CIE5050-09 Additional Thesis

An Overview of the Zinc Smelting Industry in the European Union

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Abstract

Zinc smelters in the European Union are now facing a lot of problems, especially under the attack of the Covid-19. This study reviewed the situation of the zinc smelting industry in the EU, including production methods, application of raw materials, pollution control, and waste treatment. The vast majority of smelters use hydrometallurgical process to obtain high-purity zinc products. Roasting – leaching – electrowinning method is well developed, accepting a large range of raw materials and also has economic advantages. However, the problem with this method is the generation of large amounts of leaching residues. Many researchers have been worked on this and proposed many solutions. It can be improved by increasing leaching efficiency and can better recover valuable metals from the leaching residues. As for environmental pollution in the zinc smelting industry, sulphur emissions have been under well control, and both waste water and solids can be partly recycled in the process. But the storage and disposal of leaching residues are the main problems that still exist and need to be resolved.

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1. Introduction

1.1. Background

Zinc is of great importance in many industrial processes. According to the International Zinc Association (2017), more than 60% of the annual total zinc production is used for galvanizing of all forms of steel to protect it from rust and corrosion, 17% for die casting, 9% for brass and the rest is used for other manufacturing purposes, such as electrical conductors, primers and paints, and vulcanization of rubber. Hence, the smelting of zinc is an important part of industrial production nowadays.

As a natural resource, zinc can be found in the earth's crust and do not move along with environmental changes. The smelting of zinc starts with mining. Some of the zinc smelting companies own zinc ores, while some of them purchase ores from independent mines. But in many cases, both sources of ores are used. Asia, North America and Australia occupy large proportions of zinc production all around the world. Regulations and policies in different regions are different, so are the smelting methods and waste treatments.

Zinc ores are smelted for the primary processes, while recycled metal products are used for secondary production. However, in many cases, both primary and secondary raw materials are applied at the same time. It is difficult to distinguish between primary and secondary zinc production. Overall, about 30% of the total zinc consumption in EU comes from secondary zinc (Sahu et al., 2004), and about 50% of the secondary zinc is recycled (European Environment Agency, 2019). Nowadays, the secondary zinc production has been increasing all around the world (International Zinc Association, 2017).

The traditional zinc smelting processes include pyrometallurgical processes and hydrometallurgical processes. The pyrometallurgical zinc smelting process produces zinc by taking advantages of the differences in the boiling points of zinc and other components. It mainly includes three processes of roasting, reductive distillation and refining. Higher energy consumption and lower product purity are the two major drawbacks (European Environment Agency, 2019). Therefore, it has been gradually eliminated and replaced by hydrometallurgical methods.

Roasting – leaching – electrowinning (RLE) process of zinc sulphite concentrates is the most commonly used zinc production method nowadays, which produces more than 90% of zinc globally. In 2007, a total production of 2.1 million tons zinc in EU was achieved by applying hydrometallurgical routes (European Commission, 2017). This method offers more economic and environmental benefits. However, it also brings a serious problem of the production of large amounts of zinc leaching residues (Jha et al., 2001; Turan et al., 2004).

1.2. Problem Statement

With the advancement of science and technology, yield and quality of zinc products have been greatly improved. It is getting easier than ever to achieve high-purity zinc products. But at the same time, there are still many tricky issues regarding the environment and production constraints. Especially under the current attack of the Covid-19, more problems have been raised. The Tara mine in Ireland was shut down. It is reported to be the largest zinc mine in Europe, as well as one of the largest zinc mines in the world. Besides, the shortage of raw material supply, the decline of grade, the lack of confidence in the current market, and the restrict environmental regulations all pose great challenges to the industry.

Fig 1. The image of Tara mine in Treland
(Image source: https://www.boliden.com/operations/mines/boliden-tara)

The environmental problems include pollutants emission into air and water, the generation of hazardous waste, and a serious risk of soil contamination. The presence of iron and sulphides in zinc ores rises big problems. Roasting and smelting of sulfidic concentrates contributes to the emission of sulphur dioxide and cause air pollution. However, it has been effectively controlled in EU by the higher fixation of sulphur and producing sulphuric acid as well as liquid sulphur dioxide (European Commission, 2017).

Iron should be separated away from zinc during the smelting processes, to avoid cross-contamination and reduce resource loss. However, the formation of zinc ferrite during zinc smelting makes it difficult to recover Zn and Fe, because of the insoluble characteristic of zinc ferrite in the traditional leaching process (Chen & Dutrizac, 2004). As the main leaching residue, pyrometallurgical, hydrometallurgical and combined processes have all been applied to recover valuable metals from it and achieve safe disposal.

