Effect of Lead and Zinc Impurities in Ironmaking and the Corresponding Removal Methods: A Review

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Abstract: This paper reviews the effects of Pb and Zn impurities and their removal in the ironmaking process. The phase changes during ironmaking were investigated, along with the removal techniques of such impurities and their environmental impact. Results show that distribution of Pb–Zn–Fe in Fe ore is complicated, the particles are fine, and the removal of mineral phase at high temperature is difficult. Therefore, the production and occurrence of Pb and Zn impurities in the ironmaking process were analyzed; such impurities reduced the overall productivity of the process. In addition, the important treatments for the removal of these impurities were investigated. Most of these processes eliminated the Pb and Zn impurities from the dust or sludge, but the main impact of the reduced productivity of the ironmaking process in the furnaces was still observed.

Keywords: ironmaking; impurities; iron; Zn; Pb; reduction roasting; phase changes

1. Introduction

A mineral is a naturally occurring chemical compound that has specific atomic structure, chemical composition, and physical properties [1]. Minerals can be found in different areas and phases. Most minerals (e.g., Fe) have wide industrial application in many aspects of the social economy, such as in steel making. Abundant iron-containing minerals are present in Fe ore, which mainly occurs in the form of rocks, magnetite (Fe3O4), hematite (Fe2O3), siderites (FeCO3), and limonite (2Fe2O3·3H2O) [2]. However, the ironmaking process causes environmental problems. The growing need for a dramatic reduction of greenhouse gas emissions leads to the development of innovative technologies to reduce energy consumption and emissions in this process [3].

1.1. Ironmaking Process

Fe is extracted from Fe ore and converted into alloys. This metallurgical process is important. The raw materials of the iron-bearing mineral are introduced in the blast furnace (BF), wherein aside from Fe and C, other elements are also subjected to roasting in the furnace [4]. Therefore, steel is produced by pig iron or hot metal and steel scrap. These methods can be performed using two types of furnaces, namely, basic oxygen (or basic oxygen steelmaking) and electric arc furnaces (BOF and EAF, respectively) [2,5]. In BOFs, approximately 75% of Fe comes from the hot metal produced during the BF process. In fact, BOF plays a key role in steel production [6] and produces almost 66% of the total crude steel. At present, over 93% of the total Fe production from ores is performed using BF. BF uses several Fe ores, such as magnetite (Fe3O4) and hematite (Fe2O3), as iron-bearing raw materials. These materials can use coke, pulverized coal, and lime or limestone as reducing agent, heat source, and fluxing agents, respectively. BF ironmaking mainly aims to produce a hot metal with consistent quality [5].
Pb–Zn refractory iron ore presents a complicated relationship because of Pb–Zn–Fe inlay, fine particles, and variable contents of lead and zinc impurities. Such variations influence the difference of migration and enrichment, which are important problems in Fe ore beneficiation and processing. Reduction roasting technology has become an important method for refractory Fe ore dressing because of its remarkable sorting index and the high utilization of Fe resources [7,8]. Fe can also be extracted from cyanide gold tailings through magnetization roasting process or by using sulfuric acid slag [7,9]. Fe and Zn are also recoverable through selective reduction and calcination from the Zn tailings in Ni Fe ores [10,11]. Fe and Ni can be recovered using microwave carbothermal reduction [8], in which a refractory Fe ore that contains Pb and Zn as impurities is subjected to roasting and reduction processes because of high temperature. Various types of Zn and Pb minerals influence complex intercalation relationships and diverse morphological changes. However, the phase transition and migration of Pb and Zn impurities have not been explored. With the breakthrough of flash magnetization, relevant analysis can improve the efficiency of the magnetization roasting process and enhance the resources.

1.2. Impurities in the Ironmaking Process

The reactivity of coke in an operating BF is not only affected by an inherent mineral matter but also by recirculating alkalis [12]. BF sludge (BFS) is a dangerous waste product of pig ironmaking. In addition to Fe, BFS contains Zn, CaO, S, Pb, Cd, Cr, As, and alkali metals (e.g., K, Na, etc.) [13]. Cu, Ni, Cr, Cd, Pb, and Zn are among the most common heavy metal contaminants of industrial pollution [14,15]. The impacts of these chemicals in terms of impurities can be arranged according to the environmental risk indicator for heavy metals, where Cd > Zn > Cu > As > Pb [16]. Moreover, the deleterious elements that enter the smelting furnace include K, Na, Zn, and Pb [17].

2. Effect of Pb and Zn Impurities on the Ironmaking Process

The Fe and steel industry can directly determine the industrialization foundation of a country. In 2018, China’s crude steel output reached 928 million tons; the Fe ore dependence outside the country exceeded 80%. Given the complex metallogenic reasons and sources, Pb and Zn impurities are more or less contained in the raw materials for ironmaking. Both chemicals are harmful to BF ironmaking. The allowable amount of Pb and Zn in the raw materials should be less than 0.15 kg/t. The effect of these impurities on the furnace is evident, especially in refractory areas [18]. Traditional refractory materials for BF hearth lining comprise carbon bricks and ceramic cup. Nevertheless, these materials cannot meet the requirements for a long service life design of blast furnaces [19].

Pb and Zn are considered harmful impurities in BF ironmaking. Pb impurities can easily reduce, oxidize, expand, and form Pb-containing precipitation. Zn-containing dust seriously affects BF production. At present, problems related to the use and recycling of mineral wastes are common in integrated steel mills. The continued emphasis of environmental regulations on landfills and their storage has rendered the effective management of these wastes a high priority [20]. The direct recycling of Fe wastes in BF is disserved by their corresponding chemistry (0.1% Zn in the charge), as well as the presence of Pb [13]. To achieve effective continuous recycling of Fe units, the sources should be identified, and the structure should be determined to develop a device and suitable technology for the processing of Zn and Pb [21].

