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Technology Selection for Slag Zinc Fuming Process

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Abstract. Circular economy and multi-metal extraction philosophies more and more encourage smelters to reprocess their by-products most significant of which is slag for recovery of valuable metals. Zinc, for instance, can be introduced to lead and copper smelting operations through different sources, including the recycling of waste electric and electronic equipment. During the conventional smelting processes from primary resources, or even those that are particularly developed for recycling purposes, e.g., Black Copper route, the zinc is typically deported to the slag phase as zinc oxide. Recovery of zinc from slag is typically carried out via a slag zinc fuming operation, where a reductant is used to reduce zinc oxide and volatilize zinc metal. In most cases, volatilized zinc is re-oxidized to produce zinc oxide, which can then be sent to hydrometallurgical unit processes for refining. Several technologies and reactors have been developed for efficient and cost-effective fuming processes, none of which can be considered the “best” and most suitable technology for all applications and smelter conditions/slag compositions. This paper reviews the advantages and disadvantages of each of the available technologies and recommends the most suitable process for common conditions.

1. Introduction

Zinc is the fourth most produced metal after Fe, Al, and Cu with a wide range of applications in metallic products, rubber, and medicine, and is primarily produced from the smelting of Zn sulfide concentrates. The main primary Zn smelting processes were the electrolytic process (i.e., roasting, leaching, and electrowinning), imperial smelting process or ISF (i.e., the blast furnace), and retort processes including vertical, electrothermic, and horizontal. The retorting processes have disappeared, and the main production route, today, is the electrolytic process. The ISF process is used for the separation and concentration of Zn values from complex, mainly higher lead-containing zinc sulfide concentrates, the production rate of Zn to Pb is around 2:1. The use of low-cost secondary feeds makes an ISF smelter, consisting of 3 steps of concentration, final reduction, and recovery of Zn metal, competent with the electrolytic process.

Secondary resources, e.g., industrial residues and end-of-life (EoL) products, are of increasing interest because of the depletion of primary sources, ever-increasing demands for materials and especially metals, the importance of sustainable and intelligent resource utilization, and the negative impact of



waste on the environment. The main secondary feeds for Zn production are galvanizing ashes and dross and dust from scrap-based electric arc furnace (EAF) steelmaking. Galvanizing ashes are generated from the oxidation of Zn hot dip galvanizing bath, and contain 65-75% of Zn in the form of mainly oxide and some metal and Zn chloride. Galvanizing dross is a Zn-Fe alloy collected from the bath bottom, and contains 3.5% Fe and 96% Zn. The EAF dust consists of mainly oxides of Fe (25-35%) and Zn (10-35%), some volatile chlorides, and slag formers such as lime (5-20%). Other industrial residues such as diecasting scraps, Zn-rich slag from the Pb blast furnace, leach residues containing Zn ferrite, Sb slag, and slag from dirty Cu concentrates and secondary Cu recycling are also treated for recovery of Zn. Oxidized Zn ores such as silicates or carbonates, difficult to separate by flotation, can be treated by fuming too [1,2].

Zinc fuming processes are highly flexible for fuel use and the application of in-situ combustion, and can be used for recovery of Zn metal from ZnO found in low-grade ores or secondary complex materials of low or negative value. The low-value feeds can be treated to cover the operational costs of fuming and reduction. Zinc fuming is based on carbothermic reduction and selective volatilization of ZnO to Zn metal vapor (the overall reaction: $\text{ZnO} + \text{C} = \text{Zn(v)} + \text{CO(g)}$), reoxidation of vapor to fine ZnO particulate matters or fume ($\text{Zn(v)} + 0.5\text{O}_2 = \text{ZnO}$), and condensation of fume from the gas phase. Zinc oxide in the feed can be reduced to Zn(v) via the addition of C, or by the use of CO or natural gas (the reaction: $\text{Zn} + \text{CO(g)} = \text{Zn(v)} + \text{CO}_2\text{(g)}$). Direct condensation of Zn metal from vapor is favorable in high-grade materials processing, eliminating the need for subsequent reduction of ZnO to Zn metal. For the contaminated low-grade feeds and high levels of dross-forming compounds such as dust and halides, high-grade ZnO fume containing submicron-size particles will be produced followed by a reduction stage. The fume often contains Pb, Ag, and Cd and minor impurities such as As and Ge, and an additional refining stage is required [1]. The fume is either cooled and filtered or scrubbed from the gas phase for recovery of ZnO. The ZnO fume can be also used as feed to an ISF or an electrolytic Zn plant [3]. Oxidation of Zn(v) is an exothermic reaction and the generated heat can be used for the reduction of ZnO, which is an endothermic reaction, or recovered as steam.

