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MECHANO-CHEMICAL AND THERMAL TREATMENT OF IRON BEARING WASTE MATERIALS: ECOLOGICAL BENEFITS AND SYNERGETIC EFFECTS

Ph.D. Thesis

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To the main supporter and the finest
in the world, my parents, who do
not find the words to express my
gratitude, God bless you.

To my wife and my children

To all my brothers and sisters
I dedicate this modest effort

Abstract

Steel scrap recycling is generally performed by direct smelting of scrap in electric arc furnaces, generating about 2% of dust per charge. Electric arc furnace dust (EAFD) is characterized as a hazardous material, due to its heavy metals content and a powder form.

This PhD thesis presents the study of Serbian electric arc furnace dust (EAFD) management trough some conventional and innovative technologies.

The investigated EAFD was brought from Serbian carbon steel making and that is way the zinc percentage it was 30.34%, which is in the standard range of typical chemical analysis of EAFD from carbon steelmaking. The analysis also shows that zinc, iron and chromium are mainly present as ferrites which are very resistant against to any kind of treatment. Because of that, it is necessary to use more aggressive conditions (high temperature or stronger leaching reagent) for metals recovery.

Solidification/Stabilization (S/S), a widely used treatment technology, of EAFD was investigated in two ways; first as cement replacement in grout mixture and the replacement percent was set up to 80%. Results of compressive strength testing showed that the best maximum replacement of cement with EAFD is 20%. With a higher amount of EAFD in mixture compressive strength decreases rapidly. According to leachability results, Pb was stabilized in a cement matrix even at 80% of cement replacement with EAFD.

Second way of (S/S) of EAFD by using cement as the main stabilizer, fly ash as an additive, and controlling the EAFD particle size by milling. EAFD replaced 0-50 % of fine aggregate and fly ash replaced 10-25% of cement in mixtures, with different milling times applied. S/S samples were tested for compressive strength and heavy metals leachability. The results of compressive strength testing showed that the best maximum EAFD replacement is 15%, after which compressive strength decreases rapidly. The best fly ash compressive strength was attained at 10% replacement of both fine aggregate and cement. The milled EAFD produced the best results at three hours of milling; however, the addition of fly ash resulted in

a slight compressive strength decrease in these samples. Leachability results of concrete samples indicated that Zn and Pb were stabilized in the cement matrix even at 30% of fine aggregate replacement with EAFD.

Also sintering of EAFD was investigated by using conventional methods for (EAFD) and electronic waste (e-waste) valorization trough stabilization process, in order to achieve concurrent management of these two serious ecological problems. Based on the results, it was found that materials suitable for use in ceramics industry as a partial substituent of quartzite and fluxing components can be produced. Besides solving the environmental problem related to EAFD and liquid-crystal display (LCD) disposal, by replacement of raw materials, certain economic effects can be achieved.

Innovative technology for EAFD treatment proved the possibility of separate zinc and lead recovery from coal composite pellets, made of EAFD with other synergetic iron-bearing wastes and by-products (mill scale, pyrite cinder, magnetite concentrate), in two-stage process. The first, low temperature, stage performed in electro-resistant furnace enabled removal of lead due to the presence of chlorides in the system, and in second stage at higher temperature in DC plasma furnace, zinc was valorized. By Presented technology several final products were produced including higher purity zinc oxide corresponded to wash Waelz oxide.

Finally, a methodology was established for a relationship between the composition of mixtures of iron-bearing non-standard dispersed raw materials for production of sinter and its most important metallurgical properties, in accordance with the appropriate phase of the production technological process. Using an appropriate software package, the database of available resources is formed. Raw data in the database include: chemical composition, bulk density, grain size distribution, moisture content and the annual quantity generated. The base is divided into basic raw materials and additives. Basic, iron-bearing, raw materials are electro-arc furnace dust (EAFD), pyrite cinder and mill scale, and additives are: flux (lime), binders (cement, bentonite) and reducer (coke). For the study of these relations the planned experiment is conducted, based on the Simplex plane. The connection between the composition of the dispersed iron-bearing mixture, as an

independent variable, and dependent variables (metallurgical properties such as resistance to impingement and compression strength) was determined using correlation and regression analysis, where mathematical models for fast and reliable projected synthesis the required metallurgical properties of sinter were obtained.

Key words: EAFD, Solidification/Stabilization, Metallurgical properties, Zinc, Lead, Process modeling, Concrete, Fly ash, LCD glass, Sintering, Ceramic materials, Thermal treatment.

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1. Introduction

Historically metals have been linked with industrial development and improved living standards, and thus play an important role in our modern societies. Human civilizations have been known after their concurrent metals' use, such as the copper age, Bronze Age and Iron Age, etc. Due to shortage of metals sources, recycling became the most important source of metals and raw material for industry. Metal recycling has several potential benefits, primarily due to:

(a) Its ability to direct the end-of-life wastes (scrap) away from landfills and

(b) Achieving resource stewardship through conservation [1].

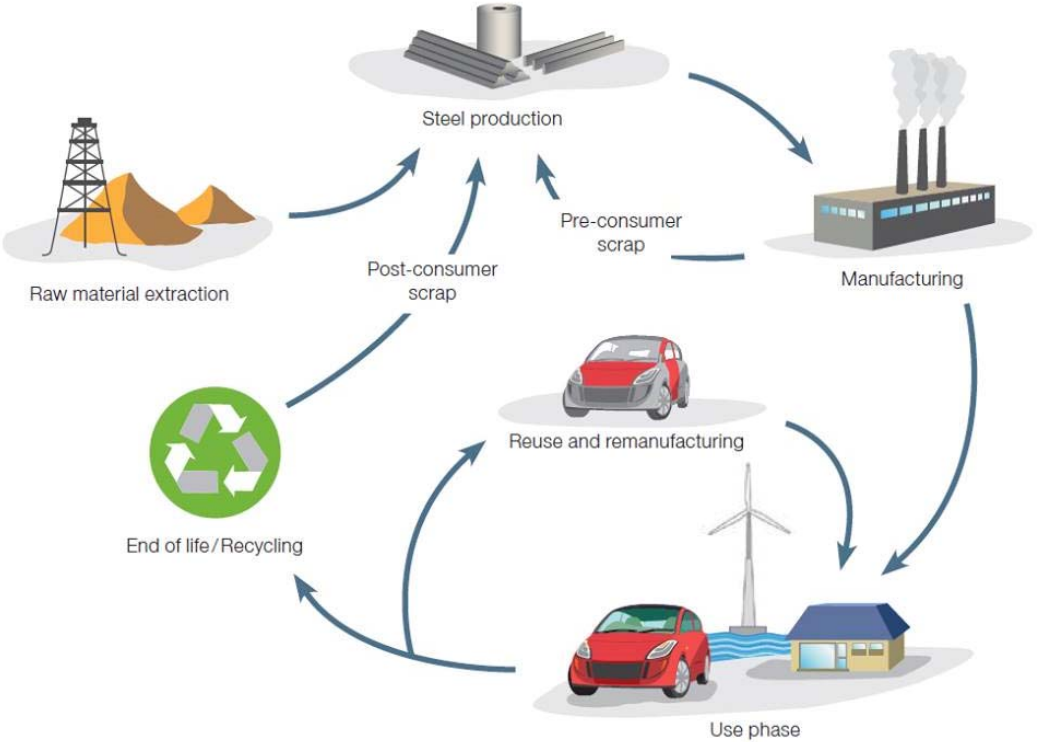


Figure (1-1). Steel's life cycle

Metal recycling is undertaken mainly because of altruistic reasons, economic imperatives and legal considerations [2], argued that from an economic perspective it is always cheaper to recycle steel than to mine virgin ore and move it through the process of making new steel. Steel is the world’s most used and recycled metal. The recycling of scrap metal is an integral part of modern steelmaking, improving the industry's economic viability and reducing environmental impact. Moreover the recycling of steel scrap reduces the need for iron ore extraction, significantly reducing CO_2 emissions, energy and water consumption and air pollution. However, the critical limiting factor is the availability of sufficient steel scrap, as much steel remains locked in its current use (such as in durables, automobiles and bridges), compelling the steel industry to rely on mining virgin ore to supplement the production of new steel.

According to the Turkey Statistical Institute, from January to December 2012, Turkey imported 22.42 million tonnes of scrap, representing a 6% increase year-on-year and according to the China Association of Metal Scrap Utilization, China’s scrap imports decreased 26% year-on-year from 6.77 million tonnes in 2011 to 4.97 million tonnes in 2012. Also China’s scrap ratio decreased from 135.5 kg per metric ton of steel in January 2012 to 112.2 kg in October 2012 [3].

Steel production is associated with a significant accumulation of wastes, as slag, sludge, flue dust and gasses. Some of these are recyclable, others are toxic, constituting hazardous wastes, which should be processed, in order to be reutilized or discarded properly in order to avoid environmental impact.

Steel production can occur at an integrated facility from iron ore or at a secondary facility, which produce steel mainly from recycled steel scrap. Integrated facilities typically include coke production, blast furnaces (BFs), and basic oxygen steel making furnaces (BOFs), or in some cases open hearth furnaces (OHFs). Raw steel is produced using a basic oxygen furnace from pig iron produced by the blast furnace and then processed into finished steel products. Secondary steel making most often occurs in electric arc furnaces (EAFs).

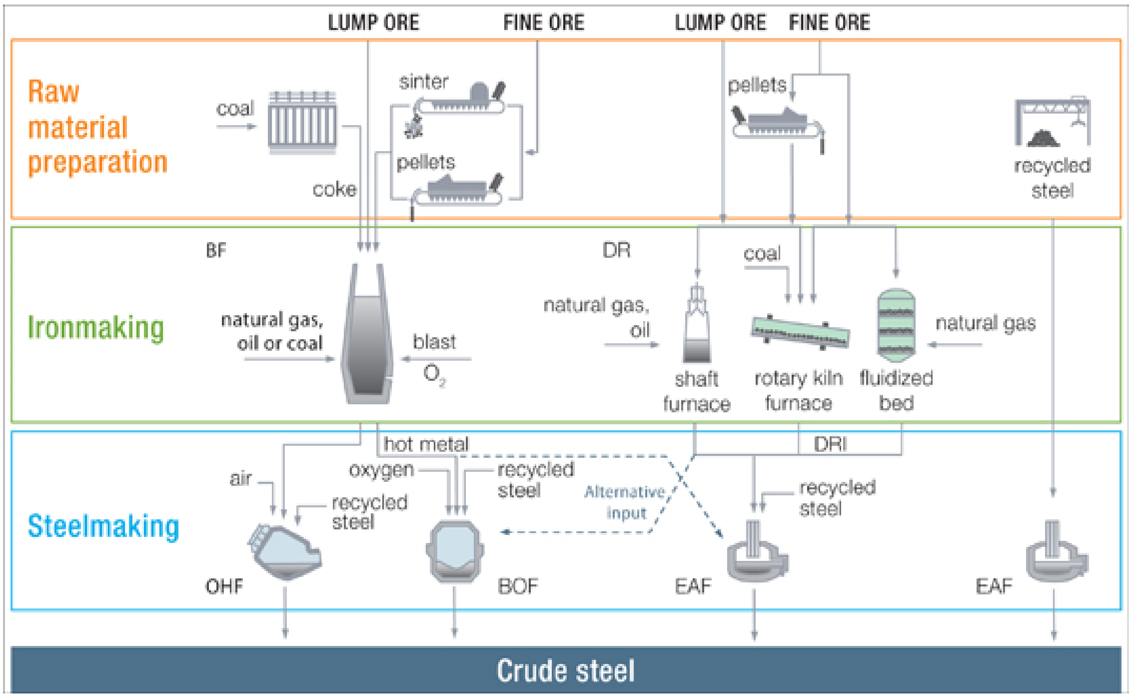


Figure (1-2). Steel production (variations and combinations of production routes)

All of these production methods can use recycled steel scrap as an input and most new steel contains recycled steel.

Based on statistics from World Steel Association, world crude steel production was 1 665 million tons in 2014, an increase of ~1% compared to 2013. Also according to the World Steel Association, in 2014 more than 1.1 billion tonnes was produced in Asia, of which China alone accounted for 822.7 million tons (Mt), i.e. 49.4% of total global production. In the Europe 169.3 Mt of crude steel was produced during the year, with Germany the biggest producer at 42.2 million tonnes, followed by Italy at 23.7 Mt and France at 16.1 Mt [4].

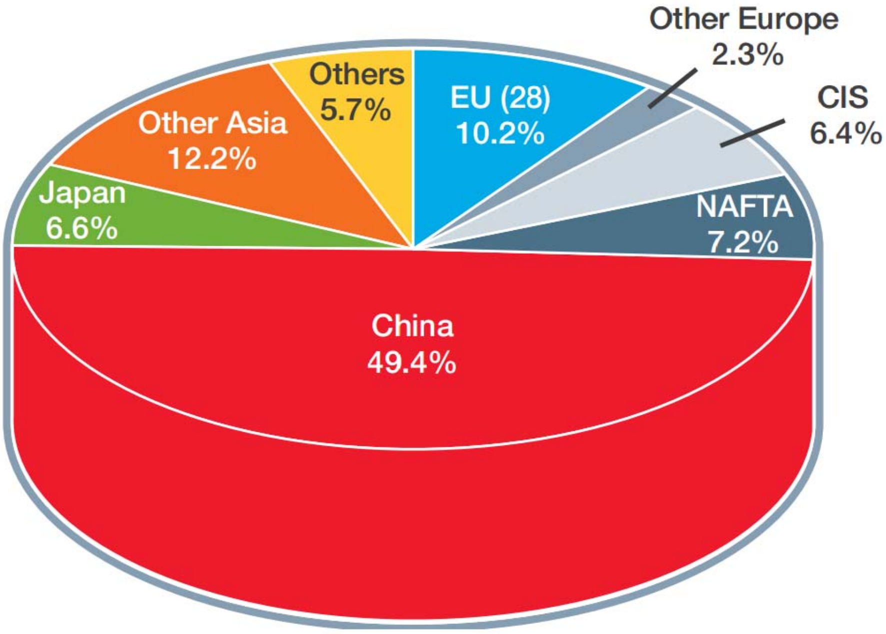


Figure (1-3). World steel production 2014

For various reasons, electric-arc furnace technology is currently used in most global steel production worldwide. BOFs currently produce about 70% of the world’s steel and 29% of steel is produced in EAFs and the BOFs process uses up to 30% scrap and around 90-100% is used in EAFs production [5].

The production of steel in electric arc furnace (EAF) generates a by-product called EAF dust. This EAFD is collected in bag house and amounts to approximately 2% of the produced steel are generated in typical EAFs operations. These steelmaking flue dusts are classified in most industrialized countries as hazardous residues according to the USA Environmental Protection Agency (US EPA) classification, dated-back 1980 because the heavy metals contained in them, tend to leach under slightly acidic rainfall conditions.

It is estimated that the world-wide total production of EAF dust could be as high as several million tons, all of which must be treated, recycled or land-filled.

EAFD can vary greatly in composition of the metallic charge, the furnace additives used and the type of steel produced. Several researches reported that about 15-20 kg of dust is produced for each ton of steel produced [6, 7, 8] and about 3,000,000 tons of EAFD are generated worldwide every year [9].

It is a complex, fine-grained, high-density material containing high amounts of zinc and iron, and significant amounts of calcium, manganese, magnesium, lead, and chromium. The phase identification of the EAFD samples indicates the presence of complex minerals such franklinite ($ZnFe_2O_4$), magnetite (Fe_3O_4), magnesium-ferrite ($MgFe_2O_4$), chromite ($FeCr_2O_4$), calcium-magnetite ($Ca_{0.15}Fe_{2.85}O_4$), periclase (MgO), manganese oxide (Mn_3O_4), quartz (SiO_2) and zincite (ZnO) [10, 11, 12]. The typical chemical composition of EAFD from the production of carbon steel/low alloyed steel and high alloyed steel is presented in table (1-1).

Table (1-1). Typical chemical composition of EAFD from the production of low alloyed steel and high alloyed steel.

Component	Dust from alloy steel production (Wt- %)	Dust from stainless steel production (Wt- %)
Fe_{tot}	17 - 37	20 - 33
SiO_2	1.7 - 5	3 - 9
CaO	2 - 16	8 - 18
Al_2O_3	1 - 4	0.4 - 2
MgO	1.2 - 3	1 - 4
P_2O_5	0.01 - 0.1	0.03 - 0.1
MnO	1.5 - 6.9	2.2 - 6.3
Cr_2O_3	0.12 - 6	9 - 20
Na_2O	n/a	0.6 - 2
K_2O	n/a	0.7 - 3
Zn	2 - 15	2 - 25
Pb	0.05 - 3.6	0.2 - 4.5
Cd	0.01 - 0.04	0.01 - 0.05
Cu	0.01 - 0.8	0.015 - 0.5
Ni	0.01 - 0.5	1 - 4
V	0.01 - 0.2	0.05 - 0.12
W	0.5 - 1.5	n/a
Co	0.01 - 0.2	0.02 - 0.04
As	0.001 - 0.01	n/a
Hg	0.05 - 0.7	0.0002 - 0.015
CI	0.7 - 1.7	0.8 - 1

F	0.01 - 0.65	0.3 - 0.7
S	0.25 - 1.42	0.2 - 0.5
C	0.5 - 3.1	0.05 - 1.3
Basicity	n/a	n/a
Moisture	n/a	n/a

Beside its high levels of zinc, steel industry wastes can include lead, arsenic, cadmium, chromium, nickel and dioxin, among other toxic substances. Some smelters have reported dioxin emissions. Reclamation smelters should therefore be monitored for dioxin emissions.

Annex C of the Stockholm Convention on Persistent Organic Pollutants lists, among the source categories with potential for comparatively high levels of formation and release of dioxins to the environment:

- Secondary copper production.
- Sintering plants in the iron and steel industry.
- Secondary aluminium production.
- Secondary zinc production.

Electric arc furnace (EAF) dust with high chloride content increases the threat of dioxin emissions and the high chloride content reduces the value of recycled zinc oxide produced by EAF dust recycling plants. Moreover because EAF dust includes dioxin, plants in Japan that recover Zinc from EAF dust are designated as special facilities under the law concerning special measures against Dioxins [13, 14].

Several treatment technologies have been developed and can be divided into two main groups; processes which recover the metals and solidification/stabilization processes.

The greater part of EAFD presently is treated by a high temperature metal recovery (HTMR) process and successive condensation. For treatment of EAFD with high zinc content, Waelz process prove to be the best available technique [15, 16]. This technology allows the recovery of elements with high vapor pressure, such as Zn and Pb and the remaining material called Waelz Iron Product can be used in the manufacture of cement and asphalt. This process is efficient for the treatment of dust generated in carbon steel production when the percentage of Zn and Pb is between 15–20% [17, 18]. The amount of Zn and Pb contained in the dust can be increased by a direct recycling of EAFD in the furnace, if the steel quality is not influenced [19-21]. Metal recovery is also accomplished by several hydrometallurgical processes. Pyrometallurgical and hydrometallurgical processes have been applied for treatment of EAFD in order to produce either zinc oxide or metallic zinc. The hydrometallurgical processes are regarded as more eco-friendly for treating materials having relatively low zinc content. They are based on leaching methods as the main extraction process and the problem of this process is that it can recover zinc only from the zinc oxide in EAFD [9, 22, 23, 24].

When metal recovery is not profitable a stabilization process in a cement matrix can be used as well as vitrification, which is acquiring importance as metals contained in the EAFD [25-29].

Therefore, the treatment and stabilization of this industrial residue is necessary. The increasing use of zinc-containing scrap for steel production has lead to high zinc content in the electric arc furnace and converter flue dusts. The cost of disposing of this residue is high due to environmental restrictions. Various recycling processes have been developed for these dusts, but most never reached the pilot plant stage and many investigations were stopped because of metallurgical and economical inefficiencies.

Generally if economical considerations do not justify any recycling process, the best option is to convert EAFD to non hazardous form by Solidification/ Stabilization procedure before permanent disposal.

The base of presented research in this dissertation is EAFD and the research about chemical and physical properties of the EAFD after application of currently existing treatment ways of EAFD. They were:

1) Solidification/Stabilization of EAFD by replacement of cement in mortar for landfilling and with concrete, by replacement of fine aggregate, for using in building industry.

Concrete is a well-known suitable environment for Solidification/ Stabilization, which is favorable for some materials that have leachable elements and need fixation. Moreover, the properties of the concrete may be enhanced due to the zinc and pozzolanic compounds present in the waste. Therefore, the use of EAFD in concrete is an interesting option.The effects of a small amount of EAFD on the properties of concrete have been investigated [8, 9, 12, 30, 31].

The dust has been used as a replacement for cement by mass in 2 and 3%, and the results obtained indicate that the EAFD retards the setting time and enhances the compressive and shearing strengths as well as resistance to abrasion. Another advantage of using EAFD in concrete is that a partial replacement of cement raw materials in concrete reduces the high CO_2 emission generated during manufacture.

Some environmental agents can induce concrete degradation, which significantly impact the performance of concrete structures. Corrosion of reinforced bars can cause failure and increase costs as support and repair are needed. The pitting corrosion in the reinforced bars caused by the penetration of chloride ion is a serious concrete degradation problem as pitting acts as a point of stress concentration, which can lead to a significant decrease in mechanical strength. Some researches have been performed to investigate the effect of EAFD addition on corrosion of reinforcement embedded in concrete contaminated with EAFD [32-35].

Based on the existing studies, the results show that improvement in the corrosion resistance of steel bars embedded in EAFD-concrete compared to those bars embedded in plain concrete. This improvement in corrosion resistance attributed partly due to the influence of the EAFD particles in improving the physical properties of the EAFD-specimen, such as porosity.

Due to the high content of zinc, (up to 30% by weight), and iron (about 40% by weight) it’s rational to consider reuse of EAFD or valorization of these elements from EAFD, which will have the sustainable economic feedback.

2) Vitrification of EAFD with LCD residue glass also for using and we have got row material for bricks.

The vitrification process was selected as the inertizing process because it permits the immobilization of the hazardous elements in the glass network and represents an environmentally acceptable method for the stabilization of this waste.

Classes of various compositions were obtained by mixing EAFD with glass cullet and sand.

Worldwide, tremendous amounts of waste of electronic and electrical equipment (WEEE) are generated, of which modern TV sets and computer monitors represent a significant source [36]. Liquid crystal displays (LCD) nowadays are widely used, but due to complexity of the process, only a part of discarded LCD monitors is being recycled. In last several years, end-of-life LCD's are identified as a potential source for indium recovery, why various studies focused on indium recovery from discarded LCD's are reported [37, 38, 39]. However remaining solid material, LCD waste glass, is not suitable for landfill, incineration or composting [40]. Appreciable quantities and diversity of metallic materials and high content of SiO_2, Al_2O_3 and CaO indicate the possibility of valorization of these components in production of ceramics, but also synergistic effects in metallurgy [41].

According to available literature overview, different studies for EAFD and LCD treatment were reported, but all mainly focused on process of stabilization [42] and re-utilization of the individual waste streams in asphalt mixtures [43], production of high grade materials [44], foamed glass [45] and as cement replacement [46]. Nevertheless, appropriate selection of materials combined for "disposal for the future", will allow highest possible degree of valuable materials recovering while minimizing wastes production.

Therefore, a part of this study is development of the optimal technological procedure for stabilization and valorization of EAFD and LCD trough conventional methods of synthesis and sintering, which will enable their transformation into inert materials suitable for use in ceramic industry.

3) Thermal pretreatment of EAFD with iron bearing materials by using pelletization technique to extract zinc and lead and the residue material was used as the row material for reuse in the furnaces for iron recycling.

Resource recovery is an innovative industry and a natural trend; all countries have to switch from waste disposal and treatment to resource recovery, life cycle assessment, clean production and environment friendly products.

Many economies are developing vigorously the resource recovery, regeneration, recycle and reuse of waste. Besides establishing laws and regulations, they promote technologies for resource recovery.

However, to understand the property of wastes and value added technologies is the prerequisite to resource recovery in order to maximize the advantages of resource use, to minimize impacts on environment, and so to achieve sustainable development of industries.

Waste treatment has been expanded from source control in the past into resource reuse and sustainable development following the rise of the environmental awareness across the globe.

Due to the overuse in the past few decades, resources on the earth are drying out, whether coal, petroleum or natural gas. Based on the current consumption rate, the remaining petroleum and major metals will be used up within the next five decades [22]. For this reason, waste reuse and development has become the main stream in the future.

From this point of view, EAF dust issue is considered as a resource reuse opportunity to convert all components of EAF dust into value and resource for other industries such as steelmaking and zinc smelting. Existing waste EAF dust treatment practices namely to use it in the feed material composition of cement, Rotary Kilns and as raw material in the production of concrete based building materials like bricks, tiles etc., cannot prevent leachability of heavy metals such as Cd, Co, Pb, Dioxin and others, but by using resource reuse technologies all valuable resources can be used within the limits of environmental regulations as explained above.

Besides the fact that the EAFD has been characterized and investigated very intensively in the last decades, still there is no simple, sufficient, economical, technical, and environmental solution for processing EAFD [9, 47]. However, all EAFD treatment processes, except recovering Zn and Fe, needs to immobilize the toxic metals in any product, which contain this type of waste, before landfilling. EAFD cannot be treated in conventional pyrometallurgical metallurgical process due to EAFD's fine granulometry [12, 48, 49] and the high specific surface area (between1 and 8.1 m^2 g^{-1}) [50]. In order to overcome this problem the dispersed materials are agglomerated applying the cold bond techniques using one of two known processes, pelletization or briquetting. Due to final target, EAFD with iron-bearing wastes are mixed with carbonaceous material (coal, coke, char), and binders (cement, hydrated lime, or organic binders) to produce the material known as "composite pellet" [51]. Produced pellets are dried in order to achieve sufficient green strength to enable handling, loading, high temperatures and stress during reduction in furnaces, even though the heat treatment of pellets it is an optional process. Several studies have concluded that pellets with sufficient green strength could be an appropriate charge for any kind of furnaces [51].

2. Overview of literature and available data

2.1 Steel making furnaces

Steel is an essential material for modern life. It is an alloy of iron usually containing less than 1% carbon. It is used most frequently in the automotive and construction industries. Steel can be cast into bars, strips, sheets, nails, spikes, wire, rods or pipes as needed by the intended user. Based on statistics from World Steel Association, world crude steel production was 136 million tons in May 2013, an increase of 2.6% compared to May 2012 and forecasts that global apparent steel use will increase in 2014 to reach 150million tones with growth of 3.2% [4].

Still is produced via two main routes:

- Integrated smelting involving blast furnace (BF) iron-making followed by basic oxygen furnace (BOF).
- Electric arc furnaces (EAF).

2.1.1 Blast furnace (BF):

Steel production at an integrated steel plant involves three basic steps. First, the heat source used to melt iron ore is produced. Next the iron ore is melted in a furnace. Finally, the molten iron is processed to produce steel. These three steps can be done at one facility; however, the fuel source is often purchased from off-site producers.

The blast furnace is basically a counter-current reactor; raw materials are charged into the furnace top, molten products are tapped from the bottom and gases pass from bottom to the top of the furnace. The raw materials consist of ferrous materials (iron oreas sinter or pellets), fuel (coke) and fluxes (limestone, dolomite). Other materials, like coal, oil and natural gas may be co-injected with air through the tuyeres at the base ofthe furnace. The reducing gases and heat required for the process are generated at the bottom of the furnace by combustion of the fuels. These pass upward, counter-current tothe raw materials, exiting at the furnace top after imparting heat and enabling therequired chemical reactions on the raw materials.

The main product of the blast furnace is molten pig iron and the by-products are molten slag and gas. Iron is produced via direct and indirect reduction of iron oxide. Coke is the main source of carbon, for the direct reduction, and carbon monoxide, for the indirect reduction.

The blast furnace can be divided into six zones, from the relatively cool zone at the top, to the intensely hot zone at the bottom [52]:

- Granular zone.
- Cohesive zone.
- Active Coke zone.
- Raceway.
- Deadman zone.
- Hearth.

About 70% of the iron oxides are reduced by indirect reactions with carbon monoxide and hydrogen (in a small contribution) before the cohesive zone (1250^{o}-$1300^{o}C$); whereas the remaining 30% of FeO is reduced via the direct reduction with coke within the cohesive zone [53]. The gases that exit from the top of the conventional furnace are mostly formed of 20-30% CO, 10-20% CO_2 and the rest is nitrogen [54].

2.1.2 Basic Oxide Furnace (BOF):

Molten iron from the blast furnace is sent to a basic oxide furnace, which is used for the final refinement of the iron into steel.

In the basic oxygen furnace, the iron is combined with varying amounts of steel scrap (less than 30%) and small amounts of flux. A lance is introduced in the vessel and blows 99% pure oxygen causing a temperature rise to1700°C. The scrap melts, impurities are oxidized, and the carbon content is reduced by 90%, resulting in liquid steel.

Other processes can follow secondary steel-making processes where the properties of steel are determined by the addition of other elements, such as boron, chromium and molybdenum, amongst others, ensuring the exact specification can be met.

Optimal operation of the blast furnace demands the highest quality of raw materials, the carbon content of coke therefore plays a crucial role in terms of its effect in the furnace and on the hot metal quality. A blast furnace fed with high quality coke requires less coke input, results in higher quality hot metal and better productivity. Overall costs may be lower, as fewer impurities in the coke mean smaller amounts of flux must be used.

Around 770 kg of coal are used to produce 1 ton of steel through this production route. Basic Oxygen Furnaces currently produce about 70% of the world's steel. A further 29% of steel is produced in Electric Arc Furnaces [5].

The major component of the waste produced in BOFs is slag. Because of its composition, this slag, unlike that from the blast furnace, is best used as an additive in the sintering process. As its metallic content is lower, it does not make a good raw material for the construction industry.

Hot gases are also produced by the BOF. Furnaces are equipped with air pollution control equipment that contains and cools the gas. The gas is quenched and cooled using water and cleaned of suspended solids and metals. This process produces air pollution control dust and water treatment plant sludge.

2.1.3 Electric arc furnace (EAF):

This furnace can be described as a furnace heating charged materials by the way of an electric arc. The first electric furnaces came into being in 1907, at the hands of Paul Heroult of French origin. The commercial part of these furnaces was established in the USA.

These furnaces exist in all the sizes-right, from the smallest one having a capacity of around 1 ton to the largest one having a capacity of 400 tons (approx.)

An electric arc furnace used for steelmaking consists of a refractory-lined vessel, usually water-cooled in larger sizes, covered with a retractable roof, and through which one or more graphite electrodes enter the furnace. The furnace is primarily split into three sections:

- **The shell**, which consists of the sidewalls and lower steel 'bowl';
- **The hearth**, which consists of the refractory that lines the lower bowl;
- **The roof**, which may be refractory-lined or water-cooled, and can be shaped as a section of a sphere. The roof also supports the refractory delta in its center, through which one or more graphite electrodes enter.

By recycling scrap, electric steel production makes a significant contribution toward protecting raw material resources. In addition, electric steel plants are not dependent on coal. Further increasing productivity and energy efficiency in electric steel production can be achieved by newly developed electric arc furnaces. Not only does this lower the cost per ton of steel produced but it also substantially reduces energy consumption and CO_2 emissions. With advanced modernization solutions, can be potentials for leveraging optimization in existing electric steel plants.

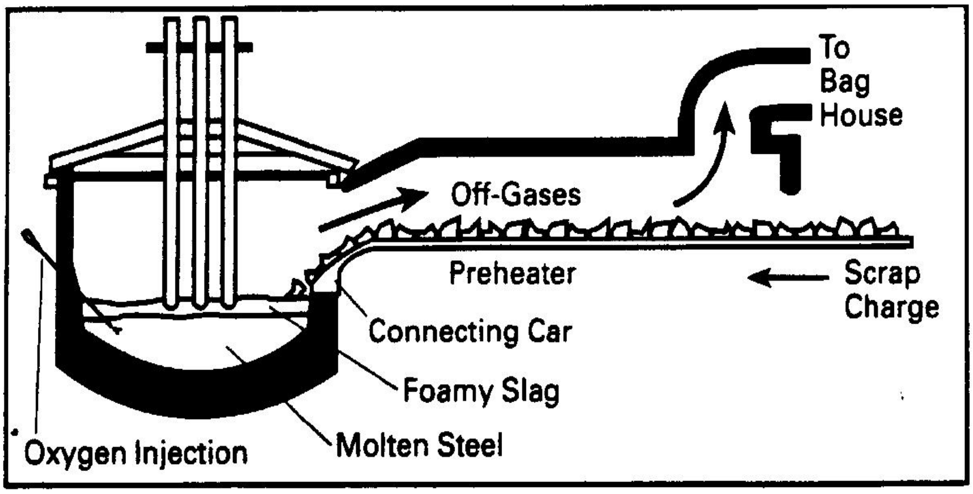


Figure (1-4). Schematic diagram of the EAF

The electric arc furnace operates as a batch melting process producing batches of molten steel known "heats". The electric arc furnace operating cycle is called the tap-to-tap cycle and is made up of the following operations:

- Furnace charging
- Melting
- Refining
- De-slagging
- Tapping
- Furnace turn-around

Details of EAF construction and the modes of operation are given later.

2.1.4 Energy Optimizing Furnace (EOF):

EOF was developed to replace the electric arc and other steelmaking furnaces. The EOF is an oxygen steelmaking process. Carbon and oxygen react to preheat scrap metal, hot metal and/or pig iron. These furnaces reduce capital and conversion costs, energy consumption and environmental pollution, while increasing input flexibility.

The energy optimizing furnace (EOF) burns coal, enhanced by oxygen injection, to generate the thermal energy needed to preheat and then melt a mixture of scrap and pig iron, or other steelmaking raw materials, in an enclosed hearth.

It is a vertical process with the hearth at the base, and chambers above in which scrap etc, is preheated by off-gases before descending into the melting zone. Steel is tapped off at the bottom of the vessel. The technology was pioneered in Brazil, but most working examples are in India, and commercial units are typically in the 500,000-600,000 tons/year range [55].

The EOF is recognized as a way of producing good quality steel with relatively low investment and operating costs, and is ideal where power networks cannot support the heavy electrical loads imposed by electric arc furnace (EAF) steelmaking. However, the EOF may be more environmentally damaging than the EAF.

The following are some important features of the EOF:

- Combined oxygen blowing (submerged and atmospheric);
- Maximum utilization of the sensible heat from all reactions;
- Scrap preheating, using the sensible heat from the waste gases;
- Production of liquid steel combining hot metal and scrap in charge;
- Possibility of using high percentage of solid charge (> 40 %);
- Special submerged tuyeres for oxygen blowing, with long life;
- Efficient wet de-dusting system;
- De-slagging and formation of second slag during blow;
- Liquid steel of highest purity, with very low level of phosphorous and sulfur;
- Very low noise level;
- Highest productivity - up to an average of 42 heats per day.

Combining the above features, the EOF presents a lower cost than any other route, combined with great flexibility with regard to the metallic charge mix.

2.1.5 Plasma Furnaces

Plasma is a partially ionized (up to 50 %) gas that contains electrons, ions, energized molecules, dissociated molecules, neutral molecules, and atoms (→Plasma Reactions). The plasma operates at atmospheric pressure and is sufficiently conducting to permit stable transfer of electric power between two or more electrodes. The plasma attains temperatures >2000K (e.g., 10 000 – 20 000K for an argon plasma operated at an arc voltage of 25V and current of 1.5 kA).

Basic Principles and Construction:

The principal difference between plasma furnaces and arc furnaces is the use of a plasma torch instead of electrodes. In a plasma torch thermionic electrons are emitted from a cathode and accelerated towards the anode. They collide with gas molecules and ionize them. The positively charged gas ions are accelerated in the opposite direction towards the cathode with which they collide, releasing their energy and hence sustaining the thermionic emission.

Depending on the type of torch and its construction materials, water cooling may be applied. Various AC or DC torches are available; they include transferred arc, nontransferred arc (Figure 1-5), and superimposed arc [56, 57].

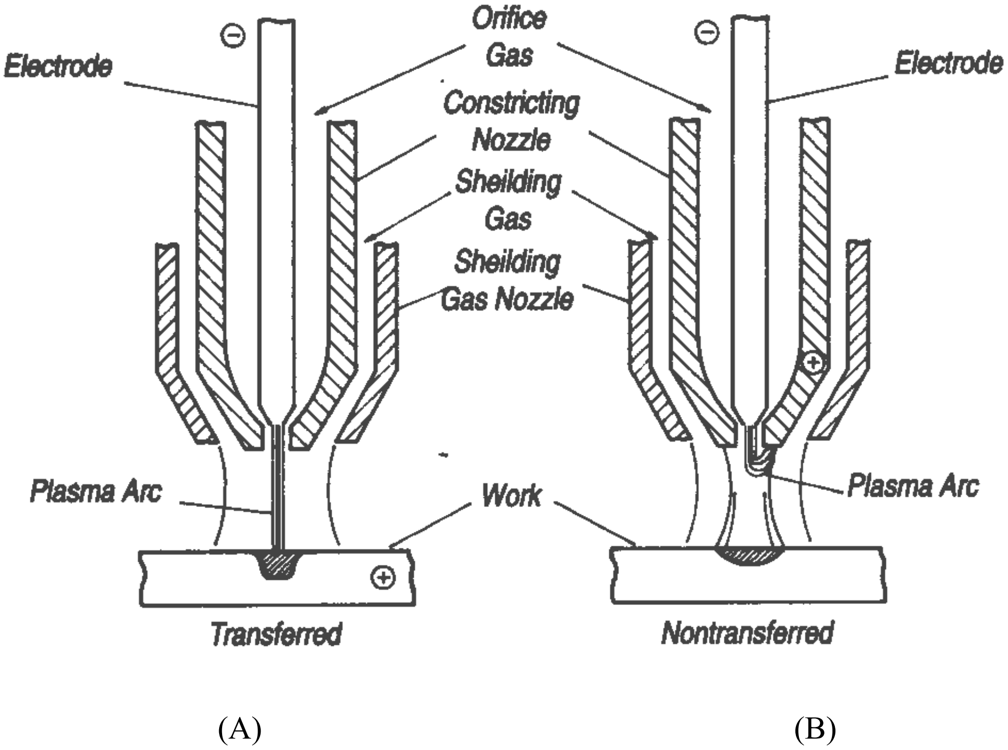


Figure (1-5). (A) Transferred arc torch (B) nontransferred arc torch

Furnace construction is similar to that of arc resistance and arc furnaces. Refractory and other components are selected to suite the specific application.

