

Enhancing Zinc Extraction Efficiency from Insoluble Zinc Cake through Citric Acid Leaching: A Hydrometallurgical Approach

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Abstract— The present study employs the zinc cake leaching method as a means to enhance the extraction of zinc from insoluble to soluble forms. Citric acid, identified as a water-soluble local reducing agent, facilitates this process, with a sulfuric acid solution serving as the solvent. Optimal results were obtained when the concentration ratio of sulfuric acid to citric acid was maintained at 28.7:4, resulting in an 86% dissolution rate of zinc cake. This technological advancement signifies a more efficient hydrometallurgical processing method for zinc cakes. Thermodynamic analysis elucidated that the limiting stage in the chemical reactions, involving zinc ferrite and a mixture of citric and sulfuric acids, is the mutual chemical interaction between zinc ferrite and citric acid. Complete reaction occurred at an optimal temperature of 338 K (65 °C). A kinetic study revealed that equilibrium constants for dissolving reactions of zinc and iron oxides in sulfuric acid exhibit high values, undergoing changes due to the recovery of zinc ferrite at the specified temperature. Quantitative analyses of the solution and secondary residual cake were conducted to ascertain the solubility of the zinc cake. To enhance the efficiency of hydrometallurgical processing at the optimal temperature, the impact of intensive mixing of the solution was investigated. Consequently, at 65 °C, the maximum average melting rate of zinc cake, reaching 90.3%, was achieved with a solution mixing speed of 55-65 times per minute. The proposed improvement method, if implemented on an industrial scale, holds the potential to significantly augment zinc production productivity.

Keywords— zinc cake, zinc ferrite, citric acid, sulfuric acid, reduction, leaching, thermodynamics, kinetics, Gibbs energy, equilibrium, intensive mixing.

1. INTRODUCTION

Hydrometallurgical processing plays a pivotal role in the global extraction of zinc from industrial residues, particularly zinc cakes an integral by-product of the zinc production process, encompassing diverse mixtures comprising lead, iron, and various metals. This method involves leveraging chemical reactions in aqueous solutions to extract and refine metals from their ores or residues. Specifically applied to zinc cakes, the process typically entails the selective dissolution of cakes through an acidic solution, facilitating the dissolution of zinc along with other impurities. Subsequent stages involve subjecting the resultant solution to a series of separation and purification techniques to yield pure zinc. The hydrometallurgical processing of zinc cakes holds substantial significance for multiple reasons. Firstly, it facilitates the recovery of precious metals from industrial residues, thereby mitigating waste generation and conserving natural resources. Secondly, this approach proves economically viable, especially when juxtaposed with traditional pyrometallurgical methods that demand elevated temperatures and substantial energy consumption.

Uzbekistan exemplifies the relevance of this process, as substantial quantities of industrial waste in the form of zinc cakes from the production activities of “Almalyk MMC” JSC are diligently collected. Engaging in the processing of these cakes enables the enterprise to markedly augment metal production without resorting to primary raw materials, flues, or incurring exorbitant energy costs. The hydrometallurgical processing of zinc cakes emerges as both pertinent and imperative for the recovery of zinc and other valuable metals from industrial residues. Its advantages over traditional pyrometallurgical processes, coupled with its contribution to resource conservation and economic feasibility, underscore its importance in contemporary metallurgical practices. Some researchers have conducted studies on the processing of zinc cakes (zinc ferrite) formed in the production of zinc [1-2].