2. Zinc fuming technologies

Fuming processes can be categorized into three major classes: (a) direct fuming from solid/gas reactions (Waelz kiln and shaft furnace processes), (b) fuming from a molten slag (the conventional slag fuming furnace, the submerged lance slag fuming, O₂-enriched air side blown smelting, and submerged plasma fuming), and (c) fuming from particles suspended in a gas phase (Horsehead Flame Reactor and Contop Cyclone Reactor). The most important operational features and advantages and disadvantages of these technologies are summarized below.

2.1. Waelz kiln

The Waelz Kiln is the most often used process for Zn recovery from secondary materials and industrial residues. It is a long rotary kiln similar to cement or lime kiln, patented in Canada in 1909 but developed in Germany with the first real-scale production in 1925 [1].

The charge (ZnO-containing residues, a low volatile anthracitic coal or coke fines, and flux) is dried and preheated to the reaction temperature of 1150 °C in the first section of the kiln. Flux like lime or limestone is added to increase the melting temperature of the generated slag. The process can operate well at the (CaO+MgO)/(SiO₂+FeO) ratios of 0.1-0.2 or >1.3, either the acidic or basic slags, respectively [4]. The feed moves slowly in a countercurrent flow against the heated air. In addition to ZnO→Zn(v) reduction, FeO→Fe(v) reduction also occurs, where Fe helps in reducing ZnO and other base metal oxides (e.g., $\text{Fe} + \text{ZnO} = \text{Zn(v)} + \text{FeO}$). Zinc vapor is directed toward the gas space of the freeboard where it is oxidized into ZnO fume by the excess oxygen in the gas stream above the tumbling bed. Other metals with high vapor pressures such as Pb, In (80%), Tl (80%), and Cd (97%) are also volatilized and reported to the fume. Iron and Cu form the FeS-Cu₂S matte phase containing Ag, Sb, and As. Germanium partly (33%) reports to the fume and partly stays in the residual slag [1].

2.1.1. Advantages and disadvantages. Waelz process requires a simple installation, and a wide range of feed materials can be treated via process modification (e.g., temperature, residence time, reductant quantity). However, the formation of a molten phase should be minimized for the charge could maintain an open structure, a dry and tumbling condition, and good kinetics of solid-gas reactions. The formation of eutectic compositions at 1180 °C, especially in the presence of Fe, can lead to accretion on the kiln walls avoiding gas and solid proper movements which requires shutdown and accretion removal. The feed Pb content higher than 5% should be also avoided. Lead-containing phases accumulate in the bottom of the kiln and attack the refractory. Particularly in the presence of Cu, they form low melting temperature matte phase eutectics. Excess coke (as large as 40% of the charge in comparison to the normal addition of 25%) can be used as a conditioning agent to absorb molten phases, decreasing the strengths of accretions, or reducing the accretions and enabling their removal from the furnace wall.

The particle size distribution of the feed must be also carefully evaluated to avoid large amounts of feed carryover to the off-gas system and excessive dusting. This consequently lowers ZnO concentration in fume which at the same time may negatively affect the oxidation reactions of the fumes and requires a large volume of the furnace. It is needed to loosely agglomerate the feed in a drum conditioner [1, 5]. It was reported that pellets allow fast reduction and high metallization rates due to high and uniform porous structure [5]. The particle size distribution of coke is also very important (2-6 mm with at least 60% above 2 mm). Too coarse particles remain unreactive while too fine coke will burn excessively and increase the extent of melting.

The oxidation reaction of $Zn(v) \rightarrow ZnO$ is very exothermic [5], and heat energy is partly recovered to the bed for compensation for heat consumed by the endothermic reaction of $ZnO \rightarrow Zn(v)$ reduction. The overall thermal efficiency of the process is relatively low per tonne of Zn recovered due to various heat losses [1]. The energy consumption is relatively low but the burner needs to run. Modern furnaces require <200 kg of coke per 1 ton of EAF dust [5].

The refractory lifetime was reported to be an issue, which is about 12 months. About 67% replacement is necessary requiring a shut-down time of about 4 weeks [1]. For Waelz kilns designed for the treatment of Zn-residues, it has been reported that the refractory lining in the feed end area (subject to the abrasive effect of the tumbling material) of the kiln may last between 2 and 2½ years, while other types of refractory material used in the most aggressive zones (e.g., main reduction zone) within the kiln may need replacement between 2½ and 3 months [6]. The most important causes behind the wear and failure of the refractory lining are the deformation of the kiln shell, abrasive properties of the load, chemical aggressiveness of the load, and thermal shocks due to sudden changes in process operating conditions. Failure of the refractory lining may also be caused by the penetration of metallic fumes within the bricks [7]. However, it is not completely clear to what extent is this problem avoidable via the substitution of bricks for a castable refractory.