To remove iron from leaching residues, another leaching process is mostly applied. Reactions happen in hot concentrated sulphuric acid, followed by precipitation of the dissolved iron and formed large volumes of jarosite (Dutrizac & Jambor, 2000; Pappu et al., 2006), goethite (Davey & Scott, 1976; Pradel et al., 1993) or hematite (Ismael & Carvalho, 2003). Although these methods show a high leaching rate of both zinc and iron, it is difficult to remove iron and other unwanted metals from leaching solution (Filippou & Demopoulos, 1997). Disposal of such waste requires a very high containment and monitoring standard.

In this study, the situation of the zinc smelting industry in the EU is reviewed, including production methods, application of raw materials, pollution control, and waste treatment. The research questions are:

1. In the current industrial market in EU, what are the complete processes of zinc smelting, from collection and transportation of raw materials, smelting technologies to waste treatment and disposal?
2. How to achieve better resource recovery from zinc smelting industry to reduce waste?

2. Primary Zinc Production

Primary zinc is produced from natural zinc ores, mostly in the form of sulphide and a small amount of oxidized ore. The ores normally contain more than 50% zinc, as well as iron, lead, cadmium, copper, silver, arsenic and some other metals. The main raw material is sphalerite (ZnS). Smithsonite ($ZnCO_3$), hydrozincite ($3ZnO\cdot 2ZnCO_3\cdot 3H_2O$), willemite ($2ZnO\cdot SiO_2$) and hemimorphite ($4ZnO\cdot 2SiO_2\cdot 2H_2O$) are also widely used. The separation and concentration of ores include size reduction and selective physiochemical separation. Through crushing, grinding and flotation processes, the zinc concentration is achieved from ores at or near the mines. And the concentrates are transported to smelters and storage.

The first step at the smelters is always roasting, by results in oxidation of the concentrates and forms zinc oxide. Among all the roasting system, like sintering, fluidized bed and so on, the selection highly depends on the following zinc extraction methods. Sintering is often used to prepare materials for pyrometallurgical processes, and not suitable for leaching processes which require extensive grinding and retain the material finely divided. After roasting, the zinc calcine can be produced by pyro- or hydro- metallurgical processes.

2.1. Pyrometallurgical processes

Although pyrometallurgical processes have been gradually eliminated in the EU due to the relatively low purity and efficiency, it shows advantages in the co-smelting of zinc and lead. There is still one plant in Poland applying Imperial Smelting Furnaces (ISF). In this part, the ISF processes will be further discussed.

2.1.1 Sintering

By partially melting the material, a porous cake with sufficient cohesion and strength can be formed for the following carbothermic reduction process. Sintering can also reduce sulfur from the feed. Zinc sintering has been largely applied these days with more demanding controls and performance to produce high quality sinters.

2.1.2 Blast furnace

The blast furnace in the Imperial Smelting Process was developed from a standard lead smelting blast furnace, but completely sealed. The reason is that the produced zinc is recovered as vapour and the presence of oxygen in the exhaust gas leads to the formation of zinc oxide. ISF has higher operating intensity than the standard lead blast furnace, as well as the air blowing rate and coke consumption (Sinclair, 2005). Zinc produced by ISF is more expensive than electrolytic zinc, so several smelters using this technology have closed in recent years. However, it is sufficient for the co-smelting of Zn and Pb, which requires raw materials contain certain amount of both Zn and Pb. But the decline of traditional raw materials has become a problem.

One inherent advantage of ISF is that vaporization separates zinc from other components, and only volatile compounds can be collected with zinc. Though part metals are not volatile, their compounds might lead to contamination. While the major contamination is lead, which is used as collector in lead splash condenser. Since cadmium is more volatile than zinc, all the cadmium from feed ends up in the zinc product. The fuming of a large proportion cadmium during sintering will lead to the reduce of load on the refining and also in the final level. Tin compounds are volatile, and 20% from the feed can be reported to zinc products. Tin is separated from zinc by distillation refining. It may be necessary to limit the feed to keep the content within specifications.

Lead-zinc sulphide or oxide concentrate is transferred from the top of ISF, while the hot air at about 1100 °C is blown into the chamber from bottom to top by the furnace air dust. Sintering is then carried out, and the agglomerate is redacted by coke in the closed blast furnace. Zinc vapour is produced and passed through a fine spray of molten lead which dissolves the zinc and prevents reversion. Then the zinc-lead solution goes through a separating bath, zinc is evaporated, collected, and heated until about one-third has been boiled off and condensed. The condensate can be used to produce high-grade zinc (up to 99.95%) and also pure cadmium. The remaining zinc can produce less pure zinc for galvanizing, brass and so on.

2.1.3 Thermal refining

As mentioned above, zinc products by pyrometallurgical processes contains certain level of impurities, and a following refining operation is needed to meet the market demand. The major contamination involves lead and cadmium, with also a significant proportion of iron, copper, arsenic and tin. The presence of non-volatile elements might be caused by the dust carryover to the condenser. The thermal refining is usually achieved by liquation refining, chemical precipitation and distillation.

