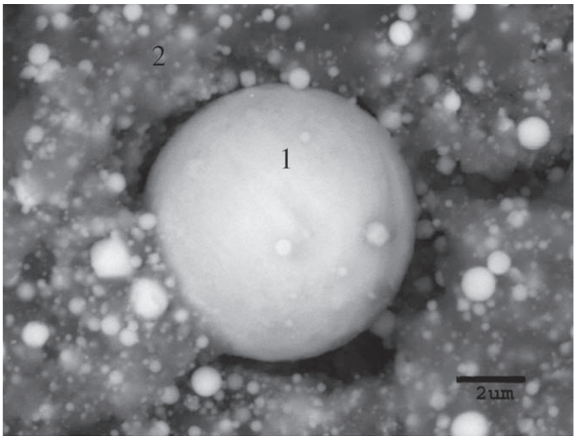


Figure 6. A spherical EAFD particle (area 1: rich in Fe and O, area 2: rich in Fe and Zn) [25].

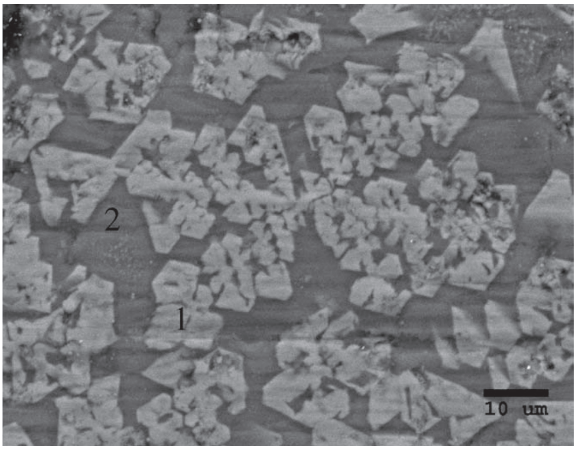


Figure 7. Dendritic structure in a EAFD particle (area 1: rich in Fe, Cr and O, area 2: rich in Fe, Ca, Si and O) [25].

3. Treating of steelmaking dusts

The possibilities for treating the steelmaking dusts are recovering the valuable metals from the dusts, recycling them back into furnace, or placing them on the dump. However, due to the chemical nature of the dusts, only small quantities of dust are possible to charge back to the furnace. The common practice has been to throw the collected dust near to the factory on the dump. Earlier the EAF dust was not processed further because that was considered uneconomical and unnecessary from the point of view of the law.

Nowadays, the steelmaking dust particles are classified as hazardous waste due to their chemical nature [14]. Because these dusts are containing toxic elements such as heavy metals that could dissolve to ground water it is necessary to treat them in order to eliminate the toxic compounds. This is why the dusts are not possible to be used straightly as landfill today [1].

As the environmental protection regulations have become more stringent, the disposal of the dust has become an expensive option [4]. On the other hand, dusts are containing valuable metals and they can be used as a source of raw materials in metal production. The pressure to reduce pollutants has increased more interest for further utilizing of dusts as sources of metals or as secondary raw material [27].

As alternative to landfill, various processes have been developed for treating these dusts. The target with these treating processes is to produce a residue that could be recycled further or safely disposed-off without affecting the environment. The most important stage is the separation of non-ferrous metals, such as zinc and lead, from iron in the dust.

The most harmful element in the carbon steelmaking dusts is zinc as it hinders the direct recycling of the dust back into the furnace. Still, it is also the most valuable element in the dust. The main purpose of treating carbon steelmaking dusts is to remove zinc so that iron-containing materials can be recycled and zinc recovered.

The recovery of zinc from the dust does not only save natural resources and eliminate environmental problems. Production of zinc from the secondary waste materials, such as steelmaking dusts, also consumes less energy. The energy savings can be about 30 % compared to manufacturing from primary sources. The process costs and profitability are extremely dependent on the zinc content of the waste and on the market price of zinc. [39]

3.1 Treating processes today

Both pyrometallurgical and hydrometallurgical processes or their combination have been used for dealing with the secondary materials, such as steelmaking dusts [4]. Numerous processes have been developed to treat this material but only a limited number of these have reached commercialization and the majority of them have been pyrometallurgical. Some of these processes have been commercialized for a period of time and then abandoned or have only reached the pilot scale [9]. There are some plants in commercial operation for processing EAF dusts in the USA, Sweden, Germany and Japan [27].

The pyro- and hydrometallurgical treatment processes for EAF dust developed today are represented in Figure 8. Both the commercial operation processes and the pilot plant operation processes are included. The processes at laboratory scale and under developing are not listed in Figure 8 [26]. In addition to pyro- and hydrometallurgical processes, the other options currently for treating these materials are stabilization or vitrification processes as well as other miscellaneous processes [6,9,14,38,40,41]. But in these options the valuable metals may not recovered and thus lost.

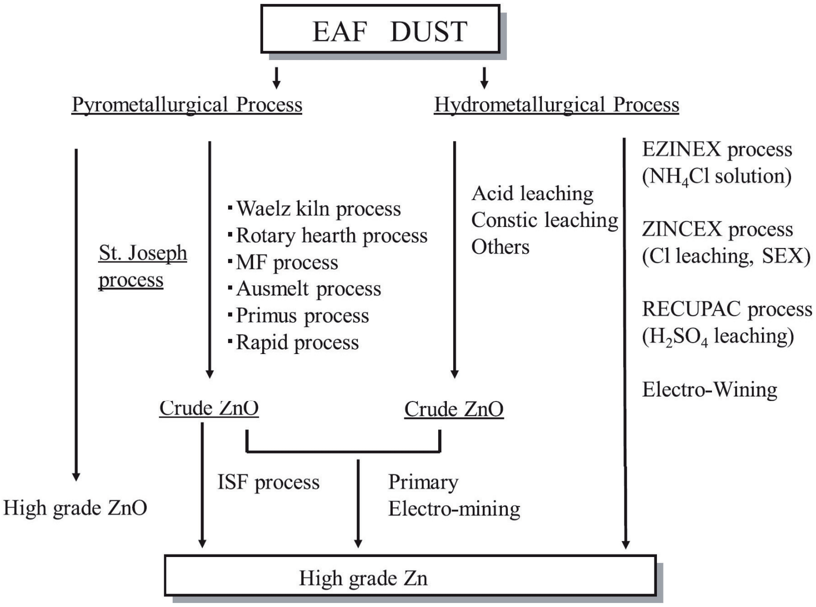


Figure 8. Pyro- and hydrometallurgical treatment processes or EAF dust [26].

3.1.1 Pyrometallurgical processes

Today the dust treating processes are predominately pyrometallurgical and they present over 99 % of the recycling capacity. Most of these are based on rotary kilns, plasma, and flame reactor processes [42]. Pyrometallurgical processes in dust treatment usually produce an upgraded zinc oxide. The ZnO in the EAF dust is enriched to around 90 % grade ZnO with these processes [29]. They perform well when a huge amount of EAF dust is treated at one time [29].

The Waelz kiln process is worldwide the most important and oldest method for treating the waste dust from steel mills. It has been shown to be possible to volatilize 95 % of Zn and Pb by Waelz kiln, when the dust contained 4.5 % Zn and 2 % Pb [43]. A schematic presentation of steel mill dust recycle via Waelz Kiln is shown in Figure 9.

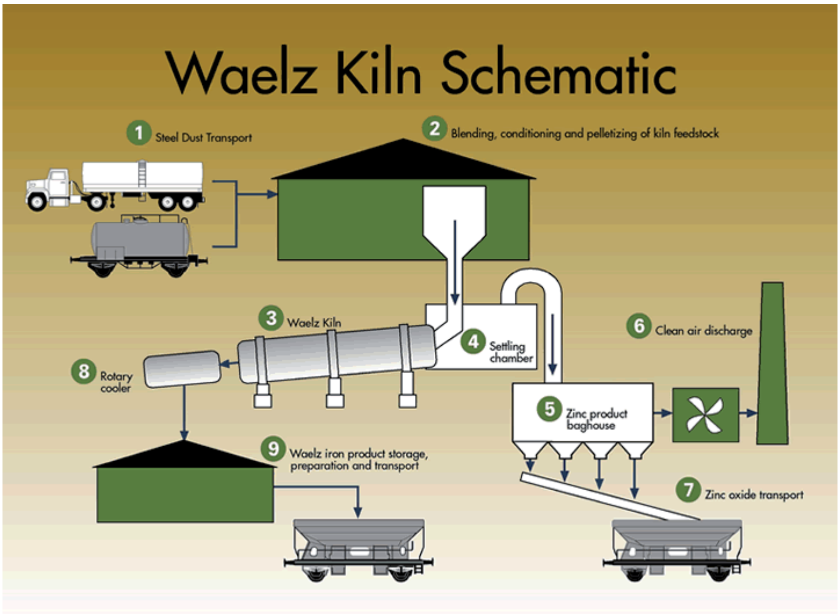


Figure 9. A schematic presentation of dust recycling route via Waelz Kiln [44].

There are, however, some drawbacks with pyrometallurgical processes that drive for developing and searching new options. Pyrometallurgical processes face problems such as high energy consumption and a need of a dust collection/gas cleaning system, and generation of worthless residues [4,45]. Also, the presence of chloride and fluoride salts cause severe corrosion problems and thus necessitates the use of expensive alloys as construction materials [4].

In addition, pyrometallurgical processes usually require a large feeding quantity in order to be economical and thus the treatment plant may have distant location from the steel factories. For example the Waelz kiln process requires a large quantity feed with high zinc content to be economical. Zinc content should be higher than about 15 – 20 % in the dust in order for the process to be economical and the plant must process at least 50 000 tons of feed per year [14,19].

A short-term solution could be to recycle the dust in order to increase the zinc content. Sometimes poor wastes (BOF dusts containing 2 to 5 % of zinc) are recirculated to the converter until they reach a zinc content up to 20 % [46]. But in this case the normal operation of the steelmaking furnace is disturbed.

Moreover, pyrometallurgical processes require some reducing agents and relatively high temperatures to produce raw zinc oxide of low commercial value [45]. Usually, they produce only crude ZnO and to supply metallic zinc later treatments are needed and at least one process step more is necessary. In addition, their separation capability is not always good. An insufficient zinc yield and numerous impurities in the final product with the pyrometallurgical processes are reasons why the search for an alternative process is still important [46].

3.1.2 Hydrometallurgical processes

The impetus for developing hydrometallurgical processes is that they can fit on smaller scale and an on-site process could be possible. Hydrometallurgical processes on a small scale are regarded as more environmentally suitable and economical for treating materials having relatively low zinc content. An on-site type process is desired to reduce treatment cost and cost of transportation of the dust [26]. These processes are more compact and easy to make a closed system [4,46]. They can also provide a good selectivity in metal separation and flexibility in end products [5-7].

In hydrometallurgical processes metals are extracted by a leaching stage and then recovered in metallic form by electrowinning or other reduction methods [27]. Hydrometallurgical route could offer an interesting alternative for zinc recycling if iron dissolution can be controlled [14,45]. Although many hydrometallurgical processes for EAF dust treatment have been proposed, most of them have not been commercialized [26].

More detailed description of hydrometallurgical processes is given in chapter 4, in which the focus is on alkaline leaching.

3.2 Choice of treatment

The choice between the processing routes depends strongly on the dust characteristic. Therefore a detailed characterization is important, including the particle size, the number of valuable elements and mineralogical phases. These characteristic may indicate the amount of leachable constituents [14].

