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Critical review on secondary zinc resources and their recycling technologies

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A R T I C L E I N F O

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A B S T R A C T

In a race to save the earth of its rapidly depleting natural resources, the use of Secondary Raw Materials (SMRs) as alternative replacements in several processes is currently intensively pursued. The valorization of SMRs is consistent with the sustainable circular economy, where resource efficiency is maximized for the benefit of both the economy and green environment. In line with this mandate, this article focuses on investigating recent studies on secondary zinc (Zn) resources and describing state-of-art Zn recycling technologies. Globally, some of the main Zn-containing secondary raw materials are mine/concentrator/smelter tailings, wastes, slags, scraps, dust, etc.

Although the pyrometallurgical process has been dominant in the secondary metal recycling processes, there has been growing interest and pressure to achieve sustainable and greener recycling methods to remediate the environmental problems caused by emissions of toxic heavy metals and sulfur oxides in the traditional smelting process. In the last decades, many sustainable and environmentally friendly novel hydrometallurgical processes for Zn extraction were developed to overcome tougher legislation and meet cost competitiveness. Secondary Zn recycling focuses on the development of selective Zn-rich but Pb, Fe, As-lean recovery processes.

1. Introduction

Metals play an important role in industrial development and improved living standards. Society can draw on metal resources from Earth's crust as well as from metal discarded after use. New routes for metals recycling are continually investigated not only for lowering costs but also to prevent environmental pollution (Larba et al., 2013). The increasing demand for metals and metallic compounds in the world has recently required intensive studies for the extraction of metals from ores.

The Zn industry has two main types of end-user: first users and end-users. First users include galvanizers, die-casters, brass-makers and relatively smaller applications like chemical manufacturing. Galvanizing involves coating other metals such as steel or Fe in molten Zn to form a protective layer to prevent corrosion. Zn-coated steel can also tolerate higher loads and is fire resistant. Die-casters manufacture strong, complex and intricately shaped metal components such as key rings, screws, seatbelt buckles and so on. Combining Cu and Zn creates brass alloy, which is used for radiator tubes and tanks, musical instruments, clock mechanisms, pipe or water fittings, and nuts-bolts. The proportions of Zn and Cu can range from 35:65 to 50:50 by weight percent to create different types of brass alloys with varying mechanical and electrical properties. End-users of Zn take the output of the first users as an input of their manufacturing processes for example in the construction, automotive, hardware, furniture, electronics, medical, toy, and clothing industries. Zn can be repeatedly recycled without any detriment to its chemical and physical properties. According to the International Zinc Association, approximately 70% of the Zn produced

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Abbreviations: HAC, Acetic acid; AR, Aqua-regia; AA, Ascorbic acid; BOF, Basic Oxygen Furnace; BAT, Best Available Technology; Bt, Billion ton; C, Carbon; CO_2, Carbon dioxide; CMC, Carboxymethyl cellulose; CGG, Continuous Galvanizing Grade; CA, Citric acid; CZO, Crude Zinc Oxide; EAF, Electric Arc Furnace; EW, Electrowinning; EoL, End-of-life; EPA, Environment Protection Agency; EC, European Council; EU, European Union; FA, Formic acid; IRM, Fe-rich material; PbS, Galena; HCl, Hydrochloric acid (HA); HG, High Grade; ISP, Imperial Smelting Process; IPS, In process separation; ISL, In-situ-leach; IZA, International Zinc Association; IX, Ion-exchange; IL, Ionic Liquid; Fe, Iron; Kt, Kilotonnes; Pb, Lead; LCA, Life Cycle Assessment; LME, London Metal Exchange; Mt., Million ton; MJ, Mega Joule; HNO_3, Nitric acid (NA); H_3NTA, Nitriloacetic acid; OA, Oxalic acid; PLS, Pregnant Leach Solution; PFA, Primary flyash; RLE, Roast, Leach and Electrowinning; RHF, Rotary Hearth Furnace; SFA, Secondary flyash; Ag, Silver; NaEX, Sodium ethyl xanthate; SX, Solvent extraction; SHG, Special High Grade; ZnS, Sphalerite; SAF, Submerged Arc Furnace; H_2SO_4, Sulfuric acid (SA); SO_2, Sulfur dioxide; USGS, United States Geological Survey; USA, United States of America; WEEE, Waste Electrical and Electronic Equipment; WOX, Waelz Oxide; Zn, Zinc; ZnO, Zinc oxide, zincate; ZPR, Zinc Process Residue

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worldwide originates from mined ores and the other 30% from recycled or secondary Zn (https://www.lme.com/en-GB/Metals/Non-ferrous/Zinc#tabIndex=0).

In the world, 95% of metallic Pb and Zn production come from sulfide type of ores (i.e. galena and sphalerite), only 5% of Pb and Zn come from oxidized (i.e. non-sulfide) ores (http://zinc.org.in/why_zinc/production/). In 2018, according to the USGS; Zn reserve of the world is about 230 Mt. and global Zn production was estimated to be 13.42 Mt., and metal consumption was estimated to be 13.74 Mt., respectively (www.usgs.gov). Approximately, 25–30% of global Zn demand is supplied from recycled Zn (https://www.nrcan.gc.ca/our-natural-resources/minerals-mining/minerals-metals-facts/zinc-facts/20534). In 2018, 32.000 tons of secondary Zn from galvanizing residues and crude Zn-oxide recovered from electric arc furnace (EAF) dust recycled in the USA.

European Commission (EC) Communication in 2015 addresses the “Closing the loop – A European Union (EU) action plan for the Circular Economy” Policy:”… where the value of products, materials, and resources is maintained in the economy for as long as possible, and the generation of waste is minimized… to develop low carbon, resource-efficient and competitive economy”. Towards a circular economy, “Metals are the ideal candidate: ‘ETERNALLY’ recyclable, no down-cycling, no material quality issues”. But, certain conditions need to be met for the Circular Economy. From metals perspective physical, economical and recycling aims are important. Waste needs to find its way into new products from a physical point of view. Therefore, we focus on the quality and performance of applied recycling processes. Economically, revenues need to match/surplus costs of the entire recycling chain (i.e. comprehensive collection, chain optimization, economies of scale, a special challenge for high-quality recycling of complex waste streams and need to generate adequate recycling drivers). Recycling is a key contributor to resource efficiency. For the supply side, primary and secondary raw materials are complementary and for the demand side, resource-efficient materials, substitution, product design, and resource-efficient use.

Table 1 shows the effect of metal recycling on CO_2 savings from both primary and secondary sources according to the 2018 report on the Environmental Benefits of Recycling Bureau of International Recycling (https://www.mgg-recycling.com/wp-content/uploads/2013/06/BIR CO2_report.pdf; Nilsson et al., 2017). Benchmark data are reported per 100,000 t of material produced to provide a means of direct comparison between primary and secondary metal production. The total estimated reduction in CO_2 emissions obtained from these data is approximately 500 Mt. CO_2 per annum. Recycling Sn, Pb, Al and Ni saves more than 90% CO_2. Zn recycling saves 76%, Cu recycling saves 65% and Fe (steel recycling) saves 58% CO_2.

Recovery of valuable metals and/or energy from SMRs has a two-fold effect on natural resources. Firstly, using SMRs lessens the pressure on the earth's fast depleting raw materials, thereby ensuring the extended supply of metals and other products for a foreseeable future. Secondly, since SMRs emanate from waste streams, removing resources from them ensures a cleaner environment (Hamuyuni et al., 2018).

Table 1
Carbon footprint and savings expressed in Kilotonnes of CO_2 (kt CO_2)/100,000 t from both primary and secondary metal sources (https://bir.org/publications/brochures/).

Metal	Primary sources	Secondary sources	Savings (%)
Sn	218	3	99
Pb	163	2	99
Al	383	29	92
Ni	212	22	90
Zn	236	56	76
Cu	125	44	65
Ferrous	167	70	58

Using SMRs also keeps metals in circulation, a process often referred to as a sustainable circular economy. Rising waste volumes require Metal Recycling Concepts. The increasing amount of production waste, steel scrap, batteries, e-waste, industrial residues, mine tailings, metallurgical slags/dust, bottom ash process, etc. require efficient recycling technologies. In these wastes, heavy metals threaten the environment, create risks for human health and induce significant storage problems. These wastes also have a significant amount of valuable metals, which make recycling economically feasible and lucrative.

Secondary Zn recycling contributes to a sustainable circular economy. Unlike a traditional linear economy (extract, make, use, dispose of), in a sustainable circular economy, each new object is designed for maximum longevity and future reuse and, at the end of its life, becomes a potential secondary resource, rather than an item of waste for disposal. The sustainable circular economy encompasses more than the production and consumption of goods and services; it aims to disconnect economic growth from the depletion of natural resources. Given its many attributes, including being essential, versatile, durable, and infinitely recyclable, Zn contributes to a circular economy in numerous ways.

In this review paper, the specific problems associated with oxidized and/or mixed types of Pb—Zn ores (i.e. non-sulfide ore) are described and methods for solving their recycling problems, combining economic and technical considerations, are discussed. This manuscript's main task is the development and assessment of ecologic, economic and resource-efficient hydro metallurgical processes for the treatment of low grade oxidized Pb—Zn flotation tailings or metallurgical wastes (i.e. EAF dust, Waelz leach residues, galvanizing wastes, slags, bottom ashes, etc.) for the raw material sector. To be able to meet this objective, this paper will focus on the best available Zn recycling technologies (BAT). This keeps the Zn processing industries' chain closed and future generations do not lose any valuable raw materials: an important contribution to a better environment and a greener future. Most of the countries in the world have very high import dependency on some metals and have limited primary raw material (i.e. not self-sufficient). The exclusive concentration of natural reserves is in particular countries (i.e. > 90% of world demand is covered by three countries). Continuous population increases, rising raw material prices, and unpredictable shortages are increasing the societies' demand for metals every day. Therefore, secondary Zn resources and their recycling technologies are gaining attention.

2. Global Pb—Zn reserves and production

According to the International Zinc Association, there is an estimated 1.9 Bt of Zn contained in the earth's crust and natural waters. Zn extracted from the 12th century to present is about 500 Mt. (https://www.zinc.org). Globally, Zn is the fourth most consumed metal. Pb and Zn are two of the most extensively used commodities throughout history and have a major significance for mining and metallurgical industries. According to the United States Geological Survey, in the world, there are more than $86*10^6$ tons of Pb and more than $230*10^6$ tons of Zn reserves. Those mineral deposits are mainly located in the USA, Australia, China, Canada, Peru, India, Mexico, and other countries. China, Australia, Peru, the USA and Canada are the most Zn producing countries; while, China, the USA, Japan, S. Korea, and Germany are the most Zn metal consuming countries in the world.

Pb—Zn ore deposits occur in five different types: massive sulfide type, sedimentary exhalative type, Mississippi valley type, intrusion type, and supergene non-sulfide type. In 2017, the cut-off grade for open mines was 4% Zn, for underground mines 6% Zn and an oxidized type of ores 10–32% Zn. China produced 37%; Peru 11%; India 7%; Australia, the USA, and Mexico 6% of Zn ore globally in 2017. The ten largest primary Zn mining operators were Glencore, Hindustan Zinc, Tech, Boliden, Sumitomo, Minera Volcan, Votorantim, Industrias Penoles, Zijin Mining and Zhongjin Lingnan Metals in 2017. The ten

Table 2
Location of non-sulfate Pb and Zn mineral deposits in the World (compiled from Mondillo, 2013; http://www.geo.tu-freiberg.de/oberseminar/OS_09/Andreas_Nuspl.pdf).

Supergene origin	Hypogene origin
N. America	N. America
➢ Remac, Reef Ridge, Santa Eulalia, Siera Mojada, Torion and Tintic.	➢ Franklin, Sterling Hill, Balmat
S. America	S. America
➢ Accha Yanque	➢ Vazante
Europe	
➢ Olkusz, Sardinia, Belgium, Poland, Turkey (Oreks, Belen, Dedeman), Silvermines Tynagh	
Africa	Africa
➢ Skorpion, Morrocco	➢ Tsumeb, Kabwe, Berg Auchas
Asia	
➢ Shaimerden ➢ Angouran ➢ Mehdi Abad ➢ Jabali ➢ Mae Sod ➢ Jinding ➢ Lanping	
Australia	
➢ Hypergene ➢ Aroona Beltana, Magellan	

largest Zn smelting operators at that year were Korea Zinc Group, Nyrstar, Glencore, Hindustan Zinc, Shaanxi Boliden, Votorantim, Hechi Nanfang, Teck and Huludao Zinc (Yener, 2018).

In the world, although almost all of metallic Pb and Zn production (i.e. 95%) come from galena (PbS) and sphalerite (ZnS), non-sulfide forms also have a considerable potential for producing Pb and Zn concentrates (Yin et al., 2010; Ma et al., 2011; Abkhoshk et al., 2014). Location of some non-sulfide Pb and Zn mineral deposits (smithsonite, hemimorphite, hydrozincite, cerussite, anglesite, etc.) according to the origin in the world is given in Table 2.

Pb and Zn resources have been continuously exploited and the high-grade ores have gradually become depleted, and low-grade oxide ores have been developed as important sources. Every year, more than 13.6 Mt. of refined Zn and 11 Mt. of refined Pb are produced worldwide (https://www.statista.com/statistics/264634/zinc-production-by-country/). Pb—Zn resources are found together and are scarce increasingly, and World's Pb—Zn reserves are insufficient. Global Zn reserve lifetime was 24 years in 1960 and 19 years in 2010 (http://minerals-usgs.gov/minerals/pubs/commodity/zinc/index). Therefore, the secondary recovery of Pb—Zn resources is of great practical significance.

At present, approximately 70% of the Zn and 40% of the Pb produced originate from mined ores. 15–35% of Zn and 60% of Pb come from a recycled or secondary sources (Worell and Reuter, 2014). Such relatively low recycling rates are due to long term of end uses and product lifespan of typical Zn products (Gordon et al., 2003; Meylan and Reck, 2017). Zn concentrates contain 48–56% Zn and 3–15% (ave. 10%) Pb; while Pb concentrates contain 55–75% Pb and 1–3% Zn. Report prepared by the Bureau of International Recycling (www.bir.org) indicated that the total energy requirement for secondary Zn production represents only 75% of the energy consumed for Zn production from ores with simultaneous reduction of CO_2 emission. Therefore, it is essential to explore new sources of easily available metal waste and to develop efficient methods of processing (Queneau and Downey, 1994).

2.1. Pb—Zn ores

The minerals of Pb and Zn are naturally associated with each other. Three types of mineralization are distinguished for every Pb and Zn deposit:

- ➢ Sulfide minerals, which are mainly found in the hypogene primary sulfide ore body and mineralization occurs during several successive stages, with Pb and Zn being derived from this ore body. Sphalerite and galena are the major sulfide minerals of Zn and Pb, respectively.
- ➢ Non-sulfide ores (often known collectively as “Zinc Oxides”), which fall into two types, hypogene or supergene weathering. The primary sulfide ore body is usually sheltered from supergene weathering by the cap of hypogene oxidized ores. Supergene oxidation ores are evidenced by the absence of sulfide minerals and their outcropping at the surface or their near-surface occurrence.
- ➢ Mixed sulfide–oxide ores with very complex mineralogy that are most often found in the transition, and occasionally in the oxidized, zones of deposits (Moradi and Monhemius, 2011).

3. Primary zinc production

The minerals of Pb and Zn are naturally occurring together. 80% of Zn mines are underground mines, 8% are of the open-pit type and the remainder is a combination of both. In terms of production volume, underground mines account for as much as 64% of overall Zn production, combined underground/open pit mines provide 21%, and the remaining 15% is sourced from open-pit mines. Thus, Zn production from primary sources is quite difficult and expensive. Rarely is the ore, as mined, rich enough to be used directly by smelters; it needs to be concentrated. Zn ores only contain 5–15% Zn when mined first. The most abundant source of Zn is the mineral sphalerite or Zn blende. Zn is mainly recovered through pyrometallurgy or hydrometallurgy. To concentrate the ore by froth flotation, it is firstly crushed and then ground to enable optimal separation from the other minerals. A typically, Zn concentrate usually contains roughly 55% of Zn, usually in the form of ZnS. Zn concentration (i.e. size reduction and flotation) is generally done at the mine site to keep transport costs to smelters as low as possible. About 25–30% is sulfur, which needs to be removed either by roasting or sintering to convert ZnS to ZnO. Zinc oxides are then processed in either pyrometallurgical or more commonly hydrometallurgical processes to produce Zn metal or Zn-salt products.

3.1. Pb—Zn oxidized/mixed ore concentration methods

Before the development of flotation and smelting processes for ZnS ores at the beginning of the 20th century, the non-sulfide deposits were the principal source of Zn in the world. From Roman times up to the 18th century, the non-sulfide Zn-ores, a mixture of silicates and carbonates known as “Lapis Calaminarius”, “Calamine”, “Galmei”, or “Galman”, in the Latin-, French-, German-, and Polish-speaking world respectively, were used as the source minerals for the production of brass, a Zn-Cu ± Sn alloy fairly widespread throughout Europe and the Mediterranean area over the centuries (Boni and Large, 2003). Later, the non-sulfide ores were processed to produce high-grade ZnO in Waelz furnaces, using a technology that was discovered in Belgium and then developed throughout Europe during the 19th century. Jean-Jacques-Daniel Dony, a chemist from Liège, invented the first process, patented in 1810 by Napoléon I, to transform the ores from the rich Belgian deposits (notably from “LaCalamine”, Moresnet) into malleable Zn. The metallurgical transformation of the “calamine” concentrates was done in horizontal crucible melting furnaces, operating for the first time in a factory at the Saint Léonard wharf in Liège (Dejonghe, 1998).

Currently, Zn is produced mostly from ZnS ores because sulfides are easy to separate from gangue and to concentrate by conventional flotation techniques. Oxidized Zn ores, such as smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), hydrozincite ($2ZnCO_3.3Zn\ OH$), zincite (ZnO), and hemimorphite ($Zn_2SiO_3.H_2O$), have also long been an important source of Zn. The depletion of these sulfide ores has brought more emphasis on Zn extraction from oxidized Zn ores or tailings. There are three basic ore varieties of Zn-oxide which are of economic value:

- Hemimorphite (gangue minerals: dolomite, goethite, quartz, and kaolinite),
- Smithsonite (gangue minerals: goethite, quartz, calcite, and kaolinite), and
- Willemite (gangue minerals: quartz, barite, goethite, and feldspar) (Bulatovic, 2010).

However, their concentration was difficult and, until relatively recently, only rich ores were exploited, using limited concentration by washing and gravity methods. For the low-grade oxidized Zn ores, their exploitation and metallurgy are very limited. Non-sulfide Zn deposits including oxides, silicates, and carbonates constitute approximately 5% of the world metallic Zn production. With the depletion of natural sphalerite and increasingly stringent environmental legislation for SO_2 emission, Zn-oxide ores have become important and attractive alternative resources for sulfide ore. Although there are numerous unexploited or abandoned reserves in the world, they are not widely used for lack of suitable processing methods, especially for the low-grade Zn—Pb oxide ore with high Si. The growing demand for Zn—Pb has required intensive studies on the recovery of Zn—Pb metal from these low-grade ores. Much effort has been expended in an attempt to exploit unconventional Zn resources by hydrometallurgical and pyrometallurgical methods.

None of the oxidized Zn—Pb minerals lend themselves very readily to any known concentrating method. Their specific gravities are too low for good gravity separations. Although many other carbonates and silicate minerals have yielded Zn—Pb oxidized ores. Often, all three minerals (i.e. carbonate, oxide, and silicate type) are simultaneously present in a single ore sample, although one mineral generally predominates. The Zn from all three must be extracted if a high overall recovery is going to be obtained. Along this line, it should also be noted that, although smithsonite may be the principal mineral in one part of a large ore body, hydrozincite or calamine may predominate in some other part. This further complication limits the chances of working out a successful concentrating method. Given these conditions, a hydrometallurgical process would seem to offer a reasonable solution to the problem if a suitable solvent were available (Moghaddam et al., 2005; Moghaddam et al., 2005a).

For smithsonite ores, the content of Zn and Pb is usually low-20% Zn and 5% Pb, respectively. High-grade concentrates cannot be obtained without heavy losses, regardless of the techniques used. Hence, in many locations that treat smithsonite ores to produce Zn, high Zn grade concentrates are produced from low-grade ores by volatilization techniques at high temperatures in a Waelz-type kiln. The Zn content in the collected dust can be as high as 65–70%, in comparison with the original Zn content of around 20% in the ore. The dust is dissolved in an H_2SO_4 solution, followed by purification and EW to produce Zn metal powder. The volatilization process is very effective, but heavy pollution may occur. Capital investment is also high, and it seems difficult for small and medium enterprises to use this process to produce Zn metal.

Mixed sulfide–oxide Pb and Zn ores are most often found in the transition, and occasionally in the oxidized, zones of Pb—Zn ore-bodies. They are of great importance because there are numerous unexploited or abandoned reserves of these ores in the world. However, they present difficulties for conventional mineral processing due to complex mineralogy. Despite the large reserve, mixed sulfide-oxide ores have not been utilized efficiently because of the complex mineralogy which causes difficult beneficiation. The intricate composition, fine particle size and serious sliming of ores/tails usually induce a poor flotation effect. Therefore, elimination of the flotation stage and direct extraction of Zn—Pb from the mixed ores might be a more suitable method (Jia et al., 2016). The dissolution of sulfides in mixed ores is more difficult than oxides due to their covalent crystal structure. Although the primary sources of the metals are Pb and Zn concentrates from sulfide and oxidized ores, as supplies of these deplete, the processing of mixed ores must be considered (Li, 2008). There is great potential to exploit many well-scattered small reserves of mixed ores. There are also numerous stockpiles, tailing ponds and buried mine tailings of mixed ores that are important enough to receive attention. To date, no research on the hydrometallurgical processing of mixed sulfide–oxide Pb and Zn ores appear to have been done, despite an obvious need among the Pb and Zn industries in the world.

Pb—Zn ores are concentrated adopting grinding followed by sequential flotation technique in which Pb minerals are floated in the first stage further followed by flotation of Zn minerals. In this process, some portions of Pb and Zn are also lost as sulfide, oxide and mixed minerals into the tailings as metal losses. The mixed sulfide–oxide Zn ores are found with the main sulfide and/or oxidized ore bodies. Because of complex mineralogy, treatment of mixed sulfide-oxide deposits is very difficult from a mineral processing point of view and consequently, they are mostly left untreated as a result of the metallurgical difficulties encountered in extracting Zn from them (Asadi et al., 2017).

In the World, up until now, the Zn grades of oxidized ores/wastes exploited > 20%. As far the low-grade Zn, they have much difficulty in mineral processing, high mineral processing costs, low utilization ratio (50–60%) and a serious waste of the resource (Yanbo and Xia, 2016). There is no economic and environmentally friendly technology yet to directly treat the low-grade Zn oxide ores/wastes. Oxidized ores/wastes are: heterogeneous, deep oxidized and have complex properties.