Plasma furnaces have been employed commercially, e.g., to produce ferrochromium, to melt steel scrap and to recover valuable metals from steel flue dust.

2.2 Electric Arc Furnace (EAF) Steelmaking:

Steel is 100% recyclable, the recycling of scrap metal is an integral part of modern steelmaking, improving the industry's economic viability and reducing environmental impact. The recycling of steel scrap reduces the need for iron ore extraction, significantly reducing CO_2 emissions, energy and water consumption and air pollution.

Figures from the Bureau of International Recycling show that total world steel scrap use increased 7.6% in 2011 to reach 570 million tones. The BOFs process uses up to 30% recycled steel (scrap) and around 90-100% is used in EAFs production [58].

As a result of these efficiencies, steel scrap is increasingly being regarded as a raw material for manufacturing new products worldwide.

Steelmaking from scrap metals involves melting scrap metal, removing impurities and casting it into the desired shapes. The EAFs melt scrap metal in the presence of electric energy and oxygen. The process does not require the three step refinement as needed to produce steel from ore. Production of steel from scrap can also be economical on a much smaller scale. Frequently mills producing steel with EAFs technology are called mini-mills, which melt scrap metal via the heat produced by an electric arc.

The Electric Arc Furnaces process, or mini-mill, do not involve iron-making. It reuses existing steel, avoiding the need for raw materials and their processing. The furnaces are charged with steel scrap, it can also include some direct reduced iron (DRI) or pig iron for chemical balance.

In 2010, around 400 million tons of electric steel were produced worldwide, just fewer than 29 percent of total steel production. The share is close to 50 percent in Europe and to some extent even significantly higher in North America, Africa, India and the Near East [59].

2.2.1 Scrap and steel production:

The recycling of scrap metal is an integral part of modern steelmaking, improving the industry's economic viability and reducing environmental impact. The recycling of steel scrap reduces the need for iron ore extraction, significantly reducing CO_2 emissions, energy and water consumption and air pollution.

As a result of these efficiencies, steel scrap is increasingly being regarded as a raw material for manufacturing new products worldwide. Ferrous scrap (iron and steel) has become a globally traded commodity. The increased demand for steel scrap is reflected in recent trade statistics.

The United Nations Commodity Trade Statistics Database shows that the volume of global scrap exports increased from 9.3 million tons in 1990 to 106 million tons in 2011. Figures from the Bureau of International Recycling show that total world steel scrap use increased 7.6% in 2011 to reach 570 million tons [58].

The globalization of the ferrous scrap market, however, also places stresses on the system. The long lifespan of steel products means that the amount of steel available for recycling cannot keep up with the current world demand for new steel products. With steel, structures can last longer than 60 years and cars often last longer than 12 years; steel products can be seen as scrap-in-inventory, meaning that the steel will not be ready for recycling until the long life of the product comes to the end.

A positive aspect of steel is the ease of recycling when products finally do reach the end of their life. The ability to recover and collect old steel products for subsequent recycling is greatly enhanced by the inherent magnetic properties of steel; consequently, a large tonnage of steel becomes available for recycling every year.

Figures from the US Census Bureau and the US International Trade Commission demonstrate that the US is the world's largest exporter of ferrous scrap; exporting nearly 23 million tons of iron and steel scrap in 2011. Globally, China, Taiwan, South Korea, India, Canada, and Turkey are the largest markets for exports of US steel scrap in that same period.

Ferrous scrap exports from the EU to third countries reached a record high in 2012. The 27 member states exported around 19.22 million tons of iron and steel wastes and scrap valued at €6.8 billion/year to countries outside the Union (extra-EU trade), according to preliminary figures released by the European Statistical Office. The export volume exceeded the 2011 amount of 18.81 million tons by 407,000 tons or 2.2%. The UK was by far the largest exporter of the EU-27, shipping nearly 5.2 million tons of ferrous scrap outside the EU. The most important destination country for EU ferrous scrap was Turkey. At 11.05 million tons and a value of €3.3bn, around 58% of all extra-EU ferrous scrap exports headed to this country (2011: 9.97 million tons, €3.1billion).

North America is also one of the largest consumers of its own steel scrap, recycling more than 70% of that scrap domestically, with mini-mills being the primary source of recycled steel. Mini-mills use electric arc furnaces, which melt scrap metal via the heat produced by an electric arc. US producers Nucor (one of the world's largest steel producers), as well as one of its competitors, Commercial Metals Company (CMC) use mini-mills exclusively. Since the electric arc furnace can be easily started and stopped on a regular basis, mini-mills can follow the market demand for their products easily, operating on 24 hour schedules when demand is high and cutting back production when sales are lower. “This high level of scrap consumption is a reflection of the steel industry’s commitment to conserving energy and natural resources,” said Gregory Crawford, executive director of the Steel Recycling Institute in North America. “Scrap steel is used in everyday products, including packaging, appliances, automobiles and construction. Each year, more steel is recycled in North America than paper, aluminum, plastic and glass combined.”

This flow of scrap also faces challenges in the form of trade restrictions. The Organization for Economic Cooperation and Development (OECD) reported in 2012 that North American and European ferrous scrap is traded openly, but that about 19 percent of the scrap trade is burdened by various trade restrictions [56]. The 2012 OECD report noted that “waste and scrap exports are restricted in many parts of the world. Waste and scrap trade involving iron and steel and non-ferrous base metals (copper, aluminum, lead and zinc) tends to be more regulated than trade involving other metals.”

The OECD found that, in 2009, at least 19% of scrap of iron and steel, exported by a total of 34 countries, was subject to export restrictions. “Export restrictions dampen trade flows,” stated the report [58]. “In fact, some exports actually will not take place due to the very fact that export restrictions are in place. Export activity would be higher if restrictions did not exist.”

The rationales that governments cite most frequently as motivating their use of the restrictions include safeguarding domestic supplies, controlling illegal exports, and protecting local industry. Non-automatic export licensing, export taxes and other export prohibitions were among the measures used to regulate the export of iron and steel scrap, according to the OECD.

Due to the high value of metals, scrap has been recycled whenever possible since the existence of the metal production itself. Given the chemical and physical properties of metal, the metal scrap can be recovered becoming secondary raw material which can, in almost all applications, compete with virgin material. Although scrap can be processed with high efficiency and little loss, this highly depends on the cleanness of the scrap, which is determined by separate collection and scrap treatment. Different scrap types (defined by scrap source) are the bases for the collection system and technologies employed in scrap processing, as well as being the starting point of the scrap sector.

2.2.1.1 Scrap source

Generally, steel scrap can be divided into three categories:

A) Home scrap (plant scrap)

B) Process scrap (prompt scrap)

C) Obsolete scrap (capital scrap)

A) Home scrap is generated in steel mills during the production of steel. It is relatively pure and its chemical composition is known, so it can be easily recycled.

B) Process scrap is generated in the manufacturing of products made from steel. This scrap occurs during production of both industrial and consumer end products. Process scrap is available for recycling in relatively short time after its generation. However, scrap preparation and classification are essential before melting. The rate of process scrap generation will be decreasing due to the better steel utilization in steel processing.

C) Obsolete scrap consists of iron or steel products discarded after the end of their service life. Post-consumer steel products include old passenger cars, steel cans, electric appliances and other items. Obsolete scrap is often mixed or coated with other materials, such as copper, zinc, tin, glass and plastics. For this reason the content of tramp elements in obsolete scrap is usually high. Moreover, the chemical composition of obsolete scrap fluctuates widely depending on its origin and degree of processing. Obsolete scrap, especially the one originating from old passenger cars, is usually processed by shredding.

2.2.1.2 The key sources of scrap:

1) Vehicles and transportation:

The automobile industry is by far the largest market for metals application and the largest source of metals scrap. When a car has come to its end of life, it is collected and dismantled. The amount of scrap that is collected depends on the yearly number of end-of life- vehicles (ELVs) and their metals' content. The average lifetime of vehicles is estimated to be 12-15 years, however many vehicles may be used longer.

2) Construction and buildings:

In some countries, especially those without an automobile industry, the building and construction sector is probably the largest market for metals.

3) Packaging materials:

Metal packaging waste is a large short term source of scrap. Most of the products used in food packaging have less than one year of life time.

4) Cables and wires:

When buildings and old installations need to be demolished, renewed and/or upgraded, scrap is generated. Since the current demand is mainly driven by new installations in developing countries, the available scrap from this sector may expect to rise in the future.

5) Electrical and electronic equipments (EEE):

The electrical and electronic waste is growing very fast, this rapid growth rate is due to the fast pace of technological development, especially in information technology which has resulted in the more frequent replacement of electrical and electronic equipment by industry

6) Equipment and appliances:

This category covers a wide range of products from home appliances, such as fridges, washing machines, ovens and microwaves, etc. to industrial and agricultural machinery and structure, such as earth-moving and quarrying equipment, cranes, farm vehicles and machinery, storage tanks, tools, etc.

2.2.2 Electric arc furnaces:

Electric Arc Furnace (EAF) is a steel making furnace, in which steel scrap is heated and melted by heat of electric arcs striking between the furnace electrodes and the metal bath. Two kinds of electric current may be used in Electric Arc Furnaces: direct (DC) and alternating (AC). Three-phase AC Electric Arc Furnaces with graphite electrodes are commonly used in steel making.

The main advantage of the Electric Arc Furnaces over the Basic Oxygen Furnaces (BOF) is their capability to treat charges containing up to 100% of scrap, easy temperature control, deep desulfurization and precise alloying.

About 33% of the crude steel in the world is made in the Electric Arc Furnaces. The capacity of Electric Arc Furnace may reach 400 ton [60].

2.2.2.1 Structure of EAFs:

The furnace consists of a spherical hearth (bottom), cylindrical shell and a swinging water-cooled dome-shaped roof. The roof has three holes for consumable graphite electrodes held by a clamping mechanism, the mechanism provides independent lifting and lowering of each electrode. The water-cooled electrode holders serve also as contacts for transmitting electric current supplied by water-cooled cables (tubes). The electrode and the scrap form the star connection of three-phase current, in which the scrap is common junction. The furnace is mounted on a tilting mechanism for tapping the molten steel through a tap hole with a pour spout located on the back side of the shell. The charge door, through which the slag components and alloying additives are charged, is located on the front side of the furnace shell. The charge door is also used for removing the slag (de-slagging).

The scrap is charged commonly from the furnace top. The roof with the electrodes is swung aside before the scrap charging. The scrap arranged in the charge basket is transferred to the furnace by a crane and then dropped into the shell. The scheme of an EAF is presented in the figure (1-6).

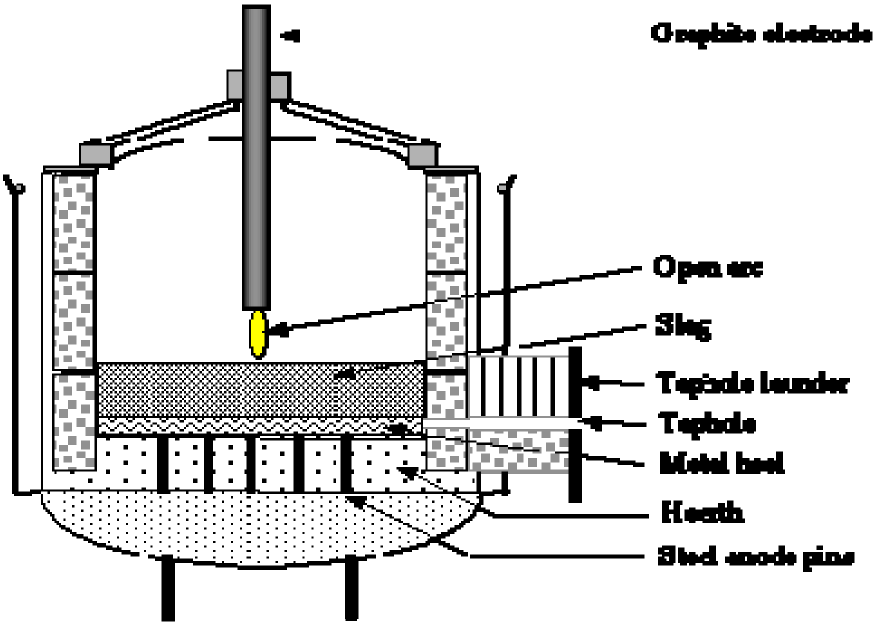


Figure (1-6). Schematic of an Electric Arc Furnace [62]

2.2.2.2 Refractory lining of EAFs:

Refractory linings of Electric Arc Furnaces are made generally of resin-bonded magnesia-carbon bricks. Fused magnesite grains and flake graphite are used as raw materials. When the bricks are heated the bonding material is cooked and turns into a carbon network binding the refractory grains, preventing wetting by the slag and protecting the lining from the erosion and chemical attack of the molten metal and slag [60].

2.2.2.3 Chemical and physical processes in EAFs:

A) Melting:

Melting process starts at low voltage (short arc) between the electrodes and the scrap. The arc during this period is unstable. In order to improve the arc stability small pieces of the scrap are placed in the upper layer of the charge. The electrodes descend melting the charge and penetrating into the scrap forming bores. The molten metal flows down to the furnace bottom.

When the electrodes reach the liquid bath the arc becomes stable and the voltage may be increased (long arc). The electrodes are lifting together with the melt level. Most of scrap (85%) melts during this period. Temperature of the arc reaches 6300ºF (3500ºC) [60].

B) Oxidizing stage:

At this stage excessive carbon, phosphorous, silicon and manganese oxidize. The process is similar to that in Basic Oxygen Furnace. Basic oxidizing slag composed of lime (CaO) and iron ore (FeO) is used during the oxidizing period. Gaseous oxygen may be blown into the melt for additional oxidizing iron oxide causes increase of Oxygen content in the molten steel according to the reaction:

$$\mathbf{FeO = Fe + O} \qquad (1\text{-}1)$$

Oxygen dissolved in the melt oxidizes carbon, phosphorous, silicon and manganese:

$$\mathbf{C + O = CO} \qquad (1\text{-}2)$$

$$\mathbf{Si + O_2 = SiO_2} \qquad (1\text{-}3)$$

$$\mathbf{Mn + 1/2O_2 = MnO} \qquad (1\text{-}4)$$

$$\mathbf{2P + 5/2O_2 = P_2O_5} \qquad (1\text{-}5)$$

Carbon monoxide partially burns in the atmosphere:

$$\mathbf{CO + O_2 = CO_2} \qquad (1\text{-}6)$$

The formed oxides are absorbed by the slag. CO bubbles floating up through the melt result in refining of the steel from non-metallic inclusions and hydrogen removal. Gaseous products CO and CO_2 are removed by the exhausting system.

The oxidizing slag enriched with phosphorous and other oxides formed during this period is removed from the furnace to a slag pot (de-slagging) [60].

C) Reducing stage:

New slag composed mainly of lime CaO, CaF_2 (as slag fluidizer) is added at this stage for formation of basic reducing conditions. The function of this slag is refining of the steel from sulfur and absorption of oxides, formed as a result of deoxidation ("killing"). The excessive oxygen dissolved in the melt during oxidizing period is removed by metallic deoxidizers Mn, Si, Al:

$$\mathbf{Mn + O = MnO} \qquad (1\text{-}6)$$

$$\mathbf{Si + 2O = SiO_2} \qquad (1\text{-}7)$$

$$\mathbf{2Al + 3O = Al_2O_3} \qquad (1\text{-}8)$$

Basic reducing slag is favorable for desulfurization in accordance to the reaction:

$$\mathbf{S + CaO = CaS + O} \qquad (1\text{-}9)$$

Oxide and sulfide non-metallic inclusions are absorbed by the slag. Alloying elements (Cr, Ni, Mo, V, etc.) are added after deoxidation. In many cases the processes of "killing" (deoxidation), desulfurization, alloying and final heating are performed outside of the furnace - Ladle refining [60].

2.2.2.4 Operation of an Electric Arc Furnace:

It consists of charging, melt down period and refining. The large baskets containing heavy and light scrap are preheated through the exit gas. Burnt lime and spar are added to help early slag formation. Iron one or mill scale may also be added if refining is required during melt- down period.

The roof is swung off the furnace, and the furnace is charged. Some furnaces are equipped with continuous charging. Hot metal is also charged as per the requirement.

In the meltdown period, electrodes are lowered and bored into the scrap. Lower voltages are selected in order to protect the roof and walls from excessive heat and damage from the arcs. Once the arc is shielded by scrap, voltage is increased to form molten metal pool to reduce the meltdown period. During meltdown period, silicon, manganese and carbon oxidizes. Also oxidizing and limy slag is produces which promotes dephosphorization as well. Melt- down time depends on

- Arc conditions: larger arc requires lower current and lower heat losses
- Deep or shallow bath: deep bath shortens the meltdown period.

Refining continues even during melting. Removal of phosphorus must be complete before the rise in temperature and carbon boil.

The single oxidizing slag practice is employed when removal of sulphur is not required. When both P and S are required to be removed double slag practice is used. In double slag practice, oxidizing slag is removed and reducing slag is formed after deoxidation with ferrosilicon or ferromanganese or aluminum. Reducing slag helps to avoid loss of alloying elements.

Once the bath chemistry and its temperature are attained, heat is deoxidized and finished for tapping.

2.2.3 Emission control in EAFs.

Electric furnace production will produce a lot of smoke, and serious pollution of the natural environment of the production site and the plant, more importantly, is directly harm the operating health of workers, the electric furnace with the charge back charge, scrap miscellaneous materials, waste oil . A higher proportion of dirt and oxide, the smelting process with the electric arc steelmaking furnace, converter, open-hearth, its large number of flue gas and a higher concentration of dust generated by the chemical reaction between the molten iron oxide slag.

Scrap containing dust, oxide particles, residual substances, these substances will be generated with the hot gas stream and the molten steel in the melting process of the bubbles floating in the explosion, some residual oil and oxidation in the process of dumping of electromagnetic stirring and liquid steel, scrap kinds matter and other substances release a lot of smoke, dust concentration and flue gas temperature is high. In addition, the various stages of the flue gas, soot emissions are changing; the flue gas also contains small particles of iron oxide dust, dust of manganese oxide, silicon oxide dust, and other oxides, etc.

Second, the design principles and indicators, provided that ensure reach the premise of "GB9078-1996 industrial furnace smelting region emission standards", "reliable operation does not affect the smelting process and workers to operate" is considered as an important design goal, while minimizing operating costs, savings Engineering investment. If steelmaking furnaces feeding artificial feeding from the furnace upper portion, molten steel after smelting is inclined from the front portion of the furnace, the material, in order to not affect the normal process and operational requirements, we believe that the ideal way to the collecting, is the use of thermal processes mushroom cover as catching dust. In order not to affect the human operator and feeding, the umbrella cover is movable, and the material is stainless steel. The trap cover has been used in the multi-the Taichung frequency steelmaking furnace flue dust collection, the trapping efficiency is high, and the flue gas temperature is low.

Key equipment in the system, the effect of conditions directly affect the success or failure of the entire system, so every aspect of the design, manufacture, installation, commissioning and running precipitator need to be carefully arranged. In order to improve the job conditions and plant self-natural environment, equipped with three sets of bag filter system is now ready for its electric furnace [61].

2.3 Electric arc furnace dust (EAFD):

Steel production by electric-arc furnace (EAF) technology has been increasing in importance over the past 20 years at the expense of traditional open hearth and basic oxygen converter technology. When steel is produced using an electric arc furnace, about 15 - 20 kg of dust is formed per tons of steel [6]. This dust is considered as a toxic waste due to its content of heavy metals. It is estimated that the world-wide total production of EAF dust could be as high as several million tones, all of which must be treated, recycled or land-filled.

2.3.1 Mechanism of dust formation.

The dust collected in bag filters at the end of the EAF fume extraction system is the final product of a series of phenomena, such as the emission of particles from the steel bath, the transport of these particles from the steel bath, the transport of these particles by the gas flow in the fume extraction system, the in-flight physico-chemial transformations they undergo, etc (Figure (1-7)). The results of the morphological analysis of the EAF dust show that the dust formation process takes place in two steps: first, the emission of dust ” precursors”, i.e. vaporous, metal droplets, and solid particles, inside the furnace; second, the conversation of those precursors into dust by agglomeration and physico-chemical transformations.

Dust formation is strongly linked to the process which can be divided into five steps:

1. Furnace charging: the scrap and the additives (lime, coal, etc.) are loaded into special charging buckets which are then emptied into the furnace;
2. Melting: an electric arc is created between the graphite electrodes and scrap which entails the charge melting and the formation of a steel bath covered by a slag of layer, volatile solute species (e.g.) zinc begin to be removed;
3. Refining: in this step of the process, phosphorus is removed from the steel bath by interfacial reactions between the slag and liquid metal, injection of oxygen promotes the decarburization reaction with dissolved carbon and bubbles of carbon monoxide (CO) are formed, which helps to remove other dissolved gases;
4. Slag forming: the CO-bubbles crossing the slag layer make it foam, the foaming process being enhanced by the addition of coal powder;
5. Casting: after the composition and the temperature of the bath have been controlled, the liquid steel is cast.

The projection of liquid steel and slag droplets by bursting of CO bubble has been recognized as the principal mechanism of dust emission in EAF.

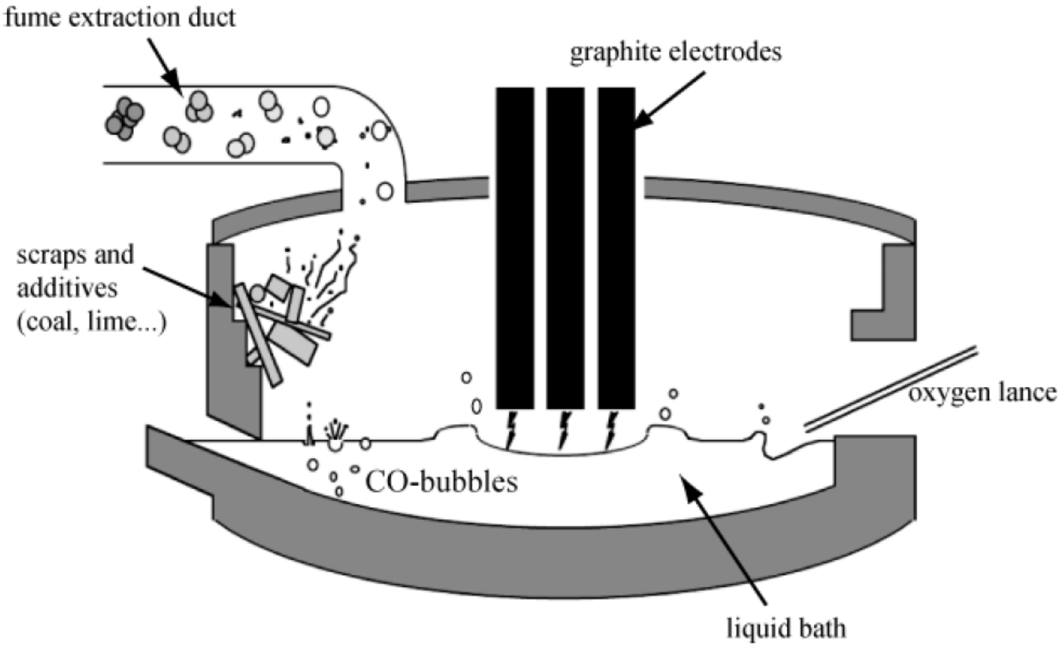


Figure (1-7). Schematic representation of an Electric Arc Furnace

Very few studies about bubble-burst at the surface of liquid metal have been reported [62]. However, in order to understand the phenomenon, useful results and observations can be found in the abundant literature about the air-water system. From these studies, the bubble/burst process can be split up to three steps which give rise to two types of droplets (Figure (1-8)).

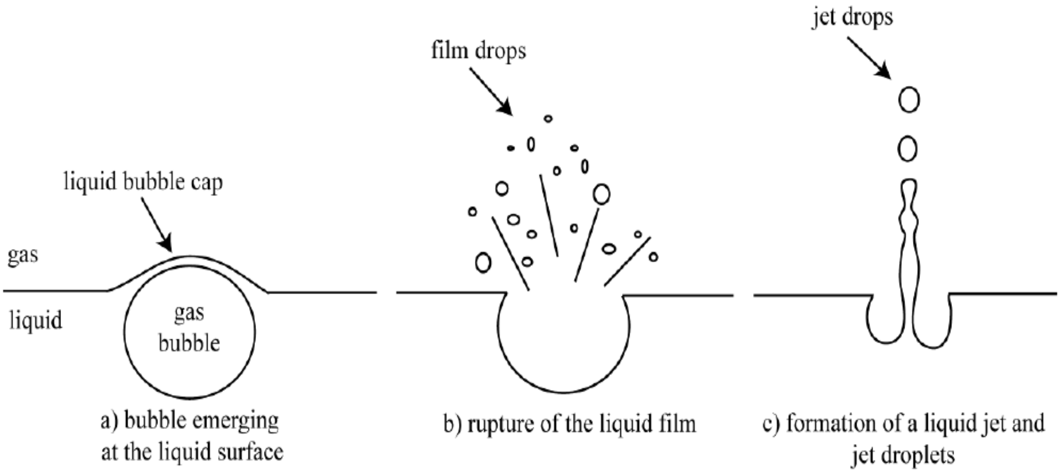


Figure (1-8). Schematic representation of the burst of a bubble of a liquid surface

When emerging at the surface (Figure (1-8-a)), a bubble lifts up a liquid that progressively gets thinner under the influence of drainage, when the bubble comes to rest. The shape of a bubble floating at the surface of a liquid can be determined by following the approach proposed by [63].

As the film reaches a critical thickness, it breaks up and the bubble cap is disintegrated into fie droplets called film drops (Figure (1-8-b)). Many authors [64-67] studied the number and size of film drops as a function of the bubble size. The number is proportional to the surface of the film. The size distribution is wide: from 0.3 to 500µm.

After the disruption of the bubble cap, the cavity remaining at the liquid surface closes up; creating an upward Rayleigh jet that is unstable and can break up into droplets usually called jet drops (Figure (1-8-c)). The number of jet drops never exceeds ten and decreases when the bubble size increases [64, 67]. Their sizes have been found to range between 0.1 and 0.18 times the diameter of their parent bubble for air-water system.

Jet drop come from the disintegration of the upward jet created after the removal of the bubble cap. Their number increases when the bubble size decreases, and their size represents 12 to 18% of the parent bubble size. The size of CO-bubbles formed in EAF remains little known. However, analysis of foaming slag samples and numerical calculations indicate that their sizes are probably between 2 and 20 mm [7]. Jet drops are not exhausted by fume extraction system and are likely to fall back into the steel bath.

Jet drops can thus hardly contribute to dust formation from bubble burst in EAF. Film drops are emitted during the disintegration of the liquid cap high covers the bubble at the surface of the bath. Their morphology and size range are very close to those of the particles contained in EAF dust. The amount of projections produced by bubble burst in EAF varies between 0.016 and 0.028 kg m^{-3} [7].

2.3.2 Physical and chemical characteristics of EAFD:

There are a number of factors that lead to a considerable variation in the properties of the EAFD. For instance, EAFD sources could differ from one plant to another and from one melt to another, and also, type and amount of scrap material used in the electric arc furnace.

The EAF dust forms as a result of volatile metals like zinc and lead, passing into the vapor phase at the operating temperature of the furnace and being oxidized and cooled in the extractive air flow. These metals are therefore found in the resulting dust both as free oxides and in the form of composite structures with iron oxides. These latter compounds are notably of the spinel type, MFe_2O_4 (M = Fe, Zn, Ni, Mn or Cd). Overall, EAF dusts contain major elements of the type iron, zinc, calcium and silicon (these last two from the degradation of the refractories) in the form of simple or mixed oxides, and minor elements like copper, manganese, chromium, cadmium and lead present in the scrap iron raw material or introduced as additives. The dusts also generally contain significant amounts of chlorides [6].

The morphology of the EAF dust was observed from SEM analysis and it was concluded that the dust generally contains very tiny (less than 2 μm) spheroids, some of which agglomerate into relative large particles (10-100 μm) and composition variations of particles in different sizes. The small particles mainly consist of $ZnFe_2O_4$ and Fe_3O_4, which fill about 80-90% of the whole dusts. Medium size particles are metal oxides or silicates. The big particles are mostly Fe enriched silicates or oxides and there are fine oxides particles attached on them. In general, EAF dust contains mainly of $ZnFe_2O_4$, Fe_3O_4, FeO, ZnO, minor amount KCl, Fe-Al-Ca-Zn-Mg oxides, and trace amount of Fe_2O_3 and various silicates. However, nearly none of these compounds was found to be pure in composition. Element substitution for each other is common in these compounds [68]. For example, in a typical $ZnFe_2O_4$ particle, 1.33 % Ca, 1.2 % Mg, 1.78% Mn was observed to substitute for Zn and Fe. These substitutions indicate the complexity of the dust compositions.

The results of the X-ray diffraction phase analysis show that the basis of the examined EAF dust samples is made of a mixture of metal oxides, silicates and sulphates. It has been done more analyses of EAF dust to point out metals content in more integrated iron and steel work. All concerns are focused on iron and zinc since they are the most abundant valuable elements in the dust [24].

The most common phases found in the EAFD are; franklinite ($ZnFe_2o_4$), magnetite (Fe_3O_4) and zincite (ZnO). Most of the metals present in the dust, such as iron, are present in several valence states, which additionally complicates the development of suitable processes for the treatment of EAF dust. For example, iron is present as metallic form and as metal oxides of various oxidation states. The chemical complexity of the dust is enhanced by the amphoteric nature of these metals, the reducing or oxidizing conditions in the furnace and the presence of large quantities of metal oxides such as calcium oxide and magnesium oxide. These alkaline earth metal oxides also make the EAF dust suspensions highly alkaline [6].

2.3.3 EAFD and environment:

Electric arc furnace dust (EAFD) is one of the wastes generated by the steelmaking industry. The waste is in the form of fine powder accompanied by fume gas during steel scrap melting in an electric arc furnace (EAF) and collected in the bag house for further treatments. Collecting the smoke and the dust, that emits frome electric arc furnaces in special filters, it was the first step to protect the environment. After reviewing the results of tests and analyzes of EAFD, the results showed that the dust contains high amount of zinc and small amount of some heavy metals, i.e. chromium, mercury, cadmium, and lead. Therefore, the environmental protection agencies have classified the EAFD as a hazardous solid waste, 10 09 09 HM or, as a flue gas dust containing dangerous substances, K061 [69]. This leads to the incapability of EAFD being disposed of in landfills and should not be allowed in the environment untreated.

Electric arc furnace dust from steel production is generated in considerable amounts worldwide. It contains some heavy metals which could leach to groundwater and contaminated the environment and human health. With the large increase in steel production using EAF technology during the last few years, the problem of managing EAFD is now a serious environmental challenge both locally and internationally.

According to US Environmental Protection Agency, the constituent concentrations measured in EAFD by Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), must not exceed any of the levels listed in table (1-2) [70].

Table (1-2). Maximum Constituent Concentrations in TCLP Extracts

Element	**TCLP limit, mg/L**
Antimony	0.206
Arsenic	0.0936

Element	**TCLP limit, mg/L**
Barium	55.7
Beryllium	0.416
Cadmium	0.15
Chromium(total)	1.55
Lead	5.0
Mercury	0.149
Nickel	28.3
Selenium	0.58
Silver	3.84
Thallium	0.088
Vanadium	21.1
Zinc	280

Source: [68].

2.3.3.1 EAFD Element Toxicity and Biological Effects:

It is not only radioactive elements that pose a major risk to health and the environment. The main emphasis of this part is to highlight the many EAFD elements and compounds that are particularly hazardous and which may pose a considerable threat to the environment and to human and animal health if not treated in a sensible manner. Paradoxically, most EAFD toxic elements in trace quantities are also essential to healthy living.

Heavy metals in particular pose a significant threat, although many of the lighter metals and elements also constitute a significant hazard. The extensive industrial use over many years of metals such as lead, mercury, cadmium, chromium, nickel, copper, zinc and arsenic, has led to these elements being found in the environment in concentrations far higher than would normally be found in nature.

Exposure to these elements beyond certain limits can lead to many health-related problems. This has led to a much greater awareness and understanding of health and environmental issues, and significant steps are now being taken to control the use of heavy metals and other potentially toxic elements over the whole life cycle, ranging from the original mining and smelting of ores to the production and application of materials and components, and ultimately to their recycle or disposal.

When formulating risk assessments, a realistic estimate of exposure to a given pollutant is often the weakest link. The use of biological markers, defined as observable end points in a series of events leading from environmental exposure to ill health, once verified through laboratory studies, can aid in quantifying actual effects [71]. A typical exposure biomarker would be the concentration of an element, for example lead, in the blood of an individual, whilst an effective biomarker would be the biological response to this exposure.

Biological exposure to chemical elements or compounds may be through external contact with the skin through which certain compounds may subsequently be absorbed into the bloodstream either by direct diffusion through the skin or via the presence of cuts or wounds. Direct internal exposure may be as a result of ingestion of food or particulate matter such as dust, or by inhalation into the lungs of contaminated air. Once in the bloodstream, these elements will be transported around the body where they may accumulate in specific organs, to be slowly eliminated through urine or faeces. The overall toxicity of a given substance and its effect will depend on a number of factors including its absorption, distribution, metabolism and excretion by the body. In assessing the risk to an individual such factors as age, sex, nutrition and general health, genetic and susceptibility influences, and the nature and duration of exposure, need to be taken into account. Several heavy metals pose particular health risks, with Pb exposure, for example, leading progressively to delirium, paralysis, kidney failure, coma and death at levels > 429 µg/L in the blood. Heavy metal ions including lead are also thought to affect enzymes by mimicking and thereby inhibiting the effect of essential elements such as Mg, Ca, Fe, Cu and Zn [71].

One particular source of metal exposure commonly occurs in industrial facilities such as foundries, shipyards and metal-working plants involving welding, brazing or soldering operations, where metals are melted or heated to high temperatures, consequently giving off metal or oxide fumes. Symptoms described as ‘metal fume fever’ may be caused by exposure in this way to Zn, Cu, Mg, Cd, Ni, Al, Mn, Be, Ag, V, etc. These metals also find their way into many of the wastes associated with metal fabrication and finishing processes and may therefore pose an environmental threat beyond the facility itself, particularly as in the past many wastes of this nature have been disposed of with very little thought of the environmental consequences. Another major source of heavy metal contamination arises from the burning of fossil fuels. Coal fired power stations have in the past released significant quantities of these metals into the environment, as has the use of coal in residential areas as a source of heat.

However, although most elements pose a biological threat in one form or another, it should be borne in mind of course that many of the (nonradioactive) elements are in fact absolutely essential in trace or greater quantities for biological health. In this respect there is therefore a balance to be made.

The detailed hazards associated with toxic materials are generally well known and documented, and therefore only a brief summary of some of the more serious consequences of exposure are provided here as a guide to the types of effect that can be expected from elements and compounds present in EAFD.

1. Vanadium (V):

Vanadium and its compounds are not usually regarded as being particularly dangerous in the quantities normally found in the environment, although there may be some dependence on oxidation state. Acute exposure to vanadium, however, particularly in the form of vanadium pentoxide, can lead to heart disease, damage to the nervous system, the kidneys and the liver, together with inflammation of the stomach and intestines. There is also evidence for oxidative damage to biological systems, with the formation of free radicals. Symptoms resulting from exposure may include, trembling and paralysis, headaches, dizziness and nose bleeds. It is found in nature in the form of many different minerals and soils and is also present in coal - and oil - related deposits. It is also used as an alloying addition to steel and titanium alloys, and is employed in nuclear reactors as a structural material due to its low neutron absorbing properties and high temperature creep resistance. It is also employed as a catalyst in the manufacture of sulphuric acid and in the glass industry as a colorant.

2. Chromium (Cr):

Although chromium metal itself is usually regarded as nontoxic, when present in compounds its toxicity is known to be very dependent on its oxidation state, with some states posing little if any potential risk, whilst other states are highly toxic. Chromium (III), for example, is thought to be an essential trace element and occurs naturally in many vegetables and fruit, in addition to cereal grains and meats. It is believed to pose a toxic threat only in relatively high concentrations; however, it may be reduced to Cr (II) in some biological processes, where it can then react with hydrogen peroxide to produce hydroxyl radicals. Chromium (VI), however, is known to be both toxic and carcinogenic, with exposure implicated in increased risk of lung cancer. Cellular uptake of Cr (VI) is followed by reduction to Cr (III) with the formation of reactive Cr (V/IV) intermediates which can lead to genetic damage and damage to chromosomes and DNA [72]. Oxidative stress is also believed to play a major role in its toxic behavior. Exposure can lead to allergic reactions, respiratory problems, a weakened immune system, and kidney and liver damage. Excessive exposure may ultimately lead to death. Work exposure in air should be kept at less than 0.1 mg/m^3, whilst concentrations in drinking water should not exceed 0.1 mg/L. Chromium is a major constituent of stainless steels and superalloys, and is also employed extensively in chromium compounds used by the electroplating, leather tanning, textile and paint industries; it is also used as a corrosion inhibitor. The oxide is used as a colorant in the glass industry. A major occupational source of exposure results from welding operations involving stainless steel. Contamination of soil by Cr can result from industrial activities.

