ENERGY AND ENVIRONMENTAL ASSESSMENT OF PROCESSING THE SECONDARY RAW MATERIALS IN HYDROMETALLURGICAL ZINC PRODUCTION

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Abstract

An energy and environmental assessment of the processing of secondary raw materials during hydrometallurgical zinc production using the Waelz process was made. The exergy method of thermodynamic analysis was used as a research method. A real operating installation at KCM SA - Plovdiv, Bulgaria serves as a model flowchart. The research aims to carry out a precise assessment of the internal energy resources of the processes, suitable for carrying out work under the given environmental conditions. This fact allows to determine the thermodynamic improvement of the processes, as well as to evaluate the internal (irreversible) and external (effluent) losses of available energy. The data obtained from the study were used in the assessment of the anthropogenic load on the environment, influenced by the real production processes of processing of secondary raw materials. The assessment was made by varying the amount of input secondary raw materials. Residual anthropogenic emissions in the environment, namely heat emissions, gas emissions and solid waste, deserve serious attention. The process of processing a larger amount of secondary raw materials is characterized by higher energy efficiency and lower environmental impact.

Keywords: Secondary raw materials, hydrometallurgical zinc production, exergy analysis, environmental impact

1. INTRODUCTION

Sustainable development, imposed in the current century, implies preferential use of renewable and secondary resources; minimization of emissions entering the environment; optimization of the energy and technological efficiency of the chemical technological processes used. The transition to ecologically sustainable technologies means replacing the open technological system *resources → production → consumption* (which corresponds to the already outdated and rejected material model) with the closed cyclic system *resources → production → consumption → secondary resources* (corresponding to the modern sustainable development model) [1, 2].

The circular economy encourages the use of waste materials as resources, transforming our economy from a linear to a circular model. It is based on the responsible use of all resources – human, natural and economic. It aims to control and limit our negative impacts on the planet and ensure the well-being of future generations. No such cycle can be completely closed, since any real transformation process is subject to inevitable losses and relative inefficiencies. Our goal should be to identify and minimize them throughout the product life cycle [3-5].

Metallurgy is a key driver of the circular economy:

Mine *(ore)* - **Flotation plant** *(concentrate)* - **Metallurgical plant** *(metal, alloy)* - **Processing plant** *(product)* - **Industry or household** *(waste)* - *secondary raw material* - to the **metallurgical** or **processing plant.**

It is distinguished by a significant consumption of primary material and energy resources, a variety of used processes and equipment, significant amounts of emissions (gas, liquid and solid) entering the environment.

At the same time, there are many existing options for replacing some of the used processes with more efficient ones, opportunities to use secondary resources, energy-technological combination of chemical-technological processes, and maximum utilization of primary and secondary energy resources [6].

The present study presents an energy and environmental assessment of the processing of secondary raw materials in the hydrometallurgical extraction of zinc using the Waelz process. The exergy method of thermodynamic analysis was applied. A real operating installation at KCM AD - Plovdiv, Bulgaria serves as a model flow chart. KCM is the largest lead and zinc production company in Southeast Europe and exports to almost the whole world [7, 8]. The absolute and relative exergy characteristics were calculated. The data obtained from the study were used in the assessment of the anthropogenic load on the environment, influenced by the real production processes of processing of secondary raw materials.

2. METHODOLOGICAL BASES

The processing of secondary raw materials by the Waelz process has been analysed using the exergy method of thermodynamic analysis. The methodology described in [9] was used.

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

$$\sum\varepsilon' \geq \sum\varepsilon'' + \Delta\varepsilon \qquad (1)$$

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 ε 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.

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

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

The exergy efficiency η_ε has been determined through the ratio of the exergy of the usable output flows (ε_{ut}) to the exergy of the input flows ($\sum\varepsilon_{i\ input}$):

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

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

Exergy efficiency and exergy losses illustrate the possibility of exergy improvement of the system, defined by the improvement potential P_{ot} [10]:

$$P_{ot} = D_{irr}(1 - \eta_\varepsilon) + D_{effl} \qquad (4)$$

3. EXPERIMENTAL PART

This study was carried out on a real functioning chemical-technological unit of hydrometallurgical zinc production, namely the Waelz process, according to the scheme in **Figure 1**.