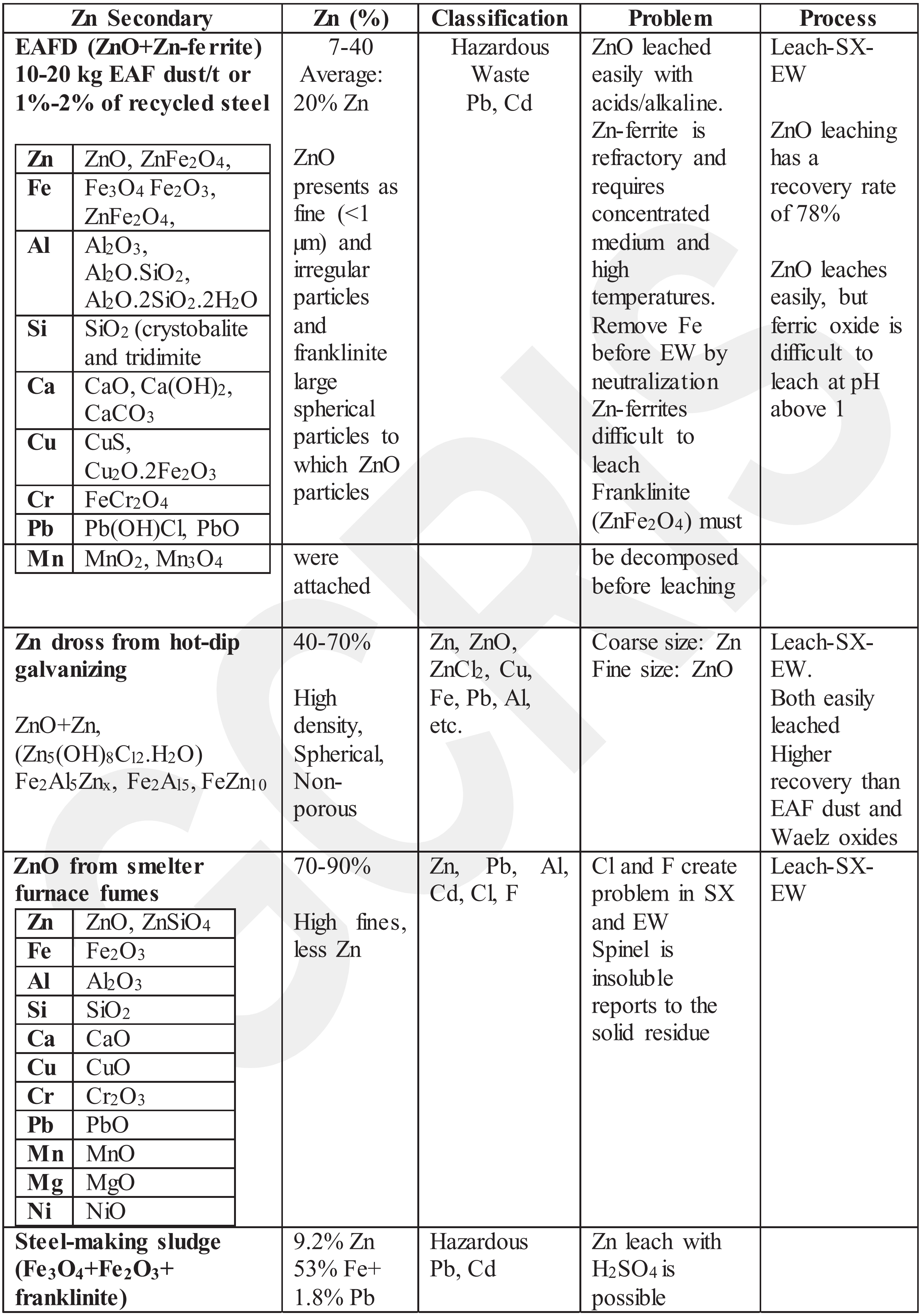
Previously, physical separation methods, such as gravity concentration, were used at pre-concentration and concentration stages without any success (Farag et al., 2011). In practice, the commonly used method for the recovery of oxidized Pb and Zn ores at present is froth flotation in the World. The degree of oxidation in Pb ores may range from slight tarnishing of the galena to complete oxidation. Semi-oxidized ores are still more complex than oxidized ores because they present the complexities of both sulfide ores and oxidized ores. Flotation tests aim at concentrating sulfidic Pb and Zn, and oxidized Pb; while, almost all oxidized Zn remains in the flotation tailings due to the complexity and fineness of the ores. 97% of liberation was obtained at −74 µm particle size (Talan, 2016). In the Pb flotation, sulfidizing agents (i.e. Na_2S or NaHS from 500 to 4500 g/t); promoters (Aero 407 (mercapto benzothiazole), Aero 404 and Aero 412); collectors (i.e. Amyl Xanthate, Iso Propyl Xanthate); depressant (i.e. $ZnSO_4$) and control reagents (i.e. CMC and Na_2SiO_3) are generally used. Remaining Zn oxide ores in the flotation tailings can be beneficiated using flotation with very low efficiency at four or five stages of cleaning, leaching or directly exporting to foreign smelters (Şentürk et al., 1993; Onal et al., 2005; Fa et al., 2005; Karaoğlu et al., 2006; Hosseini and Forsberg, 2007; Navidi Kashani and Rashchi, 2008; Shahsavari et al., 2010; Yang et al., 2013; Shu-Juan et al., 2014; Mehdilo et al., 2014). These researchers obtained Zn grade between 31% and 67% and recovery between 64% and 97%.

3.2. Roasting, calcining & sintering

Over 95% of the world's Zn is produced from ZnS. Apart from Zn, the concentrate contains more than 25–30% different amounts of Fe, Pb, and Ag as well as other minerals (http://zinc.org.in/why_zinc/production/). Before metallic Zn is recovered, by using either hydrometallurgical or pyrometallurgical techniques, sulfur in the concentrate must be removed, which is done by roasting or sintering. The ZnS concentrate is heated strongly to more than 900 °C (below the melting point of 1185 °C) with a sufficient supply of air in blast furnaces where ZnS converts into the more active ZnO (Eq. (1)) when combined with oxygen. At the same time, S reacts with oxygen giving out $SO_{2(g)}$ which

Table 3

Zn secondaries from metallurgical processes (compiled from Lottering, 2016 and Langova et al., 2007).



Zn Secondary	Zn (%)	Classification	Problem	Process
EAFD (ZnO+Zn-ferrite) 10-20 kg EAF dust/t or 1%-2% of recycled steel **Zn**: ZnO, $ZnFe_2O_4$, **Fe**: Fe_3O_4 Fe_2O_3, $ZnFe_2O_4$, **Al**: Al_2O_3, $Al_2O.SiO_2$, $Al_2O.2SiO_2.2H_2O$ **Si**: SiO_2 (crystobalite and tridimite **Ca**: CaO, $Ca(OH)_2$, $CaCO_3$ **Cu**: CuS, $Cu_2O.2Fe_2O_3$ **Cr**: $FeCr_2O_4$ **Pb**: Pb(OH)Cl, PbO **Mn**: MnO_2, Mn_3O_4	7-40 Average: 20% Zn ZnO presents as fine (<1 μm) and irregular particles and franklinite large spherical particles to which ZnO particles were attached	Hazardous Waste Pb, Cd	ZnO leached easily with acids/alkaline. Zn-ferrite is refractory and requires concentrated medium and high temperatures. Remove Fe before EW by neutralization Zn-ferrites difficult to leach Franklinite ($ZnFe_2O_4$) must be decomposed before leaching	Leach-SX-EW ZnO leaching has a recovery rate of 78% ZnO leaches easily, but ferric oxide is difficult to leach at pH above 1
Zn dross from hot-dip galvanizing ZnO+Zn, $(Zn_5(OH)_8Cl_2.H_2O)$ $Fe_2Al_5Zn_x$, Fe_2Al_5, $FeZn_{10}$	40-70% High density, Spherical, Non-porous	Zn, ZnO, $ZnCl_2$, Cu, Fe, Pb, Al, etc.	Coarse size: Zn Fine size: ZnO	Leach-SX-EW. Both easily leached Higher recovery than EAF dust and Waelz oxides
ZnO from smelter furnace fumes **Zn**: ZnO, $ZnSiO_4$ **Fe**: Fe_2O_3 **Al**: Al_2O_3 **Si**: SiO_2 **Ca**: CaO **Cu**: CuO **Cr**: Cr_2O_3 **Pb**: PbO **Mn**: MnO **Mg**: MgO **Ni**: NiO	70-90% High fines, less Zn	Zn, Pb, Al, Cd, Cl, F	Cl and F create problem in SX and EW Spinel is insoluble reports to the solid residue	Leach-SX-EW
Steel-making sludge (Fe_3O_4+Fe_2O_3+ franklinite)	9.2% Zn 53% Fe+ 1.8% Pb	Hazardous Pb, Cd	Zn leach with H_2SO_4 is possible	

is subsequently converted to sulfuric acid (H_2SO_4) – an important commercial by-product. In the case of $ZnCO_3$ ore, it is calcined to get ZnO (Eq. (2)):

$$3ZnS_{(s)} + 3O_2(g) \rightarrow 2ZnO + 2SO_{2(g)}\uparrow \quad (1)$$

$$ZnCO_{3(s)} \rightarrow ZnO + CO_2(g)\uparrow \quad (2)$$

Hot roasted material is cooled down, ground and transported to the leach tanks. ZnO is dissolved in cascading tanks containing H_2SO_4. Impurities are precipitated. Zn metal is produced by electrolysis. Electrodeposited pure Zn sheets are melted over 420 °C in an induction furnace and cast in slabs weighing from 1 to 6 t.

3.3. The hydrometallurgical process

Hydrometallurgy is currently the main method of Zn recovery in the world, and more than 80% of Zn is obtained by hydrometallurgy (Jha et al., 2001). In a leaching stage, the ZnO is separated from the other calcines by H_2SO_4. The Zn content dissolves whereas Fe precipitates and Pb and Ag remain undissolved in the impure $ZnSO_4$ solution. The leach solution contains some impurities which need to be eliminated to obtain a high-purity Zn product by electrowinning (EW) at the end of the production process. Impurity metals (i.e. Fe, As, Pb, Cd, Cu, Mn, Co, etc.) in leach solution are removed by precipitation with NaOH (± H_2O_2) at pH about 3.5 and/or adding Zn powder at pH 5.0 for cementation purification. As all the elements to be removed lie below Zn in the electrochemical series they can be precipitated by cementation. The purified solution then passes an electrolytic process where it is electrolyzed between Pb alloy anodes and Al cathodes. An electrical current is circulated through the electrolyte by applying an electrical difference of 3.3–3.5 V between the anode and cathode causing the Zn to deposit on the Al cathodes in high purity. The deposited Zn is stripped off, dried, melted and cast into ingots. The Zn ingots may have different grades: Continuous Galvanizing Grade (CGG) with 0.1–1.0% Al. High Grade (HG) minimum 99.95% of Zn and Special High Grade (SHG) minimum 99.99% of Zn (http://zinc.org.in/why_zinc/production/).

3.4. The pyrometallurgical process

The Imperial Smelting Process (ISP) is based on the reduction of Zn and Pb into the metal with carbon (C) in a specially designed Imperial Smelting Furnace (ISF). The ISP process is an energy-intensive process and thus became very expensive following the rise of energy prices. Today, Imperial Smelting furnaces are only in operation in China, India, Japan, and Poland.

4. Zinc secondaries and their recycling technologies

Zn is an inherently recyclable non-ferrous metal and can be recycled indefinitely without any loss of physical or chemical properties across its life cycle. At present, approximately 70% of Zn comes from the primary refining of Zn ores (including 10–15% from recycled sources) and about 30% comes directly from recycled Zn (representing 80% of the Zn available for recycling). The recycling level continues to increase each year as technology improves. This mature recycling infrastructure results in reduced energy use reduced emissions and minimized waste disposal. The amount of Zn on steel products is often too small to be recovered and recycled. The long life of Zn coated steel products in construction also makes a forecast of their emergence in waste streams difficult to model, hence more work will be required on this (http://www.egga.com/wp-content/uploads/2014/06/4.SD_Brochure_Update_Final_web.pd_. pdf and https://www.lme. com/en-GB/Metals/Non-ferrous/Zinc#tabIndex = 0).

Zn and/or Pb metals are recovered from various secondary resources (i.e. off-cuts from die-casting, scraps, wastes, tailings and residues) at all stages of production and use with different levels of impurities. The main secondary sources of the metals are sludge and tailings from the processing of some non-ferrous metals (such as Zn, Pb, and Cu), remelted Zn/Pb ingots or pigs, dust from EAF, Waelz slags and brass smelting, dross/waste from hot-dip galvanizing, spent batteries, EoL automobile shredder scrap, rayon industry sludge, cathodic tubes from Waste Electrical and Electronic Equipment (WEEE), appliances, die-cast parts, trimmings, offcuts, metallic scraps, etc. (Nilsson et al., 2017). For example, Zn content in such materials ranges from 20 to 30% in EAF dust via 60–75 wt% in galvanizing ashes, up to 92–95 wt% in Zn dust (oversprays), and galvanizing dross (Trpcevska et al., 2018). 5–15% Zn may be found in oxidized mine/flotation tailings (Kaya et al., 2019; Hussaini et al., 2019). Table 3 shows Zn secondary compositions, Zn contents, classification, problems, and process used for Zn extraction. Recovery from secondary Zn sources eliminates the option of disposal which today is considered expensive and environmentally unacceptable because of the increasingly stringent environmental protection regulations. Furthermore, most of these materials are classified as hazardous wastes due to their increased toxicity as a result of the presence of different metals including Pb, As, Cd and Cr (Nilsson et al., 2017). This keeps the Zn processing industries' chain closed and future generations do not lose any valuable raw materials: an important contribution to a better environment and a greener future.

Zn, Pb, and Cd containing wastes are generated in various metallurgical industries. These materials contain different levels of impurities depending on sources. The production of steel in EAF generates a by-product called EAF dust. Leaching residues of roasted Zn using Waelz technology also produces Zinc Plant Residues (ZPR). Hot-dip galvanizing also generates Zn ashes and bottom drosses. Due to the presence of significant amounts of leachable compounds of Zn, Pb, Cd, Cr, and Ni; EAF dust, ZPR, and galvanizing wastes are classified as hazardous wastes. Therefore, these wastes must be stored in a specialized landfill. Hydrometallurgical processing is effective and flexible for treating such secondaries as it can control the different levels of impurities. The major obstacle in the hydrometallurgical extraction and beneficial reuse of Zn is the presence of highly stable Zn-ferrite ($ZnFe_2O_4$), which is insoluble in most acidic, alkaline and chelating media under mild conditions and creates problems in Zn recovery. The amount of Zn in this form is about 50% of the total Zn. High-temperature acidic leaching dissolves both Zn and Fe together, which is not targeted.

Globally, one of the main Zn-containing secondary raw materials is galvanized steel and scrap brass (OECD, 1995; Gordon et al., 2003). Zn recycling is predominantly conducted by employing a Waelz kiln reactor (OECD, 1995; Doug, 1996), but other technologies have also been developed to treat such hazardous material, e.g., the rotary hearth furnace (RHF) or in-process separation (IPS) (Suetens et al., 2014). Another way to recycle Zn is the leaching of scrap galvanized steel in an alkaline medium followed by electrowinning (EW) (Gordon et al., 2003; Halli et al., 2020). EAF dust, galvanizer dross, flue dust, and steelmaking sludge are also important Zn secondaries, which may be processed with natural primary Zn-oxide ores by leaching. These wastes are classified as hazardous because of toxic elements such as Pb and Cd. However, they contain a high concentration of Zn, Fe, and other metals which can potentially be recovered from these materials (Langova et al., 2007).

The discharge and accumulation of a large amount of smelting waste residues lead to a serious waste of resources and prominent environmental issues. Zn-smelting slag (contains 44% Zn, 4.8% Cd, 0.74% Cu, 0.38% Co, etc.) belongs to hazardous solid waste (Song et al., 2019). Smelting slag containing a high content of Zn as the secondary resource has to undergo further processing and recycling for the sustainable development of the Zn industry in the future. The energy consumption of Zn secondary production is about 25% lower than that of the primary production of Zn (Rudnik et al., 2017), thereby, indicating the significance of processing the smelting slag containing a larger amount of Zn. On the other hand, the accumulation of slag containing Zn generated from metal smelting has reached more than 10 Mt. (NG et al., 2016), and it is still growing at a rate of 320,000 tpy. The long-term storage of Zn waste slag not only occupies a large amount of land but also causes heavy metal pollution damage to the water system, further affecting human health (Dessouky et al., 2008). If the Zn waste residue is stored for a long time, then its soluble components will penetrate downward with water, migrate to the soil, and enrich harmful substances, thereby acidifying, alkalinizing, and hardening the nearby soil. All these effects indicate that the treatment and recovery of Zn slag will significantly protect natural resources and energy, as well as reduce the impact on the environment and human health (Broadley et al., 2007).

4.1. Electric arc furnace dust (EAFD)

Recycling of steel from end-of-life (EoL) products saves the world from its fast-depleting natural resources. Currently, more than 600 Mt. of annual global steel production is from secondary raw materials (Holappa, 2017). The dominating technology for the production of steel from scrap is the EAF dust (Oustadakis et al., 2010; Havlik et al., 2005; Jha et al., 2001). The production of carbon steel from scrap using EAF dust technology typically generates 10–20 kg of dust (1–2%) per ton of steel. (Leclerc et al., 2003). EAF dust is a potential and important SMR. Classification of EAF dust as a pollutant is based on the content and toxicity of metals such as chromium (Cr^{6+}) and Pb present (E. U. Council, 2003; Ruiz et al., 2007). Hexavalent Cr has been restricted to 0.1% due to health and safety issues. The main source of these elements is the scrap metal fed into the EAF. A practical integrated solution for EAF dust reuse and the optimized recycling of the major metals present in the dust is to recycle the material back to the steelmaking process, which would facilitate clean steel production. Zn renders direct EAF dust recycling process impracticable; Nevertheless, as about one-third of the dust can comprise high Zn content in recycled scrap would react and cause damage to the refractory bricks of the electrical furnace due to scaffold formation. It will also choke the gas uptake, which may lead to the entire process shut down (Halli et al., 2017; Hamuyuni et al., 2018). The presence of several other metals like Fe, Cr and Mn are advantageous as these are all common steel alloying elements. But, the presence of Zn in EAF dust compromises the economics of the furnace operation (Dutra et al., 2006).

Selective leaching of metals is seen as one of the most lucrative solutions to solving the challenges related to EAF dust recycling (Havlik et al., 2005; Halli et al., 2017; Hamuyuni et al., 2018). The twofold benefit of this method is that dissolved metals Zn and Pb can separately be recovered from the solution as products while at the same time the Fe rich residue can be used as a secondary raw material for the EAF process.

EAF, which is one of the largest and fast-growing hazardous waste fractions produced, is predominantly used in steel production. When smelting scrap steel in an EAF, three output streams are produced: iron matte, slag, and dust. The global production of EAF dust in steel production is approximately 12 Mt./year (Dutra et al., 2006; Holappa, 2017; Halli et al., 2018) and therefore, recycling it could bring new secondary raw material streams into steel, Zn, and Pb production. The quantity of EAF dust generated per year around the world represents a possible recovery of about 900 t of Zn (Leclerc et al., 2003). The dust is rich in Fe but also contains toxic and volatile metals. The main components in the dust include Fe, Mn, Zn, Pb, and Cr. However, Zn and Pb in the dust inhibit its recycling back to the steel process (Halli et al., 2018). Landfilling such material should not be promoted due to the toxic and carcinogenic nature of the dust. Besides, both the EC and EU strongly regulate the amount of Pb fed into EAF processes, as well as it's content in the final product (E. U. Council, 2003; European Commission, 2002). According to the EU Commission CE Directive, EAF is the efficient Fe (scrap) processing technology. Submerged Arc Furnace (SAF) is the best available technology for ferroalloy production and recycling of ferrous waste streams. Scrap material is charged to the heated EAF. Temperature is more than 2000 °C. This technology is a highly flexible operation. There is a simple power control in a defined atmosphere. Process advantages are high process throughput, flexible input materials, high energy efficiency and produced minimized waste.

EAF dust is generated by at least three mechanisms. Atomization of liquid steel by “boiling” gas evolution, the dusting of finely divided solids (mainly lime, CaO) added to the steelmaking furnace and fuming of the volatile metals (Zn, Cd, and Pb) which can form gases at steelmaking temperatures. Dust particles produced by these mechanisms agglomerate to some extent to produce very fine, chemically complex assemblages. This dust has historically been impounded in landfill sites. Carbon steel EAF dust is quite variable in composition depending upon the steelmaking practice and the source of scrap used in the furnace. Generally, the dust contains significant amounts ($>$ 10%) of Fe, Ca and Zn and lesser amounts ($<$ 10%) of Cd, Pb, Ni, Cu, Mg, Mn, Na, K, Cr, and Cl. Typical composition of EAF dust is 19.4% Zn, 24.6% Fe, 4.5% Pb, 0.42% Cu, 0.1% Cd, 2.2% Mn, etc. (Jha et al., 2001). 50% of this Zn is in the Zn-ferrite form. The dust is generally regarded as toxic waste because of the leachability of toxic elements such as Pb, Cd, and Cr from landfill sites. For this reason, under environmental pressure, the secondary steel industry has been seeking process alternatives for treating the dust. The objectives of most of the proposed processes are to recover valuable metals such as Zn, Cd, and Pb from the dust, to render the dust non-toxic according to current environmental legislation (always changing), and to process the dust with the minimum economic penalty (or maximum benefit) to the steelmaker.

4.2. Galvanizing process wastes

Zn ash is also termed skimmings. A solid by-product formed at the surface of the galvanizing bath as a result of the reaction between Zn and air. It is removed from the surface of the bath periodically metallic Zn occurs as droplets. Zn ashes are a loss for the galvanizing company if they are not recycled. Zn flux may reduce the Zn ash and dross formation and melt the metallic Zn and return to the Zn bath. Crude skimmings with Zn total of ± 80% and Zn metal of ± 50% are saleable to recyclers in bulk or drums or big bags. Crushed skimmings with Zn of ± 70% are saleable to recyclers in bulk or drums or big bags. Small globules of Zn can be entrained in the ash that is removed for recycling. This entrained Zn is separated from the ash and remelted for re-use.

Zn bottom dross is a solid by-product of the reaction during hot-dip galvanizing between Fe and molten Zn. Dross contains about 96% Zn and 4% Fe and is removed from the bottom of the bath periodically and recycled. Minimum 94% Zn ingots or big blocks of maximum 1–2.5 t in bulk or on pallets can be saleable to recyclers.

Upon withdrawal from the galvanizing bath, a layer of molten Zn will be deposited on top of the alloy layer. Often this cools to exhibit the bright shiny appearance associated with galvanized products. Fig. 1 shows a schematic section through a typical hot-dip galvanizing

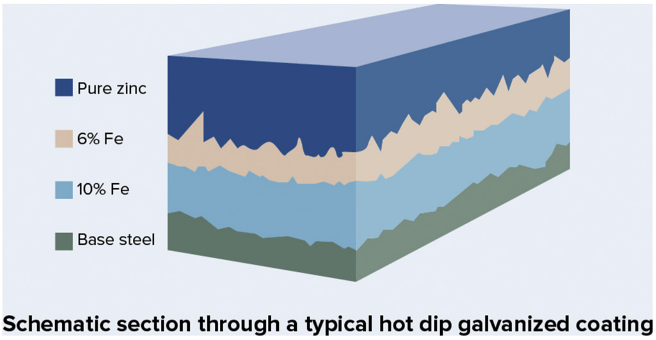


Fig. 1. Schematic section through a typical hot-dip galvanizing coating.

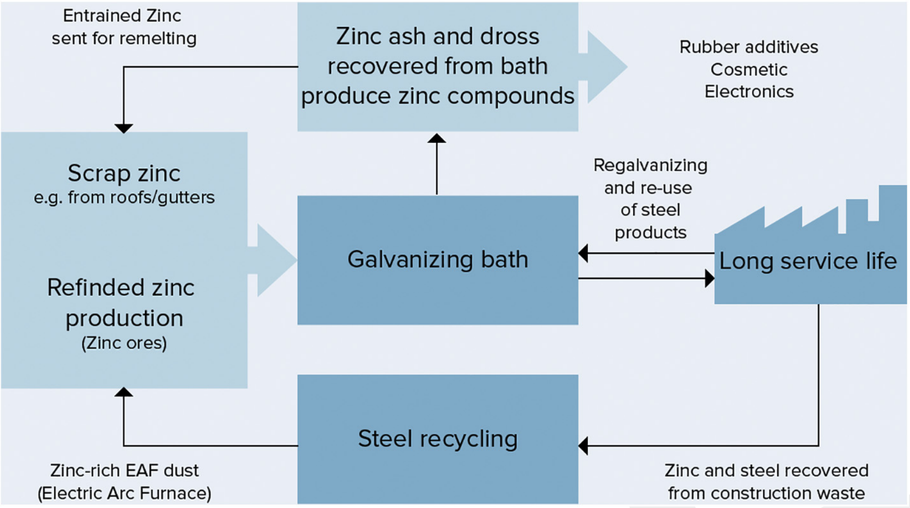


Fig. 2. Flows of recycled Zn within the galvanizing process and at the end of life.

coating. In reality, there is no demarcation between steel and Zn but a gradual transition through the series of alloy layers that provide the metallurgical bond. 45–200 µm Zn coatings stop corrosion of steel in two ways–a physical barrier and electrochemical protection (www.egga.com). Typical values for galvanizing of one kg of steel to EN ISO 1461 require Gross Energy of 3.4–5.3 MJ and global warming potential of 0.1–0.33 kg CO_2 equivalent (https://www.egga.com/wp-content/uploads/2014/06/6.-ga_sustain_eng_lr.pdf).

Process energy use, emission control; regeneration and recycling of process solutions/wastes, and water use are important environmental aspects of the galvanizing process. All of them have important recycling and regeneration routes. Flows of recycled Zn within the galvanizing process and at the end of life are given in Fig. 2.

4.2.1. Use of recycled zinc in the galvanizing process

There are two important sources of Zn used in the galvanizing process:

- ➢ Refined/Primary Zn: Metallic Zn produced from both mined ore concentrates or recycled feedstock. It is estimated that, on average, refined Zn contains about 10–15% of recycled feedstock
- ➢ Remelt/Secondary Zn: Metallic Zn that has been recovered from end-of-life (EoL) or process scrap and remelted for re-use scrap. Galvanizers are also important purchasers of remelting Zn – that is scrap Zn from, for example, old Zn roofs that have been cleaned and remelted into ingot form.

So, the refined Zn purchased by galvanizing plants contains a high proportion of recycled Zn and fully recycled Zn is often purchased to supplement the use of refined Zn. The production of one kg of refined Zn (from ore) requires gross energy of 50 MJ, although only 20 MJ of this energy is used directly in Zn production. Secondary (remelted) Zn used by general galvanizers requires just 2.5 MJ to produce.

4.2.2. Recycling of process residues

During the galvanizing process, any Zn that does not form a coating on the steel remains in the bath for further reuse. There is no loss of materials that may occur during the spray application of other coating types. Zn ash (from surface oxidation of the galvanizing bath) and dross (a mix of Zn and Fe that accumulates at the bottom of the galvanizing bath) are fully recovered onsite or at specialist recyclers. Any Zn metal within the crude ash is directly recycled for further use, often in the same galvanizing process. Some plants operate small furnaces to recover metallic Zn from process ashes. The fine ash and dross are then sold to make Zn dust and compounds for a variety of applications such as rubber additives, cosmetics, and electronic components.

Many galvanized steel products can be removed, re-galvanized and returned to use. For example, highway guard rails are often removed and replaced during routine highway maintenance and resurfacing. The redundant barriers are returned to the galvanizing plant for re-galvanizing and are then used again in similar applications. The Zn-rich acid that is produced by stripping the remaining coating is used for the production of Zn compounds for the chemical industry. Galvanized steel can be recycled easily with other steel scraps in the EAF steel production process. Zn volatilizes early in the process and is collected in the EAF dust that should be then recycled in specialist facilities and often returns to refined Zn production.