3. Manganese (Mn):

Manganese is an essential trace element, being a constituent of many enzymes required for normal amino acid, lipid, protein and carbohydrate metabolism [73]. It is also an essential nutrient for maintaining the proper function of many biological processes including blood clotting. Although manganese deficiency is rare, overexposure can result in toxic effects, with the brain being particularly vulnerable, excessive exposure leading to symptoms similar to Parkinson ’ s disease. Exposure to concentrations of Mn in drinking water in excess of 300 µg/ L has been shown to have an adverse effect on the mental performance of children. Manganese is commonly used in many industries including as an alloying addition to steel, in batteries and glass and ceramics manufacture, and in welding operations.

4. Nickel (Ni):

The literature on the effects of nickel exposure is very well documented [74]. Nickel is not recognized as an essential element in human biochemistry and it is not clear how it is metabolized. All nickel compounds are classified as carcinogenic, although nickel metal itself is not. Excessive exposure to nickel can result in lung embolism, lung fibrosis, respiratory failure, asthma, bronchitis, heart disorders and allergic reactions, and it also increases the risk of lung, nose, larynx and prostate cancer, with typical symptoms including dizziness, itching, skin ulceration, swelling of the legs, and vomiting. Exposure to Ni has been known specifically to lead to lung and nasal cancers in refinery workers. It can also induce allergic reactions on skin contact, with 'nickel dermatitis' a well known skin condition. It is also responsible for oxidative stress due to the production of free radicals, it can trigger changes in intracellular calcium levels, and it may damage DNA. At high doses, nickel may even cause death; for example, the oral and intraperitoneal LD_{50} doses of nickel acetate and nickel chloride in rats is of the order of 350 and 11 mg/kg, respectively. It occurs naturally in the environment in minerals but only in relatively small concentrations, with industrial applications involving nickel leading to much higher concentrations in the environment. Power stations and municipal incinerators, for example, release nickel into the environment, as does metal extraction and smelting operations. In addition, environmental nickel contamination occurs through the mining, production and processing of nickel, and the recycling of nickel – containing scrap, but the burning of fossil fuels undoubtedly generates the greatest concentration of atmospheric nickel, with the concentration in the air around industrialized areas being typically of the order of 120 – 170 mg/m^3. Plants also accumulate nickel, and tea is known to contain around 7.6 mg/kg of dried leaves. It occurs in small concentrations in cigarette smoke where it may combine with carbon monoxide to form nickel carbonyl, a known carcinogen. Nickel is widely employed as a major constituent of many important metal alloys, including stainless steels and the superalloys. It is also widely employed in coins and jewellery, in electroplating and electroforming, and is used in the manufacture of Ni-Cd and Ni-metal hydride batteries and electronic equipment.

5. Copper (Cu):

Copper is an important trace element, regarded as essential in the catalytic and transport functions of cells [75, 76]. It is also essential for brain metabolism. A deficiency of copper can lead to the development of diseases such as anemia, diabetes and cardiovascular conditions, and in pregnancy it can lead to problems with fetus development. Excessive amounts of copper in cells can, on the other hand, result in the formation of reactive oxygen species that may damage lipids, nucleic acids and proteins. Long - term excessive exposure to copper can give rise to liver and kidney damage with symptoms including headaches, dizziness, breathing difficulties, vomiting, abdominal pain, and diarrhoea. Chronic poisoning can result in cirrhosis of the liver, together with brain damage that may result in Alzheimer's, Parkinson's and Creutzfeldt-Jakob related diseases, and can ultimately lead to internal bleeding, liver and kidney failure, coma and death. As well as being absorbed through ingestion, copper can also be absorbed via the skin and by respiration. Small amounts of copper in water can lead to nausea and gastric irritation. It occurs naturally in the environment and is widely used in current everyday life, ranging from electrical and electronic equipment and wiring to coinage. It is also employed in the building and construction industries, a range of metallic alloys, and in industrial machinery. Additional copper enters the environment through mining and smelting operations, phosphate fertilizer production, and directly in households due to the use of copper plumbing. Copper contamination also poses a serious threat to farmland where it can disrupt soil activity by adversely influencing the beneficial effects of micro - organisms and earthworms.

6. Zinc (Zn):

Zinc is not regarded as being a particularly toxic element, and is in fact an important and essential trace element, with the average body containing around 2-3 g of Zinc. Excessive exposure to Zinc can, however, result in damage to the pancreas and lead to arteriosclerosis, in addition to disturbing protein metabolism, with symptoms including stomach cramps, vomiting, nausea and anemia. It is a very abundant element and occurs naturally in Zinc ores and, through natural weathering, is present in the air, soil, water, animals and plants. Industrial sources include mining, galvanizing of metals, batteries, automobiles, paint pigments, burning of coal and waste and the building and construction industry. The waste water of many industrial plants gives rise to Zinc-contaminated river sludges.

7. Cadmium (Cd):

Unlike many metals, cadmium is believed to have no essential biological function. Cadmium is now recognized as a carcinogen, exposure leading to increased incidence of lung and prostate cancers. Exposure may also lead to genetic damage including damage to chromosomes and DNA, bone disease, brain damage,

damage to the central nervous system, the kidneys and the immune system, and it can promote pneumonia and emphysema. It may also interfere with the function of enzymes and induce the formation of free radicals. Chronic symptoms of cadmium poisoning include weakness, fever, headaches, muscular and stomach pains, gastric and intestinal hemorrhaging, diarrhoea and vomiting. Natural exposure to cadmium occurs through the weathering of cadmium-containing rocks where it is washed into rivers and may enter the water system and hence food chain; in particular, such foods as liver, mushrooms, fish, shellfish, grain cereals, potatoes and other vegetables. Cadmium is also released through human activities including zinc, lead and copper metal smelting and refining operations where Cd is a by-product. Cadmium is also present in cigarette smoke, with an estimated dose of 1.7 μg Cd per cigarette. The maximum allowable exposure in air is 0.1 mg/m^3. It is considered immediately dangerous to life and health at concentrations of 9 mg/m^3. Cadmium salts and compounds including cadmium chloride, cadmium nitrate, cadmium sulphide and cadmium selenide, are used as pesticides and in the production of artificial phosphate fertilizers. It has also been used in paint pigments, Ni-Cd batteries, and silver solder. Other applications include electroplating and coating, and it is used in the manufacture of certain plastics.

8. Mercury

It occurs in three major forms, as elemental Hg, inorganic mercurial salts and minerals, and organic mercurial compounds including methyl mercury [77]. Mercury vapor is particularly hazardous as it is almost completely absorbed through inhalation. It was recognized from early times that mercury could cause neurobehavioral disorders and exposure to vapor could induce ‘hatter’s shakes’ or ‘mad hatters disease’, mercurous nitrate once being used in making felt hats. It may induce delayed neurotoxic effects years after original exposure or as a result of low level exposure over a prolonged period of time. Mercury poisoning was endemic in Japan in the 1960s and 1970s and was traced to methyl mercury chloride released into Minamata Bay in the effluent from a chemical factory. This concentrated in marine plankton and then fish that subsequently entered the human food chain. Prenatal exposure to as low as 10 ppm methyl mercury can affect fetus brain development and many children born to mothers who had eaten contaminated fish had serious nervous system damage, later referred to as Fetus Minamata Disease. The major effects of exposure to mercury include damage to the central nervous system and the brain, liver and kidney damage, and damage to DNA and chromosomes, leading to neurodevelopment disorders including dyslexia, intellectual retardation, attention deficit and hyperactivity disorders, and autism. Other effects include raised blood pressure. It can also promote allergic and autoimmune responses in susceptible individuals, with symptoms including skin rashes and headaches, in addition to personality changes, tremors and blurred vision, loss of hearing, memory loss, muscular weakness, lethargy, confusion, delirium, seizures, insomnia, and loss of teeth. Exposure may also lead to sterility, birth defects and miscarriages.

Initial short term exposure to mercury vapor in concentrations as low as 1 mg/m^3, can cause chest pain, inflammation of the lungs, coughing up blood, and accumulation of fluid in the lungs. Longer term exposure to vapor at levels of around 0.03 mg/m^3 can lead to muscle tremors affecting the hands and arms or even the whole body. In addition to inhalation of vapor, absorption of mercury vapor or liquid can also occur through the skin. Interestingly, direct ingestion of liquid mercury may not lead to harmful effects, as it is not easily absorbed by the gastrointestinal tract. Elemental mercury has an elimination half - life in the human body of 40 – 60 days. The FDA limit of methyl mercury in fish for human consumption is 1 ppm, with levels for most fish of the order of 0.1 – 0.5 ppm.

Levels of mercury in drinking water should be no more than 2 ppb. Human related sources of mercury are many as it is found in such household appliances as thermometers, barometers, paint pigments, batteries and fluorescent lighting. Industrial uses include a liquid electrode in the manufacture of sodium hydroxide and chlorine by electrolysis of sodium chloride solution, electrical switches and rectifiers, catalysis, explosives, and medicines.

Natural sources include the weathering of mercury-containing minerals. Combustion of fossil fuels and solid waste incineration also releases mercury into the environment, as does its use in agricultural fertilizers. It is not normally found to any great extent in plants, but can, for example, accumulate in fish. Another major source has been its use as an amalgam in dental restoration, with mercury concentrations in amalgam of around 50% mass, although it is believed that the solubility of Hg from amalgam in teeth is vanishingly small and therefore does not pose a significant health issue. Mercury has undoubtedly been a source of environmental contamination from dental practices in the past, although controls in most countries are now far tighter on the use and disposal of amalgam wastes.

9. Aluminum (Al)

Aluminum is the third most abundant element and is extracted from bauxite ore. It is not normally regarded as an essential trace element, but may be required in very small quantities to activate certain enzyme systems. Humans are exposed to considerable amounts both in food and non-dietary sources. Various aluminum compounds are also used in antacid formulations, an emulsifying agent in processed cheeses, cake mixes, self – raising flour, shampoos, and urban water treatment. It is also readily absorbed by foods cooked in aluminum cookware. Dermal exposure occurs through use of antiperspirants and deodorants. Aluminum smelting and the aluminum industry also generate wastes. Although aluminum toxicity is generally considered to be low, there is considerable controversy over its potential role in Alzheimer's disease or in speeding its progression. Dementia has been observed in some dialysis patients and this has been related to the amount of aluminum in the dialysis fluids used. Excessive uptake can lead to decreased liver function, anemia, gastroenteritis, colic with symptoms including headache, loss of appetite and muscle aches. Due partly to its ionic size, it may also compete with a number of essential trace elements including magnesium, calcium and iron in bodily functions.

10. Lead (Pb):

A significant body of evidence exists for the toxic effects of lead [77-80]. Lead is an Anglo-Saxon word for the element known by the Latin name plumbum. Everyday exposure to lead has occurred throughout the ages by various routes including boiling grape juice in lead pots and storing foodstuffs in lead vessels common in Roman times, use of lead - glazed ceramic vessels or high lead glasses in food and drink storage, use of lead water pipes and, more recently, use of lead in petrol. In ancient times, lead salts were even used to sweeten wine ('sugar of lead'). Fortunately, most of these routes for lead exposure are now appreciated and in general exposure is minimal.

Due to its chemical similarity with calcium, exposure to lead results in the body incorporating it into bone marrow, the kidneys, nerve tissues and the brain. In chronic exposure lead may be deposited in significant quantities in teeth and bones. Absorbance may occur by ingestion or inhalation of lead - contaminated dust or fumes, car exhausts being a major contributing factor before the banning in many countries of lead compounds in petrol, e.g. tetraethyl lead or lead bromochloride. Lead and its compounds may also be carcinogenic, and it has been associated with increased risk of lung, stomach and bladder cancer; it is also implicated in tumors of the liver and kidney. The central nervous system is particularly vulnerable to lead exposure, where it is deposited in the hippocampus region of the brain. Children are particularly vulnerable because more lead is effectively absorbed into the bloodstream than is the case for adults. Concentrations in the blood as low as 10 μg/dL, can impair mental and physical development in children, leading to reading and learning difficulties and lowered IQ. Moderate to high exposure to lead is also now known to induce the formation of free radicals which result in oxidative damage to critical biomolecules, lipids, proteins, chromosomes and DNA [80]. Heavy metal ions including lead are thought to effect enzymes by mimicking and thereby inhibiting essential elements such as Mg, Ca, Fe, Cu and Zn. Oxidative stress occurs when the generation of free radicals exceeds the ability of antioxidant defense mechanisms. Lower exposure is also thought to lead to oxidative stress, and this might be associated with many human diseases including hypertension and artery and kidney disease; levels in the blood as low as 3.5 μg/dL are likely to lead to increased risk of heart disease. Exposure to lead has also been shown to weaken the immune system resulting in increased susceptibility to bacterial and viral infections. Chronic symptoms of lead poisoning include intense thirst, headaches, high blood pressure, anemia, weight loss, poor attention span, memory loss and irritability, delirium, tremor, muscular weakness or paralysis, abdominal pain and vomiting, and sterility. At high concentrations in the blood, > 80 μg/dL, lead can cause convulsions, coma and ultimately death. Current major sources of lead that can result in environmental exposure include lead paint and lead water pipes. Additional sources result from industrial activity including metal extraction and smelting processes, together with the manufacture of lead glass, lead - acid storage batteries, and electrical and electronic equipment with soldered connections. In the form of lead acetate, lead has also been used extensively in dyeing and printing of cotton, and in varnishes, pesticides, antifouling paints, and even hair dyes, whilst lead nitrate is used in textile printing. Various lead – based compounds are also used in explosives, catalysts, photography, thermoelectric and piezoelectric devices, and coatings. In the 1960s a blood level of 60 μg/dL was considered acceptable, but with increasing awareness of lead toxicity the acceptable level was reduced to 25 μg/dL in 1985 and 10 μg/dL in 1991, which is nevertheless still above the level at which clinical effects may be noticed.

11. Arsenic

The name arsenic is derived from the Greek word for potent, arsenikon. It was used extensively in the past in various forms and concentrations as a general medicinal tonic and for the treatment of ulcers and syphilis. It has also been used in chemical warfare and deliberately as a poisoning agent. Arsenic is, in fact, regarded as one of the most toxic elements known.

Exposure to arsenic can result in a range of health related effects including decreased production of red and white blood cells, diabetes, brain damage, loss of resistance to infections, and heart problems. It may also cause damage to DNA and increased chance of developing certain cancers. Inorganic arsenic compounds are known carcinogens with increased risk of lymphatic cancer and those of the skin, lung, digestive tract, prostrate, colon, bladder, kidney and liver. It can result in bronchitis, laryngitis and rhinitis. Arsenic contamination in natural water is a worldwide problem. Exposure in drinking water can lead to thickening of blood vessels, characterized by a progressive loss of circulation in the hands and feet and leading ultimately to gangrene in the extremities. Exposure to arsenic of around 1 mg kg^{-}1 day^{-1} can, over a period of time, lead to seizures and coma, whilst lower exposure, 0.05–0.5 mg kg^{-1} day^{-1}, may lead progressively from numbness in the hands and feet to loss of reflexes. There have been many reported incidences of arsenic exposure around the world, often from contaminated drinking water [82]. In the Cordoba province of Argentina, for example, incidences of skin cancer in the 1950s were traced to drinking water containing > 100 μg L^{-1} of arsenic from natural ground waters. Symptoms of arsenic poisoning include dehydration and thirst, severe gastric pain, inflammation of the eyes and nasal membranes, loss of appetite, nausea, vomiting, diarrhoea, loss of hair and nails, delirium, pulmonary oedema, and seizures. Arsenic is cumulative in animal tissue and may concentrate in hair and nails. Concentration of arsenic over the length of hair may be used to determine the exposure to arsenic over a period of time and has been used as an indicator of deliberate poisoning. It is generally recognized that soluble inorganic arsenic compounds are more toxic than organic arsenic; however, inorganic trivalent arsenic is converted to mono-and dimethylated species in biological processes and it is now believed that rather than being a detoxifying mechanism, these methylated arsenic compounds are more potent inhibitors of certain enzyme functions than the inorganic variety. Trivalent arsenic interferes with enzyme function by bonding to SH and OH groups, resulting in cell damage. It also induces oxidative stress by the generation of reactive oxygen species. Arsenic is known to cross the placental barrier and can affect the fetus and may lead to deformities or spontaneous abortion.

The maximum permitted concentration in air is 0.5 mg m^{-1}, whilst in drinking water it is only 50 µg L^{-1}, with $\leq$ 10 µg L^{-1} recommended. Arsenic is found naturally in soils and minerals and may be present in the air through volcanic activity and the action of certain micro - organisms which release methyl arsine. It is also released into the environment through the burning of fossil fuels, as a by-product in the refining of lead and copper ores, and in arsenic-containing pesticides and insecticides. Other commercial applications include its use as an additive in glass manufacture, as a wood preservative, and in the manufacture of GaAs semiconductors. Levels of arsenic in certain foodstuffs, in particular fish, may be relatively high; for example, 77 µg g^{-1}, as arsenic can be absorbed from the water in which they live. It may also be present in plants.

2.4 Electric arc furnace dust management:

Electric arc steelmaking flue dust is a type of solid waste produced during the purification of gases given off in furnaces used in the manufacturing of steel from smelting scrap metal. Environmentally speaking, this flue dust is a toxic and hazardous product. The hazardous nature of electric furnace dust is caused by the generation of soluble oxides such as Pb, Cd, and Zn, mainly, formed at high temperatures above the steel bath and in the off gas systems of the electric arc furnace. After disposal of the flue dust in landfills, these soluble oxides find their way into the water table, causing pollution. Because of the large quantities of dust produced (figure (1-9)), its non-ferrous metal content, and the way it is dumped, technical solutions must be found so that it can be dealt with in a suitable manner.

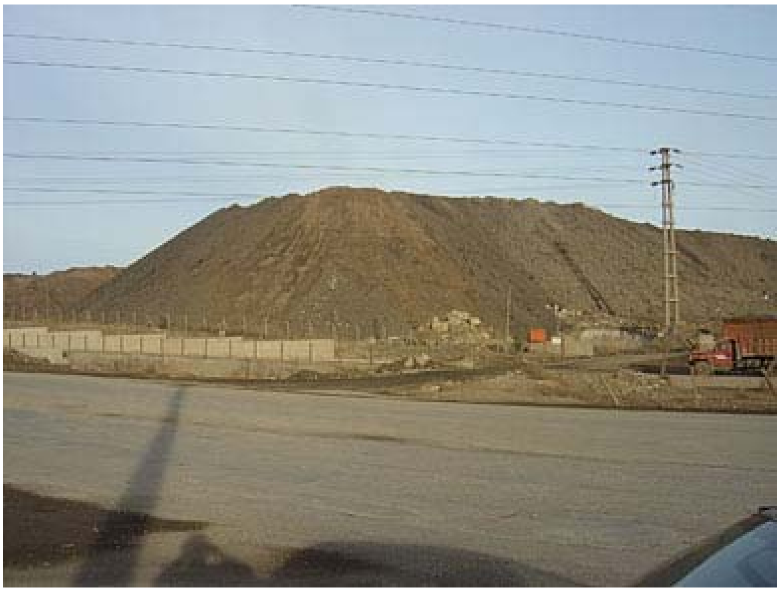


Figure (1-9). EAFD Dump

Since legislation in the past was not enforced, the disposal of EAF dust was not a technical issue. With future regulations, however, the steelmaker will require an understanding of the many options for dust disposal that are available to him. These options may include scrap selection, scrap pre-treatment, suppression of dust formation, recycling, thermal treatment, hydrometallurgical treatment, zinc recovery, and secure landfill disposal. Each steel company has its set of constraints and requirements. The common denominator is that dust disposal is not regarded as a commercial opportunity, but rather a requirement or problem to be solved. The decision regarding a process route will largely depend on minimizing cost and maximizing convenience. An intelligent decision will require at least a cursory knowledge of the technical aspects of EAF dust disposal [82].

Generally, there are several ways of handling EAF dust, which can be classified roughly into three categories [83]:

- Solidification/stabilization or vitrification of the dust to allow "delisting" and disposal,
- Recycling of dusts by returning them to the EAF,
- Hydrometallurgical and pyrometallurgical processes for zinc recovery and removal of heavy metals.

These options are desirable to different degrees according to their potential to satisfy the aim of prevention and control of environmental pollution.

2.4.1 Disposal of the dust:

In most cases, the cost for disposal of EAF dust is related to the zinc content. With a very high zinc oxide level (around 50%), EAF dust may be sold to major zinc smelters at a profit. If the dust is to be processed by a regional facility, then the cost increases significantly as the zinc level falls below about 25%. The average zinc content of EAF dust is under 20%, so the cost of regional processing is typically high [82].

Although some steel companies dispose of dust in secure landfills or sell it to fertilizer manufactures, these outlets are limited, costly and diminishing with time. Because of regulatory pressures and the value of the zinc in the EAF dust, the desirable treatment method, if practical, is on site zinc recovery.

The two fundamental alternatives for disposing of EAF dust are landfilling and recycling. When deciding between these alternatives, several factors are essential. The main factors are economic (treatment and transportation costs), environmental (regulations and conservation), long term liability, and concerns over public opinion. The availability of landfill sites is a factor in the decision to recycle or landfill EAF dust. The distance that EAF dust must be shipped is a factor in the cost of landfill disposal.

Electric arc furnace dust has been disposed of in hazardous waste dumps. It has been estimated that there are approximately 2 million tons per year of electric arc furnace dust accumulated in the United States. Disposal of electric arc furnace dust in a hazardous waste dump may cost upwards of $150 to $200 per ton.

2.4.1.1 Solidification/Stabilization (S/S):

S/S is a widely used treatment technology to prevent migration and exposure of contaminants from a contaminated media. Solidification refers to a process that binds a contaminated media with a reagent changing its physical properties by increasing the compressive strength, decreasing its permeability and encapsulating the contaminants to form a solid material. Stabilization refers to the process that involves a chemical reaction that reduces the leachability of a waste, so it chemically immobilizes the waste and reduces its solubility; becoming less harmful or less mobile.

S/S treatment typically involves mixing a binding agent into the contaminated media or waste. Common types of binder materials used are organic binders that include asphalt, organophilic clay, or activated carbon; and inorganic binders that may include cement, fly ash, lime, phosphate, soluble silicates, or sulfur.

S/S has been tested and evaluated for its effectiveness in containing and treating a wide array of contaminants. For metals, S/S is most often selected for treatment of these contaminants because metals form insoluble compounds when combined with appropriate additives, such as Portland cement [84].

Perhaps the most unique application of cement in waste management is for solidification/stabilization (S/S) treatment of waste. S/S treatment of waste involves mixing cement into contaminated media or waste to immobilize contaminants within the treated material. By mixing Portland cement into a waste containing free liquids, the waste gains physical integrity or become more solid. The chemical properties of hydrating Portland cement are used to lower the solubility of toxic contaminants in the waste and in some cases, to also lower the toxicity of hazardous constituents.

Stabilization processes rely on the principles of encapsulation, ion exchange, precipitation and polymerization. The fine EAF dust particles are incorporated into an aluminosilicate network. This reduces the surface area (encapsulation) and can immobilize the heavy metal ions, if the process is correctly done.

Typically, EAF dust is a basic oxide mixture with a simple structure. The heavy metals are largely ionically bonded, allowing them to leach in mildly acidic aqueous solutions. To change this structure, the dust is mixed with water and a soluble silicate. A Portland cement, pozzolanic cement or other bonding agent is then added, along with "proprietary chemicals" that optimize the curing process and enhance cross linking. The additives must be correctly proportioned and the components very thoroughly mixed for successful results. The slurry is cast into forms for solidification, precipitation, and curing. The resulting structure is largely covalently bonded, with complex aluminosilicate chains that immobilize the basic oxides, including the heavy metals.

Low temperature stabilization is a relatively low cost method of EAF dust treatment that can be carried out on site. If the product is to be recycled, then other steel mill wastes can be incorporated into the mixture. By incorporating mill scale and other magnetic wastes, the solidified product becomes magnetic and can be easily handled by a scrap crane.

The curing process for solidified EAF dust may take a very long time to proceed to completion. If the heavy metals are not completely incorporated into the structure, they may be leachable on physical breakdown of the solidified mixture. Process control is therefore important to ensure effective immobilization of the heavy metals [82].

The S/S process performs well at certain concentrations but poorly at others. For example, solidification of copper, lead, and zinc using cementations materials is effective at low to moderate concentrations. However, these metals interfere with the immobilization process at higher concentrations and render it less effective.

Some autors summarized the advantages and disadvantages of S/S technology. S/S technology has the following advantages [85]:

- Low cost because the reagents are widely available and inexpensive
- Can be used on a large variety of contaminants
- Can be applied to different types of soils
- Equipment is widely available and simple
- High throughput rates
- However, it still has the following disadvantages:
- Contaminants are still in the soil, not destroyed or removed
- Volume of the treated wastes usually increases significantly
- Volatile organic compounds and some particulates may come out during treatment process
- Delivering reagents deep into the wastes and mixing them evenly is difficult
- In situ S/S site may not be redeveloped
- Long-term efficiency of S/S is still uncertain

However, the S/S processes can generally be divided into five categories based on the additives used:

(1) Sorption,

(2) Lime-fly ash pozzolan process,

(3) Pozzolan-portland cement systems,

(4) Thermoplastic microencapsulation, and

(5) Microencapsulation.

2.4.1.1.1 Sorption:

Sorption is often used to eliminate free water and improve handling of wastes, such as limiting the escape of volatile organic liquids. Sorbents are also used to modify the chemical environment to limit the solubility of the waste [86].

The wastes considered for S/S treatment are mainly liquids or sludges [86]. In order to prevent the liquid from draining from the wastes, and to improve the handling properties of the waste, sorbents are added to the wastes. This process is referred to as sorption. Sorption may be realized through a chemical reaction between wastes and sorbents or by sorbent molecules retaining moisture as part of the capillary liquid [86]. Some typically used sorbents are activated carbon, anhydrous sodium silicate; various forms of gypsum, celite, clays, expanded mica, and zeolites [87]. Sorption can be divided into two different processes based on physical mechanisms: absorption and adsorption.

According to [86], most large, hazardous waste landfills are using sorption to satisfy requirements regulating burial of liquid wastes.

2.4.1.1.2 Cementations Stabilization/Solidification:

USEPA [88] defines cementations S/S technologies as those that use "inorganic reagents to react with certain waste components; they also react among themselves to form chemically and mechanically stable solids." This is a conventional method used for S/S. Common reagents include Portland cements, fly ash, and lime and kiln dust. These reagents usually react to form a solid matrix, which is often stable and has a rigid, friable structure like many soils and rocks [91]. Cementations S/S reagents are often called "inorganic polymers". Typically, the S/S process is realized through hydration of Portland cement. In the presence of water, C_3S and C_2S in cement hydrate to form calcium silicate hydrate gel (C-S-H gel) and $Ca(OH)_2$. C_3A hydrates to form calcium trisulfoaluminate hydrate, or calcium monosulfoaluminate hydrate, or tetracalcium aluminate hydrate [89]. These products form hardened paste, mentioned as a solid matrix previously.

Advantages of cementations S/S include the wide availability of cementations reagents, which are inexpensive and can be operated simply. Among them, Portland cement is the most commonly used [89].

The final pH of the system may not be desirable. There is an optimum pH range to precipitate amphoteric metals is about 10, such as Cd, Cr, Cu, Pb, Ni, and Zn. However, the pH value of a hardened Portland cement is over 12.5 [89].

Many contaminants interfere with the hydration of Portland cement [89]. Portland cement cannot control the oxidation state of metals [89]. As recommended by [89], these disadvantages can be solved by adding various additives into Portland cement, which includes blast furnace slag, pozzolan and fly ash. These additives not only serve to improve the performance of Portland cement as S/S reagents, but also help to cut down the cost.

2.4.1.1.3 Polymer Stabilization/Solidification

As defined by [88], "polymer S/S technologies process waste at relatively low temperature by combing or surrounding wastes with liquid polymers. Cooling or curing of the polymer then produces a solidified final waste form product".

Polymer S/S is a versatile technology which can be applied for either micro encapsulation or macro encapsulation; also can be accomplished ex situ or in situ [88]. USEPA [88] divided polymers into two categories: thermoplastic and thermosetting. Thermoplastic binders can be melt to a flow able state when heated and harden to a solid when cooled, while thermosetting binders require the combination of several ingredients to polymerize and harden (irreversible).

When the waste particles are small solid particles (<60 mm) and homogeneously distributed, the organic polymer matrix is known as micro encapsulation. In micro encapsulation, individual waste particles are fully surrounded and encapsulated by the polymer matrix. When the waste particles are large (>60 mm), clean polymer can be placed around the waste and this process is usually called macro encapsulation. USEPA has identified micro encapsulation as the best demonstrated available technology (BDAT) [89].

Polymer S/S is useful because of its broad application to diverse waste streams. Additionally, polymer S/S results in waste products with improved durability and leachability characteristics compared to cementitious techniques [89]. Polyethylene, one of the most common polymers used for S/S, is relatively inexpensive.

Both thermoplastic polymers and organic polymers are hydrophobic after curing and thus resist leaching, even at very small particle sizes. This property makes polymers ideal for trapping highly toxic metals and organic compounds. Organic polymer micro encapsulation, specifically, is a useful method to encapsulate waste because it is well-suited for many types of applications, including liquid waste solidification; it exhibits a high degree of impermeability, and can quickly attain physical strength. Organic polymer-treated wastes typically remain in solid/monolithic form because of their high strength and elasticity properties. Because organic polymers can be synthesized in a wide variety of compositions, they can be tailored to meet different requirements for wastes. This is advantageous for solidifying liquid wastes, which can have highly variable characteristics and remediation requirements [90].

One disadvantage of polymer S/S technologies is sensitivity to particle diameter. Micro encapsulation can typically effectively treat particles between 50 µm and 3mm, while micro encapsulation is best for particles >60mm [88]. Particles outside of these size ranges are best treated after processing or with different methods. Polymer S/S treatment also presents the problem of volatilized moisture release, which can be hazardous. It is best to pre-treat wastes with more than 2% moisture [88].

One nearly obsolete method of organic polymer micro encapsulation, Urea-Formaldehyde S/S, expels free water during the condensation reaction of stabilization. This method requires large quantities of resin dispersion for solidification and is expensive for drumming radioactive wastes compared to cementations processes. Lastly, these systems have generated concern for the environment due to the use of formaldehyde [88].

Organic Polymer Systems are also relatively unfashionable in recent years. In some cases, waste components may interfere with polymerization by reacting with catalysts or taking up free radicals. Polymer S/S processes often require roughly 25% by weight of polyester resin in the waste mixture, which can significantly increase costs due to chemical requirements [88].

The selection of S/S technologies is based on several factors [91]:

Waste characteristics (both chemical and physical) Waste characteristics are the most important factor in determining S/S treatment technology. Process type and processing requirements, the types of S/S activity (in-drum, in-plant, etc.) and processing requirements (waste modification, mixing models, waste transportation/storage) should be considered during selecting a S/S technology.

The S/S product can be disposed in a landfill, stored, or transported elsewhere. According to regulatory requirements, the S/S products for landfill disposal and for delisting may not require the same degree of treatment. Delisting requires that the waste materials are no longer hazardous, while disposing in a RCRA hazardous waste landfill does not [91].

There are numerous regulations relevant to S/S processes, such as the EP, MEP, TCLP, and chemical reaction requirement for waste treatments, but these are not performance criteria which S/S products must meet. Generally, a designer will produce an S/S waste product meeting minimum requirements, i.e. removing free liquids and/or produce a solid which can be transported or stored [91].

2.4.1.2 Vitrification:

Vitrification or glassification is a high temperature stabilization process. The concept is similar to that of chemical stabilization, in that the zinc and heavy metal oxides are incorporated into an aluminosilicate network.

Hazardous constituents can be immobilized in vitrification processes by two main interactions with the glass matrix:

A. Chemical bonding
B. Encapsulation

EAF dust is mixed with a silica source and heated to form a molten glass. Depending on the temperature, slag basicity and oxygen potential in the system, a portion of the heavy metals may fume and report to the gas phase. To minimize fuming, a low temperature and diffuse heat source are desirable. The slag basicity should be low and the oxygen potential of the system high. Thus, a gas burner operated with a lean mixture is an appropriate heat source and silica sand is a good fluxing agent.

EAF dust in the molten state behaves like an ionic soup. The degree of covalent bonding between species is quite small. When an acid substance like silica sand is added, the ionic species bind together to form long chain polymers of aluminosilicates. This glass network incorporates the heavy metals, providing them with a higher degree of covalent bonding, thereby reducing their leachability. In addition, the glass has a much lower surface area than the EAF dust from which it was made, thereby further reducing the leach rate of the heavy metals.

The oxygen potential is an important consideration in vitrification. If there is sufficient chromium in the EAF dust to cause concern, then a high oxygen potential is to be avoided since it encourages the formation of hexavalent chromium, which is more leachable than the trivalent form [82].

Hazardous constituents may also be immobilized without direct chemical interaction with the glass network. Since vitrification constitutes a molten phase during some portion of the process, materials that do not interact chemically or have not completely entered solution can be surrounded by a layer of vitrified material and encapsulated, as the melt cools. This layer of vitrified material protects the encapsulated constituents from chemical attack and inhibits their ability to escape from the vitrified product [92]

The glass formed from a successful vitrification process can be delisted and landfilled. Alternatively, it may be used as an industrial raw material, or can be made into useful glass wool or ceramic products.

2.4.2 Dust treatment:

Zinc-coated galvanized steel scrap is the most widely used feedstock for Electric Arc Furnace (EAF) steel production.

The EAF dust generated by steel mills can be treated in an economically viable way. The treatment processes is part of the larger steel industry loop that allows the reuse of two important natural resources, zinc and iron.

Historically, in most developed countries, manufacturers landfilled EAF dust at a significant financial cost. However, increased landfill costs, governmental, environmental and social pressures placed on steel producers are encouraging steel companies to take advantage of sustainable disposal options that allow for the recovery of valuable recyclable components, such as zinc and iron units.

The opportunity to treat EAF dust reduces the steel companies' cost of disposal and closes the industry loop, resulting in an environmentally friendly outcome.

2.4.2.1 Recycling

The variable nature of primary zinc oxide deposits has required the evaluation and modification of numerous metallurgical techniques. These methods have enabled Zinc Oxide to consider the recovery of zinc a very broad spectrum of materials including industrial wastes. Most of these wastes are generated in small quantities that are insufficiently large to be of commercial interest. The one notable exception is electric arc furnace dust (EAFD).

The dominant EAFD processing technologies are specialty smelters or Waelz kilns, which use high temperatures to convert EAFD into crude zinc oxide for further processing and iron slags. However, the Waelz kiln technology (and all pyrometallurgical processing technologies) is prone to the formation of dioxins and does not extract other materials than zinc forms. These kilns need very large scale to be economic, and mostly produce low-grade intermediate zinc products (termed 'crude zinc oxide'), losing other metals extraction. As such, these kilns solutions cannot be considered as true 'recycling' operations for EAFD secondary treatment.

However, this new proposed advanced halide hydrometallurgical zinc process is where possible designed as a zero-waste industrial recycling process. The metal produced is fluoride free and low to ultra-low chloride content which facilitates their reuse in secondary applications.

Generally speaking at historical zinc prices, the recovery of zinc from EAFD has not been possible without a subsidy, i.e. it has no value and is therefore considered to be a waste. Since it also contains traces of toxic elements such as cadmium, arsenic and mercury, it is classified as a hazardous waste. EAFD has been processed for many years using Waelz kiln technology but this does not recover the iron and due to the addition of fluxes the residue created by the process is greater than the tonnage of EAFD treated. As a hazardous waste, international transportation of EAFD is subject to legal restrictions. The Zinc Oxide approach recovers:

- A superior zinc oxide concentrate that can be sold to zinc smelters
- Pig iron, the basic intermediate feed for the steel industry
- Building aggregate that can be sold to the construction industry.

There is no waste from the process. As such it represents a major advance in waste and metals recycling.

The traditional methods used in the production of zinc from oxide Waelz are mainly two: the Imperial Smelting process and the traditional and wide extended RLE (Roasting-Leaching-Electro wining). The traditional zinc refinery, where the Waelz oxide, together with the zinc oxide, is fed in the stage of leaching of the electrolytic process in order to obtain bleach electrolytic from which you can obtain the zinc metal is the target customer for a Waelz plant. It is a way to cheapen the provisioning of the main raw material, the concentrated ore of zinc, without reducing the metallurgical performance of the process. But due to the short allowable limits of halogens, mainly chlorine and fluorine, the amount of Waelz to treat here it's seriously restricted.

The economic margins of these industries, higher than in the Waelz process, are based on two factors. On the one hand they are based on the premiums for sale with which the market appreciates your product, higher in the case of alloys than in the high-quality metal. On the other hand, they are based on the procurement margin that presents the formula of purchase of the ore, the costs of treatment (treatment charges) and zinc content not payable in the ore depending on zinc content. Therefore the equation is clear. We need an integrated industry that its supply consists of these wastes, which are rich in zinc, where in most cases the producer pay for its disposal and recycling, in order to obtain the contained zinc like pure metal or metal alloys, with their corresponding premium of sale, all of this through a hydrometallurgical process with high-performance and economically profitable. Thus, the expected economic results will be truly spectacular.

2.4.2.2 Metal recovery.

Processing of EAFD for recovery of valuable metals such as Zn and Pb could be beneficial to both resource and environmental conservation.

Processes for zinc recovery and removal of heavy metals are suitable options for reclaiming valuable resources, which have already been mined and treated, at least once. Pyrometallurgical and hydrometallurgical options exist for the recovery of zinc, in principle. Important parameters of these processes are temperature, heat source (if any), oxygen potential, consumables (energy, flux, etc.), pH-value or basicity, end product forms and uses, and disposal options for off gas and residues. Zinc recovered by the different technologies can be in the form of metal or oxide. An economic viable recovery of the zinc content of EAF dust requires a minimum percentage of zinc available in the dust. Commercially viable hydrometallurgical technologies are not available at this time [83].

The objective of the (pyrometallurgical) high temperature recovery processes is to reduce and fume away the heavy metals (i.a. zinc and lead), leaving an oxide and/or metallic residue substantially free of heavy metals. First of all the dust is optionally mixed with a reductant and fluxes, then it is heated in a fuming reactor.