2.1.4 Other methods

The use of an electric furnace can effectively provide heat to the carbothermal reduction process. In general, this method is only economically reasonable if zinc is recovered as metal by condensation rather than re-oxidized from the furnace gas and collected as zinc oxide fume. To recover zinc by condensing, the furnace must be airtight to prevent oxygen from entering. High temperatures can be easily reached in electric furnace, providing opportunities for a wider range of slag components. However, this requires more attention for the protection method of the refractory oven. Resistance heating, induction heating as well as plasma or arc heating, are the three principle methods of electrical heating.

2.2. Hydrometallurgical processes

Most of the EU smelters apply RLE method, which is a continuous process. The overall process is shown in the figure below. The details about each step will be analysed in this part.

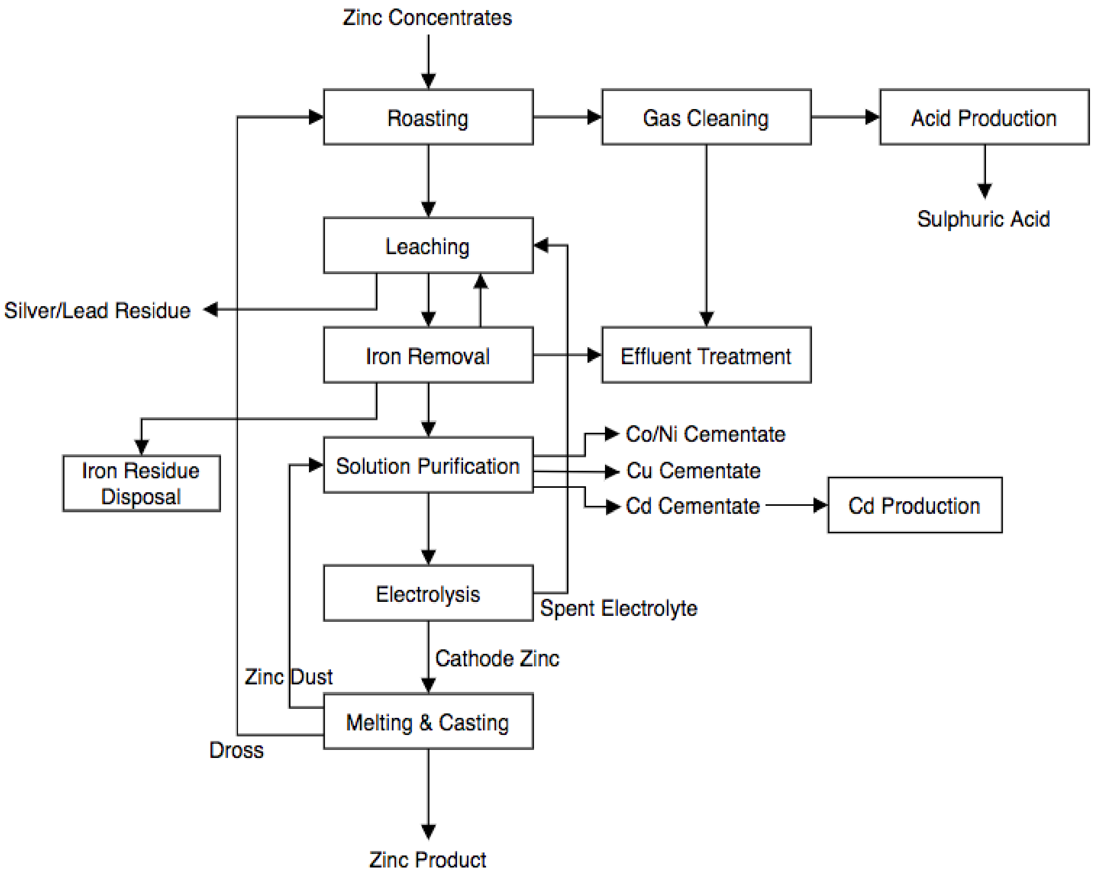

Fig 2. A general sketch of the traditional RLE process

2.2.1 Roasting

The process starts with roasting to remove sulphur by a highly exothermic oxidation reaction and convert zinc sulphide concentrate into zinc oxide (Eq.1). However, due to the presence of iron in the ores, hematite (Fe_2O_3) will also be produced and then reacts with zinc oxide to form zinc ferrite ($ZnFe_2O_4$) (Eq.2). Zinc ferrite is hardly soluble for the common acid leaching and poses a big problem. Another by-product is sulphur dioxide (Eq.3), but it can be further treated and produce sulfuric acid for sale. The gas produced during roasting contains the carryover calcine dust and certain volatile elements, including chlorine, fluorine, mercury, selenium and so on. Those impurities need to be removed before producing sulfuric acid.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \qquad \text{(Eq.1)}$$