According to the Gesellschaft für Bergbau, Metallurgie, Rohstoff - und Umwelttechnik in Germany, in 2006, the European steel industry (EU-27) produced 1,29 Mt. of EAF dust, which contained 296,872 tons of Zn (i.e., 23%). 93% of this Zn (276,920 tons) was recycled. (http://www.gdmb.de). There are more than 650 general galvanizing plants in Europe. Plants are located near to steel fabrication and manufacturing facilities to minimize the economic and environmental cost of transport.

4.3. Hydrometallurgical Residues (Waelz Oxide (WOX))

The amount of solid wastes from the non-ferrous industrial activities, especially from Pb/Zn mining and smelting activities, is increasing currently with industrialization and the rapid development of the economy. The hydrometallurgical residues from smelting activities are often stockpiled and pose potential environmental risks due to the toxic elements, such as As, Cd, Cr, Cu, Ni, Pb, Sb, and Zn, which are contained in the residues. With the rapid depletion of geogenic rich ore resources in recent years, it has become increasingly more financially attractive to recover valuable metals from previously stockpiled hydrometallurgical residues, while simultaneously reduce the potential of environmental pollution of toxic elements from the residues (Guo et al., 2010).

Most Zn refining plants operate a roasting–leaching–electrowinning (RLE) process for Zn—Pb oxidized ore concentrates. If Fe is present in the Zn ore concentrate, Zn-ferrite will be produced upon complete roasting at 950 °C. It accounts for approximately 15% of the total Zn produced. After roasting, the solid is leached at 70 °C with dilute H_2SO_4 to solubilize Zn in the ZnO form. ZPR is produced during Co elimination stage is about 70 kg per ton of produced Zn and this is dumped into tailing site daily (Ruşen, 2007).

WOX (sometimes called crude zinc oxide or CZO) is produced from the recycling of EAF dust in Waelz kilns, which is a high-temperature metals recovery process designated as Best Available Demonstrated Technology by the U.S. EPA for managing EAF dust, a listed hazardous waste under EPA regulations. EAF dust is blended with a carbon source and water, heated to approximately 1200 °C in the Waelz kiln where the non-ferrous metals volatilize into the counter-current air stream inside the kiln and captured in product collectors. The Zn-rich WOX is used as a feedstock to produce Zn metal or sold to other Zn smelters for use as an alternative to Zn concentrates in Zn production. WOX typically contains approximately 60% Zn, as compared to 20% Zn contained in EAF dust (http://azr.com/american-zinc/eaf-dust-recycling/products/waelz-oxide).

Zn calcine can be produced from the further refining of WOX in a calcining kiln. The process separates the residual Pb, Cd, and chlorides from the Zn to produce Zn calcine, a 65–70% Zn content product sold to other Zn smelters as an alternative to Zn concentrates for Zn production.

Several hundred-thousand tons per year of Fe-rich material (IRM) as a by-product of the EAF dust recycling process are produced. By selling IRM to asphalt, cement, and aggregate companies as well as steel producers as a source of low-cost Fe units to supplement their use of scrap metal, it closes the recycling loop (http://azr.com/american-zinc/eaf-dust-recycling/products/iron-rich-material/).

Silver/lead concentrate is manufactured by processing the separated solids from the Zn metal production process with a hot-brine (NaCl) leach solution to dissolve the Pb and Ag, then separating the aqueous solution from the remaining solids. Pb and Ag carbonate will be precipitated from the aqueous solution with soda ash. The Pb—Ag carbonate will be separated from the brine solution and further processed with soda ash to remove remaining impurities. The purified Pb—Ag concentrate is expected to be sold as moist solid (> 60% Pb, > 50 tr. oz./ton Ag) to Pb producers.

4.4. Pb—Zn mining tailings and metallurgical wastes

As the high-grade primary resources diminished, the treatment of processing plant tailings can be considered as a metal significant secondary source. Mining and metallurgical treatment of ores generate millions of tons of ore processed every year which are contained considerable amounts of significant losses of non-ferrous and precious metals. Nowadays, mining wastes can be considered as a technogenic source of metals. This growing interest in metallurgical tailings is due at the first instant to depletion of mineral resources in the most industrialized. Zn and Pb are usually concomitantly present in Zn—Pb ores, wastes and tailings.

As the primary sources of Zn and Pb, natural high-grade sulfide ores are steadily becoming, depleted. Recovering Zn—Pb from mine tailings and/or metallurgical wastes of low-grade ores are recognized as a needed alternative to meet future demand. Oxidized ores are the main source of Zn—Pb after sulfides and are generally found in silicate or carbonate forms in different parts of the world. In the past years, many processes have been tested for treating the oxide ore, such as flotation, gravity separation combined with flotation, hydrometallurgy, and pyrometallurgy, etc. It is generally known that oxidized minerals of Pb—Zn are more difficult to float than their sulfide counterparts. This fact is due to the higher solubility of oxidized minerals as well as the extensive hydration of surfaces (Liu et al. (2011). However, it is expensive to use traditional processes to recover Zn—Pb from mine wastes or metallurgical tailings or low-grade ores. Different methods are used to recover metals from mine tailing or metallurgical tailings, including leaching. Each method has its limitations. Compared with physical and chemical processes, leaching is relatively inexpensive, safe, simple to operate, and environmentally friendly. There is a poorly soluble $PbSO_4$ formed during the leaching stage and leads to a high concentration of Pb in the leach residue. Approaches to recover metals from leaching residues should be developed in mines to reduce environmental problems as well as creating a new source.

5. Lice cycle assessment

The concept of sustainable development encompasses the need for a careful balance of social, economic and environmental aspects considering both present and future needs. Recognizing this, the Zn industry has engaged in a long-running and growing sustainable development program that has had many key activities and achievements. Increasingly the Zn industry is being asked to provide information to downstream users of Zn and Zn-containing products on the environmental footprint of the materials it produces. Understanding the environmental footprint of Zn starts with documenting the resource requirements (energy and non-energy) and environmental releases associated with upstream operations i.e., mining, mineral processing, and refining; but it also involves understanding the impacts and benefits of using Zn during other stages in the product life cycle. These benefits can arise in use e.g. extending the life of galvanized steel products, and through EoL recycling e.g. by utilizing recycled Zn to create new products. Data for the most recent Life Cycle Assessment (LCA) for primary Zn production was provided by the International Zinc Association (IZA) members. Participants represented mining, mineral processing and smelting operations in Asia, Australia, Europe, N. America, Africa, and S. America. The study represented 4.9 Mt. of Zn concentrate production and 3.4 Mt. of Special High-Grade Zn production. Relative to the previous LCA for primary Zn, primary energy demand and emissions to air decreased by 15% or more. The 24% reduction in primary energy demand was accompanied by a 34% increase in the use of renewable energy resources (hydro, wind and solar). Similarly, all LCA indicators, except for a relatively stable result for Eutrophication Potential, also decreased by up to 26%. In particular, the Global Warming Potential decreased by 15%. These results show that the Zn industry is making progressive improvements to production technologies that benefit both downstream users and global sustainability goals as a whole (www.egga.com).

6. Treatment of mining and metallurgical wastes

Extraction of Zn from oxidized Zn ores can be performed by pyrometallurgical and hydrometallurgical methods. Though a high Zn recovery can be obtained by the pyro- metallurgical process, huge energy consumption and high production costs prevent its wide industrial application. In the hydrometallurgical process, the ore is first leached and then a purification process by precipitation or SX is carried out to prepare solutions for the subsequent EW (Abkhoshk et al., 2014).

Metal oxides are insoluble in most molecular solvents and generally strong aqueous mineral acids are used for their dissolution. There are lots of recovery techniques of Zn and Pb from secondary resources, especially leaching residues and oxidized ores/tailings. For this purpose, the hydrometallurgical method is the most convenient. Generally, the hydrometallurgical leaching process is technically more exact, highly predictable, more flexible and easily controllable in metal extraction from primary and secondary resources. Hydrometallurgy uses various lixiviants (such as strong acids, caustic watery solutions, halides, chelating agents/ligands or microorganisms) to selectively dissolve and precipitate base metals. Cyanide, thiourea, and thiosulfate are used for precious metal leaching (Kaya et al., 2019). Strong mineral acids and bases are conventional; but, not environmentally friendly leachates. Inorganic acids, ligands, etching agents and microorganisms (bioleach) are more green and emerging alternative leachates. Corrosivity, toxicity, high consumption, slow leaching rate, high cost, low stability, and environmental irritations are the main disadvantages for leaching solvents. Corrosion causes problems for the equipment when several kinds of leaching reagents are used. Also, the leaching process normally takes a long time to obtain the metal-rich solution due to the slow leaching rate, which makes the process a time-consuming one as compared to the pyrometallurgy. Therefore, accelerating/catalyzing the leaching rate with oxidants is important. For example, extensively used

H_2O_2 has low toxicity and is environment-friendly. Due to high consumption rates, H_2O_2 is expensive and easily decomposes into water and oxygen at temperatures higher than 45 °C. As oxidizing agents, $KMnO_4$ gives Mn^{2+} and HNO_3 gives NO and NO_2 as the reaction product. Fe^{3+} has low cost, purified by goethite and jarosite precipitation before EW and can be regenerated.

After leaching, some impurities containing a pregnant leach solution (PLS) should be purified. The major aim of purification is to produce a pure electrolyte for SX and/or EW. Chemical precipitation, cementation, and SX are some purification methods. In chemical precipitation of metals from PLS, the pH of the solution is adjusted by the hydrolytic precipitation of metals. For example, Sn, Fe, Cu, and Zn can be precipitated at a pH of 1.5, 3.0, 6.0 and 8.0, respectively. After precipitation, filtration (solid-liquid separation) can be performed to remove precipitated metals from the PLS. The pH of the medium is adjusted by NaOH or H_2SO_4. Cementation is a type of precipitation, a heterogeneous process in which ions are reduced to zero valences at a solid metallic interface. The process is often used to refine leach solutions. For example, Ag and Cu in solution are precipitated with Zn powders or Cu in solution is precipitated with scrap Fe. Activated carbon adsorption and ion exchange are also other metal recovery methods from the PLS. EW is the recovery of metals from solution by passing a direct current through the solution. Electrons from the current chemically reduce the metal ions, to form a solid metal compound on the cathode. In EW, the solution base is HNO_3, H_2SO_4, ammoniacal solutions, etc.

7. Previous research studies for Pb—Zn oxide ores/metallurgic wastes/tailings

Previous research studies for Zn and Pb oxide ores/wastes/tailings showed that Zn can be beneficiated using flotation and leaching processes. Even though the leaching method is more effective, because of the high consumption of chemicals, flotation before hydrometallurgical processes is preferred. Also, hydrometallurgical processes are preferred instead of pyrometallurgical ones due to high smelting costs and strict regulations about disposal and environment (Ma et al., 2011; Moradi and Monhemius, 2011; Abkhoshk et al., 2014). The hydrometallurgical Zn extraction process mainly contains three steps; leaching, purification, and electrolysis. During the leaching process, the most common leaching agent is sulfuric acid (SA). However, for low-grade Zn oxide ore, especially those with high contents of Fe, Ca, and Si, excessive acid consumption and complex purification process have caused significant concerns (Xu et al., 2010). Leaching selectivity and effectiveness of valuable metals are always important in hydrometallurgical processing. Leaching is faster, flexible, environmentally-benign and more efficient; however, wastewater and waste gas (H_2, Cl_2, etc.) are generated invariably during the process. Leaching requires corrosion-proof equipment and complicated flowsheets. The diffusion speed and chemical reaction rate during the leaching process can be accelerated by an increase in temperature, finally leading to a rapid leaching process.

Low solubility product (K_{sp}) for some ionic compounds in water at ambient conditions means precipitation of that compound without dissolution during the leaching process. Zn compounds with F^-, Cl^-, Br^-, I^-, SO_4^{2-}, CH_3CO_2, SO_3^-, and NO_2^- ions are soluble in water. But, Zn compounds with OH^-, S^{2-}, PO_4^{3-}, CO_3^{2-} and CrO_4^{2-} ions are insoluble in water. Pb compounds with Cl^-, NO_3, $CH_3CO_2^-$, ClO_3^-, SO_3^- and NO_2^- ions are soluble in water. However, Pb compounds with OH^-, S^{2-}, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, CrO_4^{2+} are insoluble in water. NO_3^- anions, which may come from HNO_3, make soluble compounds with all-metal cations in water. Thus, there is no selectivity between Zn and Pb with HNO_3 leaching. Chlorides of Pb^{2+} and Ag^+ are insoluble in water. Hydroxides and carbonates of most metals are also not soluble. Most of these compounds precipitate during the leaching process.

Solubility rules of common ionic compounds show that for the Zn dissolution without Pb ions, only halogens (F^- and I^-) and SO_4^{2-} ions have required selectivity. But, Cl^-, NO_3^-, and $CH_3CO_2^-$ do not have selectivity and they dissolve both Zn and Pb ions together. It seems that SO_4^{2-} and I^- have the best selectivity among Zn, Pb and Ag. The best and cheapest SO_4^{2-} the source that can be used in leaching is H_2SO_4. Halogen I^- is more toxic than Cl^-, and Br^- and not environment-friendly. Mineral acids of H_2SO_4, HNO_3, and HCl all dissolve Zn; but, selective Zn and Pb leach can be achieved with only H_2SO_4.

Hydrometallurgical treatment of secondaries and wastes is an economical option for the recovery of metals even at their small concentrations in raw materials (Agarwal et al., 1974; Conrad, 1992; Kim and Lee, 2016). It operates at relatively low temperatures (below 100 °C) by using aqueous solutions containing cheap chemicals without generation toxic and volatile solid particles, whereas the process is cost-effective also in small-scale production. Most typical Zn compounds can be easily dissolved in acid and alkaline/ammoniacal solutions due to the amphoteric character of the species. Jha et al. (2001) reviewed the hydrometallurgical Zn recovery from industrial wastes. They described that various leachates could be used to recover Zn from secondary resources. Zn ions can form a variety of soluble complexes. According to this review paper, in all of the reagents, H_2SO_4 (SA) was the best and most commonly used leachate to recover Zn from leach residues (Frenay, 1985; Espiari et al., 2006; Kukurugya et al., 2015; Abd El Aal et al., 2013; Kim and Lee, 2016; Ghasemi and Azizi, 2017; Rudnic, 2019a). But in recent years, because of some drawbacks of acid leaching such as Si releasing into solution and causing silica gel forming, many researches had been performed using different chemicals like chloride (HCl, CaCl2, etc.) (Dhawan et al., 2011; Ghasemi and Azizi, 2017; Halli et al., 2017; Trpcevska et al., 2018), ammonia, ammonium salt (NH4CO3, NH4Cl, etc.) (Frenay, 1985; Ju et al., 2005; Moghaddam et al., 2005; Feng et al., 2007; Wang et al., 2008; Ding et al., 2010; Yin et al., 2010; Ma et al., 2011; Liu et al., 2012a; Liu et al., 2012b; Xia et al., 2015), HNO_3 acid (NA) (Zárate-Gutiérrez et al., 2010; Jha et al., 2012; Ghasemi and Azizi, 2017), caustic soda (NaOH) (Ju et al., 2005; Dutra et al., 2006; Chen et al., 2009; Santos et al., 2010; Dhawan et al., 2011; Liu et al., 2012; Abkhoshk et al., 2014; Ghasemi and Azizi, 2017), citric acid (Irannajad et al., 2013; Halli et al., 2017; Ghasemi and Azizi, 2017), boric acid (Abalı et al., 2017), sulfamic acid (Wu et al., 2014), methane sulfonic acid (Feng et al., 2015), trichloroacetic acid (Deng et al., 2015), 5-sulphosalicylic acid (Wu et al., 2015), and gluconic acid (Hursit et al., 2009), diethylenetriamine (Frenay, 1985), weakly alkaline aqueous iminodiacetate solutions (Dou et al., 2011), ammonium carbonate solutions (Ruiz et al., 2007; Havlik et al., 2018), etc. for the dissolution of Zn from different samples. However, in some cases efficiency of Zn leaching is insufficient due to existence of refractory minerals in the waste, e.g. acid or ammoniacal leaching of franklinite (Zn-ferrite $ZnFe_2O_4$) from steelmaking flue dust (Kukurugya et al., 2015; Halli et al., 2017; Havlik et al., 2018).

Although some of above chemicals (H_2SO_4, alkaline, and ammoniacal solutions), due to some advantages such as low corrosion, low toxicity, and low pollution, have found commercial usage in plants, the remaining processes are not applicable industrially due to insufficient recoveries or high costs (Moghaddam et al., 2005; Wang et al., 2008; Ma et al., 2011). As stated and approved by many researchers, H_2SO_4 has been employed mostly for the hydrometallurgical extraction of Zn from ores or secondary resources since Zn-oxide/Zincite (ZnO) and Zn-ferrite/Franklinite ($ZnFe_2O_4$/$ZnO.Fe_2O_3$) being the most important compounds are soluble in concentrated H_2SO_4. Zn-oxide can be dissolved even with dilute H_2SO_4; but, not Zn-ferrite (Havlik et al., 2004). The leaching was more effective in hot conditions with both acid and ammoniacal solutions. A recovery of > 98% of metallic values were obtained in the acidic solutions (Jha et al., 2001).

7.1. HCl leach

Cl^- anions, which may come from HCl or brines, make soluble compounds with Al^{3+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Hg_2^{2+}.

Table 4
Chronological summary of the previous leach studies using HCl as a lixiviant for Pb–Zn oxide ores/tailings/wastes with tested ranges and optimal conditions.

Material used	Conc. method used	Pb Dissolution	Zn Dissolution	Optimum reagents/dosages	Part. Size	Reference
Smithsonite ore 16.5% Zn, 4.2% Pb and 3.5% Ca	HCl atmospheric leach		D > 95% Zn	1.5 M HCl, 45 °C, 25 g/L S/L, 500 rpm E_a: 59.58 kJ/mol	180 + 150 µm	Dhawan et al. (2011)
Oxidized Pb–Zn Flotation tailings, Turkey Zn: 5.8% Zn, 7.5% Pb, 21.3% Zn	HCl atmospheric leach	D: 10% Pb	D: 92% Zn 12% Fe	0.5–1.0 M HCl, 30–180 min., S/L: 1/10–3/10, 25–80 °C, 400 rpm Optimum: 1.0 M HCl, 1/10 S/L ratio, 80 °C, 30 min.	d_{80}: − 13 µm	Kaya et al. (2020)
Synthetic Zn-Ferrite			D > 90% Zn, < 8% Fe	0.5–1.0 M HCl, 90–100 °C, 1–2 h. E_a: 83 kJ.mol^{-1}		Nunez and Vinals (1984)
EAF dust (15.9–32.3% Zn, 32.3–37.7% Fe, 1.9–3.2% Pb)	Two stage HCl atm. Leach, ZnO and Zn-ferrite leachs		R: 90% Zn	0.5–10 M HCl, 25–90 °C, 1–2 M HCl first stage for ZnO, 4–6 M HCl second stage Zn ferrite leach EW: 2.7–4.9 kWh/kg Zn, 300–2000 Am^{-2}		Baik and Fray (2000)
$ZnFe_2O_4$ (28% Zn + 50.3% Fe) + tandem furnace sludge (14.1% Zn + 52.1% Fe)	HCl atm. and pressure leaching using microwave heating (600 W)		93% Zn	20 °C, S/L: 1/50, 7 days, 260 °C, 85 bar, 0.3 M HCl, 100 min.	− 0.18 mm	Langová et al. (2009)
Zn ash, Kovotvar Kuty, v.d. Slovakia (77.7% Zn, 0.5% Al, 0.2% Fe)	HCl atmospheric leach		D > 99% Zn, impurity (Pb, Fe, Al, Cd, Cu)	5–15% HCl, 10 -150 min., 20 °C, S/L: 1/10 Optimum 10% HCl, 20–30 min.	0.25–0.125 mm	Takacova et al. (2010)
Zn ash (High-dip galvanizing) 55% Zn, 14% Cl	HCl atmospheric leach		D: 100% Zn, 60% Pb, 40% Fe	2.0 M HCl, 20 °C, S/L: 1/20, 30 min, 300 rpm	< 1.25 mm	Trpcevska et al. (2018)

Only AgCl is insoluble in water. With HCl leach, there is no selectivity among Zn, Pb, Fe, Al, and Cu. Table 4 summarizes previous studies for concentrating Zn from oxidized ores, flotation tailings, and different metallurgical wastes using an HCl lixiviant and chronological development. Maximum target metal dissolution rates, main operating variable ranges, optimum conditions, particle sizes, etc. are also given in this table. Chloride-based leaching systems have advantages over sulfate-based systems. Most metal chlorides are considerably more soluble than sulfate salts. It is easy to regenerate brine leaching reagents using cyclic processes. $PbSO_4$ is insoluble in water; but, soluble in saturated chloride solutions. HCl leach is performed at pH < 1. Leach solution chlorinated to precipitate Fe. Zinc SX and electrolysis are followed by the HCl leaching. Chlorine handling and SX/EW in chloride solutions are expensive and complicated for small producers (Dreissinger et al., 1990).

The reaction between smithsonite ore and HCl, and Zn-ferrite and HCl (Nunez and Vinals, 1984; Langová et al., 2009) can be written as:

$$ZnCO_{3(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{3}$$

$$ZnFe_2O_{4(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + Fe_2O_{3(s)} + H_2O_{(l)} \tag{4}$$

$$ZnFe_2O_{4(s)} + 8HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + 2FeCl_{3(aq)} + 4H_2O_{(l)} \tag{5}$$

HCl is a very effective lixiviant for the leaching of zinc ferrite. Hematite can be formed also by precipitation from the $FeCl_3$ solution.

$$2FeCl_{3(aq)} + 3H_2O_{(l)} \rightarrow Fe_2O_{3(s)} + 6HCl_{(aq)} \tag{6}$$

It is desired to suppress reaction (5) in favor of reaction (4) (i.e. to shift the equilibrium of reaction (6) to the right). $Fe_2O_3/FeCl_3$ ratio increases with increasing temperature. The equilibrium constant of the reaction (6) can be expressed as $K_3 = a^*(HCl)^6 = a^*(FeCl_3)^2$. Hence it follows that the dilute acid must be used to minimize $FeCl_3$ content; but, the amount of HCl must be sufficient to extract all Zn (Langová et al., 2009).

In Table 4, one ore, flotation tailing, synthetic Zn ferrite, EAF dust, synthetic Zn ferrite-tandem furnace sludge, and two Zn ashes leach results with HCl were presented. HCl can be used as lixiviant especially for chlorine-containing Pb–Zn materials (Jha et al., 2001; Takacova et al., 2010; Dhawan et al., 2011; Trpcevska et al., 2018) where Zn dissolution could be much faster and with higher leaching efficiency due to aggressive action of chloride ions in acidic medium. Zn ash from Slovakia was leached with 10% HCl for 20 min. More than 99% of Zn dissolved along with impurities Pb, Fe, Al, Cd, and Cu (Takacova et al., 2010).

Dhawan et al. (2011) studied the kinetics of HCl leaching of smithsonite ore containing 16.5% Zn. They used 0.25–1.5 M HCl, 25–45 °C leaching temperature, 25–150 g/L S/L ratio, 150–450 µm particle size and 500 rpm mixing speed. More than 95% Zn extraction was obtained at 1.5 M HCl concentration, 45 °C temperature, − 180 + 150 µm particle size, 25 g/L S/L ratio at 500 rpm mixing speed. The rate of reaction based on and controlled by the shrinking core model for the surface chemical reaction. The activation energy was calculated as 59.6 kJ/mol. In this study, HCl dissolved the smithsonite ore without any filtration problems.

Kaya et al. (2020) leached Turkish Pb–Zn flotation tailings by inorganic and organic acids. 92% Zn dissolution and 12% Fe and 10% Pb co-dissolutions were obtained at 80 °C leaching temperature and 1/10 S/L ratio for 30 min. Leaching time. Nunez and Vinals (1984) reported the preferential extraction of Zn (about 90% total Zn) and low solubilization of Fe (about 8% total Fe) when HCl concentrations between 0.5 and 1.0 M were used at 90–100 °C for synthetic Zn-Ferrites. The activation energy was 83 kJ/mol.

Baik and Fray (2000) used hot HCl solutions to extract Zn from EAF dust containing ZnO and Zn-ferrite. A two-stage process was designed for complete Zn extraction from the dust by counter-flow leaching between the dust and the leaching agent. The dust undergoes two leaching processes: the first leach the ZnO from the dust and in the second hot HCl solution reacts with the Zn-ferrite residue from the low-acid leaching vessel. Fe in the residue from the hot acid leaching was found in the form of hematite, Fe_2O_3, and goethite, FeOOH. The filtrate from the hot acid leaching had a low pH, and high content of iron chlorides, which other workers have found effective in the leaching of sphalerite and pyrite. This solution was used to leach fresh EAF dust, mainly free ZnO particles in the low-acid leaching vessel, where the pH can exceed 4.0. To remove Fe from the filtrate the solution was aerated with air or oxygen and to remove other elements the filtrate from the low-acid leaching was treated with ZnO and Zn metal powders or sometimes with activated carbon to remove organic species. The purified solution was transferred to an EW cell with an ion-exchange (IX) membrane, which produced HCl and Zn. HCl is a very effective lixiviant for the leaching of Zn-ferrite in EAF dust, giving a high Zn yield without jarosite formation.