Dusts containing many elements make metal extraction complex and difficult. In addition, each dust is unique, which makes finding a suitable treatment process even more complicated. The problem in the processing of dusts is the fact that their chemical and mineralogical composition varies widely even if the dust has been taken from the same process. Because of the wide range of composition within the dust it is necessary to make accurate and precise analysis of each individual case in order to optimize any recycling or recovery process. Thus, also flexibility for handling different source material is desired from the treating process [37].

Although many pyro- and hydrometallurgical processes have been developed, none of them have been entirely satisfying. The reason for failures could be that it is still more economical to extract zinc from the naturally occurring raw materials [5]. Also the secondary raw materials have much more complex structure than primary ones. Agglomeration and inclusion of small particles inside large matrix phases are typical for flue dusts. Besides the valuable metals, for example the EAF dust is also containing numerous other non-ferrous elements (sodium, potassium, chlorine, fluorine) that complicates any process which is developed to recover valuables metals [5].

A process can mature into a full-scale only if it is economically viable and if it can compete on a global scale with other processes. The criteria by which a process concept can be evaluated is represented in Figure 10, initially the technical feasibility must be proved. In case of dust treating processes, the economically viable process can be achieved if the operating costs for the process are less than the costs for dumping it. [47]

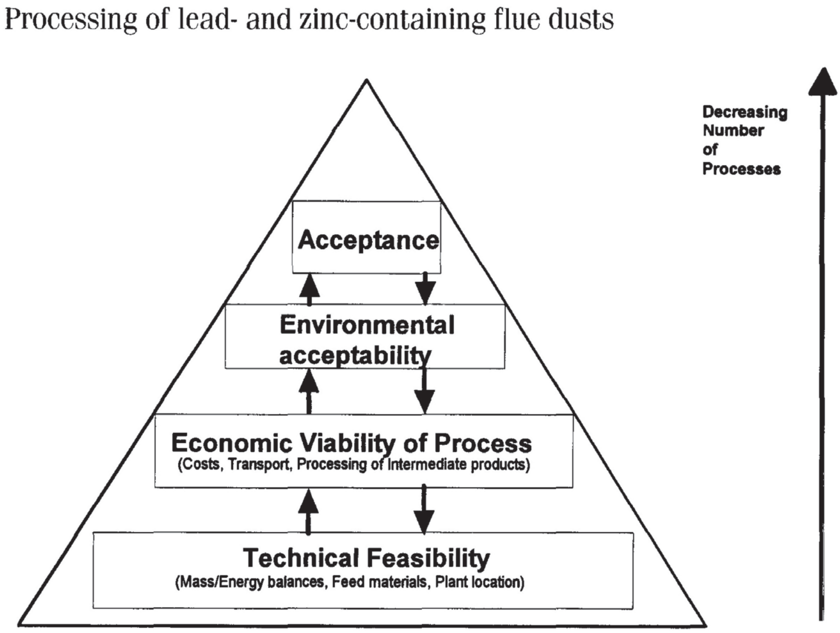


Figure 10. A process evaluating for the iron and steelmaking dust processing [47].

The mineralogical form of the zinc seems to be a basic indicator to the effectiveness of dealing the EAF dust. Zinc is present mainly as two compounds as oxide ZnO and ferrite $ZnFe_2O_4$. The zinc oxide and the ferrite behave in a different way, which causes difficulties in dust treating. The zinc oxide can be easily handled with both pyrometallugical and hydrometallurgical methods, but the zinc ferrite is extremely stable and significantly complex and difficult. The major obstruction in the hydrometallurgical extraction of zinc is the presence of zinc ferrite ($ZnFe_2O_4$) in the dust which is a highly stable compound [48].

Despite the benefits with hydrometallurgical processes there have been very few commercial processes because they are essentially dependent on the characteristic of EAF dust. If zinc in the dust occurs mainly as ZnO high recoveries are expected, but if zinc ferrite is the main component the recoveries remains low. [29]

The carbon steelmaking EAF dust contains in average 20 % of zinc and the amount of zinc in ferrite form is about 50 % of the total zinc [48]. When zinc particles are in contact with iron particles at high temperatures (800 – 1300 °C) in an oxidizing atmosphere, zinc ferrite formation will occur in the furnace and in the evacuation system [48]. Regarding zinc emission, the latter mechanism is particularly important at steelmaking temperatures in the 1600 °C range [48].

Because dust from iron and steelmaking consist of very fine particles the physical concentration techniques, such as gravity or magnetic separation, may not be suitable for treating this material and exhibits poor recoveries [14,38]. Furthermore, the fine size distribution suggests that the material will be difficult to handle dry, if no previous agglomeration is used [14]. On the other hand, the reaction kinetics involving these dusts should be fast, which suggest that leaching may be an attractive route to treat this material, if the zinc can be leached selectively [13,14]. Thus the hydrometallurgical processes offer some potential advantages, especially caustic leaching due to its selectivity to iron.

4. Hydrometallurgical processing of iron and steelmaking dusts

Hydrometallurgical processes are effective and flexible for treating the steelmaking dusts as they can control different levels of impurities. Dusts from steelmaking are containing impurities in different levels depending on the source. Depending on a character and composition of the secondary raw material, a suitable solution can be chosen to dissolve the desired metals leaving the gangue in the solid residue. The dissolved metal can be recovered with different methods as precipitation, crystallizing, extracting on selective solvent, ion exchange, electrolytic precipitation etc. [4]

Hydrometallurgical processes are considered to be suitable for such an on-site treatment [26] and they offer an interesting alternative for zinc recycling if iron dissolution can be controlled [14,45]. In the recovery of zinc the hydrometallurgical processes have been considered as more pro-environmental and economical for dealing of materials even with low zinc content on small scale [4].

The aim of hydrometallurgical treating of dusts is to recover the valuable elements contained in the dust and to obtain a non-hazardous residue that can be stored without problem or can be used in agglomeration units in iron-making industries. The leaching process should produce iron-bearing residue with maximum of 0.4 – 1 wt-% zinc in order to recycle it into steel plant furnace [4,17].

To reach this objective a sequence of unit operations, such as leaching, filtration, purification, extraction, stripping and electrolysis processes is required [16]. In the first step leaching is used to transfer zinc to the solution phase and selective solubility of zinc relative to iron compound in this step is very critical. Precipitation and cementation techniques can be carried out for the removal of the impurities from the leach liquor. The common stages in a hydrometallurgical process are shown in Figure 11.

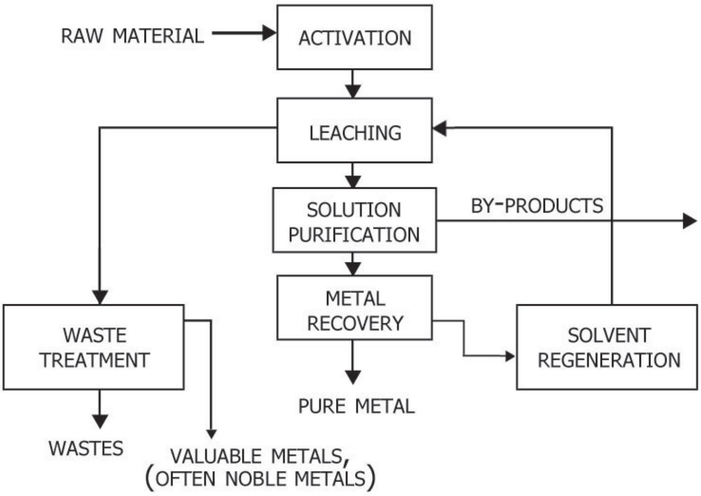


Figure 11. The common stages in a hydrometallurcal process.

4.1 Various leaching methods

Hydrometallurgical processes can be roughly divided into four groups in terms of leaching agent and electrochemistry, namely acidic or alkaline leaching and oxidative or reducing leaching. Type and concentration of the leaching agent is dependent on chemical composition of source material and mineral from which the metal has to be extracted [37]. Sulfuric acid, hydrochloric acid, ammonia, ammonium carbonate, ammonium chloride, sodium hydroxide, carboxyl acid etc. have been used for the dissolving of zinc [4]. Different processes have been developed with planning stage, pilot plant and commercial levels [4]. Table 6 shows an overview of different leaching processes with their typical features.

Table 6. Overview of several hydrometallurgical processes [49].

Leaching agent	Feature
sodium hydroxide leaching	leaching by NaOH cementation of ZnO electrolysis of Zn from solution selective reduction of rests leaching by dilute NaOH Zn recovery > 95 %
ammonium carbonate leaching	reduction roasting into Fe_3O_4 leaching by $(NH_4)_2CO_3$ cementation of ZnO calcination into ZnO alternative production of other Zn compounds Zn recovery 70 – 75 %
sulfuric acid leaching	neutral leaching (pH=3) oxidative acid leaching in autoclave simultaneous precipitation of hematite
acetic acid leaching	leaching by acetic acid ion exchange Zn recovery 70.5 % extraction of Pb,Cd,Cu,Ni,Mn,Ca,Mg,Na,K
chloride leaching	leaching by HCl (98 % extraction) pressure leaching and hematite precipitation solvent extraction and Zn electrolysis

Principally, the two most used leaching methods for treating carbon steel dusts are sulfuric acid (H_2SO_4) and caustic soda (NaOH) leaching. Both laboratory and pilot set-ups have been constructed with these leaching methods two in previous researches.

The major advantages with acidic solutions is that they are very familiar and cheap and also with sulfuric acid solutions the traditional electrowinning is applicable to obtain metallic zinc [26]. The other advantages of acid leaching are better kinetics and recycling of the solution, and as well less concentrated solutions. Also, generally, the recovery of zinc is enhanced in acidic leaching as compared to alkaline leaching.

However, there are problems with treating the iron if it is dissolved into leaching agent. The amount of zinc is often low compared to iron in dust and in acid leaching only a small share of zinc can dissolve without dissolving iron and other materials [7]. Furthermore, a large amount of acid will be consumed when other elements are dissolved in addition to zinc [7,38]. In addition, the high alkalinity of many dusts consume a lot of acid for pH adjustment [2,25].

The main problem with dissolved iron is that it makes the solution purification process very difficult and complex. The dissolved iron disturbs the removal of Cu, Cd and Co ions in the cementation process [50]. Even though iron removing processes have been developed and have been used in the industry for decades, none of them is completely satisfactory [50]. If high-quality zinc is wanted to produce, a considerable cleaning system will be required in acidic leaching and thus it will not seem economical [27]. In addition, the dissolved iron promotes the corrosion of anodes and increases the lead and iron content of the cathode in the zinc electrolysis [50].

Alkaline leaching has the advantage that iron does not dissolve. They can be used to separate non-ferrous metals, such zinc and lead, from iron-based materials. Thus, a relatively clean and iron-free leach solution can be achieved by alkaline leaching and the complicated iron removal process is avoided. Therefore NaOH leaching could be a promising leaching method and sodium hydroxide is one of the common bases used for leaching amphoteric hydroxides or oxides [51]. However, there are also disadvantages with alkalis such as more concentrated liquor is needed and the poor recycling of the liquor. Also the cost of leaching agent is higher than that of acids and some technical problems lie in recovering metallic zinc with the electrowinning process [26].

Many pilot plants have been built to test hydrometallurgical technologies. In Table 7 several processes used for treating iron and steelmaking dusts are compared. The status of the process is symbolized as once tested in laboratory (o), tested on pilot scale (ooo), and in use of technical scale (oooo). The zinc products received are divided into low grade (l) and refined (h) metals, for all the processes iron products are oxides (o). Also the environmental effects are indicated in respect of possible problematic water pollution (wp). [37]

Table 7. A comparison of different hydrometallurgical treatment processes for treating steelmaking dusts [37].