Waelz slags often conform to leaching requirements from the environmental point of view. Calcium oxide reduces the leachability of heavy metals in slag, reducing the environmental impact.

Overheating could be identified as a potential problem although it may be controlled by allowing excess air ingress [8].

2.2. Conventional slag fuming furnace

The original test work behind the conventional slag fuming furnace technology was developed by the Sulphide Corporation at Cockle Creek (Australia) between 1906 and 1920 [9]. The furnace was developed for Zn recovery from Pb blast furnace slags containing 10-18 wt% Zn and other Zn-rich secondary materials. The first large-scale conventional slag fuming furnace was installed by the Anaconda smelter in Montana (USA) in 1925 [1, 9, 10]. The furnace has been used since then at major lead smelters. Other operations that use this furnace are Boliden's Ronnskar smelter (Sweden), the Filn Flon smelter of Hudson Bay Mining and Smelting Company (Canada), Teck's Pb and Zn metallurgical complex in Trail (Canada), Nyrstar's Port Pirie smelter (Australia), and the Non-ferrous Metals Smelter at Plovdiv (Bulgaria). Since 2018, a fuming furnace has been installed in Guangxi raw antimony-rich Polytron Technologies Inc. (China) to smelt and fume the slag from the Sb blast furnace [2].

The Zn recovery is maximum at the residual Zn level in slag between 2.5 and 3 wt%, below this level, there will be a large drop in furnace capacity. In the case of charging hot slag to the furnace, e.g., from an electric furnace connected to Kivcet Pb processing, the Zn residue in slag can be as low as 2 wt% [11]. Common to the majority of fuming technologies, the furnace should not exceed a limit of Zn recovery (often recommended at 1 wt% Zn in the final slag) to prevent the generation of metallic Fe. The heat extracted from cooling the furnace (40 GWh/year) was recovered at the Boliden plant and used for central heating in the neighbourhood [12].

2.2.1. Advantages and disadvantages. This process is only economic for high concentrations of Zn in slag (a minimum of 16% of Zn in feed is needed). Agglomeration or screening of charged slag should be done to have the proper feed size distribution and prevent it from going to the off-gas system. Too coarse particle size distribution reduces the production capacity due to a slow melting rate [2]. Low ash content coals are preferred due to the dilution effect of ash on the slag Zn content, reducing Zn recovery [1]. If pulverized coal is selected as the source of heat and reduction, then considerable operating and safety issues must be taken into account. Industrial facilities often pulverize coal for their own consumption, and although different pulverizing technologies may be available, all of them require precise controls of free oxygen in the milling and off-gas systems to avoid hazardous conditions that could result in severe explosions. Furthermore, coal pulverization plants are designed with standard inert-gas (usually nitrogen) blanketing systems for additional explosion risk mitigation, which may significantly add to the overall operating cost. Despite a proper design, the risk of explosions is not completely mitigated in this type of facility.

The Zn recovery rates of 85%-90% and 88%-95% were reported at Teck's Trail operation (Canada), and in Guangxi (China), respectively [1, 2].

The slag freezing line on the furnace's inner surface provides extra protection against the aggressiveness, turbulence, and abrasive nature of the slag bath, increasing the lifetime of water-cooled jackets over 10 years and even up to 20 years [1, 12]. However, additional fuel and costs are required for the associated heat loss for forming the slag freeze line.

The best capacity has been reported for batch operation. Operation in continuous mode is not common and often lower capacities were experienced however this can be the subject of further study case by case from one smelter to another. Overall plant availability has been reported at 88% [1].

Conventional fuming furnaces are generally regarded as having relatively high maintenance requirements for tapping blocks, cooling jackets, and waste heat boilers. Tapping blocks are subject to high-temperature stress and the corrosive nature of the slag, which is plant-specific. The failure of cooling jackets has been reported as a common problem in conventional slag fuming furnaces which has been attributed in part to sudden temperature changes associated with the loss of the protective slag layer [13]. Regular inspection and maintenance of water jackets are mandatory to guarantee the furnace's integrity. Continuous cleaning of the boiler tubes and walls is needed because of sticky accretions on the ducts which reduce the boiler's heat extraction efficiency. Soot is often extensively blown away using saturated steam [1].

2.3. Submerged lance slag fuming

The submerged lance slag fuming technology can be used for treating the leach residues from an electrolytic Zn plant, low-grade complex ores or concentrates, and any difficult-to-process feeds [14]. The process principles were developed by Commonwealth Scientific and Industrial Research Organization (Australia). The process was originally applied to Sn fuming in 1978. Later on, it was further developed to Zn fuming by Ausmelt (Whyalla, Australia); the first commercialization was performed by Onsan Smelter of Korea Zinc (South Korea). Mitsui at the Hachinohe ISF smelter (Japan) and Young Poong Corp. (Sukpo, South Korea) also use this technology for Zn fuming. The process was later applied to Pb and Cu smelting by Mount Isa Mines (i.e., Isasmelt process) [1].