The main advantages expected from the use of HCl are: (Baik and Fray, 2000).

- ➢ The chemical activity coefficient of HCl in 0.5–5.0 M aqueous solution does not decrease greatly with increasing acid concentration, unlike that of H_2SO_4,
- ➢ Chlorides contained in the dust are beneficial to the leaching process,
- ➢ Washing the dust to remove chlorides is not necessary,
- ➢ Toxic elements, such as Pb and Cd, can be removed from the dust as soluble chlorides,
- ➢ The formation of jarosite can be avoided,
- ➢ S/L separation by filtration in chloride systems is easier than in sulfate systems, and
- ➢ Chloride solutions with HCl have higher equivalent conductivities than sulfates with H_2SO_4, which reduces the cell voltage in electrolysis.

Selective leaching of Zn from Zn ferrite in HCl was studied by Langová et al. (2009). Synthetic Zn ferrite and the dried sludge from a tandem furnace were used. Selective leaching required > 250 °C and a pressure of about 85 bars. The best results were obtained for leaching in 0.3 M HCl solution at 260 °C temperature for 100 min. When 93% Zn was solubilized from synthetic Zn ferrite while Fe remained as hematite. Under the same conditions, > 99% Zn was removed from the dried Tandem furnace sludge. The solid residue from the sludge contained 98% α-Fe_2O_3 and < 0.2% Zn allowing it to be directly recycled for Fe smelting or used as a pigment.

Trpcevska et al., 2018 leached Zn ash containing 55% Zn with HCl solutions. The best results (full Zn dissolution) were obtained for 2.0 M HCl concentration at 20 °C temperature, 1:20 S/L ratio, and 30 min. Leaching time. The presence of Fe ions is usually disadvantageous for the metal EW stage due to possible reduction from Fe^{3+} to Fe^{2+} at the cathode and Fe^{2+} to Fe^{3+} oxidation at the anode. The cathodic reaction of Fe^{3+} results in a decrease in the current efficiency of the Zn electrodeposition. In turn, Pb ions do not show a negative effect on the zinc EW due to high hydrogen overpotential on metallic Pb. The presence of chlorine in the raw material and further, in typical acidic sulfate leachate leads to some problems during subsequent zinc EW. To overcome this problem, washing of the ash with distilled water and Na_2CO_3 or pyrometallurgical pretreatment can be helpful (Trpcevska et al. (2018)).

As a conclusion, leaching low-grade Zn oxide ores with more than 90% Zn dissolution is possible at low (45 °C) temperature with 1.5 M HCl concentration. Synthetic Zn-ferrite and EAF dust require a high temperature, high HCl concentration and sequential (two-stage) leaching to dissolve more than 90% Zn with low Fe contamination. Zinc EW requires 2.7–4.9 kWh/kg Zn energy consumption at a cathodic current density of 300–2000 $A.m^{-2}$. Fe can be removed from the solution as FeO.OH and Fe_2O_3. The use of low-acid leaching stage with H_2O_2 or air/oxygen bubbling oxidation enables effective Fe removal. The presence of metal-organic complexes in EAF prevents cementation of Fe and can be removed by active carbon addition without Zn loss. The HCl loss in the EW is around 2% and can be decreased by increasing the current density (Baik and Fray, 2000).

HCI leach should be performed at pH < 1. Leach solution can be chlorinated to precipitate Fe. Chlorine handling is difficult and SX/EW in chloride solutions are expensive and complicated for small plants. Some of the problems of HCl leaching–EW is the generation of Cl_2 gas and not HCl during the EW step, and corrosion of anodes and cathode substrates (Mackinnon et al., 1982; Majima et al., 1990; Mirza et al., 2016). This requires an application of more resistant electrode materials or special cell construction and obeying safety restrictions.

7.2. H_2SO_4 leach

SO_4^{2-} anions coming from H_2SO_4 make soluble compounds with Al^{3+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+} and Zn^{2+} cations in water. Sulfates of Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+}, Ag^{+}, and Hg^{2+} are not soluble in water at ambient conditions, they precipitate during leaching with H_2SO_4 (Sillen and Martell, 1964). With H_2SO_4 leach there is a good selectivity between Zn and Pb + Ag. Although Fe, Al, and Cu impurities co-dissolve along with Zn. After H_2SO_4 leach, purification of impurity metals (i.e. Fe, Al, Cu, etc.) by precipitation/cementation/SX is required.

In order to find out the stability areas of Zn, Fe, and Ca in the Zn–Fe–Ca–S–H_2O system, the standard Gibbs free energy change (ΔG^0) values can be determined from thermodynamic calculations. The value of ΔG^0 is the main criterion for the spontaneity of a reaction ($\Delta G^0 < 0$) in a closed system at constant pressure and temperature. Table 5 shows the values of ΔG^0 at 20, 40, 60, 80, and 95 °C. The values of ΔG^0 refer to 1 mol of H_2SO_4. The following possible reactions describe the possible reactions of Zn in an H_2SO_4 solution (Trung et al., 2011; Kukurugya et al., 2015):

$$ZnO_{(s)} + H_2SO_{4(aq)} = ZnSO_{4(aq)} + H_2O \tag{7}$$

$$ZnO.Fe_2O_{3(s)} + 4H_2SO_{4(aq)} = ZnSO_{4(aq)} + Fe_2(SO_4)_{3(aq)} + 4H_2O \tag{8}$$

$$ZnO.Fe_2O_{3(s)} + H_2SO_{4(aq)} = ZnSO_{4(aq)} + Fe_2O_{3(s)} + H_2O \tag{9}$$

$$ZnO.\ Fe_2O_3(s) + H_2SO_{4(aq)} = ZnSO_4(aq) + Fe_2O_{3(s)} + H_2O \tag{10}$$

$$3ZnFe_2O_4(s) + A_2SO_4(aq) = 2A[Fe_3(SO_4)_2(OH)_6] + 2ZnSO_4 \tag{11}$$

where A is an alkaline metal (Nunez and Vinals, 1984).

Fe passes into the solution together with Zn from franklinite (Eq. (8)) and/or from iron oxides. Reaction (8) is thermodynamically preferable to reactions (9) and (10) within the whole temperature range for

Table 5
Calculated ΔG^0 values for some of the reactions given above at different temperatures.

Temp. (°C)	7	8	9	12	13	14	15	16	17
20	−134.57	−67.07	−74.66	−36.24	−62.19	−71.51	−253.62	−195.70	−122.40
40	−132.04	−61.70	−69.90	−31.62	−56.24	−65.05	−251.47	−194.05	−123.45
60	−129.36	−56.20	−64.90	−26.90	−50.15	−58.46	−249.08	−192.19	−124.25
80	−126.55	−50.57	−59.65	−22.08	−43.94	−51.74	−246.46	−190.16	−124.82
95	−124.36	−46.27	−55.58	−18.40	−39.19	−46.61	−244.37	−188.52	−125.12

dissolving both Zn and Fe together from Zn-ferrite. Reaction (7) occurs slowly at room temperature and runs at a high rate and elevated temperatures. It is important to note that most of the Fe remains as $Fe_2(SO_4)_3$ and Fe_2O_3. Both $PbSO_4$ and $CaSO_4$ formed have a limited solubility and remained in the residue:

$$Fe_2O_3 + 3H_2SO_{4(aq)} = Fe_2(SO_4)_{3(aq)} + 3H_2O \quad (12)$$

$$Fe_3O_4 + 4H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad (13)$$

$$4Fe_3O_4 + 18H_2SO_{4(aq)} + O_{2(g)} = 6Fe_2(SO_4)_{3(aq)} + 18H_2O \quad (14)$$

$$CaO + H_2SO_{4(aq)} = CaSO_4 \downarrow + H_2O \quad (15)$$

$$Ca(OH)_2 + H_2SO_{4(aq)} = CaSO_4 \downarrow + 2H_2O \quad (16)$$

$$CaCO_3 + H_2SO_{4(aq)} = CaSO_4 \downarrow + CO_2 + H_2O \quad (17)$$

$$CaFe_2O_4 + 4H_2SO_{4(aq)} = CaSO_4 \downarrow + Fe_2(SO_4)_{3(aq)} + 4H_2O \quad (18)$$

The thermodynamic values given in Table 5 have negative values of ΔG^0 at all given temperatures. From these values, it is possible to get an idea of which reactions are more likely to take place than others. Reaction (15) has the highest probability of proceedings, which indicates that acid can be preferably consumed by leaching of Ca from its oxide. If only values of ΔG^0 would be taken into account, neglecting other factors (kinetics, system complexity, and side effects), the main mineral dissolution order between ambient temperature up to 100 °C and atmospheric pressure changes in the following order $CaO > Ca(OH)_2 > CaCO_3 > ZnO > ZnFe_2O_4 > Fe_3O_4 > Fe_2O_3$ (Kukurugya et al., 2015).

Eh-pH diagrams of the Zn–Fe–Ca–S–H_2O system at 20 and 100 °C show that Zn and Ca are present in the form of soluble compounds in a wide range of pH, from 0 to 5.0, practically in the whole range of the water stability area. However, the case of Fe is more complex. In very acidic areas and with a potential higher than 0.77 V, Fe creates the area of ferric ions. After leaching out Zn, Fe and Ca into the solution, according to Eqs. (7), (8), (15), free acid is partially consumed what leads to increase pH and subsequent hydrolytic precipitation of Fe from the solution. Zn and Ca remain in a soluble form while the pH value is in the range 0 to 4.0. After pH $>$ 4.0, there could be precipitation of Zn, which should be avoided by choosing suitable leaching conditions.

Secondary Zn treatment processes can be divided into pyrometallurgy and hydrometallurgy (Jia et al., 2016). In the case of pyrometallurgy, it can obtain direct metal recovery and more stable wastes. But compared with hydrometallurgy, it consumes more energy. Hydrometallurgy mainly consists of four basic processes: roasting, leaching, purification, and EW (RLE). Leaching with acid is reported to be effective for the slag (Havlik et al., 2005). Given its effectiveness, lower cost, and wide availability relative to other acids, H_2SO_4 is selected as the main leachate. However, when leaching Zn-slag with H_2SO_4, other impurity ions, such as Fe, Cd, and Co, still inevitably enter the leachate along with Zn (Zhang et al., 2016). These impurity ions, especially Co, will cause serious damage to the EW of Zn. An oxidized material that contains a great amount of Zn, and Fe was leached with H_2SO_4, and $ZnSO_4{,}7H_2O$ (which was 99.5% pure) was obtained (Goldstein et al., 1980).

In Table 6, EAF dust, Waelz leach plant residues, leach residues, ores, slags; flotation tailings, Zn ashes and brass slags, Zn ash, smelter slag, BOF sludge, brass waste, Zn dross, brass flyash, incinerator flyash, As-rich Cu smelting dust H_2SO_4 leach results were presented. A maximum Zn recovery of 98% was obtained by leaching with 2.0 M H_2SO_4 at 2 h, 60 °C, 1/4 S/L ratio, and 480 rpm for Angouran–Iran smithsonite ore by Espiari et al. (2006). The rate-controlling step used to describe this leaching process is a physico-chemical desorption process with the activation energy of 23.5 kJ/mol. For the silica coagulation stage, lime was added to raise the pH and a maximum filtration rate was obtained at pH 5.3 in 2 h residence time and at 75 °C temperature. The low-grade ZnO ore with high Si from China was treated through the process of H_2SO_4 curing and water leaching (Zhang et al., 2016). The ore was firstly cured for 3 h by 55.2% H_2SO_4 and consumption of 1288 kg/t, and then leached using water for 3 h at 50 °C with 1/5 S/L ratio. Under optimal conditions, a Zn recovery of 99.2% was obtained and the dissolution of silica was as low as 0.56%. A good separation of Zn from silica was reached.

Yanbo and Xia (2016) used both mineral processing and metallurgical technologies (flotation + leach + SX + EW) for low-grade refractory Chinese Zn oxide ore. From this ore, total 81% Zn recovery was obtained using bulk sulfide flotation, magnetic separation, Zn oxide flotation, neutral and H_2SO_4 leaching, SX and EW. Neutral leaching was performed at 30–40 °C temperature, 60 min. Leaching time, S/L ratio of 1/3–1/4 and final pH of 5.2–5.4. H_2SO_4 leach was performed at 80–85 °C temperature, 60 min. Leaching time, S/L ratio of 1/2–1/3 and final pH of 1.0–1.5. Asadi et al. (2017) leached Pb—Zn flotation tailings from Iran containing 8.3% Zn using $H_2SO_4 + Fe_2(SO_4)_3$ together. 94.3% Zn dissolution was obtained using 1.14 M H_2SO_4 and 2.49 acid/$Fe_2(SO_4)_3$ ratio at 80 °C leaching temperature. Dilute acid concentration and high temperature were required to leach Zn. Kaya et al. (2020) leached Turkish Pb—Zn flotation tailings by inorganic and organic acids. 92% Zn and 12% Fe dissolutions without any Pb dissolution was obtained using 1.0 M H_2SO_4 at 40 °C leaching temperature and 1/10 S/L ratio for 60 min. Leaching time.

The Zincex process (Nogueira et al., 1982) was originally developed to recover the Zn from the chloride-sulfate solutions. As applied to the EAF dust, this approach serves to leach the EAF dust in dilute H_2SO_4 to solubilize the ZnO-component that is then treated directly by SX. The leaching of the EAF dust using an H_2SO_4 solution (0.1 to 2.0 M) in the temperature range of 18–61 °C has been carried out by Cruells et al. (1992). The EAF-dust containing zincite and Zn-ferrite is used for this leaching test. The sample containing 22% Zn and 3% Pb is used for these experiments. The results reveal that for the Zn species, the reaction rate is virtually independent of the H_2SO_4 concentration and for the Fe species, the reaction rate is a function of the acid concentration and temperature. The achieved Zn dissolution amounts to around 90%, whereas the Fe co-dissolution is within the range of 20–50% in 1 h leaching. The Modified Zincex Process is a hydrometallurgical process to obtain high-quality SGH Zn-slabs from secondary raw materials. The process has the direct and atmospherical dilute H_2SO_4 leaching, in mild conditions. Al and Fe impurities are precipitated for PLS purification. Selective Zn extraction from the PLS by a liquid cationic exchanger (D_2EHPA) is carried out. Stripping, EW, melting and casting are the other step for 99.99% Zn commercial slabs production (Díaz and Martín, 1994).

Lupi et al. (1996) have leached EAF dust containing a high proportion of ZnO and being poor in Zn-ferrite. This material is leached in 1.5 M H_2SO_4 at 30 °C to provide an aqueous solution, being rich in Zn, Fe, and Mn and a sludge containing $PbSO_4$ and $CaSO_4$. Depending on the H_2SO_4 concentration the extraction yield of Zn is between 73.9% (0.5 M H_2SO_4) and 95.6% (1.5 M H_2SO_4), while the Fe extraction is between 47.3% and 59.7%, respectively.

Jandová et al. (2002) have leached EAF dust containing 14% Zn, 57% Fe and 1.7% Pb. The Zn occurs mostly as Zn-ferrite, while Fe as magnetite and as ferrite. The Zn dissolution is between 45% and 90% at 80 °C depending on the H_2SO_4 concentration that is used in the range 0.5 M and 3.0 M. The Fe dissolution is between 10% and 90%. Almost 90% of Zn extraction efficiency was achieved in 20 using 3.0 M H_2SO_4 at 80 °C, S/L ratio of 1/10 and that almost 70% Zn extraction efficiency was achieved during 5 h if leaching was performed in returned leach solutions at 80 °C and S/L ratio of 1/10. Leach residues were Fe_3O_4 and $PbSO_4$. Pressure leaching the dust at 120 °C, S/L ratio of 1:10 in 1.0 M H_2SO_4 provided only 75% Zn extraction while leaching in 2.0 M H_2SO_4 made possible 95% Zn extraction into the solution.

Havlik et al. (2004) used high-pressure autoclave leaching for EAF dust containing 20.9% Zn at 150 °C temperature and 4.1 bar pressure using 0.4 M H_2SO_4. The effect of temperature and pressure on the yield

Table 6
Chronological summary of the previous leach studies using H_2SO_4 as a lixiviant for Pb−Zn oxide ores/tailings/wastes with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
Angouran Mine, Iran Smithsonite, hemimorphite, cerussite, 37% ZnO, 23.7% SiO_2, 6.2% Al_2O_3, 3.85% Fe_2O_3, 3.75% PbO	H_2SO_4 atmospheric leach		D: 98% Zn	0.125–3.0 M H_2SO_4, 75–180 min., L/S: 2–5, 0–750 rpm Optimum: 2 M H_2SO_4, 2 h, 60 °C, L/S: 4, 480 rpm E_a: 23.5 kJ/mol	- 300 µm 53–75 µm	Espiari et al. (2006)
Low-grade Zn ore with high Si, Yunnan, China	H_2SO_4 curing and water leaching		D: 99.22% Zn 0.56% Si	30–100% H_2SO_4, 500–2100 kg H_2SO_4/t ore Optimum: 3 h, 55.17% H_2SO_4, 1288 kg H_2SO_4/t ore, 50 °C, L/S: 5/1 mL/g, 400 rpm	−200 µm	Zhang et al. (2016)
Low-grade refractory Zn oxide ore 6.5% Zn, 0.92% Pb, 6.72% Fe, 27.2% CaO, 0.81% MgO	H_2SO_4 atmospheric leach + SX + EW		$Zn_{overall}$: 80.95%	Neutral leaching: 30–40 °C, L/S: 3–4: 1, pH 5.2–5.4 Acidic leaching: 80–85 °C, 1 h, L/S: 2–3:1, pH: 1–1.5 SXfeed: 25–30 g/L Zn, 30–50% P_2O_4 + keresene EWfeed: 50 g/L, 300–500 A/m^2, 3 V, 35–40 °C, 2500–3000 KWh/t Zn		Yanbo and Xin (2016)
Pb-Zn Flot. Tails Bama-Isfahan-Iran 8.26% Zn, 4.18% PbO	H_2SO_4 + $Fe_2(SO_4)_3$ atmospheric leach		D: 94.3% Zn	320 rpm, 1.14 M H_2SO_4, 2.49 Acid/$Fe_2(SO_4)_3$ ratio, 10.10 mL/g L/S ratio, 80 °C	−150 µm	Asadi et al. (2017)
Oxidized Pb−Zn Flotation tailings, Turkey Zn: 5.8% Zn, 7.5% Pb, 21.3% Fe	H_2SO_4 atmospheric leach	D: 0% Pb	D: 92% Zn 12% Fe	0.5–1.0 M H_2SO_4, 30–180 min., S/L: 1/10–3/10, 25–80 °C, 400 rpm Optimum: 1.0 M H_2SO_4, 1/10 S/L ratio, 40 °C, 60 min.	d_{80}: −13 µm	Kaya et al. (2020)
EAF dust	H_2SO_4 atmospheric leach + SX (Zincex process)					Nogueira et al. (1982)
EAF dust (ZnO and Zn-ferrite)	H_2SO_4 atmospheric leach		D: 90% Zn, 20–50% Fe	0.1–2.0 M H_2SO_4 leach, 18–61 °C, 1 h		Cruells et al. (1992)
EAF dust, galvanizing ash, waelz oxides and Zn and Cu residues.	H_2SO_4 atmospheric leach + SX + EW (Modified Zincex process)		Waelz oxide > 95% Gal. ash > 98% EAFD > 70–91%	0.5 N H_2SO_4, 40 °C, 1 h, pH: 2.0		Díaz and Martín (1994)
EAF dust, 63.1% ZnO and poor in Zn-ferrite	H_2SO_4 atmospheric leach		73.9% Zn 95.6% Zn, 47.3–59.7% Fe	0.5 M H_2SO_4 1.5 M H_2SO_4		Lupi et al. (1996)
Steelmaking dust, Zn ferrite + Fe_3O_4, Czech, Nova Hut Plant, 14% Zn, 1.7% Pb, 57% Fe	H_2SO_4 atmospheric leach		D: 45–90% Zn, 10–90% Fe	0.5 M–3.0 M H_2SO_4, 80 °C 1st stage: 80 °C, 3 M, L/S: 10/1, 30 min. 2nd stage: 80 °C, L/’: 10/1, 5 h Na_2SO_4, NaOH Na-jarosite precipitation, pH: 2, 95 °C, 8 h, seed $FeSO_4$, NaOH conversion to Fe_3O_4 (64% Fe and 0.2% Zn), pH: 5.5–6.5, 90 °C, 1–2 h Fe precipitation of Zn PLS at pH: 4, 40 °C, ZnO/Zn powder cementation 60 °C for EW.	d_{75}: −100 µm	Jandová et al. (2002)
EAF dust (ZnO and Zn ferrite) 20.9% Zn, 2.7% Pb, 27.8% Fe, 4.3% Ca	High pressure H_2SO_4 leach in autoclave		D: 84% Zn	0.4 M H_2SO_4, 700 rpm, 150 °C, 4.1 Bar		Havlik et al. (2004)
EAF dust	H_2SO_4 atmospheric leach		D: 75% Zn	0.5 M H_2SO_4, 70–90 °C		Havlik et al. (2006)
EAF dust + Steel making sludge 8.08% Zn, 45.24% Fe, 2.12% Pb 9.15% Zn, 52.50% Fe, 1.75% Pb	H_2SO_4 atmospheric leach		D: 100% Zn and 90% Fe	0.1–4.0 M H_2SO_4, 20–80 °C, 15 min.-6 h Optimum: 3.0 M H_2SO_4 leach, S/L: 1/5, t: 6 h, 80 °C		Langova et al. (2007)
EAF dust 25.3% ZnO, 24.8% Fe_2O_3, 18.6% CaO, 6.02% PbO	H_2SO_4 atmospheric leach		E: 30% Zn, Zn/Fe: 9 D: 80% Zn, 45% Fe	0.1–0.3 M H_2SO_4, 80 °C 3 N H_2SO_4, S/L: 1/10, 60 °C	d_{90}: −100 µm	Oustadakis et al. (2010)
EAF dust, Podbrezova	H_2SO_4 atmospheric leach		95% Zn, > 66% Fe 65% Zn, ˜5% Fe			Havlik et al. (2012)

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Table 6 (*continued*)

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
				0.05–1.0 M H_2SO_4, 20–95 °C, S/L: 1/10 1.0 M H_2SO_4, 80 °C, 60 min., 1/10 S/L 0.1 M H_2SO_4, 1/10 S/L		
EAF dust 17.1% Zn, 27.2% Fe, 1.28% Pb	H_2SO_4 atmospheric leach		D: 87% Zn	20–95 °C, 0.05–1.0 M H_2SO_4, L/S: 50 Optimum: 1.0 M H_2SO_4, 80 °C, L/S: 50	99% -50 µm 37% (− 22 + 2 µm), 35% (− 47 + 28 µm	Kukurugya et al. (2015)
EAF dust 33.16% Zn, 1.64% Pb, 17.89% Fe, 3.4% Ca, 0.23%Cr	Inorganic acids: HCl, AR, HNO_3, H_2SO_4, H_3PO_4; organic acids: citric, acetic, formic, oxalic acids; acetone, glycol, ethanol; KOH, NaOH, ammonium, and distilled water	18–60% Pb 18–60% Pb	$>$ 75% Zn (Fe $<$ 6%) $>$ 75% Zn (Fe $<$ 15%)	S/L: 200 g/L, 400 rpm, 168 h, ambient conditions 1.2 M HCl or 10% AR 0.94 M citric acid or 1.5 M HNO_3		Halli et al. (2017)
Zinc ash from hot-dip galvanizing plant, Poland 61.5 ± 8.0% Zn	H_2SO_4 atmospheric leach + purification + EW		R: 95–97% Zn G: 99.5% Zn	20–25% H_2SO_4, 150–500 g/L, 21 °C, 300 rpm Optimum: 20% H_2SO_4, 150–200 g/L Purification: 2 mL 30% H_2O_2, 10 min, 300 rpm EW: 1–5 A/dm^2, Pb and Al electrodes, current efficiency 92%, 21 °C.		Rudnic (2019a)
Metallic Zn and Zn-oxide dusts and Zn ash (60–80% Zn)	H_2SO_4 atmospheric leach + purification + EW		D: 92–98.9% Zn	20–25% H_2SO_4		Rudnic (2019b)
Turkish Zn Waelz leach residue	H_2SO_4 atmospheric leach for Zn Chloride leach for Pb	D: 87% Pb	D: 47% Zn; 53% Fe 52% Zn	5.0 M H_2SO_4, 40 °C, 1/10 S/L, 4 (1 M $FeCl_3$ + 200 g/l NaCl + 10 g/l HCl) mixture, 100 °C, 2 h		Kahraman (1980)
Cinkur, Turkey neutral leach residue	H_2SO_4 leach and water leach in two steps		D: 90% Zn, $<$ 7% Fe	Baking (150–250 °C) with H_2SO_4 Water leach (600–650 °C)		Addemir (1982)
Zn leach waste	Flot. + H_2SO_4 atmospheric leach for Zn NaCl leach for Pb and Ag Cementation of Pb and Ag	D: 90% Pb D: 80% Ag	D: 80% Zn	200 g/l H_2SO_4, 2 h, 80–85 °C 300 g/l NaCl, 30 min., 1.5 $<$ pH $<$ 2.0 with HCl	− 150 µm	Raghavan et al. (1998)
Turkish Zn Waelz extraction residue 24.64% Pb; 11.3% Zn; 8.34% Fe; 5.21% S	1 stage leach: H_2SO_4 roasting + water	8 mg/l Pb	R: 86.32% Zn-46.04% Fe ext.	Roasting: H_2SO_4/waste: 1; 200 °C; 30 min Water leach: 25 °C; 60 min.		Turan et al. (2004)
Turkish Zn Leach residue 12.34% Zn; 15.51% Pb; 6.27% Fe	Water leach Hot H_2SO_4 leach for Zn Brine leaching residue for Pb	D: 84.9% Pb	D: 18% Zn (Water leach) D: 71.9% Zn	150 g/l H_2SO_4, 95 °C, 2 h, 200 g/l pulp density 300 g/l NaCl, 10 min., 95 °C, 200 g/l pulp density		Aydın (2007)
Turkish Cinkur Leach Residue 20.3% Pb, 12.7% Zn, 8.4% Fe	H_2SO_4 leach			N: 1000 rpm, S/L: 2/10, 0–100 g/L H_2SO_4, 1 h	− 20 µm	Güler et al. (2011)
	Sulfating roasting leach Water leach NaCl brine leach		R: 90% Zn	Roasting: 100–700 °C, 0.5–2.0 h with H_2SO_4 and 5–200% water Water leach: 25–90 °C, 2/L: 1/10–5(10, 1000 rpm, 0–8 h Optimum: H_2SO_4/sample: 1/1, humidification: 10%, 200 °C roasting, 1 h, leaching 1 h, 30 °C, S/L: 1/5		
30.56% Pb; 1.6% Zn; 4.69% Fe; 7.31% S	2 stage leach: NaCl leach	D: 89.34% Pb; 1–2 mg/l Fe	D: 17.49% Zn	Leach: 20 g/l waste/NaCl sol.; 200 g/l NaCl; 25 °C; 10 min.		
Leach residue, Zn: 12.43%, Pb: 15.51%, Fe: 6.27%	Water leach of $ZnSO_4.7H_2O$ H_2SO_4 atmospheric Zn leach		D: 18.4% D: 71.9%	Reaction time: 60 min, T:95 °C Reaction time: 120 min, T:95 °C, reagent concentration: 150 g/L, Pulp density: 200 mg/L		Ruşen et al. (2008)
	NaCl for Pb leach	D: 98.9%		Reagent Concentration: 300 g/L, T: 95 °C, pulp density: 50 g/L, Reaction time: 10 min, addition of 30 mL HCl		
Iranian Zn plant residue (ZPR) 9.21% Zn, 12.37% Pb, 5.31% Fe	H_2SO_4 + water + brine atmospheric leaching			C_{brine}: 50–300 g/L, 10–50 min., 25–200 g/L, pH 1–5, 100–500 rpm.	− 118 µm	Farahmand et al. (2009)
		89.43% Pb, 3.84% Zn	69.3% Zn, 0.1% Pb and 10% Fe	Optimum: 25 g/L S/L, pH: 1, t: 30 min., C_{brine}: 300 g/L, 400 rpm		
		2.99 g/L Pb,		pH: 2.5, 200 g/L pulp density, 60 min, 80 °C H_2SO_4 leach 70 °C, 60 min. 200 g/L pulp density water leaching		

