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ZINC RECOVERY TECHONOLOGIES FROM SOLID WASTES OF HOT DIP GALVANIZING

TRABAJO FIN DE MÁSTER (TFM)

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RESUMEN

PALABRAS CLAVE

Zinc; Galvanizado en caliente; Tecnologías de recuperación; Cenizas; Matas; Economía circular; Reciclaje.

PLANTEAMIENTO DEL PROBLEMA

El presente trabajo consiste en un análisis crítico de la bibliografía científico-técnica sobre las tecnologías disponibles para la recuperación de zinc de los residuos sólidos generados en el proceso de galvanizado en caliente, con el objetivo de diagnosticar cuál podría ser, a día de hoy, la mejor alternativa. Dentro del conjunto de residuos sólidos a tratar, son considerados las cenizas de zinc, las matas y los polvos de zinc. Asimismo, la recopilación de información se ha orientado a los datos necesarios sobre la composición química de dichos residuos junto con la tecnología de recuperación que los trata, para una futura investigación que pueda valorizar el zinc metálico recuperado, fomentando así la transición hacia una economía circular de los procesos industriales de fabricación en los sectores químico y metalúrgico.

RESULTADOS

En primer lugar, se describe la situación del zinc como materia prima a nivel global hoy en día, así como la situación de la galvanización, en concreto de la galvanización en caliente en España, junto con sus factores medioambientales.

Posteriormente, y con vista a futuros estudios, se ha elaborado una tabla donde se recogen la composición química de cenizas, matas y polvos de zinc provenientes en su mayoría de los procesos de galvanizado en caliente. Esta tabla, se ha realizado con el objetivo de identificar una posible valorización de impacto y rendimiento de las tecnologías que se presentan a través de un estudio de análisis de ciclo de vida.

Una vez se introduce el problema, se plantean diferentes rutas de reciclaje para cada fracción de residuo. Las tecnologías descritas se clasifican en (Trpčevská, 2015).

- Procesos fisicometalúrgicos

- Procesos pirometalúrgicos

- Procesos hidrometalúrgicos

Por último, y en base a los métodos de recuperación de zinc propuestos, se presenta una comparación de las tecnologías entre sí, teniendo en cuenta las siguientes características: su capacidad de recuperación y purificación de zinc, simplicidad que pueda presentar el proceso, sus requerimientos energéticos, sus necesidades de instalación de equipos y si está o no implementada a escala industrial.

CONCLUSIONES

Como conclusión final, se determina que, a pesar de que en general la eficiencia de los métodos fisicometalúrgicos puede parecer bastante alta, estos aún se encuentran en fase experimental y no se ha avanzado lo suficiente como para implementarlos a escala real, lo que lleva a descartar estas tecnologías.

Por otro lado, los procesos hidrometalúrgicos y pirometalúrgicos parecen los más prometedores. Los primeros por la alta pureza del zinc que recuperan y los segundos por su gran cobertura a escala industrial en otras aplicaciones. Sin embargo, ambos dos continúan teniendo sus limitaciones en cuanto a la generación de residuos o a su ineficiencia energética.

Por ello, este proyecto propone para estudios futuros la idea de combinar los métodos más novedosos con los convencionales, aprovechando la ventaja de los convencionales por su ya implantación a escala industrial y la ventaja de los más novedosos por sus altas tasas de recuperación y su sencillo procedimiento.

REFERENCIAS

Trpčevská, Jarmila, Blanka Ho͉ková, Jaroslav Briančin, Katarína Korálová, and Jana Piroškoví. 2015. The Pyrometallurgical Recovery of Zinc from the Coarse-Grained Fraction of Zinc Ash by Centrifugal Force. *International Journal of Mineral Processing* 143: 25–33.

SUMMARY

KEYWORDS

Zinc; Hot dip galvanizing; Recovering technologies; Zinc ash; Hard zinc; Circular economy; Recycle.

SCOPE

The present work consists of a critical analysis of the scientific and technical literature on the technologies available for the recovery of zinc from solid waste generated in the hot galvanizing process aiming at analyzing which one could be the best alternative today. Within the set of solid waste to be treated, zinc ashes, hard zinc and zinc dust are considered. Likewise, the collection of information has been oriented to the necessary data on the chemical composition of these wastes together with the recovery technology that treats them, for future research that can recover the recovered metallic zinc, thus promoting the transition to a circular economy of industrial manufacturing processes in the chemical and metallurgical sectors.

RESULTS

First, the current situation of zinc as a global raw material is described, as well as the situation of galvanization, in particular of hot dip galvanizing in Spain, along with its environmental factors.

Subsequently, and in light of farther studies, a table has been performed where the chemical composition of ashes, hard zinc and zinc dusts from most of the hot galvanizing processes is collected. This table has been carried out with the objective of identifying a possible impact and performance assessment of the technologies presented through a life cycle analysis study.

Once the problem is introduced, different recycling routes are proposed for each fraction of waste. The described technologies are classified in (Trpčevská, 2015),

- Physico-metallurgical processes

- Pyrometallurgical processes

- Hydrometallurgical processes

Finally, and based on the proposed zinc recovery methods, a comparison of the technologies is presented, taking into account the following characteristics: their ability to recover and purify zinc, the simplicity of the process, its energy requirements, its equipment installation needs and whether or not it is implemented on an industrial scale.

CONCLUSIONS

As a final conclusion, it is determined that, although in general the efficiency of physiometallurgical methods may seem quite high, they are still in the experimental phase

and not enough progress has been made to apply it to real scale, which leads them to be discarded.

On the other hand, hydrometallurgical and pyrometallurgical processes seem the most promising alternative. The first one because of the high purity of the recovered zinc and the second one because of its great industrial scale coverage in other applications. However, both continue to have their limitations in terms of waste generation or energy inefficiency.

For this reason, this project proposes for future studies the idea of combining the most innovative methods with the conventional ones. In this way, it could take advantage of the scope that conventional processes already have along with such high recovery rates and the simplicity of the most innovative process.

REFERENCES

Trpčevská, Jarmila, Blanka Hǫková, Jaroslav Briančin, Katarína Korálová, and Jana Pirošková. 2015. The Pyrometallurgical Recovery of Zinc from the Coarse-Grained Fraction of Zinc Ash by Centrifugal Force. *International Journal of Mineral Processing* 143: 25–33.

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1. INTRODUCTION

1.1. ZINC

Over the past fifty years the production of metallic zinc has increased by over three times with consumption levels now exceeding 7 million tons annually. However, due to this increasing demand as well as numerous other economic issues, the production supply of primary zinc has been unable to keep pace with required zinc tonnage. As shown in Figure 1, the demand for primary zinc has steadily grown over the past five years, but the zinc supply has been both erratic and diminishing. At present the scarcity of zinc is making many zinc consumers invest in secured zinc supply just to avoid a potential interruption in raw material availability (Bright et al, 2007).

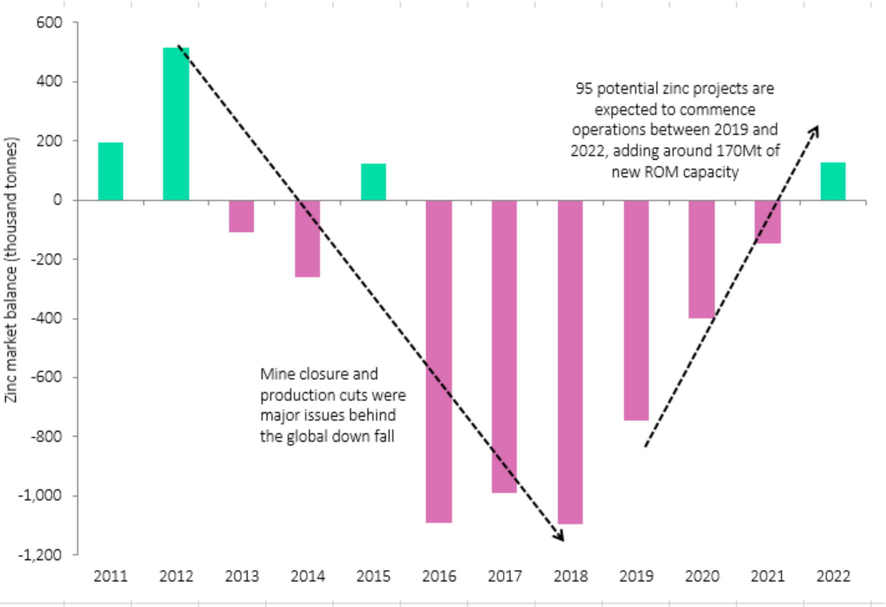


Figure 1. Global zinc market: supply and demand analysis, 2011 – 2022 (https://www.globaldata.com).

In 2018, although global zinc supply increased by 1.5% to 13.4Mt, it was still short, by 1.1 Mt, of the global demand of 14.5 Mt in that year. Increases in demand of 1.6%, 2.2%, 1.7%, and 3.2% from China, Germany, the US, and Belgium, respectively, were the major factors behind the increase in the global demand.

Over the forecast period, 2019–2022, global zinc supply is expected to grow at an annual growth rate of 3.8%, to 15.7 Mt in 2022. Simultaneously, the gap between demand and supply is expected to narrow and eventually the market will move into a surplus in 2022. This will be due to almost 100 new projects commencing operations between 2019 and 2022 where zinc is either a primary or a secondary commodity being produced. In fact, global zinc production is expected to grow at a compound annual growth rate (CAGR) of 3.8% between this period, according to GlobalData, a leading data and analytics company (https://www.globaldata.com).

Zinc has been widely used for production of numerous products such as precision die castings and zinc sheet products, brass components and platings, and industrial chemicals utilizing zinc oxide and other zinc derivatives. Moreover, due to its electrochemical features, the predominant application for zinc is as a galvanic protective coating for steel and. As outlined in figure 2, nearly 50% of the global annual zinc tonnage is consumed by galvanizing processes (Bright, 2007).

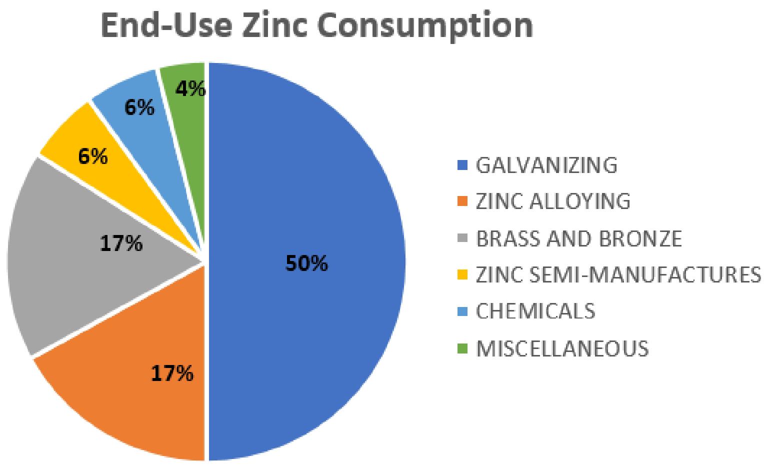


Figure 2. End-Use Zinc Consumption Distribution (Statista,2019)

To show the importance of metals recycling in the world, just give an example: a medium-sized car requires approximately 800 kg of steel and 130 kg of non-ferrous metals. If the level of possession of cars were all over the world as in the United States, let us put the case, the automobile production itself would have been exhausted by ending all known iron reserves. The recycling of metals contributes significantly to not worsen the current environmental environment. By recycling scrap, water, air and mining waste pollution is significantly reduced by 70 percent.

Zinc is a great solution to this risk of iron metal consumption thanks precisely to its role in the galvanizing industry. It is clear that prolonging the life of steel, significantly decreases its consumption, but even more impact would have if in addition to this, the metal that protects it, is also recycled and reused.

One of zinc advantages, is that this material is an inherently recyclable non-ferrous metal and can be recycled indefinitely without any loss of physical or chemical properties. At present, approximately 70% of zinc comes from primary refining of zinc ores (including 10-15% from recycled sources) and about 30% comes directly from recycled zinc (representing 80% of the zinc available for recycling).

The economic system is often considered as an open-ended system where production is aimed at producing consumer and capital goods. In turn, capital goods encourage citizens to consume more. The aim of consumption is to satisfy or create ‘‘utility’’ or welfare. When wastes derived from this system are recycled back to resources that will yield new goods, the economy becomes circular (Andersen, 2007).

Therefore, the present work intends to take advantage of this major property contributing to two fundamental features today: sustainable development and circular economy.

In figure 3, it is represented the close loop for zinc recycling. This loop is continuously improving, as knowledge is increased in zinc recovery technologies.

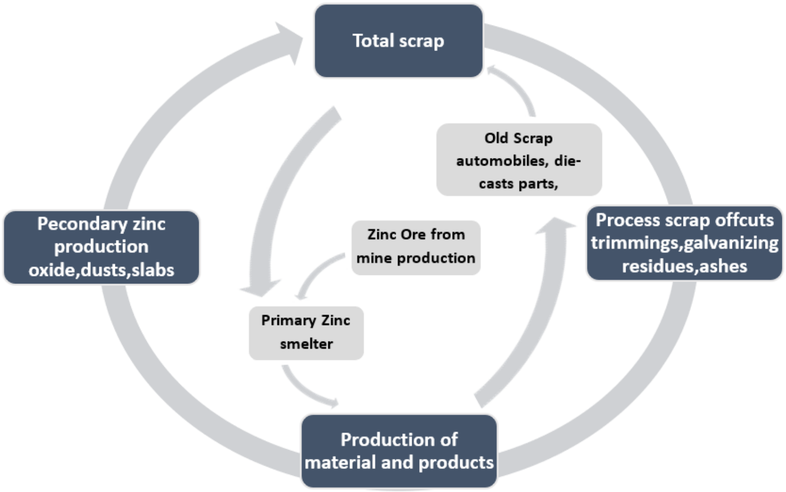


Figure 3. Zinc recycling flow loop

1.2. METAL GALVANIZING

Galvanized steel is everywhere around us and plays a vital role in our daily life. It is used in construction, transport, agriculture, transmission of electricity and in all those situations where good protection against corrosion and long duration is essential. For example, it helps to illuminate our roads looking to lighting columns, and in the provision of electricity to our homes, hospitals and offices (high voltage towers) (European General Galvanizers Association, 2016).