2.1. Effect of Pb on Ironmaking

The harmfulness of Pb to BF is mainly due to the destructive effect of liquid Pb that penetrates the furnace’s body and the oxidizing expansion. The economic and technical problems in conventional metal treatments are caused by complex compounds that are produced by a mixture of Pb sulfide and Zn ores [22]. The impact of Pb on BF can be summarized as follows. First, Pb infiltrates into the refractories of the furnace’s body. The oxidation and expansion produce internal stress, which damages the refractories, and even
cracks the furnace shell. Pb infiltration in the carbon bricks of the furnace’s bottom causes the floatation of the refractory bricks and even leakage in the entire bottom part. Second, when the liquid Pb is denser than molten Fe, the former exhibits low fluidity and becomes insoluble in the latter. Excessive accumulation of liquid Pb in the hearth and hearth bottom causes the abnormal work of the furnaces, such as iron mouth and main ditch. Maintaining and plugging the skimmer is difficult, thereby resulting in iron-running accident. Third, Pb oxide and other components in the furnace form low melting point or eutectic compounds, adhere to the sinter and pellet, reduce the soft melting temperature of the sinter and pellet, adhere to the permeability of the BF column to the coke effects, and adhere to the furnace wall to form nodules, which affect the normal production of BF. In addition, the loading of Pb increases the coke rate [23]. Lastly, Pb vapor discharges outside the furnace, thereby causing potential safety hazards, environmental pollution, and Pb poisoning [15].

2.2. Effect of Zn on Ironmaking

The Zn content in the furnace, which enters through the ore and the furnace sludge, is high. The Zn input in the BF must be limited; hence, the excess Zn must be removed [4]. The effect of Zn on the BF can be elaborated as follows. First, the simultaneous evaporation, condensation, oxidation, and Zn circulation can lead to accumulation in the furnace. Second, the deposition of extremely fine particles on other molecules with large surface reduces the life of the BF and weakens the quality of the iron pig product [21,24]. Third, the increased Zn absorption of the sinter and pellet with temperature affects the permeability of the combustion furnace [25,26]. Fourth, Zn fluctuation can cause the node collapse in the BF and block the gas pipeline [27]. Fifth, Zn expands the coke reactivity list and diminishes the coke’s quality after reaction [28]. Sixth, the Zn enhancement and development in furnace bricks are the fundamental factors that prompt a rising bull in the furnace. The behavior of Zn inside the furnace brick structure is changed from thick to free when Zn is already inside, improved, and extended [17]. Lastly, BFS cannot be directly recycled because Zn is present at a maximum acceptable concentration (approximately 0.5%) [13,29] and might form crusts inside the furnace, thereby affecting the operation. The Zn vapor penetrates the lining of the furnace and causes damage [29].

2.3. Effect of Alkaline Elements on the Pb and Zn Present during the Ironmaking Process

In a complex furnace environment, the destructive effect of Pb and Zn on the brick’s body is not only caused by both chemicals alone, but also by many factors, such as the effect of alkali metals on the penetration of Pb and Zn and on the reduction reaction. K and Na enter the furnace from coke and ore in the form of oxides, silicates, and carbonates [5]. Alkali metals, Pb, and Zn not only affect the structure of the BF body, but also present other hazards. For example, when Na$_2$O or K$_2$O increases from 1 to 3 kg/t HM, the coke ratio increases by 13.13 and 8.51 kg/t HM, the gas utilization decreases by 4.04% and 2.67%, respectively, thereby reducing the Fe content and affecting the Pb and Zn [23].

When the temperature in the BF is lower than 450 K, the deposition of Zn will lead to C deposition, which may be due to the decomposition of ZnO; that is, a small part of ZnS and ZnO.Al$_2$O$_3$ as decomposing agents of CO into CO$_2$ and C and the infiltration of the deposited C into the cracks of the lining bricks aggravate the damage in the bricks [11]. The circulation and strengthening of the alkali metals in the furnace will adversely affect the size and density of the coke, consequently reducing the Fe, Pb, and Zn contents [30].

Figures 1 and 2 show the effect of harmful elements on gas utilization and coke rate, respectively. Figures 3 and 4 show the variation of the coke rate under different Zn and Pb and Na$_2$O and K$_2$O loads, respectively.
Figure 1. Effect of harmful elements on the gas utilization under various accumulation times.

Figure 2. Effect of harmful elements on the coke rate under various accumulation times.
In steel wastes, the main constituents that are classified under the hazardous classification are potentially toxic elements (e.g., Pb and Zn) [13] and alkali metals (e.g., K) because of their concentration and potential environmental impact [31,32]. Large amounts of BF dust are landfilled, some of which contain several harmful elements [29]. The environmental impacts of these constituents strongly depend on their mineralogical and chemical forms. The analytical identification of solid matrices is a difficult and complex process [32]. The harmfulness of these elements to the environment is summarized in three aspects: (1) the leaching of Zn and Pb contaminates the groundwater [4,33,34], (2) the presence of harmful elements (e.g., Pb, Cd, Zn, and As) in a landfill violates environmental laws [20], and (3) recycling is hampered by the high Zn ratio, which causes several issues in the furnace operation because of the increase in Zn accumulation [31].

**2.4. Environmental Effect of Pb and Zn Impurities**

A rise in loading times increases the coke rate, thereby leading to the accumulation of harmful elements. The loading of Na, K, Zn, and Pb into the BF increases the coke rate by 13.99, 6.25, 3.63, and 0.02 kg/t HM, respectively. The increased coke rate and the decreased gas utilization under various loads and accumulation times of each element was also estimated [23].