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Table 6 (*continued*)

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
		0.02 g/L Zn negligible Fe				
Zn smelter residue, Guangxi-China 6.75% Pb, 6.54% Zn, 10.55% Fe	Acidic brine leach H_2SO_4 + water + brine atmospheric leaching	91.6% Pb, 93.6% Cu, 94.1% In	93.2% Zn	NaCl: 250 g/L, 1.0 M H_2SO_4, 85 °C, 100 g/L pulp density, 1 h	− 120 µm	Guo et al. (2010)
Zn leach residue 9.87%% Zn, 4.93% Fe	H_2SO_4 non-oxidative leach H_2SO_4 leach + H_2O_2 H_2SO_4 leach + MnO_2		D: 95% Zn, 72% Fe D: 90% Zn, 5% Fe D: 80% Zn, 0.4% Fe	75 °C, S/L: 1/7, t: 120 min, pH: 1.5 H_2O_2: 100 mL/kg, t: 3 h, pH: 1 MnO_2: 5 g/kg, 1.5 < pH < 2.0,		Alizadeh et al. (2011)
Zn plant residue (ZPR), Serbia 11.44% Zn, 8.81% Pb, 27.65% Fe (anglesite, Zn ferrite)	H_2SO_4 leach for Zn and Cd recovery; Pyrometallurgy (Carbothermic reduction)		D: 89.5% Zn D: 72% Zn	200 g/L H_2SO_4, 95 °C, 60 min, S/L: 1/10, Ea: 21 kJ/mol (diffusion controlled) 5 g sample + 1.5 g activated carbon, 1300 °C, Ea: 38 kJ/mol	− 74 µm	Strabac et al. (2011)
Balya-Turkey old/historical slag 13% Zn, 29% Fe, 3% Pb, 2% S	2-step H_2SO_4 atmospheric leach		D: 77.45% Zn	First stage: 1–4.07 N H_2SO_4, 55 °C, S/L: 1/10 Second stage: 1–4.07 N H_2SO_4, 95 °C, S/L: 1/10		Kurama and Goktepe (2003)
Zn smelter slag, Shanxi Zinc Shanxi Province, China 110 g/L Zn, 10.13 g/L Cd, 0.65 g/l Co, 043 g/L Fe, 0.77 g/L Cu	H_2SO_4 atmospheric leach		114.5 g/l Zn, 0.5 mg/L Co R: 98% Zn 88% Co	2 M H_2SO_4, 85 °C, 1 h, S/L: 1/4 g/mL, 300 rpm Fe removal: 80 °C, 1.5 h, 3% H_2O_2, pH: 5 Cu and Cd removal: 50 °C, 30 min, pH: 2.5, Zn excess coef. of 1.5 Co removal with 8 g/L NaEX, pH:4, 55 °C, 1 g/L K_2MnO_4		Song et al. (2019)
BOF sludge 1.4–3.2% Zn; 54–70% Fe	H_2SO_4 atmospheric leach		D: 70% Zn	0.1–1.0 M H_2SO_4, 20–80 °C, 2–60 min., L/S: 10 Optimum: 1 M H_2SO_4, 15 min., 80 °C, 300 rpm, L/S: 10	85% -22 µm	Trung et al. (2011)
Brass slag, Cairo, Egypt 11.4% Zn, 6.3% Cu, 1.3% Pb	Acid leach + H_2O_2 HCl + H_2O_2 NH_4OH + H_2O_2 leach	D: 80% Pb; 93% Cu D: 5% Pb; 99% Cu	D: 95% Zn D: 90%Zn, 85%Cu D: 98% Zn; 85%Cu	(HNO_3 > HCl > H_2SO_4) + H_2O_2 6 M HCl + 25%H_2O_2, E_a: 3.5 kJ/mol 6.8 M NH_4OH + 25%H_2O_2, E_a: 3.6 kJ/mol	-8 + 0.90 mm	Abdel Basir and Rabah (1999)
Brass slag, Cairo, Egypt 69% Zn, 13% Cu, 1.3% Fe	H_2SO_4 atmospheric leach for Zn, HCl leach for Cu Zn dust cementation		D: 95% Zn D: 99% Cu	10–50% H_2SO_4 (*V*/V), 50–450 rpm, 5–80 min, L/S: 3–8, 10–70 °C Optimum: 30% H_2SO_4 (V/V), 150 rpm, 10 min, 35 °C, L/S: 5, E_a: 59 kJ/mol	− 100 µm	Ahmed et al. (2016)
Brass Waste (Zn and Cu)	Atmospheric H_2SO_4 + H_2O_2 leach, Zn precipitation, electrowinning		D: 94% Zn D: 99.77% Cu (smelting)	1 M H_2SO_4 + 1.5 M H_2O_2, 60 °C		Kılıcarslan (2015)
Brass flyash from Turkey	H_2SO_4 atmospheric leach $(NH_4)_2CO_3/NH_4OH$ leach pH: 3.5 $Fe(OH)_3$ and $Al(OH)_3$ ↓		D > 90% Zn and D > 65% Cu	0.3–2.3 M H_2SO_4, 30–120 min. Optimum: 30% H_2SO_4, MnO_2 and $Fe_2(SO_4)_3$ oxidants Cement Cu and $ZnSO_4.7H_2O$ produced	− 200 mesh	Timur et al. (2000)
Zn Dross, Akita-Japan 64.5% Zn, 16.3% Pb, 4.8% Sn, 0.41% Al	Two-stage, H_2SO_4 for Zn and HCl for Pb and Sn atmospheric leach	D: 99.5% Pb; 99.4% Al	D: 99.1% Zn	20 ml of 3% H_2SO_4/g dross, 1 h, 45 °C 5.0 M HCl	− 0.2 mm	Barakat (1999)
As rich Cu smelting dust 23.8% Zn, 6.13% Cu, 20.9% Pb, 6.5% Bi	After alkali leach of As Two-stage H_2SO_4 atmospheric leach	99.6% Pb, 98.9% Bi	98.4% Zn, 96% Cu	130–210 g/L H_2SO_4, 0.5–3 h, 25–90 °C, 0.5–1.6 times oxidant Neutral leach: pH: 5, 1 h, 90 °C, no oxidant Residue Acid leach: 190 g/L H_2SO_4, 2 h, 90 °C, 1.4 times oxidant		Zhang et al. (2019)
Domestic waste incinerator flyash, Japan Primary: 0.8% Zn, 0.12% Pb, 1.37% Fe Secondary: 40.2% Zn, 10.7% Pb, 2.1% Fe	H_2SO_4 atmospheric leach for Zn HCl and acetic acid leach for Zn and Pb together HCl washed fly ash + dilute HCl leach NaOH for Zn and Pb	D: 77% Pb in HCl D: 98% Pb in acetic acid D: 97% Pb in NaOH	D: 94% Zn in HCl D: 97% Zn in acetic acid D: 68% Zn in NaOH	10% HCl, 20% acetic acid 3 N NaOH by washing of the residue 5 wt% HCl	primary fly ash: 0.3–2.6 µm, secondary fly ash: 0.25–4.97 µm	Nagib and Inoue (2000)

of the Zn extraction was small. Best Zn extraction of 84% was obtained at 150 °C temperature, 4.1 bar, 0.4 M H_2SO_4 concentration, and 700 rpm mixing speed. Havlik et al. (2006) extracted only 75% Zn from EAF dust with 0.5 M H_2SO_4 at 70–90 °C. Langova et al. (2007) achieved 100% Zn dissolution with 90% Fe co-dissolution using 3.0 M H_2SO_4 at S/L ratio 1/5, 80 °C temperature and 6 h leaching time from EAF dust containing 8% Zn, and TF sludge containing 9.2% Zn. 30% Zn extraction at Zn/Fe ratio of 9 was achieved in 0.1–0.3 M H_2SO_4 at 80 °C. Zn and Fe can also be almost completely extracted at 20 °C if the leaching period is long enough.

Oustadakis et al. (2010) obtained 80% Zn dissolution with 3 N H_2SO_4 at S/L ratio of 1/10 and 60 °C leaching temperature. Havlik et al. (2012) tested the possibility of acid leaching of EAF dust in dilute H_2SO_4 from steelmaking company in Slovakia. H_2SO_4 concentration chanced from 0.05 to 1.0 M at temperature between 25 °C and 95 °C. The maximum Zn extraction of 95% was achieved using 1.0 M H_2SO_4 at 80 °C after 60 min. of leaching. However, 66% Fe and 40% Ca passed into the solution. Fe dissolution depends on leaching temperature and acid concentration. Using 0.1 M H_2SO_4 at the temperature of 60 °C and the S/L ratio of 1/50, 65% Zn dissolution was achieved at 5% Fe co-dissolution.87% Zn extraction from EAF dust was achieved by using 1.0 M H_2SO_4 at the temperature of 80 °C and S/L ratio of 1/50 (Kukurugya et al., 2015). From the perspective of selective leaching of Zn, where no Fe is passing into the solution, concentration 0.1 M H_2SO_4 at S/L ratio of 1/50 and 0.25 M H_2SO_4 at S/L ratios of 1/20 and 1/10 can be considered as optimal concentrations. The rate-limiting step in the case of Zn and Ca is represented by a rate of diffusion, while in the case of Fe it is a rate of the chemical reaction.

Halli et al. (2017) tested 16 different inorganic and organic leach lixiviants (HCl, HNO_3, H_2SO_4, H_3PO_4, aqua regia (AR), citric acid (CA), ascorbic acid (AA), formic acid (FA), oxalic acid (OA), acetone, glycol, ethanol and distilled water) for EAF dust containing 33.2% Zn leaching at the S/L ratio of 1/5 for 186 h. More than 75% Zn ($<$ 6% Fe) was achieved using 1.2 M HCl or 10% AR. Rudnic (2019a, 2019b) leached Zn ash from galvanizing plant and metallic Zn and Zn-oxide dusts with 20% H_2SO_4 at the solid ratio of 150–200 g/L and 21 °C temperature. She obtained 95–97% Zn dissolution with atmospheric leaching + purification with H_2O_2 + EW.

Kahraman (1980) investigated the optimum H_2SO_4 leaching conditions to reach maximum Zn recovery from Cinkur leach residue (ZPR) in Turkey. 47% Zn and 53% Fe dissolutions were obtained using 5.0 M H_2SO_4 concentration at 40 °C leaching temperature, 1/10 S/L ratio, and 4 h reaction duration. Fe dissolution sharply increased with the increasing reaction temperature. Complex chloride solution was used to dissolve valuable Pb metals in the residue. It was reported that 52% Zn and 87% Pb were recovered by applying chloride leaching. Addemir (1982) studied the metallurgical evaluation of Cinkur-Turkey neutral leach residue by baking in concentrated H_2SO_4 in two main steps. One was baking step starting from 150 to 250 °C after mixing residue and H_2SO_4 at a predefined ratio. In this step, compounds Zn-ferrite and Fe-oxide in the residue transformed into water-soluble compounds Zn-sulfate and Fe-sulfate. In the second step, the residue obtained in the first step was heated to 600–650 °C to convert $Fe_2(SO_4)_3$ to Fe_2O_3. This baked cake was leached with water and over 90% Zn recovery was obtained at low Fe (around 7%) co-dissolution as hematite, which is not hazardous for the environment.

Raghavan et al. (1998) stated that flotation + H_2SO_4 leaching was performed to dissolve Zn and so Pb will be enriched in the residue. The residue was treated with brine (NaCl) solution to solubilize most of the Pb—Ag. Firstly, they leached the residue with H_2SO_4 (200 g/l) at a moderate temperature of 85 °C for 2 h and continued with brine leaching, 300 g/l NaCl, for 30 min. at pH 1.5–2. In addition, they tried to cement out Pb by using Zn, Fe or Al. At the end of all these trials, they recovered around 90% Pb and 80% Zn. High sponge Pb—Ag alloy, which could be processed through conventional pyrometallurgical techniques.

Turan et al. (2004) have investigated Zn and Pb recoveries from Turkish ZPR which was discarded as a cake from a Waelz kiln processing Zn—Pb carbonate ores containing 24.6% Zn. Firstly, to recover Zn from the residue, water leaching was performed at 25 °C for 60 min. With a pulp density of 20% solids after the roasting with an equal weight ratio of H_2SO_4/ZPR. The roasting step at 200 °C for 30 min. Decomposed the ferrite structure and about 85% Zn recovery was obtained. The second step was carried out to recover Pb from the secondary leach residue. At the end of experiments, about 89% Pb was recovered in 200 g/L NaCl at 25 °C within 10 min. at a low pulp density (20 g/L). Also, they recommended that Pb from the second stage leach solution could be recovered by Na_2S precipitation to obtain a rich PbS concentrate which is suitable for pyrometallurgical treatment. Aydın (2007) also used hot H_2SO_4 leach (95 °C, 2 h) for Zn and brine leach for Pb to extract Zn and Pb from Turkish ZPR. 72% Zn and 85% Pb dissolutions were obtained. Güler et al. (2011) leached Turkish Waelz Zn leach residue containing 12.7% Zn with sulfating roasting leach at 200 °C temperature and 1 h period using H_2SO_4 + water + brine leaching. They obtained a maximum of 90% Zn dissolution. Ruşen et al. (2008) leached Turkish Waelz leach residues with H_2SO_4 for Zn and NaCl for Pb at 95 °C, 120 min., 150 g/L concentration, and 200 mg/L solid ratio. They obtained a maximum 72% Zn and 99% Pb dissolutions. Farahmand et al. (2009) leached Iranian ZPR containing 9.2% Zn with H_2SO_4 + water + brine at 80 °C, S/L ratio of 1/5, and pH: 2.5 for 60 min. Period. They achieved 69% Zn and 10% Fe co-dissolution.

Zn smelter residue from China containing 6.8% Zn was also acidic brine leached using 1.0 M H_2SO_4 + 250 g/L NaCl concentrations at 85 °C temperature, S/L ratio of 1/10 for 1 h period by Guo et al. (2010). 93.2% Zn and 91.6 Pb were obtained. Alizadeh et al. (2011) recovered Zn from leach residues with minimum Fe dissolution using oxidative H_2SO_4 leaching. During H_2SO_4 leaching, Fe was dissolved as well as Zn which can reduce the Zn extraction efficiency. Leaching the residue in the presence of an oxidizing reagent such as H_2O_2 or MnO_2 significantly reduced the Fe content of the leach liquor. By using the optimum oxidative leaching conditions, Fe recovery reduced from 70% in non-oxidative leaching to 0.4 and 5% in the presence of MnO_2 and H_2O_2, respectively, with acceptable Zn recovery. This reduction in the Fe content was due to the different Fe compounds formed at different conditions. The optimum conditions in non-oxidative leaching of Zn residues were as follows: temperature: 75 °C, S/L ratio: 1/7, leaching time: 20 min., and pH: 1.5. At these conditions, the percentages of Zn and Fe extracted were 96 and 70%, respectively. The optimum conditions for H_2O_2 oxidative leaching were as follows: H_2O_2: 100 $mL.kg^{-1}$, leaching time: 3 h, and pH: 1.0. The percentages of Zn and Fe extracted were 90 and 5%, respectively. The optimum MnO_2 concentration and the favored pH were estimated to be 5 $g.kg^{-1}$ and pH: 1.5–2, respectively. The percentages of Zn and Fe extracted under this condition were 80 and 0.4%, respectively. Both oxidants, H_2O_2 as well as MnO_2, decreased the Fe recovery significantly by the formation of iron hydroxide or iron-manganese compounds, respectively.

Strabac et al. (2011) compared both hydrometallurgy and pyrometallurgy for Zn plant residue containing 11.4% Zn. They used 200 g/L H_2SO_4 at 95 °C, S/L ratio of 1/10 for 60 min. Leaching time. Maximum 89.5% Zn dissolved. The dissolution of ZPR is a diffusion-controlled process and the activation energy is equal to 21 ± 2 kJ $mole^{-1}$. The maximum Zn recovery, obtained during pyrometallurgical treatment was 72% at 1300 °C after 60 min. Kinetic investigations revealed that the ZnO reduction is carried out in the transient kinetic area, where both diffusion and the chemical reaction control the overall process rate, with an activation energy of 38 ± 5 kJ $mole^{-1}$.

By using a two-stage H_2SO_4 leach process, the recovery of Zn from Turkish historical slag which contained considerable amounts of Zn was investigated by Kurama and Goktepe (2003). In order to increase the recovery, leaching tests were performed in dilute and then hot concentrated H_2SO_4 to dissolve Zn-ferrite present in the slag. The optimal conditions were 1.85 N and 4.07 N H_2SO_4 at 1/10 S/L ratio, at a temperature of 55 °C and 95 °C in the first and second stages, respectively. It was found that about 77.5% of Zn extraction could be achieved by atmospheric leaching.

Recovery of Co and Zn from the leaching solution of Zn smelting slag was performed using 2.0 M H_2SO_4 at 85 °C, S/L ratio of 1/4, for 1 h period by Song et al. (2019). They removed Fe, Cu, Cd and obtained 98% Zn, and 88% Co dissolutions. Firstly, Fe impurity ion was removed (< 1 mg/L) from the acid leaching solution by adding H_2O_2 and controlling the pH. The Fe removal rate was 99%. Then, Cu and Cd ions in the PLS solution were extracted with Zn powder by cementation. The removal rate reached 99%, reducing the content of Cu and Cd to 1 and 5 mg/L, respectively. Finally, Co was recovered by adding sodium ethyl xanthate (NaEX). Almost 100% precipitation efficiency was obtained in this process under the optimum conditions of 8 g/L NaEX, 1 g/L K_2MnO_4, pH 4.0, 55 °C, and 5 h. After precipitation, the Co ion concentration of the solution decreased to less than 1 mg/L, and a pure Zn solution with a concentration of 114.5 g/L was obtained.

Trung et al. (2011) leached BOF sludge with 1.0 M H_2SO_4 at 80 °C, S/L ratio of 1/10 for 15 min. and obtained a maximum 70% Zn dissolution. Brass slag was leached with HNO_3, HCl, H_2SO_4, and NH_4OH with H_2O_2 oxidant by Abdel Basir and Rabah (1999). They found that ($HNO_3 > HCl > H_2SO_4$) + H_2O_2 leaching order achieved the maximum 95% Zn, 80% Pb, and 93% Cu dissolutions together. 6.8 M NH_4OH + 25% H_2O_2 achieved 98% Zn, and 85% Cu dissolutions together. Cu, Zn and Pb were successfully recovered by hydrometallurgical treatment using acid or alkali lixiviants. Mineral acids leach almost all metals in hot conditions while ammonia selectively leaches Cu and Zn in the same order. The activation energy values of acid leaching are lower for Zn than for alkali leaching. In both cases, the activation energy value decreases in the order Zn, Cu and Pb with acid and Zn, and Cu with alkali leaching. Ahmed et al. (2016) leached brass slag containing 69% Zn with H_2SO_4 for Zn and HCl for Cu using 30% H_2SO_4 at 35 °C temperature, and S/L ratio of 1/5 for 10 min. Leaching time. 95% Zn dissolution, and 99% Cu dissolution were achieved with Zn dust cementation. The leaching process was well interpreted with the shrinking core model under chemically controlled processes. The activation energy of Zn was 59 kJ/mol.

Kılıcarslan (2015) used H_2O_2 as an oxidant in the H_2SO_4 leaching system for both Zn and Cu extraction from Turkish brass waste. Optimum conditions for both Cu and Zn extraction are 1.0 M H_2SO_4 concentration, 60 °C leaching temperature, and 1.5 M H_2O_2. Leach liquors have been purified via adding Zn powders following by the leaching of wastes. Finally, Zn EW performed with 94% of current efficiency from the purified leach liquors. Since the Cu presents as the metallic form in the wastes, only 7.5% of Cu extraction has been accessed in the absence of H_2O_2 and undissolved Cu remained in the leach residues. Therefore, to recover of Cu from these residues, they have been mixed with several fluxes such as calcium oxide (CaO), borax ($Na_2B_4O_7.10H_2O$) and salt (NaCl) and melted. By melting leach residues Cu has been recovered with an efficiency of 99.79%. Timur et al. (2000) leached brass flyash from Turkey with H_2SO_4 and $(NH_4)_2CO_3/NH_4OH$. Air, MnO_2, and $Fe_2(SO_4)_3$ were used as oxidants. Cement Cu and $ZnSO_4.7H_2O$ compounds were produced. Maximum Zn dissolution was $> 90\%$, and Cu dissolution was $> 65\%$.

Barakat (1999) used a two-stage acid leach (H_2SO_4 + HCl) for Zn dross and obtained 99.1% Zn and 99.5% Pb dissolutions at 45 °C temperature for 1 h leaching time. Zn and Al dissolved into solution, whereas Pb and Sn remained with the residue. Al was selectively precipitated as calcium aluminum carbonate by treating the sulfate leachate with $CaCO_3$ at pH 4.8. $ZnSO_4$ solution was either evaporated to obtain $ZnSO_4$ crystals or precipitated as basic $ZnCO_3$ at pH 6.8. The undissolved Pb and Sn were leached with 5.0 M hot HCl. About 73% Pb $(OH)_2$ was separated by cooling the leached products down to room temperature. From the soluble fraction, Sn was recovered as hydrated SnO_2 by alkylation with NaOH at pH 2.4, while the remaining Pb was separated at pH 8.5 as $Pb(OH)_2$. A process flowsheet had been suggested which involved two-stage hydrometallurgical treatment. The recovery efficiency of the metal salts was 99.1, 99.4, 99.6, and 99.5% for Zn, Al, Pb, and Sn, respectively.

In order to efficiently recover Zn and Cu from As-rich Cu-smelting hazardous dust after alkali leaching of As, an optimum two-stage H_2SO_4 leaching process was developed by Zhang et al. (2019). The results indicated that 98.4% Zn and 96% Cu were leached using the first-stage of neutral leaching at pH 5.0, 90 °C temperature for 1 h duration and the second-stage of H_2SO_4 leaching at 190 g/L, 2 h leaching time, 90 °C temperature and 1.4 times oxidant addition. Meanwhile, 99.6% Pb and 98.9% Bi have remained in the H_2SO_4 leaching residues, which can be recovered by pyrometallurgical processes.