The zinc contained in the flue gas is then collected as condensed metal or oxide. It can be used to produce a wide range of products. Further residues of pyrometallurgical processes may also be utilized, depending on the process.

The major impetus for the development of hydrometallurgical processes for the treatment of EAF dust is that, a small scale, on-site process could be economic, because of its low capital and operating costs as well as the recovery of the valuable metal containing products. Also, there may be some environmental benefits of hydrometallurgical processes in comparison to pyrometallurgical processes. Although today's commercial EAF dust treatment processes are predominantly pyrometallurgical, hydrometallurgical processes are gradually replacing these pyrometallurgical counterparts for the treatment of EAF dust.

Hydro- metallurgical processes are:

- Leaching in NH4 Cl(Ezinex , HST)
- Leaching in H2SO4 (Recupac , Hydromet, ZincOx)
- Leaching in NaOH(Zimaval)

Advantages of Hydro-metallurgical process are Lower capital & operating costs, halides can be removed (“washing”) but disadvantages are low Zn recovery (zinc ferrite cannot be easily leached), Fe not recovered, it lost the value, significant waste disposal, waste water issues.

2.4.2.3 Thermal treatment.

A method for the separation and recovery of metals selected from the group consisting of iron, cadmium, zinc, and lead, from raw material comprising a mixture of metals, which comprises the steps of heating the raw material to a temperature sufficient to substantially vaporize cadmium, zinc, and lead, and insufficient to substantially vaporize iron; separating secondary dust and vapors produced during the first step from the residual sinter mass, which mass comprises iron, slurring the secondary dust in an aqueous solution of ammonia ammonium carbonate to dissolve zinc and cadmium; separating a zinc/cadmium bearing leach liquor from substantially insoluble lead containing particles by filtration; treating the zinc/cadmium bearing leach liquor to recover cadmium by adding metallic zinc to the leachate to produce a cadmium containing cement; separating the cement from the leach liquor; and removing ammonia from the leach liquor to precipitate basic zinc carbonate. As known very well, Steel melts at approx. 1480°C but zinc boils at 907°C, Volatile impurities vaporize, oxidize and form dust (Zn, Pb, Cd, etc) The main pyrometallurgical technique is Waelz process, which represents more than % 80 of the recycling capacity. The other techniques are:

- Rotary Hearth (Kobelco, Inmetco)
- Multiple Hearth (PaulWurth PRIMUS)
- Shaft Furnace (Cupola Oven , IS Zinc Smelter, Mitsui)
- Melting Cyclone (VAI; HRD)
- Plasma Furnace (Mintek)
- Electrothermal(Toho)

Advantages of High temperature process are Zn and Fe is highly or completely recovered, and disadvantages are high capital and operating costs, air emissions.

2.4.2.3.1 Waelz process:

Most zinc oxide (ZnO) is made from zinc metal derived from ore or scrap zinc metal resources. Zinc metal is an internationally traded commodity, where prices are set by the London Metal Exchange and at any point in time will reflect supply and demand balances. ZnO is also found in a wide range of chemicals and pharmaceuticals used for medical and cosmetic purposes such as wound healing and sunscreen. Emerging ZnO markets include ITO replacement for displays and photovoltaic panels, as a semiconductor for making inexpensive transistors, and as applications in thin-film batteries. Before entering the description of the Waelz technology and its applications on the treatment of EAFD, a short definition is required for clarifying the difference to other techniques. Waelz Technology is volatilization of non –ferrous metals like Zn, Pb, Cd, etc out of an oxidized solid mixture by means of reduction by coke breeze in a rotary kiln without generating a liquid slag must be disposed of in special landfills; figure (1-10).

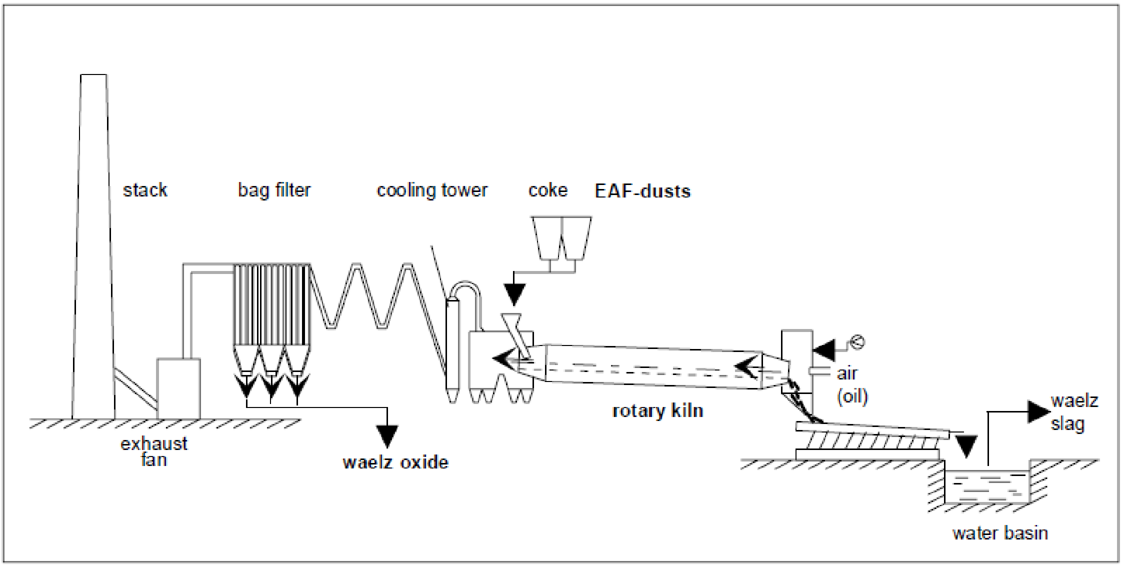


Figure (1-10). Schematic view of a Waelz-plant

Waelz Technology is in use since many years, originally introduced for the enrichment of low grade Zinc ores, further adopted on the re-processing of the neutral leaching residues of Zn Smelter residues and for the past 30 years successfully applied on the treatment of EAF dust. The Waelz Kiln process is a well-established technology that uses a Rotary Kiln to treat steel mill dust. Dust containing Zinc Oxide and a carbon source, such as coke, are charged into the Rotary Kiln and heated by combustion heat. Compared to the RHF process, the rotary kiln has lower productivity because of a lower operating temperature and less contact between dust and coal.

The temperature in the kiln is generally below 1200°C. Because of lower temperature and inferior dust and coal contact the Waelz process achieves lower iron metallization and less dezincification than RHF. Therefore Iron product cannot be used as a metallic at EAF and it must be disposed of in special landfills.

The accumulation of EAF dust and its disposal have become a serious issue worldwide. EAF dust contains valuable metal resources such as Iron, Zinc, Lead, and other elements. Effective recovery of these metals would contribute to the development of a sustainable society.

From the viewpoint of ecology, low carbon requirements and resource recovery are naturaltrends in the future, and the prospect of the resource recovery industry is very promising.

However, to understand the property of wastes and value added technologiesis the prerequisite to resource recovery in order to maximize the advantages of resource use, to minimize impacts on environment, and so to achieve sustainable development of industries. Waste treatment has been expanded from source control in the past into resource reuse andsustainable development following the rise of the environmental awareness across the globe.

Due to the over use in the past few decades, resources on the earth are drying out, whether coal, petroleum or natural gas. Based on the current consumption rate, the remaining petroleum and major metals will be used up within the next five decades. For this reason, waste reuse and development has become the main stream in the future. Therefore, countries in the world have gradually made the effective use of resource the new direction of environmental policies and the focus of environmental management.

Existing waste EAF dust treatment practices namely to use it in the feed material composition of cement Rotary Kilns and as raw material in the production of concrete based building materials like bricks , tiles etc, can not prevent leachability of heavy metals such as Cd, Co, Pb, Dioxin and others, but by using RHF technology all valuable resources can be used within the limits of environmental regulations as explained above. As the products of RHF process; Zinc oxide will be used to feed Smelters to produce metallic Zinc and DRI will be used as raw material for existing steelmaking operations to produce steel.

2.4.2.3.2 Sintering:

In the iron and steel industry, burden preparation produces an enormous amount of fines. Agglomerating these fine materials is necessary for the shaft furnace operation, particularly for the blast furnace. As the blast furnace is a countercurrent process in which solids descend against a rising gas flow, it is imperative that the burden is supplied in a lump form [93]. Sintering is the most widely used agglomeration process. It serves to do more than simply to bring about the agglomeration of fine-grained materials. Ores with elevated concentrations of hydration water and carbon dioxide are often crushed and sintered integrally to achieve higher concentrations of iron by extracting the volatile components. By means of sintering, ores which are difficult to reduce or tend to disintegrate or grow in volume during reduction can be transformed into a stable and easily reducible burden. By-products generated in steel plants, such as furnace dust, steel mill dust and mill scale, can be included in the sintering process and thus reused. The fluxes required to liquefy the slag are added to improve the properties of the agglomerates.

2.4.2.3.2.1 Sintering process:

In the sintering process, the temperature of a micropelletized sinter mix is raised to achieve partial fusion and produce partially molten material which, on cooling, crystallizes or solidifies into various mineral phases that bond the structure together. The process heat is supplied by combustion of coke breeze, one of the components of the sinter mix.

Due to complete combustion of carbon, a temperature in excess of 1400°C is easily attained. The temperature profile of the sinter bed has a significant effect on the type of sinter produced and on its physical and reduction properties. Other factors which significantly affect the sintering process and sinter quality include:

(1) The size and composition of micropellets or granules;

(2) The chemical composition and size of raw materials;

(3) The mineral composition of ores; and

(4) The relative proportion of ores, fluxes, and coke used in the blend.

The following processes take place in the formation of iron ore sinters:

(a) Solid state reactions: solid-solid and solid-gas;

(b) Partial melting of materials to form primary liquid;

(c) Dissolution of solids in the melt to form secondary liquid;

(d) Crystallization of mineral phases from this liquid on cooling and solidification of final liquid.

It is assumed that the sintering process is complete when the temperature drops to 1100°C. Depending upon whether fluxes have been incorporated in the sinter mix, iron ore sinters are divided into two broad classes: non-fluxed or acid sinters and fluxed sinters. Depending upon the relative amounts of bases and acids, fluxed sinters are further categorized into two sub-classes according to basicity: self-fluxing sinter and super-fluxed sinter [94].

2.4.2.3.2.2 Binders:

As raw materials constitute up to 80% of the sinter cost, many operators have attempted to increase the use of low cost ores such as concentrates, pellet feed, and in-plant dusts and sludge, etc. Fine materials create problems in sintering because they decrease permeability and productivity. Consequently, improved granulation techniques have been developed for these materials. In addition to improving agglomeration by optimizing the method of water addition and the residence time in the drum, much attention has focused on binders such as lime or bentonite [95].

Traditionally, burnt lime has been used to increase sintering rates, to facilitate the use of thicker beds and to allow more fine ore to be used [96]. For best results, the burnt lime needs to be:

(1) Sufficiently fine to be completely hydrated while in the mixing/granulation drum(s)

(2) Highly reactive, aiming at burning to the extent of residual CO_2 content less than 2% [97].

2.4.2.3.2.3 Flux and coke size:

The chemical and size analyses of fluxes can influence the energy requirements for sintering. The particle size of fluxes needs to be optimized for higher bed permeability which leads to decreased power consumption. For silica sand, it is generally accepted that silica should be crushed fine in order to promote its reaction in the sintering process [98]. Similarly, fine serpentine is preferred, particularly if the ore mix contains a large amount of limonitic ore [99]. Limestone is more reactive and does not require to be as fine as serpentine or silica. As limestone is a major component of the ore mix, it is preferable to use a coarser material in order to maintain good raw mix permeability.

With regard to coke breeze, it has been found that coarse material is preferable and results in lower coke consumption [100]. The optimal size range for coke breeze was reported to be 0.25-3mm by [101]. Using different size fractions of coke breeze, Autor [98], found that the coarse (-3.15 +1.0mm) gave the best result while fine coke (-1.0 mm) gave the worst results. Fine coke can be considered mainly as adhering fines which form the surface coating around granules.

The fine coke burns quickly. Very coarse coke burns slowly and may widen the flame front with a possible loss of productivity. Further trials clearly demonstrated that coarsening of the fuel reduced the amount required, enhanced sinter output, improved the reduction degradation index (RDI), and decreased SO_2 emissions [102].

Some autors conducted an extensive sinter pot test programme to investigate the effect of coke particle size on sintering productivity, coke requirements, and quality [103]. They found that coarse coke breeze gave the highest flame front speed and the highest combustion efficiency. Fine coke gave low combustion efficiency and therefore produced less heat and a lower sintering temperature. As a result, coke rate must be increased when using finer coke in order to maintain sinter quality. In order to change the distribution of coke particles in the granules, split coke can be added [104]. In this system some of coke is added in the normal way to the ore mix before the granulation drum, while the remainder is added close to the discharge end of the drum, so that much of the coke breeze is bound to the surface of granules and the amount of coarse coke coated by ore fines is minimized. Generally, this procedure has led to improvements in productivity but not to a significant reduction in coke consumption.

2.4.3 Minimization of dust formation:

Minimization of dust formation In order to minimize dust formation, it is suggested that violent carbon boils should be limited [105], the size of the bursting bubbles be reduced by controlling the decarburization reaction (and therefore controlling the ratio of chemical to electrical energy in the EAF) [106, 107], the position of the oxygen lance, blowing time [108], and intensity of blowing should be optimized [109], a slag layer that covers the metal bath should be formed early on in the heat [108], (a foamy slag practice would therefore be beneficial as well as slag of higher viscosities [105]), slopping should be limited, and friable additives and fluxes should be bottom injected [106-112].

3. Methodology and experimental setup

This part of research includes all procedures that were followed for testing raw material and products.

3.1 Characterization:

Samples of EAFD were obtained from Serbian steel making company, equipped with electric arc furnace with capacity of 260,000 tons/year. As a precursor to fundamental studies of the potential and alternative methods to EAFD treatment, EAFD was characterized. The EAFD samples were subject to many tests, optical microscopy was used to inspect the nature and the wettability property of EAFD; particle size analysis was done through sieving; elemental analysis of the dust was performed using X-ray fluorescence (XRF); phase composition was achieved through X-ray diffraction (XRD); scanning electron microscope (SEM) was used to look at particle morphology and leachability tests were performed on the samples through to the standard Toxicity Characteristic Leaching Procedure (TCLP).

3.1.1 Sampling:

Samplings were made in three consecutive days. The dust of each cycle was collected in silos and then transferred to a truck and weighed. Each sample consisted of a bag of 20 kg that was filled in three spots of the truck.

3.1.2 Optical microscopy:

Laboratory optical microscope X700 resolution was used to get primary information about EAFD in terms of the general form. EAFD sample was placed in a thin layer as it was brought from the factory on graphic paper to estimate the size of the granules; also another sample was washed and sieved to 36 µm to get rid of fine materials and to make sure of the presence of the spherical particles. Moreover the magnetization property of the spherical particles was observed by placing a steel knife above the particles. Furthermore the EAFD was found hydrophobic, this property was investigated by using optical microscopy also where a thin layer sample was placed under the microscopy and single drop of water was dropped then series of photo were taken , and the interval between the each photo and which followed by was 15 sec.

3.1.3 Sieve analysis:

Tyler Canadian Standard Sieve Series screens (Figure (3-1)), were used in order to dry-screen the EAF dust samples and separate them into size classes. The screen sizes, which are identified by their grid opening, started at a size of 1.0 mm and went down to a size of 36 µm. The largest size class which did not pass through the initial 1.0 mm screen, was labeled +1.0 mm, while the smallest size class which passed through the 36 µm screen into a pan was labeled -36 µm.

Figure (3-1). Tyler Canadian Standard Sieves

3.1.4 Scanning electron microscopy (SEM):

Morphology of the samples was analyzed by scanning electron microscopy (SEM) using JEOL JSM-5800 at 20 kV ((Figure (3-2)). Prior to the SEM analysis, samples were coated with gold using a spatter coater ((Figure (3-3), POLARON SC502, Fisons Instruments).

Figure (3-2). JEOL JSM-5800

Figure (3-3). POLARON SC502

3.1.5 Chemical analysis:

Chemical composition was analyzed by X-ray fluorescence, (XRF, Thermo Scientific Niton analyzer Figure (3-4)), and atomic absorption spectrometry (AAS, Perkin Elmer 4000 spectrometer). Phase composition was analyzed using Jenapol U-Carl Zeiss polarizing microscope.

Figure (3-4). Niton XL3t XRF Analyzer

3.1.6 XRF Spectrometer:

Energy dispersive X-ray fluorescence technology (ED-XRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples. It can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously.

3.1.7 X-ray diffraction (XRD):

X-ray diffraction is a method used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. X-ray diffraction XRD analysis was performed using "Philips PW 1050" diffractometer, Cu-Kά1, 2 radiations were used, measuring in 2θ range 15-100°, step 0.02° and exposition 10 sec.

3.1.8 Leachability test (TCLP):

The TCLP or Toxicity Characteristic Leaching Procedure is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. The TCLP analysis determines which of the contaminants identified by the United States Environmental Protection Agency (US EPA) are present in the leachate and their concentrations. In the TCLP procedure the pH of the sample material is first established, and then leached with an acetic acid or sodium hydroxide solution at a 1:20 mix of sample to solvent.

Heavy metals leachability was tested according to the standard Toxicity characteristic leaching procedure (TCLP), US EPA method 1311[113], where 50g of sized reduced samples were placed in polyethylene bottle with 1000 ml of leaching fluid #2 (glacial acetic acid, pH value of 2.88±0.05), L/S ratio of 20. The mixture was agitated at 300±2 rpm for 18±2 h.

3.2 Solidification/Stabilization experiments:

Solidification/Stabilization (S/S) treatment is used to treat hazardous wastes for disposal. S/S treatment involves mixing a binding reagent into contaminated media or waste. The treatment protects human health and the environment by immobilizing hazardous constituents within the treated material. S/S has been effective in treating a variety of hazardous constituents in many different forms of waste and contaminated media. Portland cement is the most common used as the S/S binding reagents due to its ability to solidify and stabilize the wastes. Portland cement is not only used alone, but also with fly ash, lime, soluble silicates, clays, and other materials [114, 115].

Portland cement is a generic material principally used in concrete for construction. Portland cement-based mix designs have been the popular S/S treatments and have been applied to a greater variety of wastes than any other S/S binding reagent.

In presented research the commercial Ordinary Portland cement, (CEM II B-M (V-L) 32.5 R), was used in all mixtures.

3.2.1 Cement grout S/S:

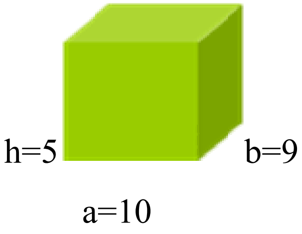
Cement-based "grout" systems have been used for so many years. Cement grout is a mixture of Portland cement and water. This technique is commonly called grouting, and the mixtures so obtained, grouts. Cement-based "grout" systems have been used for so many instances for S/S. EAFD the target waste for treatment was mixed with varying percentages of cement with and without another combined materials. Lime used to adjust pH or to drive off water utilizing the high heat of hydration produced by S/S binders [114].

3.2.1.1 Experimental set-up & Methods:

Fourteen mixtures were made according to the designed program. The EAFD and lime were dried at 105°C for 24 hours. Materials were mixed dry by electronic mixer for about five minutes the proportion of water added with continued mixing until the mixture became homogenous; the specimens were casted and compacted into two portions with vibration for about 30 sec. After curing for 28 days, in accordance with the standard SRPS U.M1.005, the samples were tested for compressive strength and leachability.

Based on values of designed program and cube dimensions, the quantity by weight of EAFD, cement, lime and water are calculated and shown in table (3-1).

Cement: Water ratio was 1: 0.4.



Cube dimensions= (10*9*5) cm

Cube volume= 450 cm^3

Cube surface area= 0.009 m^2

Table (3-1). Percentages by weight of used materials.

No.	Cement%	Lime%	EAFD%	Water, g	Cement, g	Lime, g	EAFD, g
D1	100.0%	0.0%	0.0%	252.00	630.00	0.00	0.00
D2	80.0%	0.0%	20.0%	322.46	644.91	0.00	161.23
D3	70.0%	0.0%	30.0%	357.69	625.95	0.00	268.26
D4	60.0%	0.0%	40.0%	392.91	589.37	0.00	392.91
D5	30.0%	0.0%	70.0%	498.60	373.95	0.00	872.55
D6	20.0%	0.0%	80.0%	533.83	266.91	0.00	1,067.66
D7	10.0%	0.0%	90.0%	569.06	142.26	0.00	1,280.38
D8	40.0%	40.0%	20.0%	355.94	355.94	355.94	177.97
D9	35.0%	35.0%	30.0%	386.98	338.61	338.61	290.24
D10	30.0%	30.0%	40.0%	418.02	313.52	313.52	418.02
D11	60.0%	20.0%	20.0%	339.20	508.80	169.60	169.60
D12	52.5%	17.5%	30.0%	372.33	488.69	162.90	279.25
D13	45.0%	15.0%	40.0%	405.47	456.15	152.05	405.47
D14	15.0%	5.0%	80.0%	538.01	201.76	67.25	1,076.03

3.2.2 CONCRETE S/S:

Concrete is an artificial conglomerate stone made essentially of Portland cement, water, sand, and aggregates. The mixing of all the materials is placed into a plastic form; a chemical reaction called hydration takes place between the water and cement, and concrete normally changes from a plastic to a solid state in about 2 hours. Concrete has been used for S/S for many years for waste treatment. In this research Raw and milled EAFD was replaced of fine aggregate with different percentages with and without fly ash.

3.2.2.1 Experimental set-up & Methods:

Four concrete mixtures were prepared, according to percentages presented in table (3-2), with different replacement percentages of EAFD, fly ash and deferent EAFD surface area. Cement-aggregate-water ratio was 1:5:0.6 by mass was used for all concrete mixtures. 1-2 mm the size of coarse aggregates and 0,25-0,75 mm fine aggregates were used, the coarse aggregates constituted 60% by weight of the total aggregates. 810 ml of water and 3645g of coarse aggregate were used for every sample. EAFD was used as a replacement of fine aggregate, while fly ash was cement replacement. Milling was applied in series III and IV for EAFD size reduction. From each series, six samples were prepared and presented results represent mean values.

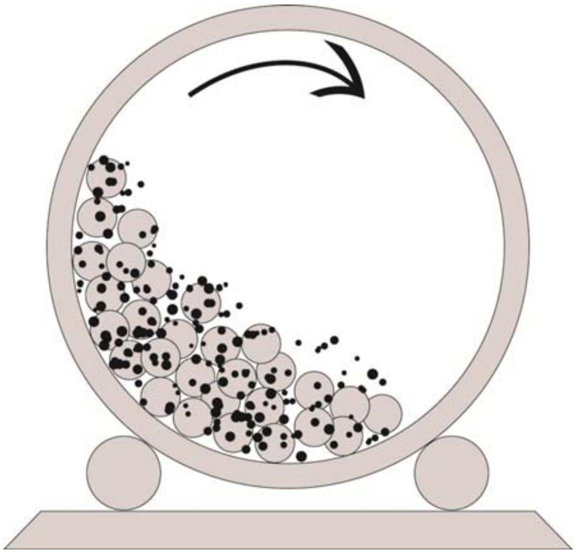
Table (3-2). EAFD S/S experimental set-up

Mixtures	Additions, %		Milling time, min
	EAFD	Fly ash	
I	0-50	-	-
II	10-15	10-25	-
III	10	-	60, 300
IV	10	0, 10	0-180

3.2.2.1.1 Material preparation:

The EAFD and fly ash were dried at 105°C for 24 hours; the fly ash was sieved to -45µ and EAFD was divided into two parts: the first part was used without milling and the second part was milled for 30, 60, 120, 180, 300 minutes. The milling was performed in a steel ball mill, figure (3-5), (Ø160 mm, height 270 mm, ball diameter 10 mm, EAFD + balls material charge 60%) at 300 min^{-1}, where the dust to balls ratio was 1:1.

The mixing of prepared materials was performed in an electronic mixer with dry materials until the mixture became homogeneous. After that, a defined amount of water was added. All materials were mixed for about three to five minutes. Cubes size 15×15×15 cm, were cast for each concrete mixture.



Figure(3-5). Steel ball mill.

The specimens were cast and compacted into two portions with vibration for about 30 sec. After curing for 28 days, in accordance with the standard SRPS U.M1.005, the samples were tested for compressive strength and leachability.

The four concrete mixtures were prepared is:

- Mixture I with EAFD varying between 0% and 50% of the aggregate weight.
- Mixture II with EAFD between 10 and 15% and fly ash varying between 10% and 25%.
- Mixture III with 10% EAFD and different milling time.
- Mixture IV with 10% EAFD, different milling time and 10% fly ash.

Designed program and quantities of used material are presented in tables below.

1) First mixture:

Preliminary mixture with wide range of EAFD replacement was prepared for previews of the affecting proportions. 1215g of cement and 135g of coarse aggregate were used for every sample without any additives. First mixture’s design is shown in table (3-3).

Table (3-3). First mixture’s design

No.	EAFD%	Fine aggr, g	EAFD, g
B1	0	2,430.0	0
B2	10	2,178.0	243.0
B3	13	2,114.1	315.9
B4	15	2,065.5	364.5
B5	17	2,016.9	413.1
B6	20	1,944.0	486.0
B7	25	1,822.5	607.5
B8	30	1,701.0	729.0
B9	40	1,458.0	972.0
B10	50	1,215.0	1,215.0

2) Secondary mixture:

According to the first mixture’s results secondary mixture was prepared with addition of fly ash as a binding agent and 10- 15 % EAFD replacement. Design of second mixture is presented in table (3-4).

Table (3-4). Second mixture's design

No.	EAFD%	Fly ash%	Fine aggr, g	Cement, g	EAFD, g	Fly ash, g
B2	10	10	2,178.0	1,093.5	243.0	121.5
		15	2,178.0	1,032.8	243.0	182.3
		20	2,178.0	972.0	243.0	243.0
		25	2,178.0	911.3	243.0	303.8
B3	13	10	2,114.1	1,093.5	315.9	121.5
		15	2,114.1	1,032.8	315.9	182.3
		20	2,114.1	972.0	315.9	243.0
		25	2,114.1	911.3	315.9	303.8
B4	15	10	2,065.5	1,093.5	364.5	121.5
		15	2,065.5	1,032.8	364.5	182.3
		20	2,065.5	972.0	364.5	243.0
		25	2,065.5	911.3	364.5	303.8

3) Third mixture:

Third mixture was designed as a preliminary test to investigate the effect of surface area or the difference between coarse and fine EAFD on the concrete's property without any addition of fly ash. EAFD was milled for one and five hours and added as a replacement from 10- 15 % to concrete mixture. The design of third mixture is presented in table (3-5).

Table (3-5). Third mixture's design

No.	EAFD%	Milling time, min	Fine aggr, g	EAFD, g
B2	10	60	2,178.0	243.0
B3	13		2,114.1	315.9
B4	15		2,065.5	364.5
B2	10	300	2,178.0	243.0
B3	13		2,114.1	315.9
B4	15		2,065.5	364.5

4) Fourth mixture:

According to results that obtained from previous mixtures, final mixture was prepared by adoption EAFD percentage at 10%, 10% of fly ash and different milling time. Fourth mixture's design is presented in table (3-6).

Table (3-6). Fourth mixture's design

No.	EAFD %	Fly ash %	Milling time, min	Cement, g	Fly ash, g
B2	10	0	0	1,215.0	0
		10	0	1,093.5	121.5
		0	30	1,215.0	0
		0	30	1,215.0	0
		0	60	1,215.0	0
		10	60	1,093.5	121.5
		0	120	1,215.0	0
		0	180	1,215.0	0

3.2.2.1.2 Compressive strength:

Compressive strength may be defined as the measured maximum resistance of a concrete specimen to axial loading. It is generally expressed in Megapascals (MPa) or pounds per square inch (psi) at an age of 28 days. One Megapascal equals the force of one Newton per square millimeter (N/mm^2) or 1,000,000 N/m^2. Other test ages are also used; however, it is important to realize the relationship between the 28-day strength and other test ages. Seven-day strengths are often estimated to be about 75% of the 28-day strength and 56-day and 90-day strengths are about 10% to 15% greater than 28-day strengths. Compressive strength of concrete is a primary physical property and frequently used in design calculations for bridges, buildings, and other structures. Compressive strength was tested after 28 day and it was determined based on results obtained by testing 3 cubes for each concrete type.

The compressive strength testing was performed in accordance with the SRPS U.M1.020 standard at servo tensile machine INSTRON 1332 with maximal load of 100 kN. Testing compressive strength, i.e. determining breaking force, was done using hydraulic press capacity of 3000 KN (Figure (3-6)). The load was added continually, with constant increase of stress from 0.6 ± 0.4 MPa/s until breaking.

Figure (3-6). Examining compressive strength on hydraulic press

3.3 Sintering of EAFD within LCD waste glass matrix:

Samples of EAFD were obtained from Serbian steel making company, equipped with electric arc furnace. The LCD waste glass was obtained from the local WEEE recycling company.

3.3.1 Materials preparation:

Both raw materials were sieved on standard mesh type sieve in order to obtain -100µm fraction and subsequently dried in laboratory oven at 105 ºC for 24 hours. Prior to sieving and drying, raw materials were milled in a steel ball mill, figure (3-1), (Ø160 mm, height 270 mm, ball diameter 10 mm, material + balls material charge 60%) at 300 min^{-1}.

In order to investigate the possibility for EAFD-LCD stabilization and valorization using conventional methods of synthesis and thermal treatment, testing mixtures were prepared according to mixing matrix presented in Table (3-7).

Table (3-7). EAFD and LCD glass mixing matrix

Series	Temp.	Sample No.	EAFD	LCD
			%	
I	600 ºC	1.1	75.00	25.00
		1.2	68.75	31.25
		1.3	62.50	37.50
		1.4	55.00	45.00
II	650 ºC	2.1	75.00	25.00
		2.2	68.75	31.25
		2.3	62.50	37.50
		2.4	55.00	45.00
III	700 ºC	3.1	75.00	25.00
		3.2	68.75	31.25
		3.3	62.50	37.50
		3.4	55.00	45.00
IV	750 ºC	4.1	75.00	25.00
		4.2	68.75	31.25
		4.3	62.50	37.50
		4.4	55.00	45.00
V	800 ºC	5.1	75.00	25.00
		5.2	68.75	31.25
		5.3	62.50	37.50
		5.4	55.00	45.00
VI	900 ºC	6.1	75.00	25.00
		6.2	68.75	31.25
		6.3	62.50	37.50
		6.4	55.00	45.00

3.3.2 Experimental set-up & Methods:

As presented, six series with four different mixtures for each temperature were prepared providing a total of 24 mixtures. The dry homogenization of predefined quantities of EAFD and LCD glass was performed in an electric mixer. After homogenization, mixtures were compressed using two-sided uniaxial pressing machine under pressure of 300 MPa, to form 32×13×10 mm cubic samples. Afterward, the pressed samples were heated to the temperatures of 600, 650, 700, 750, 800 and 900ºC, at a rate of 10ºC/min, in Marshall 9000 tube electro-resistant furnace. After reaching the defined temperature, samples were kept at constant temperature for 1 h, than cooled to 200°C in the furnace, and finally removed from the furnace to cool to room temperature.

In case of Series VI, samples sintered at 900ºC, 20 min after reaching defined temperature, started to melt, and were not used in further tests.

3.3.2.1 Analytical methods:

Both, raw materials and sintered samples, were characterized in order to determine chemical and phase composition, morphology, mechanical properties, mass differences and heavy metals leaching degree. Chemical composition was analyzed by X-ray fluorescence (XRF, Thermo Scientific Niton analyzer) and atomic absorption spectrometry (AAS, Perkin Elmer 4000 spectrometer). Phase composition was analyzed using Jenapol U-Carl Zeiss polarizing microscope. Morphology of the sintered samples was analyzed by scanning electron microscopy (SEM) using JEOL JSM-5800 at 20 kV. Prior to the SEM analysis, samples were coated with gold using a spatter coater (POLARON SC502, Fisons Instruments). X-ray diffraction (XRD) analysis was performed using "Philips PW 1050" diffractometer. Cu-Kά1, 2 radiations was used, measuring in 2θ range 15-100°, step 0.02° and exposition 10 sec. Mechanical properties (compressive strength) of sintered samples were analyzed according to ASTM C1358-11 standard at servo tensile machine INSTRON 1332 with maximal load of 100 kN. Heavy metals leachability was tested according to the standard Toxicity characteristic leaching procedure (TCLP), US EPA method 1311 [113].

3.4 Sintering of EAFD within iron-bearing waste composite pellets:

The subject of this part is to investigate the separation of zinc and lead recovery from coal composite pellets, made of EAFD with other synergetic iron-bearing wastes and by-products (mill scale, pyrite cinder, magnetite concentrate), in two-stage process. The first, low temperature, stage should enable removal of lead due to the presence of chlorides in the system and in the second stage at higher temperature, zinc should be valorized. Using HSC chemistry 6.12, a model of two-stage process was developed. Model was verified in semi-industrial conditions.

3.4.1 Materials preparation:

All by-products materials and additives which were used in this research are obtained from the Serbian production lines.

EAFD is hazardous waste generated in steel plant in Serbia in amount 4800tpa, and is valuable source of zinc.

Mill scale is formed during hot rolling process of steel in Serbian rolling mill plant in amount of 1000 tpa.

Pyrite cinder was generated in the process of sulfuric acid production in Šabac and due to its composition belongs to the technogenic waste; this material is used as iron source in defined mixture.

Magnetite concentrate, which is used in one mixture, was brought from newly opened mine in western Serbia; this concentrate due to its chemical composition is not suitable for usage in blast furnaces, and in defined mixture was used as iron source.

Used additives, flux (lime), binder (cement) and reducing agent (coke) were commercial grade. All used materials were dried for 24 hour at 105^{o}C, and weighted in dry room condition.

Three different test mixtures (marked P1, P2, and P3) were made and tested at different process temperatures and times. The quantity of every mixture was 50 kg, and the composition of materials is presented in table (3-8). Definition of feed mixture was guided with maximal annual amounts of EAFD and mill scale generated per year, iron content in mixture of 45% and mixture basicity of 0,75.

Basicity was calculated using formula:

$$B = \frac{(CaO + MgO)}{SiO_2}$$

Using Solver function of MS Excel software which by means of what-if analysis tools and pre-set constrains finds optimal value of target cell.
According to Solver results, mixture composition was as follows:

Table (3-8). Percentage by weight of used materials

Mixture	EAFD, %	Mill scale, %	Pyrite cinder, %	Coke, %	Magnetite, %	Lime, %	Cement, %
P1	20	4	62	10	-	2	3
P2	20	4	42	10	23	2	0
P3	86	-	-	10	-	2	3

Suspension was prepared by adding flux lime as 1% lime milk.

3.4.2 Experimental set-up & Methods:

Semi-industrial pelletizing disc (Ø100×22 cm) was used to agglomerate the materials. The pelletizing disc was placed at an angle of 45° with a speed of 15r/min (Figure (3-7)). All raw materials and additives were mixed dry for 10 minutes before start of suspension spraying. In the first few minutes of spraying micro pellets were formed, and after calculated quantity of lime milk added and at the end of spraying process; the bigger pellets began taking shape. Produced pellets were dried, in the room temperature for 2 days and at 105°C/3h in the dryer, before tests started. Before thermal treatment the particle size analysis was performed and fractions between 6 -10 mm (>75% of material) have been selected as sample for further testing.

Figure (3-7). Used pelletizing disc

Process modeling:

For process modeling in HSC Chemistry 6.12 software input data, chemical compositions of charge components derived from Solver functions were used.

HSC Chemistry is designed for various kinds of chemical reactions and equilibria calculations. The name of the program is based on the feature that all calculation options automatically utilize the same extensive thermochemical database which contains enthalpy (H), entropy (S) and heat capacity (C) data for more than 17000 chemical compounds. This database is equivalent to more than seventeen thick data books.

HSC Chemistry offers powerful calculation methods for studying the effects of different variables on the chemical system at equilibrium. For example, if the user gives the raw materials, amounts and other conditions of almost any chemical process, the program will give the amounts of the product as a result. HSC also makes heat and material balance calculations of different processes much more easily than any manual method.

Using HSC chemistry 6.12, a model of two-stage process was developed. Model was verified in semi-industrial conditions.

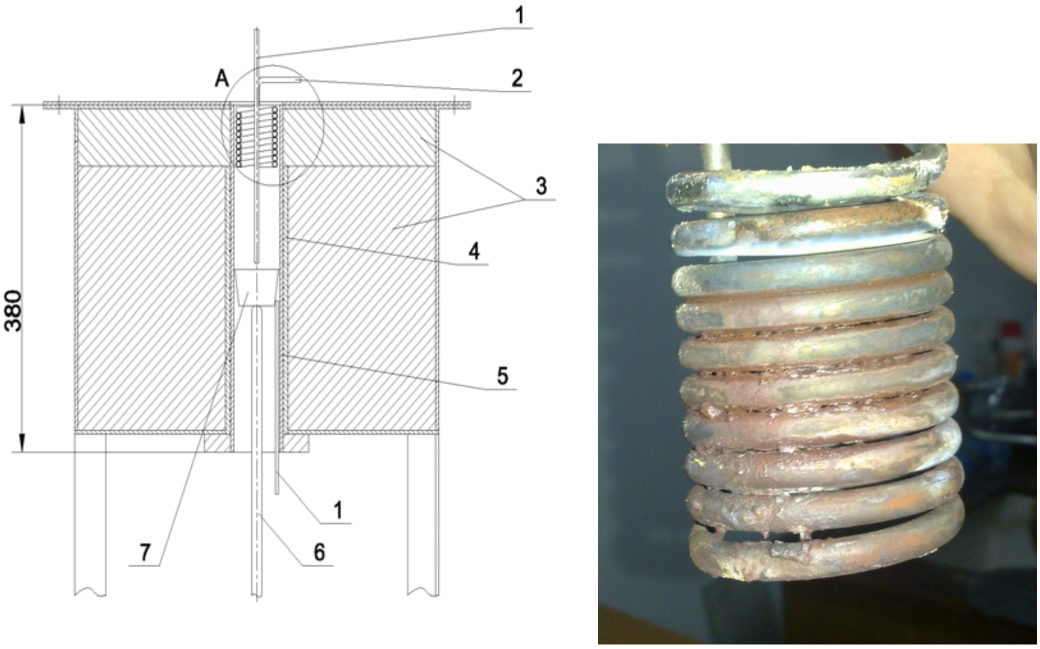
Presented process is highly suitable for locally available zinc rich and iron-bearing wastes and by-products and production of lead-chloride, zinc-oxide, pig-iron and slag, all as commercial grade products.