**Figure 3.** Variation of the coke rate under various Zn and Pb loads.

**Figure 4.** Variation of the coke rate under various Na₂O and K₂O loads.
Further research should focus on the relevance of the process conditions (e.g., different counter pressure at the blast furnace top) and input composition with respect to the damage mechanism of the elements present in the BF lining. Such information can lead to the generation of the limits for these elements in the BF, as well as to the development of an improved internal recycling strategy (e.g., additional knowledge about the maximum chargeable Zn content, which can improve the amount of top gas dust internally recycled at the sinter plant) [18].

3. Phase Changes and Characteristics in Metallurgical Reduction

Zn and its compounds are widely used in high-performance alloys, battery materials, confidential instruments, and microelectronics industries [35]. China has become the largest Pb–Zn producer and consumer in the world. The country’s Pb–Zn smelting output also demonstrated a rapid increase [36].

As previously mentioned, the distribution of Pb–Zn–Fe in Fe ore is complicated, the particles are fine, and the removal of mineral phase at high temperature is difficult. Therefore, the production and occurrence of Pb and Zn impurities in the ironmaking process are analyzed, and the process of metallurgical reduction of Pb–Zn minerals is described in this paper. The phase evolution of the Pb–Zn minerals during the metallurgical reduction process is summarized, and their transformation characteristics during the ironmaking process are analyzed. Understanding the variation characteristics of Pb–Zn reduction process at high temperature and controlling the Pb–Zn technology for Fe-containing raw materials is essential and can provide theoretical support for controlling the Pb–Zn impurities in Fe-containing raw materials and promote the level of their comprehensive utilization.

3.1. Characteristics of Pb and Zn Minerals during Ironmaking

In nature, Pb and Zn mostly exist in sulfide state, and the occurrence of both in Fe ores is complex. The Pb in iron concentrate mainly exists as galena. Lead jarosite and Al also exist. Zn mainly exists in sphalerite and Zn carbonate, as well as Zn in sinter, pellet, and furnace dust. The formula for Zn is in the form of silicate and spinel mineral, whereas that for Pb mostly exists in the form of Pb oxide. The mineral characteristics of Pb–Zn-containing materials in BF during ironmaking are summarized in Table 1. Given that the Pb and Zn impurities in Fe ores are mostly coexisting and interpenetrated with other minerals in fine grain size, such impurities are often disseminated in the grain edge of Fe oxide ore [37]. In general, BFS (dry solid) contain 21–32% of Fe, 15–35% of C, 1.0–3.2% of Zn, and 0.3–1.2% of Pb [4].

Table 1. Characteristics of Pb and Zn minerals in BF ironmaking.

| Fe Concentrate | Sinter and Pellet | Ironmaking Furnace Dust | Furnace Tumor |
|----------------|-------------------|-------------------------|---------------|
| PbS, PbO, PbSO₄ | PbSiO₃            | PbO                     | Middle part of the furnace’s body is CaSiO₃ |
| ZnS, ZnCO₃     | ZnS, ZnFe₂O₄, Zn₂SiO₄ | ZnO, ZnFe₂O₄, Zn₂SiO₄ | Upper part of the furnace’s body is ZnO |

In BFS, Zn is commonly present in various phases. Zn can be obtained in the liquid, solid, or gaseous form depending on the temperature through BF recycling [20]. Figure 5 shows the sources of Pb and Zn that enter the furnaces, as well as the corresponding cycle course during processing.
3.2. Production and Occurrence State of Pb and Zn

The sources of Pb and Zn in ironmaking include natural Pb–Zn minerals, Pb–Zn–Fe ore, Pb–Zn in sinter and pellets, and Zn/Pb dusts [38]. The production and occurrence of typical Pb–Zn impurities during the ironmaking process are presented in Table 2.

Table 2. Output and occurrence status of Pb and Zn elements.

| Source                          | Component                                  | Specificity                                                                 |
|---------------------------------|--------------------------------------------|-----------------------------------------------------------------------------|
| Natural Pb mineral              | PbS, lead oxide ore, and bauxite (PbCO₃)   | Most of the Pb in nature exists in the form of PbS                             |
| Fe ore                          | PbS, PbO, PbSO₄, and PbCO₃ or basic lead carbonate and lead silicate | The Pb content in BF is minimal. The main Pb minerals are PbO and Pb          |
| Pb-bearing sinter and pellet    | The order of mineral the content of Pb is PbO > PbO·SiO₂ and 2PbO·SiO₂ > lead ferrate > PbSO₄ | Roasting causes desulfurization of sulfides to form oxides                     |
| Natural Zn mineral              | Mainly sphalerite (ZnS), part red zinc ore ZnO, rhombohedral (ZnCO₃), Zn₂SiO₄, and ZnFe₂O₄ | Zn in nature often exists in the forms of ZnS, but some exist as oxidized ores |
| Fe ore                          | Zn exists in the form of ZnCO₃, ZnS, ZnFe₂O₄, and Zn₂SiO₄ | The content of Zn in BF is minimal, mainly in the form of ZnO and Zn           |
| Zn-bearing sinter and pellets   | ZnO, Zn₂SiO₄, ZnFe₂O₄, and a small amount of ZnS | The ZnSO₄ and ZnS contents given good desulfurization by sintering is minimal |
| Zn dust                         | The order of the contents of Fe and Zn minerals is ZnFe₂O₄ > ZnO > Zn₂SiO₄ > ZnS and ZnSO₄ | ZnO is easy to leach, but ZnFe₂O₄ is difficult to dissolve                     |

Figure 5. Source, impact, and cycle route diagram of Pb and Zn.
Fe coexisting with Fe-containing Zn in the raw materials are in the forms of Fe$_3$O$_4$, Fe$_2$O$_3$, FeO, and ZnFe$_2$O$_4$ [39]. The use of spinel-like material ZnFe$_2$O$_4$ is difficult, in which oxygen ions are packed closely, the lattice is highly stable, and are difficult to dissolve in acid leaching. Similarly, separating Fe and Zn is difficult [40] but recovering both is feasible [41].