Nagib and Inoue (2000) leached domestic waste incinerator primary (PFA) and secondary (SFA) flyash with H_2SO_4 for Zn; HCl and acetic acid for Zn and Pb together; HCl washed fly ash + dilute HCl leach and NaOH leach for Zn and Pb. This is more effective than alkaline leaching, which suffers from low solubility of Zn. It was found that 10% HCl dissolves 62.5% Zn and 39.5% Pb from PFA and 94% Zn and 77% Pb from SFA while leaching using 20% acetic acid dissolves 62% Zn and 94% Pb from PFA and 97% Zn and 98% Pb from SFA. But unfortunately, the acids also dissolved some impurities such as Fe, Mg, and Al. Alkaline leaching has the advantage that it dissolves only Pb and Zn from the fly ash leaving all other impurities in the solid residue. It is a potentially feasible method for simultaneous detoxification and metal recovery. Alkaline leaching using 3.0 N NaOH followed by washing of the residue using 5% HCl dissolves 98% Pb and 68.6% Zn, while that followed by water washing dissolves 81.4% Pb, and 35.3% Zn from SFA.

From previous Zn secondaries H_2SO_4 leach results the following conclusions can be drawn. Low-grade Zn ores with high silica can be leached in one step with more than 98% Zn dissolution using 2.0 M H_2SO_4 at S/L ratio between 1/2 and 1/5 at 50–60 °C for 2 to 3 h. Low-grade Zn ores with high CaO can be leached with H_2SO_4 in two stages around 81% Zn dissolution. In the first stage, low temperature (30–40 °C) and high pH (5.2–5.4) at S/L ratio of 1/3–1/4, and in the second stage, high temperature (80–85 °C) and low pH (1.0–1.5) at S/L ratio 1/2–1/3. 25–30 g/L Zn for the SX stage and 50 g/L for the EW stage can be obtained. Oxidized Pb—Zn flotation tailings contain 5.8–6.3% Zn, 4.3–7.5% Pb and can be leached directly with 1.0 M H_2SO_4 or 1.14 M H_2SO_4 + $Fe_2(SO_4)_3$. More than 92% Zn dissolution without any Pb contamination can be obtained at 40 °C and 60 min. Leaching time. But, a small amount of Fe also co-dissolved with Zn. The use of low temperature and acid concentration and oxidant addition (H_2O_2, MnO_2 etc.) decreases Fe impurity dissolution.

EAF dust contains high Zn and Fe contents as compared to the oxidized low-grade Pb—Zn ores/tailings. Zn-ferrite is insoluble in most acidic, alkaline and chelating media under mild conditions and creates problems in the Zn recovery. Also, it is difficult to leach Zn-ferrite at ambient temperatures. Selective leaching of Zn and Pb from hazardous waste EAF dust is a lucrative business. At the same time, Fe-rich residue as a by-product of EAF dust recycling can be used as a secondary feed for EAF steel production. Previous studies used H_2SO_4 concentrations from 0.1 to 4.0 M, temperatures from 18 to 90 °C and leach period 15–300 min. 95.6% Zn and 60% Fe dissolutions were achieved with 1.5 M H_2SO_4 concentration and 100% Zn and 90% Fe dissolutions were achieved with 3.0 M H_2SO_4 concentrations. For EAF dust, elevated leach temperature of 80 °C, long leach time and low percent solid are better to obtain high Zn extraction with high Fe containing PLS. 84% Zn dissolution from EAF dust can be achieved with high-pressure leaching in the autoclave with a much lower H_2SO_4 (0.4 M) concentration at 150 °C and 4.1 bar pressure. Pressure leaching at high-temperatures and low acid concentrations achieves high Zn dissolution for shorter leaching periods. However, autoclave leaching requires extremely high investments (CAPEX) and operating (OPEX) costs.

High-grade Zn ash from a high-dip galvanizing plant and metallic Zn, ZnO dust and Zn ash from Poland were leached with 20–25% H_2SO_4

concentration at atmospheric leaching conditions. 92–97% of Zn dissolution can be obtained. After leaching, H_2O_2 purification and EW can produce very pure Zn grade. WOX is produced from the recycling of EAF dust in Waelz kilns. This ZPR can be leached after H_2SO_4 roasting (200 °C) to decompose Zn-ferrite structure and then 60 min. Water leaching at ambient conditions for about 86% Zn dissolution. Turkish ZPR was also leached with hot H_2SO_4 for Zn and brine for Pb. Almost 72% Zn and 85% Pb can be achieved with 150 g/L H_2SO_4 and 300 g/L NaOH in 120 and 10 min. Leaching times. Sulfating roasting with H_2SO_4 at 200 °C for 1 h duration, water leaching at 30 °C for 1 h period at S/L ratio of 1/5, and then brine leach (200 g/L) at 25 °C for 10 min. The duration can achieve 90% Zn, and 89% Pb extractions. Water, H_2SO_4, and brine leach at 95 °C can achieve 72% Zn and 99% Pb dissolutions without roasting. Iranian ZPR also leached by H_2SO_4 + water + brine and 69% Zn and 89% Pb dissolutions were obtained at 80 °C. Chinese ZPR acidic brine and water leaches with 1.0 M H_2SO_4 concentration at 85 °C temperature for 1 h duration dissolved 93% Zn and 91% Pb. Thus for ZPR leach, either H_2SO_4 sulfating roasting or high-temperature acidic brine leaching and water leaching are required for high Zn and Pb dissolutions.

Zn from historical Pb—Zn slags can be extracted in two stages with low temperature dilute and high temperature concentrated H_2SO_4 leaching with/without H_2O_2 oxidant addition. Zn smelter slag can be leached with 2.0 M H_2SO_4 at high temperature (85 °C). Fe removal at 80 °C with H_2O_2 and Cu and Cd at pH: 5.0 and 50 °C and Co at pH: 4.0 with NAEX and K_2MnO_4 can be performed. Leaching Zn from slags requires either a two-stage leach or high-temperature concentrated H_2SO_4 leach. BOF sludge contains high Fe and low Zn. About 70% of Zn can be dissolved with 1.0 M H_2SO_4 at 80 °C for 15 min. Leaching time. Brass slag, waste, and fly ash can be leached with mineral acids and H_2O_2 oxidants. HNO_3 dissolves all Zn, Pb and Cu metals together. $NH_4OH + H_2O_2$ can leach 98% Zn and 99% Cu. Zn and Cu can be extracted from brass slag, waste and fly ash more than 94% with 30% H_2SO_4 at 35 °C for 10 min. 90% Zn can be leached with 1.0 M H_2SO_4 + 1.5 M H_2O_2 at 60 °C and 65% Cu with $(NH_4)_2CO_3/NH_4OH$. From As-rich Cu smelting dust, 98% Zn and 96% Cu can be extracted with two-stage neutral and H_2SO_4 + oxidant leaches.

7.3. H_3BO_4 leach

Boric acid is a very weak mineral acid. Abalı et al. (2017) used 0.9 M H_3BO_4 to leach high-grade Turkish smithsonite ore containing 37.7% Zn at 40 °C temperature, 60 min. Leaching time, and 1% solid ratio. They achieved a 94.8% Zn extraction (Table 7).

7.4. Citric acid (CA) leach

As an alternative to mineral acids, weak and partially dissociating organic acids mainly di/tri-carboxylic acids have been studied as a lixiviant in hydrometallurgical processes. Carboxylic acids are HC derivatives and these structural features make them di−/tripolar and acidic. Citric acid is a weak organic tricarboxylic acid with three different values of pK_a. Tricarboxylic acids show significantly lower pK_{a1} value and higher pK_{a3} value resulting from the stabilization of monoanionic form by an intramolecular hydrogen bonding. Two carboxylic groups serve as a proton donor. (https://www.sciencedirect.com/topics/engineering/mineral-acid). The cost of CA is about 700–750$/t and expensive than inorganic acids (www.alibaba.com).

Citric acid with low molecular weight is a naturally occurring fruit acid, produced by microbial fermentation and is biodegradable organic products. It is one of the world's largest-tonnage fermentation products. In hydrometallurgical treatments, the ability to recover metals or metal oxides depends on their chemical reactivities. When the metal treated is known to be easily dissolved then it seems more appropriate to use a less costly and more environmentally friendly leachate such as CA (Larba et al., 2013). CA offers a more ecological treatment for Zn wastes.

The reaction steps between ZnO and CA can (pH < 3) be written as follows (Demir et al., 2006; Larba et al., 2013):

$$C_6H_8O_{7(s)} + H_2O_{(l)} \leftrightarrow H_3O_{+(aq)} + C_6H_7O_7{}^{-}{}_{(aq)} \quad pK_a: 3.128 \tag{19}$$

$$C_6H_7O_7{}^{-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O_{(aq)} + C_6H_6O_7{}^{2-}\,(aq) \quad pK_a: 4.761 \tag{20}$$

$$C_6H_6O_7{}^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^{+}(aq) + C_6H_5O_7{}^{3-}(aq) \quad pK_a: 6.396 \tag{21}$$

$$3ZnO(s) + 2C_6H_8O_{7(aq)} \rightarrow 3Zn^{2+} + 2C_6H_5O_7{}^{3-}{}_{(aq)} + 3H_2O_{(l)} \tag{22}$$

Organic citric acids are highly selective for Zn (Halli et al., 2017) while containing elements fully compatible with the EAF. However, there are no previous observations in which satisfactory Zn extractions (> 80%) from the EAF dust by organic acid leaching. In order to make the dust suitable as feed material for steel plant, Zn content needs to be decreased to ≤10%. The main cause of the insufficient Zn extractions is the existence of Zn-ferrite (or with isomorphously substituted metals i.e. $(Zn_x,Me_y)Fe_2O_4$), from which Zn is not fully leachable in organic acid (Havlik et al., 2005; Halli et al., 2018).

Table 8 presents CA, alkaline roasted CA and CA in Cl^-, $NO_3{}^-$ and $SO_4{}^{2-}$ leaching media results. Larba et al. (2013) were observed that at low concentration (0.05 M) CA was able to dissolve 90.4% of ZnO after 1 h leaching time at 50 °C temperature. The addition of chlorides, nitrates, and sulfates enhanced the dissolution to 98%, 84%, and 67%, respectively attained after 15 min. at 40 °C. H^+ ion from CA and Cl^- and NO^{3-} anions have a significant effect in the dissolution of Zn. Anions have catalytic effects in Zn dissolution. The dissolution was controlled by a surface chemical reaction in the case of Zn dissolved by CA mixed with chloride and nitrate ions. The activation energy of ZnO dissolution with CA and chloride ions were found to be 96.9 kJ/mol (Larba et al., 2013). Irannajad et al. (2013) also leached low-grade Iranian smithsonite ore containing 16.1% Zn with 0.5 M CA concentration at 80 °C temperature, and S/L ratio of 1/10 for 60 min. Duration. They achieved 82% Zn extraction. Kaya et al. (2020) leached Turkish low grade oxidized Pb—Zn flotation tailings using CA in the presence and absence of NaCl. 91% Zn and 12% Pb dissolutions were obtained using 1.0 M CA concentration at 80 °C temperature, and S/L ratio of 1/10 for 180 min. Leaching time. Addition of 0.05 and 2.0 M NaCl to 0.5 M CA did not improve metal dissolutions.

Several studies have been conducted to offer a solution to use EAF dust as an SRM. However, these studies are dominated by direct inorganic acids (H_2SO_4, HNO_3 or HCl). The problems and limitations related to inorganic acids, such as poor selectivity, low Zn recovery and problematic leach residue. In a quest to overcome these limitations, a method that is both selective and generates a recyclable Fe-rich residue is to use citric acid (CA). EAF dust from Finland also leached using CA with and without alkaline roasting with NaOH (EAF/NaOH: 1.94). Finish EAF dust with 33.2% Zn and 1.6% Pb was leached with only 0.4 M CA and after NaOH roasting at 450 °C for 60 min. + 0.8 M CA leaching at 40 °C for 60 min. With only CA leach 78% Zn and with alkaline roasting + CA leaching 100% Zn, > 80% Pb and < 5–10% Fe dissolution was obtained (Halli et al., 2017; Halli et al., 2018; Hamuyuni et al., 2018).

Table 7
Summary of the previous leach studies using H_3BO_4 as a lixiviant for Pb—Zn oxide ore.

Smithsonite, Turkey 37.74% ZnO, 19.46% PbO, 2.05% Fe_2O_3	H_3BO_4	94.81% Zn	S/L: 1%, 700 rpm, 40 °C, 60 min, 200 μ, 0.9 M boric acid E_a: 62.03 kJ/mol	200–1000 μm	Abalı et al. (2017)

Table 8
Chronological summary of the previous leach studies using organic citric acid as a lixiviant for Pb−Zn oxide ore/EAF dust/ZnO and metallic Zn with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum Reagents/Dosages	Part. size	Reference
ZnO/αAl $_2O_3$	Citric acid atmospheric leach with $Cl^-/NO_3^-/SO_4^{2-}$		D: 90.4% D: 98%	0.05 M citric acid, 1 h, 50 °C, 350 rpm 0.05 M citric acid + 0.05 M NaCl, 1 h, 50 °C, 350 rpm		Larba et al. (2013)
Zn from low-grade oxide ore, Smithsonite, Iran ZnO: 16.1%	Citric acid atmospheric leach with/without NaCl		D: 82%	Reagent Concentration: 0.5 M, 80 °C, Reaction Time: 60 min, S/L:1:10,	40–350 µm	Irannajad et al. (2013)
Pb-Zn oxidized flotation tailing, Turkey 5.8% Zn, 7.5% Pb, 21.3% Fe	Citric acid atmospheric leach	D: 12% Pb	D: 91% Zn	0.5–1 M CA, 30–240 min., 25–80 °C, 400 rpm, S/L: 1/10–3/10, NaCl: 0.05–2 M Optimum: 1.0 M CA, S/L: 1/10, 80 °C, 180 min.	d_{80}: 57 µm d_{50}: 13 µm	Kaya et al. (2020)
EAF Dust 33.16% Zn, 1.64% Pb, 17.89% Fe, 3.4% Ca, 0.23%Cr	Citric acid leach Alkaline roast + citric acid leach	> 80% Pb	78% Zn 100% Zn, < 5% Fe	Alkaline roasting, EAF/NaOH: 1.94, 450 °C 0.80 M CA, 40 °C		Hamuyuni et al. (2018)
EAF dust, Ovako Imatra Oy, Finland 33.2%Zn, 1.64% Pb, 17.9% Fe, 0.23% Cr	Without roasting with citric acid only NaOH roasting + citric acid leach		78% Zn	0.4 M citric acid, 40 °C	-80 µm	Halli et al. (2017, 2018)
		> 80% Pb removal	100% Zn (< 10% Fe)	Roasting: 450 °C and 60 min. EAF/NaOH: 2/1 0.05–0.8 M CA, 40 °C, O_2 purging 2 L/min, 2 h, S/L: 100 g/L Optimum: 0.8 M CA, 40 °C, 60 min.		
Metallic Zn 99.99% Zn	Citric acid atmospheric leach in NaCl, $NaNO_3$ and Na_2SO_4		34% Zn 100% Zn 91.85% Zn 13.15% Zn	0.2–2 M CA, 350 rpm, 30–80 °C 0.5 M CA, 270 min. 0.5 M CA + 2 M $NaNO_3$, 30 min. 0.5 M CA + 2 M NaCl, 270 min. 0.5 M CA + 2 M Na_2SO_4, 270 min.	3 mm	Boukerche et al. (2018)

In order to recover base and precious metals and recycle Fe to the steel process, the desirable behavior of flotation tailing/EAF dust leaching process is one that possesses (a) high Zn dissolution, (b) good selectivity towards Fe, (c) ability to decrease Pb content and optionally (d) retains some Mn and Cr in the solids depending on the steel process. 0.94 M CA shows high Zn extraction (> 75%) and low Fe dissolution (17%) whilst maintain approximately half of the Mn, Cr, and Pb within the solids (Eq. (23)). Nonetheless, regardless of the lower selectivity towards Fe, the advantage of CA over 1.2 M HCl and 10% AR is the absence of chlorides in the leaching media. Chloride circulation into the EAF should ideally be avoided due to its corrosive nature, thus the selection of a chloride-containing lixiviant increases the requirements for an efficient leach residue washing process (Halli et al., 2017).

$$0.94\text{ M CA} > 1.5\text{ M HNO}_3 > 1.75\text{ M HAC} > 2.7\text{ M FA} > 1.2\text{ M HCl} > 12\text{ M NaOH} \tag{23}$$

Boukerche et al. (2018) leached metallic Zn (99.99%) with CA in NaCl, $NaNO_3$, and Na_2SO_4. 0.5 M CA + 2.0 M $NaNO_3$ achieved 100% Zn dissolution in 30 min. Period. Yang et al., 2016 used 0.25 M nitrilotriacetic acid (NTA) for low-grade Zn oxide ores containing 10.8% Zn at 40 °C temperature, and S/L ratio of 1/10 for 2 h leaching time. 91% Zn and 4.1% Fe extractions were obtained. Halli et al. (2018) used CA and NaOH roasting (450 °C, 1 h) and 0.8 M CA leach for Finnish EAF dust containing 33.2% Zn at 40 °C temperature for 60 min. Leaching time,100% Zn with < 10% Fe was achieved.

From previous CA leaching results of Zn secondary following conclusion can be drawn. At 80 °C temperature, 82% and 91% Zn dissolutions can be obtained using 0.5 and 1.0 M CA for 60 and 180 min. Leaching from the low-grade ore and flotation tailings, respectively. Alkaline roasting at 45 °C and 0.8 M CA leach at 40 °C dissolves 100% Zn, > 80% Pb and < 5% Fe from EAF dust. Only organic CA leaching achieves much lower Zn dissolution as compared to the NaOH roasted CA leaching. Metallic Zn and ZnO can be leached with 0.5 M CA in NaCl, $NaNO_3$ and Na_2SO_4 solutions. Almost full Zn dissolution in 30 min. Can be possible. The use of H_2SO_4 at pH: 4–5 for secondary Zn resources followed by purification and EW usually generates low Zn dissolutions. Decreasing pH below 2 with H_2SO_4 significantly increases Zn dissolution.

7.5. Acetic acid (HAC) and nitriloacetic acid (H_3NTA) leach

Another hydrometallurgical process of steelmaking EAF dust treatment is based on a diluted acetic acid leaching (Table 9). This method dissolves the lime as calcium acetate and is followed by an ammonia leach that serves to remove the Zn from the residue (Dreissinger et al., 1990). The UBC-Chaparral Process for treating EAF dust was designed to meet the objectives of detoxifying the dust and maximizing the recovery of metal values (Zn, Pb, Cd, etc.) This process has the following steps: selectively remove metal chlorides ($PbCl_2/ZnCl_2$) by hot/cold water washing, selectively remove free lime as Ca-acetate (gypsum is precipitated from the Ca-acetate solution with H_2SO_4 regenerating HAC), selectively leach ZnO in an ammoniacal-ammonium carbonate solution, clean up the solids to render the dust non-toxic, and precipitate final products in high purity and saleable form. Pb is solubilized slightly as plumbate (PbO_2^{2-}) and Zn as zincate (ZnO_2^{2-}) at pH about 12.5. Cd is not solubilized at all from the EAF dust. This small Zn and Pb contamination can be removed by precipitating metal carbonates with carbonic acid or sodium bicarbonate. Ca is also removed by carbonate addition. Dilute 3.0 M HAC leaching complexes Pb and forms $ZnAC_2$ and $CaAC_2$. Cd and Pb were cemented by Zn powder at room temperature. Gypsum is precipitated by adding H_2SO_4 to $CaAC_2$ solution. Zn from lime leach residue is leached with NH_3-$(NH_4)_2CO_3$ lixiviants. Second cementation completely removes Cd and Pb ahead of the Zn precipitation step. In the presence of an excess of Zn dust. The approximate individual metal recoveries achieved by the UBC-Chaparral

Table 9
Chronological summary of the previous leach studies using acetic acid as a lixiviant for EAF dusts with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
EAF dust 20.5% Zn, 4% Pb, 21% Fe	Dilute HAC leach and NH_3/$(NH_4)_2CO_3$ leach UBC-Chaparral Process (chloride wash, lime leach, cementation, gypsum leach, Zn leach, cementation, and steam precipitation)	D: 55–60% Pb and Cd	D: 55–60% Zn as ($ZnCO_3$ or $Zn(OH)_2$)	3.0 M HAC and NH_3-$(NH_4)_2CO_3$		Dreissinger et al. (1990)
EAF dust, USA 17.3% Zn, 2.1% Pb, 0.083% Cd	Concentrated HAC leach	76.3% Pb, 85.2% Cd	70.5% Zn	3.0 M HAC, 150 g/L,		Barrett et al. (1992)
Low-grade Zn oxide ore 10.82% Zn, 7.38% Fe, 7.80% Pb	Nitrilotriacetic acid leach		D: 91% Zn, 4.1% Fe	0.25 M Nitrilotriacetic acid leach, 40 °C, 2 h S/L: 10 mL/g	- 74 µm	Yang et al., 2016

process are 55–60% Zn recovered as a $ZnCO_3$-$Zn(OH)_2$ product, 55–60% Pb recovered as Pb—Cd cement, 80–85% Cd recovered as Pb—Cd cement and 95–100% Ca recovered as $CaSO_4.2H_20$. After Zn leach, Zn powder cementation for Pb and Cd and steam precipitation for $ZnCO_3$ production stages are used. Ammonia and CO_2 are produced as a by-product. This process is very complex and time-consuming. Also the product recovery rates are low.

A small amount of Cd and Pb are also solubilized, which are removed by cementation with Zn powder. Zn is recovered from the solution as a hydroxide–carbonate mixture by steam stripping. The process does not recover Zn from its ferrite but the residues generated could be safely disposed of. NH4Cl solution has also been used for the recovery of Zn from secondary resources. For this purpose, Ezinex process has been developed by Engitec Implant. Olper (1993) explained that this process was operated at 70–80 °C temperature for 1 h period and main leaching reaction was between ZnO and NH4Cl by following reaction. Other metals present in the dust i.e. Cu, Cd, Ni, Pb, and Ag also react with the same mechanism. The Fe oxides, the ferrite, and silica are not dissolved during this step. The leach solution is purified by the Zn cementation process. Zn metal is produced from the purified Zn-amino chloride electrolyte by electrolysis in an open cell without the evolution of chlorine at the anode. The anodic oxidation of the NH_4Cl to $N_{2(g)}$, passes through chloride oxidation to chlorine and this reacts with ammonia giving nitrogen and chloride ions. This reaction depolarizes the anode, lowering the cell voltage of about 1 V, compared to that of oxygen evolution in the conventional $ZnSO_4$ electrowinning. The impurities in the electrolyte did not affect the current yield like in H_2SO_4 electrolyte, and these impurities were co-deposited with Zn. The process is more energy-efficient than sulfate EW (Jha et al., 2001).

Similar research work is also published by Barrett et al. (1992). A steelmaking EAF dust containing 17.3% of Zn, 2.09% of Pb, and 0.083% of Cd is used in this process. The key differences are that a simple, one step, strong HAC leach at ambient temperature is used to separate easily removable elements and the residue is recycled to the electric furnace to recover Fe values from the contained oxides and Zn-ferrite. Cr returns to the slag or melt. The heavy metals in solution (Zn, Pb, Cu, and Cd) are precipitated as a bulk sulfide product (while regenerating HAC) for delivery to a Zn-plant. Pb can be removed separately by cementation from solution with Zn-dust if required. The HAC solution is treated in two steps to remove Ca and Mg, and the concentration is adjusted before returning it to the strong HAC leach. Briefly, the process is based on the concept of recycling the dust to the electric furnace, while removing the components not wanted in steelmaking. Useful products are produced where possible, and the main bulk of the dust becomes steel or slag. Zn extraction was 70.5%, Pb 76.3%, and Cd 85.2%.

Yang et al. (2016) used 0.25 M H_3NTA concentration at 40 °C temperature for 2 h leaching time. They achieved 91% Zn and 4.1% Fe dissolutions from low-grade Zn oxide ore containing 10.8% Zn. Selective high Zn and low Fe extraction are possible with this new process. The leaching reagent was regenerated by adjusting the pH of the solution to 1.0 with H_2SO_4. H_3NTA leach residue contains less than 1.5% Zn. $PbSO_4$ and $CaSO_4$ white precipitates can be purified with an ammoniacal solution and H_3NTA can be recycled. $ZnSO_4$ solution can be purified with ZnO powder and EW can be used to obtain Zn metal. The spent electrolyte can be recycled to the EW circuit.

7.6. *Alkaline leach (NaOH and Ammoniacal solutions)*

Fe, Al, Mg, Ca, etc. will not be dissolved in alkaline solution. Hence, the consumption of the leaching agents will be reduced to a minimum value, and a leach solution containing only Zn and Pb as predominant elements will be obtained (Liu et al., 2011). Although it is known that the most important leachate is H_2SO_4 to dissolve Zn-ferrite, different leachates were examined by some researchers. Caustic soda (NaOH) is an example of these studies. In the caustic soda leach process, Zn and Pb are selectively dissolved in NaOH rejecting Fe in the residue. The leach solution after purification with Zn powder is electrolyzed to produce metal regenerating NaOH according to the reactions:

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \quad (24)$$

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O \quad (25)$$

$$2Na_2ZnO_2 + 2H_2O \rightarrow 2Zn + 4NaOH + O_2 \quad (26)$$

NaOH leach can be used for the recovery of metal from EAF dust, BOF dust, and galvanized steel scrap (Jha et al., 2001). Zn can be present in EAF dust as an oxide (ZnO) and/or as a ferrite ($ZnFe_2O_4$). This selective extraction of Zn can be achieved by alkaline leaching, as metals like Zn, Pb, and Cd pass into a solution while Fe remains in a solid residue. However, these methods require very concentrated solutions, which cause some technical problems. Moreover, Zn in the ferritic form is not leached out during alkaline leaching and therefore, it is necessary to use pyrometallurgical reduction as an intermediate step. Complicated recycling of solutions and high cost of reagents are other disadvantages of alkaline leaching (Havlik et al., 2004, 2005, 2006). Recently, extensive researches have been conducted on the treatment of Zn-oxide ores by alkaline agents including NaOH (Santos et al., 2010; Chen et al., 2009) and ammoniacal solutions (Ding et al., 2010; Liu et al., 2012a; Liu et al., 2012b; Yin et al., 2010). Chen et al. (2009) studied the leaching process of refractory hemimorphite in NaOH solutions.