$$Fe_2O_3 + ZnO \rightarrow ZnO{\cdot}Fe_2O_3 \qquad \text{(Eq.2)}$$

$$ZnS + O_2 \rightarrow Zn + SO_2 \qquad \text{(Eq.3)}$$

2.2.2 Leaching

1). Conventional leaching

The conventional leaching uses sulfuric acid as leaching agent (Eq.4), and usually consists of two stages, neutral leaching and strong leaching. The primary goal is to dissolve as much zinc as possible into the solution. While the leaching residues usually contain about 20% zinc, which mostly in the form of zinc ferrite. The second stage uses strong sulfuric acid to leach rest of the zinc oxide and zinc ferrite. The leaching products need to be further purified, due to the presence of other metals.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \qquad \text{(Eq.4)}$$

After electrowinning processes, the spent electrolyte usually contains about 150 g/L sulfuric acid as well as 50 g/L zinc. The variation of these numbers highly depends on the producers. However, a severe leaching condition is needed due to the presence of zinc ferrites, while a secondary leaching is also needed to extract more zinc from the primary leaching residue.

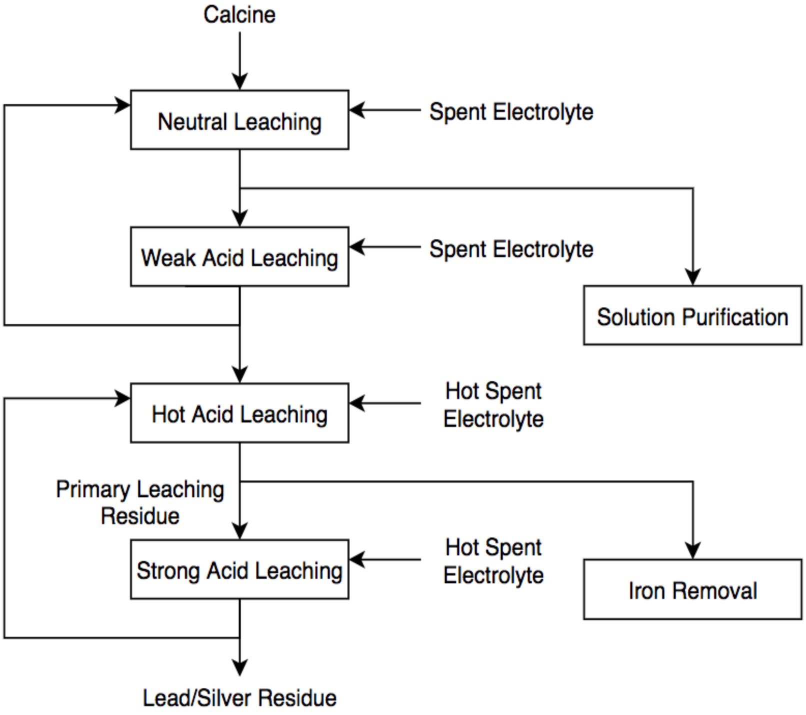

Fig 3. Flow of the conventional leaching process

a. *Primary leaching*

Iron and silica are precipitated during neutral leaching. Apart from removing those elements, this purification also helps in scavenging of other minor impurity elements, e.g., antimony, arsenic, aluminium, indium, gallium, germanium and so on. Good pH control is required during the leaching operation to achieve satisfactory electrolyte quality.

b. Secondary leaching of primary leaching residue

Hot strong sulfuric acid solutions have been proved to be effective in dissolving zinc ferrites from primary leach residue.

$$ZnO{\cdot}Fe_2O_3 + 4H_2SO_4 \rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad \text{(Eq.5)}$$

c. Iron removal

In the pressure leaching process, iron is used as a medium for the transportation of oxygen. The sulphur compound is oxidized to element sulphur, through which sulphur can be recovered. Zinc sulphide reacts with sulfuric acid under a certain oxygen pressure, zinc sulphide exists in the form of soluble zinc sulphide, and sulphur in the form of compound exists in the form of elemental sulphur (Langová & Matýsek, 2010).

Higher setting and filtration rates can be achieved by separating iron precipitate as coarse as possible. In general, to minimize nucleation requires iron to be precipitated from the low iron concentration. The growth of crystal can be promoted by adding seed material in the form of recycle precipitate.

Selective solvent extraction has also been widely researched to remove iron. Versatic acid and D2EHPA have both been considered. However, there are some issues like the relatively low loading of solvents, organics introduced might influence electrowinning, and the costs of reagents.

2). Direct leaching

As alternatives to the conventional method, direct atmospheric leaching and pressure leaching have been proposed, and proved to be applicable by few large-scale applications (Filippou, 2004). Direct atmospheric leaching is easy to operate and maintain, as the pressure is kept at the atmospheric pressure. Under this circumstance, the temperature is then increased to 100 ºC. This method can also process materials with low zinc content, and can convert sulphur into element, instead of sulphur dioxide remaining in the residue (Santos et al., 2007).