3.3. Present Situation of the Pb–Zn Metallurgical Reduction Process

Pb–Zn sulfides are converted into oxides through oxidation roasting. Then, PbO and ZnO are converted into Pb solution and Zn steam through a carbonaceous reductant, respectively. Under high-temperature reduction, ZnO and ZnFe$_2$O$_4$ are reduced to Zn steam [15]. Pb is directly produced by the interaction reaction among PbS, PbO, and PbSO$_4$. The reduction process of the Pb–Zn metallurgy can be divided into three types: pyrometallurgical smelting of lead, pyrometallurgical Zn refining, and pyrometallurgical recovery of Zn-containing dust. The technical characteristics of these processes are provided in Table 3.

| Classification                  | Characteristics                                                                                       | Technology          | Specificity                                      |
|---------------------------------|-------------------------------------------------------------------------------------------------------|---------------------|-------------------------------------------------|
| Pyrogenic process of Pb smelting | Modern Pb productions are almost in the form of pyrometallurgical lead smelting, which can be divided into BF and direct Pb smelting | Kivcet method       | Oxygen-rich smelting                             |
|                                 |                                                                                                       | QSL method          | Oxygen-rich bottom blowing furnace              |
|                                 |                                                                                                       | ISA, Asmelt method   | Oxygen-rich top blowing furnace                 |
|                                 |                                                                                                       | Vanukov method      | Oxygen-enriched side blowing furnace            |
|                                 |                                                                                                       | SKS method          | Bottom-blowing oxidation BF reduction           |
| Both                            | Kaldo method                                                                                          |                      | The recovery rate of Zn is 95% and the utilization rate of sulfur is more than 94% |
| Pyrogenic process of Zn smelting | Accounts for 30% of the total Zn production in China. The vertical tank method accounts for 60%, the ISP method accounts for 31.6%, and the other methods cover a small percentage | Vertical tank method| The recovery rate of Zn is 93.8%, Pb and Zn can be produced at the same time, and the processing cost is low |
| Electric furnace method         | Zn products containing more than 99.99% Zn can be obtained                                           | ISP method          |                                                |
| Other soil methods              | Small-scale and requires low investment                                                               | Electric furnace method |                                                |
| Rotary kiln                    | Comprehensive utilization of Fe and Zn from low Zn dust                                               | Rotary kiln         |                                                |
| Rotary hearth furnace           | High efficiency and low energy requirements, effective recovery of metals (e.g., Fe and Zn)         | Rotary hearth furnace |                                                |
| Circulating fluidized bed       | Use of good gas dynamics conditions in fluidized bed to reduce energy consumption                     | Circulating fluidized bed |                                                |
| Melt reduction                  | Zinc removal complete and the hot metal quality is high, but the object contains abundant Zn dust     | Melt reduction       |                                                |

Table 3. Technical characteristics of the Pb–Zn metallurgical reduction process.
3.4. Reduction of Pb-Containing Minerals

PbS is the main raw material in lead smelting by fire; the corresponding reduction, however, is extremely complicated because PbS is not only reduced by metal Cu, Zn vapor, metal Fe and Na₂CO₃ to form Pb solution but can also react with the Pb oxide to form Pb liquid.

At 700–900 °C, the metal Cu and PbS were replaced to form Pb solution and Cu₂S. At approximately 1000 °C, volatile PbS was replaced by the Zn vapor formed by ZnO reduction. PbS is sintered at 648–760 °C to produce metal Pb and SO₂ flue gas, and can also be oxidized by O₂ in furnace gas to form PbO. At 1250 °C, Fe can replace Pb in the PbS. PbS can also be reduced to Pb steam by Na₂CO₃. The thermodynamic calculation suggests that the lowest temperature of spontaneous occurrence is 1429 °C. At 1050 °C, PbS easily reacts with the Pb oxide (i.e., PbS is partially oxidized to PbO and PbSO₄ to react with PbS). This characteristic is widely utilized in direct lead smelting. The basic reaction can be represented as follows.

\[
PbS(s) + 2PbO(s) = 3Pb(l) + SO_2(g) \quad (1)
\]

The thermal decomposition of Pb carbonate is accompanied by the continuous decomposition of several intermediate products to form PbO. The initial decomposition temperature of PbSO₄ is 750 °C, whereas that of intense decomposition is 950 °C [41]. At 800 °C, PbO-SiO₂ and 2PbO-SiO₂ begin to melt and decompose the PbO dissociated from PbO and SiO₂ before reducing to metal Pb. PbO.

Fe₂O₃ can melt and decompose PbO below 1000 °C. Metal Fe can reduce PbO to Pb solution [39]. The natural presence of PbO, as well as the oxidation, reduction, and decomposition of Pb-containing minerals into PbO, carbothermic, or CO reduction can be defined by the following formulas [42].

\[
PbO(s) + C(S) = 2Pb(l) + CO(g) \quad (3)
\]

\[
PbO(s) + CO(g) = Pb(l) + CO_2(g) \quad (4)
\]

The addition of chlorination agent, such as CaCl₂, for chlorination reduction roasting can convert PbO into PbCl₂ with low boiling point and high volatility under high-temperature chlorination condition (i.e., PbCl₂ steam can be formed and recovered) [43]. The migration and enrichment of Pb in the reduction process of Pb-bearing minerals are illustrated in Figure 6.