M. Deniz Turan et al. Mechanical activation of zinc production solid waste via ball milling, followed by a two-step hydrochloric acid (HCl) washing process, resulted in the solubilization of 74% zinc in the first step. Subsequently, the second step yielded 56% lead and 53% silver from the solution residues, highlighting a potential resource recovery pathway outlined in a conceptual flow diagram [3]. In the present investigation led by Ali Reza Eivazi Hollagh et al. an examination of the dissolution kinetics of zinc from Zinc production residue (ZPR) in a dilute sulfuric acid solution was conducted. Through an analysis of reaction rates and experimental observations, it was deduced that the leaching reactions are predominantly governed by the diffusion process within the porous product layer. The determined activation energy for the melting process was approximately 1 kJ/mol within the temperature range of 298 - 353 K, indicating efficient zinc extraction from ZPR in a dilute acidic sulfate solution. Additionally, employing the model-

free method revealed an estimated activation energy of 2.9 kJ/mol [4]. Hana Rigoulet et al. initiated acidic leaching experiments with elevated zinc, iron, and metal concentrations. The recommended galvanic sludge treatment involves washing in 20-25% NaOH or KOH (L:S ratio 4:1) at 60-70 °C for 8 hours. H₂O₂ aids in separating liquid from residue through roasting glass or pressurized water flow. Electrolysis (3.5-4 V, 300-400 A/m², stainless cathode, nickel anode, 25 °C, 3-4 hours) produces cathodic zinc, safeguarded from oxidation. Redissolution in an inert atmosphere enables compact metallic zinc reuse, distillation, or rectification [5]. Mahmut Sami Alkan et al. investigated lead and zinc leaching from zinc filter cake using eco-friendly ammonium acetate. The sample contained 13% lead, 10.7% zinc, and various other elements. PbSO₄ and ZnSO₄·7H₂O, ZnFe₂O₄, and Zn₂SiO₄ were identified as lead and zinc phases. Optimal leaching conditions were determined: 3 M ammonium acetate, 70°C, 1-hour duration, and 1/10 g/mL solid/liquid ratio. Leaching efficiencies were 81% for lead and 34% for zinc. Lead recovery via cementation with 10 μm zinc powder had an activation energy of 33.4 kJ/mole. Zinc entrapped in lead contributed to successful recovery. A zinc-rich solution remained for potential electrochemical recovery. Ammonium acetate proves advantageous for lead recovery from zinc filter cake [6].

Asadollahfardi et al. investigated electro kinetic enhanced remediation of arsenic-contaminated sediment from a zinc refinery, assessing various enhancement agents and conditions for sediments with 5,700 mg/kg arsenic. Leaching experiments aimed to identify optimal enhancers and solution concentrations, revealing insights into soil-metal interactions. Electrolyte conditioning solutions (ethylene diamine tetra acetic acid, citric acid, and sodium hydroxide) were studied, with sodium hydroxide employed as pre-treatment. The study also evaluated the impact of increasing the voltage gradient from 1 to 1.5 V/cm over an 8-day period. Results showed limited effects of pre-treatment and voltage increase on arsenic removal efficiency. However, the use of citric acid (0.5 M) as the catholyte solution significantly increased efficiency by 33.51% [7].

The hydrometallurgical processing of zinc production cakes emerges as a pivotal practice, contributing to resource conservation, environmental amelioration, economic viability, and regulatory adherence. Its implementation provides an efficient avenue for extracting precious metals from waste materials, thereby mitigating the environmental footprint of industrial processes

2. MATERIALS AND METHODS

The primary focus of this study is on the waste cakes derived from the hydrometallurgical washing process conducted at the "Almalyk MMC" JSC Zinc plant. The chemical and material composition of the zinc plant cakes, specifically selected for experimentation, is detailed as follows: Zn-19.4%, along with ZnO-1.72%, ZnSO₄-0.74, ZnO·Fe₂O₃-15.3%, Pb-5.8%, inclusive of PbO-0.54%, PbS-0.45%, PbSO₄-0.21%, Cd-0.20%, along with CdO-0.019%, CdSO₄-0.007, CdS-0.015%, CdO·Fe₂O₃-0.154%, Cu-1.57%, as well as CuO-0.144, CuSO₄-0.052, CuS-0.12, CuO·Fe₂O₃-1.25%, S-7.7%, Fe-23.2%, CaO-2.7%, MgO-1.0%, Al₂O₃-2.2%.

