# HYDROMETALLURGICAL ZINC PRODUCTION - ENVIRONMENTAL AND EXERGY ANALYSIS

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**Abstract**

The metallurgical industry is characterized by significant consumption of material and energy resources. The natural resources used are primarily non-renewable. The hydrometallurgical zinc extraction is distinguished by a variety of processes and equipment, possible options for replacing some of them with more efficient ones, opportunities for maximum utilization of energy resources. The object of the present analysis is the actually functioning chemical-technological system - KCM - SA, Plovdiv. The fundamental production units, namely roasting of zinc sulphide concentrates, sulphuric acid leaching of the obtained calcine, electrowinning of zinc, ecologically oriented units - processing $SO_2$ - containing gases to sulfuric acid and waste zinc cakes via Waelz process, as well as the system as a whole, have been analysed. The exergy method of thermodynamic analysis was applied as a research method. The obtained results are compared with those from our previous studies, as well as with literature data on similar processes. Higher energy-technological efficiency and reduction of the harmful impact on the environment can be achieved by increasing the share of renewable energy resources and processed secondary raw materials and reducing specific energy consumption.

**Keywords:** Environmental Impact, hydrometallurgical zinc production, emissions, sustainability, exergy analysis

## 1. INTRODUCTION

Energy intensity and anthropogenic load are dominant criteria for evaluating the competitiveness and efficiency of any modern technology. This applies with might and main to metallurgy, which is characterized by a high consumption of primary material and energy raw materials and, at the same time, the emission of significant amounts of harmful substances into the environment. Currently, there are difficulties and problems in the production of metals from both primary and secondary raw materials due to high energy and labour costs, strict safety regulations, complicated approval and permission procedures, lack of new or improved processing concepts [1].

The continuous growth of the economy and population at the same time leads to an increase in the demand for natural resources, such as fossil fuels, minerals and metals. This raises the question of the depletion of natural resources and the impact on the environment and climate. Thinking in circles is an approach that helps us understand the path of a material, for example a metal, from mining, through production, processing, use and recycling, and to take effective life cycle optimization measures [2].

Sustainability is to "meet the needs of the present without compromising the ability of future generations to meet their own needs". Sustainable development of the system technology - nature can be achieved only by maintaining the state of consumption of resources, less than their recovery from the environment, as well as when waste emissions do not disrupt the biogeochemical cycles of the earth. The criteria for an ecologically sustainable technological process emphasize the ratio between the use of renewable, non-renewable and reused resources, the quantity and quality of waste released into the environment and the energy-technological efficiency of the processes. The exergy method of thermodynamic analysis is a possible option for characterizing the technogenic load on the environment. It takes into account the interaction of each system with the environment (**Figure 1**) [3,4].

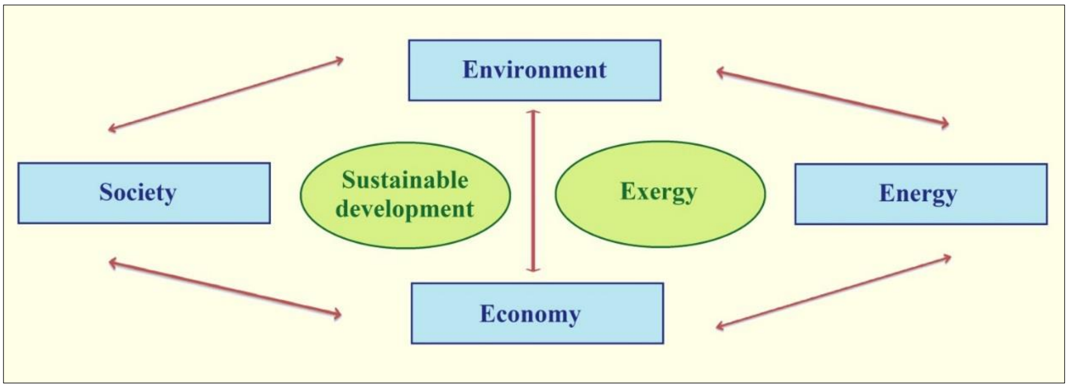


**Figure 1** The place of sustainability and exergy in modern social economic development

Exergy is a general criterion by which the resources and energy entering the production system can be evaluated. Exergy can also be used to quantify the environmental sustainability of the external environment in terms of the waste emitted in it, i.e. to show the norm of what nature can "recycle". Exergy analysis is a strategic tool to assess the real efficiency of a given process [3,5].