Figure 6. Migration and enrichment changes in the reduction of Pb-bearing minerals.
3.5. Reduction of Zn-Bearing Minerals

ZnS is reduced to Zn steam [44] under the presence of CaO and C or CO within 900–1000 °C for Zn-containing minerals. When the temperature exceeds 1167 °C, simple Fe replaces Zn in ZnS to generate Zn steam. Zn-smelting raw materials are mainly composed of Zn sulfide ores, which always contain Fe [45] during the oxidation roasting stage of Zn-smelting by fire or wet process. ZnS will oxidize and become ZnO at 750 °C and inevitably form ZnFe₂O₄ with Fe₂O₃ [46]. The reduction of ZnFe₂O₄ is not simple and involves the reduction of C and CO to ZnO. Typical reactions are defined by the following formulas.

\[
\text{ZnFe}_2\text{O}_4(s) + C(s) = \text{ZnO}(s) + 2\text{FeO}(s) + \text{CO}(g) \quad (5)
\]

\[
3\text{ZnFe}_2\text{O}_4(s) + C(s) = 3\text{ZnO}(s) + 2\text{Fe}_3\text{O}_4(s) + \text{CO}(g) \quad (6)
\]

\[
3\text{ZnFe}_2\text{O}_4(s) + \text{CO}(g) = 3\text{ZnO}(s) + 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g) \quad (7)
\]

\[
\text{ZnFe}_2\text{O}_4(s) + \text{CO}(g) = \text{ZnO}(s) + 2\text{FeO}(s) + \text{CO}_2(g) \quad (8)
\]

When ZnFe₂O₄ decomposed into Fe₃O₄ and ZnO at 650 °C, Reactions (6) or (7) will occur. The ZnO on the surface of the ZnFe₂O₄ particles will gradually increase with temperature. When the temperature is higher than 850 °C, Reactions (5) and (8) will take place. FeO will be produced and partially reduced to primary Fe. If the temperature reaches 950 °C, then ZnFe₂O₄ can be completely reduced to simple Fe.

Thermodynamic calculations show that the decomposition temperature of ZnSO₄ into ZnO and SO₂ is 1194 K, and that ZnSO₄ can also be reduced to ZnS by C or CO. When the temperature is within 700–950 °C, two reaction steps are involved in the decomposition process of Zn₂SiO₄: (1) Zn₂SiO₄ decomposes into ZnO and (2) SiO₂ and ZnO decomposes into Zn steam [23]. When heated at low temperature, ZnCO₃ can completely decompose to form ZnO [47]. The thermal decomposition of the basic Zn carbonate ([2ZnCO₃·3Zn(OH)₂]) in the atmosphere is completed in one step and accords with the stochastic nucleation mechanism. ZnO, gaseous CO₂, and H₂O can be produced by the thermal decomposition between 220 and 260 °C.

The reductants of ZnO include C, CO, CH₄, H₂, and Fe, wherein the main reductants are C and CO [39]. The natural existence of ZnO, as well as the corresponding oxidation, reduction, and decomposition from Zn-containing minerals are the main reactions of pyrometallurgical Zn smelting, comprehensive utilization of Zn-containing dust, and Zn cycle in BF ironmaking through carbothermal or CO reduction [5,42].

\[
\text{ZnO}(s) + \text{CO}(g) = \text{Zn}(g) + \text{CO}_2(g) \quad (9)
\]

\[
\text{ZnO}(s) + C(s) = \text{Zn}(g) + \text{CO}(g) \quad (10)
\]

Similar to the chlorination and reduction roasting of PbO, ZnO is converted into ZnCl₂ with low boiling point and strong volatility; high-temperature chlorination is required to form and recover ZnCl₂ steam [48]. The migration and enrichment changes of Zn during the reduction process of Zn-bearing minerals are displayed in Figure 7, whereas the migration and enrichment changes of different Pb–Zn materials in BF are shown in Figure 8.

When the Pb–Zn material enters the blast furnace from the furnace mouth, the reduction reaction of Pb and Zn will not occur because of the low temperature in the upper part of the furnace. The water that entered and the chemical crystallized water will begin to evaporate. When the temperature reaches 400–700 °C, the reduction and decomposition of ZnFe₂O₄ by C/CO will occur to form ZnO with the decrease in charge. At this time, the carbonates of Pb and Zn have been decomposed and PbSO₄ is reduced and PbO is reduced to Pb solution by C/CO. When the charge continues to decrease at approximately 700–900 °C, all reactions will intensively occur in this region. When PbSiO₃ and Zn₂SiO₄ melt and decompose at this temperature region, PbO, ZnO, SiO₂, PbSO₄, and ZnSO₄ will begin to decompose. When the temperature reaches 900–1300 °C, the above reactions
will be completed. The reduction of ZnO by C/CO to Zn steam will also occur in this temperature range. Moreover, PbS, PbO, and PbSO\(_4\) will react with one another to form Pb solution and SO\(_2\).

**Figure 7.** Migration and enrichment changes during the reduction of Zn-bearing minerals.

**Figure 8.** Reduction process of Pb and Zn materials in BF.

4. Removing Lead and Zn Impurities from the Ironmaking Process

With regard to the reduction characteristics of Pb and Zn impurities in different mineral forms in refractory Fe ore, the causes, migration trend and enrichment regularity, and phase transition and residual characteristics of the reduced products are rarely investigated. The removal of Pb and Zn impurities in the mine is not yet solved. The main problems are listed below.

Fe ore that contains Pb and Zn impurities has many kinds of iron-bearing minerals, and many types and combinations of Zn and Pb minerals exist. Zn and Pb minerals have different calcination and reduction properties.