Solid feed (Zn-containing materials, coal, and fluxes) is added via a feed port in the roof of the furnace. Fuel (gas, oil, or pulverized coal) is injected with O₂-enriched air through a vertical submerged

lance into a molten slag bath in a cylindrical vessel. Bath is highly turbulent with high reaction rates and mass transfer rates. The chemical reactions are similar to the conventional slag fuming furnace and fuming rates are in a similar order. The final slag contains < 3% Zn and <1% Pb [1].

A slag freeze line protects the refractory outer layer of the tube, forming under the cooling effect of air injection [1].

The gas handling and fume collection systems are very similar to the conventional slag fuming furnace. The cooling system consists of a waste heat boiler, a water tube section, and humidification using water sprays. For small plants, only cooling by humidification can be used due to the high cost of a waste heat boiler. Using electrostatic precipitators allow for fume collection at temperatures as high as 400-500 °C, higher than the bag filter, minimizing the required cooling degree [1]. The heat from the secondary post-combustion can be recovered to generate electricity [15, 16].

2.3.1. Advantages and disadvantages. It is a flexible and rather simple technology and can be easily integrated into existing flowsheets. It can also incorporate both solid and liquid feeds and can be applied to a wide range of feed materials from primary resources to secondary Zn leach residues, Zn slags, EAF dust, and complex EoL products. The lowest-cost available fuel sources can be used and difficult-to-source and high-cost cokes are not required. High feed flexibility leads to optimum productivity and economic performance [15, 16]. It was reported that the partial pressure of O₂ can be precisely controlled to achieve the desired bath chemistry and products [15, 17]. Volatile species can be recovered in the fume, valuable non-volatiles in metal, and low-value non-volatiles in slag [1].

Early recoveries at Korea Zinc QSL's slag fumers in series, which at the time were treating granulated slag combined with other Zn residues, were reported at 61% and 55% for the first and second fuming stages, respectively, which corresponds to a global recovery of 83% [18]. Korea Zinc also reported a zinc recovery of 49% for the first stage fuming furnace, which was increased to 64% by using 100% powdered coal [19]. In general, a typical zinc recovery range is given from 85% to 90% for the Korea Zinc fuming plant [20]. A more recent test developed at Onsan with EAF dust resulted in a zinc recovery of 90% [21].

The refractory lifetime is the primary concern in the application of this process and often relining is required. For the submerged lance vessel, the high turbulent bath reduces the life of refractory to below 3 months in some cases, leading to plant availability of less than 80% [1, 18]. The refractory lining of the furnace wall is not possible and water-cooling jackets are mandatory. Using water jackets alone limits the operating temperature, which can barely exceed the slag liquidus temperature. This limitation can be overcome if the refractory lining is used and the temperature is not above the bricks' degradation temperature. Using chrome magnesite fused grain re-bonded bricks, the resistance against iron silica slags, and the lifetime has increased to over 2 years. If the refractory lining is backed up with water-cooling jackets, the lifetime would further increase. Using water jackets, the formation of metallic Fe in fume should be avoided because Fe fuming leads to accretion formation and furnace blockage. Consequently, the residual slag's Zn content will be more than 2%. For refractory lined vessels, Zn content as low as 1% and below can be obtained in the final slag but even with having a refractory lining, Fe fuming should be avoided over a long period of time. Due to the exothermic reaction between Zn and CO(g) in the upper part of the reactor (secondary combustion), the gas reaches a high temperature affecting negatively the refractory lining. Therefore, a water-cooled refractory lining with a slag freeze line has been proposed as a solution, also assisting in cooling the gas and separation of fume [17, 19]. Hachinohe claimed to have achieved a 2-year lifetime for one single campaign [22].

The lance consumption rate is high, and lance design to reach stable operation and long lifetime plays a key role in the process [18, 23].

It was reported that the capital and operational costs are low. Low capital cost is due to simple furnace construction and peripheral system arrangement. Operational cost is low due to low energy consumption and low manpower needs [1, 15, 18]. Having a very turbulent bath, the slag can splash into the gas outlet causing accretion formation and blockages [1, 18]. Therefore, the reactor needs to be tall (height/diameter ~ 3.0). The lance needs to be completely withdrawn from the bath, thus, a high plant

structure is needed. Hughes et al. [15] reported that in comparison to conventional slag fuming furnaces, the furnace gas volume can be significantly reduced due to high O₂ enrichment and having a more gas-tight system limiting the air ingress. They did not explain why submerged lance slag fuming is tighter than any other stationary slag fuming furnace.