The object of the analysis is a real functioning system - the zinc production plant in KCM - SA, Plovdiv. KCM is the largest lead and zinc Production Company in South Eastern Europe and exports to almost the entire world [6,7]. The choice was made due to the complexity of the process (diversity in the raw materials used, the products obtained and the waste emitted; the use of different chemical-technological processes) and its great economic, social and ecological importance [8-10].

## 2. METHODOLOGICAL BASES

The chemical-technological system "Hydrometallurgical zinc production" was analysed by applying the exergy method of thermodynamic analysis. The methodology described in [11] was used.

The exergy balance based on the second law of thermodynamics, in the most general way, has been presented by equation (1):

$$\sum\varepsilon' \geq \sum\varepsilon'' + \Delta\varepsilon \tag{1}$$

where $\sum\varepsilon'$ and $\sum\varepsilon''$ are the sums of the input exergy and the output exergy, respectively, while $\Delta\varepsilon$ is the change of the exergy of the system. In stationary processes $\Delta\varepsilon = 0$.The exergy of the material flow $\varepsilon$ is the sum of its physical and its chemical exergy.

The absolute losses (irreversible and effluent) and the relative exergy characteristic (exergy efficiency) of the individual stages as well as of the system as a whole were estimated on the basis of the exergy balance.

The irreversible losses $D_{irr}$ have been calculated from the difference in the exergy values of the input ($\sum\varepsilon_{i\ input}$) and the output ($\sum\varepsilon_{i\ output}$) flows of each considered stage as in equation (2).

$$D_{irr} = \sum\varepsilon_{i\ input} = \sum\varepsilon_{i\ output} = T_0\Delta S \tag{2}$$

The effluent losses $D_{effl}$ include the exergy of the unusable material and energy flows, penetrating into the environment.

The exergy efficiency $\eta_\varepsilon$ has been determined through the ratio of the exergy of the usable output flows ($\varepsilon_{ut}$) to the exergy of the input flows ($\sum\varepsilon_{i\ input}$) as in equation (3):

$$\eta_\varepsilon = \frac{\varepsilon_{ut}}{\sum\varepsilon_{i\ input}} \cdot 100\% = \frac{\varepsilon_{ut}}{\varepsilon_{ut}+D_{irr}+D_{effl}} \cdot 100\% \tag{3}$$

The exergy losses and the thermodynamic degree of perfection characterize the corresponding chemical-technological system quantitatively and qualitatively.

## 3. EXPERIMENTAL PART

The studies were carried out on a real functioning system for the production of zinc by the hydrometallurgical method with a Waelz process for the processing of waste zinc cakes. **Figure 2** shows the scheme of interaction of the production system "Hydrometallurgical extraction of zinc" with the surrounding ecosphere.