The first, low temperature, stage:

Laboratory electro resistant furnace (ERF) (Morgan type 1), upgraded with a condenser system, was used for pellets pretreatment and lead volatilization is shown in figure (3-8).

The annealing program, for lead valorization, was performed in temperature range of 850- 1200^{o}C for 30-60-90 min. Retention time was varied in order to optimize process parameters, necessary for design of industrial plant.

The process conditions during the laboratory experiments were maintained constant. Every sample from every mixture was fed from the furnace's bottom and at the end of designed temperature and time, the samples were left in the furnace to cool gradually for 24 hr. Pellets were taken out from the furnace and subjected to many tests.



(a) (b)

Figure (3-8). (a) Technical drawing of (ERF) with details:
1- Thermocouple, 2-Water cooled condenser, 3-Insulation, 4-Heater,
5-ceramic tube, 6-crucible holder, and 7-crucible. (b) Condenser.

Condensed gases were scraped from the condenser and chemically analyzed. Produced pellets were grinded and sieved through a sieve 50 µm to give homogenous powder for chemical analysis.

The second, high temperature, stage:

In order to valorize zinc, electro resistant furnace was connected with semi-industrial DC plasma furnace, figure (3-9), capacity of 50kg, equipped with gas cooling system and bag filter.

Charge materials for DC plasma furnace were start slag and pretreated pellets, materials were added in portions, and smelting campaign lasted for 6 hr at 1490ºC.

Start slag originated from previous smelting of similar material. After smelting, materials were cast into casting crucible, and left for metal and slag separation. Condensed gases were collected from the bag filter and chemically analyzed. No additional reducing agent was added, due to the pellets contained 10% of coke.

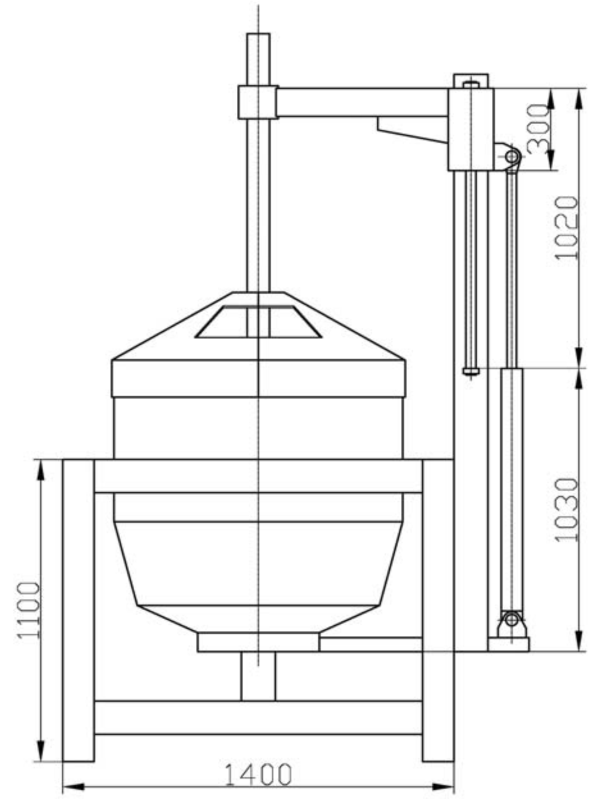


Figure (3-9). Technical drawing of DC plasma furnace.

For second stage of the process 40 kg of pretreated pellets were charged in DC plasma furnace in the molten start slag bath. After finishing the smelting campaigns metal and slag were cast, dust from off-gasses was collected at the bag filter. Obtained metal and slag were analyzed.

Efficiency of zinc and lead separation during these experiments were established by measuring variations of metal content retained in the pellets.

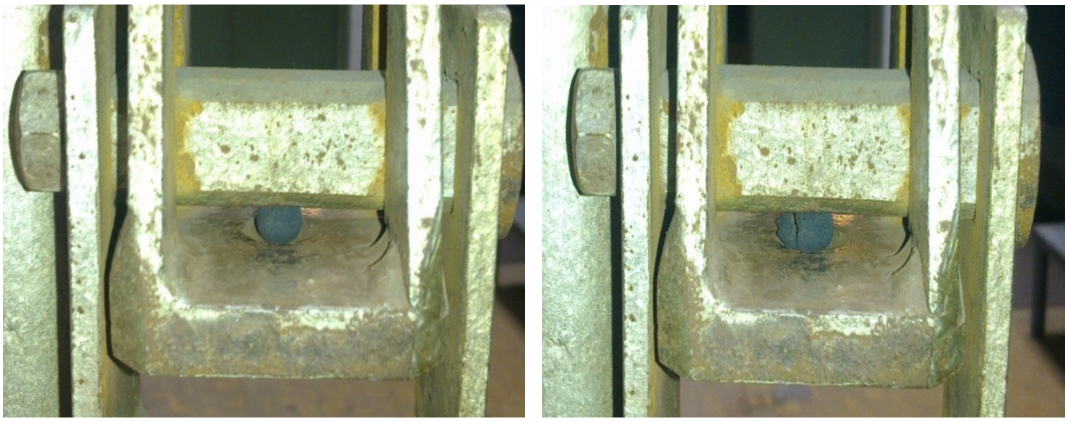
3.4.2.1 Drop strength:

Pellets drop strength represents its ability to survive multiple drops in material handling systems, is determined by dropping number of pellets from different heights on a solid surface and accounting the number of pellets that have survived from fracture. Green pellets were characterized by drop strength; ten pellets for every height were subjected to drop from 1, 1.5 and 2 meter for every mixture.

3.4.2.2 Compressive strength:

Compressive strength test was performed at laboratory testing instrument shown in figure (3-10, A-B-C).

(A)



(A) (C)

Figure (3-8). (A). Compressive strength machine, (B). Pellet before crashing, (C). Pellet after crashing

Ten pellets from every mixture were chosen and by electronic vernier diameter were measured from three different sides; the average value was calculated as a diameter for a pellet. Every chosen pellet was held between the two jaws and the weights were added by grams until the pellet crash, then weights calculated and the compressive strength calculated as an average for ten tested pellets. Both green and annealed pellets were characterized by compressive strength.

3.4.2.3 Abrasion test:

Pellets were analyzed for abrasion. Test was performed by weighting a defined amount of pellets in the plastic bag. The bag was manually shacked for 5 minutes. After that time pellets were weighed again and the losing weight is calculated. Abrasion test was applied on annealed pellets.

4. Results

Based on planned laboratory experiments and measurements, obtained results are presented in the following. Testing results of the characteristics of EAFD, additives, mortar, hardened concrete, LCD glass sintered products, green& annealed composite pellets are shown in a form of tables and graphs, which are formed in a way so that they can be directly used for analysis and conclusions.

4.1 characterization of EAFD:

The treatment policy of waste is closely associated with the characteristics of the wastes. It is therefore important to know the physical and chemical properties of the wastes before a treatment method is developed or chosen. EAFD, intended for study, was obtained from Serbian steel making company, equipped with electric arc furnace with capacity of 260,000 tons/year. EAFD was characterized by X-ray diffraction, grain size analyses, chemical analysis, leaching test, optical microscopy and scanning electron microscopy (SEM) techniques.

4.1.1 Physical properties:

EAFD is typically chocolate-brown in color, fine-grained material (Figure (4-1)), and emits foul gases (presumably acetylene) [116].

Figure (4-1). EAFD raw material

4.1.1.1 Humidity (%):

Humidity was analyzed by drying the raw sample at the temperature of 105^{o}C, which is the standard procedure. Results are presented in table (4-1).

Table (4-1). Humidity test results for the EAFD

Sample wet weight	300 g
Sample dry weight	296 g
Humidity	1.33%

4.1.1.2 Density (g/cm^3):

Bulk density is a measure of the weight of the material per unit volume (g/cm^3), usually given on an oven-dry (110°C), Results are presented in table (4-2).

Table (4-2). Bulk density test results for the EAFD

Tube volume (ml)	sample weight (g)	Density(g/cm^3)
50 ml	30	0.60
250 ml	154	0.616
500 ml,	296	0.592
Density average		0.602

4.1.1.3 Wettability:

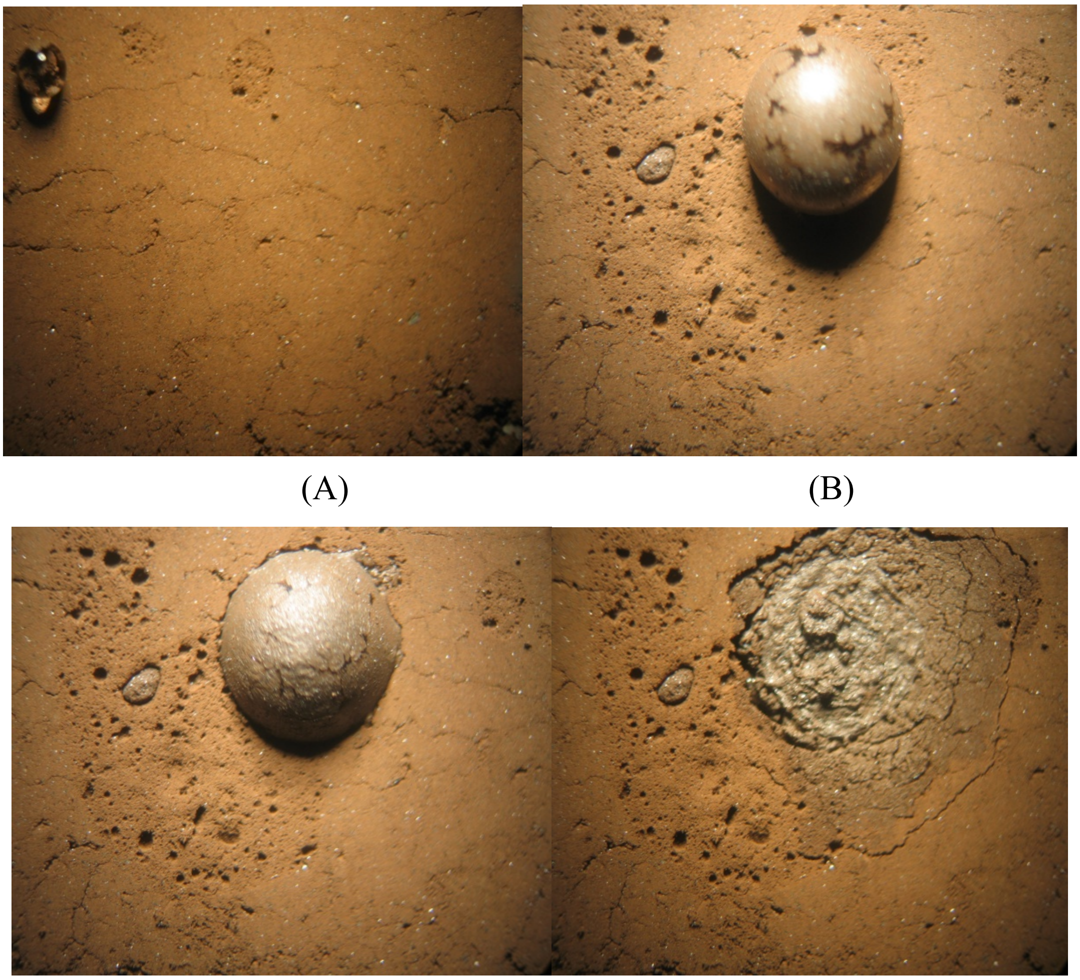
Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. Wetting deals with the three phases of materials: gas, liquid and solid. Wettability is property of any solid surface to be wetted when in contact with a liquid; that is, the surface tension of the liquid is reduced so that the liquid spreads over the surface.

Wetting is best explained with a drop of water on a plastic film. The liquid volume remains the same, the drop base diameter will increase and the contact angle will decrease as a function of time. When the liquid volume is reduced as a function of time, the base diameter of the drop is studied. When this diameter remains constant, the absorption is dominating. When the drop is spreading across the surface (increasing base diameter), the interaction is based on adsorption

Wettability can be estimated by determining the contact angle or calculating the spreading coefficient. Wetting or spreading of a liquid on a solid surface or material depends on the solid surface properties as well as the liquid used.

The wetting or sorptive behavior between a liquid and a particular sheeted substrate is dependent, at least in part, upon the relationship of the surface energy (tension) of the liquid and the surface energy of the substrate. The theoretical relationship of these energies is complex, and the different mathematical models which have been proposed for adhesion, wettability, and sorption are beyond the scope of this test method, but may be found in standard texts in these areas. In many cases, however, the contact angle of the fluid which will be in contact with the substrate, or the contact angle of a liquid of known surface tension, when placed in contact with a substrate of interest, is used to understand or predict in-process or end-use results of a particular printing, adhesion, or sorptive application [117].

Wettability in this case was analyzed by the visual changes in bulk sample of the EAFD, which is presented on the figure (4-2) A, B, C and D.



(A) (B)

(C) (D)

Figure(4-2). Wettability of EAFD

4.1.1.4 Loss of ignition (750^{o}C for 1hr):

The loss of ignition is reported as part of an elemental or oxide analysis of a mineral. The volatile materials lost usually consist of "combined water" (hydrates and labile hydroxyl-compounds) and carbon dioxide from carbonates. It may be used as a quality test, commonly carried out for minerals such as iron ore. For example, the loss on ignition of a fly ash consists of contaminant unborn fuel. In this research the materials for LOI test were treated at 750°C for 1hr. Results are presented in the table (4-3).

Table (4-3). Loss of ignition (750°C for 1hr)

Sample No.	Sample weight (g)	After burning for 1 hour at 750°C
		Sample weight (g)
1	2	1.80
2	3.01	2.78
The total percentage of lost weight		8.58 %

4.1.1.5 Grain size analysis:

Sieve analysis of EAFD and cumulative undersize& oversize are presented in table (4-4) and figures (4-3) and (4-4) respectively.

Table (4-4). Sieve analysis and cumulative undersize & oversize of EAFD

Sieve's size mm	Wt, g	Wt, %	Cumulative undersize %	Cumulative oversize %
1	2.00	0.84	99.16	0.84
0.5	2.00	0.84	98.32	1.68
0.25	32.00	13.45	84.87	15.13
0.125	58.00	24.37	60.50	39.50
0.1	36.00	15.13	45.38	54.62
0.063	44.00	18.49	26.89	73.11
0.045	26.00	10.92	15.97	84.03
0.036	27.00	11.34	4.62	95.38
0.01	11.00	4.62	0.00	100.00
Total	238.00	100.00		

The sieve analysis shows that approximately 54% of the EAFD particles were larger than 100 μm.

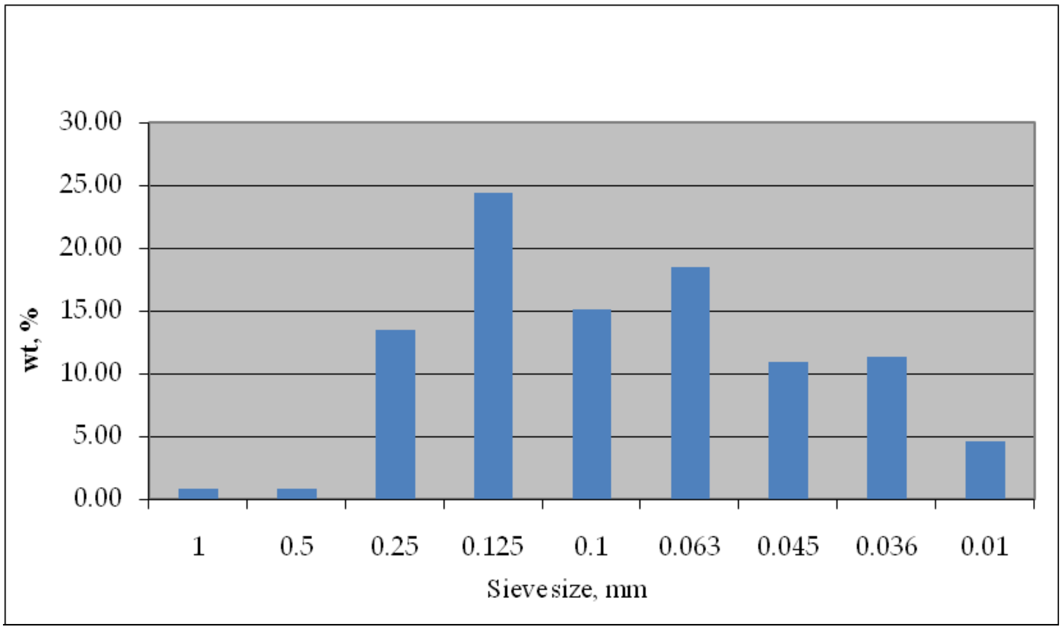


Figure (4-3). Sieve analysis of EAFD

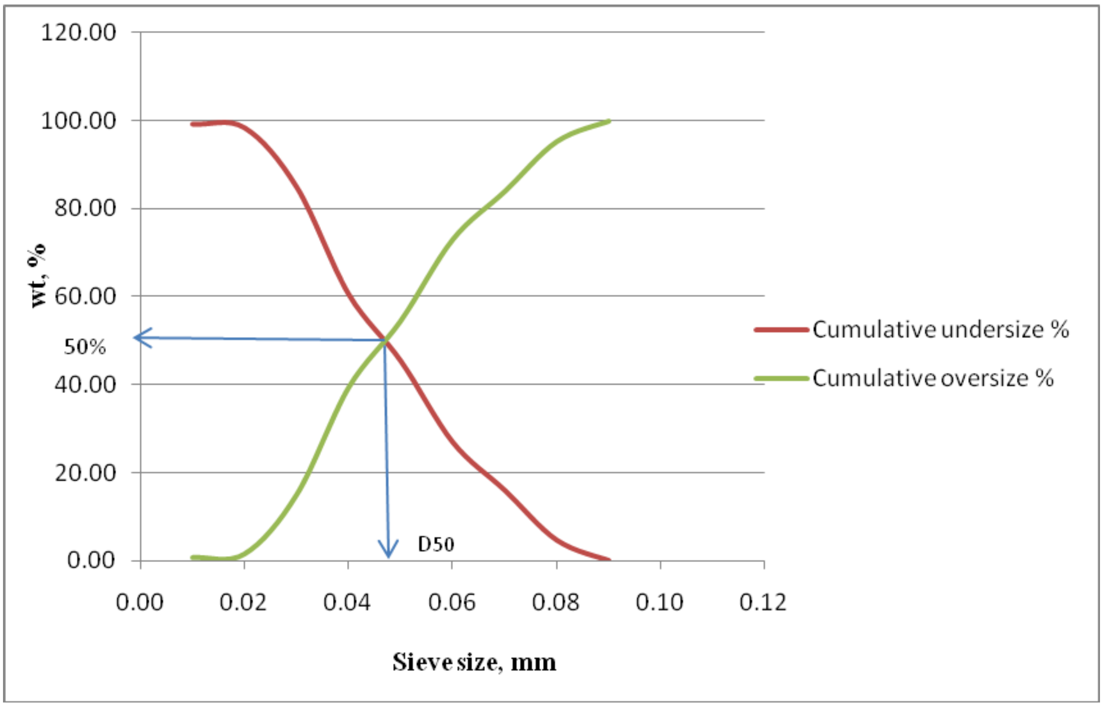


Figure (4-4). Cumulative under size and cumulative over size of EAFD

By carrying out standard calculations, the surface area and particles quantity per one gram of EAFD were obtained:

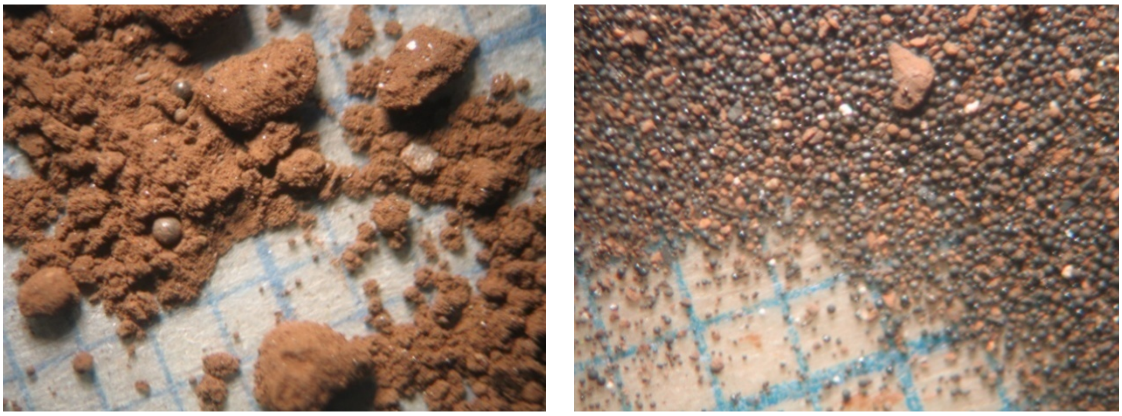
Surface area = 1.40E+06 (cm^2/g)

Particle/gram = 5.37E+16

4.1.2 EAFD morphological analysis:

4.1.2.1 Optical microscopy:

If the size and distribution analysis enable to characterize quickly and reliably a powder, they don't give any information on particles shape. Though, particle morphology is also an important parameter to explain a physical behavior or a physical property. A microscopic analysis enables to visualize some particles, but no operator will analyze enough particles to obtain a representative analysis. Figure ((4-5) a, b) shows optical microscopy images of EAFD sample before and after washing.



a) Before washing b) After washing

Figure (4-5). Macro optical images of EAFD samples

As can be seen from the Figure (4-5) a, b), particles in sample has predominantly spherical shape where bigger particles are covered with the smaller ones. Also the presence of small white spots in the sample was observed, which represent CaO, whose presence was confirmed by XRD analysis.

4.1.2.2 Scanning electron microscope (SEM):

The SEM micrograph of an EAFD sample was carried out by using (JEOL JSM-5800 at 20 kV, figure (3-2)).

The SEM photograph of EAFD samples is presented in figure (4-6). Prior to the SEM analysis, samples were coated with gold using a spatter coater (POLARON SC502, Fisons Instruments, figure (3-3)).

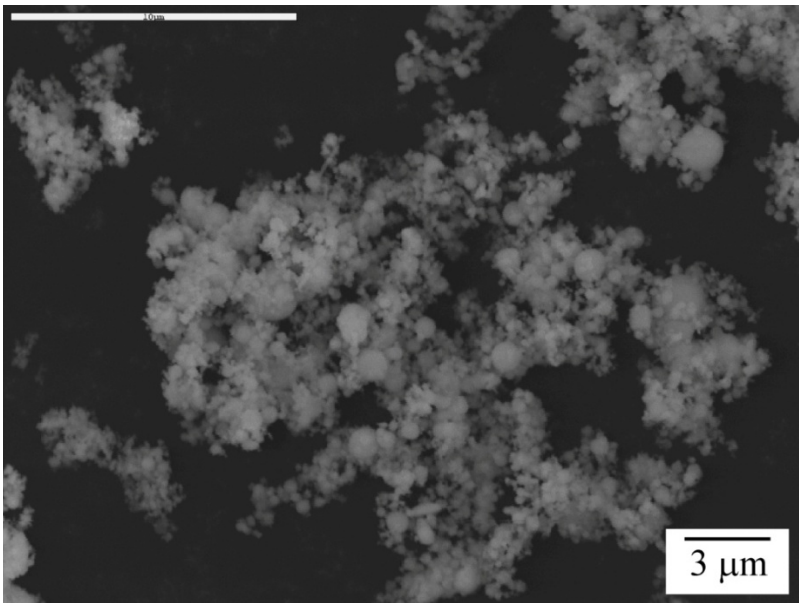


Figure (4-6). SEM micrograph of EAFD

Used EAFD is characterized with spherical particles of slag and flakelike particles of ZnO and PbO, size in range from 0.20 to 1.20 μm, average particle size 0.45μm. Due to the relatively small size, but high surface, i.e. surface area particles are partially agglomerated.

4.1.3 EAFD Chemical characterization:

The chemical properties of EAFD dust vary considerably, depending on the steel grade produced, raw materials used, operational parameters, furnace type and heats [114]. The chemical analysis of utilized EAFD is presented in table (4-5), along with the TCLP analysis of EAFD. Typical chemical composition of EAFD is presented in table (4-6).

Table (4-5). Chemical analyses of utilized EAFD with TCLP limits

Component	%	TCLP, ppm	Limits, ppm
Si (as SiO_2)	4.89		
Al (as Al_2O_3)	0.27		
Fe (as oxides)	17.75		
Ca (as CaO)	9.79		
Mg (as MgO)	4.78		
Cd	0.10	74	1
Cl-	0.98		
Cr	0.05	<0.5	5
Pb	3.52	147	5
Ni	0.01		
Cu	0.18		
Zn	30.34	253	
As	0.004	<0.05	5

Table (4-6). Typical chemical composition of EAFD

Component	Dust from carbon/low alloyed steel production (Wt- %)
Fe_{tot}	10 - 40
SiO_2	0.6 - 5.1
CaO	3 - 17
Al_2O_3	0.3 - 3
MgO	0.5 - 6
P_2O_5	0.1 - 0.37
MnO	1.1 - 6
Cr_2O_3	0.13 - 2
Na_2O	0.3 - 3
K_2O	0.5 - 2.3
Zn	21 - 43
Pb	0.4 - 10
Cd	0.02 - 0.18
Cu	0.08 - 0.5
Ni	0.01 - 0.05
V	0.01 - 0.035
W	n/a
Co	0.001 - 0.01
As	0.001 - 0.02
Hg	0.0001 - 0.005
CI	0.8 - 5
F	0.02 - 0.9
S	0.1 - 3
C	0.4 - 3.3
Basicity	2.0 - 6.5
Moisture	6 - 16

*n/a = not available

For presented research, samples of EAFD with high Zn content were used in order to fully determine the properties of mixtures and final products with extreme Zn content. Usual Zn content is between 18-40%, so investigated samples were in upper part of this range.

4.1.3.1 XRF Spectrometer analysis:

Energy dispersive X-ray fluorescence technology (ED-XRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples. Characteristics of standard Zn solution are presented in table (4-7). The Zn concentrations for different fractions of EAFD are presented in table (4-8).

Table (4-7). Standard Zn solution

Solution	1ppm	5ppm	10ppm
Zn concentration	0.081	0.387	0.543

Table (4-8). Zn concentration for different fractions of EAFD

No	Sieve’s size mm	Zn concentration
1	Raw material	0.667
2	- 0.036	0.590
3	+ 0.036	0.665
4	+ 0.045	0.650
5	+ 0.063	0.655
6	+ 0.1	0.663
7	+ 0.125	0.668
8	+ 0.250	0.660

4.1.3.2 X-ray diffraction:

X-ray diffraction XRD analysis was performed using "Philips PW 1050" diffractometer. The XRD pattern of EAFD is presented in figure (4-7).

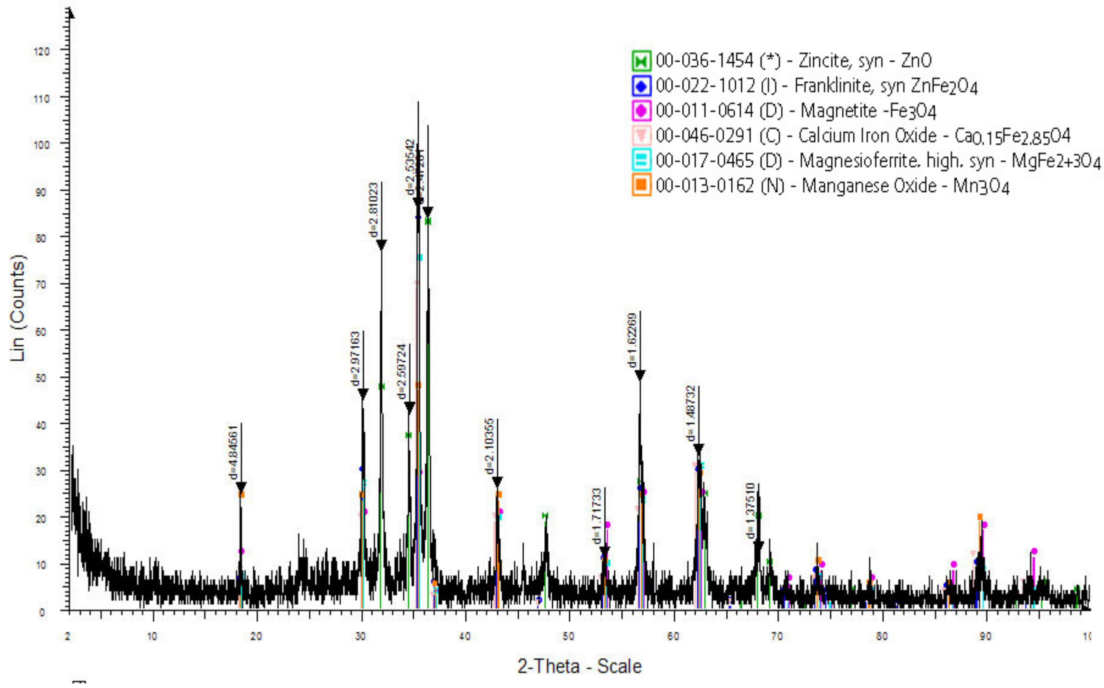


Figure (4-7). XRD of EAFD

The mineralogical analysis of EAFD shows that it contains a high content of zinc and iron, together with slight quantities of calcium, manganese and magnesium. These elements are presented as complex minerals such as: franklinite ($ZnFe_2O_4$), magnetite (Fe_3O_4), magnesium-ferrite ($MgFe_2O_4$), calcium-magnetite ($Ca_{0.15}Fe_{2.85}O_4$), manganese oxide (Mn_3O_4) and zincate (ZnO).

4.2 Analysis of process products:

4.2.1 Solidification/Stabilization products analysis:

Portland cement is the most common used of all S/S binding reagents because of its ability to both solidify and stabilize the wastes. Portland cement is not only used alone, but is also used as the main component in a number of proprietary S/S systems. Many formulations combine Portland cement with fly ash, lime, soluble silicates, clays, and other materials. For the most part, however, Portland cement remains the backbone of S/S technology, whether used alone or in combination with other constituents. First, the characterization of used additives for S/S process was realized.

4.2.1.1 Cement:

Portland cement is well known for its use in concrete. It is the “glue” that holds the mass together. Concrete’s high strength, low permeability, and resistance to most chemicals make it an ideal material for waste containment. Commercial Ordinary Portland cement, (CEM II B-M (V-L) 32.5 R), was used in all mixtures. Characterization of used cement is presented in table (4-9).

Table (4-9). Characterization of used Portland cement

Component	%	Component	%
SiO_2	21,6	MgO	1,76
Al_2O_3	4,35	Na_2O	0,09
Fe_2O_3	2,95	K_2O	0,51
CaO	63,81	SO_3	2,06
Bulk density, t/m^3			1,50
Specific surface area, m^2/kg			320-380
Granulometric analysis, μm			15% <5 15% >45

4.2.1.2 Fly ash:

Fly ash class F (-45μ), originating from burning of ‘Kolubara’ coal at the Bor heating plant, was used in designed concrete mixtures as the binding agent in the S/S process. The chemical analysis of utilized fly ash is presented in table (4-10), along with the TCLP analysis. Sieve analysis of fly ash is presented in table (4-11) and graphically on figure (4-8).

Table (4-10). Chemical analyses of utilized fly ash with TCLP limits

Component	%	TCLP, ppm	Limits, ppm
Si (as SiO_2)	28.17		
Al (as Al_2O_3)	9.28		
Fe (as oxides)	6.72	<0.1	
Ca (as CaO)	4.44	1784.7	
Mg (as MgO)	0.72		
Pb		<0.3	5
Ni		<0.2	
Cu		<0.1	
Zn		0.05	
As		<0.1	5

Table (4-11). Sieve analysis of fly ash

Sieve's size, mm	Wt, g	Wt, %
250	4	2
125	26	13
100	14	7
63	52	26
45	32	16
36	16	8
-36	56	28
Total	200.00	100.00

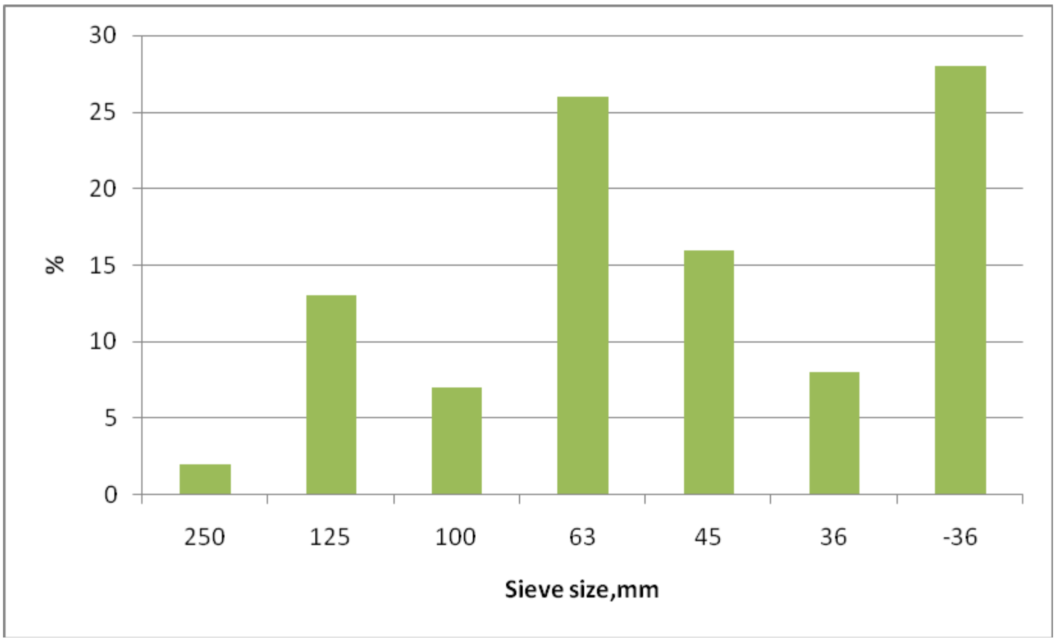


Figure (4-8). Sieve analysis of fly ash

4.2.2 Cement grout S/S products analysis:

Cement grout is a mixture of Portland cement and water. This technique is commonly called grouting, and the mixtures so obtained, grouts. Cement-based "grout" systems have been used for so many years in so many instances for S/S.

4.2.2.1 Grout hardened testing results:

After curing for 28 days, in accordance with the standard SRPS U.M1.005, the samples were tested for compressive strength. The compressive strength testing was performed in accordance with the SRPS U.M1.020 standard at servo tensile machine INSTRON 1332 with maximal load of 200 kN.

Compressive strength results are presented in table (4-12) and graphically in figure (4-9)

Table (4-12). Compressive strength results

Series No.	Sample No.	Cement %	Lime %	EAFD %	Maximum load, kN	Compressive strength, MPa
Series I C:L=1:0	D1	100.0	0.0	0.0	105.71	11.75
	D2	80.0	0.0	20.0	84.21	9.36
	D3	70.0	0.0	30.0	57.84	6.43
	D4	60.0	0.0	40.0	3.64	0.40
	D5	30.0	0.0	70.0	3.83	0.43
	D6	20.0	0.0	80.0	3.78	0.42
	D7	10.0	0.0	90.0	1.54	0.17
Series II C:L=1:1	D8	40.0	40.0	20.0	69.70	7.74
	D9	35.0	35.0	30.0	39.35	4.37
	D10	30.0	30.0	40.0	25.86	2.87
Series III C:L=3:1	D11	60.0	20.0	20.0	67.70	7.52
	D12	52.5	17.5	30.0	71.67	7.96
	D13	45.0	15.0	40.0	43.13	4.79
	D14	15.0	5.0	80.0	2.78	0.31

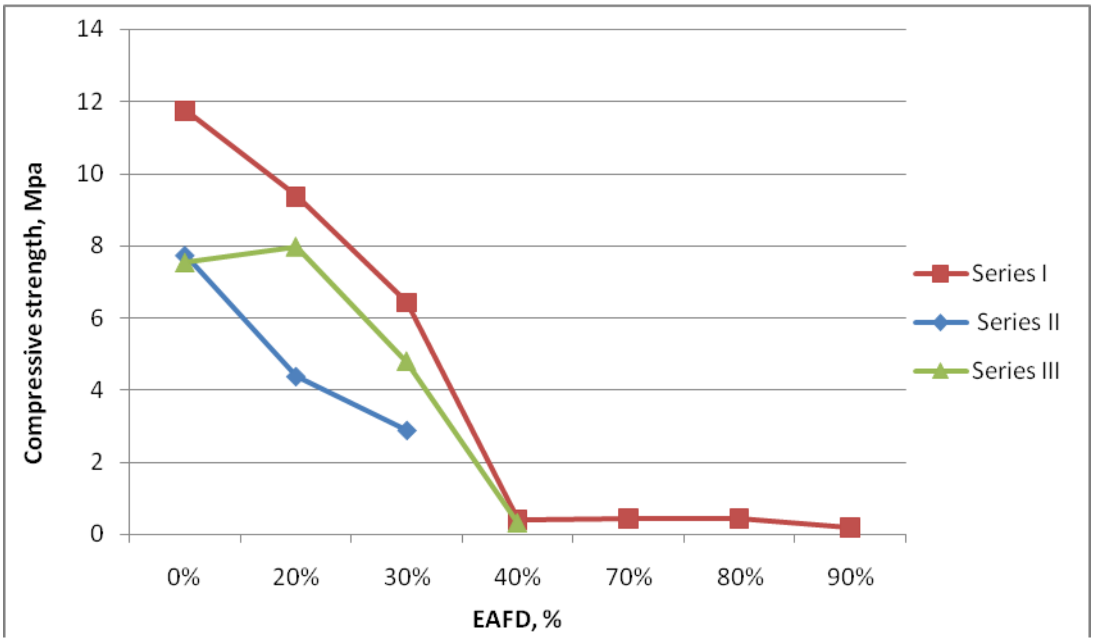


Figure (4-9).Compressive strength results with different cement: lime percent

As can be seen in figure (4-9), compressive strength in series I achieved the highest value with 20% of cement is replaced with EAFD. Whereas in series II the highest compressive strength was with 20% of EAFD and 40% lime replacement. On the other hand, in series III the best compressive strength was with 17.5% addition of lime and 30% of EAFD replacement.