The process can be operated in batch or continuous mode depending on the plant preference and furnace availability [15, 16]. If multiple vessels are used, the process can be operated in a continuous mode where the first reactor is used for sulfur removal (if the feed contains sulfur) and Zn and Pb fuming, followed by the second step where Zn fuming is completed and low Zn in residual slag is obtained. It is favorable to operate in a continuous mode rather than batch mode. The major plant cost can be reduced because the need for charge slag holding facilities and larger gas handling volume capacity is decreased. In batch mode operation, the fuming rate for the submerged lance slag bath furnace is similar to the average rate in the conventional fuming furnace in batch mode. This leads to a decrease in Zn content of 6 %/h between 17 and 3 % Zn content. For slag containing 2% Zn, the continuous fuming rate leads to 4 %/h decline in Zn content [1].

The environmental and workplace impact is minimal. Fugitive emissions are low because of well-sealed and stationary reactors. The slag is benign and can be used in the construction industry [15, 16]. However, this can be different depending on each country's policy (*private communication*).

An additional design problem, that affected the operation at Hachinohe, was the generation of sulfuric acid (from SO₂ and H₂O) in the off-gas system which resulted in the corrosion of the equipment parts. An adequate off-gas temperature must be maintained in order to avoid the formation of acid [22].

2.4. Oxygen-enriched air side blown technology

The O₂-enriched air side blown smelting was developed based on the Vanyukov process by the former Soviet Union, and has been used for Cu and Ni smelting since 1976. The re-innovation and improvement were performed by CINF Engineering Co. (Changsha, China), and in 2002, it was used for the reduction of hot high Pb slag. The commissioning of the furnace for treating the Pb-bearing polymetallic materials was performed in 2014 [24, 25].

The hearth and body of the furnace are made of refractory materials and Cu and steel water cooling jackets, respectively. Several tuyeres embedded in the copper water jacket provide O₂-enriched air into the slag bath. The feed enters the furnace from the upper port and reacts with the O₂-enriched air.

The process is performed continuously in three O₂-rich side-blown furnaces linked by chutes: oxidation-melting-desulfurization (to produce Pb-rich slag), reduction melting (to produce crude Pb and reduction slag), and slag fuming (to produce ZnO). Fuming is carried out in the last furnace of the three furnaces (i.e., only one furnace is required for fuming). During slag fuming, pulverized coal is added through the nozzle to reduce ZnO into Zn(v), which is further oxidized in the tertiary tuyere of the fuming furnace to form ZnO fume. The heat energy of the high-temperature fume is recovered by the waste heat boiler followed by the fume desulfurization and dust collection. The off-gas is emitted after desulfurization. Figure 1 depicts a schematic of an O₂-rich side-blown furnace [24, 25].

Lead slag with 15-17% Zn and 1.5-2.5% Pb was treated together with pulverized coal in the fuming smelting furnace. The residue slag contained <1% and <0.1% Zn and Pb, respectively, and was water-quenched after tapping (to be dumped or sold). The Zn recovery rate was reported to be more than 92%.

The furnace's lifetime was reported to be up to 5 years. The main equipment, process parameters, and main techno-economic indicators of the process are provided by Zhang et al., 2020 [25].

2.5. High temperature submerged plasma fuming

High temperature submerged plasma fuming is an intensified version of conventional slag fuming processes. The feed contains Zn-containing residues (e.g., Pb blast furnace slag, secondary Cu smelting slag, EAF dust), petcoke, and fluxes. For enhancing the fuming rate, a bath temperature as high as 1350 °C is required, and the thermal energy is provided via thermal plasma and chemical reactions. Inside electric plasma torches, the cold blast air is transformed into a high enthalpy plasma gas which together with fuel is injected into the slag bath to provide heat and slag agitation for mixing. Consequently, the

ZnO reduction and volatilization occur followed by the afterburning of Zn(v) to ZnO fume, and part of the heat is recycled back to slag increasing the energy efficiency. Slag phase, matte and ZnO fume are the products. The off-gas is treated in an electrostatic precipitator. Figure 2 illustrates a schematic of the submerged plasma fuming process [26, 27].