It is known that metal materials are susceptible to experiment the natural phenomenon of corrosion which can be simply defined as rust. Metallic corrosion is an electrochemical process that involves both chemical reactions and the flow of electrons as the materials seek to reach a state of lower energy potential. This phenomenon can lead to material destruction among other problems (Salazar-Jiménez, 2015). In fact, corrosion and repairing of corrosion damage are multi-billion-dollar problems – the most recent assessments indicate corrosion costs about **3% of each nation's GDP**. Notwithstanding, the cost of materials consumption is significantly more prominent than simply monetary, it can also lead to waste of natural resources, hazardous failures, and many other indirect costs. In addition, this natural phenomenon is unavoidable. The only thing that can be done is utilizing the proper protection well in advance to reduce these yearly expenses (American Galvanizers Association 2012).

Then, there are several methods of applying metal coatings on steel. It is important to know the differences between them, because they have different durability and may be suitable for specific applications.

Within construction field, the most commonly used zinc coatings are the following described ones.

Continuous galvanization, which are thin zinc coatings applied to sheet metal or steel strip. They are used for products that must be bent or shaped after the coating has been applied (coatings, car bodies, household appliances).

Zinc thermal spray coatings are sprayed onto the steel surface with molten zinc droplets, using a special spray gun that is fed with zinc wire or powder.

Electrolytic zinc deposits are thin coatings applied by electrolysis. They have no metallurgical bond between the zinc layer and the base steel. The thickness of zinc electrolytic coatings is significantly less than that of the corresponding hot dip galvanizing coatings, so they are not usually suitable for outdoor exposure or in applications where a certain service life is required, unless they are additionally protected by painting to prolong their useful life. It is the most widely employed zinc coating method for car components. Its adhesion to the steel substrate is good and its surface appearance smooth and shiny (European General Galvanizers Association, 2014).

Sherardization is a solid phase diffusion process, in which small parts are treated in rotating drums with a mixture of zinc, silica and / or carbon dust, at temperatures between 380 ° C and 400 ° C (European Commission , 2001). Under these conditions, layers of zinc-iron alloys are formed on the surface of the steel with varying thicknesses that depend on the temperature and the duration of the treatment. The coatings thus obtained are similar to those of hot dip galvanizing, although generally of a lower thickness and do not have the outer layer of pure zinc. They are very resistant to abrasion.

On the other hand, there other methods that do not imply zinc. **Aluminium** and **aluminium alloy coatings** are also used in automobile, construction industries as an alternative for zinc coating in order to reduce weight, provide better mechanical properties and yield high temperature oxidation resistance compared to hot dip zinc coating (McCann et al., 1999).

Apart of this, **chromium passivation** is also presented as method to provide anticorrosive properties for metals. The toxicity of hexavalent chromium is well-known. Workers exposed to the substance daily are more likely to develop lung cancer and allergy. Instead new concepts, as for example, organic, inorganic and combinations of the both, have been developed. In most cases these concepts are based on barrier effects, where the metal surface is protected from oxygen and water by a dense coating. One method for replacing hexavalent chromium in passivation for hot-dip galvanized steel is to use formulations based in trivalent chromium, a much lesser dangerous chromium state than hexavalent chromium (Berger et al., 2007).

However, the life and durability of steel increases significantly when coated with zinc. Although nowadays, there are several studies looking for new alloys against corrosion, there is no other material, for now, that can provide steel with such efficient and economical protection such as zinc. It is known that if the steel is left unprotected, it will corrode in almost any environment. In order to avoid the corrosion, the zinc coatings stop the corrosion of the steel in two ways: by means of a physical barrier and by electrochemical protection.

Zinc coatings provide a continuous and impermeable metal barrier that does not allow moisture and oxygen to penetrate to the based steel. The metallic zinc surface reacts with the atmosphere and forms a compact and adherent patina that is insoluble against rainwater. The typical thicknesses of these coatings are between 45 μm and more than 200 μm.

On the other hand, zinc has the property of galvanically protecting steel. When bare steel is exposed to moisture, such as at the edges of cuts or in damaged areas of the coating, a galvanic battery is formed. The zinc that surrounds these bare areas is corroded in preference to steel, and forms corrosion products that are deposited on the surface of the steel and protect it. In the bare areas, corrosion does not progress in the transverse direction (EGGA, 2011).

In Europe there are more than 650 general galvanization plants, each of which makes an important contribution to the industrial economy and employment. The plants are located near the factories of articles and steel constructions in order to reduce as much as possible the environmental and economic costs of transport. They are distributed between Portugal, Spain, United Kingdom, Sweden, Norway, Estonia, Netherlands, Germany, Switzerland, Belgium, Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Greece, Bulgaria and Romania. The higher concentration of them is located in central and south Europe.

These companies deal with many polluting emissions, composed primarily of zinc (gas or particles) and other element traces such as lead, aluminum, tin, nickel or hydrogen chloride and ammonia (Ministerio de Medio Ambiente, 2005).

According to E-PRTR database, there are 39 hot dip galvanizing companies in Spain and 25 of them report zinc emissions (http://www.prtr-es). They are located mainly in Cataluña, Basque Country, Asturias and Murcia as it is shown in figure 4. All these 25 companies indicated in the map, have been collected in table 1 to analyze the distribution of zinc and metal galvanizing industry in Spain.

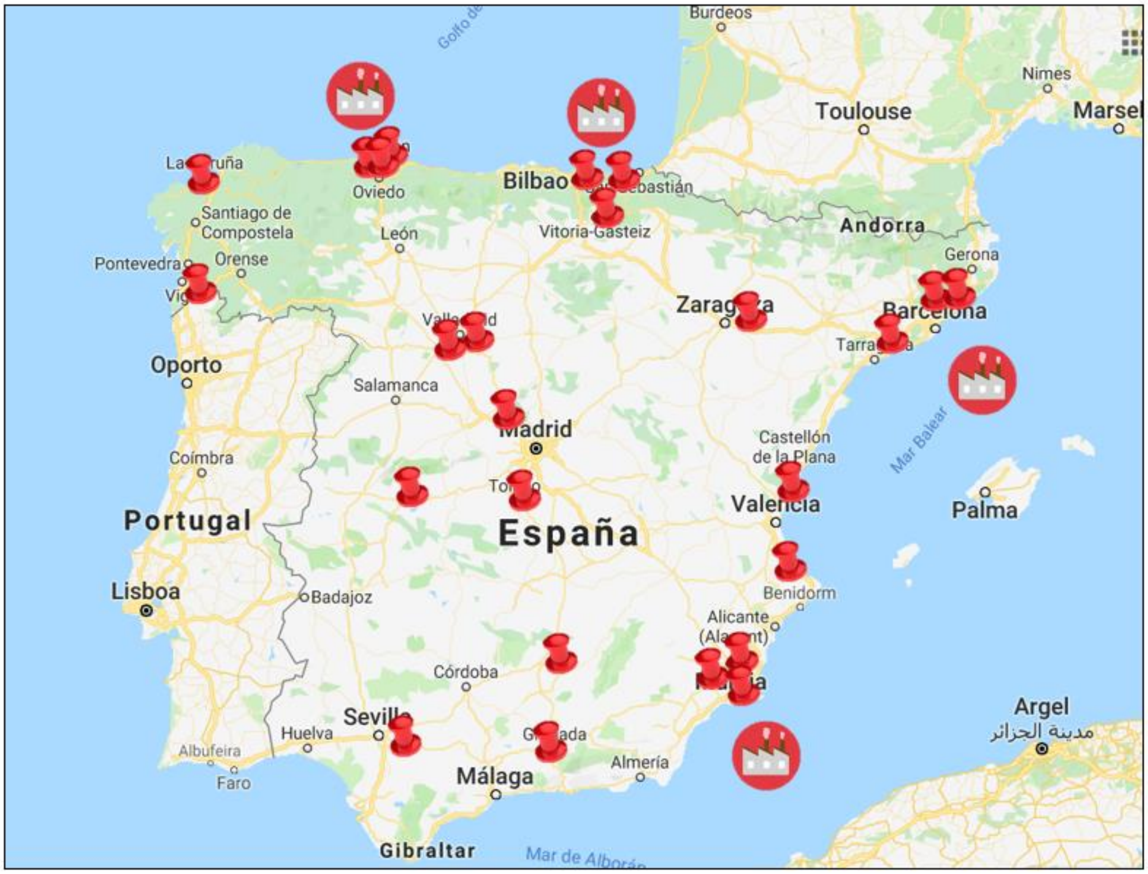


Figure 4. Hot Dip Galvanizing plants distribution in Spain

One of the main problems from the galvanizing processes are their environmental impacts, which are emissions to air and the generation of wastes, in most cases classified as hazardous (Dallin, 2015).

Although, this issue is discussed in a section below, table 1 is presented to gather the total Zn emissions per year and the receiving environmental compartment from companies illustrated in the map. It is important to notice that the most recent data found in E-PRTR about Zn emission per year are from 2017 (http://www.prtr-es).

There are two possible environmental compartments receiving the Zn emissions: water and air. In addition, the companies whose main activity is the hot dip galvanizing are emphasized in bold.

Table 1. *Galvanizing plants located in Spain and its corresponding zinc emissions*

	Company	**Total Zn emissions (kg/year)**	**Receiving environment**
1	MOREDA RIVIERE TREFILERIAS (BCN)	11.51	Water
2	GALVANIZADORA VALENCIANA SLU	11.78	Water
		1580.46	Air
3	**UNIZINC**	**0.000002**	**Water**
4	INDUSTRIAL GALVANIZADORA	9.49	Water
		11.96	Air
5	RETSA-II, S.L.	4.44	Air
6	MEGALTA	8.53	Air
7	EUROTÉCNICA DE GALVANIZACIÓN, S.A.	46.50	Air
8	INDUSTRIAS ALGAMA, S.L.	2.05	Air
9	**GALVANIZADOS DEL SURESTE, S.A.**	**130.15**	**Air**
10	**GALVANIZADOS DEL MEDITERRANEO, S.L.U.**	**13.10**	**Air**
11	HIERROS Y APLANACIONES (HIASA)	2.60	Water
12	EUROPEA DE CONSTRUCCIONES METÁLICAS, S.A. (EUCOMSA)	158	Air
13	**INDUSTRIAL GOÑABE S.L.**	**3.34**	**Air**
14	ISOWAT MADE, S.L (ANTES MADE TORRES Y HERRAJES)	0.53	Air
15	GALVANIZACIONES ARAGONESAS, S.A. - GALVASA	4.86	Air
16	MOREDA RIVIERE TREFILERIAS (ASTURIAS)	335.62	Water
17	SOPORTES METÁLICOS TUBULARES, S.L.	0.80	Air
18	**CABARRI, S.A. (CABARRI, S.A.)**	**0.002**	**Air**
19	**GALVANIZADOS ALAVESES CABA, S.A.**	**0.003**	**Air**
20	**GALVANIZADOS OLAIZOLA, S.A.**	**8.29**	**Water**
		143.95	**Air**
21	**GALVANIZACIÓN TOLEDO S.L.**	**20.23**	**Water**
		23.07	**Air**
22	**INDUSTRIAS JOVIR**	**3.90**	**Air**
23	**GALVANIZADOS AVILES**	**8.31**	**Water**
24	**GALVANIZADOS DE EXTREMADURA, S.A.**	**0.003**	**Air**
25	BASOR PLANTA DE CASTELLÓN DE RUGAT	0.059	Water

Since annual production of the companies is different, the comparison between their emissions is complicated.

However, what is remarkable about this information is the scope that the galvanization industry has in our country. As mentioned, 39 companies practice galvanization and 25 specifically use zinc. Taking into account sum of all amount of zinc that is poured into the water or air, it can be said that not only is raw material being wasted, but it is also going in the opposite direction to the sustainable development and what this concept entails.

1.2.1. Hot dip galvanizing

Within zinc protection methods, hot dip galvanizing is one of the most popular treatments for steel corrosion protection and can be applied to a wide range of steel products with different dimensions, geometries and functions. The operational sequence of the plant is essentially the same in most installations, and the dimension of the kettles (i.e., the bath of molten zinc) is determined by the mix of products to be coated (EGGA, 2014).

Basically, galvanizing consists of three fundamental steps:

(1) Surface preparation

(2) Galvanizing

(3) Finishing

Figure 5 presents a flow diagram of the hot dip galvanizing process, with the most common steps and its corresponding inlet and outlet streams. In this case, the inputs and outputs of the general process have been drawn in green colour to differentiate them from the inputs and outputs of each block of the diagram. The blue colour has been awarded to the inputs, and the orange to the outputs of individual stages.

Surface preparation is the most important step in the application of any coating. In most cases of coating failure before the end of its expected service life, it is because of incorrect or inadequate surface preparation. The surface preparation step in the galvanizing process has its own built-in means of quality control because zinc simply will not react with unclean steel (American Galvanizers Association, 2019). Then, this step consists of cleaning and pickling operations that free the surface of dirt, grease, rust and scale. Furthermore, three different stages take part in surface preparation.

Degreasing can be acid, basic or biological. Figure 5 shows two of these treatments with their respective inputs and outputs. The degreasing can be accomplished by a hot alkali solution, mild acidic bath, or biological cleaning bath which removes organic contaminants such as dirt, paint markings, grease, and oil from the metal surface. However, other methods such as grit-blasting or sandblasting must be used in order to remove epoxies, vinyl, asphalt, or welding slag since degreasing cannot removed that type of dirt.