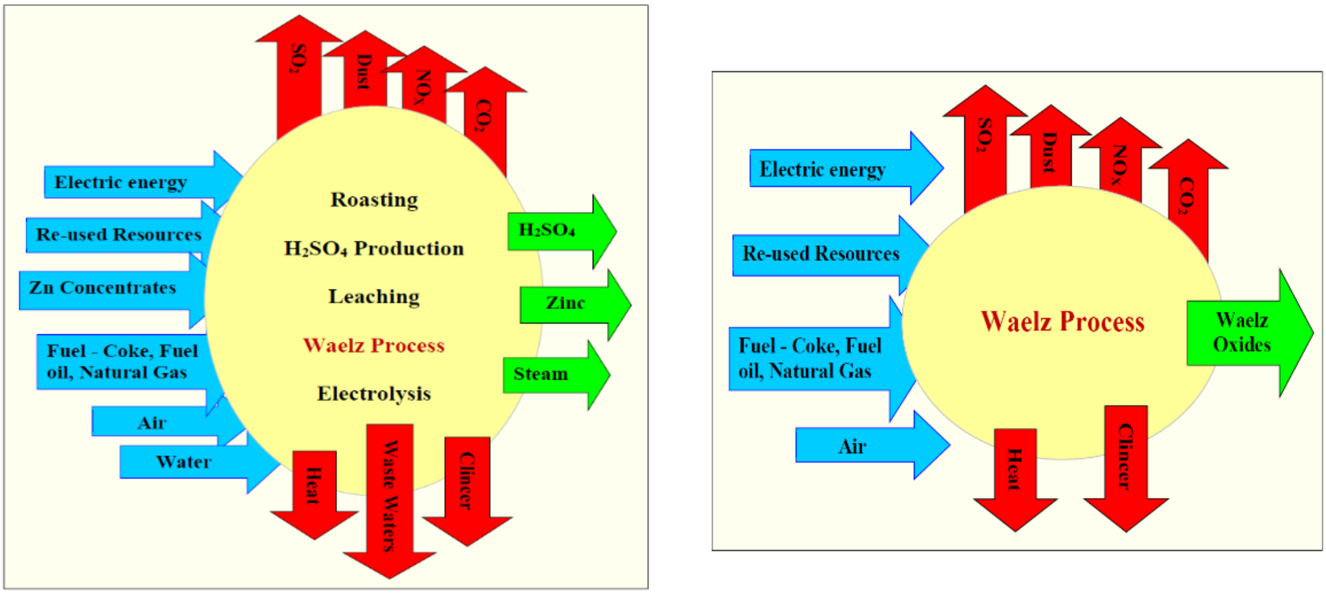

Figure 1 Left – Flow chart of the interaction between the hydrometallurgical zinc production industrial system and the ecosphere surrounding it; Right – Flow chart of the interaction between the chemical technological stage Waelz and the ecosphere surrounding it

The Waelz process is essentially an additional unit that greens zinc production. Its energy characterization gives very important information in determining the possibilities of increasing the environmental sustainability of the entire zinc production system. In world practice, pyrometallurgical and hydrometallurgical methods are currently used to process waste cakes, as well as secondary raw materials [11,12].

Zinc can be recycled to a significant extent. Estimates based on historical consumption and product life cycle indicate that a recovery rate of 80% of recoverable zinc has been achieved. Both hydrometallurgical and pyrometallurgical methods are applied [13].

The composition of secondary Zn-containing resources 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. [12].

Gas emissions from the Waelz process with processing of 24% secondary raw materials are presented in **Table 1** [14].

Table 1 Gas emissions from the Waelz process in hydrometallurgical zinc extraction [14]

Component	Unit of measure	Allowable value	Monitoring results
Dust	mg/Nm^3	5	3.0
Pb	mg/Nm^3	1.8	0.43
Cd	mg/Nm^3	0.02	0.0078
SO_2	mg/Nm^3	500	239.9
NOx	mg/Nm^3	60	43.9

4. RESULTS AND DISCUSSION

The values of the main exergy characteristics - internal and external losses, exergy efficiency and improvement potential 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 %. The results summarize the performance of the Waelz furnace over the years and our research [15].

Table 2 Exergy characteristics of the Waelz process in hydrometallurgical zinc production with varying amounts of secondary raw materials

№	Waelz Process	Losses				Efficiency	Improvement potential
		D_{irr}		D_{effl}		η_{ε}	P_{ot}
		(MJ)	(%)	(MJ)	(%)	(%)	(MJ)
1.	no secondary raw materials	13 658	59.6	3224	14.0	26.4	13413
2.	with 7% secondary raw materials	13 373	59.2	3148	13.9	26.9	12924
3.	with 12% secondary raw materials	10728	54.6	2861	14.5	30.9	10274
4.	with 24% secondary raw materials	9957	53.7	2447	13.2	33.1	9108

The place of the Waelz process from an exergy point of view among the main chemical-technological stages of hydrometallurgical zinc extraction is evident from **Figures 2** and **3**.

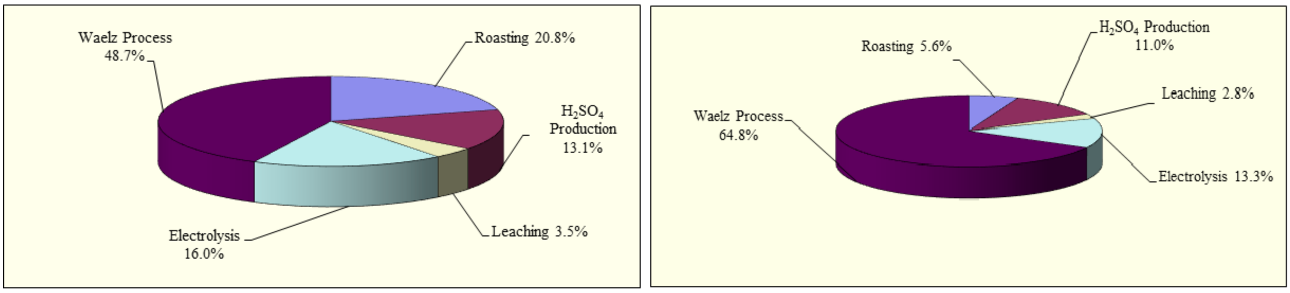

Figure 2 Distribution of irreversible (left)and effluent (right) lossesby separate stages of the chemical-technological system "Hydrometallurgical extraction of zinc"