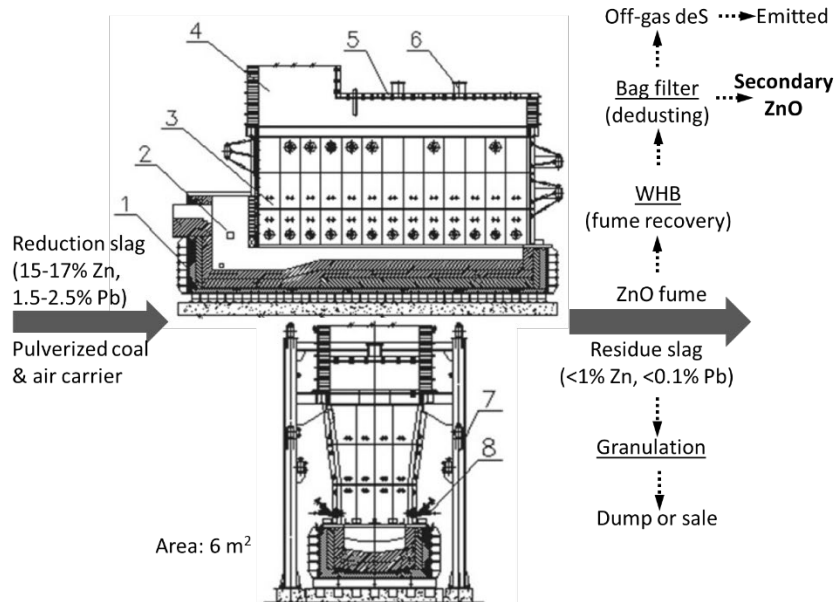


Figure 1. Oxygen-enriched air side blown furnace (adapted from [24, 25]). 1: hearth, 2: siphon chamber, 3: furnace body, 4: uptake, 5: furnace top, 6: charging opening, 7: steel frame, and 8: tuyere.

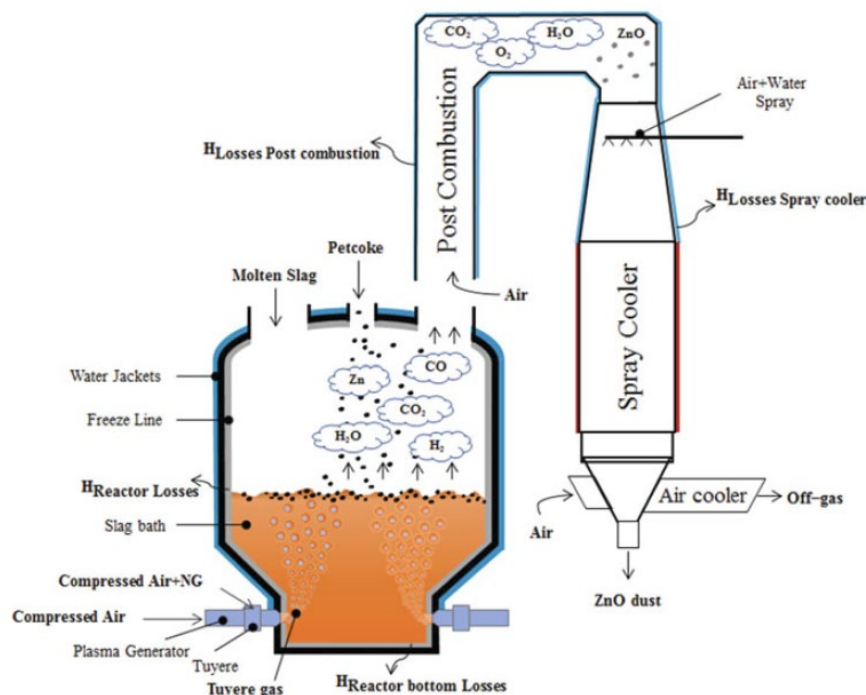


Figure 2. Schematic of high temperature submerged plasma fuming process (from [26]).

High temperature does not favor the furnace lining which could be overcome by forming water-cooled freeze linings on the smelter reactors, the stability of which can be controlled via the bath composition. Slag liquidus temperature should be controlled carefully to form a stable freeze lining to decrease the heat flux via the reactor walls and increase energy efficiency [26, 27].

Plasma-driven fuming processes are emerging as environmentally friendly processes in comparison to conventional top-blown or side-blown slag fuming furnaces. The process is especially convenient in conditions where non-hydrocarbon source electricity such as hydrogen electricity is accessible, and petcoke replaces combustion gases, reducing the net C footprint of the process [26].

The first industrial plant was built for ERAS by ScanArc [28] in Hoyanger (Norway) in 2005. Metallo Belgium also operates this furnace for recycling ZnO-containing residues [26].

2.6. High intensity fuming processes

In high intensity fuming processes, Zn-containing charges are introduced into a high-temperature reducing flame. Zinc oxide is reduced to Zn(v) reporting to the gas phase and slag suspended in the gas phase is separated in a settler or a cyclone. Zinc vapor is oxidized into ZnO fume via injection of secondary air, and the fume is filtered. The principles of carbothermic reduction and oxidation-fuming are applied to these processes like the others. The difference is that the reduction is carried out at higher temperatures, having high reaction rates, and a small equipment volume is required. High O₂ enrichment is used to reduce the gas volume and size of the gas handling system.