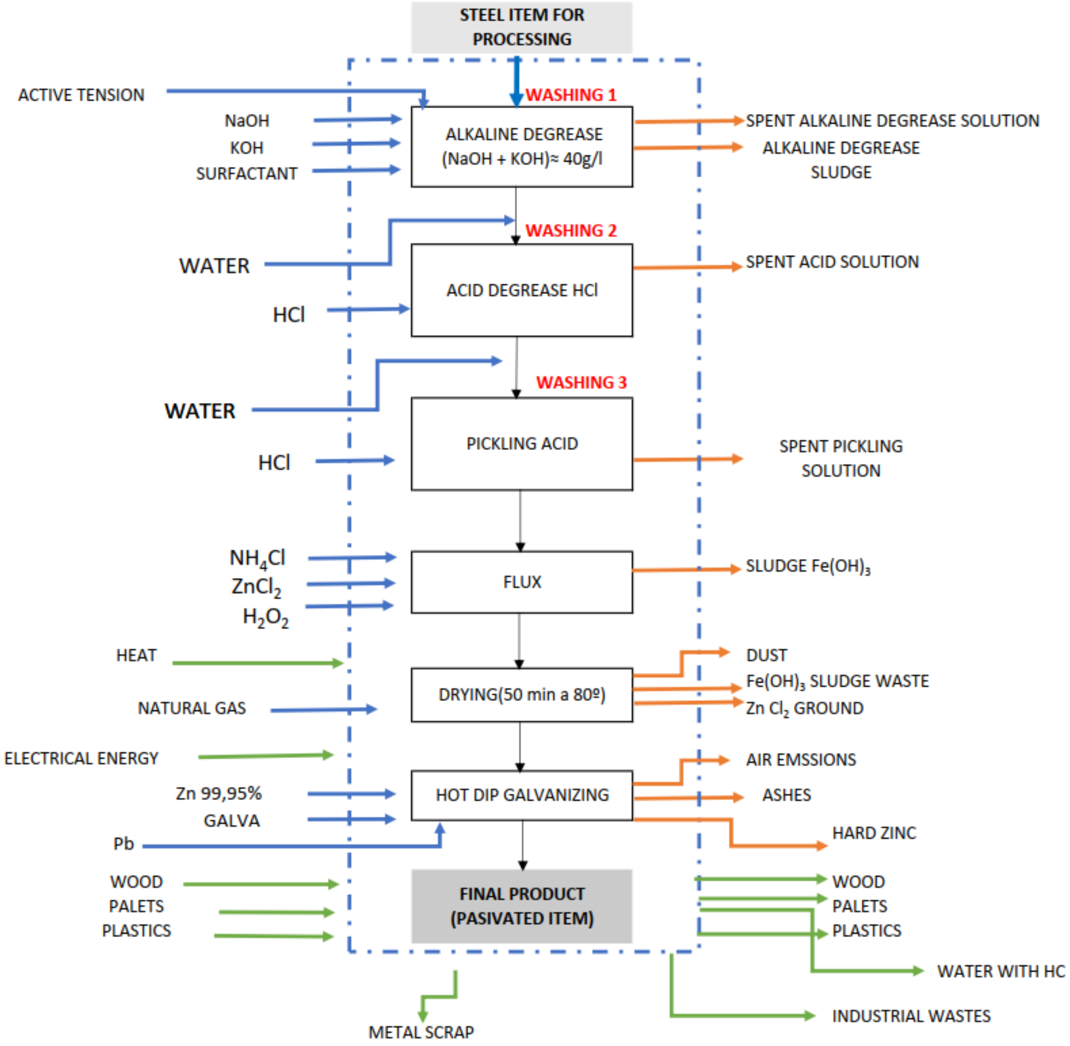


Figure 5. Flow diagram of a hot dip galvanizing process, including inlets and outlets

The pickling stage, third block according figure 5, consists of a dilute solution of heated sulfuric acid or hydrochloric acid at ambient temperature, which removes mill scale and iron oxides (rust) from the steel surface. As an alternative to, or in conjunction with pickling, this stage can also be accomplished using abrasive cleaning or air blasting sand, metallic shot, or grit onto the steel.

The final surface preparation step is fluxing, where a zinc ammonium chloride solution serves two purposes. It serves to dissolve any oxide that may have formed on the iron or steel surface after pickling and prevents further oxides from forming on the surface prior to immersion in the molten zinc. This cleaning can be accomplished with either a preflux solution, a top flux on the kettle, or both (Woods and Cole,1996).

Following the scheme represented in figure 5, the material is usually dried to continue with galvanizing. Any failures or inadequacies in surface preparation are immediately apparent when the steel is withdrawn from the zinc bath because the unclean areas will remain uncoated, and immediate corrective action can be taken.

The galvanizing step is the main phase of the process which consists of completely immersing the steel component in a minimum 98% pure zinc bath. The bath temperature is maintained at around 450 ºC or higher, in order to have zinc in the molten liquid state. The steel is lowered at an angle by crane hoist. This allows air to escape from tubular shapes or pockets that may be within the design of a fabricated piece and of course permits the molten zinc to displace the air (Grogan, 2018).

While immersed in the kettle, the zinc reacts with iron in the steel to form a series of zinc-iron inter-metallic alloy layers. Once the fabricated item reaches the bath temperature, the coating growth is complete, and the articles are withdrawn slowly from the galvanizing bath.

The final finishing stage removes excess zinc by draining, vibrating, and/or centrifuging. The metallurgical reaction continues after withdrawal from the bath, as long as the article remains near bath temperature. Articles are cooled either by immersion in a passivation solution or water or by being left in open air (European Commission, 2001).

COATING STRUCTURE

During hot dip galvanizing, even with very little contact time between steel and liquid zinc leads to the formation of intermetallic Fe-Zn in the interface substrate / coating. (Malmström et al, 2012). The coating usually consists of several layers, see Figure 6. The complex layer structure is very variable in the chemical composition, physics and mechanical properties, being affected by chemical activity, diffusion and subsequent cooling, which includes the process of solidification.

The protective zinc layer that is formed during the immersion in the bath, usually at a temperature between 450 ºC and 480 ºC, consists of a series of intermetallic layers of Fe – Zn, which have been identified as Gamma (Γ), Delta (δ), Zeta (ζ) and an outer layer of Eta (η), very rich in zinc (American Galvanizers Association ,2012).

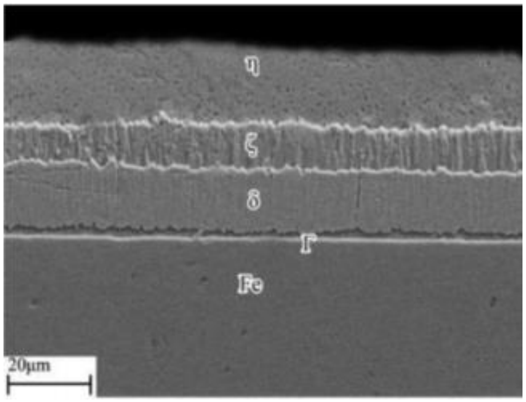


Figure 6. Micrograph view of hot-dip galvanized coating (Schmitz and Friedrich, 2007)

Gamma phase (Γ) is noticeable when the component is galvanized with a large immersion time. As its formation requires of an incubation time, in most cases, gamma phase is only observed as a line between the steel and delta phase. It has a wide range of state solid solubility and its limits have been described as $FeZn_3$-Fe_5Zn_{21}, giving an "averaged" composition of Fe_3Zn_{10}.

The Delta (δ) phase, approximately $FeZn_{10}$, and Zeta (ζ) phase, approximately $FeZn_{13}$, are visible and intermediate, unless aluminium has been added to the galvanization bath, since it decreases notably the reactivity of zinc and the formation of these phases is limited. These compounds are fragile, and, if the material deforms having a large coating thickness, cracks will form in the deposit (Schmitz and Friedrich, 2007).

The Eta (η) phase, is a solid zinc solution; it may disappear if the material undergoes a subsequent heat treatment that favours the growth of the Zeta phase at the expense of the Eta (American Galvanizers Association, 2019).

1.3. ENVIRONMENTAL CONCERNS

Sustainable development is the social, economic, and environmental commitment to growth and development that meet the needs of the present society without compromising the ability of future generations to meet their own needs. As mentioned, today is the concept that guides the way of all industrial processes.

Taking into account that the social pressure continues to construct the environment in a sustainably way, from the point of view of the process analyzed in this work, much remains to be done. In part due to increasingly restrictive environmental laws in all areas, the requirements of the materials needed for any application are becoming increasingly analyzed and strict.

This project is not focused on the study of zinc as a raw material and the knowledge of its environmental concerns probably seems negligible. However, knowledge of this fact is essential to understand the need of recycling this material.

Regarding the problems that concern primary zinc, most zinc ores and concentrates are formed by sulphides that have to be converted into oxides before metallurgical processes. This means that the metallurgy of zinc has problems similar to those found in the sulfuric acid industry: emission of residual sulphur dioxide, acid effluents and certain volatile elements such as mercury and arsenic that the raw material contains itself. In addition, zinc minerals contain iron, which constitutes the main problem of this industry due to the generation of high waste volumes such as slag, jarosite, goethite and hematite (Fundación Entorno Empresa y Medioambiente, 1996).

Therefore, sulphur oxide capture systems are required, as well as a control of the emission of particles into the atmosphere, proper management of solid waste, maintenance of safe atmospheres in work areas and limitation of fluids at acceptable levels of pH and heavy metal content (European Commission, 2001). In the same way that those solutions help to mitigate environmental impacts, raw material recycling, as this work proposes, is considered another useful alternative.

1.3.1. Environmental issues of hot dip galvanizing

Regarding hot dip galvanizing, the main environmental issues for batch galvanizing are emissions to air such as HCl from pickling or dust and gaseous compounds from the kettle (European Commission, 2001). There is also the concern about spent process solutions, degreasing solutions where oily wastes came from, or pickling baths and flux baths, with a high content of dissolved metals, including zinc. Moreover, hot dip galvanizing plants produce a great diversity of solid residual materials that contain zinc. During the drying and the final step, when anticorrosive coating is formed (Delvasto et al., 2012). The main ones being hard zinc, zinc ash and dust.

Hard zinc is also called bushes, hard dross, zinc bottom dross or hard spelter. These wastes are intermetallic compounds, which are formed between zinc and iron. This galvanizing dross is a valuable by-product because it contains high levels of zinc (more than 80 wt%) and it is of significant tonnage. Generally, about 10-20 wt% zinc in the bath is converted into dross (Wang, 2017).

According to their distributed position in the zinc bath, the galvanizing dross can be identified as surface dross (mainly $Fe_2Al_5Zn_x$) and bottom dross (mainly aluminium saturated $FeZn_7$ phase). These galvanizing dross particles are detrimental to the surface quality of the galvanized steel, since they can be easily trapped inside the coating and cause formation of swells on the galvanized surface. Conventionally, the surface dross is skimmed off by labour or machine at intervals, while the bottom dross can be removed when the operation is shut down (Schmitz and Friedrich, 2007).

The **zinc ash** or zinc top dross, on the other hand, are formed in the interface between the surface of the liquid zinc bath and the atmosphere of the tank, due to the reactions that occur between oxygen, the components of the bath and the flux additives (Meneice and Boston, 2003). The flux reacts due the high temperature of the zinc bath and alloy, which takes place as the steel is galvanized, and results in the formation of ash that ends floating on the surface of the molten zinc bath.

In addition, there is another reason to ash formation. When a fluxing compound is spread over one end of the zinc bath to create a “flux blanket”, that the steel has to go through as it is being submerged into the molten zinc to be galvanized. As the usable chemicals in the flux blanket are consumed during the galvanizing process, the flux blanket is slowly disposed of in the form of ash, and the skimming process, which clears away the flux prior to withdrawal of the steel from the zinc bath, also produces zinc oxide as the molten zinc comes in contact with the surrounding air.

Finally, the **dust,** comes from the processes of drying, draining and regulating zinc thicknesses of the steel pieces freshly extracted from the molten bath. In these processes, pressurized water vapor is usually projected on the galvanized parts, producing atomized zinc, which is later collected in the form of powders, within the systems of gas collection (cyclones and dust filters) (Delvasto et al., 2012).

Following, a typical diagram of mass flow for an HDG plant is included in figure 7. For a throughput of 1,000 kg of steel parts, the amounts of hard zinc and zinc ash are 10.1 and 9.1 kg, respectively. The metallic zinc content in theses streams accounts for 8.6 and 9.1 kg of zinc, respectively.

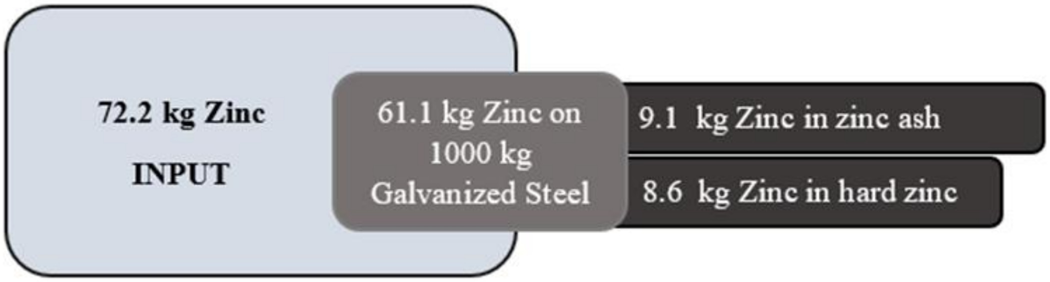


Figure 7. Mass balance (kg) of zinc in a HDG Process (Schmitz and Friedrich, 2007)

Furthermore, taking into account that a medium size HDG company has a throughput of approximately 1,500 tons of steel per month (Schmitz and Friedrich, 2007), and according the numbers presented in figure 7, it could be concluded that from a medium size HDG plant, 91.65 ton of zinc/month would be required, hence, approximately, 13.65 ton of zinc/month go to zinc ash solid waste and 12.9 ton/month go to hard zinc solid waste. That is a large amount of zinc that could be recovered and reused in the galvanized line again

As another example mentioned in Schmitz and Friedrich (2007), the biggest yearly German demand of the 700,000 tons of zinc is generated by the galvanizing industry with a share of 32 % or 224,000 tons per year. By this process about 1,600,000 tons of steel are protected against corrosion in Germany. Due to the fact that **1 ton of steel**, representing a production energy of **2,500 kWh**, can be protected over several decades of years by 30-70 kg of zinc, which is representing **125 - 300 kWh,** the galvanizing of steel parts becomes an economically very attractive process.

Then, this main area of application generates a need of 224,000 tons of zinc per year in Germany which is used in the continuous galvanizing and hot dip galvanizing industry. Amount of produced zinc ash is **12.8 wt.%** and of hard zinc **11.5 wt.%** of the zinc input. According this data, balance results are shown in figure 8.

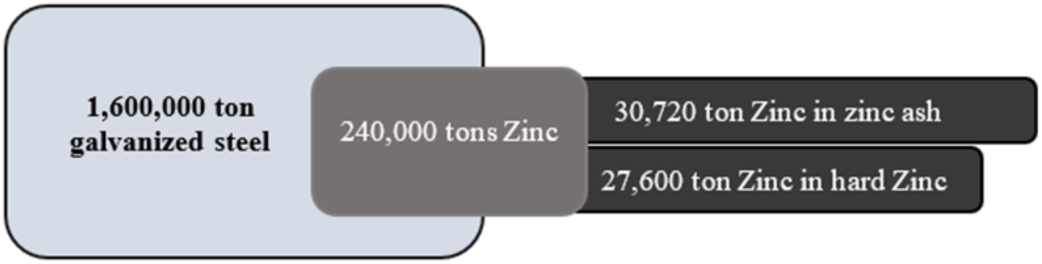


Figure 8. Mass balance, in ton of zinc consumption, in Germany by the hot dip galvanizing sector

Continuing with mass balances, a last example is presented. In this case, Delvasto et al. (2012) provide data for a mass balance which makes reference to more residues than ash zinc and hard dross. They considered wastes like zinc dust, also commented in this project. In this article (Delvasto et al 2012), it is assumed that about 7500 MT of zinc are destined annually to hot dip galvanization in Venezuela.