This detailed analysis provides valuable insights into the chemical makeup of the zinc material, aiding in its characterization and potential utilization in various industrial processes. The data concerning the chemical and material composition of the selected zinc factory cakes highlight a notable presence of iron and zinc within the chemical composition of the zinc factory cake. A substantial proportion of zinc within the cake manifests in the form of ferrite, a compound classified under the spinel category of oxides. Noteworthy is its characteristic insolubility in both acids and alkalis, distinguishing it from other oxide types [8-9].

In the course of this investigation, citric acid served as the selected reducing agent, while a 29% sulfuric acid solution was employed as the reactive medium.

The rationale behind selecting citric acid as the reducing agent for the research lies in its favorable attributes, specifically its high solubility in water and ready availability. Citric acid, with an empirical formula of C₆H₈O₇, is depicted structurally in Figure 1.

The solubility of citric acid in 100 ml of water at a temperature of 25 °C is 133 g, with the density of pure citric acid crystals recorded at 1.665 g/cm³. Citric acid undergoes liquefaction upon reaching 153°C and experiences decomposition at 175°C. The resulting salts formed through the acid's interaction with metals are termed citrates [10].

In the experimental procedure, a solution comprising citric and sulfuric acids was established, and subsequently, zinc cake was introduced into this solution [11].

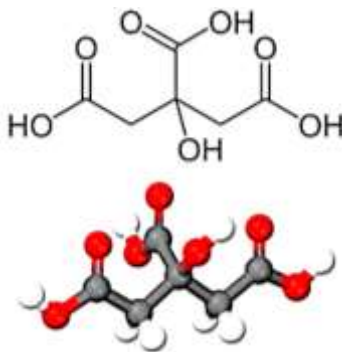


Fig.1. Molecular structure of citric acid

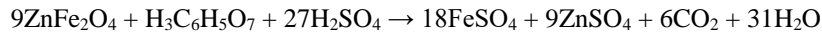
Various analytical methods were employed to ascertain the composition of the initial zinc cakes as well as the solid residue and solution derived post reductive leaching. Microscopic analysis of the cooled and crystallized cake facilitated an estimation of zinc distribution among its constituents. For the comprehensive study of the chemical and material composition of zinc production cakes and resultant products from the research, samples were meticulously collected and analyzed at the “Central Laboratory”, a state enterprise under the auspices of the State Geological Committee in Uzbekistan [12].

The solutions resulting from the research underwent analysis through a mass spectrometric analyzer (ICP-MS), while the mineral content of the zinc cake was scrutinized employing a high-efficiency energy dispersive X-ray fluorescence spectrometer, specifically the NEX CG RIGAKU model. To determine the thermodynamic values of the chemical reaction within the zinc cake and citric acid system in a sulfuric acid environment, as well as to construct their respective Ellingham graph, the ThermoBase-2.15 program and Microsoft Excel programs were deployed.

3. RESULTS AND DISCUSSION

Addressing the imperative of establishing an effective means for the hydrometallurgical processing of zinc ferrite, particularly in the context of identifying a suitable reducing agent, stands as a pivotal objective within contemporary zinc metallurgy. In this research endeavor, particular attention was directed towards the exploration of citric acid ($C_6H_8O_7$) as a recommended reducing agent, with a comprehensive investigation into its impact on the processing dynamics. Notably, citric acid presents itself as a water-soluble, benign, and economically viable reducing agent. Its distinct advantage over alternative reducing agents lies in its ability to sustain an acidic milieu within the solution.