The alkaline leaching systems are more selective for smithsonite ores when compared to acidic leaching systems, i.e. main gangue minerals, the carbonates (calcite and/or dolomite) and the iron-(hydr) oxides (goethite and/or hematite), in the ore/tailings do not dissolve and cleaner PLSs could be obtained (Zhao and Stanforth, 2000; Qin et al., 2007; Liu et al., 2011; Rao et al., 2015). Besides, the energy consumption during EW in NaOH solutions was found to be lower when compared to EW in acidic solutions (Baroch et al., 1953; Brown et al., 1983; St-Pierre and Piron, 1986; Zhao and Stanforth, 2000; Ehsani et al., 2019). Dimanche et al. (1983) found that NaOH is less effective than H_2SO_4. In another study, it has been found that H_2SO_4 or NaOH leaching reveals better results than H_2SO_3 and NH_4OH (Frenay, 1985).

Table 10 summarizes chronologically some of the NaOH leach results. Chenlong and Youcai (2009) mechano-chemically leached ZnS using 6.0 M NaOH with $PbCO_3$ additive at 90 °C and S/L ratio 1/25 for 2 h leaching period. 86% of Zn extraction was achieved. Smithsonite ore with 20.7% Zn was leached with 5.0 M NaOH at 95 °C temperature, S/L ratio of 1/10 for 2 h duration and electrowon. 99.5% Zn extraction and Pb precipitation with Na_2S was achieved by Zhao and Stanforth (2000). The leaching of refractory hemimorphite Zn-oxide ores with 5.0 M NaOH solution was studied at 85 °C temperature for 2 h, and the leaching rate of Zn, Al, Pb, and Cd were about 73%, 45%, 11%, and 5%, respectively but that of Fe was less than 1%. (Chen et al., 2009). The activation energy was 45.7 kJ/mol and the leaching was controlled by the chemical process of the reaction.

Liu et al. (2011) produced Zn and Pb concentrates from Chinese lean-oxidized Zn ores by alkaline leaching followed by two-step precipitation using sulfides. 88% Pb and 85% Zn leaching rates were obtained with 240 g/L NaOH with less than 50 mg/L Cu, Fe, Cd, Cr, Ca, Mg, and Al dissolutions. Dissolution of As is 70 g/L, and Ca is 138 g/L. As the leaching rate is 32%. Pb was precipitated with $Na_2S.9H_2O$/Pb (molar ratio) in solution is slightly higher than 1.8 at 90 °C temperature for 60 min. 99.90% of Pb in leach solution can be precipitated with Na_2S. Zn is precipitated with 2.4 $Na_2S.9H_2O$/Zn weight ratio from Pb depleted filtrate.

Ghasemi and Azizi (2018) used 4.0 M NaOH concentration at 80 °C temperature, S/L ratio of 1/20 for low-grade oxidized Iranian ore with 5.9% Zn. Maximum 85.5% Zn and 72.2% Pb dissolution were achieved. Activation energies of both Zn and Pb were very low. Ehsani et al. (2019) also leached smithsonite ore with 23.4% Zn using 3.0 M NaOH at 25 °C for 60 min. They achieved a maximum of 70.1% Zn and 43.8% Pb extractions. Lin (2000) also tried to separate Zn and Pb from industrial wastes by using alkaline leaching. He used 5.0 M NaOH as the leaching reagent. After NaOH leaching at 25 °C for 42 h, only about 53% Zn and over 70% Pb could be recovered from the dust. Pb in the solution could be removed successively as PbS by the addition of solid Na_2S. Lead sulfide could be used directly in the Pb smelters due to the presence of a high amount of Pb content.

Another caustic soda leach technique was used by Xia and Pickles (1999a). With 8–10 M NaOH only 9% Zn-ferrite decomposed. Unlike the above technique, firstly EAF dust was roasted with NaOH at low temperatures. Therefore, Zn-ferrite in the EAF dust was converted into sodium zincate (Na_2ZnO_2) and iron oxide (Fe_2O_3) as seen in reaction (27):

$$ZnFe_2O_4 + 2NaOH = Na_2ZnO_2 + Fe_2O_3 + H_2O \quad (27)$$

After caustic roasting at about 400–450 °C, dilute 4.0 M NaOH leaching process was performed to recover Zn and Pb. According to their results, about 95% Zn and 85% Pb were recovered and also the majority of iron oxide remained in the leach residue (Xia and Pickles, 1999b). Xia and Pickles (2000) also leached Zn-ferrite and EAF dust with NaOH after microwave roasting. Microwave roasting + 8.0 M NaOH leaching achieved 90% Zn and 1.02% Pb extractions. NaOH roasting succeeded 95% Zn, 65% Pb and 89% Cd dissolutions.

Youcai and Stanforth (2000b) studied caustic leaching about of EAF dust and also smithsonite containing Zn—Pb ores. They proposed that ores should be broken into particles smaller than 0.1–0.5 mm and leached with 5.0 M NaOH solution at a 90- 95 °C temperature for 1.5 h. After filtration, the leach solution was reacted with Na_2S to separate Pb as PbS and then sent to the EW process for the production of metallic Zn. They reported that over 85% of both Zn and Pb could be recovered at this leaching condition. Youcai and Stanforth (2000a) cited that Zn-ferrite can be extracted after being fused directly with NaOH pellets and dissolved in an alkaline leaching solution. They studied with EAF dust which included a high amount of Zn-ferrite. By using magnetic separator, dust was separated into two fractions, and then magnetic fraction, primarily Zn-ferrite, was leached in 11.0 M NaOH solution for 4 h at 95 °C. Other fraction, non-magnetic including mainly ZnO, was leached with 6.0 M NaOH solution for 1.5 h at 95 °C. They stated that at the end of these trials, over 80% of the total Zn and Pb recovery was obtained.

As a result, alkaline leaching with NaOH requires high reagent consumption and cost for Zn secondaries. Fe, Al, Mg and Ca cannot dissolve in alkaline solution. Zn and Pb selectively dissolved in NaOH. There are difficulties in electrolysis. Leach residues do not meet current environmental specifications for hazardous waste due to incomplete removal of Cd and Pb. NaOH leach of ZnO followed by EW of Zn powder on stainless steel electrodes. Low grade oxidized ores can be leached with dilute NaOH, but EAF dust requires magnetic separation, NaOH roasting/fusing or microwaving for high Zn and Pb dissolutions at dilute NaOH concentration. Pb can be precipitated by Na_2S and Zn EW requires a high voltage (2.4–2.6 kWh/Kg Zn). But, NaOH is less effective than H_2SO_4 for Zn secondaries.

7.7. *Ammonia/ammonium carbonate/chloride/sulphide leach*

Ammonia is a very soluble chemical in water and it is colorless in both solid, liquid, and gaseous states. When ammonia dissolves in water, it forms ammonium hydroxide (NH_4OH). Through hydrogen bonding, two substances react with each other to form NH_4^+. Reactions between smithsonite and ammonia in aqueous solution are seen in Eqs. (28) and (29).

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad (28)$$

$$ZnCO_3 + 4NH_4OH \leftrightarrow Zn(NH_3)_4CO_3 + 4H_2O \quad (29)$$

Ammonia leaching has a limited ability to recover efficiently and reuse and partial decomposition with cheaper oxidants. Ammonia is not

Table 10
Chronological summary of the previous leach studies using NaOH as a lixiviant for Pb–Zn oxide ore/EAF dust/ZnO and metallic Zn with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
ZnS mechano-chemical leach	NaOH + $PbCO_3$ additive		86% Zn	6.0 M NaOH, 90 °C, Pb/ZnS ratio: 0.9:1, 700 rpm, L/S: 25:1, 120 min.		Chenlong and Youcai (2009)
Smithsonite Ore 20.7% Zn, 2.83% Pb, 7.5% Fe, 2.5% Mg	NaOH leach + electrowinning	Pb precipitated with $Na_2S.7\text{-}9H_2O$ S/Pb ratio 1.8	99.5% Zn	5.0 M NaOH, 95 °C, 90 min., EW: 2.4–2.6 kWh/kg Zn	0.1–0.5 mm	Zhao and Stanforth (2000)
Refractory hemimorphite Zn-oxide ore	NaOH atmospheric leach	D: 11% Pb < 1% Fe	D: 73% Zn	5.0 M NaOH, 2 h, 85oC, S/L: 1/10 Ea: 45.7 kJ/mol	65–76 µm	Chen et al. (2009)
Lean oxidized Zn ore, Mengzi-China 17.3% Zn, 4.1% Pb, 3.71% Fe, 0.11% As	NaOH leaching + 2 step $Na_2S.9H_2O$ precipitation	85% Pb leaching rate 99.9% Pb precipitation	88% Zn leaching rate	90 °C, 120 min., L/S = 5:1, 240 g/L NaOH $1.8Na_2S.9H_2O$/Pb, 90 °C, 60 min. Pb precipitate $2.4Na_2S.9H_2O$/Zn, 90 °C, 180 min., Zn precipitate	0.2 mm	Liu et al. (2011)
Iranian low-grade oxidized ore Goshfil mine tailings (5.91 ZnO, 5.32 PbO)	NaOH leach (0.4–5.0 M) (3 g solid)	72.15% Pb	85.52% Zn	4.0 M NaOH, L/S = 20:1, 80 °C, 500 rpm for Pb and 400 rpm Zn E_a: 13.6 kJ/mol for Pb 13.92 kJ/mol Zn	− 150 µm	Ghasemi and Azizi, 2018
Smithsonite ore, goethite, calcite 23.4% Zn, 1.9% Pb, 18.5% Fe,7.4% CaO	NaOH leach	43.8% Pb	70.1% Zn,	1–4 M NaOH, 25–90 °C, S/L: 0.075–0.15 kg/L, t: 30–240 min Optimum: 3.0 M NaOH, 25 °C, 60 min.	d_{80}: 124.5 µm	Ehsani et al. (2019)
Industrial waste, steelmaking dust	NaOH leach for Zn + PbS separation with Na_2S + PbS smelter	D: 70% Pb	D: 53% Zn	5.0 M NaOH, 25 °C, 42 h		Lin (2000)
Zinc ferrite	NaOH leach		9% Zn ferrite decomposed	8–10 M NaOH; 60–93 °C, 120–180 min	− 74 µm	Xia and Pickles (1999a)
EAF dust (ZnO and Zn ferrite)	EAF dust + NaOH roasting EAF dust + 3% H_2O + NaOH roasting	G: 65% Pb G: 85% Pb	D: 95% Zn; 89% Cd D: 65% Zn; 89% Cd	Roasting in 400 °C, 90 min at 90 °C in 100 ml of a 4 M NaOH solution. NaOH + H_2O	− 28 mesh	Xia and Pickles (1999b)
EAF dust (ZnO and Zn ferrite)	Microwave + NaOH leach	G: 1.02% Pb	D: 90% Zn	8 M NaOH, 180 g/l solid		Xia and Pickles (2000)
EAF dust	NaOH leach		D: 70%	Fusion at 350 °C for 1 h, 5.0 M NaOH, 42 h		Youcai and Stanforth (2000b)
EAF dust	Mag. Sep. + NaOH fusing + NaOH leach	> 80% Pb	> 80% Zn	Mag fraction (Zn-ferrite) leached with 11 M NaOH,4 h, 95 °C Non-mag fraction (ZnO) 6.0 M NaOH, 1.5 h, 95 °C		Youcai and Stanforth (2000a)

Table 11
Chronological summary of the previous leach studies using ammonia/ammonium salts as a lixiviant for Pb−Zn oxide ores with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
$ZnCO_3$ + ($Zn_4Si_2O_7(OH)_2.H_2O$) + H_2O ore Angoran Mines-Iran	$(NH_4)_2CO_3$ leach		D:92% Zn R: 88.2% Zn low Fe and Pb	35–75 °C, 300–800 rpm, 2–4 M $(NH_4)_2CO_3$, 30–90 min., pH: 9–11 45 °C, 300 rpm, 3 M $(NH_4)_2CO_3$, 45 min, pH: 10, 45 °C, 300 rpm, 2 M $(NH_4)_2CO_3$, 45 min, pH: 11	−200 mesh	Moghaddam et al. (2005, 2005a)
Smithsonite ore (30.28% Zn)	NH_4Cl leach		D: 91% Zn	5.0 M HN_4Cl, 90 °C, 240 min., S/L: 1/10	84–110 µm	Ju et al. (2005)
Hemimorphite ore from Lanping, China, 49.8% Zn, 0.38% Fe	Mechanochemical activation NH_4OH and NH_4Cl leach		Unmilled: 80.5% Zn Milled: 88.2% Zn	NH_4OH and NH_4Cl ratio 2/1, pH: 10, 30 °C, 25 rpm, 180 min. Planetary milling at 400 rpm, 15–180 min.	< 70 mesh	Yuan et al. (2010)
Low-grade complex ore with 13% Zn	NH_3 + $(NH_4)_2CO_3$ leach NH_3 + NH_4Cl leach		D: 43.1% Zn	5.0 M NH_3 + NH_4Cl, 30 min., S/L ratio: 1/4		Ma et al. (2011)
Willemite (Zn_2SiO_4) 52.28% Zn (roasted hemimophite)	$(NH_4)_2SO_4$ + NH_3 + H_2O leach		G: 52,28%	Silica gel formed	−98 µm	Liu et al. (2012)
Hemimorphite ($Zn_4(Si_2O_7)(OH)_2.H_2O$	$(NH_4)_2SO_4$ leach	R: 11.20 mmole/kg Zn	25 °C; $(NH_4)_2SO_4$: 3.70 mol/kg			Li et al. (2013)
Oxide-sulphide Zn ore	Microwave heating + Na_2O_2 + NH_3/NH_4Cl leach		D: 82.06% Zn	25% Na_2O_2 + NH_3/NH_4Cl ratio: 1/1, NaClO, 1 h		Yang et al. (2016a, 2016b)
Zn oxide ore, Kashi, China	NH_3 + $(NH_4)_2SO_4$ + H_2O leach		D: 91% Zn	2.0 M $(NH_4)_2SO_4$, 4.0 M NH_3, 40 °C, 300 rpm, L/S: 4, 3 h	d_{80}: −74 µm	Song et al. (2016)
Low-grade and multiphase ZnO ore, China 6.01% Zn, 31.8% SiO_2, 12.4% (MgO + CaO), > 8% Fe	$(NH_4)_2SO_4$ + NH_3 and Na-citrate		D: 96.91% Zn	S/L: 1/10, 25 °C, 300 rpm, $NH_3/(NH_4)_2SO_4$: 2:1 0.2 M Na-citrate		Yang et al. (2017)
Low-grade oxidized Zn ore, China 1.81% Zn, 0.26% Pb, 1.49% Fe, 0.37% S	$(NH_4)_2SO_4$-NH_3-H_2O leach		 D: 91.8% Zn	4–9 M ammonia, 0/8–8/8 ammonia/total ammonia, L/S = 2–7, 0.5–4 h, 20–60 °C, 0–600 rpm Optimum: 2.0 M $(NH_4)_2SO_4$, 2.0 M NH_3, 40 °C, S/L: 1/4, 30 min, 300 rpm, 3 h	−74 µm 80%	Song et al. (2018)
Low-grade Zn oxide ore Yunnan, China, 19.5% Zn, 2.3% Pb	NH_3-NH_4Cl-H_2O leach		D: 92.1% Zn	Total ammonia: 7.5 mol/L, ammonium/ammonia: 2: 1 80 °C, 60 min., E_a: 7.057 kJ/mol	−69 µm	Wang et al., 2008
Low-grade Zn oxide ore Lanping, Yunnan, China, 10% Zn, 7.13% Pb, 21% Ca	NH_4Cl + NH_3 + nitriloacetic acid (NTA) leach		D: 90.3% Zn	200–400 rpm, 0.05–0.2 M NTA, 2–60 min., L/S: 10–40 mL/g, 30–60 °C Optimum: 0.1 M NTA, S/L: 1/20, 40 °C, 400 rpm, Ea: 22.3 kJ/mol	61–74 µm	Rao et al. (2015)
Hemimorphite ore, Yunnan, China 98.2% $Zn_4Si_2O_7(OH)_2.H_2O$	NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4HCO_3 and NH_4Cl		D > 90%	$NH_4HCO_3 < NH_4NO_3 < (NH_4)_2SO_4 < (NH_4)_2CO_3 < NH_4Cl$, NH_3/NH_4: 0.5 E_a: 57.6 kJ/mol		Ding et al. (2010)

inherently benign. It has a lower capacity of leaching of acidic compounds. The use of ammonia is limited due to its high evaporation. It may have potential at hydrostatic pressures associated with in-situ leach (ISL). There is a difficulty in maintaining high concentrations of dissolved NH_3.Table 11 shows the chronological summary of the previous leach studies using ammonia/ammonium salts as a lixiviant for Pb—Zn oxide ores. In these studies, smithsonite, willemite and hemimorphite ores alone; smithsonite + hemimorphite and mixed oxide, and sulfate ores leached with NH_3; ammonium carbonate, chloride, sulfate, and nitrate salts alone or NH_3 + ammonium carbonate, chloride, sulfate salts together were used. In order to accelerate Zn leaching microwave heating/roasting, mechano-chemical activation, strong oxidant N_2O_2 addition, Na-citrate and NTA additions were tested.

Moghaddam et al. (2005) determined the optimum conditions for the leach Angoran non-sulfide Zn ores containing 35.1% Zn with high SiO_2 content (smithsonite-hemimorphite-quartz) in ammonium carbonate medium using the Taguchi experimental design method. They obtained optimum conditions from this study were T: 45 °C, N: 300 rpm, C: 3.0 M, t: 45 min, and pH: 10. Under these conditions, the optimum dissolution of Zn was about 92%. To minimize Fe. and Pb dissolutions while keeping the dissolution of Zn, three series of experiments, in alternative conditions, were performed. Total optimum conditions that obtained from this study were T: 45 °C, N: 300 rpm, C: 2 M, t: 45 min, and pH: 11. They also found that when the ore is calcined at a temperature around 800 °C, the rate of chemical reactions was increased. No parameter had a meaningful effect for the dissolution of Zn and Pb statistically; however, pH and the $(NH_4)_2CO_3$ concentration each have a significant effect on Fe dissolution. Ju et al. (2005) conducted a study with an ore containing 30.3% Zn to observe dissolution kinetics of smithsonite in ammonium chloride. They examined the effect of particle size, reaction temperature, and NH_4Cl concentration. As a result of their study, 91% Zn was extracted using 84–110 μm sized particles at 90 °C temperature for 240 min. Duration with 5.0 M NH_4Cl solution. In all experiments, S/L ratio was taken as 1:10.

Yuan et al. (2010) demonstrated that both dry milling and mechanochemical milling can enhance the Zn extraction rate and shorten the leaching time of hemimorphite in NH_4OH-NH_4Cl leaching medium. They used 49.8% Zn and 0.38% Fe containing hemimorphite ore from Lanping in China. Mechano-chemical activation was performed with a planetary mill at 400 rpm for 15–180 min. Zn extraction of hemimorphite at the solution concentration of 5.0 M NH_4Cl, 2.5 M $NH_3{\cdot}H_2O$, S/L ratio of 1/12 (g/L) significantly enhanced by mechano-chemical activation. Mechanical activation significantly accelerated the process of ammonia leaching. There was a straightforward increase in the leaching rate and the recovery of Zn with a prolonged activation time. After leaching for 6 h, Zn extraction of 180 min. Milled sample reached 88.2%, whereas only 80.5% was achieved for the unmilled sample. In the meantime, mechanical activation shortened the leaching time dramatically. It only took activated samples 3 h to reach 80% but 6 h for the non-activated ones.

Effects of leaching time, alkaline concentration, temperature, and S/L ratio on the extraction of low-grade complex ore with 13% Zn were investigated by Ma et al. (2011). As leaching reagents, NH_3-$(NH_4)_2CO_3$ and NH_3-NH_4Cl were used. The tests were carried out with 50 g of sample in a flask. At the end of the experiments maximum of 43.1% Zn extraction was achieved with 5.0 M NH_3-NH_4Cl solution at 30 °C temperature for a 3 h period with 4:1 S/L ratio. Liu et al. (2012) studied with willemite (Zn_2SiO_4) containing 52.28% Zn. The test sample was produced from the roasting of hemimorphite and the study was conducted to investigate the dissolution kinetics of willemite in $(NH_4)_2SO_4$-NH_3-H_2O system. Since the dissolution of silica is rather low in $(NH_4)_2SO_4$-NH_3-H_2O system and formation of silica gel, the leaching rate of willemite was low. But increasing in temperature, S/L ratio and ammonia concentration increased the extraction rate. Li et al. (2013) also conducted a study to investigate the solubility of hemimorphite in ammonium sulfate solution ($(NH_4)_2SO_4$). All the experiments were conducted at 25 °C with 6 g samples. Solubility of Zn increased from 4.53 mmole/kg to 11.50 mmole/kg with an increase in $(NH_4)_2SO_4$ concentration from 0.55 mol/kg to 3.70 mol/kg.

Yang et al. (2016a, 2016b) proposed a novel combination of microwave roasting assisted phase transformation and leaching in NH_4Cl solution to recover Zn from a mixed oxide-sulfide Zn ore, and indicated both microwave heating and the strong oxidant Na_2O_2 addition level having significant effects on phase transformation and Zn leaching. The Zn leaching rate reached 82.1% under the microwave heating by adding 25% Na_2O_2 in an NH_4Cl medium with a total ammonium concentration of 7.5 M and 1:1 NH_3/NH_4Cl molar ratio. Adding of NaClO as a lixiviant and 1 h leaching time was required. In contrast, the Zn leaching degree for the ore samples roasted in a traditional electric resistant furnace is only 30.6%. Moreover, at the same oxidation degree, the total energy consumption by the proposed process is 0.78 kWh/kg·ore, which is lower than that by traditional heating.

Song et al. (2016) determined the leaching performance of low-grade zinc oxide ore from China in the system of NH_3-$(NH_4)_2SO_4$-H_2O. The mixed oxide-sulfide ore contained 60.2% amorphous smithsonite ($ZnCO_3$), 6.6% zinc silicate (Zn_2SiO_4), and 2.8% ZnS. Zn content was 1.81%, Pb 0.26%, and total Fe 1.49%. The optimum conditions for leaching were confirmed, i.e. the grinding fineness is 80% -74 μm, the concentration of $(NH_4)_2SO_4$ is 2.0 M, the concentration of NH_3 is 4.0 M, the reaction temperature is 40 °C, the ratio of L/S is 4:1; the stirring rate is 300 rpm and leaching time is 3 h. Ultimately, the leaching rate of Zn could reach more than 91.76%. Yang et al. (2017) determined the role of sodium citrate in leaching of low-grade and multiphase Zn-oxide ore containing 6.01% Zn in NH_3-$(NH_4)_2SO_4$ solution at 25 °C temperature and S/L ratio 1/10. The leaching rate can reach 96.91% with a cit^{3-} concentration of 0.2 M. Once above it, the diffusion rate of Zn would decrease, which causes the dropping of Zn leaching.

Song et al. (2018) leached low grade oxidized Zn ore containing 1.8% Zn with 2.0 M $(NH_4)_2$, 2.0 M NH_3 at 40 °C, S/L ratio of 1/4 for 30 min. Period. 91.8% of Zn extraction was achieved. Another research carried out by Wang et al. (2008), NH_3-NH_4Cl was used to recover low-grade Chinese Zn oxide ore (19.5% Zn, and 23% Pb). In this study, the effects of particle size, temperature, and concentration of $NH_{3\ -}\ NH_4Cl$ were examined. In all of the experiments, S/L ratio was taken as 1:10. The results showed that extraction efficiency decreased with the increase in particle size and optimum particle size was determined as 69 μm. The optimum temperature for leaching was determined as 80 °C although increasing temperature from 40 to 80 °C does not have a significant increase by more than 3%. Total ammonia was 7.5% M and the optimum $NH_{3\,-}NH_4Cl$ ratio was determined as 2:1. The maximum Zn dissolution was 92.1%.

Rao et al. (2015) leached low-grade Zn ore from China containing 7.0% Zn using 0.1 M (NH_4Cl + NH_3 + NTA) at 40 °C and S/L ratio of 1/20. Zn dissolution was found to be 90.3%. The result of leaching kinetics showed that the leaching process was controlled by interface transfer and diffusion through the product layer with the activation energy of 22.3 kJ/mol. Ammonia and ammoniacal solutions have been used extensively for other Zn minerals. In a study carried out by Ding et al. (2010), Zn extraction from hemimorphite ($Zn_4(Si_2O_7)\ (OH)_2.H_2O$) was aimed considering the effects of ammonia-ammonium ratio, ammonia concentration, temperature, and ammonia ions. Highest Zn recovery was observed at an ammonia-ammonium ratio of 0.5. Effects of NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4HCO_3 and NH_4Cl as ammonia ions and according to the results, the most effective one was determined as NH_4Cl. Order of ammonia ions on the basis of effectiveness is $NH_4HCO_3 < NH_4NO_3 < (NH_4)_2SO_4 < (NH_4)_2CO_3 < NH_4Cl$. Also with the increase in temperature and NH_4Cl concentration, the extraction rate of Zn was increased visibly.