	Raw material	Status	Zn product	Fe product	Zn yield	Pre-treatment	Effect on environ.
Pressurised leaching	BFD	ooo	1	o	>95	no	
Chlorine leaching	BF/BOFD	ooo	1	o	90	no	
NH_4Cl-leaching	BF/BOFD	o	1	o	90	no	wp
NaOH-leaching	BF/BOFD	oooo	1	o	85	no	
NH_4Cl-Ezinex	EAFD	oooo	1	o		no	wp
Zincex	Pyrite	oooo	1	o	96	no	wp
UBC	EAFD	ooo	h	o	60	no	wp
Unimetal	EAFD	ooo	h	o	75	no	wp

However, in general, there still does not exist an effective and economically advantageous method for the treatment of these wastes. Many of built pilot plants had to stop production after only a few years because of various problems. The key problem with hydrometallurgical processes is to maximize the recovery of zinc at the same time when the dissolving of iron is minimized.

The presence of zinc ferrite in the iron and steelmaking dusts is the major problem with hydrometallurgical processing of these dusts. Zinc is occurring predominantly in two phases, zincite and zinc ferrite. From those zincite easy to dissolve in many solvents, both in acid and alkaline solutions but the zinc ferrite is very difficult to decompose by leaching [45]. The ferrites are very stable and insoluble and will usually dissolve only in very strong acids [50]. However, the strong acids will also leach the other metals as well from the dust.

In a view above, the zinc recoveries with hydrometallurgical processes depends on the form of zinc in the dust. If zinc in the dust occurs mainly as ZnO high recoveries are expected, but if zinc ferrite is the main component the recoveries remain low [29]. The content of zincite can vary from about 30 % to 70 % of the total amount of zinc in the dust [26].

4.2 Commercialized and pilot scale alkaline leaching processes

Despite that the steelmaking dusts often contain valuable metals in same or even higher concentrations than the ores, only few developed processes for dust treatment have reached commercialization. Many proposals have been done for hydrometallurgical processes [46] but still commercial processes are limited. Some alkaline leaching processes have been developed earlier and used for the leaching of zinc from the different oxidized ores and secondary materials. However, they have faced difficulties and have closed down.

In the 1960's the U.S Bureau of Mines investigated the recovery of zinc from the oxide ores using caustic soda (NaOH) as a leaching reagent [52]. The zinc oxide ore contained 21.2 wt-% zinc and zinc recovery of 85 % was obtained using 4 - 6 M NaOH solution [3]. The process has also been tested to secondary materials, such as EAF dust [30,53] and to galvanized steel scrap [54].

Amax Co. operated a pilot plant in the 1970's, which was based on caustic leaching and purification of alkaline solutions by removal of lead with zinc dust and followed by electrowinning. However, this development faced technical and economical problems and was eventually abandoned. Later in France was built up a similar plant, based on direct caustic leaching, but it has also been abandoned [7].

Frenay et al. [53] developed the Cebedeau process (Figure 12) for the recovering metals from EAF dust. In the process the dust was leached to dissolve zinc and lead in hot 95 °C concentrated 6 - 12 M NaOH solution for 1 - 2 hours. After leaching the solution purification, in order to remove lead, was done using cementation with zinc powder. From the purified solution zinc was produced, as a powder, by electrolysis as on semi-pilot plant scale and the process was economical if dust contained 20 % zinc [3,4]. In 1986 a commercial plant was built up in France but was discontinued within a short time. The Cebedeau process faced problems with the filtration for solid-liquid separation [4].

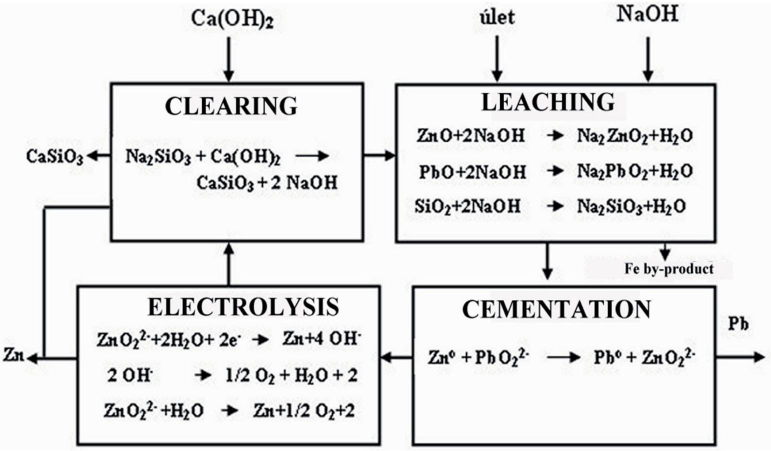


Figure 12. Principle of the Cebedeau-process [53].

Due to the filtration problems in Cebedeau process in Cardiff was used a high intensity magnetic field to settle the slurry after leaching when 80 % of zinc and 90 % of lead recoveries were obtained. The unrecovered zinc was mainly as zinc ferrite and the process was developed further. [4,55]

The Cardiff process was proposed of two-stage leaching (Figure 13) with an intermediate reducing roasting to decompose ferrites and to enhance lead extraction. By reducing roasting zinc can be recovered from ferrites, but if it is done before leaching lead oxides will reduce to metallic lead. The behavior of trace elements, including cadmium, during the leaching has not been reported. However, the iron rich residue is said to be suitable for disposal in a landfill. [4]

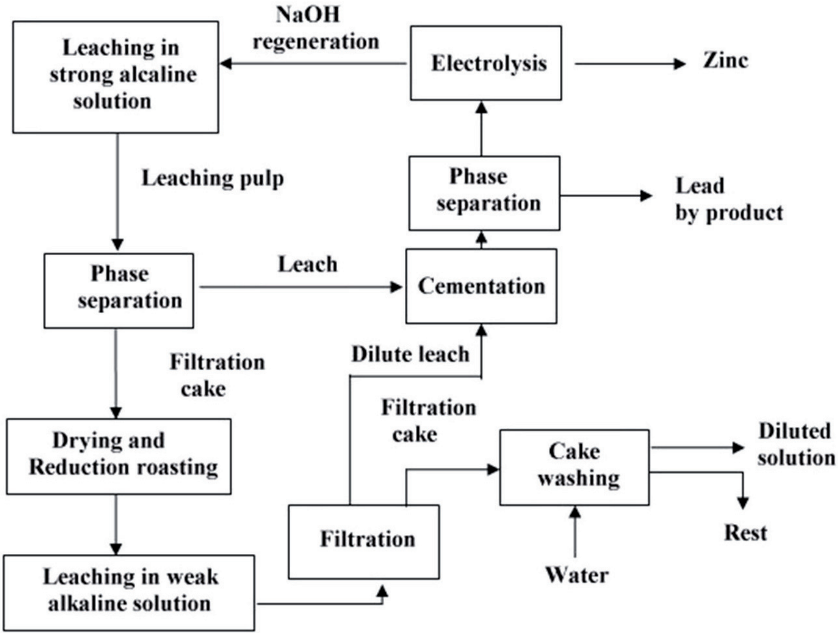


Figure 13. Cardiff process [49].

Also certain kind of direct alkaline leaching – electrowinning process for treating of EAF dusts has been developed in order to release zinc from zinc ferrites with strong alkaline solution. In the process the dust is first separated into two fractions using a magnetic separator. The magnetic part consisted primaly of the zinc ferrite and it was leached in 11 M NaOH solution for 4 hours at 95 °C. The non-magnetic part was thought to be ZnO and was leached with 6 M NaOH solution for 1.5 hours at 95 °C. [56,57]

In that direct alkaline leaching - electrowinning process around 80 to 85 % of the total amount of Zn and Pb were recovered from the dust when the dust contained 21.2% Zn, 21.8% Fe, 3.6% Pb and 2.5% Mn. However, in some earlier laboratory experiments in which the dust contained 24 % Zn and 33 % Fe only 50 % of zinc was recovered, and when the dust contained 16 % Zn and 39 % Fe only 32 % of zinc was recovered. Supposedly, higher iron content in EAF dust reflects higher zinc ferrite content because the zinc ferrite dissolves not in alkaline solution and lowers the zinc recovery. [56]

Despite that technical and economic problems have emerged, caustic soda leaching, could offer some potential advantages for treating the dusts. An important factor will be the costs imposed to landfill today. Reduction of these by using dust treatment can be decisive to process economics.

5. Alkaline leaching of zinc from steelmaking dusts

The alkaline leaching offers a method for separation of zinc and lead from the oxidized zinc ores and waste materials. The major advantage of sodium hydroxide leaching is the good selectivity between iron and zinc, because of the insolubility of iron compounds. Because very few other elements are leached the consumption of the leaching agent is low and a solution containing only zinc and lead as main elements is obtained [38]. Thus a relatively clean and iron-free leach solution can be achieved and the very complicated iron removal process is avoided. Zinc extraction from iron and steelmaking dust using alkaline leaching could be a promising method for dust treatment and sodium hydroxide is one of the common bases used for leaching amphoteric hydroxides or oxides [6].

The previous researching and processing of steelmaking dusts using the alkaline leaching have focused on zinc recovery by electrolysis. The hydrometallurgical principles of caustic soda leaching - electrowinning process are described in this chapter 5. The emphasis has been on the leaching stage as it is considered to be the most important stage in extracting zinc from the steelmaking dusts.

5.1 Caustic soda leaching – electrowinning process

Dusts from steelmaking can be treated by caustic soda leaching - electrowinning process in order to recover zinc as a marketable product such as zinc dust, powder or cast shapes. A simplified general process flow sheet of caustic soda leaching – electrowinning process is illustrated in Figure 14. The main stages in the process are: water leach, caustic leach, purification of the leachate by cementation, and electrolysis to deposit zinc while regenerating the caustic for re-use. [30]

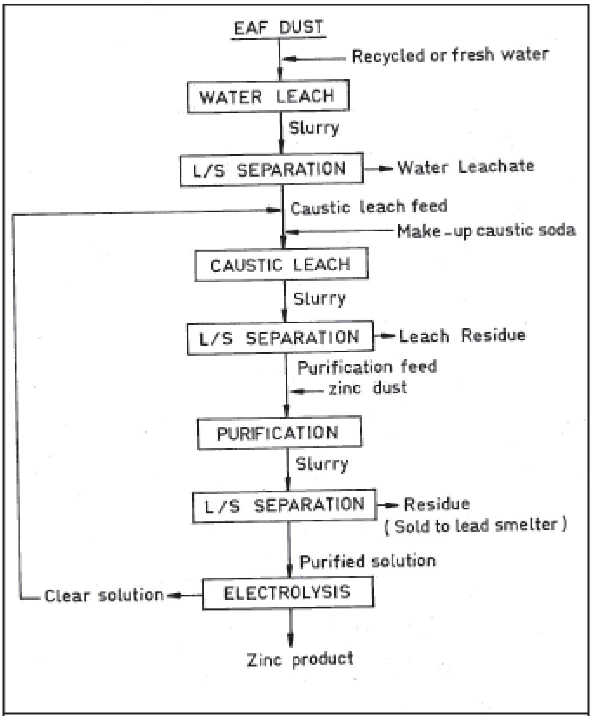


Figure 14. A principal flowsheet of caustic leach-electrolysis process [30].

5.1.1 Water leach

The water leach/wash stage has been seen necessary prior to NaOH leaching because there can be a substantial amount of NaCl and KCl salts in the dust [9]. Elements such as Na, K and Ca are also soluble in caustic soda and thus consuming the caustic. Also the presence of chlorides is detrimental to electrolysis and poses health risks due to formation of toxic chlorine gases [30,37]. After washing the dust, the water leachate is thickened and filtered, and it is recycled and eventually bled-off [30].