In addition, Delvasto et al. (2012) claimed that previous studies indicated that typical values for an annual production of **11,500 MT** of galvanized steel products implies a consumption of near of **750 MT** of zinc per year, of which only **54%** refers to galvanized products. The remaining **46%** of zinc goes to the waste generated. The distribution among different types of wastes is as follows: **4%** in the hard zinc, **17%** in zinc ash and **19%** in dust, the remaining **6%** considers that it corresponds to coatings that do not pass quality controls. All these data are summarized in the following figure 9.

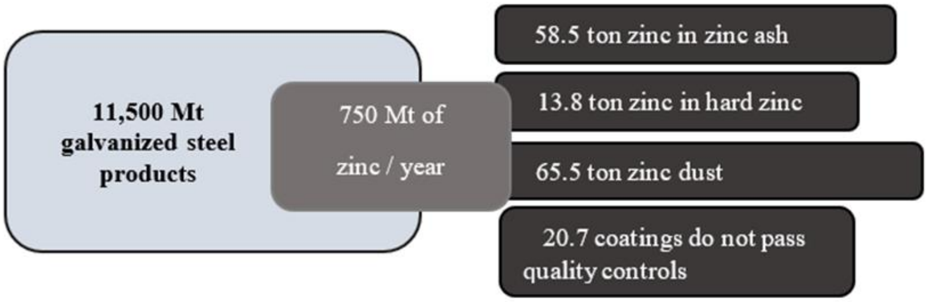
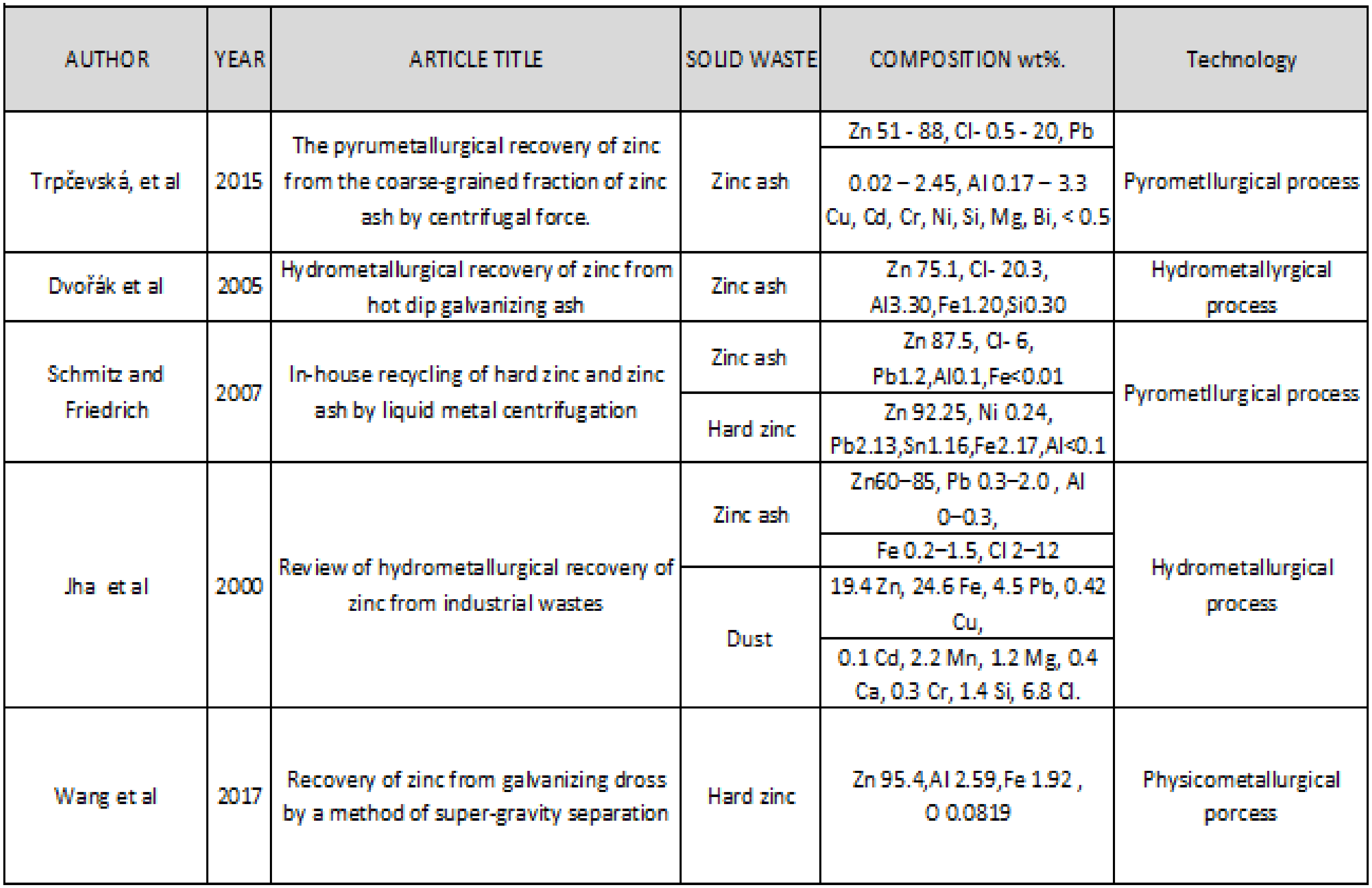


Figure 9. Balance mass flow 3 of zinc from HDG in Venezuela

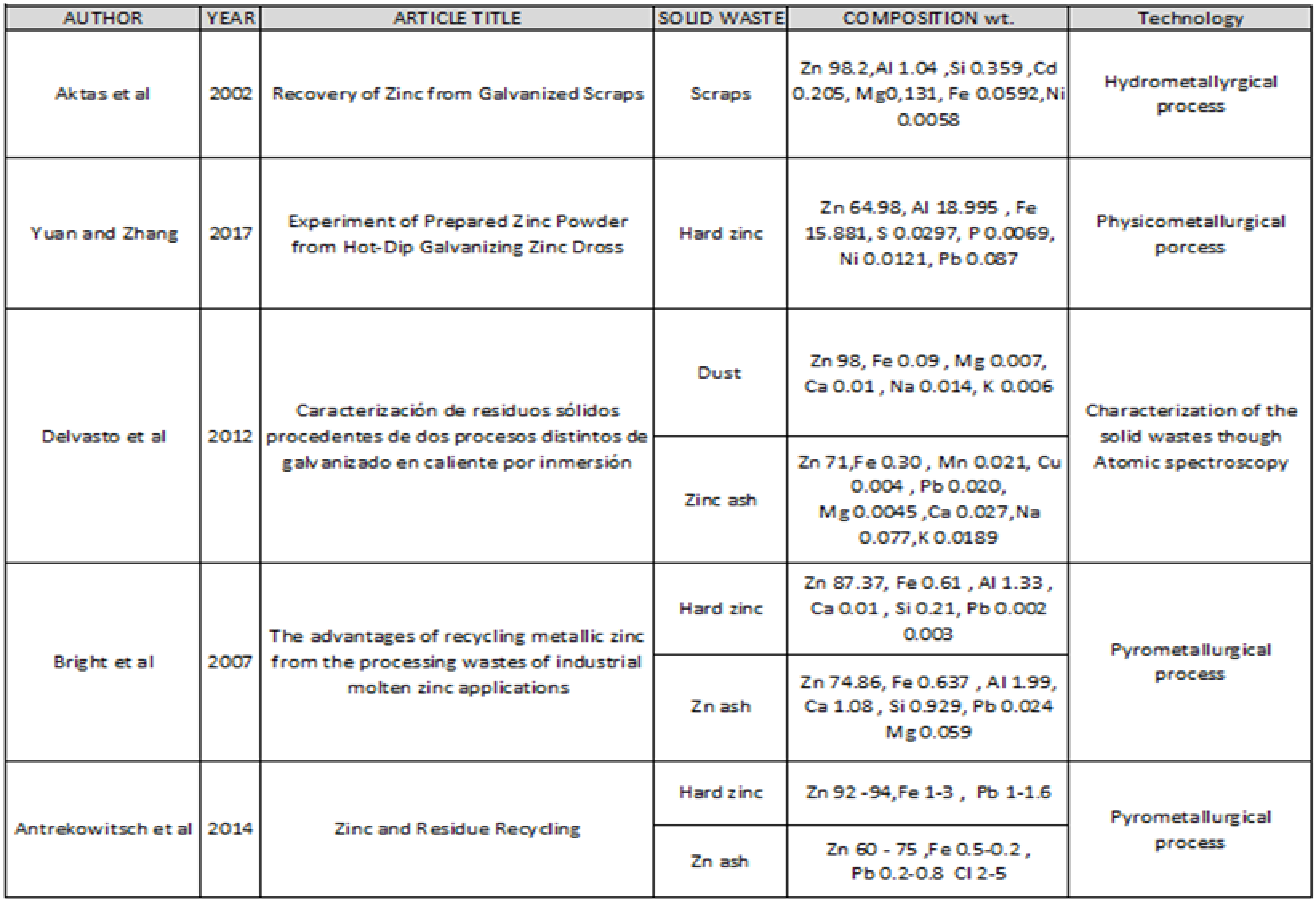
Additionally, to the loss of zinc in the solids wastes, hot dip galvanizing also has zinc losses in the stage of acid pickling. Project Life2acid estimated zinc losses in spent pickling acids to be 6-8 % of total zinc input to the hot dip galvanizing process (http://www.life2acid.eu).

Because, of high heterogeneity of all these zinc wastes, it is very difficult to define precisely its chemical phase and granulometric composition. Therefore, it is very difficult to determine the optimum conditions for processing them. Table 1 gathers the information on typical composition of zinc ash, hard zinc and dust, data were obtained from different references.

Table 2. *Chemical composition of zinc ash, hard zinc and dust from hot dip galvanizing*



AUTHOR	YEAR	ARTICLE TITLE	SOLID WASTE	COMPOSITION wt%.	Technology
Trpčevská, et al	2015	The pyrumetallurgical recovery of zinc from the coarse-grained fraction of zinc ash by centrifugal force.	Zinc ash	Zn 51 - 88, Cl- 0.5 - 20, Pb 0.02 – 2.45, Al 0.17 – 3.3 Cu, Cd, Cr, Ni, Si, Mg, Bi, < 0.5	Pyrometllurgical process
Dvořák et al	2005	Hydrometallurgical recovery of zinc from hot dip galvanizing ash	Zinc ash	Zn 75.1, Cl- 20.3, Al3.30,Fe1.20,Si0.30	Hydrometallyrgical process
Schmitz and Friedrich	2007	In-house recycling of hard zinc and zinc ash by liquid metal centrifugation	Zinc ash	Zn 87.5, Cl- 6, Pb1.2,Al0.1,Fe<0.01	Pyrometllurgical process
			Hard zinc	Zn 92.25, Ni 0.24, Pb2.13,Sn1.16,Fe2.17,Al<0.1	
Jha et al	2000	Review of hydrometallurgical recovery of zinc from industrial wastes	Zinc ash	Zn60–85, Pb 0.3–2.0 , Al 0–0.3, Fe 0.2–1.5, Cl 2–12	Hydrometallurgical process
			Dust	19.4 Zn, 24.6 Fe, 4.5 Pb, 0.42 Cu, 0.1 Cd, 2.2 Mn, 1.2 Mg, 0.4 Ca, 0.3 Cr, 1.4 Si, 6.8 Cl.	
Wang et al	2017	Recovery of zinc from galvanizing dross by a method of super-gravity separation	Hard zinc	Zn 95.4,Al 2.59,Fe 1.92 , O 0.0819	Physicometallurgical porcess



AUTHOR	YEAR	ARTICLE TITLE	SOLID WASTE	COMPOSITION wt.	Technology
Aktas et al	2002	Recovery of Zinc from Galvanized Scraps	Scraps	Zn 98.2,Al 1.04 ,Si 0.359 ,Cd 0.205, Mg0,131, Fe 0.0592,Ni 0.0058	Hydrometallyrgical process
Yuan and Zhang	2017	Experiment of Prepared Zinc Powder from Hot-Dip Galvanizing Zinc Dross	Hard zinc	Zn 64.98, Al 18.995 , Fe 15.881, S 0.0297, P 0.0069, Ni 0.0121, Pb 0.087	Physicometallurgical porcess
Delvasto et al	2012	Caracterización de residuos sólidos procedentes de dos procesos distintos de galvanizado en caliente por inmersión	Dust	Zn 98, Fe 0.09 , Mg 0.007, Ca 0.01 , Na 0.014, K 0.006	Characterization of the solid wastes though Atomic spectroscopy
			Zinc ash	Zn 71,Fe 0.30 , Mn 0.021, Cu 0.004 , Pb 0.020, Mg 0.0045 ,Ca 0.027,Na 0.077,K 0.0189	
Bright et al	2007	The advantages of recycling metallic zinc from the processing wastes of industrial molten zinc applications	Hard zinc	Zn 87.37, Fe 0.61 , Al 1.33 , Ca 0.01 , Si 0.21, Pb 0.002 0.003	Pyrometallurgical process
			Zn ash	Zn 74.86, Fe 0.637 , Al 1.99, Ca 1.08 , Si 0.929, Pb 0.024 Mg 0.059	
Antrekowitsch et al	2014	Zinc and Residue Recycling	Hard zinc	Zn 92 -94,Fe 1-3 , Pb 1-1.6	Pyrometallurgical process
			Zn ash	Zn 60 - 75 ,Fe 0.5-0.2 , Pb 0.2-0.8 Cl 2-5	

Then amount generated from this kind of waste depends on how the galvanizing process is carried out in each plant. In addition, it depends on several factors such as the bath temperature or the chemical composition of the baths. However, this kind of data are difficult to obtain, due to reservations presented by some industrialists to make them known.

Finally, solid residues from the galvanizing process have a usable metal fraction that is generally recycled by zinc primary suppliers however, little is known about the destination that is given to the non-metallic fractions contained in these materials. Said fractions, not directly usable, present very high contents in heavy metals, which can generate a negative impact on ecosystems, if they are not arranged safely. To mitigate the impact, alternatives are sought and among them we find numerous studies dedicated to the finding of innovative efficient solutions.