3). Leaching residues treatment

Neutral leaching residues can be treated by pyrometallurgical methods, like ISF or Waelz Kiln. Zinc, lead, silver, copper and other metals can be further recovered. All the pyrometallurgical methods show similar shortcomings of high energy requirement for maintaining reaction temperature and the large iron-bearing residue generation (Beşe et al., 2010). Besides, due to very limited availability of ISF plants and Waelz plant with SO_2 adsorption step, it is mostly treated by hydrometallurgical methods. For example, with hot acid leaching, a relatively high content of zinc can be recovered, as well as potential recovery of In, Ga, and Ge. However, volume and environmental stability of the produced iron residues are of significant concerns.

Jarosite, goethite and hematite are three mainly used processes to remove iron. Among all the methods, the most widely used one is to form jarosite ($Fe_3(SO_4)_2(OH)_6$) (Eq.5). It is simple to operate and requires low costs. Sulphate in the zinc hydrometallurgical system can be removed while maintaining the acid balance of the system. However, this method consumes alkali to remove iron, and generates a large amount of iron slag, which will cause secondary pollution. Besides, various metal ions (Cu, Zn, Co, Ni, Mn, In, Ga, Ge, Al) will also co-precipitate in this process.

$$12Fe^{2+} + 8SO_4^{2-} + 3O_2 + 4xOH + 14H_2O \rightarrow 4xFe_3(SO_4)_2(OH)_6 + 8H^+ \quad \text{(Eq.6)}$$

The formation of goethite (FeOOH) (Eq.6) generates toxic iron-rich residues of moderate volume. Reduction and oxidation are repeated, the cycle is long, the steam consumption is large, and the oxygen utilization rate is low, only about 3%.

$$2Fe^{2+} + \frac{1}{2}O_2 + 3H_2O \rightarrow 2FeOOH + 4H^+ \quad \text{(Eq.7)}$$

The advantage of the hematite (Fe_2O_3) method (Eq.7) is the production of iron-rich slag, with possibility to be used in the cement, iron industry and/or as pigment. But it is the most expensive option due to high temperature and pressure requirements. All three iron removal technologies involve additional costs and at least 1% of total zinc is lost in the residue (Graydon & Kirk, 1988).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+ \quad \text{(Eq.8)}$$

The storage of jarosite and goethite residues has become arising issue, due to the increasing environmental constrictions on the lines ponds and tailings dams. To solve this problem, it is necessary to treat the residue so that it is inert and can be landfilled. The term "inert" refers to long-term chemical stability and adherence to leaching test standards to prevent groundwater contamination. Alternatively, the residue can be processed into inert materials suitable for the construction industry, such as concrete aggregates or road base materials. Two extensively used methods of residue treatment are: 1. chemical treatment by mixing with other materials to change physical and chemical properties, 2. pyrometallurgical processing, which usually involves conversion to inert slag, with potential zinc, lead and silver recovery.

2.2.3 Solution purification

The purpose of solution purification is to minimize co-deposition and increase electrodeposition efficiency by removing irrelevant elements. In addition, impurities like Cl, F, Al, Mg and Mn, need to be removed in case they accumulate in the closed circuit. The iron concentration should also be kept at low levels, because of the potential competition of Fe2+ oxidation at the anode and Fe3+ reduction at the cathode. Impurity can be removed by precipitation in the form of hydroxides or other specific compounds. Normally, adjusting pH to remove impurities can be used as part of the solution preparation procedure.This is applicable especially during the iron removal phase, where iron is the main impurity to be removed by this method.

2.2.4 Electrolysis

Then, electrodeposition of zinc is performed in a simple open electrolytic cell. Zinc sulfate solution releases zinc ions at the cathode (Eq.9), while water decomposes and release oxygen at the anode, forming hydrogen ions and releaseing electrons (Eq.10). Because of the existence of many competing ions at the cathode, there is the possibility of discharging other metal ions into solution, especially the discharge of hydrogen ions to release hydrogen.

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad \text{(Eq.9)}$$

$$H_2O - 2e^{-} \rightarrow 2H^{+} + \frac{1}{2}O_2 \qquad \text{(Eq.10)}$$

Sulfuric acid is also produced here and then returned to the leaching phase. Acid mist can be minimized by using different coverings or preserving a foam layer. During the electrolysis process, heat is generated and dissipated in the cooling circuit. The cooling circuit is designed to optimize the water balance in the process, but it can also be another source of mists. Produced zinc is normally deposited on cathode and removed by stripping the cathode every day. For further melting, low-frequency induction furnaces are commonly applied (Sinclair, 2005). While a small part of the zinc is used for the purification step by producing zinc powder or dust.