5.1.2 Caustic soda (NaOH) leaching

Leaching stage is applied to extract the desired metals from the dust. An aqueous solution containing a suitable leaching agent (NaOH) is used. The major advantage with alkaline leaching is its selectiveness in leaching zinc compared to iron compounds.

The selectivity of alkaline leaching in dissolving zinc compared to iron compounds is depicted in equilibrium diagrams (Figure 15 and Figure 16), which show that speciation and dissolution of iron hydroxide and zinc oxides are dependent on pH. These diagrams indicate that zinc can be dissolved in either acidic or alkaline media, whereas iron is more readily soluble in acidic media [14].

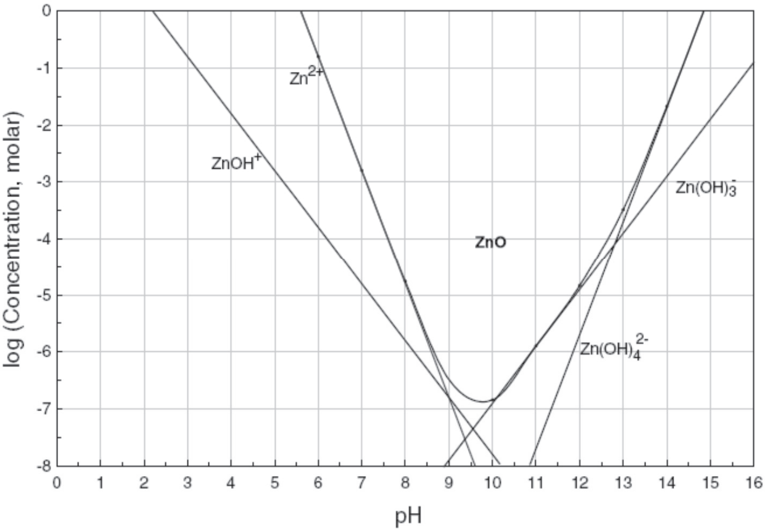
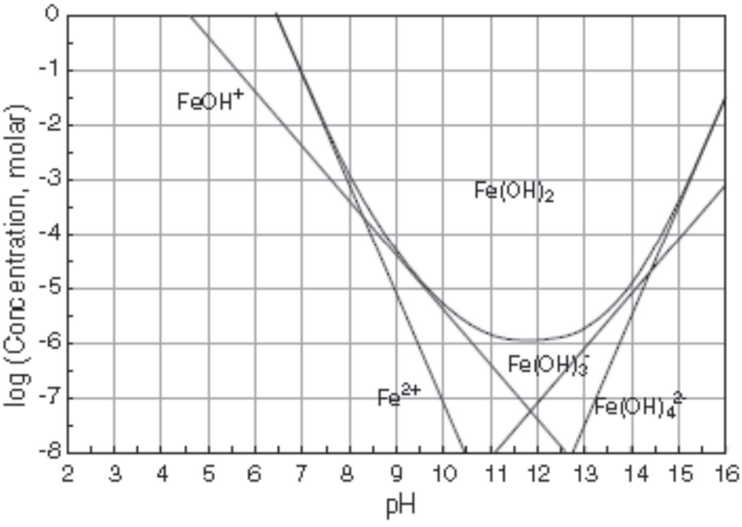
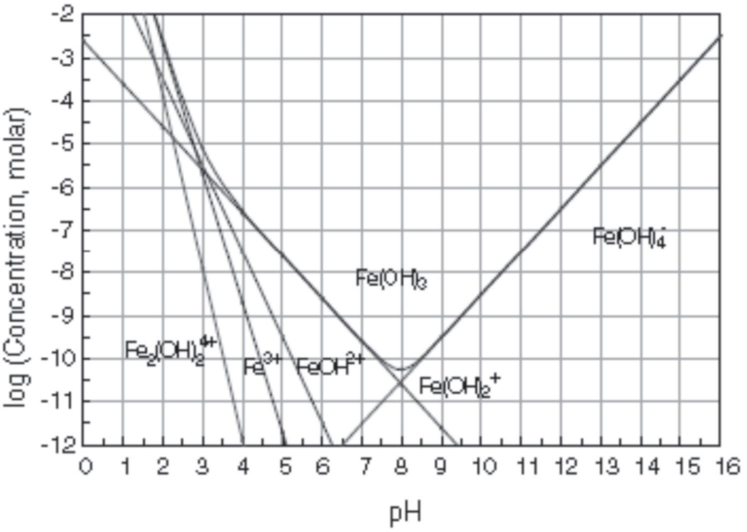


Figure 15. Solubility of ZnO as a function of pH, at 25 °C [14].



a)



b)

Figure 16. Solubility of ferrous (a) and ferric (b) hydroxides as a function of pH, at 25 °C [14].

Alkaline leaching, using sodium hydroxide as a leaching agent is seen effective in the dissolution of heavy metals, without significant dissolution of iron [14]. Oxides of Zn, Pb and Al can be dissolved effectively in strong NaOH solution and in limited cases Cr and Cu can be dissolved. Thus, the consumption of leaching agent decreases and a solution containing Zn and Pb as predominant elements will be obtained. Considering these, it would be appropriate to use the alkaline processes to leach zinc and lead selectively from the dusts [7].

The earlier experiments have shown that the solubility of the certain amphoteric elements in strong alkaline solution decreases in the following sequence Zn > Pb > Al > Cr(III) > Cu [7]. The solubility of Cr(III), Cu and Cd are found to be negligible in the presence of zinc and lead. Also the solubility of lead is decreased if the zinc content in caustic solution is relatively high. Fe, Cd, Ca and Mg have found to remain in the leaching residue [7].

Zinc and lead oxides dissolve easily in alkalis. The main dissolution reactions (1) and (2) in caustic soda leach can be expressed as follows [4,30]:

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \tag{1}$$

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O \tag{2}$$

The other form of zinc, which is present in the dust, is zinc ferrite ($ZnFe_2O_4$). Zinc ferrite is a very stable compound and only partial amount will dissolve in alkalis.

If dust contains aluminum hydroxide or silica they are dissolved in alkaline solutions in similar fashion, reaction (3) and (4) [37]. However, aluminum and silica have found to dissolve relatively little from EAF dust [56].

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{3}$$

$$Al(OH)_3 + NaOH \rightarrow Al(OH)_4^- + Na^+ \tag{4}$$

After NaOH leaching the solids are separated from the leachate. A residue enriched in iron and depleted in zinc and lead is obtained and it may be suitable for recycling or more suitable for disposal than the original material. [30]

5.1.3 Solution purification

After leaching solids are separated and a purification process is conducted to remove other dissolved heavy metals such as lead, cadmium and copper from the leachate. These metals can cause operational difficulties when zinc is electrowon and thus should be removed before that. In hydrometallurgical processes the solution purification can be done using crystallization, cementation, solvent extraction or ion exchange *etc*. [4]

Lead, cadmium and copper can be removed from the leach solution by cementation with zinc powder [4] and lead containing purification residue may be a suitable feed to a lead smelter [30]. Cementation is suitable to remove metals that are more noble than zinc from the solution, reaction (5) [4].

$$Me^{2+} + Zn^0 \rightarrow Me^0 + Zn^{2+} \quad (5)$$

Me = Cu, Pb, Cd, Ni, Co

Solution purification studies for leachate after EAF dust leaching with NaOH solution showed that amount of zinc powder required for remove Pb, Cu and Cd was stoichiometrically four times greater. The Zn, Pb, Cu and Cd concentrations of caustic leachate before and after purification are shown in Table 8. After cementation using zinc powder, the cement obtained was seen a suitable raw material for further recycling of Pb and Cd. The cement contained 75.4% Pb, 5.8% Zn, 1.6% Cu, 0.12% Fe and 0.21% Cd. [27]

Table 8. Concentrations of certain elements before and after cementation of caustic leachate [27].

Metal	Before	After
Zn (g/l)	18.00	22.00
Pb (g/l)	3.20	0.21
Cu (mg/l)	0.70	0.20
Cd (mg/l)	22.00	1.00

The other method for solution purification would be precipitating lead using sodium sulphide. According to Youcai and Stanforth [7] the cementation with zinc powder leads only to partial removal of lead (20%) in alkaline solution. They have investigated solution purification using sodium sulphide as precipitant for selectively removing of lead and almost 100% removal of lead was achieved. The concentrations of other elements (Fe, Ca, Cu, Cd, Mn) in leach solutions were all less than 0.5 g/l and it could be reduced further to less than 0.1 g/l after sodium sulphide was added.

Sodium sulphide was not able to remove aluminium together with lead from the leach solution. However, aluminium is not considered as a harmful element in the subsequent treatment of leach solutions (purification and electrolysis), but if it is not removed before electrowinning, it may accumulate when the leach solutions are recycled after zinc electrowinning. [7]

5.1.4 Electrowinning zinc from leach solution

After solution purification zinc can be recovered as solid zinc by electrolysis or precipitated as its pure compound. Electrowinning is the most important method in producing zinc and around 80% of produced zinc in the world is obtained by this technology [7]. This technology usually uses acidic sulfate solution but a sponge-like, particulate zinc deposit can be produced in caustic soda solution [30]. The quality of zinc powder from alkaline solution is much more stable than that from acidic solution [7].

The reactions during the electrolysis at anode (6) and cathode (7) are given as follows:

Anode reaction: $2OH^- \rightarrow H_2O + ½O_2 + 2e^-$ (6)

Cathode reaction: $Zn(OH)_4^{2-} + 2e^- \rightarrow Zn_s + 2OH^- + H_2O$ (7)

According the total reaction (8) zinc can be precipitated from caustic soda solution by applying an electric potential of 1.6V [37].

Total reaction: $NaZnO_2 + H_2O \rightarrow Zn + 2NaOH + ½O_2$ (8)

Zinc recovery by electrowinning provides an opportunity to produce a premium product without the costs for melting, casting and atomizing [30].

5.2 Effect of leaching parameters

The most important parameters controlling the efficiency of the leaching process are oxidation potential, concentration of leaching agent, temperature, and pH [37]. Also other factors, such as particle size, agitation and pulp density, are affecting the efficiency of leaching process as having influence on leaching rate. If an insoluble reaction product is formed on the particles during leaching, the dissolution rate depends on the nature of this product [51]. The mineralogical phases indicate the amount the leachability and the mineralogical form of the zinc seems to be a basic indicator to the effectiveness of dealing the EAF dust.

5.2.1 NaOH concentration

The concentration of leaching agent should set up to optimum level in order to maximize the selectivity [51]. Generally the increase of NaOH concentration increases dissolution of zinc from the dust. However, with higher than 5 M concentrations, further increase has only little effect on the leaching (Figure 17). Thus, a concentration of 5 M NaOH should be sufficient for optimum extraction of zinc and lead from dust. In leaching zinc to reach maximum leaching and extraction for sufficient phase weight ratio of NaOH/dust was considered the ratio of 3 [7]. In several experiments using NaOH concentrations around 6 M gave zinc recoveries above 65 %, but to reach recoveries of this level also increased temperature is needed [14,27,46].