2. OBJECTIVE

The main aim of this work is to perform a technical assessment on the applied technologies to recover zinc from the residues that come from hot dip galvanizing process. Both the most commonly applied processes and the recently developed ones will be discussed. This project is focused mainly in three types of wastes: zinc ash, hard zinc and dust. All of them are solid wastes with an elevated mass fraction of zinc.

To fulfill this general objective, several specific objectives need to be achieved:

- Firstly, it is necessary to gather all the available information regarding what happens to the wastes once they are generated and collected after the hot dip galvanizing process.

- The second objective is to describe all the founded technologies with all the relevant information in order to compare which ones are currently the best ones to recover zinc.

- Once it has been performed the literature review for zinc recovery technologies, it is needed to gather the chemical composition of the relevant wastes in a table.

- Finally, in order to complete the information needed to support the main purpose of this project, it is performed a table where recovery technologies are analyzed according some selected characteristics.

Therefore, this work focuses on the waste treatment stage to contribute in the subsequent introduction of the recovered materials into the production systems, which is the cornerstone of the circular economy.

3. METHODOLOGY

The methodology that has been followed in the initial phase of the project corresponds to a systematic literature search. Articles in scientific and technical journals, engineering web sites, encyclopedias and science reviews have been used to search the required information. To start the search, headlines/keywords such as “recovery of zinc”, “zinc ash”, “hot dip galvanizing process”, “hydrometallurgical process” or “review of technologies to zinc recovery” have been written in the Scopus and Google search engines.

Additionally, the best available technique reference document in the Ferrous Metals Processing Industry (European Commission, 2001), has been thoroughly reviewed, given that this source provides information about the general hot dip galvanizing process and wastes generation. In addition, it has been searched in several scientific articles to accomplish a table with the composition of the correspond wastes according each author.

4. RESULTS AND DISCUSSIONS

With the rising cost of zinc, reaching historic levels (Figure 10), more emphasis is being placed on technologies to increase the efficient utilization of zinc (Bright et al., 2007). Figure 10 present the average prize of metal zinc, in USD per ton, as extracted from the London Metal Exchange for the period 2010 to 2019.

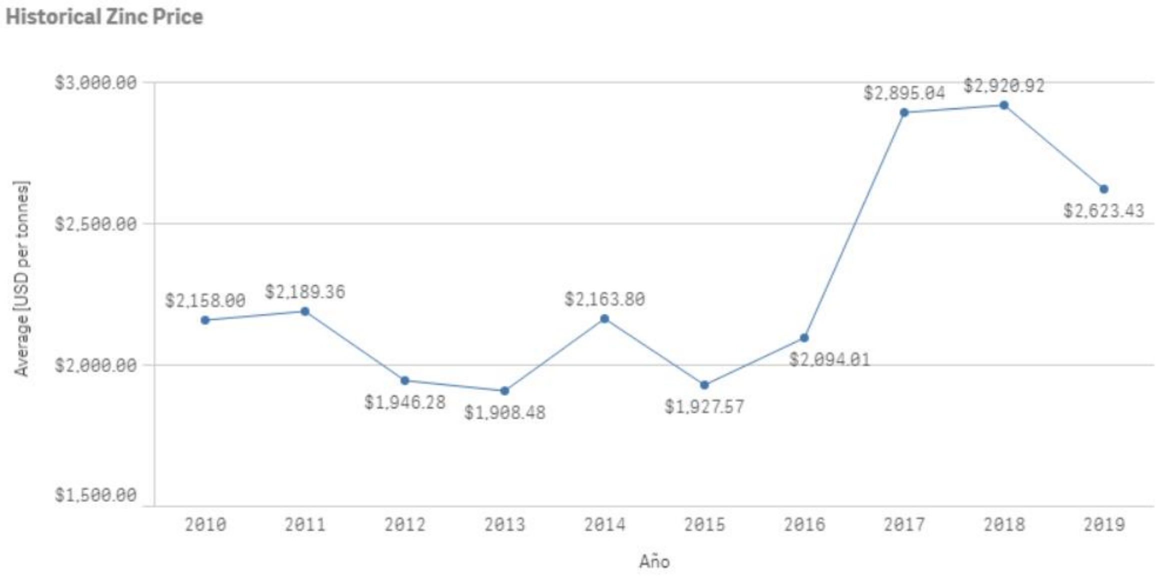


Figure 10. Historical zinc price (The London Metal Exchange - an HKEX Company, 2019)

In the last decade, the price of zinc reached its highest value in 2018, exceeding 2,900 USD/ton.

However, at present, its price is around 2,600 USD/ton, which is still higher than the average in the last ten years. Zinc prices fell as an increase in Chinese production and the collapse of the cash metal premium on the London Metal Exchange (LME) pointed to a market with higher supplies. Zinc quotation has sunk by more than 30% since a peak in early 2018 as the trade war between the United States, China weakened the outlook for demand, and operators expected an increase in refined metal for end up with a supply deficit.

The high volatility of zinc prices recommends assuring the supply of this essential metal. In Europe, primary zinc sources are scarce, after many years of exploitation. In this context, the production of secondary zinc from industrial wastes is considered of upmost importance. To this end, several zinc recovery technologies are discussed in the following section, considering three types of wastes to manage: zinc ash, hard dross and dust.

Current zinc residues recycling technologies are primarily aimed at recovering metallic zinc or its compounds (Trpčevská, 2015). According to that paper, industrial zinc ash processing technologies are divided into:

- Physico-metallurgical processes
- Pyrometallurgical processes
- Hydrometallurgical processes

However, because the classification could be confusing, since three different residues will be managed, this section follows a structure where the technologies are described meanwhile the corresponding residues are indicated.

4.1. DESCRIPTION OF ZINC RECOVERY TECHNOLOGIES

Some of the following technologies are the processes, techniques, and alternatives that either because of their poor implementation, either because they are in the pilot phase or at the laboratory scale, they should be considered as emerging techniques within the zinc metallurgy sector.

4.1.1. Physico-metallurgical

a. Super-gravity separation

Super-gravity technology is presented as a physical method to enhance separation and mass transfer which can effectively separate different components from complex materials. In recent years, super-gravity separation has been successfully applied in removing impurities from metal melt, owing to the difference of densities between impurities and melt.

Then, this method is proposed to recover zinc from galvanizing hard zinc. Ideally, the solid dross particles (hard zinc), can be removed at the galvanizing temperatures (440-460 °C) from the molten zinc under a super-gravity field, and the purified zinc with iron content lower than 0.1 wt% can be directly returned into the galvanizing bath for coating production.

Research in the area of pyisicometallurgical methods of zinc ash processing is oriented on the study of parameters influencing the efficiency of smelted zinc recovery, such as the temperature, the time period and the usage of gravity coefficients (Trpčevská, 2015).

Then Wang et al. (2017) examined the feasibility of applying super-gravity separation to recover zinc from the hard dross residue of hot dip galvanizing. That study investigated in detail the influences of gravity coefficient, separation time and separation temperature on the separation efficiency. Besides, the mechanism of super-gravity separation of galvanizing dross was also examined.

After separation, the filtered zinc with high purity is collected and a small amount of residue is intercepted by the filter medium. The procedure is presented in the flow chart shown in figure 11 and the used equipment in figure 12. Furthermore, the method is described step by step.

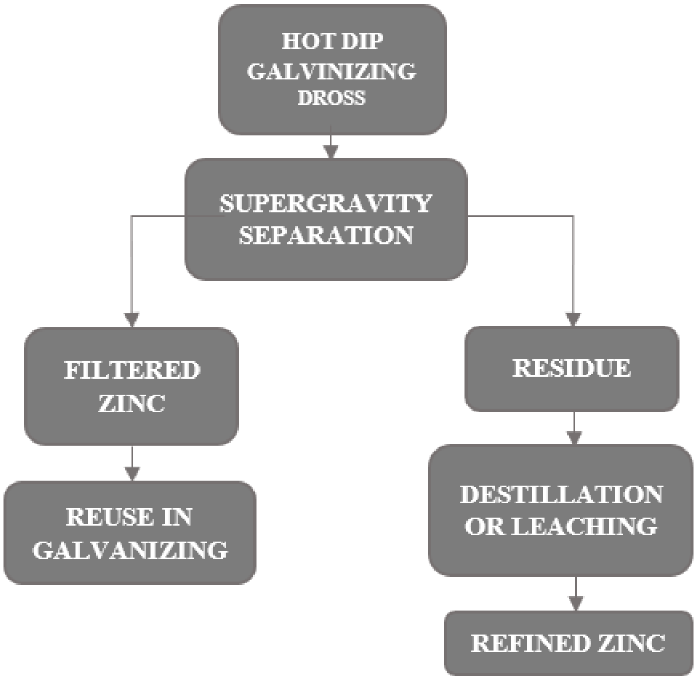


Figure 11. Flow chart of recycling zinc dross by super-gravity separation

Firstly, a centrifugal apparatus generates the super-gravity field. It is mainly constituted by a heating furnace (5) and a counterweight (1) which is installed symmetrically onto the centrifugal rotor (3). The heating furnace has a cylindrical alumina chamber of 40 mm diameter and 150 mm length and is heated by the resistance wire with the isothermal zone of 80 mm long. A program controller with a type R thermocouple (10) controls the temperature of the furnace, which is within the observed precision range of ±3°C. Once the centrifugal rotor starts running, the heating furnace and counterweight change from vertical to horizontal and rotate therewith. During rotating, the transmission of power and electrical signals is realized by the slip ring (12) fixed on the centrifugal axis (2).

In order to conduct the super-gravity separation experiment, a galvanizing dross sample is firstly placed into a self-design graphite filter crucible (9) consisting of two small crucibles (8) with the same internal diameter of 21 mm.

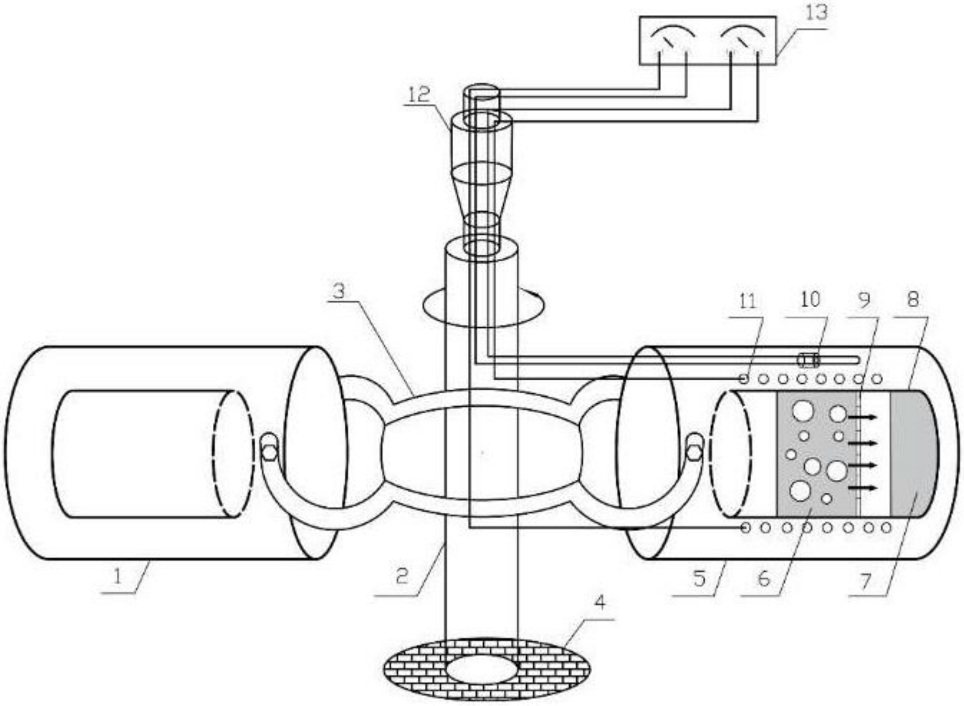


Figure 12. Schematic diagram of the centrifugal apparatus: counterweight (1), centrifugal axis(2),centrifugal rotor (3), base (4), heating furnace (5), galvanizing dross sample (6), filtered zinc (7),graphite crucible (8), filter (9), type R thermocouple (10), resistance coil (11) ,slip ring (12), temperature controller (13).

Following with the procedure, 20 holes with a diameter of 1 mm are evenly distributed in the bottom of the upper crucible. A carbon fiber felt, CFF, with a thickness of 5 mm is used in this work as the filter medium. The graphite crucible (8) is then heated to the target temperature for 15 min in the heating furnace of the centrifugal apparatus. Afterwards, the centrifugal apparatus is started and adjusted to the desired rotational speed to conduct separation isothermally. The centrifugal apparatus is not shut-off until the target separation time. After that, the graphite crucible is taken out from the furnace and quenched in water.

The residue and filtered zinc (zinc with iron content lower than 0.1 wt%) is collected from the upper and lower crucibles, respectively, in preparation for further characterization or further refined by conventional methods, such as distillation, leaching or electrorefining, later discussed.

It is noticed that Wang et al. (2017), analyzed the chemical composition of the filtered zinc and separation efficiencies obtained at different gravity coefficients, t = 180 s and T = 510 °C. The zinc hard sample chemical characteristics are shown in table 3. The content of zinc in this dross sample is very high, accounting for 95.4 wt%, followed by aluminum, 2.59 wt%, and iron ,1.91 wt%. The low oxygen content of 0.0819 wt% indicates the dross sample mainly consisted of metals with a small amount of oxide.

Table 3. *Chemical composition of hard zinc sample for super-gravity separation*

Chemical composition of the original galvanizing dross sample (wt%)			
Zn	**Al**	**Fe**	**O**
95.4	2.59	1.91	0.0819

The results of this article are summarized in the following figures. As it was mentioned before, in order to know the separation efficiency of this method the influences of gravity coefficient (G), separation time (t) and separation temperature (T) have been studied.

Then, the yield of purified zinc (Y_{zinc}) and the recovery rate of zinc (R_{zinc}) are represented against these three variables.