Pb–Zn minerals are symbiotic with other minerals, and the Pb–Zn–iron intercalation relationship is complicated.
The Pb and Zn mineral particles in Fe ores are fine. Thus, satisfying the standard sorting requirements is difficult. For example, some of the particles are less than 2 µm, and crystals are variously produced.

During the high-temperature roasting of Pb and Zn minerals, both minerals can undergo multiphase change and transfer, adhere and melt with temperature or atmosphere, and easily form solid solution using gangue minerals, thereby making the separation of Pb, Zn, and Fe difficult.

In Pb–Zn mineral chemical leaching, although the effect of Pb-extracting Zn is satisfactory, the acid consumption cost and environmental pollution are substantial [49].

The separation of ultra-fine magnetic particles is greatly influenced by particle agglomeration due to different external and molecular forces, such as van der Waals, magnetic gravity, double-layered electric, hydrodynamic, and brown forces. Theoretical and empirical analyses showed that the efficiency of the magnetic separation of nanoparticles greatly decreases with the particle size [50].

4.1. Removing Pb and Zn from Fe Dust

The treatment of iron produces dust that contains Fe-associated metal residues. EAF dust (EAFD) contains metallic elements, such as Zn, Pb, Fe, Cr, and Cd [51]; hence, the elimination of such harmful impurities is crucial for industries.

In steel industries, Cl is used to remove Zn from BOF dusts. Cl roasting indicates relative selectivity, and the recovery percentage of Zn is higher than that of Fe. High levels of Zn recovery (53–99%) were obtained on wide ranges within 10–18 min. Zn recovery can also reach 93% at roasting temperatures above 650 ºC [52].

A new three-step process was developed to remove Zn and Fe from ZLR. First, Zn ferrite is converted to Zn sulfate and Fe sulfate at 450–500 ºC by roasting ZLR with ammonium sulfate. Then, ferric sulphate is analyzed to ferric oxide without Zn frit production, and Zn sulfate is analyzed at 600–650 ºC. Selectively roasted ZLR is sprayed to separate Zn and Fe using water. The ratio of ammonium sulfate/ferric sulfate is 4:1; the roasting temperature is 450 ºC; the roasting time is 1.30 h; the degradation for Zn ferrite, Zn, and Fe extraction are 81.36%, 89.61%, and 56.13%, respectively. A total of 2.04% for iron extraction, 87.03% for Zn fructite degradation, and 92.63% for Zn extraction are required under ideal experimental conditions for sulfate baking at a roasting temperature of 650 ºC and roasting time of 1 h [53].

In solvent-based treatments, dissolved dust in a eutectic solvent (DES) consists of 1 M choline chloride, 1.5 M urea, and 0.5 M ethylene glycol. A total of 38% DES (by weight) was extracted from the Zn in the dust after stirring for 48 h at 60 ºC. The resulting electrolyte was then subjected to periodic voltage measurements to characterize its electrochemical behavior. The Zn layers were discharged in large quantities with high current efficiency from the electrolyte DES by applying moderate fixed reduction potentials. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) investigations indicated that the Zn layers deposited in moderate reduction potentials possess high purity with soft and smooth morphologies as shown in Figure 9 [29].

A statistically designed experiment was performed to investigate the recovery of Zn from EAFD using diluted sulfuric acid leaching. A total of 80% Zn was extracted under the following ideal conditions: natural acid 3 N, temperature was 60 ºC, and solid-to-liquid ratio was 10%. Under experimental conditions, the filtration of Fe was approximately 45%. The leaching results, as well as the SEM/EDS and XRD results, indicated that the Zn in the EAFD easily dissolved, and the decomposition of Zn–Fe was low. The main stages of the synthesized minerals were in the forms of basanite (CaSO₄·0.5H₂O), anhydrite (CaSO₄), and anglesite (PbSO₄) [54].
Figure 9. X-ray diffraction (XRD) pattern of (a) as-received cupola dust and (b) dust residue after extraction from DES.

At present, the Waelz process is a widely used recovery technique, which includes Kawasaki, SL/RN, and SDR methods. The basic principle of the direct reduction method is to discharge ZnO and ZnFe$_2$O$_4$ as metal vapor at high temperature so that Zn can be separated from the slag solid phase [55]. The melting reduction method refers to the reduction, separation, and oxidation enrichment of ZnO or ZnFe$_2$O$_4$ in the dust during the molten state.

The other process that uses organic ligand and Zn ions is BF dust leaching in a 0.2 M-imododetic acid vinegar solution at 20 °C for 120 min with a liquid-to-solid ratio of 10 mL/g at leaching rates of 62.78% and 6.07% for Zn and Fe, respectively. The optimum conditions for leaching 65.58% Zn were extracted using a solution with NH$_4$Cl: NH$_3$·H$_2$O at 0.2: 2: 2 M and a 20:1 liquid-to-solid ratio at 40 °C for 120 min [15].

4.2. Selective Reduction of ZnFe$_2$O$_4$

High amounts of Zn-containing dust are produced in China every year. The Zn in ZnFe$_2$O$_4$ generally accounts for approximately 15% of the total Zn in raw materials, which sometimes reaches up to 50% [46]. Therefore, the comprehensive utilization of ZnFe$_2$O$_4$ is the key to control the content of Zn and Fe in the raw material that contains Fe. The reduction of ZnFe$_2$O$_4$ using carbon-reducing agent is feasible. Given the strong reduction atmosphere, ZnFe$_2$O$_4$ can be easily reduced to metal iron and Zn vapor. Although the separation of Zn and Fe is realized, the economic benefit is hardly achieved. The separation of Zn and Fe can be achieved through magnetic separation or leaching only by reducing...
Fe$_3$O$_4$ and ZnO, which greatly increases the economic benefit. Therefore, scholars are paying increasing attention to the selective reduction roasting of ZnFe$_2$O$_4$.