Heavy metals leachability was tested by standard toxicity characteristic leaching procedure (TCLP) [111]. Leachability results are presented in table (4-13).

Table (4-13). Leachability results

Sample No.	Cement %	Lime %	EAFD %	TCLP, ppm	
				Pb	Zn
D1	100.0	0.0	0.0	0.74	0.07
D2	80.0	0.0	20.0	0.74	0.23
D3	70.0	0.0	30.0	0.37	1.16
D4	60.0	0.0	40.0	0.74	2.04
D5	30.0	0.0	70.0	1.47	1.41
D6	20.0	0.0	80.0	1.10	0.38
D7	10.0	0.0	90.0	5.93	6.19
D8	40.0	40.0	20.0	1.29	0.26
D9	35.0	35.0	30.0	1.93	2.82
D10	30.0	30.0	40.0	0.70	2.49
D11	60.0	20.0	20.0	0.69	1.12
D12	52.5	17.5	30.0	1.20	2.03
D13	45.0	15.0	40.0	2.32	2.56
D14	15.0	5.0	80.0	1.55	0.47

From table (4-13), it could be seen that leachability of lead from all concrete samples is far below the limit of 5 mg/L, except for sample D7 with 90% of EAFD is above the limit. Pb was stabilized in a cement matrix even at 80% of cement replacement with EAFD. Lead leachability is reduced comparing to initial values

(Table (4-5)), but for Zn there are no TCLP limits. In general, increases of EAFD amount in mixture; Zn leachability increase.

4.2.3 Concrete S/S product analysis:

Concrete is an artificial conglomerate stone made essentially of Portland cement, water, sand, and aggregates. The mixing of all the materials is placed into a plastic form; a chemical reaction called hydration takes place between the water and cement, and concrete normally changes from a plastic to a solid state in about 2 hours. Concrete has been used for S/S for many years for waste treatment. In this research Raw and milled EAFD was replaced of fine aggregate with different percentages with and without fly ash.

4.2.3.1 Testing results for hardened concrete:

Four concrete mixtures were made with different replacement percentages of EAFD, fly ash and different EAFD surface area.

The four concrete mixtures were prepared as:

- **Mixture I** with EAFD replacement of fine aggregate varying between 0% and 50% of the aggregate weight.
- **Mixture II** with EAFD replacement of fine aggregate varying between 10 and 15% and fly ash replacement of cement varying between 10% and 25%.
- **Mixture III** with 10% EAFD replacement and different milling time.
- **Mixture IV** with 10% EAFD replacement, different milling time and 10% fly ash.

After curing for 28 days, in accordance with the standard SRPS U.M1.005, samples were tested for compressive strength and leachability.

The compressive strength testing was performed in accordance with the SRPS U.M1.020 standard at servo tensile machine INSTRON 1332 with maximal load of 200 kN. Compressive strength results for all mixtures are presented below.

- **Compressive strength results for the first mixture:**

Compressive strength results for the first mixture are presented in table (4-14) and illustrated in figure (4-10).

Table (4-14). Compressive strength results for the first mixture

Sample No.	EAFD, %	Load, kN	Compressive strength, MPa
B1	0		19.78
B2	10		20
B3	13		19.96
B4	15		17.5
B5	17		3.3
B6	20		3.1
B7	25		2.6
B8	30		2.38
B9	40		2.35
B10	50		2.1

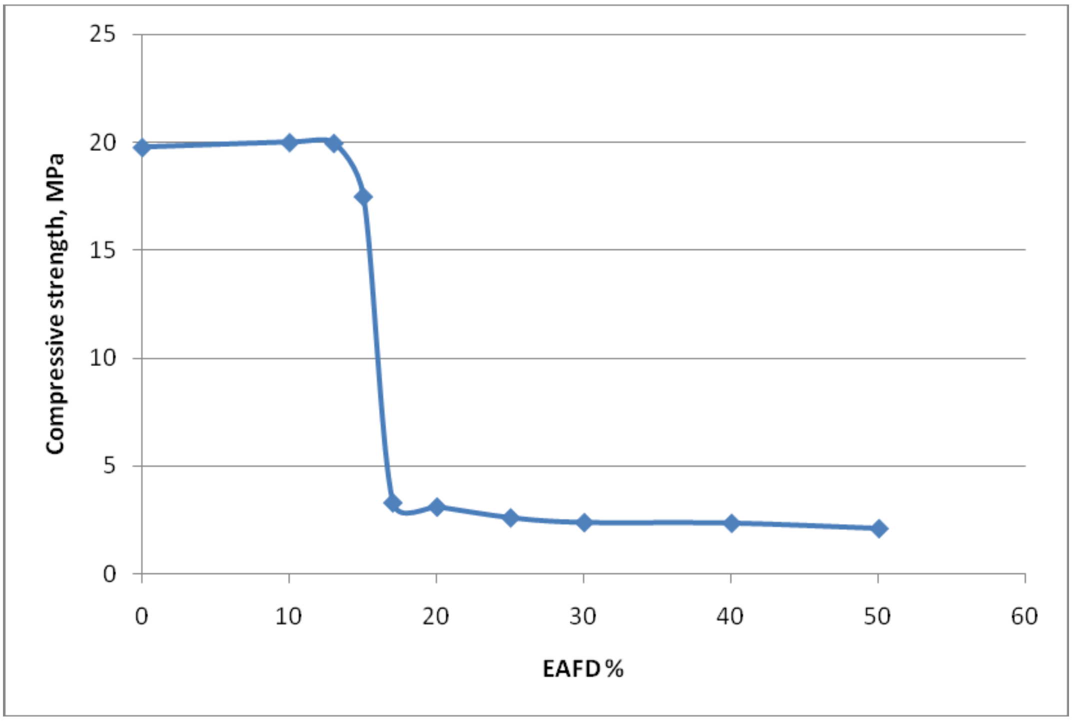


Figure (4-10). Compressive strength results for the first mixture

As can be seen in Figure (4-10), the highest compressive strength for the first mixture was for sample B2 with 10% of fine aggregate replacement and compressive strength rapidly decreased when more than 15% replacement of EAFD. For this reason, samples containing 10-15% of fine aggregate replacement were further investigated.

- **Compressive strength results for the second mixture:**

Compressive strength results for the second mixture are presented in table (4-15) and illustrated in figure (4-11).

Table (4-15). Compressive strength results for the second mixture

Sample No.	EAFD,%	Fly ash, %	Load, kN	Compressive strength, MPa
B2	10	10		16.18
		15		11.64
		20		10.23
		25		8.73
B3	13	10		7.91
		15		10.91
		20		9.77
		25		10.85
B4	15	10		10.05
		15		12.47
		20		10.96
		25		5.37

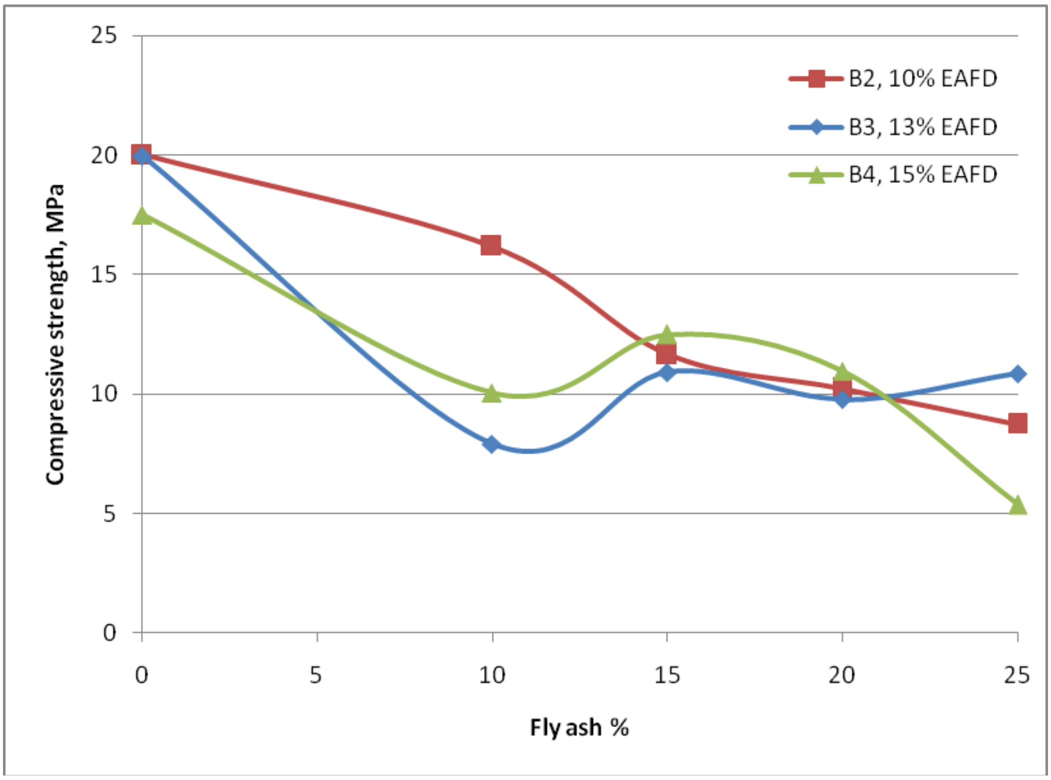


Figure (4-11). Compressive strength results for the second mixture

As presented in Figure (4-11). The best compressive strength was 16.18 MPa with addition of 10% of fly ash to sample B2 with a combination of 10% EAFD. For sample B3 with 15% fly ash has got the value of 10.91 MPa. Finally 12.47 MPa was recorded for sample B4 with 15% of fly ash.

- **Compressive strength results for the third mixture:**

Compressive strength results for the third mixture are presented in table (4-16) and illustrated in figure (4-12).

Table (4-16). Compressive strength results for the third mixture

Sample No.	EAFD, %	Milling time, min	Load, kN	Compressive strength, MPa
B2	10	60	42.919	17.17
B3	13		30.648	12.26
B4	15		26.399	10.56
B2	10	300	0.733	0.29
B3	13		0.811	0.32
B4	15		2.4	0.96

In mixture III, the sample B2 with 10% and one hour milled EAFD has recorded 17.17 MPa and it is the best compressive strength in the group after that, as the percent of EAFD increased as the compressive strength decreased. Whereas for the five hour milled EAFD, compressive strength was very poor.

- **Compressive strength results for the forth mixture:**

Compressive strength results for the forth mixture are presented in table (4-17) and illustrated in figure (4-12).

Table (4-17). Compressive strength result for the forth mixture

Sample No.	EAFD, %	Fly ash, %	Milling time, min	Load, kN	Compressive strength, MPa
B2	10	0	0	450	20
		10	0	364	16.18
		0	30	334	15.84
		10	30	164	7.29
		0	60	360	17.17
		10	60	316	15.04
		0	120	316	15.04
		0	180	412	18.31

As can be seen in table (4-17) the percentage of EAFD was set on 10% for different milling time with and without 10% of fly ash, it found that the presence of fly ash has negative impact.

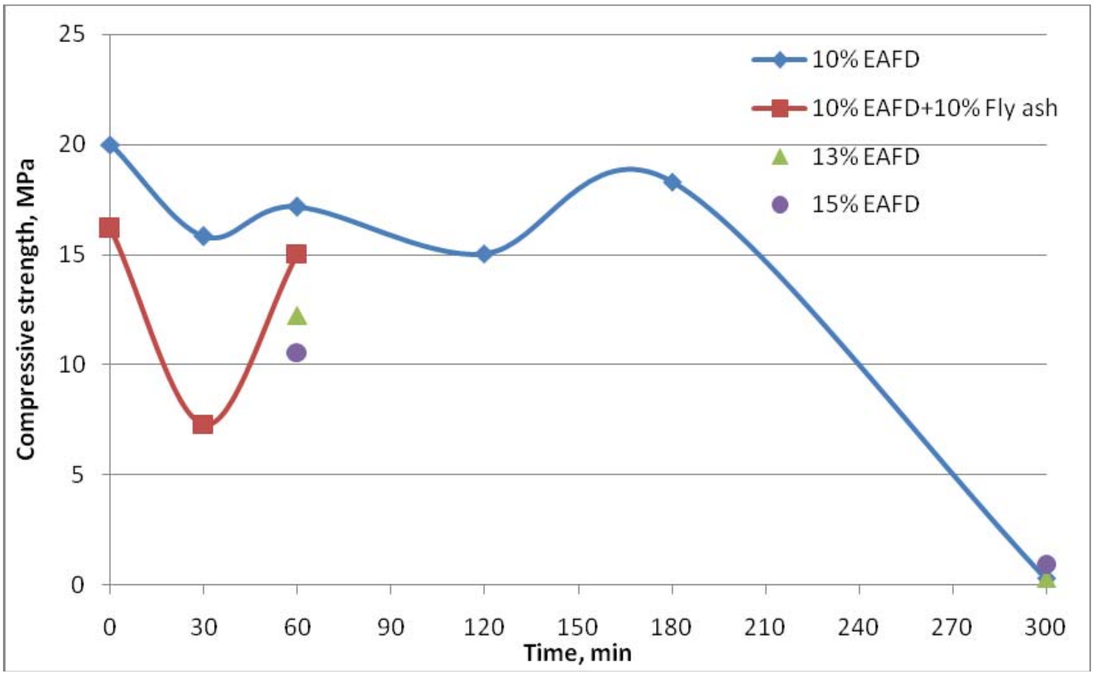


Figure (4-12). Compressive strength results for the third and fourth mixtures

The best compressive strength was attained with fly ash was at 10%, with replacement of both components and three hours of milling of EAFD, whereas the compressive strength decreases slightly with the further addition of fly ash.

The results show that the replacement of fine aggregate with more than 15% of EAFD results in a rapid decrease of compressive strength

Heavy metals leachability was tested according to the standard Toxicity Characteristic Leaching Procedure (TCLP), US EPA method 1311[113]. The TCLP results of zinc and lead leachability are presented in table (4-18).

Table (4-18). The TCLP results of Zinc and Lead

Mixture	Sample No.	EAFD, %	Fly ash, %	Milling time, min	TCLP		PH
					Zn, mg/L	Pb, µg/L	
Mixture I	B1	0			9	20	7.33
	B2	10			25.32	75	7.30
	B3	20			181	261	7.77
	B4	30			189.1	261	7.75
	B5	40			226.3	274	7.78
	B6	50			234.1	298	7.74
Mixture II	B7	0			9	20	7.33
	B8	10			25.32	75	7.30
	B9	13			30.7	81	7.84
	B10	15			31.2	93	7.77
	B11	17			179.8	280	7.86
	B12	20			181	261	7.77
	B13	25			194	264	7.72
	B14	30			189.1	261	7.75
Mixture III	B15	10	10		12	55	7.69
	B16		15		7.7	43	7.45
	B17		20		3.8	41	7.38
	B18		25		3.1	35	7.52
	B19	13	10		26	59	7.40
	B20		15		15	40	7.52
	B21		20		8.8	41	7.34
	B22		25		6.1	36	7.30
	B23	15	10		29	76	7.34
	B24		15		27	68	7.43
	B25		20		21	49	7.31
	B26		25		29	59	7.42
Mixture IV	B27	10		60	27.04	65	7.33
	B28	13			34	76	7.44
	B29	15			28.9	101	7.84
	B30	10		300	41.2	102	7.33
	B31	13			42.6	109	9.24
	B32	15			51	105	8.02

Mixture V	B33	10	0	0	25.32	75	7.30
	B34			30	26.43	70	7.45
	B35			60	27.04	67	7.09
	B36			120	29	80	7.52
	B37			180	25.88	69	7.18
	B38		10	0	12.4	54	7.63
	B39			30	14.6	49	7.71
	B40			60	12.1	37	8.60

From table (4-18), it could be seen that leachability of lead from all concrete samples is far below the limit of 5 mg/L, i.e. Pb was stabilized in a cement matrix even at 50% of fine aggregate replacement with EAFD. Zinc leachability is reduced comparing to initial values (Table (4-5)), but for Zn there are no TCLP limits. In Mixture I with increase of EAFD in mixture Zn leachability increase. In Mixture II-IV with addition of fly ash and with milling of initial EAFD, Zn leachability decreases below 50ppm.

4.2.4 Sintering results:

This part of results includes EAFD-LCD stabilization and valorization using conventional methods of synthesis and thermal treatment, to use it in ceramic industry and sintering of EAFD in synergy with other iron-bearing by-products by using pelletization technique and thermal pretreatment in tow-stage process for production of variety of final products: pig iron, slag, lead-chloride and higher purity zinc oxide..

4.2.4.1 Sintering of eafd within LCD waste glass matrix:

LCD glass and sintered samples were characterized in order to determine chemical, phase composition, morphology, mechanical properties, mass differences and heavy metals leaching degree.

4.2.4.1.1 XRF Spectrometer analysis:

Chemical composition of LCD glass was analyzed by using the XRF analyzer. The major determined elements of LCD waste glass are Si, Ca and Al, while trace elements are Fe, Zn, Pb and Cu. Chemical composition of LCD glass is presented in table (4-19).

Table (4-19). Chemical composition of LCD glass

Element	%	Element	%
Si (as SiO_2)	47.31	Ba (as BaO)	16.73
Al (as Al_2O_3)	6.29	Na_2O	3.26
Fe (as Fe_2O_3)	0.85	K_2O	4.66
Ca (as CaO)	3.66	S (as SO_3)	0.12
Mg (as MgO)	0.95	Cd	0.01
Pb (as PbO)	7.91	Cr	0.02
Zn (as ZnO)	0.22	Cu	0.03
Mn (as MnO)	0.02	Cl	0.07
Sr (as SrO)	7.60	As	0.28

4.2.4.1.2 Scanning electron microscope (SEM):

Microstructure analysis of LCD waste glass was done by SEM Microscope. According to scanning electron microscopy, SiO_2 was identified as major component, observed in form of small fractured particles; figure (4-13)

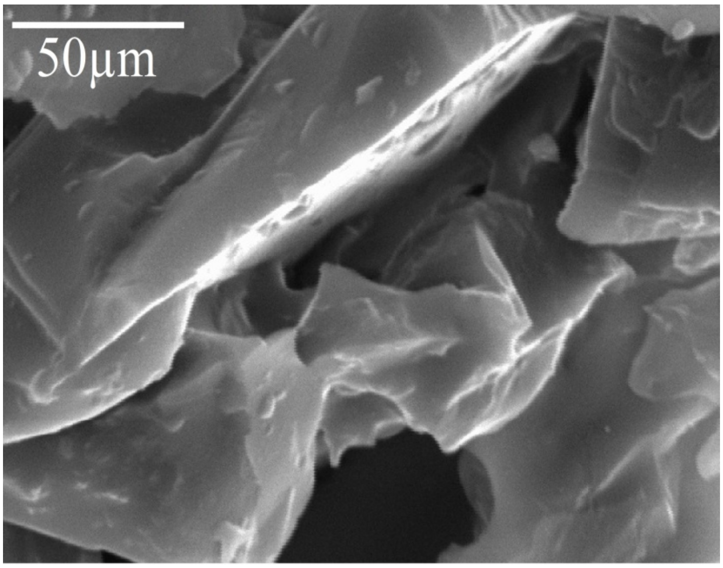


Figure (4-13). SEM of LCD glass

4.2.4.1.3 Leachability test results (TCLP):

Heavy metals leachability was tested according to the standard Toxicity Characteristic Leaching Procedure (TCLP), US EPA method 1311[113]. Results of heavy metals leachability from LCD glass are presented in table (4-20). According to obtained results of LCD waste glass, heavy metals leaching degree is far below regulatory limits.

Table (4-20). Leachability results of LCD glass.

Component	Result, mg/l	Limits, ppm [113]
Cd	<0.05	1
Cr	<0.1	5
Pb	1.0	5
Zn	11	-

4.2.4.1.4 Characterization of EAFD-LCD mixtures:

4.2.4.1.4.1 Chemical composition of EAFD-LCD mixtures:

Determined chemical composition of EAFD-LCD mixtures was calculated to oxides content, and obtained results are presented in table (4-21).

Table (4-21). Chemical composition of EAFD-LCD mixtures

EAFD/LCD	FeO	Fe_2O_3	SiO_2	CaO	ZnO	$Fe_{tot.}$
75/25	1.81	18.23	27.71	14.11	25.71	14.21
68.75/31.25	1.71	15.89	30.94	13.87	24.56	12.49
62.5/37.5	1.68	15.11	37.11	12.69	21.42	11.92
55/45	1.59	11.96	44.51	11.28	18.86	9.64

4.2.4.1.5 Characterization of sintered EAFD-LCD samples:

4.2.4.1.5.1 Chemical composition of sintered samples:

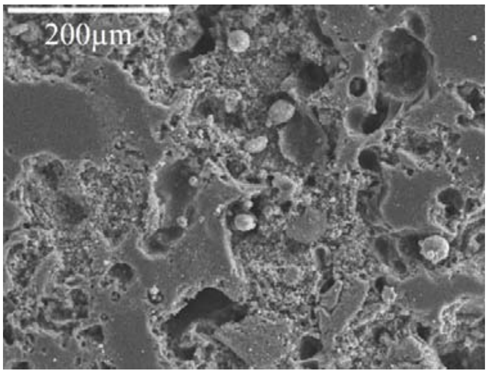
Chemical composition of samples calculated to oxides content, sintered on border temperatures, 600°C and 800°C are shown in table (4-22). Depending on the sintering temperature, volatile substances (VS) are in range from 3.17 to 6.12.

Table (4-22). Chemical composition of sintered samples on 600°C and 800°C

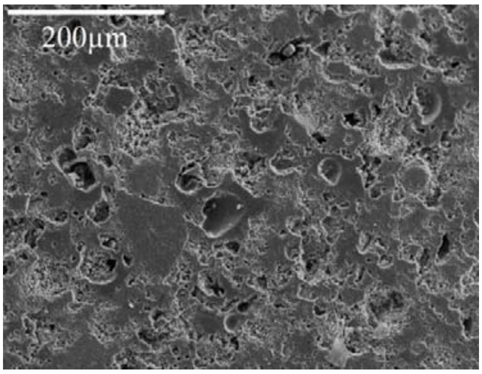
Sample No.	Fe_2O_3	SiO_2	CaO	ZnO	IM	$Fe_{tot.}$
1.1	27.56	24.55	13.56	24.55	4.36	19.29
1.2	25.18	30.71	13.11	22.94	4.02	17.63
1.3	23.95	34.58	12.84	20.39	3.98	16.77
1.4	22.39	36.16	12.21	18.84	3.17	15.67
5.1	21.12	28.96	13.54	25.68	6.12	14.78
5.2	20.54	30.89	13.01	24.56	5.83	14.38
5.3	18.97	33.78	12.94	21.46	5.26	13.28
5.4	16.76	39.39	12.64	19.74	4.96	11.73

4.2.4.1.5.2 Scanning electron microscope of sintered samples (SEM):

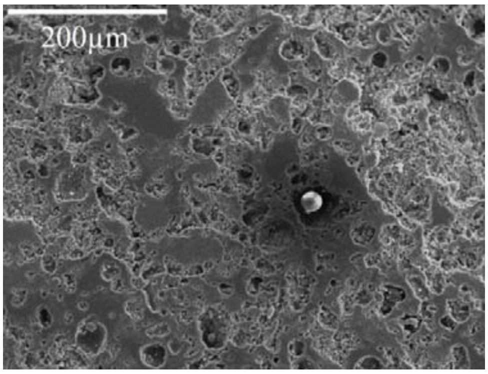
Results obtained by surface analysis at lower magnifications, of samples sintered on 600°C and 800°C, reviled structure typical for porous ceramic materials as presented in figure ((4-14), A-H).



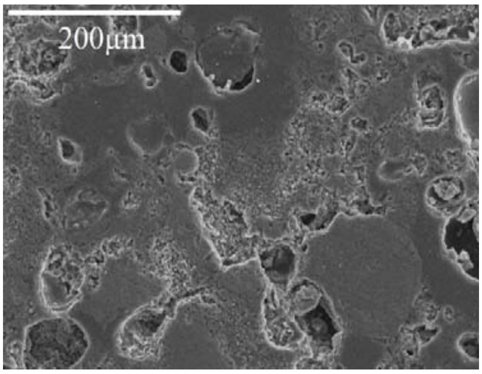
A) 1.1



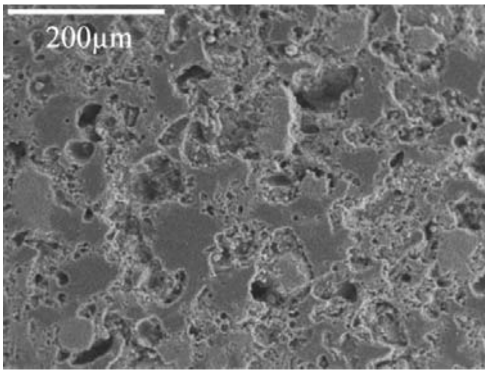
B) 5.1



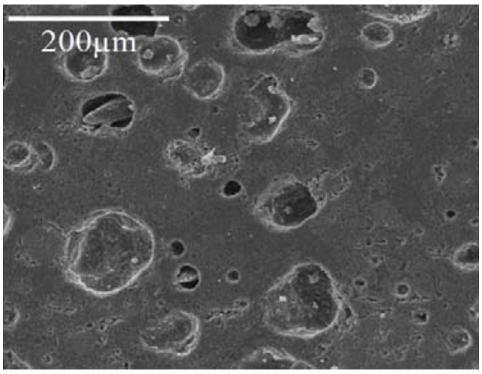
C) 1.2



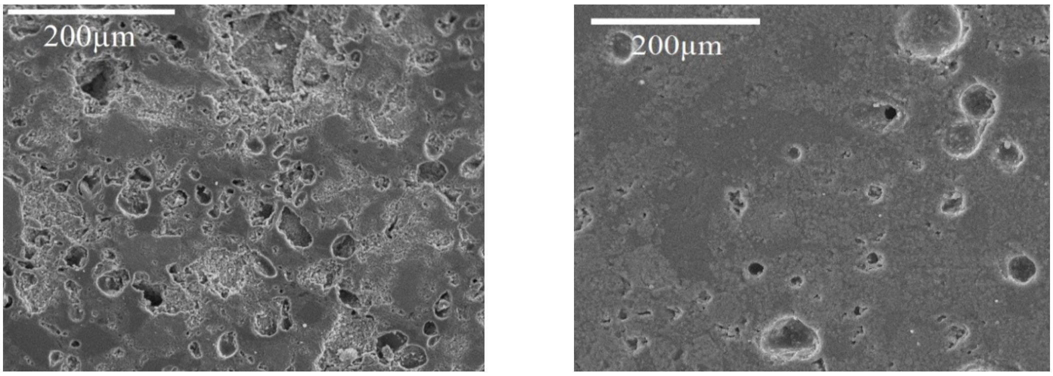
D) 5.2



E) 1.3



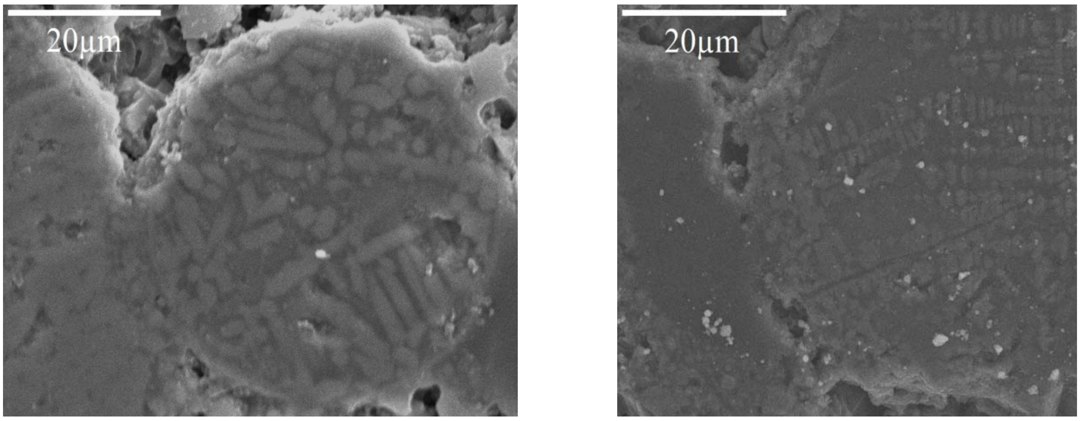
F) 5.3



G) 1.4 H) 5.4

Figure (4-14). SEM micrographs of sintered samples

Certain degree of impregnation of phase with lower melting point (Ca ferrite) in solid phase of other component was observed, Figure ((4-15), A). Also, due to the local increase of reduction potential, sporadically isolated metallic droplets (Pb) were observed, Figure ((4-15), B).



A) B)

Figure (4-15). Extraction of metallic Pb (A) and Ca ferrite (B) in iron oxide basis

4.2.4.1.5.3 Weight loss of sintered samples:

Measurements of mass differences of all sintered samples showed that weight losses generally increase with increase of sintering temperature. Results of weight losses are illustrated in figure (4-16).

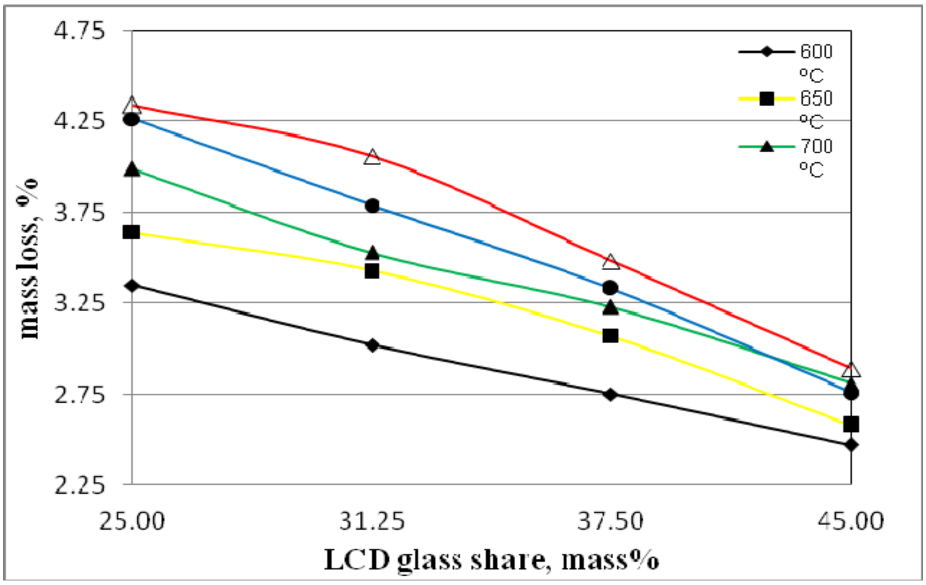


Figure (4-16). Weight loss of sintered samples

4.2.4.1.5.4 Compressive strength of sintered samples:

Compressive strength of sintered samples is presented on figure (4-17). The best compressive strength was obtained for the samples containing of 45% LCD by mass and with 800°C sintering temperature.

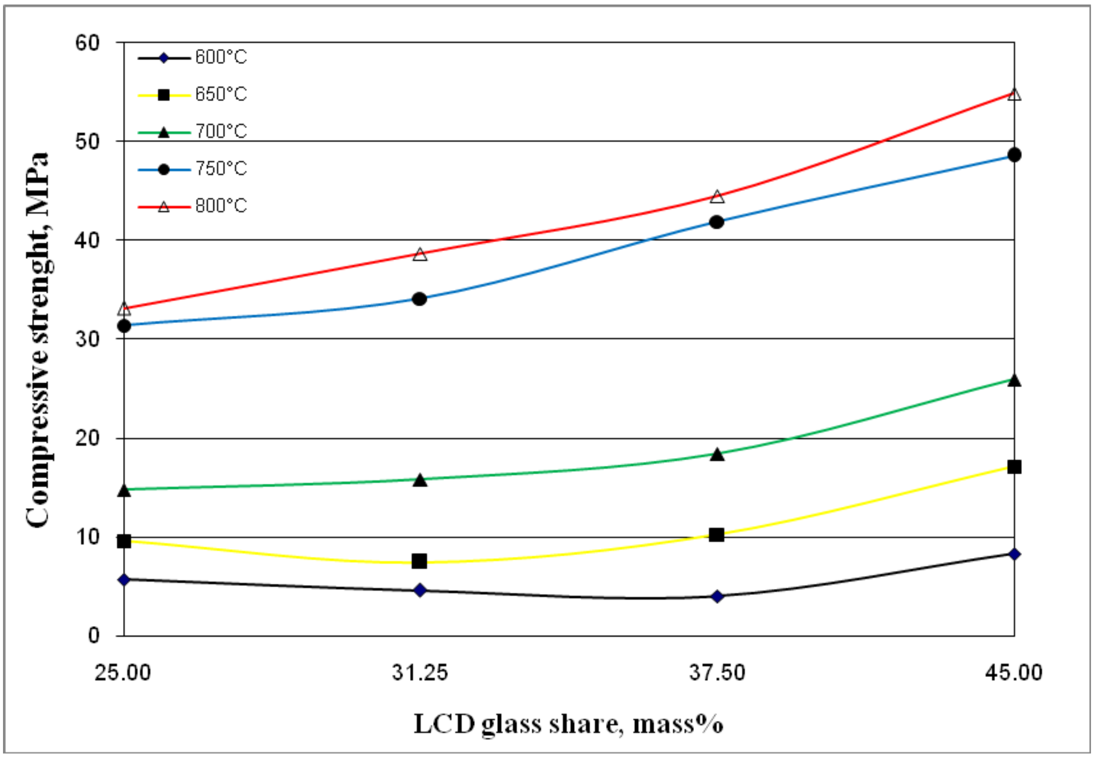


Figure (4-17). Compressive strength of sintered samples

4.2.4.1.5.5 Leachability test results of sintered samples:

Leachability results of sintered samples are presented in table (4-23). Leachability of Cd, Cr and Pb is below regulatory limits in all samples, while in a case of Zn, although there are no regulatory limits, comparing to initial values of Zn leachability from raw materials, reduced leachability was observed.

Table (4-23). TCLP of sintered samples

Sample No.	Cd, (mg/l)	Cr, (mg/l)	Pb, (mg/l)	Zn, (mg/l)
1.1	0.63	<0.1	3.1	258
1.2	0.67	<0.1	1.3	191
1.3	0.45	<0.1	2.2	152
1.4	0.67	<0.1	1.9	120
2.1	0.52	<0.1	3.2	157
2.2	0.49	<0.1	2.1	122
2.3	0.51	<0.1	2.3	148
2.4	0.29	<0.1	1.7	98
3.1	0.11	<0.1	3.4	73
3.2	0.09	<0.1	1.2	49
3.3	0.06	<0.1	4.1	114
3.4	0.41	<0.1	2.3	119
4.1	0.26	<0.1	2.4	109
4.2	0.14	<0.1	1.9	78
4.3	0.07	<0.1	1.8	86
4.4	0.11	<0.1	1.4	47
5.1	<0.05	<0.1	1.5	3.9
5.2	0.04	<0.1	1.4	51
5.3	<0.05	<0.1	1.3	4.6
5.4	0.93	<0.1	1.9	11
Limits, ppm	1	5	5	-
Method	ISO 8288	ISO 8288	ISO 8288	SM 3111b

4.2.4.2 Results of sintered EAFD within iron-bearing waste composite pellets:

This part includes the results of using the EAFD in synergy with other iron-bearing waste by-products, by using pelletization technique, in two-stage process. The first, low temperature, stage performed in electro-resistant furnace enabled removal of lead due to the presence of chlorides in the system, and in second stage at higher temperature in DC plasma furnace, zinc was valorized.

Characterization of used materials and results obtained from tested pellets are presented below.

4.2.4.2.1 Characterization of used materials:

Figure (4-18) shows all used materials in this part of work.

Figure (4-18). Used materials' photo

Limestone:

Commercial limestone from local market was used as a flux material and its chemical analysis is presented in table (4-24).

Table (4-24). Chemical analysis of used limestone

Component	CaO	MgO	SiO_2	Al_2O_3	Fe
%	94	0.91	1.1	0.66	0.59

Coke:

Coke was used as a reducing agent and its characteristic is presented in table (4-25).

Table (4-25). Characteristic of used Coke

Carbon	83%
Volatile matter	2%
Sulfur	1%
Humidity	8-10%
Ash content	13-15%

Pyrite cinder:

Chemical composition of pyrite cinder is given in table (4-27). According to chemical composition, pyrite cinder is rich of iron and silica oxide.