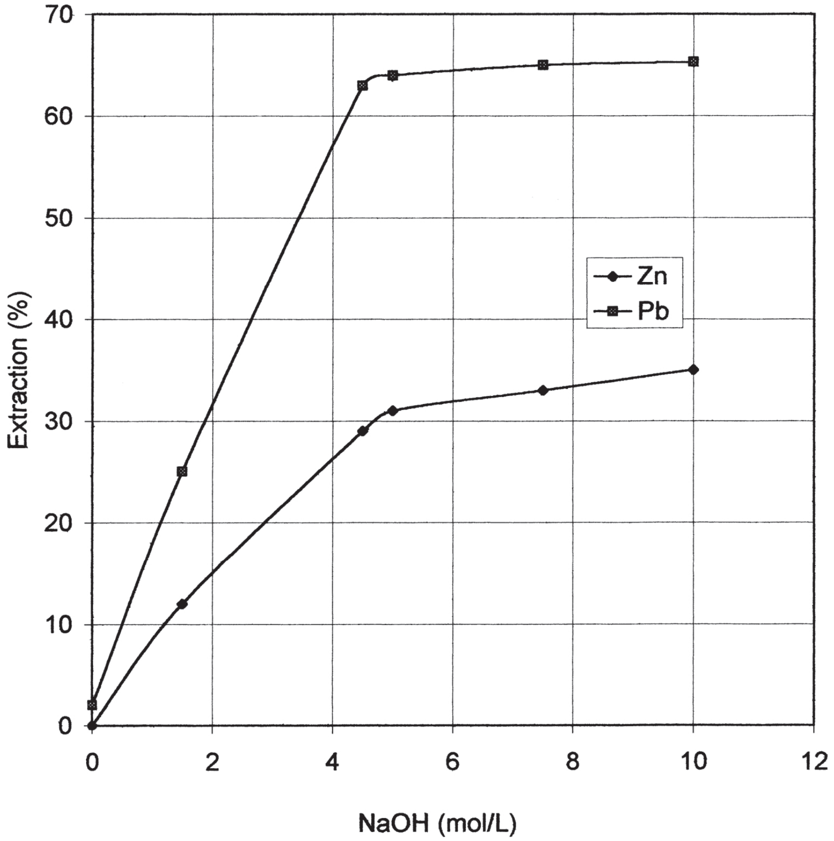


Figure 17. Effect of NaOH concentration on the extraction of Zn and Pb from steelmaking dust (25 °C, L/S 3.6, leaching time 42h) [7].

Additionally, it must be taken into consideration that the viscosity of NaOH solutions changes when concentration of NaOH increases and changes in viscosity has consequences for the diffusion rate of ions [7]. The viscosity as function of temperature and concentration of NaOH can be determined from Table 9 [58]. At temperature of 70 °C the zinc extraction was seen to increase with increased NaOH concentration up to 10 M, but to drop at 12 M, due to increased viscosity [3]. At 60 °C the dissolution of zinc was seen to decrease already in concentrations over 2.5 M NaOH [35]. There seems to be a tendency that zinc dissolution decreases with increasing solution viscosity, but no generally valid threshold value has been found.

Table 9. Viscosity of aqueous solutions of NaOH, mPa.s [58].

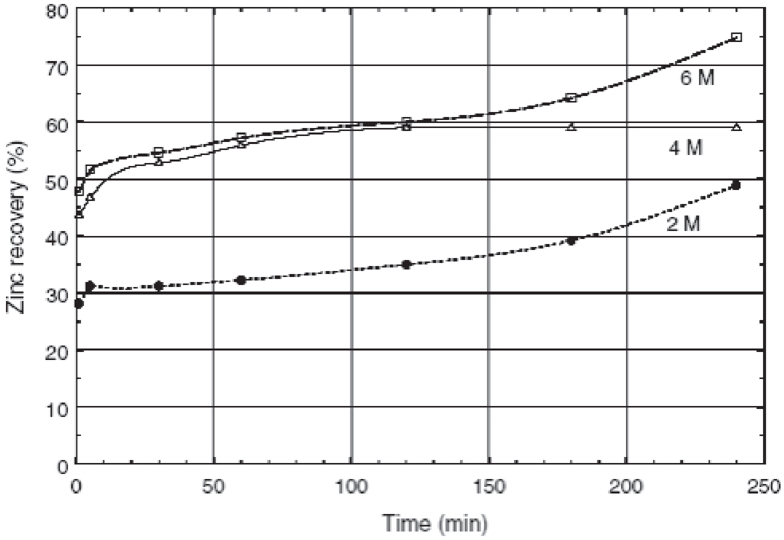
Viscosity of Aqueous Solutions of NaOH, mPa.s

Concentration kg NaOH/ kg	Temperature, °C								
	20	30	40	50	60	70	80	90	100
0,00	0,97	0,78	0,64	0,54	0,46	0,4	0,35	0,315	0,28
0,05	1,31	1,03	0,83	0,69	0,58	0,5	0,43	0,375	0,33
0,10	1,86	1,43	1,14	0,93	0,78	0,66	0,55	0,47	0,4
0,15	2,78	2,07	1,62	1,31	1,08	0,9	0,73	0,62	0,51
0,20	4,43	3,17	2,43	1,93	1,57	1,26	1,03	0,84	0,68
0,25	7,45	5,15	3,76	2,87	2,26	1,8	1,44	1,16	0,94
0,30	12,6	8,43	5,99	4,38	3,28	2,55	2,02	1,62	1,28
0,35	21,6	13,4	9,23	6,41	4,71	3,57	2,79	2,2	1,75
0,40	38,1	21,8	13,5	9	6,36	4,76	3,69	2,89	2,29
0,45	68	32,8	18,9	12,1	8,37	6,13	4,62	3,63	2,85
0,50	120	47,7	25,5	15,8	10,4	7,6	5,6	4,36	3,41

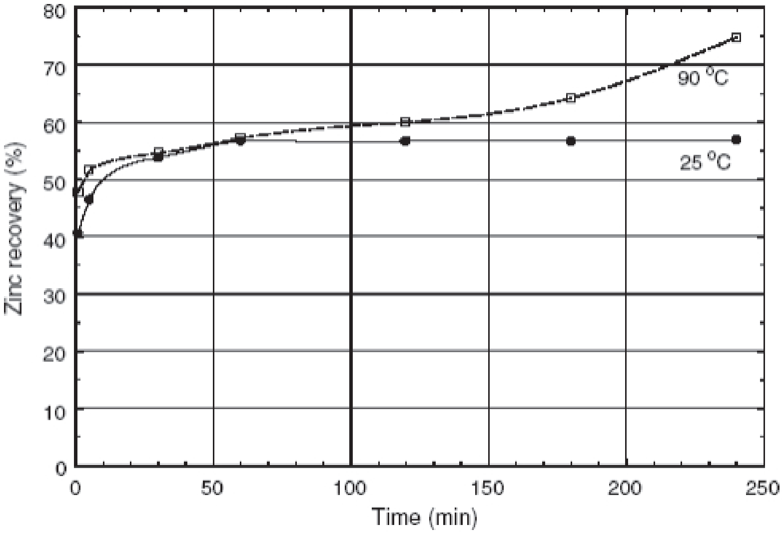
5.2.2 Temperature

In caustic soda leaching of EAF dust the solubility of zinc has seen to increase with elevated temperatures [3,27,35]. With concentrations (1 – 4 M) temperature has had a significant impact to the leaching time. At 32 °C leaching was found to be complete in 120 minutes, at 95 °C in 30 minutes [35]. The effect of temperature on leaching rate is less significant for processes that are diffusion controlled [51].

Generally, the dissolution of zinc is discovered to be very fast, tending to maximum constant value. The value is however seen to be dependent on concentration and temperature at longer leaching times (Figure 18). The additional extraction obtained after 2 hours is most likely due to dissolution of some entrapped zinc or the destruction of zinc ferrites [14]. Nevertheless, in 10 minutes more than 50 % of zinc can be dissolved and 30 – 90 minutes leaching times are reported to be reasonable for higher temperatures [3,14,27,35].



a)



b)

Figure 18. a) Influence of NaOH concentration on zinc recovery at long leaching times (90 °C). **b)** Influence of temperature on recovery of zinc at long leaching times (6 M NaOH). [14]

5.2.3 Particle size and pulp density

Small particle size and low pulp density (small volume of solids) will favor faster leaching kinetics. As the individual particles in the dust are mostly less than 10 µm, the reaction kinetics involving this kind of dust should be fast. The dissolution of soluble forms of zinc is reported to be very fast in caustic soda leaching and leaching times even 30 minutes could be sufficient. [3,9]

Commonly, the lower the solid to liquid ration is, the higher are the recovery percentage. However, the solid content have seen to have more effect on leaching time than on the maximum possible zinc extraction that can be obtained if sufficiently strong NaOH solutions is used (Figure 19) [35]. It has been also reported that no remarkable increase of zinc dissolution have been observed for the S/L ratios above 1/7, when leaching in 10 M NaOH solution for 2 h [3]. On the other hand, Mordogan et al. [27] got the best zinc yield with solid content of 10 %, when using 6.5 M NaOH solution (20 °C, 600 rpm). The solid contents above 20 % have been reported to deteriorate the recovery of zinc probably due the flocculation of fine dust particles [27,35].

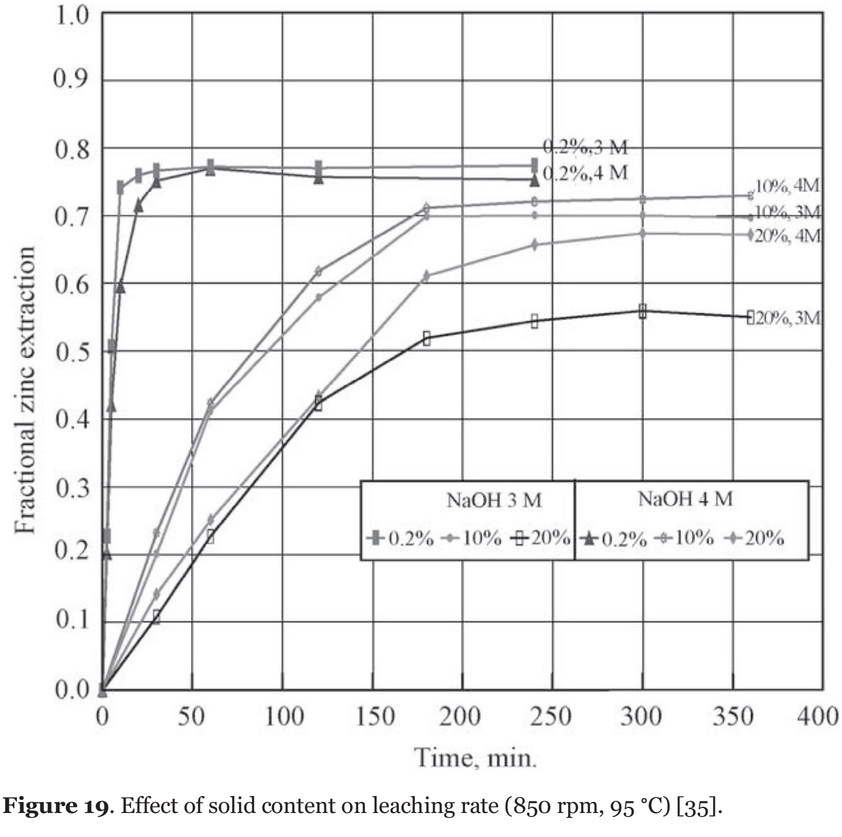


Figure 19. Effect of solid content on leaching rate (850 rpm, 95 °C) [35].

5.2.4 Agitation

Increasing speed of agitation will promote leaching rate if the leaching process is diffusion controlled [51]. Increasing agitation has been seen to increase solubility as it prevents flocculation. This indicates a relation between solid content and stirring rate. Also when using more viscous solutions (6.5 M NaOH, 40 °C, 10 wt-% solid) the increased stirring rate (from 400 to 900 rpm) increased the solubility of zinc [27]. With weaker NaOH solutions (1.5 M NaOH, 60 °C, 0.2 wt-% solid) it was found that changing stirring rate between 500 – 850 rpm stirring did not have effect on reaction rate [35].