The results of HSC and Fact Sage software show that the selective reduction of ZnFe$_2$O$_4$ to ZnO and Fe$_3$O$_4$ [11,56,57] using CO has a high spontaneity, and high temperatures can promote the reaction. When the reduction temperature is 600, 700, 800, and 900 °C, the partial pressure ratios of CO/CO + CO$_2$ in the dominant region of Fe$_3$O$_4$ is 4.4–44.5%, 3.1–38.5%, 2.3–34.1%, and 1.7–30.7%, respectively. Therefore, the CO/CO + CO$_2$ range of the selective reduction roasting of ZnFe$_2$O$_4$ should be controlled below 30% [58].

The selective reduction of ZnFe$_2$O$_4$ can be executed in medium temperature and weak reduction atmosphere at 600 °C. The reduction roasting process has been inserted between the oxidation roasting of Zn hydrometallurgy and the low-acid leaching [51]. The residual heat of oxidation roasting (above 900 °C) has been fully utilized for reduction roasting. The selective decomposition of ZnFe$_2$O$_4$ into ZnO and Fe$_3$O$_4$ associated with precious metals (e.g., Ag, Ga, Pb, and Mn) is also reduced and enriched in the magnetic separation tailings for further recovery [59,60].

4.3. Removing Pb and Zn from Sludge

Fe in solid wastes can be extracted through direct reduction or reduction roasting before applying magnetic separation [19,20]. Nevertheless, the iron concentration should be subjected to further smelting to obtain metal. Moreover, the Pb and Zn included in the wastes are prejudicial in the iron-smelting process [21]. Iron-bearing wastes, including dust, sludge, and slag, are common secondary resources that contain abundant harmful elements, such as Fe, Zn, Pb, and C [61]. Iron waste recovery can help save primary resources and greatly contributes to recycling and zero (near) waste [37]. Separation of Fe from sludge is also necessary for the recycling of precious metals resources [58].

Several hydrological and molecular mineral processes have been developed to remove Zn from BFS. For example, the BFS were utilized to remove Zn effectively by microwave heating. Analyses on the effects of temperature on the BFS dielectric properties showed that the dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) increased within the temperature range of 400–800 °C because of the gasification of carbon (CO$_2$/CO). This finding indicates that BFS microwave heating is effective in the temperature zone of 400–800 °C. BFS can be separated into two parts. One has a Zn ratio of approximately 0.108 wt.%, whereas the other has a high Zn content of about 1.02 wt.%. Microwave tests indicated that the Zn content in the separation fraction of BFS decreased from 1.02 wt.% to less than 0.13 wt.% at a Zn removal rate of 86.24% when processed for 10 min at 800 °C. This Zn content level is acceptable for material recycling [62].

BOF sludge samples were analyzed using various methods, including XRD, chemical, particle size, SEM, and X-ray energy analyses; physical separation methods are not suitable for this type of complex material. Approximately 81% of Zn can be removed from the coarse volume fraction of the BOF sludge sample through sulfuric acid filtration at an average pH of 2. The amount of Fe extracted by leaching the acid was approximately 18%. This leaching step reduces the ratio of Zn in the carrier solids to 0.39%, which is an acceptable ratio for recycling in the main iron and steel industry process [26]. The efficacy of Zn leaching depends on the stoichiometric ratio (L/S). The efficiency of iron leaching rises by increasing L/S and maintaining the acid concentration below 0.5 M. However, this factor considerably decreased when the acid concentration and L/C exceeded 1.0 M and 50%, respectively. The acid concentration was set to 1.5 M, and the L/S is fixed at 70% to maximize the selectivity of Zn. After 10 h, approximately 50% of the Zn leaching efficiency was achieved [31]. The optimal parameters for sulfate roasting are presented as follows: reaction time of 1 h, temperature of 640 °C, and ferrite sulphate/Zn ferrite mole ratio of 1.2. The use of these conditions yielded a Zn ferrite decomposition rate of 85% and ZnSO$_4$/Zn of 91.7% [63].

Another investigation was performed to eliminate Zn from BOF. The characterization of coarse and fine parts of essential BOF sludge and the crossbreed handling of slop were
conducted for this purpose. The examination demonstrated that the Fe/Zn ratios in the fine and coarse portions were 11.60 and 132.56, respectively; the proportion of Zn reaches up to 8.5 in the latter. Zn can be recognized in the slag as zincite (ZnO) and franklinite (ZnO·Fe₂O₃); the latter’s last stage is steady and insoluble in NaOH. ZnO·Fe₂O₃ must be decomposed through a thermal process to improve the effectiveness of the Zn removal. The impact of different reagents and materials on the decay of ZnO·Fe₂O₃ was evaluated, in which NaOH exhibited the most satisfactory performance. The Zn removal exceeded 90%, thereby subsequently improving the Fe/Zn proportion [64].

Bath smelting process is an efficient process for treating waste, reducing Zn and Pb oxides [21,24], and recovering of Fe from Pb slag [33]. However, the thermodynamic calculations of Gibbs free energy changes in the reduction of Zn, Pb, and iron oxides indicate that Zn and Pb oxides are easily reduced under low CO concentration, whereas the reduction of iron oxide requires a high CO concentration. Thus, Zn and Pb are reduced to metal, whereas Fe is reduced to ferrous during the bath smelting process. A large amount of carbon is necessary to simultaneously reduce Zn, Pb, and Fe oxides, which increase the C content in the metal Fe [13]. Pig iron with 93.58% Fe was obtained under a reduction temperature of 1575 °C, a C/Fe molar ratio of 1.6, and basicity of 1.2. In direct reduction, the metallization rate reached 99.79%, and the iron recovery rate reached 99.61%. The mechanism has been investigated on the bath smelting process and the recovery of lead Zn at 1550 °C for 15 min. Moreover, 96.64% of Pb and 99.99% of Zn were volatilized under optimal C/Fe molar ratio and basicity, which were 1.8 and 1.2, respectively. The liquid iron droplets play a critical role in the reduction of Zn and Pb [33]. Figure 10 illustrates the reduction mechanism of Zn and Pb during Fe oxide reduction.