2.6.1. Horsehead flame reactor

The Horsehead flame reactor was developed by Horsehead Resource Development Company Inc. (USA) for processing dust containing 10-35% Zn from scrap-based EAF. The goal was to develop technology at a small scale that can be easily installed at steel plant premises. The slag can be recycled back to the steel process and ZnO fume sold to the Zn smelter. The reductant was initially coal, and later, natural gas was also introduced leading to higher combustion rates and higher temperatures enabling the generation of molten slags without the need for fluxing. There is a possibility of sending gas from the slag separation vessel to a Zn condenser directly without forming ZnO fume. However, conditions for Zn condensation are difficult. The operational costs are largely higher than a conventional slag fuming furnace (e.g., higher energy consumption, 42 GJ of natural gas, and a need for O₂ addition, 2.5 tonne per tonne of Zn recovered) but the capital costs are lower because the plant is smaller (it was not clear with respect to footprint, equipment, or both) [1].

2.6.2. Cyclone flame reactor

The cyclone flame reactor was developed in Russia in the 1950s for flash smelting of Cu concentrates to disperse fine concentrates into suspension at the top of a smelting shaft. With the transition from air to O₂, the reactions could occur in the cyclone and there was no need for the shaft. It can treat Zn concentrates, Zn-containing residues, and secondary materials [29]. A pilot furnace was applied to fume Pb blast furnace slag at the Port Pirie smelter (Australia) [30]. It has been commercially applied as a retrofit to Cu reverberatory furnaces. The vessel walls reach very high temperatures and there is a need for an evaporative cooling system and steam rather than circulatory water cooling as used in standard water jackets. The generality of the process is similar to the flame reactor and other fuming processes but with a different initial combustion device. The use of O₂ for combustion reduces the size of the gas handling system and the large capital cost of the plant [1].

2.6.3. Shaft furnace

A shaft furnace or blast furnace has the same principles as the ISF furnace except that air or O₂ is injected near the top of the furnace to complete combustion and form ZnO fumes. It is practical for lower-grade residues and especially Zn ferrites. The charge contains the residues mixed with fluxes and coal or coke fines pelletized or briquetted with good strength and size to maintain the open structure in the shaft and good gas permeability similar to Fe blast furnace. Air is blown in the bath through tuyeres like ISF but

some amount of fuel like oil or natural gas is also injected as a coke-saving measure. Secondary air is injected at the furnace top and the generated heat of the secondary combustion is transferred to the descending charge increasing the fuel efficiency. However, ZnO sticks to the charge and is not fully recovered, leading to Zn circulation in the furnace needing extra C and leading to low fuel efficiency [1].

This is not a very favorable process. The ZnO accretion in the shaft walls requires regular shutdown for cleaning. Therefore, the shaft furnaces are small in size in a series and on a campaign basis. A variation of the process was developed by the Mitsui Mining and Smelting Company at the Miike Smelter (Japan) for treating Zn leach residues but then changed to processing EAF dust. Westinghouse has a similar process at Hamilton, Ontario (Canada) but uses a plasma torch in the base of the shaft to supply heat, similar to the SKF plasma dust processing, producing ZnO rather than condensing Zn metal [31].

3. Technology selection trade-off

The conventional and rather emerging processes for Zn fuming from secondary resources are listed in Table 1 along with important technological features. Among the above-listed technologies, Cyclone flame and Horsehead flame reactors are not included in the table because they were not commercialized. As was explained in Section 2, several technologies and reactors have been developed for Zn fuming process, each one of which shows certain advantages and disadvantages, which are compared below. It should be indicated that the volume of information available for some of the processes such as plasma fuming slag and O₂-enriched air side blown reactor is rather little making a comparison with the conventional slag fuming processes somehow challenging.

Waelz kiln and shaft furnace are not flexible in terms of feed composition, size, and morphology. On the contrary, the conventional slag fuming furnace, submerged lance slag fuming, and O₂-enriched air side blown can process a wide variety of charged materials.

In terms of the Zn recovery rate, almost all the processes show a Zn recovery rate between 85 and 95%. The reported Zn recovery for the O₂-enriched air side blown technology is the highest among all the processes. The Zn recovery rate of plasma slag fuming was not explicitly reported in the literature.

Regarding maintenance and repair requirements, the conventional slag fuming furnace has the highest furnace campaign life of 10-20 years. The O₂-enriched air-side blown fuming comes to second place with a lining lifetime of around 5 years. Submerged lance slag fuming and Waelz kiln have on average 2 years of lining lifetime. So far, based on the available information, it seems that the submerged lance slag fuming has the lowest plant availability in comparison to Waelz kiln, conventional slag fuming furnace, and O₂-enriched air side blown reactor. The lining lifetime of the plasma fuming process controlled by the slag freeze lining was not reported however failure of water-cooling jackets could be a concern because of the loss of slag freeze lining and rapid variations in temperature.