Table (4-27). Chemical composition of pyrite cinder

Component	%	Component	%
Fe	57.20	C	0.00
Zn	0.34	SiO2	8.21
Pb	0.28	Al2O3	0.82
S	1.17	MgO	0.19
Cu	0.24	CaO	0.95
Cr	0.01	MnO	0,19

Mill scale:

Characterization of used Mill scale is presented in table (4-26). As can be seen from the results the percentage of Iron quit high.

Table (4-26). Characterization of Mill scale

Component	%	Component	%
Fe	70.32	Mo	0,006
FeO	68.21	Ti	0,004
Fe_2O_3	24.00	V	0,001
MnO	0.12	Nb	0,001
CaO	0.54	W	0,008
SiO_2	0.81	S	0,023
MgO	0.22	P	0,019
Al_2O_3	0.18	Sn	0,01
C	0.02	Pb	0,0007
Cr	0.04	Sb	0,002
Ni	0.03	Co	0,006
Loss of ignition			-2.65
Organic materials			0.5
Humidity			0.895

4.2.4.2.2 Characterization of green pellets:

Produced pellets were tested before annealing for size analysis, abrasion and durability. All tests results are presented below.

Granulometric analysis:

Before the thermal pretreatment the particle size analysis was performed and fractions between 6-10 mm (>75% of material) were selected as samples for further testing. Particle size analysis is given in table (4-28).

Table (4-28). Granulometric analysis

Fraction, mm	P1, %	P2, %	P3, %
-2,5	1.04	9.31	5.43
+2,5 -4,0	35.30	15.32	68.26
+4,0 -10,0	53.37	64.3	17.17
+ 10,0	6.49	1.79	9.14

From table (4-28), the major quantity of pellets is between 4-10 mm in size.

Abrasion test results:

Abrasion results are presented in table (4-29). According to abrasion results the largest proportion of the weight losses was for the fraction + 10 mm of sample P2.

Table (4-29). Abrasion results

Fraction, mm	Weight losses, %		
	P1	P2	P3
+2.5 -6.0	3.30	5.11	1.83
+6.0 -10.0	2.11	3.17	1.12
+ 10.0	2.73	13.97	2.05

Durability:

Green pellets durability was characterized by drop strength from 1, 1.5 and 2 m and results are presented in table (4-30).

Table (4-30). Green pellets drop strength

Pellet's size, mm	Falling height, m								
	1			1.5			2		
	P1	P2	P3	P1	P2	P3	P1	P2	P3
- 2.5	10	10	10	10	10	10	10	10	10
+2.5 - 6.0	10	9	10	9	6	10	6	3	7
+6.0 - 10.0	5	1	9	4	0	10	0	0	3
+ 10.0	6	1	2	0	0	0	0	0	0

As can be seen from previous table, smallest pellets showed better durability against heights comparing with bigger pellets.

In general mixture P3 showed the best durability for all different fractions and heights comparing with mixtures P1 and P2.

Compressive strength:

Compressive strength average of green pellets results are presented in table (4-31).

Table (4-31). Compressive strength of green pellets

Pellet's size, mm	Average of compressive strength (N/cm^2)		
	P1	P2	P3
+6.0 -10.0	0.37	0.45	1.109
+10.0	0.65	0.84	1.485

Table (4-31), indicates that compressive strength for bigger pellets slightly better than the smaller. The best compressive strength was obtained from mixture P3, even though that mixture didn't stand the temperature during annealing.

4.2.4.2.3 Characterization of the products:

Green pellets were annealed for different temperatures and times. Gases were condensed and chemically analyzed as well as annealed pellets.

4.2.4.2.3.1 Process modeling:

For process modeling in HSC Chemistry 6.12 software input data, chemical compositions of charge components derived from Solver functions were used. Results of modeling are presented in Figures (4-19) and (4-20) as logarithmic function of equilibrium amount from temperature.

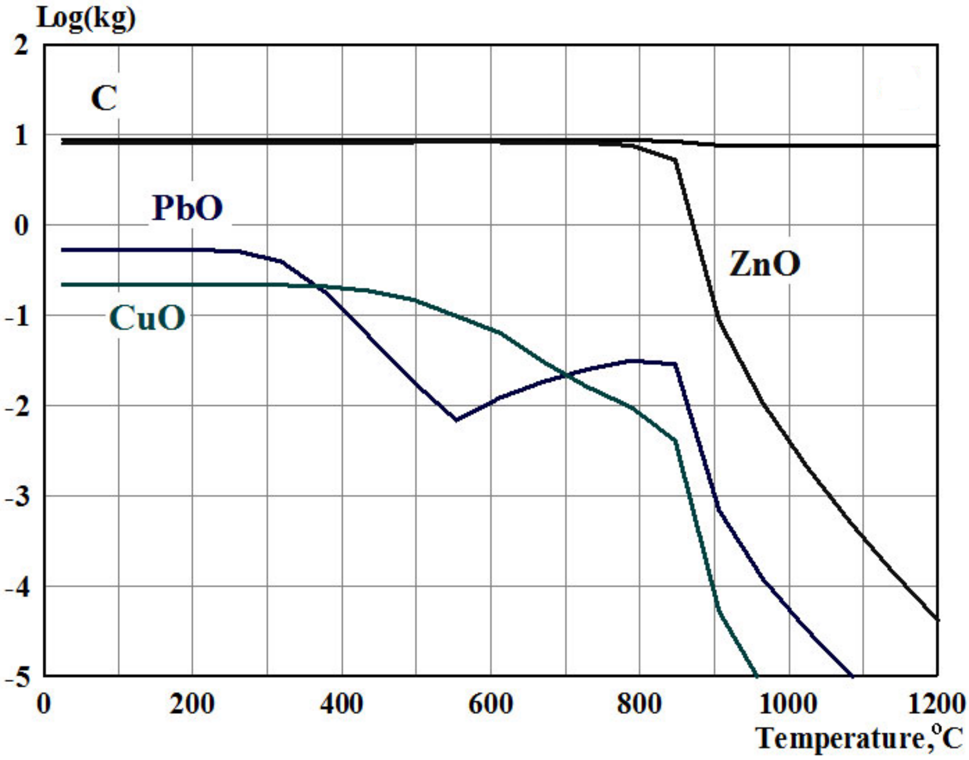


Figure (4-19). HSC modeling for a solid phase.

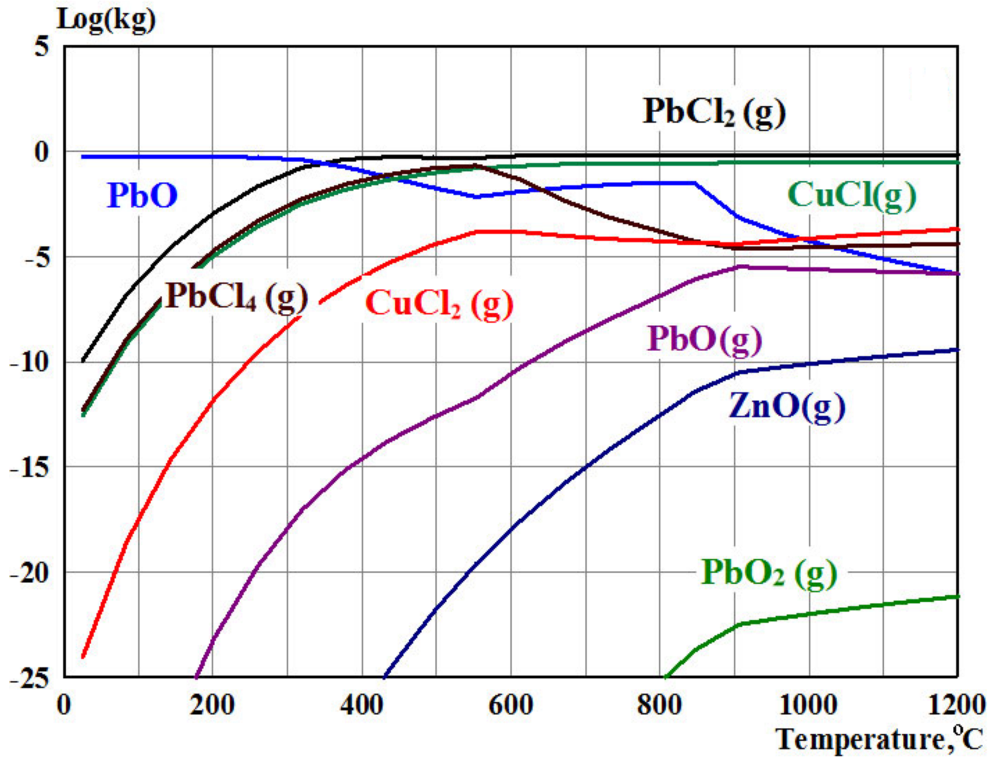


Figure (4-20). HSC modeling for a gaseous phase.

From Figures (4-19) and (4-20) it could be seen that zinc and lead could be separated during two-step heating regime, as anticipated. In the first step, lead could be vaporized in chloride form, while in second step, zinc is valorized as oxide.

4.2.4.2.3.2 The first, low temperature, stage:

Produced pellets from Electro resistant furnace (ERF), which was used for pellets pretreatment and lead volatilization, were tested for weight loss, abrasion and durability. Pellets P1 at temperatures above 1150°C started to sinter, so for further experiments maximum temperature was set to 1150°C. Also, pellets P3 even at lower temperatures started to rupture and crack, so they were not used in further experiments.

Weight losses results:

Weight losses results are presented in table (4-32).

Table (4-32). The weight losses

Tempreature, C^{o}	Weight losses, %			
	P1	P2		
	30 min	30 min	60 min	90 min
850	11.03	2.84	3.37	3.88
900	11.83	3.85	3.91	4.55
950	11.65	5.16	4.75	5.26
1000	12.62	5.61	6.23	6.41
1050	14.61	7.45	7.6	8.26
1100	14.04	12.26	9.11	11.94
1150	13.81	12.07	12.35	12.8
1200	13.55			

As can be seen from last table, mixture P1 losses the heights percentage of weight at 1050^{o}C for 30 min annealing time. For mixture P2 the percentage of weight losses increases with increasing of annealing temperature and time.

Compressive strength:

Compressive strength of produced pellets was determined and results are presented in table (4-33) and figure (4-21).

Table (4-33). Compressive strength average of annealed pellets

Tempreature, C°	Compressive strength average, N/cm^2			
	P1	P2		
	30 min	30 min	60 min	90 min
850	0.51	1.406	1.285	1.124
900	0.34	2.308	1.310	1.165
950	0.26	3.262	1.350	1.184
1000	0.51	1.182	1.552	1.695
1050	0.55	1.488	6.163	1.154
1100	1.32	4.061	4.442	6.23
1150	2.00	8.861	5.504	6.98
1200	1.06			

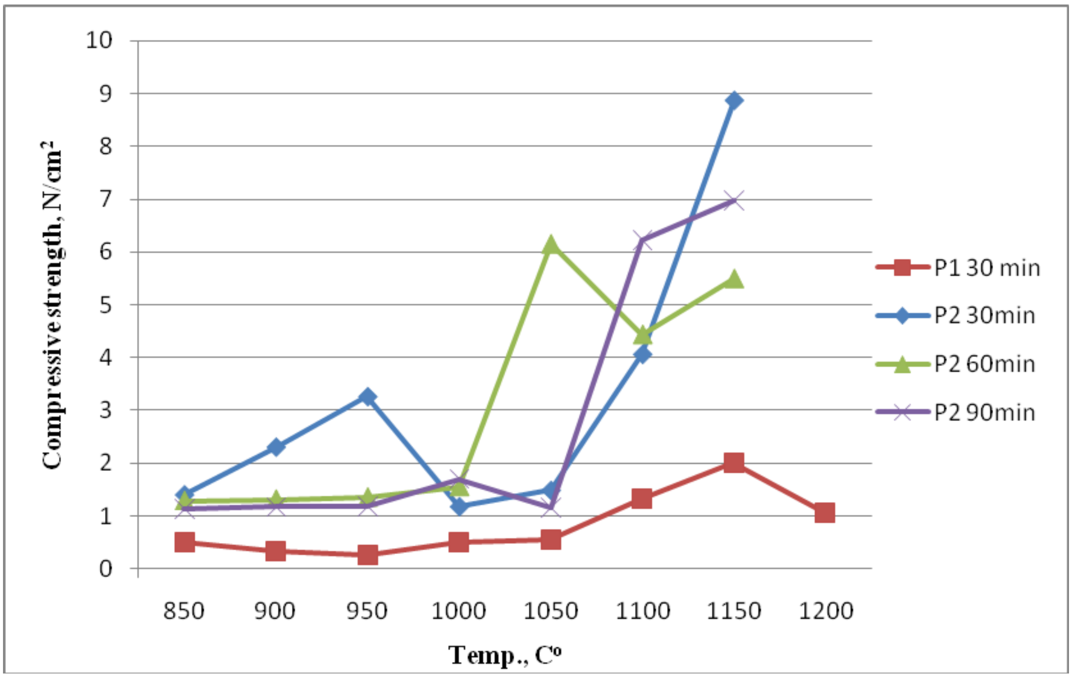


Figure (4-21). Compressive strength average of annealed pellets

In general, results showed that compressive strength of produced pellets from mixture P1 and mixture P2 increases with increasing of annealing temperature. Maximum compressive strength of both mixtures occurs at a temperature of 1150°C with 30 min annealing time. Pellets from mixture P2 have a maximum compressive strength of 8,861 N/cm^2, which is 4 times more than the compressive strength of mixture P1 at the same annealing conditions.

Chemical analysis:

Analysis results of Zn, Pb, Cu and Mn of annealed pellets and condensed gases for different temperatures and times for every mixture are presented in tables and illustrated in figures.

Zn, Pb, Cu and Mn content of annealed pellets for different temperature and time for every mixture are presented in tables (4-34), (4-35), (4-36) and (4-37) respectively and illustrated in figures (4-22), (4-23), (4-24), and (4-25) respectively.

Zn, Pb, Cu and Mn content of condensed gases for different temperature and time for every mixture are presented in tables (4-38), (4-39), (4-40) and (4-41) respectively and illustrated in figures (4-26), (4-27), (4-28), and (4-29) respectively.

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Table (4-34). The content of Zn in the pellets for different temperature and annealing time

Mixture, Time	Content of Zn in the pellets, %							
	Raw	850°C	900°C	950°C	1000°C	1050°C	1100°C	1150°C
P1 30, min	14.401	16.035	15.575	14.731	13.564	13.719	14.283	15.173
P2, 30 min	18.61	17.653	16.8	17.094	16.594	17.321	16.483	16.415
P2, 60 min	18.61	16.706	16.648	17.195	17.54	17.276	16.359	16.245
P2, 90 min	18.61	16.605	16.59	16.696	16.648	16.191	16.596	15.87

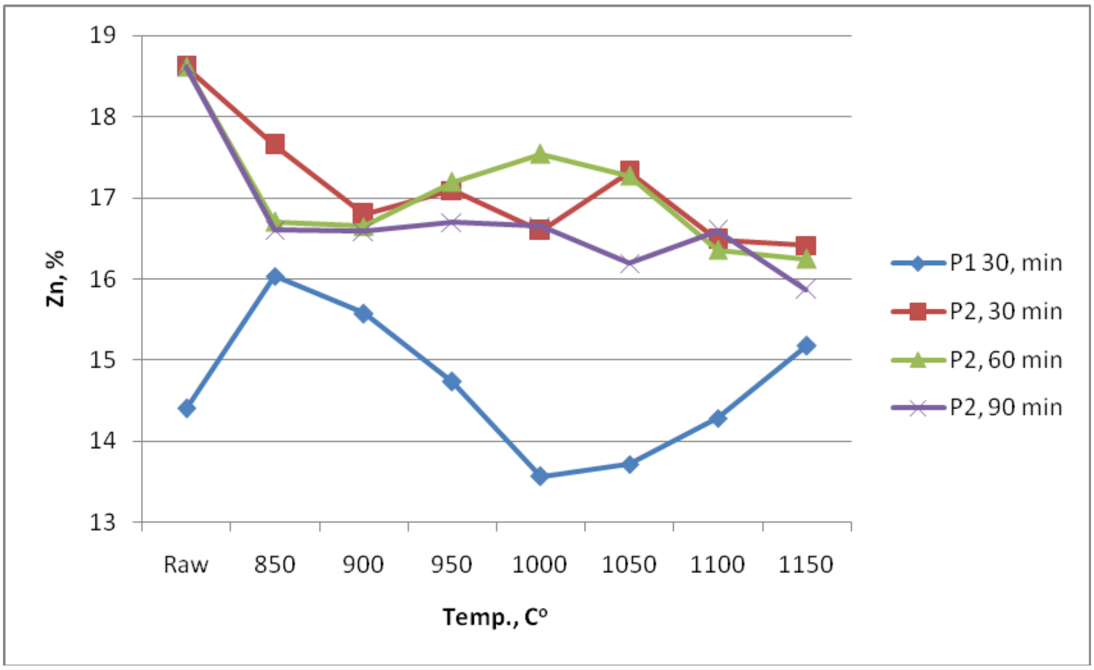

Figure (4-22). The content of Zn in the pellets for different temperature and annealing time

The percentage of residual Zn in pellets increases with increasing of temperature, which is presented in figures (4-22) and table (4-34). The largest decline and the highest percentage of Zn vaporization, for pellets P1, were observed at a temperature of 1000°C. Pellets P2 in their raw state contain 18.61% Zn. Depending on the annealing time, there is a sharp decline in the content of Zn at 850°C for 60 min annealing time and at 900°C for 30 min annealing time. With increasing of temperature there is a steady uniform loss of Zn for all tested pellets for all different process conditions. The highest loss is observed at 1150°C for 90 min annealing time, the value was 15.87% of Zn.

Table (4-35). The content of Pb in the pellets for different temperature and annealing time

Mixture, Time	Content of Pb in the pellets, %							
	Raw	850°C	900°C	950°C	1000°C	1050°C	1100°C	1150°C
P1, 30 min	0.93	0.76	0.883	0.345	0.542	0.244	0.078	0.365
P2, 30 min	1.154	1.061	1.12	0.986	0.851	0.932	0.239	0.465
P2, 60 min	1.154	0.911	0.988	1.117	0.775	0.779	0.59	0.526
P2, 90 min	1.154	1.081	1.052	1.029	0.888	0.434	0.535	0.145

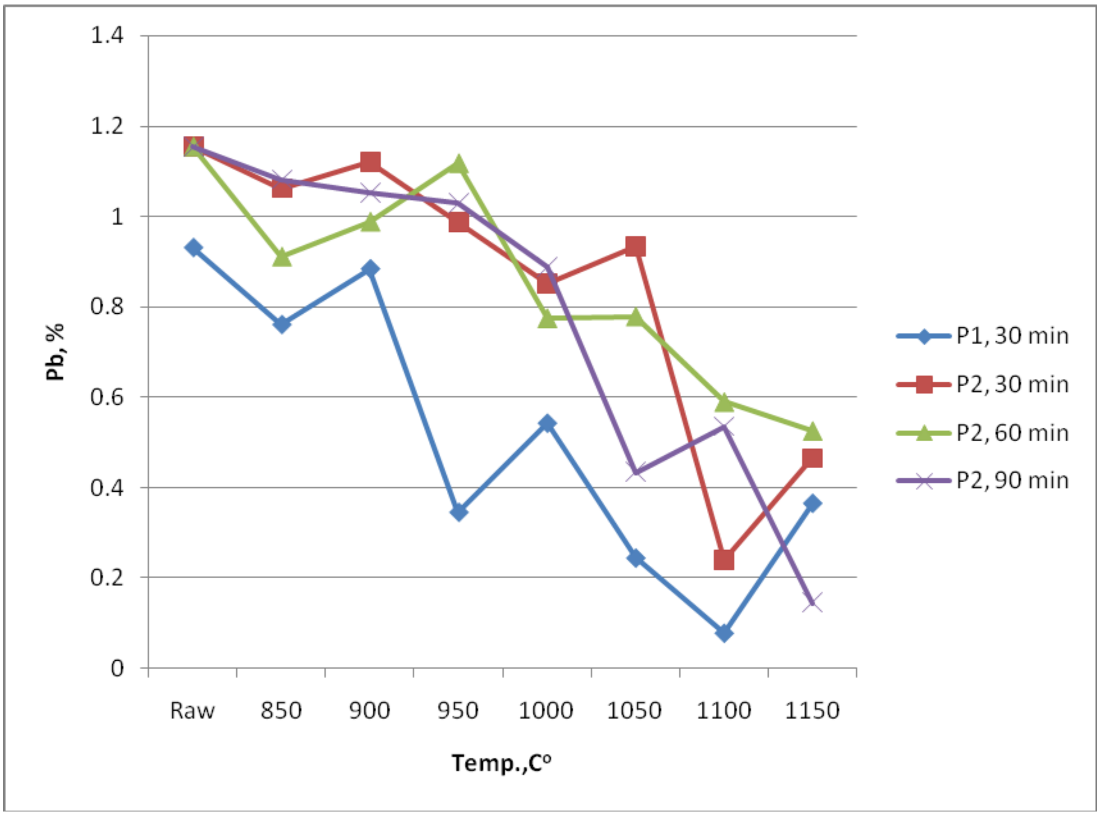

Figure (4-23). The content of Pb in the pellets for different temperature and annealing time

Chemical analysis of annealing products showed that for tested pellets P1, increase in temperature causes a decreasing in a residual amount of Pb, as presented in figures (4-23) and table (4-35). This is especially fit the two values at 950°C and 1100°C where 0.078% Pb remains in the pellets. In its raw state, chemical analysis showed that test pellets P2 contains 1.154% Pb. Depending on the annealing time a trend is observed of slight decline in the Pb content up to the temperature of 1050°C. For this temperature and for 90 min annealing time a sharp decline of Pb content is observed, while for 30 and 60 min annealing time, content decline occurs at 1100°C. For 90 min of annealing time, there is another decline at 1150°C and at this temperature the content of Pb is 0.145%.

Table (4-36). The content of Cu in the pellets for different temperature and annealing time

Mixture, Time	Content of Cu in the pellets, %							
	Raw	850°C	900°C	950°C	1000°C	1050°C	1100°C	1150°C
P1, 30 min	0.577	0.733	0.671	0.694	0.633	0.637	0.593	0.614
P2, 30 min	0.653	0.639	0.732	0.669	0.691	0.742	0.623	0.581
P2, 60 min	0.653	0.698	0.755	0.664	0.661	0.696	0.653	0.584
P2, 90 min	0.653	0.754	0.748	0.687	0.747	0.657	0.616	0.647

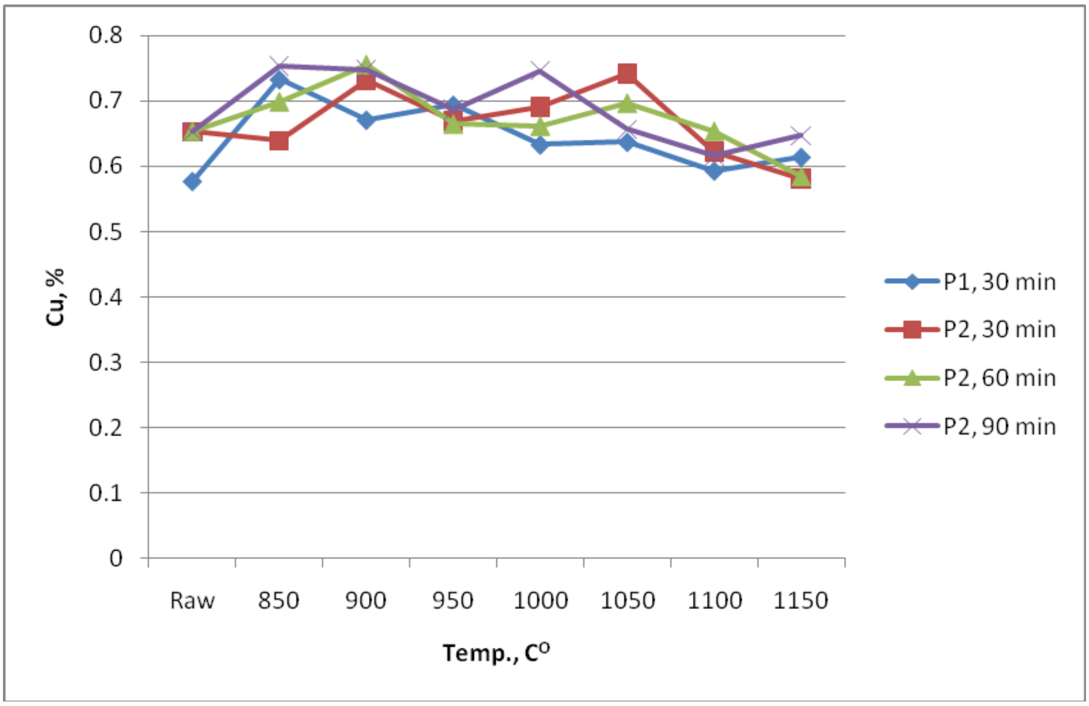

Figure (4-24). The content of Cu in the pellets for different temperature and annealing time

From table (4-36) and figure (4-24) it is clear that for every mixture of pellets there are no effect of temperature and time on the content of Cu in pellets, leads to the conclusion that increase in temperature or annealing time of pellets has unnoticeable effect on the Cu extraction.

Table (4-37). The content of Mn in the pellets for different temperature and annealing time

Mixture, Time	Content of Mn in the pellets, %							
	Raw	850°C	900°C	950°C	1000°C	1050°C	1100°C	1150°C
P1, 30 min	0.986	1.137	1.188	1.217	1.005	1.078	1.173	1.069
P2, 30 min	2.746	2.566	2.553	2.535	2.666	2.576	2.611	2.603
P2, 60 min	2.746	2.581	2.615	2.549	2.52	2.714	2.614	2.781
P2, 90 min	2.746	2.595	2.68	2.713	2.754	2.734	2.554	2.81

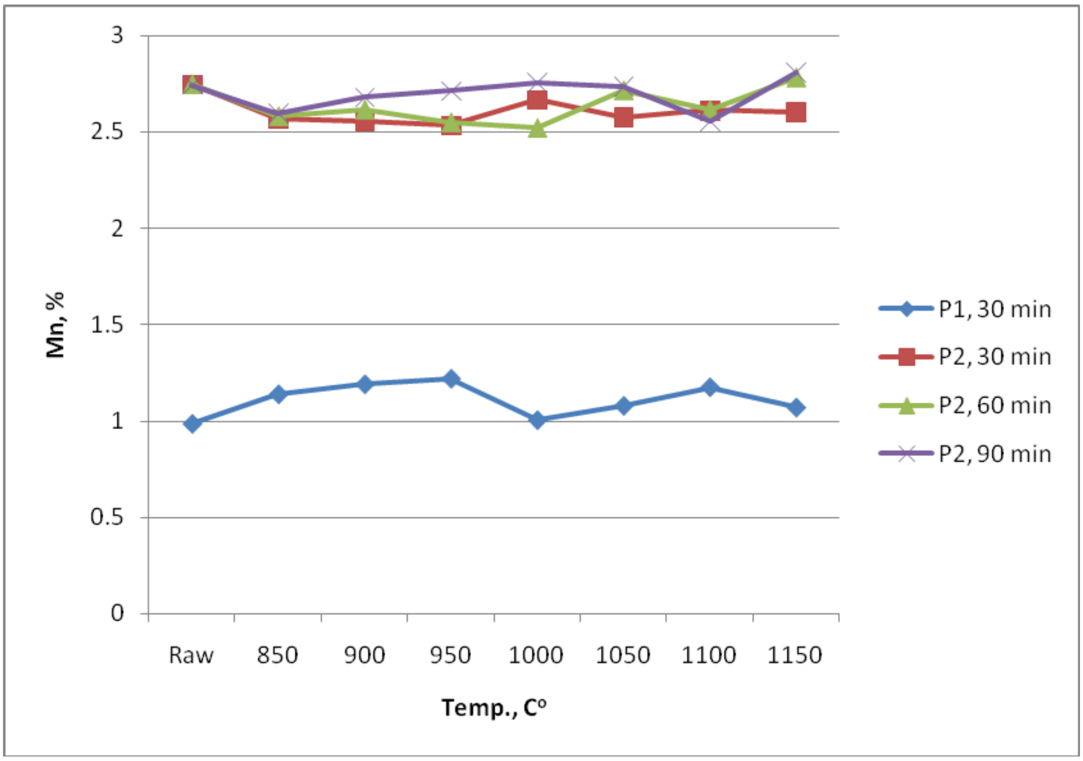

Figure (4-25). The content of Mn in the pellets for different temperature and annealing time

Just as in the case of Cu, increase in temperature or annealing time of pellets have unnoticeable effect on the Mn extraction.

Table (4-38). The content of Zn in the condensed gases for different temperature and annealing time

Mixture, Time	Content of Zn in the condensed gases, %						
	850°C	900°C	950°C	1000°C	1050°C	1100°C	1150°C
P2, 30 min	3.059	3.966	5.809	3.335	4.195	2.598	2.325
P2, 60 min	2.564	3.523	5.391	2.472	3.633	1.322	1.419
P2, 90 min	2.058	1.671	1.459	1.034	4.568	2.852	2.197

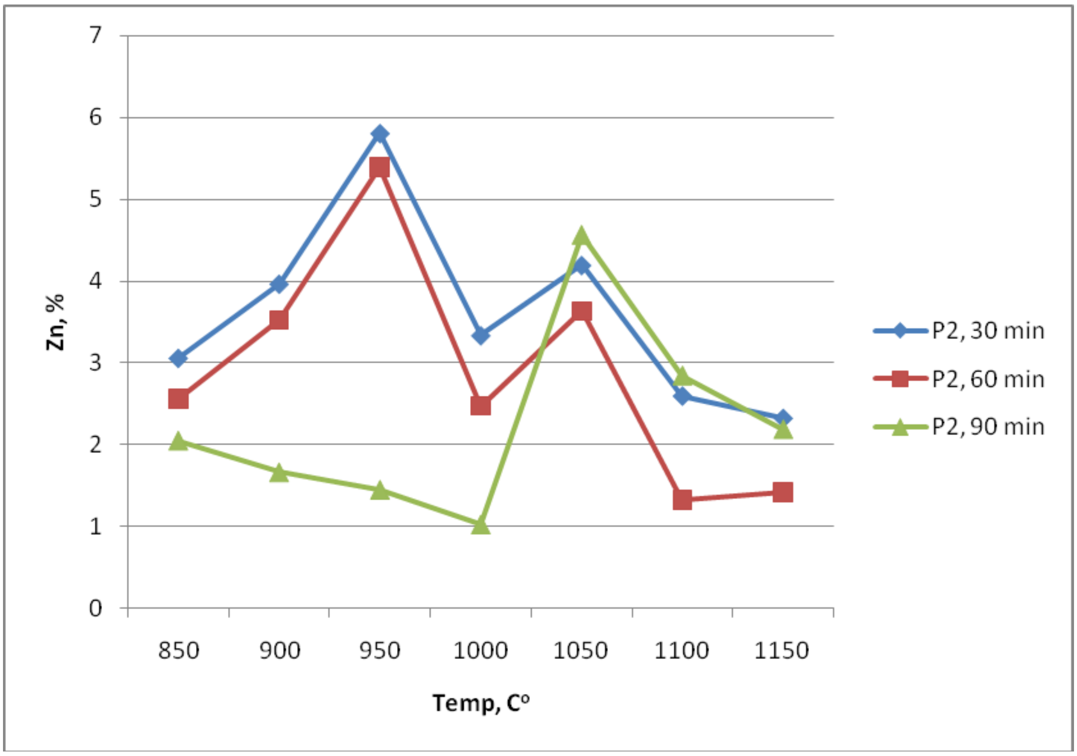

Figure (4-26). The content of Zn in the condensed gases for different temperature and annealing time

In the case of gases, gases are condensed from vaporized gases, in annealed pellets observed dependence of Zn content on weight loss. At 950°C (Figure(4-26)) obtained the highest content of Zn in the gases, with increase of temperature Zn content decreases, which is consistent with the results of annealed pellets.

Table (4-39). The content of Pb in the condensed gases for different temperature and annealing time

Mixture, Time	Content of Pb in the condensed gases, %				
	950°C	1000°C	1050°C	1100°C	1150°C
P2, 30 min	4.125	1.674	3.766	3.943	6.767
P2, 60 min	2.476	3.051	8.514	6.637	6.99
P2, 90 min	7.247	6.186	13.208	8.341	6.492

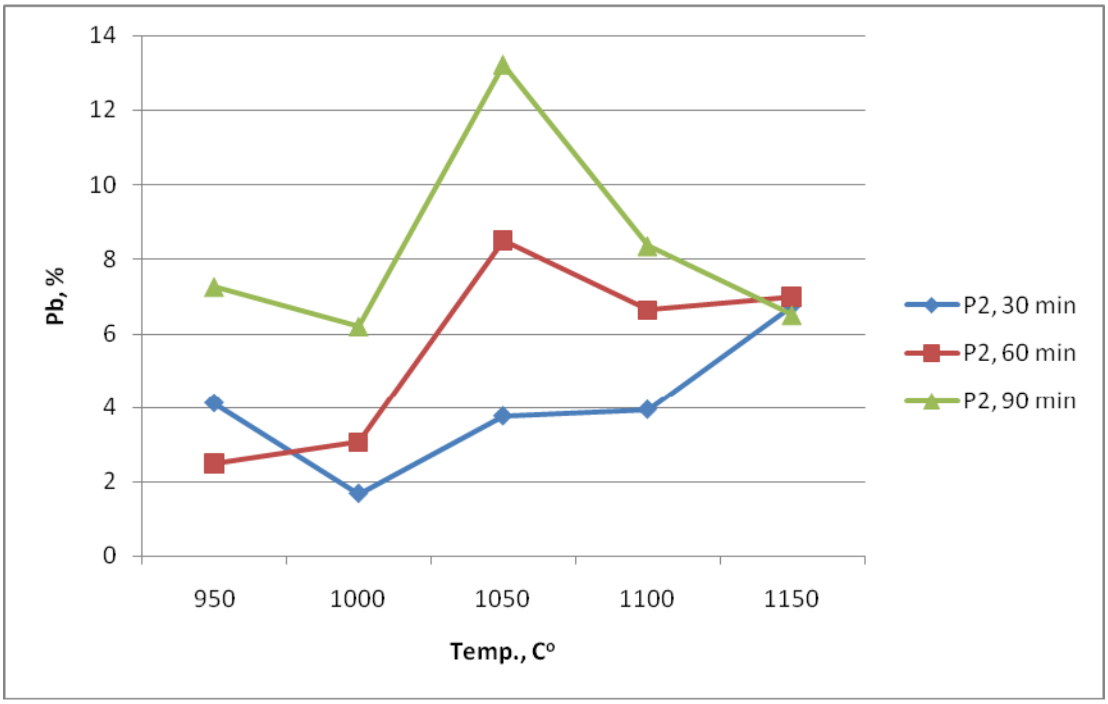

Figure (4-27). The content of Pb in the condensed gases for different temperature and annealing time

In the analysis of Pb, the highest content of Pb in the gases has detected at 1050°C. At higher temperatures a decrease of Pb content is observed, except of the 30 min annealing time, where a slight increase is marked.

Table (4-40). The content of Cu in the condensed gases for different temperature and annealing time

Mixture, Time	Content of Cu in the condensed gases, %				
	950°C	1000°C	1050°C	1100°C	1150°C
P2, 30 min	0.405	0.222	0.318	0.352	0.611
P2, 60 min	0.263	0.396	0.596	0.56	0.617
P2, 90 min	0.808	0.691	1.009	0.72	0.78

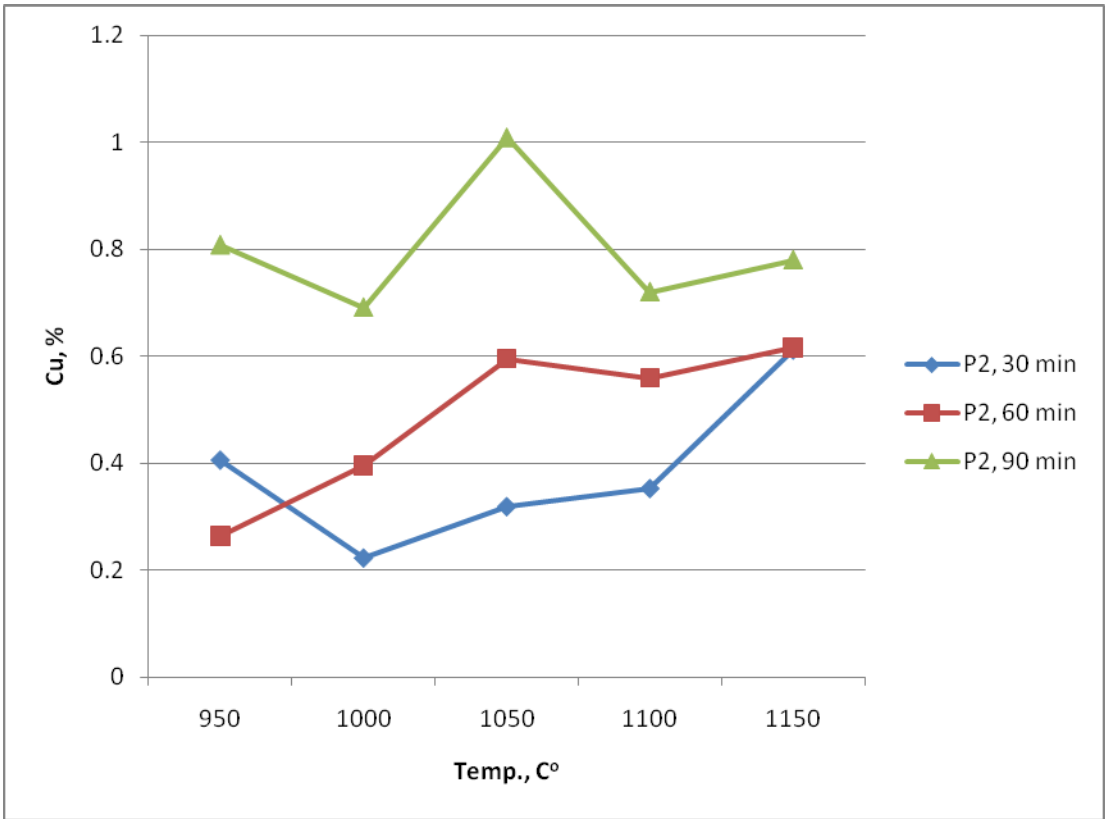

Figure (4-28). The content of Cu in the condensed gases for different temperature and annealing time

Increasing the content of copper in the gases is observed with increasing of annealing time, while the temperature increases that slightly.