**Figure 10.** Reduction mechanism of Zn and Pb during Fe oxide reduction [34].

In the hydrolysis process, the sludge is leached using HCl under oxidation conditions [4], which is another future procedure for treating the Fe concentration of Zn furnace slag using HCl leaching-spray pyrolysis [49]. After separating the solids, that contain C and Fe from the leaching solution, the latter is passed through an anion exchanger to remove Zn and Pb. The examination of the leaching behavior showed that a pH below 1.5 and a redox potential above 650 mV are required to obtain high leaching efficiencies for Zn and Pb. Sequential extraction showed that the largest part of Zn and Pb is extracted from the acid medium, whereas an additional 16–18% is extracted from the oxidizing acid medium. The XRD analysis showed that after acid leaching, Zn partially occurs as (Zn,Fe)S and as ZnFe₂O₄ [4].

A novel process was developed to strengthen the reduction and volatilization of Pb and Zn though iron oxide reduction. The impacts of temperature, C/Fe molar ratio, holding time, and basicity on the volatilization of Pb and Zn in the Fe oxide reduction system was investigated. The intensified reduction mechanism was briefly analyzed on
the basis of the results. Leaching toxicity was used to characterize the environmental impact of smelting waste slag (SWS). This ecologically friendly method can treat hazardous hydrometallurgical residues, smelting slag, and dusts effectively [34].

Another process was proposed to reduce sediment roasting to separate Zn and Fe. Thermodynamic analysis is used to determine the predominant range of Fe$_3$O$_4$ and ZnO during the reduction roasting process of Zn ferrite. The results showed that the $V$(CO)/$V$(CO + CO$_2$) ratio is a key factor that determines the phase composition in the reduction roasting product of Zn ferrite. Within a $V$(CO)/$V$(CO + CO$_2$) ratio of 2.68–36.18%, Zn ferrite is preferentially decomposed into Fe$_3$O$_4$ and ZnO. According to the thermogravimetric analysis, the optimal conditions for the reduction roasting of Zn ferrite are determined as follows: temperature is 700–750 °C, volume fraction of CO is 6%, and $V$(CO)/$V$(CO + CO$_2$) ratio is 30%. Based on the above results, the Zn leaching residue rich in Zn ferrite was roasted, and the roasted product was leached by an acid solution. The Zn extraction rate in the Zn leaching residue reached up to 70%; the Fe extraction rate is only 18.4%. The result indicates that Zn and Fe can be separated from the Zn-leaching residue effectively [58].

4.4. Factors That Affect the Roasting Process

At present, reduction roasting is a subject of interest for treating many low-grade ores [65]. Several factors affect the roasting processes. Roasting conditions, such as temperature, duration time, and usage of carbon on iron recovery, are optimized [60,66]. Roasting time significantly affects Fe recovery [67]. The flow rate ratio of CO to CO$_2$, roasting time, and temperature significantly influences the decomposition of Zn ferrite [40]. The increase of these parameters to some extent is conducive to the selective transformation of ZnFe$_2$O$_4$. However, when these parameters exceed the optimal levels, some of the Fe$_3$O$_4$ and/or ZnFe$_2$O$_4$ will be reduced to FeO excessively. Moreover, the formation of ZnS will be promoted when the temperature is excessively high [11]. The extraction rate of Zn increases with the roasting temperature and decreases with the increase in particle size [68].

The effect of smelting temperature on the volatilization of Pb and Zn was investigated. The volatilization rate of Zn increases with temperature, and even exceeds 99% at a temperature above 1500 °C [34].

Roasting temperature and reductant addition greatly influence the conversion from goethite to magnetite; the relationship between these inversely associated variables require high coal temperatures to reduce goethite to magnetite [69,70].

5. Conclusions

The phase changes of the impurities present during ironmaking were investigated in this study to apply an appropriate removal technique and reduce their corresponding impact on the environment. The conclusions drawn on the basis of the investigation are summarized as follows.

(1) The distribution of the Pb–Zn–Fe in Fe ore is complicated, the particles are fine, and the removal of mineral phase at high temperature is difficult. Therefore, the production and occurrence of Pb and Zn impurities during the ironmaking process were analyzed.

(2) The effect of Zn and Pb impurities in the iron industry, as well as the effect on the smelting output, is prominent on the melting furnace.

(3) Analyzing phase shifts is important to separate Pb and Zn impurities in the iron industry properly. Therefore, phase transformations were examined during the smelting process.

(4) Most of the removal treatments eliminated the Pb and Zn impurities on dust or sludge, but those in the furnaces remained.

(5) After this study, the removal of Pb and Zn impurities before the ironmaking process is suggested. Therefore, this implication can serve as the basis for further research.
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**Abbreviations**

- BOF: Basic oxygen furnace
- EAF: Electric arc furnaces
- BF: Blast furnace
- BFS: Blast furnace sludge
- HM: Hectometers
- EAFD: Electric arc furnaces dust
- DES: Dust in a eutectic solvent
- QSL: Queneau–Schuhmann–Lurgi
- ISA: Isasmelt process
- SKS: A method used in smelting
- SL/RN: Stelco–Lurgi/Republic–National process
- ZLR: Zinc leaching residues

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