It was reported that the capital cost of recent technologies (top submerged lance and side blown) is low in comparison to more conventional slag fuming processes. However, this can be subject to further investigation. They also have a better energy efficiency which together with their eco-friendly nature play an important role these days in technology selection because they show lower C and environmental footprint.

Considerable numbers of Waelz kiln and conventional slag fuming furnaces have been installed worldwide and are currently in operation (the exact number is not known). For EAF dust, for example, about 80% of the global capacity is treated in Waelz kilns. Also, China has numerous conventional slag fumers. However, it is clear that the top submerged lance furnace with 4 precedents has made a good place among them.

| | Waelz kiln | Conventional slag fuming furnace | Submerged lance slag fuming | O ₂ -enriched air side blown fuming | Shaft furnace | Submerged plasma fuming |
|---------------------------------|---|--|--|--|--|--|
| Feed requirements | Pb<5%, Fe control, dry, Coke (2-6 mm, >60% > 2mm), agglomerate | Solid or liquid, high Zn in slag (≥16%), low ash coal, size screening needed for solids, agglomeration | Solid, liquid, high- or low-grade, EoL products, lowest-cost available fuel (gas, oil, pulverized coal) | No need for drying, powder, lump, pulverized coal | Low-grade; coal or coke fine (+ oil or natural gas), pellets, briquettes | Zn residues, petcoke, pellets |
| Zn recovery | Up to 92%, 88-95%, low for low Zn-slag | 85-90%, 88-95% | 85-90%, 90% | >92% | 80-85% | Up to 98% |
| Maintenance & repair | Refractory-life time: 12 months, feed end area: 2-2 1/2 yrs, most aggressive zone: 2 1/2 - 3 months | Water-cooled jackets + slag freeze line: 10-20 yrs | Low lance lifetime, Refractory lining < 3 months, With chrome magnesite refractory~ 2yrs, Refractory+cooling jackets>2 yrs, refractory+water cooling jackets+slag freeze line~2yrs | Refractory+ Cu & steel water jackets: lifetime up to 5 years | Regular shutdown due to ZnO accretion on walls | Water cooling + slag freeze line (crucial and to be controlled via slag chemistry) |
| Availability | 92% | 88% | <80% | | | |
| Capital cost | | | To be investigated | Low | | |
| Operational cost | | High | To be investigated | | | |
| Energy consumption | ? | High | Low | Low | | |
| Energy efficiency | ? | Low | | | Low | High |
| Batch mode | | the best capacity | x | | | |
| Continuous mode | x | Low capacity (not common) | x (preferable) | x | | |
| Environment impact | Low | | Low | Low | | Low |
| Precedent | HorseHead Corp., Nexa Resources; Global Steel Dust Gulf; Befesa Zinc Aser SA; Befesa Zinc Duisburg GmbH; Befesa Zinc Freiberg GmbH; Befesa Zinc Korea, Ltd.; Befesa Silvermet SL; Recytech SA; Taiwan Steel Union Co., and many others globally | Anaconda, Boliden's Ronnskar, Flin Flon, Teck, Nyrstar, Plovdiv, Polytron Technol. Inc. | Ausmelt, Korea Zinc, Mitsui, Young Poong Corp. | Chenzou, China | Mitsui Min. & Smel., Westinghouse | ERAS, Umicore, Metallo |

4. Conclusions

There are six zinc fuming technologies available on an industrial scale for the recovery of zinc from secondary resources, Waelz kiln, conventional slag fuming furnace, top submerged lance slag bath, oxygen-enriched air side blown reactor, shaft furnace, and high-temperature plasma slag fuming. These technologies can treat complex zinc secondary resources such as lead blast furnace slag, secondary copper slag, electric arc furnace dust, and zinc leach residues. In the current paper, we reviewed the advantages and disadvantages of each of these technologies and provided an alternative solution to the technological challenges proposed in the literature. This study can help in the selection of an appropriate

zinc fuming process based on smelter conditions and feed availability. For common conditions, considering feed flexibility, capital cost, energy efficiency, environmental and workplace impact, and the number of previous installments, the submerged lance slag fuming can be considered a promising technology for zinc recovery from complex to process secondary residues and EoL products. The main inconvenience of this process is the high maintenance and repair and plant availability. The oxygen-enriched air-side blown fuming reactor possesses all of the advantages of top submerged lance plus a higher Zn recovery rate, as well as low maintenance and repair. However, the extent of available detailed information on this process and other rather new processes such as plasma fuming is comparatively scarce, and further information could help in better evaluating the technological pros and cons of the emerging processes.

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