Table (4-41). The content of Mn in the condensed gases for different temperature and annealing time

Mixture, Time	Content of Mn in the condensed gases, %				
	950°C	1000°C	1050°C	1100°C	1150°C
P2, 30 min	1.169	0.925	1.063	1.179	0.987
P2, 60 min	0.999	1.105	1.001	0.798	0.768
P2, 90 min	0.605	0.532	1.021	1.196	1.048

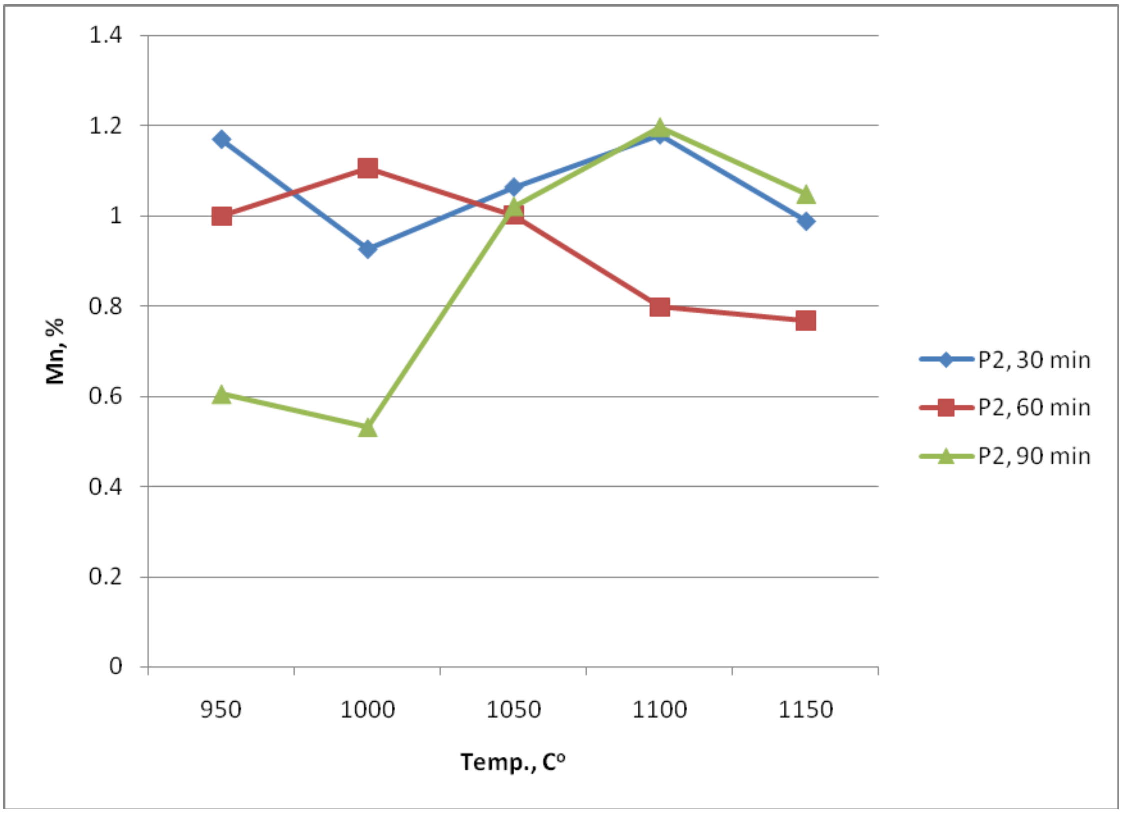

Figure (4-29). The content of Mn in the condensed gases for different temperature and annealing time

In the analysis of Mn in gases, it is noticed that the content of Mn constantly varies between 0.8-1.2%.

Concerning retention time, it is notable that with prolonged time, levels of volatilized zinc and lead increase. For design of industrial plant, time of 1hr would be suitable for achieving desired levels of lead removal from mixture. Also, in industrial scale process would be conducted in dynamic system, eg. rotary furnace, so this time and temperature level would be appropriate. For further experiments pellets pretreated at 950ºC for 60 min were chosen.

4.2.4.2.3.3 The second, high temperature, stage:

After smelting, materials were cast into casting crucible, and left for metal and slag separation. Condensed gases were collected from the bag filter and chemically analyzed. Obtained metal and slag were analyzed. Main components of start slag were FeO, SiO_2, Al_2O_3, CaO, MgO, with small amounts of Zn, Pb, Cu, Ni and Mn. Characterization of semi-industrial tests product is presented in Table (4-42) represent mean values of three campaigns.

Table (4-42) Characterization of semi-industrial test products, in wt. %

Comp	Metal	Comp	Slag	Dust
Fe	98,07	FeO	28,00	7,20
Zn	0,02	ZnO	0,32	78,20
Pb	0,10	PbO	0,02	0,37
S	0,00	S	6,38	
Cu	0,45	CuO	0,10	
Ni	0,62	C		1,30
C	0,21	Cl		0,03
P	0,05	SiO_2	31,81	0,92
Si	0,15	Al_2O_3	5,80	0,01
Mn	0,01	MgO	6,20	0,01
		CaO	19,80	0,65
		MnO	0,81	

Obtained results show that filter dust contains 78% of ZnO, i.e. 62% of Zn, which is slightly lower than the level of industrially applied processes for sole EAFD treatment. But, in presented test, mixture of iron-bearing materials was used, so the first result of Zn recovery around 95% show the possibility of industrial application for joint treatment of different materials.

4.2.5 Modeling results:

This part of work represents a methodology for establishing a relationship between the composition of mixtures of iron-bearing non-standard dispersed raw materials for production of sinter and its most important metallurgical properties, in accordance with the appropriate phase of the production technological process. Characteristics of all used materials have presented previously. Results for modeling are presented below.

Parameters set within the model were:

Fe total=55-60%
Fe met= min 50%
FeO=15-20%
Basicity CaO/SiO_2=1.2-1.35

Modeling was performed for three different FeO contents in sinter and for four different basicities (B). Results of modeling are presented in tables (4-(42-44)).

Table (4-42). Modeling of sinter process for FeO=15%

basicity	unit	1.20	1.25	1.30	1.35
mixture	kg/ 100 kg sinter	109.744	109.047	108.352	107.660
flux		11.045	12.084	13.119	14.150
coke		5.353	5.462	5.571	5.679
Fe_{total}	%	52.747	52.420	52.094	51.770
Fe_2O_3	%	58.600	58.133	57.669	57.206
heat yield/loss	MJ/ 100kg sinter	197.31	199.70	202.06	204.43
Chemical composition of sinter					
FeO	%	15.00	15.00	15.00	15.00
Fe_2O_3	%	58.88	58.45	58.02	57.60
FeS	%	0.0481	0.0478	0.0476	0.0473
FeS_2	%	0.0561	0.0558	0.0555	0.0552
S. org.	%	0.0032	0.0032	0.0032	0.0032
SO_3	%	0.0075	0.0076	0.0077	0.0077
P_2O_5	%	0.0847	0.0851	0.0856	0.0860
MnO	%	2.9042	2.8874	2.8708	2.8543
SiO_2	%	9.3507	9.3124	9.2744	9.2367
Al_2O_3	%	1.0411	1.0414	1.0417	1.0420
CaO	%	9.91	10.38	10.85	11.31
MgO	%	2.557	2.561	2.565	2.569

Table (4-43). Modeling of sinter process for FeO=17.5%

basicity	unit	1.20	1.25	1.30	1.35
mixture	kg/ 100 kg sinter	109.965	109.264	108.567	107.872
flux		11.125	12.168	13.208	14.244
coke		5.599	5.709	5.819	5.927
Fe_{total}	%	52.862	52.534	52.207	51.881
Fe_2O_3	%	55.985	55.517	55.050	54.585
heat yield/loss	MJ/ 100kg sinter	202.86	205.25	207.63	210.01
Chemical composition of sinter					
FeO	%	17.50	17.50	17.50	17.50
Fe_2O_3	%	56.26	55.83	55.40	54.98
FeS	%	0.0483	0.0480	0.0478	0.0475
FeS_2	%	0.0563	0.0559	0.0556	0.0553
S. org.	%	0.0033	0.0033	0.0034	0.0034
SO_3	%	0.0079	0.0080	0.0081	0.0081
P_2O_5	%	0.0849	0.0854	0.0858	0.0863
MnO	%	2.911	2.894	2.877	2.861
SiO_2	%	9.390	9.351	9.313	9.275
Al_2O_3	%	1.0485	1.0488	1.0491	1.0495
CaO	%	9.962	10.432	10.899	11.363
MgO	%	2.564	2.568	2.572	2.576

Table (4-44). Modeling of sinter process for FeO=20%

basicity	unit	1.20	1.25	1.30	1.35
mixture	kg/ 100 kg sinter	110.186	109.482	108.781	108.083
flux		11.205	12.253	13.297	14.337
coke		5.846	5.957	6.066	6.176
Fe_{total}	%	52.977	52.647	52.319	51.992
Fe_2O_3	%	53.371	52.901	52.432	51.965
heat yield/loss	MJ/ 100kg sinter	208.41	210.81	213.20	215.59
Chemical composition of sinter					
FeO	%	20.00	20.00	20.00	20.00
Fe_2O_3	%	53.65	53.22	52.79	52.36
FeS	%	0.0485	0.0482	0.0479	0.0477
FeS_2	%	0.0564	0.0560	0.0557	0.0554
S. org.	%	0.0035	0.0035	0.0035	0.0035
SO_3	%	0.0083	0.0084	0.0084	0.0085
P_2O_5	%	0.0852	0.0856	0.0861	0.0865
MnO	%	2.918	2.901	2.884	2.867
SiO_2	%	9.429	9.390	9.352	9.314
Al_2O_3	%	1.0559	1.0562	1.0566	1.0569
CaO	%	10.011	10.483	10.952	11.418
MgO	%	2.571	2.575	2.579	2.583

Reducibility (R) of sinter mixtures was calculated according their chemical composition using empiric equation (4-1).

Results are presented in table (4-45). Oxidation degree is also presented in table (4-45).

$$\mathbf{R=1.847-0.0572\times FeO+0.0000026476\times Fe_2O_3-0.1024\times SiO_2-0.00058031\times Al_2O_3+0.0203\times CaO+0.1643\times MgO} \qquad (4\text{-}1)$$

Results in table (4-45) show that reducibility is influenced by FeO content, increase of FeO results in increase of **R**. Also, presence of higher content of SiO_2 decreases sinter reducibility. Increase of MgO content in sinter significantly increases reduction rate of sinter.

Table (4-45). Calculated reducibility of mixtures

FeO in sinter	Basicity	R	Oxidation degree
15	1.2	0.652	92.65
	1.25	0.666	92.60
	1.3	0.681	92.56
	1.35	0.694	92.52
17.5	1.2	0.507	91.44
	1.25	0.522	91.39
	1.3	0.536	91.34
	1.35	0.550	91.29
20	1.2	0.363	90.24
	1.25	0.377	90.18
	1.3	0.391	90.13
	1.35	0.405	90.07

For sinters with lower coke addition, oxidation degree is higher, due to the fact that primary components are not affected by high temperature processes. Final sinter is characterized with higher porosity, resulting in better reducibility, which is proven by presented model.

With higher additions of coke, sintering process is conducted at higher temperatures with formation of liquid phase of iron-silicate composition. Final sinter is characterized with lower reducibility, due to the lower its porosity.

5. Discussion

EAFD, intended for study, was obtained from Serbian steel making company, equipped with electric arc furnace with capacity of 260,000 tons/year.

5.1 Characterization of EAFD:

EAFD was characterized physically and chemically by X-ray diffraction, grain size analyses, chemical analysis, leaching test, optical microscopy and scanning electron microscopy (SEM) techniques.

Humidity (%):

Humidity average of EAFD was found 1.33% and it considered a little bit low, because the samples were brought in the summer when the average of temperature was about 30^{o}C.

Density (g/cm^{3}):

The density results of the samples show that the bulk density average was 0.602 g/cm^{3}, this value refers to the used EAFD is a dense dust, that because it consists of very fine particles.

Wettability:

Wettability was analyzed by the visual changes in the sample of the EAFD, from the results; the tested EAFD considered a hydrophobic material and that because of high surface tension and very fine grain size.

Loss of ignition (750°C for 1hr):

The loss of ignition was treated at 750°C for 1hr; results show that the 8.58 % by weight was volatized and that because of carbonates, combined water, hydrates and labile hydroxyl-compounds.

Grain size analysis:

The sieve analysis shows that approximately 54% of the EAFD particles were larger than 100 µm. The analysis indicates that the major amount of used EAFD is fine powder.

The sieve analysis shows that EAF dust has contained two major sizes fraction; a fine-grained portion and a coarser part. Particles sizes range from less than 36 µm to more than 125 µm and also show that approximately 54% of the EAFD particles were larger than 100 µm. Coarse size of EAFD explained by the agglomeration of fine particles with exists of humidity.

This size distribution indicates that the physical concentration methods, like gravity or magnetic separation, are not suitable to treat such a material. Further, its size distribution suggests that the material would be difficult to handle dry, if no previous agglomeration is used.

Surface area is the area of a given surface. Roughly speaking, it is the ``amount'' of a surface, and has units of distance squares. Specific surface area "SSA" is a property of solids which is the total surface area of a material per unit of mass, solid or bulk volume, or cross-sectional area. It is a derived scientific value that can be used to determine the type and properties of a material (e.g. soil). It is defined either by surface area divided by mass (with units of m^2/kg), or surface area divided by the volume (units of m^2/m^3 or m^{-1}). It has a particular importance for adsorption, heterogeneous catalysis, and reactions on surfaces.

Results showed that; surface area it was 1.40E+06 (cm^2/g) and particle/gram = 5.37E+16, from this results it is clear that; EAFD has high surface area and very fine particles.

Optical microscopy:

A microscopic analysis enables to visualize some particles, but no operator will analyze enough particles to obtain a representative analysis.

From the microscope’s photo it is clearly that almost all particles have a spherical shape where bigger particles are covered with smaller ones. The white spots that was observed are belongs to presence of CaO.

Scanning electron microscope (SEM):

Used EAFD is characterized with spherical particles of slag and flakelike particles of ZnO and PbO and relatively small size, but high surface, i.e. surface area particles are partially agglomerated.

The small particles mainly consist of $ZnFe_2O_4$ and Fe_3O_4. Medium size particles are metal oxides or silicates. The big particles are mostly Fe-enriched silicates or oxides and there are fine oxides particles attached on them.

EAFD Chemical characterization:

The chemical analysis of EAFD shows that it is contains high amount of zinc and iron, together with slight amount of calcium, manganese, magnesium, lead, and chromium. The investigated EAFD was brought from Serbian carbon steelmaking and that is way the zinc percentage it was 30.34%, which is in the standard range of typical chemical analysis of EAFD from carbon steelmaking.

The usual Zn content is between 18-35%, so investigated sample is in upper part of this range.

X-ray diffraction (XRD):

About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others.

The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases.

From hydrometallurgical point of view it is very important to know mineralogical form of the metals in order to set up optimal leaching conditions.

According to obtained results of the XRD analysis; dominant phases of used EAFD are franklinite ($ZnFe_2O_4$) and magnetite (Fe_3O_4). Oxides of iron are also bonded with Ca and Mg in form of complex ferrites. Also, zinc is partially bonded in form of ZnO.

This material could be placed in the group of so called controlled low-strength material (CLSM). These materials are self-compacted cementations like materials used primarily as a backfill in place of compacted soil. It is also known as a flow-able fill which is usually a mixture of fine aggregates, small amount of cement and water. Usage of by-product materials is common as fine aggregates in flow-able fill materials.

The analysis also shows that zinc, iron and chromium are mainly present as ferrites which are very resistant against to any kind of treatment. Because of that, it is necessary to use more aggressive conditions (high temperature or stronger leaching reagent) for metals recovery.

5.2 Solidification/Stabilization products:

Solidification/Stabilization (S/S) is, according to the US Environmental Protection Agency (US EPA), one of the best demonstrated available technologies, to treat certain industrial wastes and contaminated soils. S/S technologies are widely used for treatment of hazardous wastes that are mostly inorganic and contaminated soils before final disposal.

The agglomerating agents used in S/S processes for the treatment of hazardous wastes that contain heavy metals are usually alkaline materials that reduce the leachability of the metals in a high-pH matrix [118].

Materials:

Commercial Ordinary Portland cement, (CEM II B-M (V-L) 32.5 R), was used in all mixtures, which is high early strength.

Fly ash class F (- 45µ), originating from burning of 'Kolubara' coal at the Bor heating plant, was used as the main aluminosilicate agent. Used fly ash had low calcium content, was predominantly in the vitreous phase and had some crystalline inclusions of mullite, hematite and quartz. The incorporation of fly ash decreased the porosity and permeability of the concrete.

5.2.1 Cement grout S/S products:

Cement grout is a mixture of Portland cement and water. Cement-based "grout" systems have been used for so many years in so many instances for S/S.

Hardened grout:

After curing for 28 days, in accordance with the standard SRPS U.M1.005, the samples were tested for compressive strength. The compressive strength testing was performed in accordance with the SRPS U.M1.020 standard at servo tensile machine INSTRON 1332 with maximal load of 200 kN.

As can be seen from the results, the highest compressive strength in series I was achieved with 20% of EAFD and rapidly decreased when more than 20% of cement is replaced with EAFD, when the lime is not included. Whereas in series II, which was the percentage of lime to cement is 1:1, the compressive strength slightly decreased. On the other hand in series III, when the lime to cement percentage it was 1:3, the compressive strength slightly increased with 17.5% addition of lime and 30% of EAFD.

According to leachability results, leachability of lead from all concrete samples is far below the limit of 5 mg/L, except for sample D7 with 90% of EAFD is above the limit. Pb was stabilized in a cement matrix even at 80% of cement replacement with EAFD. Lead leachability is reduced comparing to initial values, but for Zn there are no TCLP limits. In general, increases of EAFD amount in mixture; Zn leachability increase.

Also we can say that the leachability results without lime addition are slightly better.

5.2.2 Concrete S/S product:

Concrete has been used for S/S for many years for waste treatment. In this research Raw and milled EAFD was replaced of fine aggregate with different percentages with and without fly ash.

EAFD grain size and particles distribution allows it to replace the fine aggregate in the cement matrix.

Hardened concrete:

After curing for 28 days, in accordance with the standard SRPS U.M1.005, samples were tested for compressive strength and leachability.

The compressive strength testing was performed in accordance with the SRPS U.M1.020 standard at servo tensile machine INSTRON 1332 with maximal load of 200 kN.

Mixture I with EAFD replacement of fine aggregate varying between 0% and 50% of the aggregate weight.

Results for mixture I indicates that the highest compressive strength was with 10% EAFD of fine aggregate replacement and compressive strength rapidly decreased when more than 15% replacement of EAFD. For this reason, samples containing 10-15% of fine aggregate replacement were further investigated.

When more EAFD percentage has added, compressive strength decreased because percentage of Zn increased and due to the fact that zinc has inverse impact to concrete’s compressive strength.

In general, compressive strength has improved with addition of 10% of EAFD.

Mixture II with EAFD replacement of fine aggregate varying between 10 and 15% and fly ash replacement of cement varying between 10% and 25%.

In general, addition of fly ash to mixtures has a negative impact on compressive strength in all three researched samples, as presented in results. The addition of fly ash resulted in a slight compressive strength decrease in this mixture.

The best result was with addition of 10% of fly ash with a combination of 10% EAFD.

It is noteworthy that for addition of 15% fly ash with 15% of EAFD the compressive strength has improved to 12.47 MPa.

Mixture III with 10% EAFD replacement and different milling time.

The sample B2 with 10% and one hour milled EAFD has recorded the best compressive strength in the group (17.17 MPa), after that as the percent of EAFD increased as the compressive strength decreased. On the other hand, the milling operation to EAFD has inverse impact to compressive strength if we compared with results of mixture I (20 MPa), which is not included milled EAFD. Whereas for the five hour milled EAFD, compressive strength was very poor.

Mixture IV with 10% EAFD replacement, different milling time and 10% fly ash.

As can be seen from the results, the percentage of EAFD was set on 10% for different milling time with and without 10% of fly ash; it found that the presence of fly ash has a negative impact.

The results show that the replacement of fine aggregate with more than 15% of EAFD results in a rapid decrease of compressive strength; the abrupt decrease of compressive strength is most probably caused by the instability of hydrolysis products in concrete, due to an increased content of iron. The present alkalis, reacting with some of reactive aggregates (aggregate reaction), additionally contribute to the decrease of compressive strength.

The best compressive strength was attained with fly ash was at 10%, with replacement of both components and three hours of milling of EAFD, whereas the compressive strength decreases slightly with the further addition of fly ash. That is explained by the increase of the EAFD particle specific surface area, which affected a higher hydrolysis capacity of mineral phases.

Heavy metals leachability was tested according to the standard Toxicity Characteristic Leaching Procedure (TCLP), US EPA method 1311[113].

From the results, it could be seen that leachability of lead from all concrete samples is far below the limit of 5 mg/L, i.e. Pb was stabilized in a cement matrix even at 50% of fine aggregate replacement with EAFD. Zinc leachability is reduced comparing to initial values, but for Zn there are no TCLP limits. In Mixture I with increase of EAFD in mixture Zn leachability increase. In Mixture II-IV with addition of fly ash and with milling of initial EAFD, Zn leachability decreases below 50ppm.

Using EAFD prevents it going to landfill as waste, saves energy and natural resources, and significantly reduces CO_2 emissions in cement production. According to the EAFD Cement Association, replacing Portland cement with EAFD cement in concrete can save up to 59% of the embodied CO emissions and 42% of the embodied energy required to manufacture concrete and its constituent materials.

5.3 Sintered products:

Sintering might best be described as the synthetic manufacture of solid products using controlled heating of powdered raw materials. The proper application of sintering temperature results in the adhesion of the powder grains to each other without melting the material.

This part of results includes EAFD-LCD stabilization and valorization using conventional methods of synthesis and thermal treatment, to use it in ceramic industry and sintering of EAFD in synergy with other iron-bearing by-products by using pelletization technique and thermal pretreatment for valorization of zinc and production of a suitable input material for charging into electric arc furnaces as a partial replacement of steel scrap.

5.3.1 Sintered EAFD within LCD waste glass matrix:

Samples of EAFD were obtained from Serbian steel making company, equipped with electric arc furnace. The LCD waste glass was obtained from the local WEEE recycling company. Both raw materials were sieved on standard mesh type sieve in order to obtain -100µm fraction and subsequently dried in laboratory oven at 105ºC for 24 hours. Prior to sieving and drying, raw materials were milled in a steel ball mill (Ø160mm, height 270mm, ball diameter 10mm, material + balls material charge 60%) at 300min^{-1}.

LCD glass:

Used LCD glass was characterized in order to determine chemical, phase composition, morphology. According to attained results, the major determined elements of LCD waste glass are Si, Ca and Al, while trace elements are Fe, Zn, Pb and Cu. The major component SiO_2 was observed in a form of small fractured particles and heavy metals leaching degree was found far below the regulatory limits.

EAFD-LCD mixtures:

Chemical composition of EAFD-LCD mixtures was calculated to oxides content, it is axiomatic, as the proportion of LCD increases as the Ferrous and Zinc oxide decreases.

Sintered EAFD-LCD samples:

Chemical composition of samples calculated to oxides content, sintered on border temperatures, 600°C and 800°C. Depending on the sintering temperature, volatile substances (VS) are in range from 3.17 to 6.12 and referred to the evaporation of chloric and nitric compounds, as well on evaporation of ZnO.

Results obtained by surface analysis at lower magnifications, of samples sintered on 600°C and 800°C, reviled structure typical for porous ceramic materials. It is obvious that with the increase of EAFD overall porosity of the observed material increases. Furthermore, it was observed that with the increase of sintering temperature, apparent density decreases, as consequence of higher sintering degree.

At higher magnifications, in almost all samples, identification of individual particles is very rare, but, as a consequence of the conventional synthesis of EAFD and LCD glass, these particles are identified as agglomerates, which is typical for the reactions of solid state components during the sintering process. Nevertheless, these systems are characterized as less homogenous where it is not possible to control the stoichiometric ratio and grain growth and despite the fact that sintering was performed at temperatures below melting point, still certain degree of impregnation of phase with lower melting point (Ca ferrite) in solid phase of other component was observed. Also, due to the local increase of reduction potential, sporadically isolated metallic droplets (Pb) were observed.

Results of mass differences of all sintered samples showed that weight losses generally increase with increase of sintering temperature. Due the fact that all volatile compounds, such as nitric and chloric compounds are present in EAFD and are not contained in LCD, weight losses decrease with addition of LCD waste glass.

Compressive strength of sintered samples' results revealed that increasing of sintering temperature increases the strength of the treated material, particularly in case of decrease of EAFD, which is in accordance with results for chemical composition and sintering temperature influence on material density.

According to leachability results, leachability of Cd, Cr and Pb is below the regulatory limits in all samples, while in a case of Zn, although there are no regulatory limits, comparing to initial values of Zn leachability from raw materials, reduced leachability was observed.

5.3.2 Sintered EAFD within iron-bearing waste composite pellets:

This part of work includes the possibility of separate zinc and lead recovery from coal composite pellets, made of EAFD with other synergetic iron-bearing wastes and by-products (mill scale, pyrite cinder, magnetite concentrate), in two-stage process. The first, low temperature, stage performed in electro-resistant furnace enabled removal of lead due to the presence of chlorides in the system, and in second stage at higher temperature in DC plasma furnace, zinc was valorized.

Used materials:

Limestone:

Commercial limestone from local market was used as a flux material. Basically limestone is used as a slag former. Iron ore normally contain gangue materials such as silica (SiO_2), Alumina (Al_2O_3) along with sulphur (S) and Phosphorus (P). Removal of these impurities is done by combining the gangue materials with CaO and/or MgO to form slag which consists of low melting point complex compounds such as calcium silicate, calcium aluminates, etc.

Coke:

Coke is used chiefly to smelt iron ore and other iron bearing materials in blast furnaces, acting both as a source of heat and as a chemical reducing agent, to produce pig iron, or hot metal. Foundries use coke as a source of heat for producing metal castings. Other industrial uses of coke include the smelting of phosphate rock to produce elemental phosphorous and the production of calcium carbide. Small sizes of coke, termed breeze, are used as fuel in sintering finely sized particles of iron ore and other iron bearing material to produce agglomerates that can be used in furnaces.

Mill scale:

It is a valuable secondary material due to its high iron content, low impurities and stable chemical composition. Mill scale is formed during hot rolling process of steel in Serbian rolling mill plant. According to European Waste Catalogue and Hazardous Waste List mill scale has index number 10 02 10.

Pyrite cinder:

Pyrite cinder was generated in the process of sulfuric acid production and due to its composition belongs to the technogenic waste. This waste belongs to not listed wastes.

Green pellets:

Three different test mixtures (marked P1, P2, and P3) were made and tested before annealing.

Before the thermal pretreatment the particle size analysis was performed and fractions between 6-10 mm (>75% of material) were selected as samples for further testing.

Abrasion results indicate that for mixture P2 and P3 as the pellets become bigger as the proportion of weight losses becomes higher. Although the weight losses of mixture P2 is higher than of mixture P1. This may be due to the differences in granular analysis between pyrite cinder and magnetite.

Produced pellets must have sufficient green strength to with stand handling, loading, high temperatures and stress during reduction in furnaces, even though the heat treatment of pellets it is an optional process. In general smallest pellets showed better durability comparing with bigger pellets, that’s due good compacted pellets with very low porosity and also the less surface area exposed to the impact. That was proved by pellets of mixture P3 which showed the best green strength, due to contain mixture P3 of high amount of fine EAFD.

Green pellets’ compressive strength for bigger pellets slightly better than the smaller. The best compressive strength was obtained from mixture P3, even though that mixture didn't stand the temperature during annealing. And this is also due to the same mentioned reasons.

Process modeling:

From obtained results, it could be seen that zinc and lead could be separated during two-step heating regime, as anticipated. In the first step, lead could be vaporized in chloride form, while in second step, zinc is valorized as oxide.

With this method, produced zinc-oxide would be higher grade and washing step could be omitted. In the same time produced lead-chloride could be sent to lead smelters.

The first, low temperature, stage:

The annealing program was performed in temperature range 850- 1200°C in time 30-60-90 min at Electro resistant furnace (ERF).

Pellets P1 at temperatures above 1150°C started to sinter, so for further experiments maximal temperature was set to 1150°C. Also, pellets P3 even at lower temperatures started to rupture and crack, so they were not used in further experiments. According to literature [119], the probable reason for rupture of pellets P3 is presence of high amount of fine grain component, EAFD, that cause good compacted pellets with very low porosity and high green strength, but that resulted backfired on annealed pellets because of evaporation of lead and halogens in relatively high amounts that crushed cold intensive bonds caused by fine size and binder.

According to the results, weight losses of mixture P1 after 30 minutes annealing reached a peak at 1050°C, which means this difference in weight between the green and annealed pellets has vaporized as gasses. For mixture P2 the results were regular, as the temperature and time increase the weight losses increase, the higher amount of weight losses was 12.8% at 1150°C for 90 minutes annealing time.

In general, results showed that compressive strength of produced pellets from mixture P1 and mixture P2 increases with increasing of annealing temperature. Although the compressive strength of mixture P2 higher than mixture P1. Maximum compressive strength of both mixtures occurs at a temperature of 1150°C with 30 min annealing time. Pellets from mixture P2 have a maximum compressive strength of 8,861 N/cm^2, which is 4 times more than the compressive strength of mixture P1 at the same annealing conditions.

It is worth mentioning that, pellets of mixture P2 which is showed higher compressive strength it contain 20% of magnetite and has lost less weight after annealing, that mean it has less porosity and more dense texture comparing with P1.

To analyze the toxic elements, chemical analysis was applied for pellets and condensed gases. According to attained results, percentage of residual Zn in pellets increases with increasing of temperature. Pellets P1 has lose the highest amount of Zn at 1000°C. Pellets P2 in their raw state contain 18.61% Zn. Depending on the annealing time, there is a sharp decline in the content of Zn at 850°C for 60 min annealing time and at 900°C for 30 min annealing time. With increasing of temperature there is a steady uniform loss of Zn for all tested pellets for all different process conditions. The highest loss is observed at 1150° C for 90 min annealing time, the value was 15.87% of Zn.

Chemical analysis of annealing products showed that for tested pellets P1and P2; in general, any increase in temperature causes a decreasing in a residual amount of Pb. The less quantity of Pb was fund in pellets P1 at 1100°C where 0.078% Pb remains in the pellets. In its raw state, chemical analysis showed that tested pellets P2 contain 1.154% Pb. Depending on the annealing time a trend is observed of slight decline in the Pb content up to the temperature of 1050°C. For pellets P2 at 1150°C and 90 minutes annealing, the residual amount of Pb was the minimum, the content of Pb was 0.145%.

Copper and Manganese residue in pellets P1 and P2 were tested and from the results it is clear that for every mixture of pellets there is no effect of applied temperature and time on the content of Cu and Mn in pellets, which is due to high boiling temperature, 2595°C and 2150°C respectively.

In the case of gases, gases from mixture P2 are condensed from vaporized gases, in annealed pellets observed dependence of Zn content on weight loss. At 950°C obtained the highest content of Zn in the gases for 30 and 60 minutes annealing, with increase of temperature Zn content decreases, which is consistent with the results of annealed pellets.

In the analysis of Pb, it is noticed that with the increase of annealing time of pellets at a certain temperature gets higher proportion of Pb in the gases. Also, the highest content of Pb in the gases has detected at 1050°C. At higher temperatures a decrease of Pb content is observed except of the 30 min annealing time, where a slight increase is marked.

Analysis of copper and manganese indicates to very small amount at condensed gases, anyway residual amount of copper increases with time.

Separation of zinc and lead is based on higher affinity of lead towards chlorine than zinc, so the free energy and possibility of volatilization of lead as $PbCl_2$ is significantly higher than of the Zn and Fe chlorides.

According to the results the selectivity of zinc and lead volatilization is possible. In temperature range 850-950ºC most of lead is removed from pellets (~95%), while 80-87% of zinc remained in pellets.

Concerning retention time, it is notable that with prolonged time levels of volatilized zinc and lead increase. For design of industrial plant, time of 1h would be suitable for achieving desired levels of lead removal from mixture. Also, in industrial scale process would be conducted in dynamic system, eg. rotary furnace, so this time and temperature level would be appropriate.

For further experiments pellets pretreated at 950ºC for 60 min were chosen.

The second, high temperature, stage:

Zinc valorization was performed in DC plasma furnace at 1490ºC for 6h. Charging materials were start slag and pretreated pellets from Electro resistant furnace (ERF). In this stage no additional reducing agent was added, due to the pellets contained 10% of coke.

Obtained results show that filter dust contains 78% of ZnO, i.e. 62% of Zn, which is slightly lower than the level of industrially applied processes for sole EAFD treatment. But, in presented test, mixture of iron-bearing materials was used, so the first result of Zn recovery around 95% show the possibility of industrial application for joint treatment of different materials. Quality of produced metal is suitable for charging in to EAF, as a partial replacement of steel scrap. Obtained slag, according to its composition, is adequate for application in construction industry.

5.3.3 Modeling:

Modeling was performed for three different FeO contents in sinter and for four different basicities (B).

Results show that reducibility is influenced by FeO content, increase of FeO results in increase of reducibility. Also, presence of higher content of SiO_2 decreases sinter reducibility. Increase of MgO content in sinter significantly increases reduction rate of sinter. Reducibility is highly influenced by mineral composition (could be derived from chemical composition), process temperature, i.e coke addition to sinter mixture.

For sinters with lower coke addition, oxidation degree is higher, due to the fact that primary components are not affected by high temperature processes. Final sinter is characterized with higher porosity, resulting in better reducibility, which is proven by presented model.

With higher additions of coke, sintering process is conducted at higher temperatures with formation of liquid phase of iron-silicate composition. Final sinter is characterized with lower reducibility, due to the lower its porosity.

It is expected that with increase of reducibility mechanical properties of sinter will decrease and with this yield of conditional sinter will also decreas.

6. Conclusion

The investigated EAFD was brought from Serbian carbon steelmaking and that is way the zinc percentage it was 30.34%, which is in the standard range of typical chemical analysis of EAFD from carbon steelmaking. The usual Zn content is between 18-35%, so investigated sample is in upper part of this range.

The analysis also shows that zinc, iron and chromium are mainly present as ferrites which are very resistant against to any kind of treatment. Because of that, it is necessary to use more aggressive conditions (high temperature or stronger leaching reagent) for metals recovery.

Solidification/Stabilization in grout mixture:

With respect to mechanical and chemical properties of products, the best maximum replacement of cement with EAFD is 20%. With a higher amount of EAFD in mixture compressive strength decreases rapidly. It was found that the addition of lime slightly decreases the compressive strength.

According to leachability results, Pb was stabilized in a cement matrix even at 80% of cement replacement with EAFD. Lead leachability is reduced comparing to initial values, but for Zn there are no TCLP limits.

Solidification/Stabilization in concrete mixture:

Regarding to mechanical and chemical properties of products the best maximum replacement of fine aggregate with EAFD is 15%. With higher amount of EAFD in mixture compressive strength decreases rapidly.

Leachability of lead from all concrete samples is far below the limit of 5 mg/L, i.e. Pb was stabilized in a cement matrix even at 50% of fine aggregate replacement with EAFD. Zinc leachability is reduced comparing to initial values.

From the physico-mechanical and environmental aspects, EAFD can be used as a component in cement mixtures and the S/S process of EAFD with cement is effective.

Sintering

Sintering of EAFD was investigated by using conventional methods of synthesis and thermal treatment of EAFD-LCD waste, and by established method for EAFD treatment by two-stage process.

Sintering of EAFD within LCD waste glass matrix:

Based on the results, it was found that materials suitable for use in ceramics industry as a partial substituent of quartzite and fluxing components can be produced. Leachability of Cd, Cr and Pb is below regulatory limits in all samples, while in a case of Zn, although there are no regulatory limits, comparing to initial values of Zn leachability from raw materials, reduced leachability was observed.

Besides solving the environmental problem related to EAFD and LCD disposal, by replacement of raw materials, certain economic effects can be achieved.

Sintering of EAFD within iron-bearing waste composite pellets:

Achieved results show presence of synergy of input materials in regards to maximal metal yield, production of commercial grade products respecting principles of cleaner production and energy efficient processes. Presented technology for EAFD treatment by two-stage process show possibility of production of variety of final products: pig iron, slag, lead-chloride and higher purity zinc oxide.

Investigated process has great possibility for scale-up to industrial level, and should be considered as a potential replacement of Waelz process.

In future chlorinating components of charge could be replaced with alternative fuels, heavy metals containing waste plastics. Uncomplicated treatment of gaseous phase gives proposed process additional benefits.

Modeling results concluded that from quality aspect of final sinter from EAFD, pyrite cinder and mill scale, sintering process should be conducted under following conditions FeO=17.5% and B=1.25. Under these conditions produced sinter would possess suitable characteristics, and would enable optimal techno-economical parameters for its treatment in electric-arc furnace.

The connection between the composition of the dispersed iron-bearing mixture, as an independent variable, and dependent variables (metallurgical properties such as resistance to impingement and compression strength) was determined using correlation and regression analysis, where mathematical models for fast and reliable projected synthesis the required metallurgical properties of sinter were obtained.

7. References

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