3. Secondary Zinc Production

Secondary zinc is produced when zinc-bearing materials and zinc-bearing scraps, instead of zinc concentrates, are the raw material for zinc smelters. It usually uses oxidised and metallic products recovered from other metallurgical operations. Significant waste materials related to the secondary zinc industry include copper production dust and copper alloys, copper-lead processing slag, waste from the die-casting industry, ash from the galvanizing industry, old roofing and other laminated materials, non-ferrous metal fractions of used cars and other major steel products, electrical arc steel dust and cast iron; zinc and chemical residues from burning tires.

Secondary zinc smelters apply all kinds of zinc-containing mixed metal scraps, in the form of ingots, flashings, unqualified castings and so on (US EPA, 1995a). The recovery of zinc normally involves pre-treatment, smelting and refining. The pre-treatment of the waste includes sorting, cleaning, crushing and screening, sweating and leaching. During the sorting process, zinc dust is manually separated based on its zinc content and the following processing technology. Cleaning the scraps contributes to higher product quality and recycling efficiency. Then crushing helps to further separate zinc from other contaminants. While sweating and leaching can concentrate the zinc metal for subsequent operation. Pure zinc scrap is then melted, and impurities are trapped by flux and removed from the surface. The remaining molten zinc is heated until vaporising. The clean zinc vapour is condensed and recovered in a variety of forms (US EPA, 1995a). In general, the types of secondary raw materials decide the methods applied to recover secondary zinc (Rentz et al., 1996).

3.1. Pyrometallurgical processes

Pyrometallurgical methods are most commonly used for the treatment of smelting by-products to recover valuable metals. Reactions normally happen under high temperature and produce inert and disposal slag. It is usually carried out in Waelz furnaces, Ausmelt furnace or Imperial Smelting furnace. Secondary zinc is sometimes refined in combination with primary materials. Depending on the raw material and product specifications, various pyrometallurgical refining technologies can be applied. At a temperature of about 950 °C, zinc thermal refining can be performed by fractional distillation in a grinding tower (Rentz et al., 1996).

As the most extensively used pyrometallurgical method to treat zinc residues, the raw materials for Waelz furnace are mainly the electric arc furnace dusts and slurry from steel industry, and other Zn and Pb containing auxiliary materials. Waelz kiln process can be carried out in either one stage or two stages, while the single stage process is identical to the first stage of the two-stage process. In the first stage, the zinc plant residue is roasted to separate zinc, lead, cadmium and chloride from iron, and then bring zinc into solution by leaching. However, it consumes huge amounts of energy to maintain carbothermic reduction temperature (above 1500 K) for decomposing and reducing zinc oxide ferrite, and large amount of high iron-bearing secondary residue is generated. It usually contains around 55% zinc and 10% lead, but has a lower content of iron for steelmaking.

The system for gas treatment usually includes a settling chamber, which is used to remove the coarse dust carried by the machine and directly returned to the furnace. To cool down the hot process gases, various direct or indirect coolers are applied. Then, the Waelz oxide can be separated from the cooled gas by an electrostatic precipitator or fabric filter. The produced Waelz oxide (WO) is treated in the second stage. If no second stage applied, WO is often treated by Imperial Smelting Furnace as raw material to produce zinc and lead metal (Aota, 1997).

Most of Waelz oxides in EU are washed and then processed in the RLE plant (European Commission, 2017). Based on the counter-current flow principle, Waelz oxide can be washed with water and sodium carbonate / sodium bicarbonate / possibly sodium hydroxide by two steps or three steps. Then the metal chlorides will be precipitated by adding these chemicals, in the form of metal carbonates or hydroxides. In addition to removing chloride, fluoride, sodium and potassium can also be removed by this washing process. To treat the solution from the first washing step, the alkalis can be removed by crystallisation, and form a salt residue as well as alkali-free condensate. The residue can be directly disposed, while the condensate can be recycled. In this process, no wastewater will be produced.

3.2. Hydrometallurgical processes

Due to the complex characteristics of zinc smelting residues, it is difficult to treat with direct flotation and sulphuric acid leaching. Hot acid leaching and alkaline leaching have been applied. The hot sinters are directly mixed and washed with the acid leaching solution, and enter the leaching tank in the form of slurry. The first stage leaching is neutral leaching, and the second stage is adjusted to acid leaching under the temperature of 85 °C to 95 °C. The alkaline leaching process is mainly suitable for low-grade zinc oxide ore. The lye is mainly NaOH solution and an ammonia-carbon solution. When the zinc oxide ore is treated by the ammonia method, the zinc-ammonium complex ions formed by the reaction of zinc and ammonia are dissolved in the solution. Both methods can increase the leaching rate of zinc at relatively high temperatures.