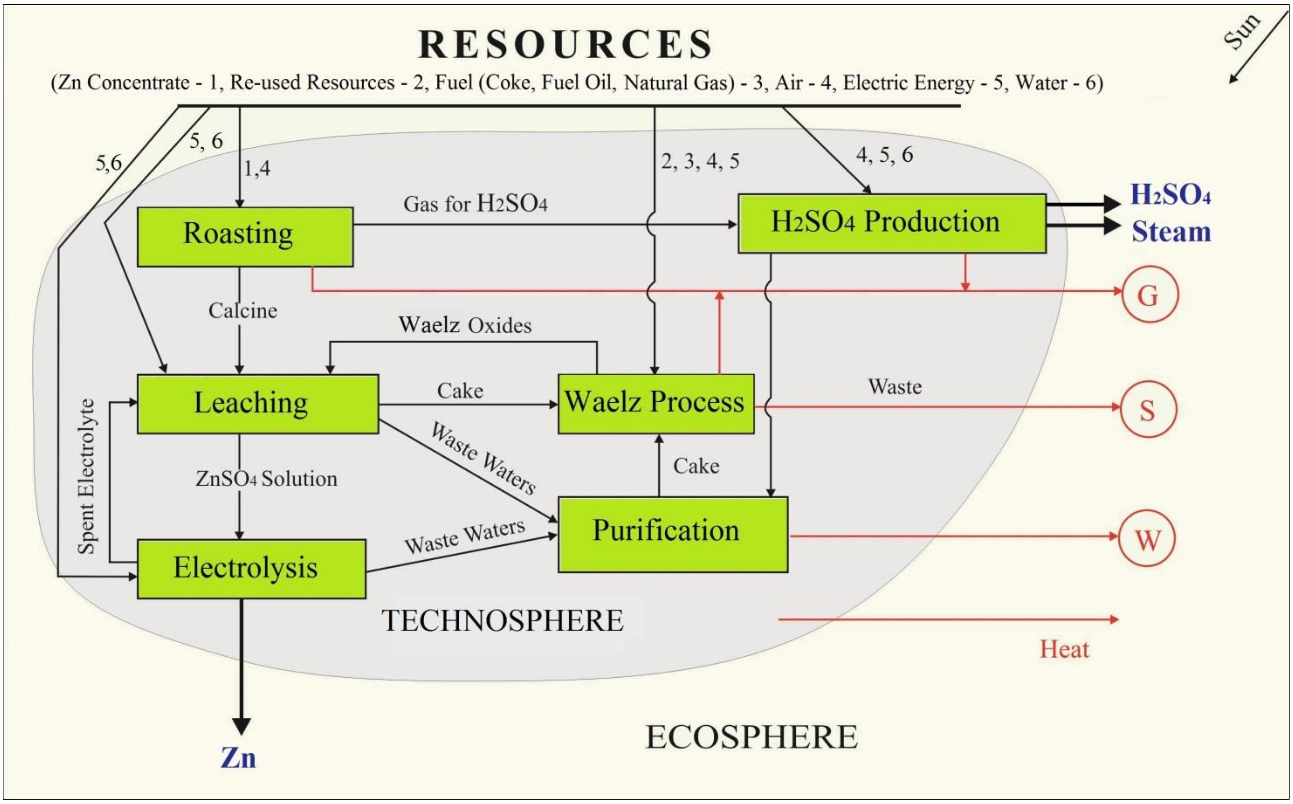


**Figure 2** Flow chart of the interaction between the hydrometallurgical zinc production industrial system and the ecosphere surrounding it (G - gases emissions, S - solid wastes, W - waste waters)

The following main stages were analyzed: roasting of the zinc sulfide concentrates in a fluidized bed furnace, sulfuric acid leaching of the obtained calcine, purification of the zinc-bearing solution from undesirable impurities, zinc electro-winning, processing $SO_2$-containing roasting gases into $H_2SO_4$ using the DKDA method ("double contact - double absorption"), processing the waste zinc cakes from leaching via Waelz process.

The main raw materials in zinc production are zinc sulphide concentrates, air and water. An important role is played by electricity - most of it is consumed during the electroextraction process. Coke, fuel oil and natural gas are used as fuel. Activated carbon, potassium ethyl xanthogenate, potassium permanganate, zinc powder, etc. are imported as auxiliary materials. Zn-containing secondary raw materials, the amount of which has been increasing in recent years, are processed in the Waelz furnace.