5.2.5 Optimal leaching conditions

In Table 10 is collected the achieved zinc recoveries in caustic soda leaching from literature. Optimal conditions can be derived as 6 – 10 M NaOH, L/S ratio of around 10, and temperature of 80 – 95 °C. When using these high concentrations and temperatures, the dissolution of zinc is fast and zinc recoveries of 80 - 85 % can be reached. Still there is a part of zinc in the dust that has not dissolved and recovered. The total recoveries of zinc are seen to be limited in alkaline solutions due to the presence of zinc ferrite. The higher is the content of zinc ferrite in the dust the lower zinc recoveries remain. [3,7,14,27,35,46]

Table 10. Conditions and recovery levels of previous caustic leach experiments for EAF dusts.

Reference	(NaOH) [M]	Temp. [°C]	L/S ratio	Leaching Time [min]	Stirring [rpm]	Recovery [%]	Zn in dust [%]
[14]	6	90	10	240	-	74	12.2
[27]	> 6.5	80	10	30	900	80 - 85	23
[7]	5	25	3	2520	-	36	24.8
[3]	10	95	7	120	600	85	33
[46]	6	80	-	10 - 20	-	65	18.54
[35]	4	95	500	240	850	75	13.6

5.3 Dissolution potential of zinc

Still, the total recoveries of zinc are limited in hydrometallurgical methods, such as in alkaline solutions, due to the presence of zinc ferrite. The presence of zinc ferrites seems to be the most important factor limiting the zinc recoveries. If the content of zinc ferrite in the dust has been high, the zinc recoveries have remained low.

Xia and Pickles [50] have leached synthetic zinc ferrite and the experiments indicated that the maximum percentage of decomposed zinc ferrite has been only about 9 % at the optimum conditions. The percentage of decomposed zinc ferrite increased with increasing temperature, caustic concentrations and leaching time, however, it is limited by high viscosity of concentrated solutions.

Zinc ferrites are insoluble into most acid and alkaline solutions. One leaching method for breaking the ferrite is dissolving it in hot and strong sulfuric acid. In order to obtain zinc recovery more than 85 % by acidic leaching, hot (about 100 °C) and strong leaching process is required and in that case iron also will dissolve considerably. As mentioned before, this consumes large quantities of acid, and iron and other non-wanted metals must be removed with solution purification treatment, which will become complex and expensive. [56]

However, these ferrites must be broken before the zinc can be collected and the breaking of the zinc ferrite is a key to the recovery of zinc from these solid dust materials [56]. When zinc is present mainly as oxide, the material can be treated directly, but when a substantial amount is combined as ferrite, a more severe alkaline leaching conditions (e.g. high temperature - high pressure leaching) or a reduction step may be desirable to maximize zinc recovery [30].

5.4 Methods to enhance leaching

Methods that are used to enhance leaching are for example pressure leaching, dust pre-treatment in a microwave oven, and leaching with ultrasonic agitation. High pressure leaching is sometimes chosen where the cost is justified by the economic value of the product. [9,14,51]

5.4.1 High temperature and pressure leaching

One method that can enhance leaching is to use high temperature and high pressure (HT-HP) conditions. The HT-HP leaching is expensive and less studied for leaching of iron and steelmaking dusts both in acid and alkaline solutions. Dutra et al. [14] have studied alkaline leaching (in 6 M NaOH solution) of zinc from EAF dust in an autoclave using temperatures of 120, 150 and 200 °C, rendering pressures of 2.0, 5.8, and 15.8 atm, respectively. The total leaching time was 4 hours and the results showed that the highest recovery of zinc (around 53 %) occurred after 30 - 60 minutes. Temperature did not affect dissolution significantly. Also a drop of about 10 % was observed at temperature of 120 °C with longer leaching times. The possible explanation for this behaviour could be that some of the dissolved zinc precipitated as zinc ferrite. For a comparison, at Dutra's study the zinc recovery of 74 % was achieved under conventional conditions of 6 M NaOH and 90 °C after 4h leaching.

5.4.2 Microwave assisted leaching

A method reported aiming to enhance leaching is to use microwave assisted leaching. The potential advantages with microwaves include among others the following [9]:

1) Rapid and selective heating of materials
2) Reactions can be catalyzed since the heating occurs on a molecular or atomic level
3) The energy source is clean and controllable
4) The gas volume is reduced and the atmosphere can be controlled as there no gaseous combustion products
5) The material is heated internally in comparison to external heating with conventional methods
6) The temperature of the container can be minimized

In microwave leaching the liquid can reach higher temperatures before boiling occurs because the vessel wall is cooler than the bulk. In the conventional boiling process many of the bubbles nucleate preferentially at sites on the vessel surface, which is usually hotter than the bulk. However, in Xia's and Pickles' study the EAF dust particles were found to promote boiling in the NaOH solution and the boiling of the solution was observed extremely violent. [9]

Materials such as metallic oxides absorb the radiation in microwave frequencies and this allows the fast heating of such materials under microwaves. The fast heating of dust can induce nucleation and propagation of cracks in the particles and making them more amenable to leaching [14]. According to Xia and Pickles [9] the EAF dust particles showed to exhibit good coupling with microwaves and this was attributed to the presence of zinc ferrite, zincite and magnetite in the dust. The solid particles and thus the interfacial temperatures could get higher than those observed in conventional leaching.

Xia and Pickles [9] leached EAF dust under microwave irradiation using 6 M and 8 M NaOH solutions with solid to liquid ratio of 180 g/l. The recoveries of zinc were 5 – 10 % higher than the maximum observed under conventional conditions/heating. The conventional conditions used as reference was: 10 M NaOH, 70 g/l solids, 93 °C and 180 minutes, and the zinc recovery reached the maximum of about 72 %. The maximum recovery that reached under microwave irradiation was 80 %. The higher recoveries with microwave leaching may indicate that some zinc ferrite has been dissolved. Using microwave had effect also on dissolution of lead. The recoveries of lead were lower than in conventional leaching and more zinc was leached than lead. This may be attributed to the different behavior of zinc and lead compounds under microwave irradiation.

Microwaves have influence on leaching rate and the effect of power level was significant. When using microwaves the leaching was very fast and reached a plateau within few minutes, while it took several hours for conventional leaching process to achieve the same recovery. The higher power levels resulted in more rapid zinc dissolution and more zinc was dissolved. At the higher power levels the irradiation time was longer in a given time period and increased temperature particularly during the initial leaching period. [9]

Dutra et al. [14] studied microwave radiation as a treatment stage prior to conventional caustic leaching. The samples were transferred immediately after heating to the leaching reactor. The leaching studies were done using NaOH solution of 6 M and temperature of 90 °C. The microwave heating prior to the caustic leaching did not improve zinc recovery in their study. One explanation to this may be that the heating time was long enough to cause an incipient sintering of the phases, which had low melting point but not sufficiently long to induce the formation of cracks in the particles.

5.4.3 Ultrasound assisted leaching

The ultra-sonic probe has been expected to improve the dispersion of fine and agglomerated particles and thus enhance zinc recovery. The effect of ultrasound is attributed to a combination of improved pore penetration capacity of the leaching agent, boundary and product layer breakdown, and localized temperature increases. Dutra et al. used ultrasonic agitation in caustic leaching of EAF dust and observed that no improvements in zinc recovery were achieved. The leaching was done at 55 °C and 6 M NaOH solutions with duration of 60 min. [14]

6. Combined processes based on alkaline leaching

Zinc ferrites can be very difficult to chemically decompose so that zinc can be recovered [56]. Hydrometallurgical processes are not able to dissolve zinc ferrite effectively. Even though the advantage of insolubility of iron oxides in caustic environment, the zinc ferrites remain also in the residue. Presence of zinc ferrites in the residue after conventional leaching indicates a need for some treatment prior to leaching (or more severe leaching conditions) [5].

Pyrometallurgical processes, such as roasting, can be used to break down the zinc ferrites. The aim of hybrid processes is to decompose zinc ferrites by pyrometallurgical process and then recover the non-ferrous metals by hydrometallurgical techniques. [5]

Some researchers have showed that by treating the dust prior to alkaline leaching higher zinc recoveries can be achieved. Converting zinc ferrites into soluble zinc oxides can increase the recovery of zinc. This can be done for example by roasting the dust under reducing conditions. By special methods e.g. by roasting with caustic soda or sodium carbonate (Na_2CO_3) zinc ferrites can be decomposed and leaching of zinc could be improved [7]. Both NaOH and Na_2CO_3 become liquids at temperatures used during roasting [37].

6.1 Roasting with caustic soda

The most promising method of the combined treatments of roasting and leaching is to convert ferrite into a soluble sodium zincate form, typically $Na_2Zn(OH)_4$, in a low temperature caustic roasting followed by caustic soda leaching. This roasted product can be dissolved together with the zincite from the dust.

6.1.1 Experiments on synthetic zinc ferrite

Youcai and Stanforth [56] have investigated the recovery of zinc from synthetic zinc ferrite by using caustic roasting and hydrolysis prior to leaching with caustic soda. The experiments showed that fusing synthetic zinc ferrite with NaOH pellets at 318 – 450 °C for 1 h the extraction reached to 70 – 82 %. With hydrolysis (water and sample are mixed and then dried) before fusing the extraction of zinc can be improved even more. The extractions increased over 90 % when the zinc ferrite was hydrolyzed with water or dilute NaOH solution prior to the fusion step.

The ferrite structure is very stable and thus the chemical extraction of zinc from it is quite difficult. When roasting the synthetic ferrite with sodium hydroxide, very little zinc was extracted at temperatures below the melting point of sodium hydroxide. The NaOH/ferrite ratio of around 1.5 was needed to reach 75 % extraction and higher NaOH/ferrite ratios did not increase the extraction significantly. Also roasting time affected on extraction of zinc and it increased during the first hour and after that was constant. [56]

Xia and Pickles [5] have also studied caustic roasting of synthetic zinc ferrite (350 – 450 °C, 30 – 60 min, with moisture of 0 – 3 wt%). Their results showed that the majority of zinc ferrite is decomposed during the roasting process and is converted into soluble sodium zincate and relatively insoluble hematite. The roast product was leached with 4 M NaOH solution for 90 min at 90 °C. Both the iron and zinc contents of the residue decreased with the increasing roasting temperature and sodium hydroxide addition. The lowest zinc content of the residue was 1.5 % [5]. For a comparison, experiments for direct caustic soda leaching of synthetic ferrite showed that only 9 % of zinc ferrites was decomposed in the optimum leaching conditions (8 – 10 M NaOH, 60 – 93 °C, 120 – 180 min) [5].