Many researches have also been conducted on leaching with different lixiviants and different conditions (Langová et al., 2007). For example, hydrochloric acid leaching (Langová et al., 2009), microwave caustic leaching (Xia & Picklesi, 2000), D2EHPA leaching (Vahidi et al., 2009), and so on. However, large amounts of waste liquid is always generated by hydrometallurgical processes (Norgate et al., 2007).

4. Environmental Impacts

The most important environmental issues related to zinc production comes from sulphur and heavy metals present in ores. Heavy metals can cause pollution through vapour formation, through leakage into water or soil, and also exist as hazardous solid waste. Overall, the environmental control during zinc smelting includes the fixation of sulphur dioxide, controlling particulates and gases emitted to the atmosphere, reducing the concentration of hazardous matter into environmentally acceptable level, limiting the discharge of wastewater, disposing solid waste safely and also considering energy consumption.

4.1. Emission into air

During the zinc smelting process, the main pollutants discharged into the atmosphere are sulphur dioxide (SO_2), metals and dusts. The main component emitted by roasters is SO_2 gas (including the emissions from roaster starting and shutting down, as well as some unplanned or emergency situations). Over 90% sulphur from zinc ores is released during roasting, and about 93 – 97% of sulphur emitted as oxides . The sulphur dioxide emitted during the roasting process is usually recovered in situ in a sulphuric acid plant. In fact, extensive desulfurization prior to electro-thermal cooking does not produce SO_2 (US EPA, 1995a).

While dusts are produced when zinc concentrates are being roasted and transported, leaching acid mist and exhaust gas are produced from cooling, evaporation and electrolysis operations (Cleven et al., 1993). Dusts are mainly composed of lead, zinc and iron oxides, in addition to a small amount of arsenic, antimony, cadmium, chlorine oxides and sulphates. Bag filters, thermoelectric dust collectors or wet scrubbers can be used for dust removal. Bag filters are widely used and have also been considered to be the best means of particle removal from the off-gases.

Fig 4. Air emission from a zinc and lead smelting and refining complex
(Image source: https://www.cbc.ca/news/canada/british-columbia/trail-b-c-smelter-decision-may-have-ripple-effect-1.1180904)

While, another method to reduce direct emission from furnaces is to take advantage of the negative pressure. When fluxes are added into the furnace or during its cleaning process, diffuse of dust and fume will happen. But maintaining a negative pressure in the furnace can control the diffuse, since it is not very significant. As for the secondary zinc smelters, most of the them usually contains a dust collection chamber or other equipment to removal dust. The exact control systems are highly dependent on the types of secondary raw materials and also the obtained products. Overall, the efficiency of the dust removal equipment is usually very high, up to 99.9%.

4.2. Emission into water

In the area near zinc mining or smelting industry, the water bodies are more potentially to be polluted by the wastewater from the industry. The main pollutants includes lead, zinc and cadmium. Most of the pollutants exist in sediments, which poses a threat of secondary environmental pollution. To treat the wastewater generated by either hydrometallurgical or pyrometallurgical production processes, the techniques are similar. For example, to pre-treat certain wastewater streams, to apply inorganic process, biological process, and so on.

In the roasting and acid production processes, wastewater is mainly produced from the air scrubbing purification and cooling water system, in which the wastewater may contain Pb, Zn, As and other metal impurities. In the pyrometallurgical processes, the quenching of slag and cleaning of acid plant blowdown are the two main sources of wastewater . Quenching is the process to cool down hot slag rapidly before disposal by using water. This process contributes to the wastewater stream. Besides, acid wastewater is generated when water is used to clean sulphur dioxide gas.

While in hydrometallurgical processes, most of the electrolyte is recycled. Wastewater comes from a small amount of waste electrolyte, waste acid from leaching process, cooling water, flushing water and so on. Pollutants include soluble metal ions, insoluble suspended solids and grease. In many installations, various types of water can be reused or recycled during the processes, including rainwater, cooling water and treated wastewater.

Still, there are some streams of wastewater containing dissolved metals and solids, that needs to be treated before discharge. Traditionally, a hydroxide / carbonate precipitation is performed. A sulphide stage be added to ensure the metals are reduced to a lower concentration. Then, the zinc production industry discharges the wastewater after to the local (industrial) wastewater treatment plant (WWTP), not the municipal sewage treatment plant (STP). The zinc content will be reduced by treating in a WWTP, normally by adsorption. While the adsorbed fraction will then be removed by precipitation (European Commission, 2008).

However, soils and plants near the industry can be seriously polluted by heavy metals, like Pb and Cd, also Zn and Cu to a lesser extent. Soil contamination from heavy metals is quite common. The risk of heavy metal transition into crops, animals and humans can be toxic. It is shown that no agricultural activity is available in such contaminated soil, due to the less of nutrients and potential toxicity. Soil pollution caused by zinc industry is more severe than water pollution and also poses a greater threat (Kachenko & Singh, 2006; Liao et al., 2008).