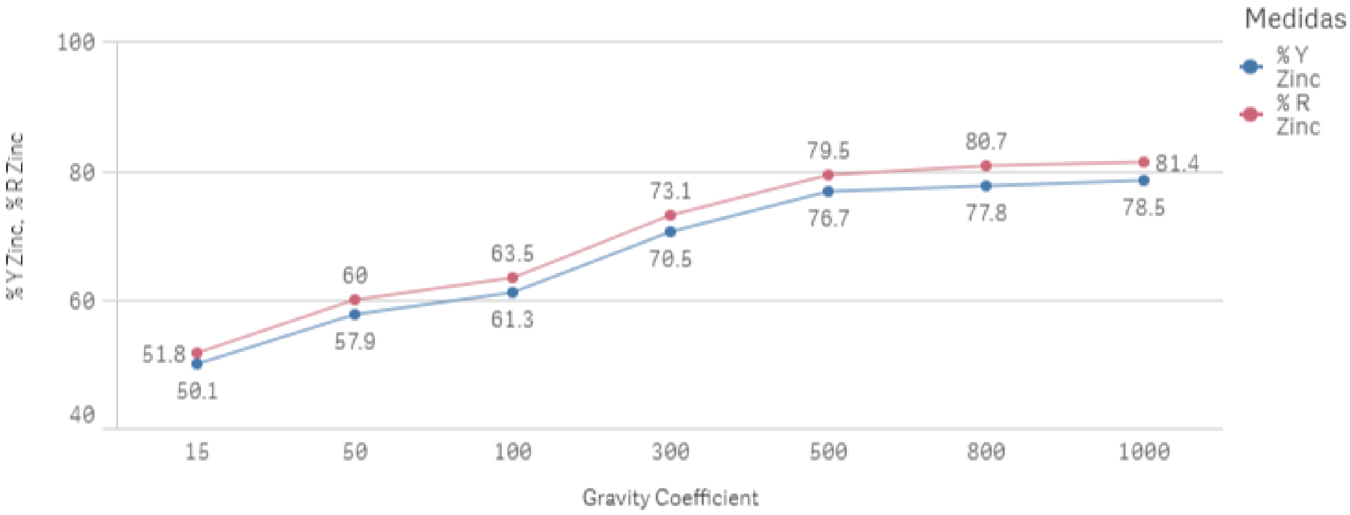


Figure 13. %Yzinc and % Rzinc evolution vs Gravity coeffiecient (t = 180 s and T = 510 °C)

Y_{zinc} increased with increasing the gravity coefficient, mainly because more molten zinc was filtered into the lower crucible when the gravity coefficient was improved. The variation trend of R_{zinc} was similar to that of Y_{zinc}. Specifically, there was a sharp increase in R_{zinc} from 51.8 wt% to 79.5 wt% with the gravity coefficient increased from 15 to 500, and beyond 500 the increase in R_{zinc} was limited.

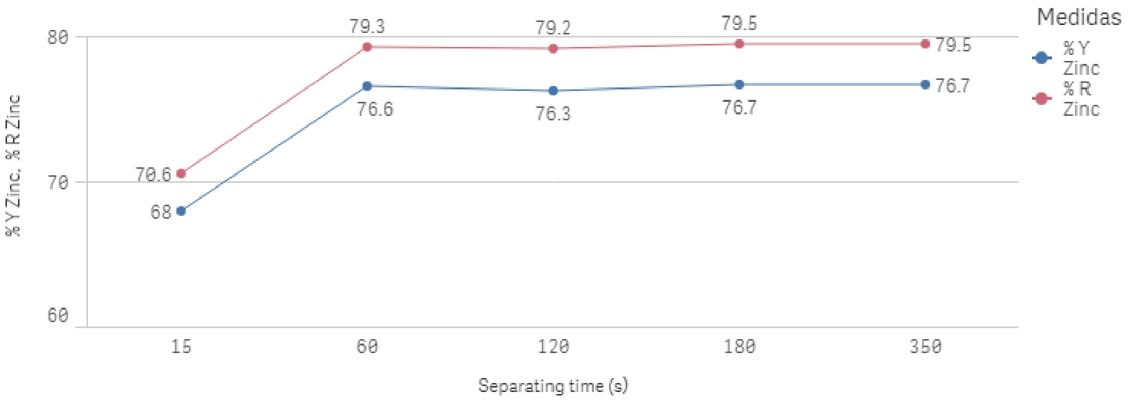


Figure 14. %Y$_{zinc}$ and % R$_{zinc}$ evolution vs separation time (s) (G = 500 and T = 510 °C)

Through figure 14 it is shown that both Y_{zinc} and R_{zinc} experienced the quick increase at the beginning of the super-gravity separation. Y_{zinc} and R_{zinc} exceeded 76 wt% and 79 wt%, respectively, in a short separating time of 60s, indicating that the super-gravity separation was a high efficient route to recovering zinc from galvanizing dross. With the separating time ranging from 60s to 350s, Y_{zinc} and R_{zinc} remained almost stable.

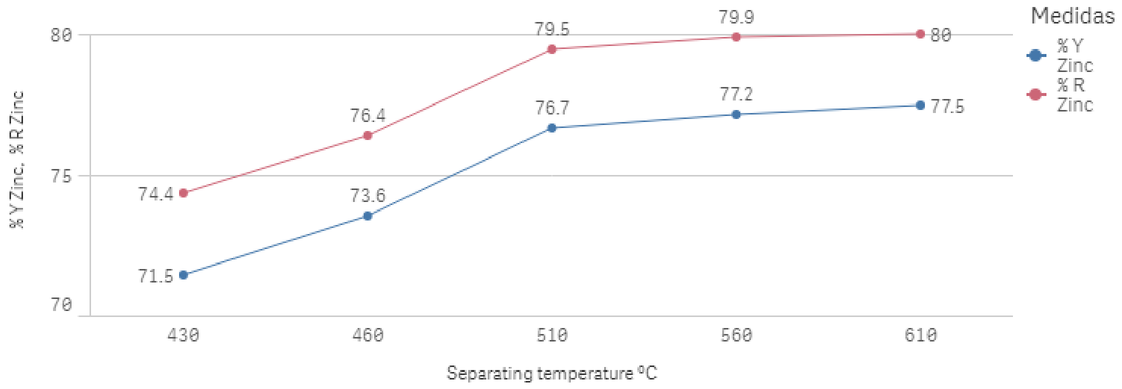


Figure 15. %Yzinc and % Rzinc evolution vs Separation temperature (°C)(G = 500 and t = 180 s)

The Figure 15 shows that temperature did not affect to Y_{zinc} and R_{zinc} compared with the other factors. It is observed that changes in temperature generate a very slow rate of increase in Y_{zinc} and R_{zinc} .

Finally, according Wang et al. (2017), who studied the super-gravity method, taking in to account the operational conditions mentioned above, over 79 wt% zinc was recovered with a high purity of about 99 wt%. In addition, although it is not shown in these figures, about 97 wt% of the iron impurity was removed.

b. Filtering centrifugation

This technology is presented for the recovery of **zinc ash** and **hard zinc** based on **filtering centrifugation**. It is a semi-continuous process where the residues can be separated from a liquid melt. The physical separation of the solid from the liquid phase in a filter is a basic technique. Due to its simplicity it can be an economical attractive technique in the predominantly small to middle sized HDG companies.

Schmitz and Friedrich, (2007), proposed a study whose objective was the recovery of metallic zinc from zinc ash and hard zinc dross, by using filtering centrifugation. For the experiments an amount of ~10 kg zinc with ~10 kg of hard zinc is heated up to 450°C. By this setup the concentration of intermetallic phases in the melt is ~12 wt.% due to the fact that they assume a concentration of zinc in the hard zinc of 24.5wt.%.

The authors explained that filtration processes can be classified in depth filtration and cake filtration. The depth filtration is frequently selected in the non-ferrous metallurgy, if a high clarification of the melt is needed; for example, in aluminum casting facilities. However, the cake filtration plays an important role if a high throughput with low residual moisture of the cake is desired.

According to this study, filtering centrifugation is carried out following a semi-continuous process where the solids are separated from a liquid melt (bath zinc). In line with the process description, the centrifuge consists of two rotating, hollow cones, also called rotors, in which the suspension of solid and liquid phases is sucked in. The liquid melt leaves the internal space through a small gap between the cones. On the opposite site, an electric drive is installed for rotation of the axis. When the cones are immersed into a liquid metal bath, melt penetrates into the hollow space by the help of collecting holes in the upper or lower cone. Because of the rotation of the cones the melt is accelerated and forced to leave the cones at the gap of the contact area of the cones.

If there are solids in the melt, such as hard zinc, which are heavier than the liquid phase, they precipitate immediately when entering the cones. Lighter particles, ash zinc, are floating inside the cones. Due to the gap size, of a few tens millimeters, the solid particles are kept within the cones and are forming a growing filter cake during the loading time. Figure 16 shows a schematic description showing how the centrifugation principle works.

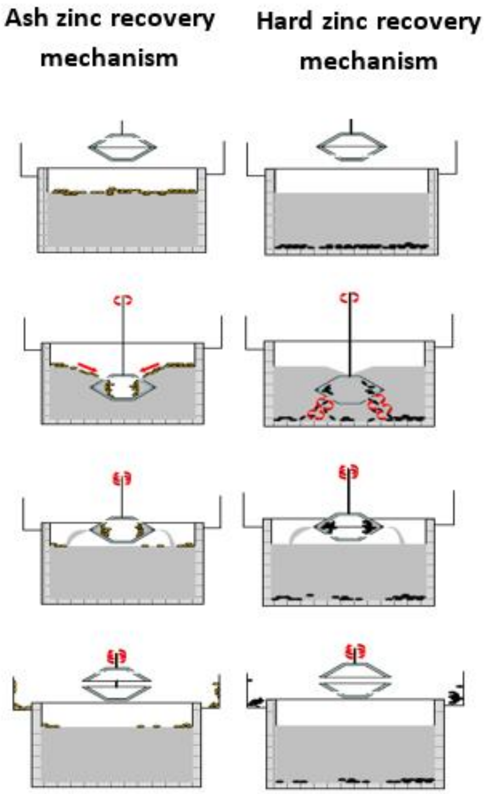


Figure 16. Schematic overview of the filtering centrifugation technology

As the filter cake gets the maximum allowable thickness the cones are removed from the melt. By accelerating the speed of the axis residual moisture can be removed from the filter cake; it flows back to the metal bath. After this ‘drying’ step, the cones are lifted further. The increasing distance of the cones initiates the automatic removal of the filter cake into a collection bin. With this last step, the separation process restarts by the penetration of the melt with the two rotating shells.

The dry filter cake is finally removed from the rotor and collected besides the bath. The melting centrifuge can be adapted to the desired characteristics of the residues hard zinc and zinc ash.

Figure 17 shows a typical sequence, lasting between one and five minutes, of these different process steps as function of time and rotating speed.

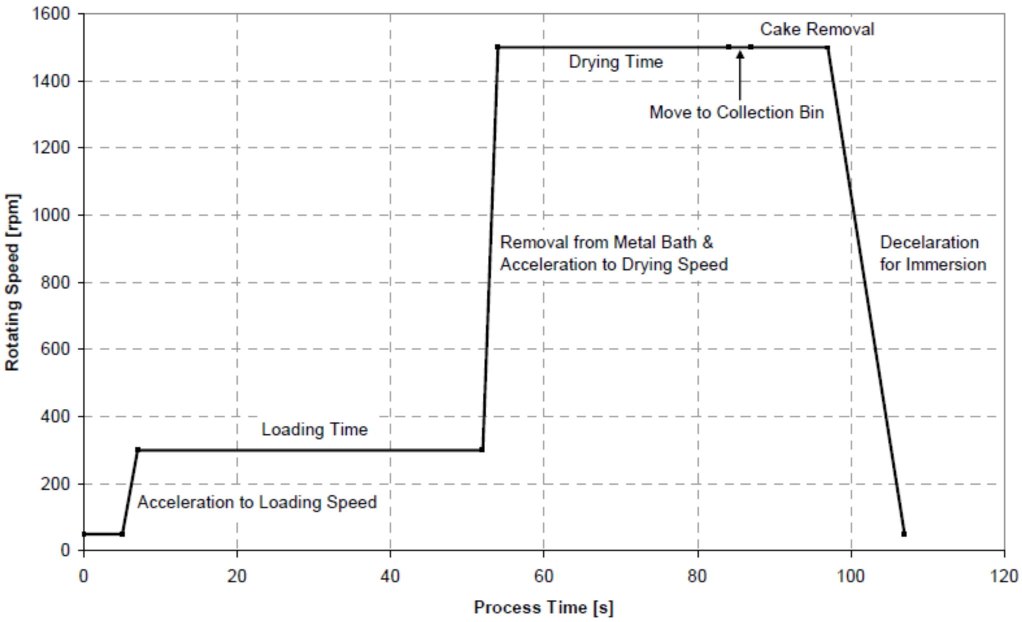


Figure 17. Typical process cycle of a filtering centrifuge (Schmitz and Friedrich, 2007)

On the other hand, figure 18 shows the equipment were the study was carried out.

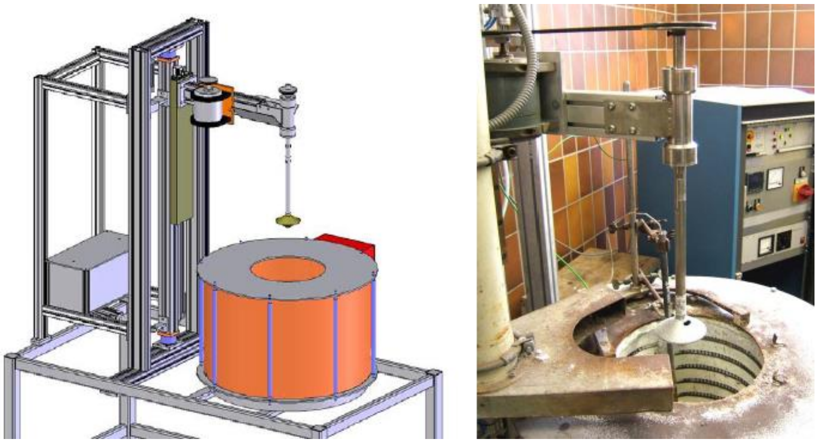


Figure 18. Sketch and picture of the laboratory centrifuge for hot melts

The results of laboratory scale tests resulted in a zinc recovery of 96 % by separating the intermetallic phases from hard zinc. The conclusion from this article is that doing the previous procedure, it could be possible at least a reduction of 9 % of the zinc input at a hot dip galvanizing company, accompanied with the reduction of the produced amount of hard zinc.

c. Vapor Pressure Separation

This method is probably closer to be a purification technique such as leaching or electrowinning (that will be mentioned later), than a zinc recovery method. However, it has been classified as a physico-metallurgical method due to the principle that governs it.