The Waelz process for the processing of zinc cakes and secondary raw materials is not energy efficient, as can be seen from the results presented. It has a low exergy efficiency and a very high potential for improvement. It accounts for the main part of the exergy losses for zinc production. These values of the main exergy indicators are mainly determined by the nature of the irreversible chemical processes taking place in the Waelz furnace (burning of fuel, reduction of metal oxides), heat exchange with the environment, non-utilization of the exergy of the furnace gases, etc.

Table 2 clearly shows the increase in exergy efficiency with increasing share of secondary raw materials.

The clinker is waste for the Waelz Section. It is passed to extract the useful components (Cu) in it. It also contains FeO, SiO_2, Al_2O_3, CaO, MgO, etc.

The way to reduce the generated emissions is through modernization and reconstruction of the applied technologies and devices - construction of purification facilities for process gases, furnace gasification, etc.

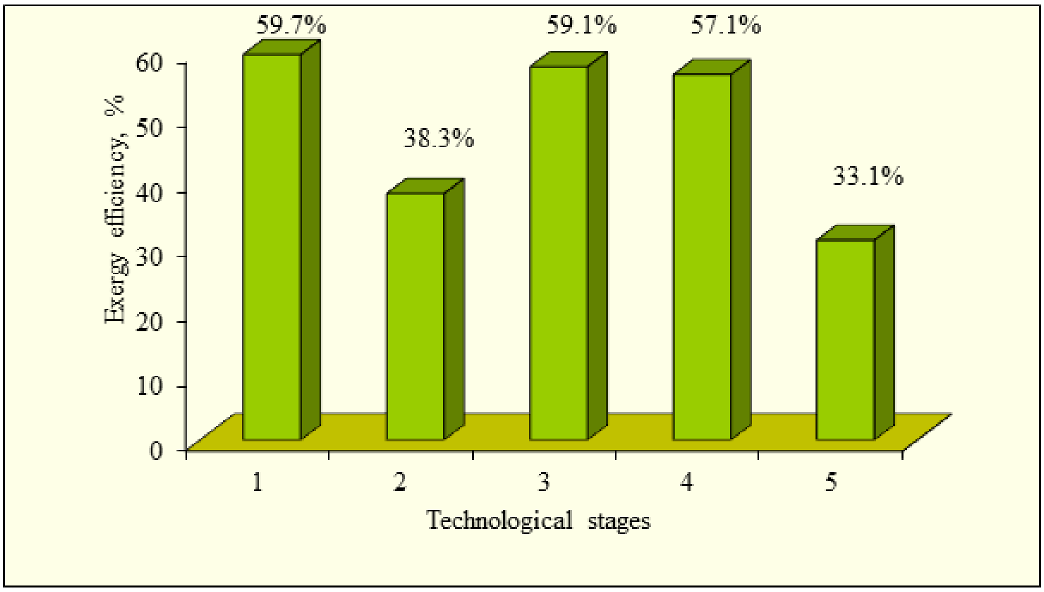

Figure 3 Exergy efficiency in the main technological stages of the chemical-technological system "Hydrometallurgical extraction of zinc": 1 - Roasting, 2 - H_2SO_4 production, 3 - Leaching, 4 - Electrolysis, 5 - Waelz process

The planned reconstruction and gasification of the Waelz furnaces and roasting ovens for the Waelz oxides in KCM was completed last year. This will allow to increase the share of processed zinc-containing secondary materials and recycled waste. This share is expected to reach 30%.

This, together with the reconstruction and modernization of the other installations of the technological scheme, will increase the degree of extraction of zinc from primary and secondary zinc-containing raw materials and waste and reduce the volume of generated waste per unit of production.

Emission limits for gases are achieved by adjusting the composition of the charge at the entrance of the respective metallurgical units, and also by optimally managing the fuel-reduction processes in the furnaces.

5. CONCLUSION

The more complete extraction of Zn from zinc concentrates, the recovery of part of the solid waste and the possible input of secondary raw materials is the reason for the presence of the Waelz chemical-technological stage in the scheme of zinc production.

The results show better exergy performance when processing secondary raw materials.

Anthropogenic emissions in the environment deserve serious attention. An ecological problem is the accumulation of solid waste (clinker after processing) in landfills, due to the lack of appropriate technologies for their processing. A large part of the heat and gas emissions and solid waste are observed in the Waelz process, which, together with the high values of the other exergy indicators, makes it inefficient from a thermodynamic and ecological point of view.

Regardless of the mentioned disadvantages, the Waelz process for processing waste zinc cakes provides a higher degree of zinc recovery and provides opportunities for recycling. This justifies the higher energy and environmental costs as well.

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