6.1.2 Experiments on EAF dust

Using caustic roasting step is also previously proven for EAF dust and the trend of using hydrolysis prior to roasting was same for both synthetic ferrite and EAF dust. The leaching of zinc has been found to increase greatly when the dust was contacted with water or dilute alkaline solution before fusing with caustic soda. EAF dust samples (25% Zn, 1.8% Pb, 33% Fe) were leached directly in caustic soda solution and using pre-treatments, such as caustic roasting or caustic roasting combined with hydrolysis. In direct leaching the amount of extracted zinc was around 38 % and was enhanced to 80 % when dust was roasted before leaching. The hydrolysis before caustic roasting increased the leaching of zinc even further to 95 %. Fusing was done at 350 °C for 1 hour. Longer fusing time improved the extraction only slightly. The chemical reactions in the fusion (9, 10) and leaching (11) processes can be summarized as follows. [7]

Fusion:

$$Zn(FeO_2)_2\ (s) + 8NaOH\ (s) = Na_2ZnO_2 + 2Na_2FeO_3\ (s) + 4H_2O \quad (9)$$

$$ZnO\ (s) + 2NaOH\ (s) = Na_2ZnO_2\ (s) + H_2O \quad (10)$$

Leaching of fused products:

$$\begin{aligned} &Na_2ZnO_2(s) + 2Na_3FeO_3 + 5H_2O \\ &\qquad = Na_2Zn(OH)_4(aq.) + 2Fe(OH)_3(s) + 6NaO \end{aligned} \quad (11)$$

After two sequential leaching steps, 94 % of the zinc can be extracted from the fused dust and about 1 % of zinc remained in the leaching residue. However, long leaching time (24h) is needed after fusing to reach the maximum extraction of the fused product when the leaching is done at ambient temperature in 5 M NaOH solution. [7]

Xia and Pickles [5] investigated caustic roasting and leaching for EAF dust when adding water 3 wt-% in part of the roasting experiments. Time for roasting was 30 – 60 min at temperatures of 350 – 450 °C. For a roasted mixture leaching was done for 90 min at 90 °C in a 4 M NaOH solution. The majority of zinc was recovered and residue contained, on average, 2.0% zinc and 19.9% iron. When the moisture was added the zinc recoveries were slightly higher and the iron recoveries were slightly lower. The higher zinc recoveries are likely due to improved contact of the reagents. The zinc recoveries were over 95 % and for iron less than 1 % when moisture was added. The major phases in the roast product were zincite, hematite and sodium zincate with some unreacted zinc ferrite.

Xia and Pickles [5] found that the effect of sodium hydroxide to zinc ferrite ratio was more pronounced for shorter roasting time and the lower roasting temperature. A weight ratio of dust to solid NaOH with higher than 1.27 does not seem unreasonable for practical application [7].

The flow sheet of a hybrid low temperature roasting process followed by dilute caustic leaching for the treatment of EAF dust is shown in Figure 20. In the process the EAF dust is first initially mixed with a fine solid caustic soda and introduced into the roasting process. After the roasting, the roast product can be easily leached with a dilute caustic solution. The majority of iron remains as hematite in the residue and could be recycled back to either the iron- or steelmaking operation. The non-ferrous metals could be recovered from the leach liquor by conventional hydrometallurgical and/or electrometallurgical techniques. [5]

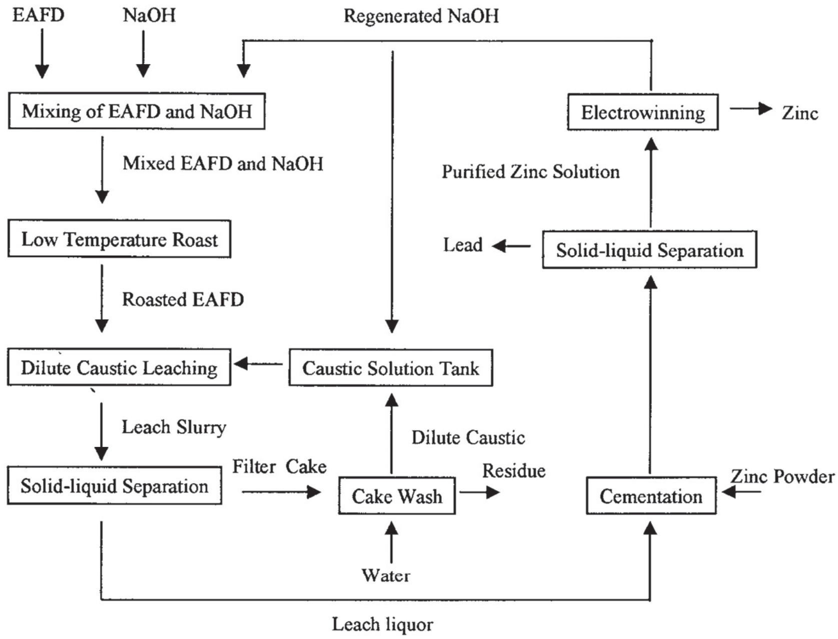


Figure 20. Flowsheet of caustic soda roasting and leaching treatment process for EAFD [5].

6.1.3 Behavior of other elements

In addition to zinc some other elements can be leached after fusing the EAF dust. Youcai and Stanforth [7] reported that the concentrations of elements such as Fe, Cu, and Cd in the solutions were lower than 0.5, 0.4, and 0.1 g/l, respectively, and the resultant leaching residue contained less than 1% of zinc, 0.5% of lead, 0.3% of copper, and 0.1% of cadmium, and over 35 % of Fe.

The use of hydrolysis or moisture combined to caustic roasting affect differently on various elements in the dust. Using hydrolysis prior to caustic roasting the lead extraction was slightly higher, 70 - 80 %, in comparison to about 65 % when leached directly with NaOH solution. When the EAF dust was directly fused the leaching efficiency of lead was found to decrease to around 30 % [7]. Similar results have been obtained when moisture was added in roasting process and the lead extraction increased to 85 % when the recovery was decreased to 63 % without moisture addition [5].

The moisture combined to caustic roasting had the opposite effect on extraction of chromium than on extraction of zinc and lead. Without moisture additions, the average chromium recovery was 80.7 % and with moisture addition in roasting the average chromium recovery was 37 %. The residue after roasting with moisture added contained on average 2.0% zinc, 19.9% iron and 0.06% cadmium and in general less than 1 % of iron was leached. The extraction of cadmium was around 89 % after roasting with moisture added. [5]

EAF dust can contain approximately 1 – 5 % of silica and part of silica may fuse with caustic soda and dissolve in solution, which will consume some NaOH. [7] Around 10 % of NaOH will be lost in the steps of fusion and leaching of the fused product. [7]

6.2 Roasting with Na_2CO_3

The other promising method to destroy zinc ferrites prior to alkaline leaching could be roasting with sodium carbonate, Na_2CO_3. According to thermodynamic calculations the conversion of zinc ferrite with addition of Na_2CO_3 is described to occur at 820 °C and for optimal roasting conditions have been reported to be 850 - 950 °C. Although higher temperature is required to decompose ferrites with Na_2CO_3 roasting, the benefits compared to NaOH roasting are that lower additions of Na_2CO_3 are required and the cheaper price of Na_2CO_3 [37,59]. It has also been reported that the hydrophobic behavior and handling of NaOH provides more difficulties. On the other hand, sintering of calcine product with Na_2CO_3 has consequences because an additional crushing step is then necessary. [37]

Kemperman [37] studied roasting of synthetic ferrite and zinc bearing wastes containing zinc ferrites followed by caustic soda leaching. The results were promising for synthetic ferrite, which was almost completely converted into soluble zinc compound and the dissolution of iron was found to be negligible. However, the results for waste materials gave incomplete conversion of zinc ferrites even when stoichiometric addition of Na_2CO_3 was increased and only around 50 % of zinc was extracted.

6.3 Other roasting methods

Some other possible methods to break the zinc ferrite are for example heating with coke or pre-treating with hydrogen-nitrogen mixture. The breaking of zinc ferrite would be facilitated by pre-reducing it by heating with coke in temperatures of 600 – 800 °C. Other method, a prior treating with hydrogen-nitrogen mixture with more than 50 % hydrogen have showed even 100 % zinc recoveries to be possible after leaching with NaOH. [13,27,46]

7. Feasibility considerations

The driving forces to treat steelmaking dusts derives from the environmental legistlation and from the economics. To these includes the market price of zinc and other metals for revenues, the cost of the treatment or land filling and also the sufficiency of raw materials from ores. The environmental side is driven also by the economics of treatments but in the future dusts can be forced to be treated due to more stringent environmental legislations.

The presence of zinc in the dust seems to be a crucial factor for the economical side as it hinders the direct recycling of dust back into steelmaking furnaces. When considering the possibility to recycle steelmaking dusts back to the process, the amount of zinc should be lowered enough in order to avoid operational problems in the steelmaking process. Also the cumulative loading of zinc in the dust may result in disposal problems if the zinc content cannot be lowered enough. [60]

Among dust treatment processes, the hydrometallurgical processes have the advantage that they are flexible in scale and are easy to make a closed system [26]. However, today's dust treatments processes are predominantly pyrometallurgical, but the disadvantage with these is the need of a large feeding of dust in order to be economical. Because hydrometallurgical processes are suitable for small-scale operations, the on-site process could be possible and thus the costs of transport are avoided. In addition, the processes can produce virgin quality of non-ferrous metals.

7.1 Caustic soda leaching process

The advantage with alkaline leaching is the selectivity in leaching zinc, which lowers the cost of solution purification as it can be done quite simply. The technical and economical profitability study of the caustic – electrowinning process showed that the process is flexible and can be applied to small, medium or large-scale operations and that it is relatively clean in term of work-place and ambient air emissions [30]. However, because a concentrated NaOH solution is needed, the solid-liquid separation is difficult and can cause some problems in industrial applications due to the high viscosity of strong NaOH solutions and extremely fine-grained solid. Despite that, the solid-liquid separation can be achieved with conventional equipment [3,4,27] and, in addition, a magnetically-induced decantation may offer some improvements in this respect [30].

Electrolysis of zinc from alkaline solution is cost-effective and around 20 % of energy saving can be achieved with electrowinning from alkaline solution. The electricity consumed for production of 1 kg of metallic zinc from the alkaline leach solution is 2.4 – 2.7 kWh, while that from acidic solution is 3.3 – 3.4 kWh [7]. However, the leaching method with NaOH needs additional developing in recovering the metal from NaZn-solution by electrowinning [4]. A commercial alkaline electrowinning plant does not exist and it can not to be connected to existing traditional zinc plants, which are based on the sulfuric acid bath [39]. About 80 % of the zinc produced in the world use the sulfate electrolysis technology [7].

For economical feasibility investigations it should be taken into considerations that NaOH is an expensive reagent, and that high concentrations are needed for sufficient recoveries [4]. Compared to acid leaching greater amount of NaOH is needed in addition to that the price of NaOH is higher. However, it should be noticed that the difficult iron removal process is present in acidic process, making it expensive [46]. The alkaline leaching seems economically possible as the solution purification is simple and easily done with zinc powder and if the solubility is more than 80 % for both zinc and lead [38].

Palencia et al. [2] have investigated the recycling of EAF steelmaking dust and the cost of their treatments. The economic analysis was carried out for both caustic soda and sulfuric acid leaching process. The breakdown of cost sections and incomes from savings and sales for alkaline process are shown in Table 11. The total cost of acidic treatment was 0.958 \$/t steel and total income 2.327 \$/t steel, when those numbers in alkaline leaching were for total cost 0.613 \$/t steel and for total income 3.149 \$/t. According to these calculations the alkaline leaching would be more favourable.

Table 11. Breakdown of cost sections and items, and income from sales and savings for the alkaline treatment and recycling [2].

Cost ($/t steel)		Income ($/t steel)	
Treatment		**Savings**	
Washing	0.065	Net fixed iron (scrap iron)	0.27
Alkaline leaching	0.026	Elimination of stabilisation	0.977
Cementation	0.079		
Electrolysis	0.444	**Sales**	
Process water	0.036	ZnO (50 % Zn)	-
Sodium hydroxide	0.1	Electrolytic Zn powder	1.738
Electric energy	0.453	Pb cement	0.119
Natural gas	0.024		
Total cost	**0.613**	**Total income**	**3.149**

The profitability of the process depends highly on the zinc content of the waste and on the market value of the recovered zinc [39]. Both dusts, BOF and EAF, contain zinc values between ore grade and concentrate grade and can be seen as a potential zinc resource [46]. To study the economic feasibility of the process the costs of the process should be compared to the zinc market price and the cost of extracting zinc from ores. Also some experiments for caustic leaching have been performed for a composite sample which contained EAF dust and Waelz oxide and was proved viable [27].