4.3. Solid waste

The solid waste slag mainly comes from smelting slag. The low Zn containing slag (about 0.5 - 0.7% Zn) can be used as filler or blasting raw material, while a high Zn containing slag (over 15%) will be further processed for metal recovery. Slags produced by pyrometallurgical furnaces usually contain a relatively low level of leachable metals. Therefore, they can be used as construction material. Zin smelting plants also generate sludge when treating the processes wastewater and the blowdown of acid plant. Most of the sludge are either recycled in process, neutralized and resold, or are non-hazardous (US EPA, 1995b).

In addition, the leaching slag generated in the leaching process and the sludge generated by wastewater treatment all need to be treated. While the largest part of solids comes from leaching residues (such as goethite, jarosite or hematite). Compositions of the used zinc concentrates to a large extent determine the volumes of wastes and residues. Most residues can be recycled upstream or downstream, while is the rest needs extra treatment before safe disposal.

Zinc content of jarosite (around 2% to 5%) is normally lower than that of goethite (7% to 8%). However, both jarosite and goethite are stored in landfills and storage tanks, due to the inability of being reused or recycled. because there is no hope of disposal in the future. With only a few alternatives to be used, such as stored in caves or used for road construction. Other wastes include neutralized wastewater residues (gypsum, zinc content around 5%), filter materials and debris, and a small amount of specific wastes (including Hg, As, Cd, Pb, etc.), to be treated in a specific way. As we all know, most landfills are monitored regularly, but the actual concentration in ground and surface water is not yet available or unknown.

Solidification / Stabilization can be used to generate non-hazardous waste without recovery. The alteration of its physical and chemical properties is achieved by blending residues with some other materials, such as cement, lime, plastic and glass. Traditionally, these residues are disposed in storage facilities, such as on-site residue areas or tailings dams. However, as continuous attention has been paid to the environmental concerns, there have been increasing restrictions on the construction and regulation of zinc residue storage.

5. Results and Discussion

Zinc smelting begins with mining. The type and composition of raw materials largely determine the subsequent processing process. Primary zinc smelting generally uses zinc ore as raw material and obtains relatively pure zinc oxide after calcination. The source of raw materials for secondary zinc smelting is more extensive and contains more impurities. Generally, methods such as physical sorting and thermal melting are used to select and melt zinc. The obtained zinc melt is then used to produce pure zinc, while some impurities will be refined.

In the history of zinc smelting, the pyrometallurgical method was initially applied and also gradually eliminated. The traditional ISF method is still used to smelt lead and zinc at the same time worldwide. However, most of the smelters use the hydrometallurgical process. The energy consumption is smaller, along with the pollution to environment. In the development of hydrometallurgical zinc smelting, neutral leaching, purification and electrolysis processes were first overcome. Then, the focus of development was shifted to the comprehensive recovery of neutral leaching residue and valuable metals. Since the main factors influencing the environmental protection and resource recovery of hydrometallurgical zinc are iron leaching residue and acid leaching residue.

Due to the large amount of neutral leaching slag and high zinc content in the slag, how to recover the zinc in it has become an important issue. Most of the hydrometallurgical zinc smelters adopt jarosite method to remove iron salt. But with the stricter environmental protection requirements and the decline of high-quality resources, it no longer meets the requirements for circular economy development. There has also some researches about leaching the residue with different kind of solvents. These hydrometallurgical processes are relatively economical due to the lower capital cost and operating cost, but the purification process becomes more complex. Therefore, it still remains to be a major challenge to recover Zn and Fe from the zinc leaching residue economically and environmentally sound.

As for the secondary zinc smelting process, the development of the secondary zinc industry mainly depends on the supply of raw materials and the assurance of product quality. Technology is a key factor to ensure that secondary zinc enterprises obtain and maintain their competitive advantages. Hence, the Walze furnace is also being widely used due to its advantages of the wide range of raw materials input and simple process.

6. Conclusion

The purpose of this current study was to look into the zinc smelting in the EU, while the second aim was to investigate on how to maximum the resources utilization. Overall, practice has proved that hydrometallurgical zinc smelting has certain advantages over the pyrometallurgical method. A whole process of hydrometallurgical method includes neutral leaching, high temperature and high acid treatment of leaching residue, iron removal, purification, and electrolysis. It is more effective to produce high purity zinc, and achieve a higher recovery rate of zinc as well as other valuable metals. This method is also more environmental friendly and energy saving compared to pyrometallurgical smelting. Besides, the growing market share of secondary zinc has proven the potential of secondary zinc smelting. To further develop the secondary zinc smelting, the sources of raw materials need to be guaranteed. And more attention can be paid on the production technology and environmental protection measures.

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