Historically, the main environmental problem associated with the production of zinc from sulphide concentrates has been the emission of sulfur dioxide into the air from the roasting process. This problem is effectively solved by high sulfur fixation and production of sulfuric acid by the DKDA method.

The main emissions to air from hydrometallurgical zinc production are - sulfur dioxide and acid mists; carbon dioxide ($CO_2$); metals and their compounds; dust. The sources of emissions depend on the process used can be - transport and handling of material; roasting and sulphuric acid plant; Waelz process; leaching, purification and electrolysis; mechanical treatments like grinding, milling and granulation. Diffuse emissions are also important and need to be considered for all of the process stages.

The main pollutants emitted into the water are metals and their compounds - Zn, Cd, Pb, Cu, Ni, Co and to a lesser extent Hg, Se, As and Cr. The possible waste water streams are - waste water from roasting and gas-cleaning steps, accidental spillage from various hydrometallurgical processes, collected and reused as filter washing water, water from general operations, including cleaning of equipment, floors, etc. The waste water from the zinc plant and the sulfuric acid plant enters the treatment plant for neutralization and purification.

Weak acid from sulfuric acid production is neutralized to technical gypsum in two stages. The cake obtained proceeds further to Waelz processing while the wastewater enters the purification station of the Metallurgical Works to be purified.

The production of zinc results in the generation of several by-products, residues and waste. Solid residues from various processes can be recycled, processed to extract other metals, final disposal after processing to ensure safe disposal. The main solid wastes generated are clinker and spent vanadium catalyst. Clinker is a waste from the Waelz process. Proceed to extract the useful components (Cu) in it. Spent vanadium contact mass is a waste product from the sulfuric acid plant. The waste is sent for vanadium extraction or recycling.

Environmental controls require systems to fix sulfurdioxide, control of particulates and gases emissions into the atmosphere, safe disposal of waste, maintain a safe work environment in the plant, and limit liquid wastewater discharges to environmentally acceptable levels of harmful substances. Air and water emissions, waste management and energy considerations are among the key factors influencing the modernization of the production process [7,8,12].

## 4. RESULTS AND DISCUSSION

The impact of zinc production on the environment can be considered in the following two directions - consumption of material and energy resources and emissions entering the environment.

The main raw material with which zinc is imported is zinc sulfide concentrate - 1.4 t/t Zn. According to the presented data, about 24% of the zinc raw materials are secondary Zn-containing resources. The tendency is for this percentage to grow to 30%. The processed secondary raw materials averaged 442 kg/t Zn. Their composition includes dust from electric arc steelmaking and cast iron-making; ashes, bottom and top dross from the galvanizing industry; old roofing and other sheet materials; non-ferrous fractions from the shredding of old cars and of other products mainly containing steel; residues from the chemical uses of zinc and other. The zinc content in them varies from 35% to 70%. They also contain iron, copper, lead, chlorine, etc. [7,12].

The energy requirements vary to a large extent. They depend on the quality of the feed and the products, the use of latent or waste heat and the production of by-products. The use of natural gas instead of fuel oil and coke, as well as low-sulfur fuel oil (sulfur content up to 1%) leads to a reduction in $SO_2$ and $CO_2$ emissions. The utilization of the heat of the off-gas flows increases the energy efficiency of the processes. Modernization and gasification of the existing Waelz furnaces are currently underway. The consumed electricity amounts to 3924 kWh/t Zn.

All emission limits imposed by national legislation as well as by best available techniques are met for gaseous emissions, waste water and solid waste. The application of the DKDA process for the extraction of sulfuric acid from $SO_2$-containing gases allows reducing $SO_2$ emissions to 140 - 280 mg/m$^3$ with a conversion rate of 99.8 %. The quantities of pollutants emitted into the air in kg for 1 ton of zinc produced are the following: dust -0.104, Pb -0.00697, Cd -0.0002, $SO_2$-8.07. The implementation of "cleaner" production processes and effective measures against pollution leads to an economic and ecological effect at the same time [7,8,12].