7.2 Presence of zinc ferrites

Despite all the advantages of hydrometallurgical processes, the recovery ratios of zinc are normally lower than those of pyrometallurgical processes. This is caused by the presence of zinc ferrites in the dust. Zinc ferrite is very stable and difficult to decompose with hydrometallurgical processes. Very strong leaching conditions, for example high concentration of solvents and high temperature, have to be applied to obtain higher leaching ratios of ferrites. However, such operations will become difficult and both capital and running costs will be high. [26]

The conversion of zinc ferrites into zinc oxides is the major importance for the feasibility. Alkaline leaching is not effective in leaching of zinc ferrite suggesting that the process should be intensified to reach these materials. For this some prior treatment could be used, such as caustic soda roasting in order to break down the ferrite structures. But, if prior treatments are needed they will increase the cost of the alkaline leaching process.

One method to enhance zinc recovery could also be to change conditions in the furnace and gas line so that the formation of ferrites could be avoided, and thereby the leaching of zinc could be be improved. Other way could be to remove zinc and other impurities from galvanized steel scrap before the scrap is feeded in the steelmaking process [54,60]. By keeping zinc out of the EAF process from the beginning, the whole process of treating the dust could be avoided but then the cost of treatments of steel scrap need to take into profitability considerations.

7.3 Wastes

The precence of heavy metals in the dust is the most crucial factor on the environmental side. If they are leached, it can cause problems with disposal of the leaching solution and if they remain in the residue, the residue cannot be land filled. By caustic soda leaching a residue enriched in iron and depleted in zinc and lead is obtained and it may be suitable for recycling and more suitable for disposal than the original material. [30]

The leach residue form caustic soda leaching is reported to contain mainly zinc ferrites and iron oxides. If zinc content can be reduced sufficiently low the residue can be recycled for reduction in the EAF steel plant. Before that it is thickened, filtered, dried and pelletized, possibly with the addition of a reductant such as a coke breeze. The solid wastes, if any, are less toxic than the feed material but bleed-off liquids may have to be treated before discharge [30]. Also other valuable metals may be recovered from the residue of caustic soda leaching - electrowinning process balancing the costs [39].

8. Conclusions

The mineralogical form of zinc seems to be a basic indicator to the effectiveness of treating the dusts from steel manufacturing. Zinc is present mainly as two compounds, zinc oxide ZnO and zinc ferrite $ZnFe_2O_4$. Because they behave differently, it causes difficulties in dust treating. The zinc oxide can be easily handled, but the zinc ferrite is a highly stable compound and thus significantly complex and difficult to handle.

Hydrometallurgical processes are not able to dissolve zinc ferrite effectively, but pyrometallurgical roasting processes can be used to break down the ferrites. From the roasted product zinc can be recovered using hydrometallurgical techniques, such as alkaline leaching. With a hybrid process using low temperature NaOH roasting followed by NaOH leaching higher zinc recoveries have been achieved. The maximum recoveries using direct leaching have been reported to be around 85 %, when the hybrid process gave around 95 % recovery of zinc (for this also hydrolysis is needed prior to NaOH roasting).

Among hydrometallurgical processes the major advantage with alkaline leaching is its selectiveness in leaching zinc compared to iron compounds. Using alkaline leaching iron remains in the solid residue and the costly and difficult iron removal process from the leachate, that is present with acidic leaching processes, could be avoided. A solution containing Zn and Pb as predominant elements will be obtained and purification off Pb can be done simply by cementation with Zn powder. From purified leach solution Zn can be recovered by electrolysis or precipitating in its pure compound.

The NaOH leaching processes have been developed before for the dissolving zinc from steelmaking dusts but they have faced technical and economical problems and have been eventually abandoned. However, there is an impetus for developing hydrometallurgical processes as they can fit a small-scale when on-site process could be possible and thus they are regarded as more environmentally suitable and economical for treating materials having relatively low zinc content. Also, dusts from iron and steelmaking consist of very fine particles (< 10 µm) and will be difficult to handle dry if no previous agglomeration is used.

Despite the benefits with hydrometallurgical processes a very few commercial processes have been successful because the processes are essentially dependent on the characteristic of dust. Thus, today the dust treatment processes are predominantly pyrometallurgical. There are, however, some drawbacks with the pyrometallurgical processes that drive for developing and searching new options. The major drawbacks with these processes are high energy consumption and need of a large feeding quantity to be economical and thus the treatment plant may have distant location from the steel factories.

The choice between the processing routes depends strongly on the dust characteristics. Dust containing many elements makes metal extraction complex and difficult. In addition, each dust is unique which makes finding a suitable treatment process even more complicated. The chemical and mineralogical composition of dust varies widely even if the dust has been taken from the same process. Although many pyro- and hydrometallurgical processes have been developed, none of them have been entirely satisfying. The target with these treating processes is to produce a residue that could be recycled further or safely disposed-off without affecting the environment and to recover zinc. The most important stage is the separation of non-ferrous metals, such as zinc and lead, from iron in the dust.

In general, there is still no effective and economically advantageous method for treating the dusts. The reason for failures could be that it is still more economical to extract zinc from the naturally occurring raw materials. But nowadays the dusts form steel manufacturings are considered as harmful waste due to presence of soluble heavy metal compounds. Thus, disposal, recycling or recovery of these dust emissions has become a major concern for the steel industry. As the environmental protection regulations have stringent, the disposal of the dust has become an expensive option and the direct recycling is limited due to accumulation of impurities (heavy metals, alkali and halides). Zinc is the main impurity in steelmaking process and should be eliminated from dust to enable dust recycling back to process.

Every day steel industry generates significant quantities of dust in in blast furnaces (BF), basic oxygen furnace (BOF) and electric arc furnaces (EAF). The use of scrap brings other elements into furnaces and they end up into dust. The steelmaking dusts are rich in zinc; in EAF dust zinc content can be even 30 % while in BF and BOF dust it is lower, around 1 – 3 % and 1.5 %, respectively. The main source of zinc is the use of galvanized steel sheet scrap as raw material in steel manufacturing. The use of this kind of scrap in steel production has been increasing, which has led to the increase of zinc content in the dusts and this trend will likely continue. However, the recycling of steel scrap has obvious economic and resource conservational benefits.

The pressure to reduce pollutants has increased more interest for further utilizing of dusts as sources of metals or as secondary raw material. The process costs and profitability are extremely dependent on the zinc content of the waste and on the market price of zinc. In case of dust treating processes, the economically viable process can be achieved if the operating costs for the process are less than the costs for the dumping it. However, the environmental side is not only driven by the economics of treatment or metals, it is also possible that in the future the landfilling of the dust will be entirely prohibited and dusts are enforced to be treated.

9. Summary

Every day steel industry generates significant quantities of dust and sludge as waste material or byproduct. Their disposal and reuse has been a serious concern for steel industry as these dusts are considered as harmful waste in most industrial countries due to presence of soluble compounds of heavy metals. On the other hand, they usually contain considerable amounts of valuable metals and the reuse of those is very much essential not only for conserving metals and minerals resources but also for protecting the environment.

Dusts from iron and steel manufacturing are generated in blast furnaces (BF), basic oxygen furnaces (BOF), and electric arc furnaces (EAF). The use of steel scrap in BOF and EAF brings other elements into furnaces and they end up into dust. A direct re-use of dust will lead to accumulation of those elements and can harm the primary processes as well as decreases steel quality. Zinc is the main impurity in the process and should be eliminated from dust in order for the dust to be viable for recycling. In this literature survey the alkaline leaching (with NaOH) of zinc from iron and steelmaking dusts is reviewed. The characteristics of EAF, BOF and BF dust and their processing based on alkaline leaching is described. Also some methods, *e.g.* pretreatments, to enhance leaching are introduced.

Dusts from iron and steel production consist mainly of ferrous oxides, mostly in Fe_3O_4 phase. In addition, they contain zinc, lead and cadmium oxides as well as minor amount of many other elements. The main source of zinc in the dust is galvanized steel scrap used in steel manufacturing. The EAF technology uses virtually 100 % recycled steel and the dust from EAF can run up to 30 % of zinc. The amount of zinc is usually lower in BOF and BF dusts containing around 1 – 3 % and 1.5 % of zinc, respectively. Zinc is present mainly as two compounds, zinc oxide ZnO and zinc ferrite $ZnFe_2O_4$.

The main target in the dust treatment is the removal of zinc so that iron containing material can be recycled and zinc recovered. Although many pyro- and hydrometallurgical processes or their combination have been developed, any of them have not been entirely satisfying and only a limited number of these have reached commercialization when the majority has been pyrometallurgical. The impetus for developing hydrometallurgical processes is that they can fit on small-scale and an on-site process could be possible. Also these processes can provide a good selectivity in metal separation and flexibility in end-products. In addition, dusts from iron and steelmaking consist of very fine particles (< 10 µm) and will be difficult handle dry if no previous agglomeration is used.

Among the hydrometallurgical methods, the alkaline leaching using sodium hydroxide (NaOH) as a leaching agent is seen effective in the dissolution of heavy metals without significant dissolution of iron, and a solution containing Zn and Pb as predominant elements will be obtained. Thus a relatively clean and iron-free solution is obtained and the complicated iron removal processes is avoided. Some facilities using NaOH leaching have build up before for dissolving zinc from the steelmaking dusts, but they have closed because of insufficiency.

For the optimal leaching conditions from literature can be derived as 6 – 10 M NaOH, liquid to solid ratio of around 10, and temperature of 80 – 95 °C. When using this high concentrations and temperatures, the dissolution of zinc is fast and zinc recoveries of 80 – 85 % can be reached. Still there is a part of zinc in the dust that has not dissolved and recovered. Methods that can be used to enhance alkaline leaching are for example pressure leaching, and microwave or ultrasound assistant leaching, but they have not seen to improve (significantly) zinc recovery.

The total recoveries of zinc are limited in hydrometallurgical methods, such as in alkaline solutions, due to the presence of zinc ferrite ($ZnFe_2O_4$) in the dust. ZnO dissolves easily in sodium hydroxide solutions, but $ZnFe_2O_4$ is highly stable compound. If the content of zinc ferrite in the dust has been high, the zinc recoveries have remained low. Around 50 – 80 % of zinc in the dust can be present as ZnO and the rest is mainly as $ZnFe_2O_4$. For breaking down zinc ferrite, pyrometallurgical processes, such as roasting, can be used prior to leaching. Roasting with caustic soda prior to alkaline leaching have showed that zinc ferrites can be decomposed and leaching of zinc could be improved.

The chemical and mineralogical composition of dust varies widely even if the dust has been taken from the same process making the processing of them difficult and complex. However, a process based on caustic soda leaching seems promising if zinc ferrite can be decomposed by relative simple treatment prior to leaching.

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Recycling of steel scrap has obvious economic and resource conservation benefits. However, steel industry generates every day significant quantities of dust and the use of scrap as raw material brings harmful elements into furnaces and they end up into dust. The dusts are considered as harmful waste and cannot directly be used as landfill today. Also a direct recycling of dust back to steel production is hindered mainly due to the presence of zinc. On the other hand, the metals recovered from the dusts may be used as raw materials. Various pyro- and hydrometallurgical processes have been developed for treating steelmaking dusts aiming to produce a residue that could be recycled further or safely disposed-off. Metal extraction from the dusts is difficult due to their complex composition and finding a suitable process is complicated as each dust is unique. The major advantage of alkaline leaching is its selectivity in leaching zinc compared to iron compounds.

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