Blanco et al. (1999) also studied the leaching behavior of Zn residue when using $(NH_4)_2CO_3$ + NH_3 media. They developed an equation for the dissolution of Zn as a function of temperature, pH and solids concentration. Considering the equation, the optimum leaching parameters to achieve maximum Zn recovery should be as follows;

- Temperature is as high as possible but less than the boiling point of the solution.
- pH is as high as possible. (Maximum pH limit 11 since NH_3 solution was buffer solution)
- Solids concentration used will determine the capacity of the process.

It was stated that the maximum Zn recovery that could be obtained was 95% from Zn waste materials.

The leaching of Zn oxide or silicate ores in alkaline ammoniacal media is a subject of considerable interest and many excellent articles have been published. As a result, alkaline ammonia + ammoniacal salt leaching achieved Zn dissolutions between 43% and 97% for oxidized, mixed and silicate type of Zn—Pb ore from different countries. Silica gel may occur from willemite or hemimorphite ore leaching. Microwave roasting and mechanochemical activation with alkaline leaching performed enhanced Zn leaching than conventional milled ores. Na_2O_2, NaClO, Na-acetate and NTA addition is helpful for high Zn dissolution. Ammonium salts effectiveness for Zn leaching is $NH_4HCO_3 < NH_4NO_3 < (NH_4)_2SO_4 < (NH_4)_2CO_3 < NH_4Cl$. However, high evaporation rate and bad smell are some disadvantages. The mechanical activation of ores/wastes represents nowadays an important contribution to different fields of solid processing technology. In extractive metallurgy, activation by intensive grinding decreases the reaction temperature in pyrometallurgy, increases leaching kinetics in hydrometallurgy and leads to alternative products and potential mitigation of the environmental impact, which is becoming increasingly important with time (Godočíková et al., 2002).

7.8. Acidic brine (NaCl) leach

Chloride systems in hydrometallurgy have been used for the treatment and recovery of precious metals for several years. In the past few years, the application of chloride hydrometallurgy for the processing of non-ferrous metals in large-scale mineral processing has been considered seriously. Different industrial wastes containing Pb have been subjected to various recovery methods. However, brine leaching (leaching by chloride solutions using NaCl, $MgCl_2$, $CaCl_2$, and $FeCl_3$) is the most recognized and widely used recovery method. The main advantages of chloride-based leaching systems over sulfate-based ones are (Godočíková et al., 2002):

- Chloride leaching is performed at moderate temperatures solubilizing all metals.
- Pyrite (FeS_2) is not attacked by chloride salts.
- Most metal chlorides are considerably more soluble than the corresponding sulfate salts.
- Easy regeneration of the leaching reagents in recycling processes.
- Most sulfide sulfur in the mineral is converted to the elemental sulfur.

However, ferric chloride solutions are corrosive to most metals, although this problem may be readily overcome with the use of plastic materials.

The effectiveness of brine leaching is based on the formation of complex chlorides of Pb in concentrated chloride solutions. $PbSO_4$ is insoluble in water; but, soluble in saturated chloride solutions acidified by HCl, H_2SO_4 or chlorine water. Nevertheless, it can be seen that the addition of chloride can lower the solubility of Pb. However, in very chloride rich media, the Pb can become soluble (Habashi, 1969). Brine leaching is based on the formation of complex chlorides of Pb and Zn. For recovery of Pb from Zn plant residue, several methods have been developed. For example, conversion of $PbSO_4$ in residue to lead chloride ($PbCl_2$) by leaching with NaCl or lead hydroxide, ($Pb(OH)_2$) by leaching with NaOH or lead carbonate ($PbCO_3$) by leaching with sodium carbonate (Na_2CO_3) has been investigated in Pb recovery. According to Abdollahi et al. (2006) considering these three methods, NaCl can be selected as the most suitable leachate due to the low cost of salt without the requirement of additional investment and any threat to the environment.

During brine leaching, the $PbSO_4$ forms sulfate ions and $PbCl_4^{2-}$, according to the reactions (30) and (33) (Sinadinović et al., 1997).

$$PbSO_4(s) + 2Cl^- \leftrightarrow PbCl_2(s) + SO_4^{2-} \quad (30)$$

$$PbCl_2(s) + Cl^- \leftrightarrow PbCl_3^- \quad (31)$$

$$PbCl_2(s) + 2Cl - \leftrightarrow PbCl_4^{2-} \quad (32)$$

$$PbCl_3(s) + Cl^- \leftrightarrow PbCl_4^{2-} \quad (33)$$

The solubility constant (K_{sp}) of $PbSO_4$ is $1.8*10^{-8}$ is lower than $PbCl_2$ ($1.2*10^{-5}$). Solubility of $PbCl_2$ at room temperature is 9.9 g/L (Habashi, 1969). An increase of Pb concentration above this amount is possible by the formation of complex ions having higher solubility, according to Eq. (33) (Sinadinović et al., 1997). (Eqs. (34)–(37)) depict the interactions by which Pb forms complex ions in concentrated chlorine solutions:

$$Pb^{2+} + Cl^- \leftrightarrow PbCl^+ \quad K_1 = 12.59 \quad (34)$$

$$PbCl^- + Cl^- \leftrightarrow PbCl_2 \quad K_2 = 14.45 \quad (35)$$

$$PbCl_2 + Cl^- \leftrightarrow PbCl_3^+ \quad K_3 = 3.98 * 10^{-1} \quad (36)$$

$$PbCl_3^- + Cl^- \leftrightarrow PbCl_4^{2+} \quad K_4 = 8.92 * 10^{-2} \quad (37)$$

The complexation equilibrium between chloride and Pb ions may be affected by chloride ions concentrations in the solution, as the solubility of $PbSO_4$ is lower than $PbCl_2$.

Table 12 shows a chronological summary of the previous leach studies using iron chloride as a lixiviant for Pb—Zn concentrates with tested ranges and optimal conditions. The Terra Gaia process is based on the dissolution of both ZnO and $ZnFe_2O_4$ in $FeCl_3$-HCl media at an elevated temperature of 175 °C (Mcelroy and Murray, 1996). The steelmaking EAF dust containing 18.5% of Zn and 8.84% of Pb is used in this process. The EAF dust is stirred by a $FeCl_3$ solution produced by the reaction of scrap Fe with chlorine gas. It is then injected into an autoclave at a temperature of 175 °C. Oxygen is also injected resulting in the oxidation of $FeCl_2$ to $FeCl_3$, which hydrolyzes extensively at 175 °C and also produces HCl. The generated HCl attacks both the ZnO and $ZnFe_2O_4$ constituents, and any residual $FeCl_3$ reacts rapidly with ZnO. Presumably, the abundant Fe_2O_3 in the EAF dust passes through the autoclave largely unaffected.

Godočíková et al. (2002) leached Slovak Cu-Pb-Zn sulfide ore after mechano-chemical activation using 1.0 M $FeCl_3$ and 0.2 N HCl at pH below 1.0. They found that the mineral dissolution order was PbS > $CuFeS_2$ > ZnS. Leclerc et al. (2003) used $FeCl_3.6H_2O$ to extract Zn from Zn-ferrites. All Zn is extracted after 8 h treatment at 150 °C with a molar ratio of $FeCl_3.6H_2O/ZnFe_2O_4$ of 10. Zn recovered as ZnCl, which can easily dissolve by water leaching and Fe remained as αFe_2O_3, which can be recycled to steel making process.

7.9. EAF dust leach

Due to the content of heavy non-ferrous metals and high dust levels during disposal, EAF dust is classified hazardous. There are three main reasons for its processing: The first reason is the recovery of Fe concentrates suitable as a raw material in the production of steel or pig Fe. The second reason is the Zn metal or salts recovery for commercial products. The current February 2020 price of Zn on the LME (London Metal Exchange) is 2200–2222 $/ton and the market price of Zn-salt ($ZnSO_4 \cdot 7H_2O$) is in the range of 300–1500 $/ton (www.alibaba.com, 2020). Content of Zn in EAF dust is in the range of 8–37%, which is

Table 12
Chronological summary of the previous leach studies using iron chloride as a lixiviant for Pb—Zn concentrates with tested ranges and optimal conditions.

Material used	Conc. method used	Pb dissolution	Zn dissolution	Optimum reagents/dosages	Part. size	Reference
EAF dust ($ZnO + ZnFe_2O_4$) 18.5% Zn, 8.84% Pb	$FeCl_3$-HCl (Terra Gaia Process)			$FeCl_3$, 175 °C autoclave, O_2 injection		Mcelroy and Murray (1996)
Cu-Pb-Zn sulphide conc., Slovakia 3,57% Zn, 4.08% Pb, 20.06% Fe, 0.93% Cu	Mechanical activation $FeCl_3$ + HCl leach		$PbS > CuFeS_2 > ZnS$	Mechanochemical activation in ball mill attritor, 600–1200 rpm, 15–60 min. 1.0 M $FeCl_3$ + 0.2 M HCl, 50–90 °C, $pH < 1$, 460 rpm, 30 min.	< −71 µm	Godočíková et al. (2002)
Zn ferrite	$FeCl_3.6H_2O$		R: 100% Zn	8 h, 150 °C, $FeCl_3.6H_2O/ZnFe_2O_4$: 10		Leclerc et al. (2003)

significantly higher than that in primary raw Zn ores (5–15%) in the world and Fe content is up to 45% (Table 13) (https://www.zinc.org/basics/zinc_recycling). The third reason is to reduce the amount of hazardous waste and/or its transformation to non-hazardous waste, i.e. saving disposal costs. In general, there are three basic ways of processing EAF dust: pyrometallurgical, hydrometallurgical and a combined method. A product of pyrometallurgical processing is usually represented by impure ZnO, which has minimal commercial value (1500–1800 $/t) (www.alibaba.com, 2020). This product has to be further processed by the hydrometallurgical method to obtain high purity metallic Zn. Hydrometallurgical processes are mainly based on acid or alkaline leaching.

A mineral acid is an acid derived from one or more inorganic compounds. All mineral acids form H^+ ions and the conjugate base when dissolved in water. Mineral acids tend to be very soluble in water and have corrosive properties. Mineral acids have been mainly used in a dilute acid form in hydrometallurgical pretreatments/processes. In 2020, mineral acid prices change in the following order HCl (170–250$/t) > H_2SO_4 (190–400 $/t) > HNO_3 (250–400$/t) (www.alibaba.com). Inorganic acids, such as H_2SO_4, HNO_3, and HCl, have previously been intensively investigated for selective dissolution of metals from the EAF flue dust (Montenegro et al., 2013, 2016; Cruells et al., 1992; Caravaca et al., 1994; Langová et al., 2009). Of the three inorganic acids, again H_2SO_4 is the most extensively studied and promising option (Oustadakis et al., 2010; Havlik et al., 2005; Montenegro et al., 2013, 2016; Cruells et al., 1992). While positive results have been observed, most inorganic acids would come at a large cost due to high consumption rates. HNO_3 and HCl acids, for example, would require water-intensive washing of nitrates and chlorides, respectively, to avoid these species ending up to furnace (Halli et al., 2017).

Secondary Zn recovery from the EAF dust was studied using either H_2SO_4 or NaOH as the leaching media (Shawabkeh, 2010; Tsakiridis et al., 2010). The motivation for the extensive research into EAF dust leaching is mainly the prospect of recycling dust into the furnace with as low Zn content as possible (Stafanova and Aromaa, 2012). Zn is known to dissolve in most acids as a result of its low reduction potential, which makes it dissolution thermodynamically favorable (Ruiz et al., 2007; Suetens et al., 2014; Dutra et al., 2006; Kukurugya et al., 2015; Mehmet et al., 2015; Stafanova and Aromaa, 2012; Shawabkeh, 2010; Oustadakis et al., 2010; Tsakiridis et al., 2010; Havlik et al., 2005; Li et al., 2015; Havlik et al., 2006; Leclerc et al., 2003; Irannajad et al., 2013). Various hydrometallurgical routes (i.e. HCl and NH_3-$(NH_4)_2CO_3$) for treating EAF dust were also tested (Baik and Fray, 2000). High reagent consumption, low Zn recovery, and toxic leach residue, which doesn't meet current environmental specifications, were some disadvantages. Treating EAF dust should meet the objectives of detoxification of dust and maximizing the recovery of metal values.

Zn should be dissolved selectively with minimum Fe and Pb co-dissolution at ambient pressure and temperature as much as possible. H_2SO_4 easily dissolve Zn without leaching Pb and Ca, which precipitates as $PbSO_4$ and $CaSO_4.2H_2O$. However, the downside to this is that most acids also co-dissolve large amounts of undesirable Fe, resulting in poor selectivity between Zn and Fe. Nevertheless, with very low H_2SO_4 concentrations (0.1 M) complete Zn recovery has been obtained with the added advantage that a minimum Fe is transferred into the solution (Havlik et al., 2006). Alkaline leaching offers the potential advantage that the Fe remains largely insoluble, and the effort to develop alkaline leaching technologies for EAF dust proceed. Such processes are limited, however, by their inability to recover Zn from Zn-ferrite unless a reducing roast is carried out first. Both approaches result in halide-containing solutions. This kind of processing is difficult. Because of the high chloride content of EAF dust, chloride-based processing technologies could offer several advantages (Havlik et al., 2004).

Jha and Duyvesteyn (1985) have explored the H_2SO_4 leaching of the U.S. steel plant dust, both at atmospheric and elevated pressures. The results showed a Zn leaching efficiency of between 32 and 76% by using

Table 13
The most common phases of metals present in previously used EAF dust (compiled from Kukurugya et al. (2015)).

Zn	Fe	Ca	Pb	Cr	Mn	Si	Cd	Ni	Cu	Reference
22–**37**	12–24	4,30	2,70							Díaz and Martín (1994)
20,90	27,80									Havlik et al. (2004)
33,00	0,90	0,90	2,17	0,20	2,30			0,10	0,20	Havlik et al. (2006)
18,96	32,09	3,42	2,05	0,12	1,68	2,50	0,05	0,07	0,30	Sedláková et al. (2006)
8,08	**45,24**		2,12				0,04			Langova et al. (2007)
28,47	36,46	0,90	4,05	0,00	1,95	1,12	0,07	0,04	0,35	Martins et al. (2008)
17,99	45,00	3,85	0,20	0,46	1,94	0,42	0,01	0,03	0,14	Sun et al. (2008)
29,10	24,00	1,73	3,64	0,14	4,11	0,34	0,11		0,25	Shawabkeh (2010)
8,00	45,00	3,70	2,10				0,04			Langová and Matýsek (2010)
17,05	27,23	**4,42**	1,28	0,81	1,03		0,09			Havlik et al. (2012)
20,32			**5,99**	0,13			0,04	0,02		Oustadakis et al. (2010)
33,16	17,89	3,40	1,64	0,23						Halli et al. (2017)
33,16	17,89	3,40	1,64	0,23						Hamuyuni et al. (2018)

the autoclave leaching (2 h, 270 °C, 2.0 M H_2SO_4) and 53–79% by using atmospheric leaching (4 h, 70 °C, 2.0 M H_2SO_4). High leaching Zn efficiencies around 97% were achieved when a high concentration of 4.0 M H_2SO_4 was used. Halli et al. (2017) found that metal dissolution orders for EAF dust using HNO_3, H_2SO_4, NaOH, CA, OA, AA and FA lixiviants as follows:

$HNO_3 \rightarrow Cr > Zn > Mn > Fe > Pb$

Citric Acid → $Zn > Cr > Pb > Mn > Fe$

Oxalic Acid → $Cr > Fe > Mn > Pb > Zn$

$H_2SO_4 \rightarrow Cr > Mn > Fe > Zn > Pb$

$NaOH \rightarrow Zn > Pb > Cr > Mn > Fe$

Acetic Acid → $Pb > Zn < Cr > Mn > Fe$

Formic Acid → $Mn > Cr > Pb > Fe > Zn$

7.10. Leaching of hydrometallurgical residues

The recoveries of Ag, Cr, Cu, In, Pb, Zn, especially Pb and Zn, from the non-ferrous solid wastes were previously investigated through pyrometallurgy and/or hydrometallurgical routes separately and in combination (Raghavan et al., 2000; Hoffmann et al., 2007; Abdel Basir and Rabah, 1999; Li et al., 2006; Turan et al., 2004; Abdollahi et al., 2006; Ruşen et al., 2008; Moradkhani et al., 2009). The Pb-bearing materials derived from hydrometallurgical processing of Zn concentrate can be reacted with Na_2S solution to recover Pb (90%–95%) and Ag (60%–70%) (Raghavan et al., 2000). Significant amounts of Pb and Zn could also be recovered from Zn plant residues using calcination with H_2SO_4 and two-stage water and brine (NaCl) leaching of the residual solids (Turan et al., 2004). With leaching conditions of 150 g/L H_2SO_4 (pH: 2.5), 80–95 °C and pulp density of 120 g/L, 69.3%–71.9% Zn was extracted from ZPR in 60–120 min (Ruşen et al., 2008; Moradkhani et al., 2009); up to 98.9% of Pb was extracted after 10 min. of treatment at 300 g/L of NaCl concentration, 95 °C, pulp density of 50 g/L with 30 mL/L HCl addition (Ruşen et al., 2008); while Pb extraction was 89.43% at pH 1.0, 300 g/L of NaCl concentration, 37 °C and stirring speed of 400 rpm. After 30 min. Leaching time (Moradkhani et al., 2009). Brine leaching, using NaCl, $MgCl_2$ or $CaCl_2$ as reagents, is generally the recognized method for the recovery of metal from non-ferrous solid wastes (Raghavan et al., 2000; Turan et al., 2004; Abdollahi et al., 2006; Ruşen et al., 2008; Moradkhani et al., 2009; Sinadinović et al., 1997). During the Zn smelting process, Pb is accumulated in the residues, which can be regarded as an alternative source of Pb mineral.

8. Summary

Clean, safe and profitable solution to the Zn secondary treatment is gaining importance. This paper covered the state-of-art recycle technology for Zn-containing secondary materials from the Zn and/or Fe-steel production/processing industry wastes/by-products, such as Zn fly/bottom ash, Zn bottom dross, EAF dust, Waelz Zn leach residue, Zn scrap, brass slag, dross, sludge, Zn flotation tailings from oxidized Pb—Zn ores, etc. These waste materials contain different levels of impurities depending on their source. Zn content in such materials ranges from 5 to 15% in ores/flotation tailings, 8–37% in EAF dust, 60–75% in galvanizing ash, 35–50% in Cu—Zn oxides from foundries, and up to 92–95% in Zn dust (oversprays and galvanizing dross).

The Zn recovery processes for Zn secondaries are normally conventional pyrometallurgy and hydrometallurgy. Pyrometallurgy is not trouble-free process for Zn secondaries. Impurities impair performance and cause serious environmental problems. Pyrometallurgical treatment is applied for high-Zn contained residues (i.e. electrothermic process); medium-Zn contained residues (i.e. imperial smelting furnace); and low-Zn residues (QSL, Waelz, HTR and SKF plasma, tetronic and electrothermic process). Pyrometallurgical processes for the treatment of Zn-containing residues have undergone more development. Technical and economical study of some possible processes shows that the hydrometallurgical process has advantages over other pyrometallurgical and conventional ways of treatment in the following aspects: higher Zn recovery, better plant flexibility, better Zn quality, better ratio profit/investment, no problems regarding F, Cl and Mg, and environmentally safer. Hydrometallurgy has been demonstrated as a complete reliable process and gaining importance everyday (Díaz and Martín, 1994).

A major drawback of the pyrometallurgical method is high energy requirement and need of dust collecting/gas cleaning system. The presence of chloride and fluoride salts in the dust causes severe corrosion problems and necessitates use of expensive alloys as materials of construction. For pyrometallurgical process, treatment of high grade secondaries is more economical. Generally large scale operations with high capital investment are required. Separation of chemically similar materials is not possible. Reaction rate is fast due to higher temperature. Handling of material is problematic. The hydrometallurgical processes are more environmentally suitable and economical to treat even low Zn containing materials on small scale. It can process Zn secondaries containing different impurities. Reaction rate is slow due to low process temperature. Handling of materials is easily handled by pipelines (Jha et al., 2001). For hydrometallurgical process low reagent consumption, temperature, time and impeller speed are targeted at high S/L ration. pH, particle size and oxidant addition significantly affects leaching kinetics, operation costs and impurity co-dissolution.

Based on this comprehensive technical review made on the hydrometallurgical processing of Zn secondaries/wastes, the following points may be highlighted. These waste materials are used for the recovery of Zn or sometimes disposed-off as a landfill. In order to recover secondary Zn, the hydrometallurgical processes have been considered which are eco-friendlier and produce residues suitable for safe disposal as Zn could be selectively dissolved in suitable lixiviants leaving other impurities in the residue. Hydrometallurgical processing is effective and flexible or treating such materials as it can control the different levels of impurities. Depending on the nature and composition of the secondary, a suitable lixiviant could be selected to dissolve the desired valuable metals leaving the gangue in the residue. The hydrometallurgical route normally has lower energy consumption and less CO_2 gas emission than a high-temperature smelting route for Zn secondaries. A suitable hydrometallurgical and the environmentally friendly process should be developed to replace the currently used practices for recycling mine/metallurgical wastes via smelting.

The widely used methods for treating and recycling Zn involve mainly acid, ammonia or alkaline leaching process. A wide series of scientific research has been carried out on the treatment of zinc sulfide and oxide ores, tailings, metallurgical industry wastes and generally secondary source by these leaching reagents on bench scale. These studies indicate that at present, dilute H_2SO_4 leaching is considered as the most viable and versatile of the available process for Zn secondary resources which is adopted by many commercial Zn plants. However, for the low-grade Zn oxide ores/tailings, especially those containing high contents of Fe, Ca and Si, the excessive acid consumption and complex purification process would cause significant concern. Besides, the formation of silica gel makes it difficult to separate the $ZnSO_4$ from the slurry. Inorganic mineral acids are strong acids and dissolve more than 90% Zn with 1.0–2.0 M concentration at intermediate temperatures (40–60 °C), at ambient pressures and S/L ratio of 1/10 in less than 60 min. Leaching time. At 1.0 M mineral acid concentration, maximum Zn dissolution is achieved in the following order: $H_2SO_4 > HCl > HNO_3$. Processes based on HCl acid has not yet found any industrial application due to non-selective leaching and costly material of construction. Green organic acids can dissolve Zn significantly at higher temperatures and pH's higher than inorganic acids. The organic acids are not economical to use as it so extracts Fe along with Zn. The leach solution so obtained during leaching could be purified by conventional Zn cementation, SX, or ion exchange (IX) process. The Zn metal or salt could be produced from the purified solution by EW or crystallization.

Alkaline NaOH solution and ammoniacal solutions may also achieve almost full Zn dissolution at alkaline pH's from Zn secondaries. Due to the relatively high pH of the leaching system, impurities such as Fe_2O_3, SiO_2, CaO, and MgO are not soluble in the leaching solutions and the following purification process is very simple. H_2SO_4 dissolves Zn, Fe, Cd, and Co together; while alkaline solutions will not dissolve Fe, Al, Mg and Ca and they remain in the residue. NaOH is selective for Zn dissolution; but, it needs further development for the metal recovery from the sodium zincate solution by EW. Sequential H_2SO_4 and brine (NaCl) leaching can be used to recover both Zn and Pb separately.

EAF dust is globally one of the biggest Zn, Pb and Fe metal-containing waste fractions, with a composition that challenges the recycling of dust back to the steel process due to the high Zn and Pb content, which also prevents it from being landfilled. With more a stringent policy on environmental protection and diminishing mineral resources, the direct leaching process becomes more attractive, especially for mine tailings. It is a known fact that H_2SO_4 is the most commonly used leaching agent for EAF dust. But in recent years, because of some drawbacks of acid leaching such as silica releasing into the solution and causing silica gel-forming, many types of research had been performed using different chemicals like ammonia, ammonium salts, nitric acid, chlorides, caustic soda, etc. Among these chemicals, due to some advantages such as low corrosion, low toxicity, and low pollution, usage of ammonia and ammonium salts has been increased. Oxidant usage, high-pressure application, microwave heating, and mechanical activation before chemical leaching have a positive influence on the leaching of Zn and Pb.

Most nonferrous metals are obtained by hydrometallurgical processes, for example, aqueous acids or alkalis are predominantly used to dissolve the metal oxides, sulfides, or silicates. EW and SX are frequently used to recover and concentrate the metals. The production of non-ferrous metals from natural mineral ores or secondary sources is of in general high energy consumption, large acid consumption, high environmental pollution, and serious corrosion. Therefore, the development of highly effective, low-temperature and environmentally benign technologies for metals processing to reduce energy consumption and to lower investment costs and the greenhouse gas emissions is urgent. Future direction of Zn secondary research will emphasis on organic acid leaching, bioleaching and ionic liquids (IL) leaching. They are considered to be the most promising candidates due to their low toxicity and little environmental impact in recent years. ILs as green solvents have shown important application in the extraction and separation of nonferrous metals. ILs can dissolve some metal oxides even in ambient conditions (Kim et al., 2018). Presently ILs are very expensive, however, when production on a mass scale will start the price of ILs is expected to drop significantly. It is believed that hydrometallurgy will gain more market share in Zn secondary recycling than pyrometallurgy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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