The first step in performing exergy analysis is the calculation of exergy value of the raw materials, electricity and fuels introduced into the system and the resulting products and waste. These values are shown in **Table 1.**

**Table 1** Exergy values of the main resources, products and emissions in hydrometallurgical zinc production

| Resources | (GJ/t Zn) | Products | (GJ/t Zn) | Emissions | (GJ/t Zn) |
|---|---|---|---|---|---|
| Zinc Concentrates | 9.785 | Zinc | 5.187 | Off-gases ($H_2SO_4$ Production) | 0.059 |
| Re-used Resources | 0.719 | Sulphuric Acid | 1.971 | Off-gases (Waelz Process) | 1.381 |
| Coke | 15.400 | Steam | 1.920 | Clinker | 5.375 |
| Fuel Oil | 0.636 | | | Heat | 2.673 |
| Electric Energy | 14.126 | | | | |

The values of the absolute and the relative exergy characteristics $D_{irr}$, $D_{effl}$ and $\eta_\varepsilon$ of the individual technological stages are presented in **Table 2**. While determining the individual indices for each technological unit, the exergy of the input flows was accepted to be 100 %.

**Table 2** Exergy characteristics for the principal stages in hydrometallurgical zinc production

| № | Stage | Losses | | | | Efficiency |
|---|---|---|---|---|---|---|
| | | $D_{irr}$ | | $D_{effl}$ | | $\eta_\varepsilon$ |
| | | (MJ) | (%) | (MJ) | (%) | (%) |
| 1. | Roasting | 3 876 | 38.2 | 213 | 2.1 | 59.7 |
| 2. | $H_2SO_4$ Production | 2 789 | 53.7 | 415 | 8.0 | 38.3 |
| 3. | Leaching | 1 016 | 37.0 | 107 | 3.9 | 59.1 |
| 4. | Electrolysis | 4 462 | 37.8 | 597 | 5.1 | 57.1 |
| 5. | Waelz Process | 9957 | 53.7 | 7 822 | 42.2 | 4.1 |

The overall exergy efficiency $\eta_\varepsilon$ of the chemical-technological system "Hydrometallurgical extraction of zinc" is comparatively low, only 22.3 %. The value is typical of metallurgical processes, but higher than that of the same chemical-technological system, without processing or to a lesser extent of secondary rawmaterials [8-10]. Main part of the losses of available energy are the irreversible ones$D_{irr}$ = 54.4 %, the remaining part are the effluent ones - $D_{effl}$ ($\varepsilon_{off\text{-}gases}$ + $\varepsilon_{clinker}$ + $\varepsilon_{heat}$) = 23.3 % (**Tables 1**, **2**). The Waelz process for treatment zinc cakes is energy inefficient. It has a low exergy efficiency - only 4.1%. The low values of the main exergy characteristics for this process are mainly determined by the nature of the irreversible chemical processes taking place in the furnace (burning of fuel, reduction of metal oxides) and heat exchange with the environment. The higher degree of extraction of Zn from zinc concentrates, the recovery of part of the solid waste (clinker) and the possible processing of secondary raw materials of various composition and origin are the reason for the presence of this chemical-technological stage in the scheme of hydrometallurgical zinc production.

## 5. CONCLUSION

An energy-technological study and assessment of the impact on the environment of the production system "Hydrometallurgical extraction of zinc with the application of a Waelz process for the processing of waste cakes and secondary raw materials" was carried out. The exergy method of thermodynamic analysis was applied.

The overall exergy efficiency of the system under study is comparatively low - 22.3 %, i.e. 77.7 % of the available input energy in the system practically degrades. The main exergy losses are irreversible - 54.4 % while the effluent losses amount to 23.3 %.

The possibilities for increasing energy-technological efficiency and limiting the harmful impact of hydrometallurgical zinc production on the environment are a higher degree of use of renewable energy and secondary raw materials, a higher degree of solid waste processing and extraction of useful components, reduction of specific energy consumption.

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