Yuan and Zhang, (2017), put forward on the concept that using hot-dip galvanizing dross (hard zinc) to prepare zinc powder directly for the reclaim and recycle of the zinc resource. Traditionally, the prepared method of zinc powder was to make the zinc dross to zinc ingot metal first, then using the zinc ingot metal to prepare zinc powder mainly. Then, this study proposed to prepare zinc powder directly using hot-dip galvanizing dross. In addition to powder preparation, the authors observed the exterior pattern of zinc powder, they analysed the distribution of grain size and determined the content of zinc in order to recover and purify the zinc from the hard zinc.

In order to prepare zinc powder from hard zinc, authors consider that when physicochemical characteristics of metal zinc are near to the melting point, the vapor pressure of hot-dip galvanizing changes exponentially. This effect allows the hot-dip galvanizing dross to prepare zinc powder according to the characteristic of zinc and zinc iron alloy. The chemical composition of hard zinc sample selected to this study is also gathered in main table of this work, table 2.

The procedure consists y basically 4 steps represented below in figure 19.

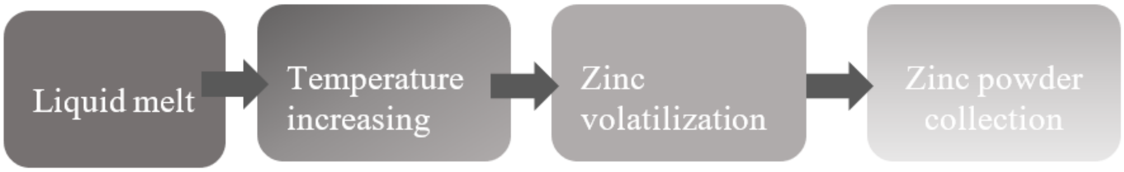


Figure 19. Procedure of Vapor pressure separation flow diagram for hard zinc

When the metal zinc was in the liquid phase, the variation of vapor pressure observed at increasing temperatures was initially very slow, although when the temperature reached a certain extent (for zinc, the temperature was 750 °C), the zinc vapor pressure increased rapidly, but other metal impurities were not evaporated or the evaporation rate was very short, so elemental zinc volatilized first. Next, zinc powder was collected in a condenser, achieving the aim of purifying the hot-dip galvanizing dross.

Table 4 shows that the content of zinc in the prepared zinc powder increased obviously, the purity increased to 99.793% from 64.988%. And the content of other impurity elements such as Al, Fe, S, P, Ni, Pb was reduced in the recovered purified zinc.

The content of the metal zinc in the zinc powder was higher to reach **99.793%,** comparing with the composition presented in table 2. The content of the impurity composition could reduce 2-3 order of magnitude than the content of the impurity in the hot-dip galvanizing dross (Yuan and Zhang, 2017).

Table 4. *Chemical composition of powder zinc after vapor separation method from hard zinc*

Power dust chemical composition (wt%)					
Zn	**Al**	**Fe**	**S**	**P**	**Pb**
99.793	0,0724	0,0561	0.0233	0,0025	0,0527

4.1.2. Pyrometallurgical process method

Currently, pyrometallurgical processing technologies are the most widely used for zinc recovery. Some pyrometallurgical processes are aimed at zinc ash in-house recovery and some of them are applied outside the place of origin. The final product of the pyrometallurgical processing can be metallic zinc or zinc compounds.

Pyrometallurgical method uses heat to separate desired metals from other materials. These processes take advantage of differences between oxidation potentials, melting points, vapor pressures, density and / or miscibility of the components of the ore when they melt (Stellman et al., 1998). Research in the area of pyrometallurgical methods of zinc ash processing is oriented on the study of parameters influencing the efficiency of smelted zinc recovery, such as the temperature, the time period and the usage of fluxes (Trpcevska et al, 2015).

Making the research for the present paper, different pyrometallurgical experiments were founded, as it is described below. As an example of pyrometallurgical process which achieve metallic zinc, is the proposed study of Trpcevska et al. (2015*).* On the other hand, Waelz method is presented as a pyrometallurgical method whose product is not metallic zinc, but zinc compound, zinc oxide.

Trpcevska et al. (2015), chose a sample from a certain Slovak hot dip galvanizing plant. The detailed chemical composition of the sample was shown in Table 2.

The aim of the pyrometallurgical process study was to investigate the effect of time (30, 60, 90 minutes) and temperature (480, 500, 550, 600, 650, 700°C) on the recovery of smelted zinc. They tried to find out the most suitable conditions of processing based on the quantitative results (mass balance), as well as on the qualitative results (chemical analysis, microstructural analysis) of smelted zinc.

In this study, two kinds of **zinc ash** samples were studied, classified according to the grain size of the solid residue; coarse-grained (particle diameter d ≥ 1.25 mm) accounted for 60% of the overall ash sample weight, while the fine-grained (d < 1.25 mm) fraction contained 40% of the total mass. The zinc ash sample was sieved on a dry mechanical apparatus using sieves with different mesh sizes.

It was observed that Zn content slightly decreased with decreasing grain size fraction. The opposite tendency was observed for the chloride content, while the content of Fe and Al slightly increased. The content of other elements (Pb, Cu and Cd) was independent of the size fraction. **Coarse-grained** fraction showed irregular particles of various sizes with light grey up to dark grey and brownish shade. Light grey areas represent metallic zinc and brownish ones represent zinc parts in the ash surface.

Finally, this research studied the pyrometallurgical processing of the coarse – grained fraction of the zinc ash residue, since processing of the fine-grained fraction could cause passing or clogging the openings of the glass-ceramic sieve.

The experiment was carried out in a thermo-mechanical laboratory. The main equipment is shown in figure 20. An electric resistivity furnace controlled by a thermoregulation unit (7) was used for melting the load and to set all the relevant melting conditions. Centrifugal force was evolved using a laboratory mixer after melting the batch of residue. The process was running in a nitrogen protective atmosphere.

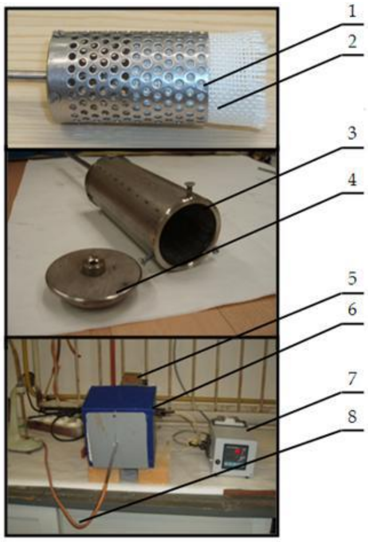


Figure 20. Main parts of equipment. (1) Perforated stainless rotating cylinder (2) Glass ceramic sieve (3) Stainless steel cylinder, (4) Lid for stainless steel cylinder, (5) Electric bender (6) Furnace with connected thermocouple (7) Thermoregulation unit, (8) Nitrogen supply. Trpcevska et al (2015).

The procedure of this method starts by weighting sample. Once the sample is weighted, it is introduced in a perforated rotating cylinder (1), lined with a glass-ceramic sieve (2), which is then closed with a lid (4). This unit is introduced in a closed stainless-steel cylinder (3) and placed into a furnace space (6). At this point, the melting process starts. After the melting process is finished, an electric mixer (5) that serves as a source of centrifugal force, is connected to the perforated cylinder for 30 seconds to centrifuge the smelted zinc. Smelted zinc is collected in the stationary cylinder. After that, cooling starts using nitrogen (8), during approximately 30 minutes.

Once the sample is cooled, the stationary cylinder with the perforated cylinder are removed out of the furnace space. They are disassembled to obtain products of melting (smelted zinc and remaining ash). The obtained products are weighed for evaluation of the process efficiency under the chosen conditions.

Trpcevska et al. (2015), observed that the most favorable conditions in terms of recovery of zinc, **88%,** were obtained at the temperature of 500°C and a melting time of 30 minutes.

The Waelz process is a method of recovering zinc and other relatively low boiling point metals from metallurgical waste such as flue dust and other recycled materials using a rotary kiln called Waelz Kiln. The zinc enriched product is referred to as **waelz oxide**, and the reduced zinc by product as **waelz slag.**

Although this technology was not initially created for the purpose of zinc recovery from ashes and hard zinc after HDG, through process modification and state-of-the-art offgas technology, it is also possible to process other zinc containing materials, including zinc sludges and drosses (hard zinc) (Mager and Meurer, 2000).

Figure 21 presents the description of the procedure. The first step in this process is an agglomeration of the raw materials with reduction agents and slag-forming additives. Dry dusts with a pneumatic conveying system to raw materials silos. After that, a homogenous mix is prepared in the form of pellets, to feed the kiln (furnace).

The pellets are charged into the feed hopper of the Waelz kiln. It is noticed that there is a prerequisite for a high zinc yield in the Waelz oxide product and a **satisfactory hard zinc** quality (Espinosa et al, 2004). Due to this fact, the pellets should exhibit a constant composition, and size to ensure uniform kiln operation, regardless of the residue to be treated. The minimum content of Zn in the feed material should not be less than 18%.

The moist material moves through the rotary kiln, being dried and preheated by the kiln gas which flows countercurrently. In the reaction zone, reduction of the metal oxides begins at about 1200 ºC with zinc and lead being vaporized as metal. The main reaction of the zinc starts in the second half of the Waelz kiln. The final step in the kiln is the reoxidation of the iron at the discharge head to form the slag at temperatures up to 1120. Minimum temperatures of 1000 ºC are necessary for a total reduction of zinc and lead containing residues.

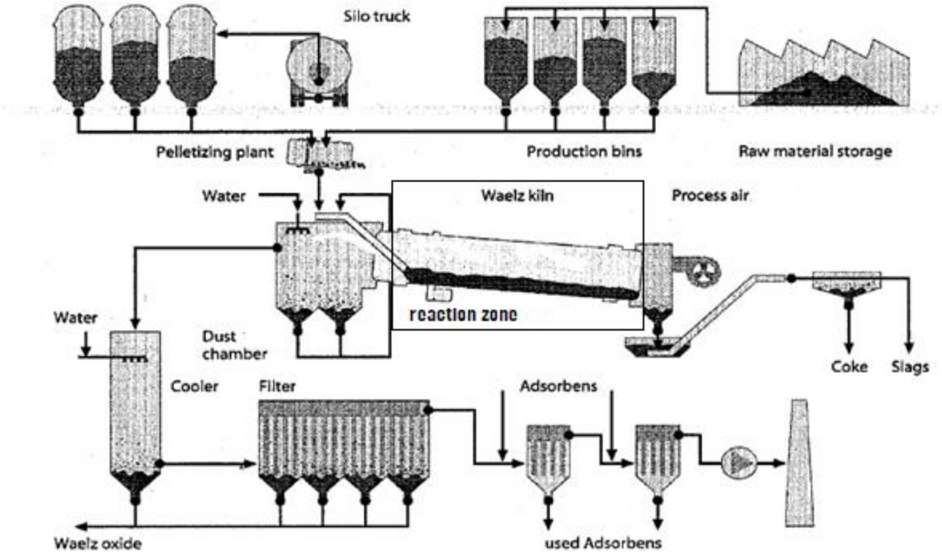


Figure 21. Simplified Flow Diagram of a Waelz Plant

In the kiln atmosphere, which is operated with excess air, process air is injected through the kiln end, zinc is reoxidized. The reduced Zn, because of its high vapor pressure, is volatilized as Zn gas and then combusted to form ZnO powder, which is collected in a filter. The combusting zinc liberates heat, which is an important part of the heat balance of the kiln (Antrekowitsch et al, 2014).

Chlorine and alkalis volatilize jointly with the heavy metals. The off-gas loaded with dust is treated in a downstream off-gas system.

In the first stage, coarse particles are separated in a dust chamber and returned to the kiln. The hot offgas, loaded with dust, is cooled down and the **Waelz oxide** is separated in a precipitator. The dust-free offgas is cleaned of dioxins, Hg or Cd. These impurities are retained using specific adsorbents. Finally, the cleaned offgas is discharged to the atmosphere through a fan, with a level of pollutants suitable to meet the corresponding environmental standards.

The retention time of the feed material in the Waelz kiln is between 4 and 6 hours depending on the bricklining, kiln length and rotary speed. The slag is discharged through a wet deslagging system.

Regarding the equipment, the Waelz kiln itself is typically 50 m long with a diameter of 3.6 m. It is slightly inclined and has a rotary speed of 1.2 rpm.

Unlike the other technologies discussed so far, the Waezl method is not a technology thought to recover zinc from the ashes and dross residues of hot dip galvanizing. Therefore, there are no literature sources with recovery yields or chemical composition data of samples to study. In other words, there are no direct studies of this application for the mentioned purpose.

4.1.3. Hydrometallurgical process

With the depletion of high-grade ores/concentrates, the hydrometallurgical processing of secondaries/wastes is gaining importance in the metallurgical industries for the recovery of metallic wastes. This is also evident for the recovery of zinc from complex secondaries/wastes, using different lixiviants (Tsakiridis et al, 2010).

Examples of technologies that are employed in hydrometallurgical processes are leaching, precipitation, electrolytic reduction, ion exchange, membrane separation and solvent extraction. Figure 22 illustrates, the possible steps for hydrometallurgical process in order to better understand this method.

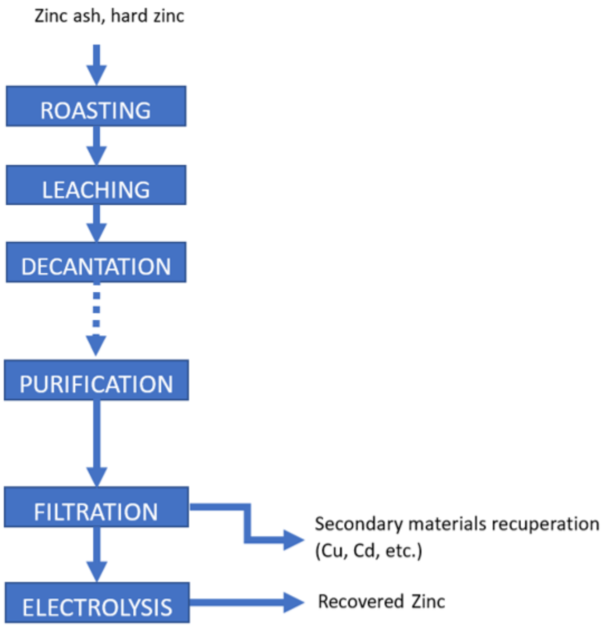


Figure 22. Schematic overview of different stages of a hydrometallurgical process for zinc recovery

The first stage of a hydrometallurgical process is usually roasting. During roasting, the concentrated sample is subjected to either low temperatures (partial roasting) or high temperatures (to achieve dead roasting). The product of this step is a calcine that is leachable. The leaching process sometimes requires high pressures, the addition of oxygen or elevated temperatures (Stellman et al, 1998).

Depending on the nature and composition of the secondaries, a suitable lixiviant could be selected to dissolve the desired metals (Ren et al ,2010). Sulphuric acid, hydrochloric acid, ammonia, sodium hydroxide has been employed as lixiviants. However, after the leaching with a lixiviant, impurities must be removed from the liquid phase by other methods such as **selective precipitation, cementation, solvent extraction, ion exchange or electrolysis**

methods (Jha et al., 2000). Finally, from the leached solution, the desired metal or its compound can be recovered by precipitation or reduction.

Following in this section, some studies dealing with the application of hydrometallurgy to zinc recovery, are presented. First of all, it must be considered that all the times, temperatures or general conditions gathered below, were used accordingly to the sample characteristics and specifics amounts of each study. The relevant information that we want to highlight through the following description is that there are many hydrometallurgical alternatives, and the variants depend on each author's approach.

The first presented article, Dvorák and Jandova (2004), is an experiment to treat zinc ashes from HDG galvanizing and the second is a review of hydrometallurgical recovery of zinc from industrial wastes, not only HDG wastes.

Dvorák and Jandova, (2004), developed a laboratory study for zinc recovery from chloride-containing **zinc ash**, formed during hot dip galvanizing. The authors carried out a procedure with several steps, very similar to the scheme in figure 22.

It is very important to take into account the chemical composition of the particular selected samples of zinc ash. As it is shown in the main table, table 2, this zinc ash sample contains chloride. Such wastes are not suitable for direct leaching with sulphuric acid since the chlorides would enter the resulting sulphate solutions. In addition, chlorides are not tolerated in the subsequent electrowinning of zinc metal, as even a very small amount in the sulphate electrolyte is extremely damaging to the electrolysis. It is possible, however, to remove chloride from this solution by solvent extraction process (not included in figure 22) using organic amines as extraction agent, dissolved in a suitable organic solvent, or to leach chloride-containing zinc wastes with a liquid organic phase containing a cation exchanger.

Then, following with the procedure:

Leaching: Firstly, the leaching step were carried out. Leaching experiments were performed in a closed, stirred, thermostated glass reaction vessels provided with pH and temperature control and with a water cooler. Standard mixing was accomplished by means of an impeller. During leaching, samples were withdrawn at selected time intervals to determine the reaction rates of zinc and impurity dissolution. The zinc ash was **leached with diluted H_2SO_4**

The conditions were as follows: 10% H_2SO_4, liquid to solid ratio of 8:1, laboratory temperature, 1 h. Such leaching conditions made it possible to generate leach liquors containing approximately 80 g Zn/L, which could be theoretically subjected to zinc electrowinning.

Decantation: The main impurities, such as iron, copper, cadmium, and organic compounds were removed from the leaching liquors by **pH-controlled precipitation** using ZnO as a neutralizing agent.

Purification and filtration: Iron was separated from zinc leach solutions by hydrolytic pH-controlled precipitation using ZnO as a neutralizing agent at pH 4 and at a temperature of 40 ^{o}C.

Subsequently, organic impurities together with Al and Si were removed at 40 ºC within 10 min using active carbon. Copper and cadmium were precipitated at pH 4 and temperature of 60 ºC using zinc powder. The cementation, which was conducted only in one step without using any activation agent, was completed within 30 min.

Table 5 gathers the final chemical composition from de zinc precipitates which consists in the compounds presented in the table and $Zn_5(OH)_6(CO_3)_2$ (hydrozincite). It is observed comparing with the initial composition of the sample given in table 2, that impurities have been reduced considerable, highlighting chloride content.

Table 5. *Composition of zinc precipitates at 40 ºC*

Element content [wt.%]					
Zn	Fe	Mn	Cu	Cd	Cl^-
61.3	0.001	0.0024	0.005	0.006	<0.01

Electrowinning: As it was mentioned before, chlorides were precipitated and chlorides present in the organic phase were readily washed out with water.

Zinc carbonate is precipitated from purified leach liquors using Na_2CO_3 as a precipitation agent at pH 8.5 and temperatures of 20, 40, 60, and 80 ºC. After that, zinc carbonate formed at 40 ºC is dissolved in diluted H_2SO_4. The ratio of zinc carbonate to H_2SO_4 and H2O was chosen to generate zinc electrolytes containing approx. 60 g Zn/ L and 10 g H_2SO_4/L.

Besides of the fact that leaching experiments were performed in a laboratory, in a closed stirred glass flask, the samples were studied and observed to determine the reaction rates of zinc and impurity dissolution taking in to account the maximum possible recovery of zinc. However, leaching conditions were selected to achieve the minimum concentration of Zn g/L that is needed for electrowinning. After the experiment, leach residues were filtered, washed with water, dried and weighed.

Electrowinning of zinc was carried out in a laboratory electrolyser without electrolyte circulation under the conditions showed in table 6.

Table 6. *Electrowinning conditions*

Electrolyte volume	**1L**
Anode	Pb 1%Ag, active area 1 dm^2
Cathode	Al,active area 1 dm^2
Current density	200,300,400 A/m^2
Electrode distance	20 mm
WElectrolyte temperature	40°C
Duration	4h

Finally, through this study the minimum purity of metallic zinc over the whole range of current densities was 99.3% and more than 98 % of zinc recovery was achieved.

Regarding the second article analysed for this section, Jha et al. (2000) studied a hydrometallurgical process for the recovery of zinc from industrial wastes. In this article, several leaching techniques were studied. The authors used different lixiviants such as sulphuric acid, hydrochloric acid, ammoniacal solution or sodium hydroxide, depending on the waste to be treated. However, as Dvorák and Jandova, (2004), Jha et al. (2000) opt for sulphur acid leaching solution, since they claimed through the article that this leaching solution is used for the recovery of zinc from secondary wastes.

A leach solution then is prepared and then purified with respect to dissolved impurities using precipitation, ion exchange or solvent extraction methods as in the previous article. What is more, the metal or salt is produced also from the purified solution by electrolysis or crystallization. It was observed that to treat a residue similar to the zinc ash or hard zinc from HDG galvanizing, sulfuric acid was also employed as lixiviant.

5. TECHNOLOGIES COMPARATION

Over the last decades, a significant number of alternative processes aimed to metal recycling have arisen. To improve the industrial process to save energy by avoiding high temperatures, numerous hydrometallurgical and pyrometallurgical concepts have been developed.

The characteristics presented in table 7 are mostly justified by the bibliography, and others are based more on the author's assumptions. For instance, there is the aspect of economic viability. Given that no economic analysis was carried out throughout this project, the notion of economic viability will be processed as three separate concepts: - simplicity of the process – equipment needs - energy requirements. As a result, they are established as positive or negative sign depending on whether or not they are characteristics favourable to the technology.

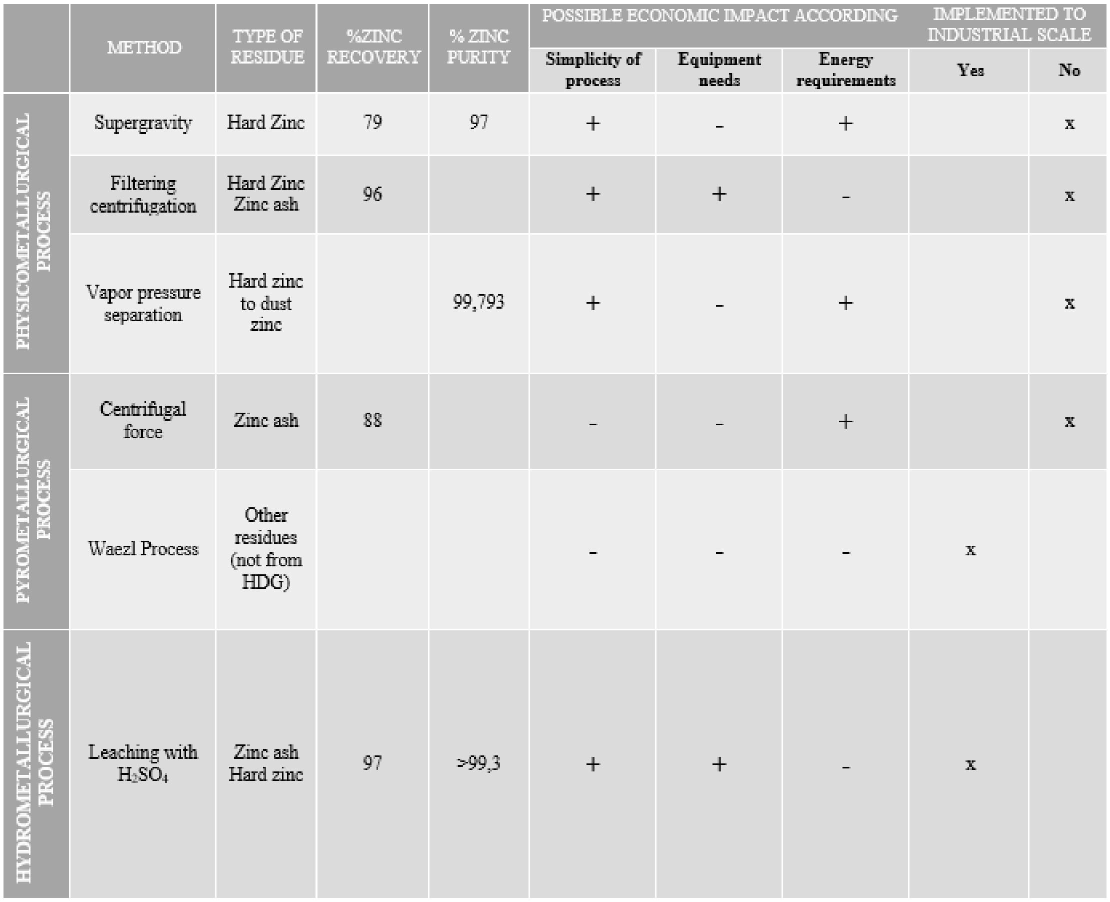
For instance, as a physical method, the super-gravity separation process is believed to be superior to the conventional methods, due to its simplicity, low energy consumption and improved environmental performance. The super-gravity separation process can contribute significantly to the recycling of hot-dip galvanizing dross. In fact, methods classified as physicometalurgical, are the most novel processes for zinc recovery. However, they are in experimental phase and have not been implemented yet at industrial scale. Therefore, although it seems that this category is suitable to achieve the best zinc recovery rates and to provide the highest zinc purity in the recovered material, it has to be further studied in order to be scaled up to the real necessities of the industrial scale.

On the other hand, there is the fact that today, it is known that most hot-dip galvanizers sell their ashes and dross to companies specialized in the recycling of these residues. Some of the methods applied by these companies is the Waelz process to recover zinc in the form of zinc oxide. That is, the product of the Waelz process cannot be reused in a hot dip galvanizing plant. However, it has been presented as an alternative in this work because since it is a really implemented method on an industrial scale, it may be a good opportunity to combine that experience of this method with some other novel process presented so far.

Regarding the main advantage offered by the hydrometallurgical processes compared to pyrometallurgical processes, in addition to the practical elimination of effluents or gaseous emissions (not studied in this project), is the high zinc purity that can be obtained in the recovered products. However, during hydrometallurgical recycling processes, by-products and other residues occur which have to be reprocessed again. Thus, the reprocessing problem is only shifted.

Meanwhile, pyrometallurgical reprocessing methods produce phases in which resources are contained in a concentrated form for nonferrous metal recovery, in addition to the advantage that the by-products are ecologically compatible. That is why pyrometallurgical processes are mainly suitable for commercial-scale application.

Table 7. *Technology recovery comparison according mainly characteristics*



	METHOD	TYPE OF RESIDUE	%ZINC RECOVERY	% ZINC PURITY	POSSIBLE ECONOMIC IMPACT ACCORDING			IMPLEMENTED TO INDUSTRIAL SCALE	
					Simplicity of process	**Equipment needs**	**Energy requirements**	**Yes**	**No**
PHYSICOMETALLURGICAL PROCESS	Supergravity	Hard Zinc	79	97	+	-	+		x
	Filtering centrifugation	Hard Zinc Zinc ash	96		+	+	-		x
	Vapor pressure separation	Hard zinc to dust zinc		99,793	+	-	+		x
PYROMETALLURGICAL PROCESS	Centrifugal force	Zinc ash	88		-	-	+		x
	Waezl Process	Other residues (not from HDG)			-	-	-	x	
HYDROMETALLURGICAL PROCESS	Leaching with H_2SO_4	Zinc ash Hard zinc	97	>99,3	+	+	-	x	

6. CONCLUSIONS

The results of the project are subjected to a number of assumptions and interpretations; thus, an uncertainty analysis could be useful to determine the accuracy of the results. However, it provides insightful conclusions that might lead to further investigations in this field.

On the one hand, public information about what happens to the solid residues of hot dip galvanizing, with its entire possibility as recycled material, is not available; only the detailed information of wastes from steel making process has such literature coverage. Above all, there is hardly any information on how to recover zinc from dust residues and reuse them with the right purity on an industrial scale. Therefore, greater knowledge about where the wastes such as zinc ash or hard zinc would be of interest is needed for a further study.

Table 7 shows all the recovery technologies that have been studied during the work in order to determine which would be the best one today, according to the characteristics that have been given.

The conclusion of the present project is that in the present day, novel technologies with capability of providing high purity and high zinc recovery simultaneously, are still in their experimental phase and not yet ready to be implemented in an industrial scale. It can be seen that any alternative for zinc recovery suits the required characteristics to be applied in a hot dip galvanizing plant.

Considering, advantages and disadvantages commented in the last section and according the relevance of the waste generation, hydrometallurgical or pyrometallurgical processes would be the best option. However, it is proposed the idea of combined procedures used for processing several zinc wastes types, including zinc ash or hard zinc. These can be based on pyro – hydrometallurgical procedures since these procedures are the most efficient in terms of completeness of processing of zinc waste and they are not still applied in galvanizing plants.

Finally, regarding the concept of circular economy within this metallurgical field, it is not possible to establish a 100% efficient waste recovery system but it should be mentioned that it is significant to continue investigate on it and efforts can be made to close the material loops to a greater extent.

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