The comprehensive molecular equation depicting the chemical reaction governing the reduction of zinc ferrite through citric acid, succeeded by the selective dissolution of the residual solid in sulfuric acid, is articulated as follows:



Derived from the aforementioned reaction, a mathematical equation encapsulating the correlation between the augmentation of temperature and the oxidation-reduction reaction is articulated as follows:

$$\Delta G^T = -2589.5 - 0.5552 \cdot T$$

Utilizing the derived mathematical expression, the likelihood of the chemical reduction process occurring was evaluated with each incremental 10-unit rise in temperature within the reaction system. The associated Gibbs energies for the chemical reaction involving the leaching of zinc ferrite with citric acid in a sulfuric acid medium, spanning the temperature range of 298 to 438 K (equivalent to 25 to 165 °C), are provided. Notably, the probability of the reaction is observed to escalate concomitantly with temperature elevation. This phenomenon is visually represented in Figure 2 through the construction of an Ellingham diagram.

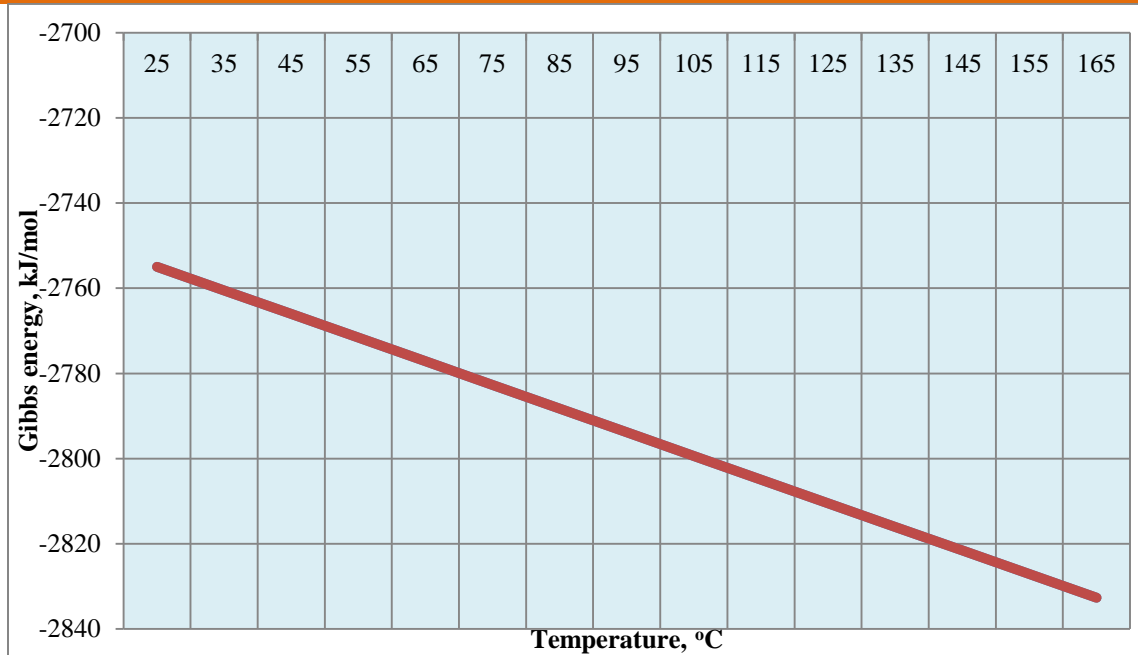


Fig.2. The Ellingham diagram portraying the reaction pathway for the reduction of zinc ferrite with citric acid.

In Fig.2 the equilibrium constants for the regenerative reactions were ascertained at specific temperatures. These values were derived from the equation establishing the relationship between temperature and the Gibbs energy of the chemical reaction involving the addition of zinc ferrite with citric acid. The resulting equilibrium constants are presented graphically in Fig.3.

The histogram format in Fig.3 elucidates that, at a temperature of 338 K (65 °C), a pivotal point is reached in typical hydrometallurgical processes. At this juncture, the equilibrium constant for the formation of metal sulfates during the leaching of zinc ferrite in the presence of citric acid within a sulfuric acid environment attains an optimal value ($K_e=2.688$).

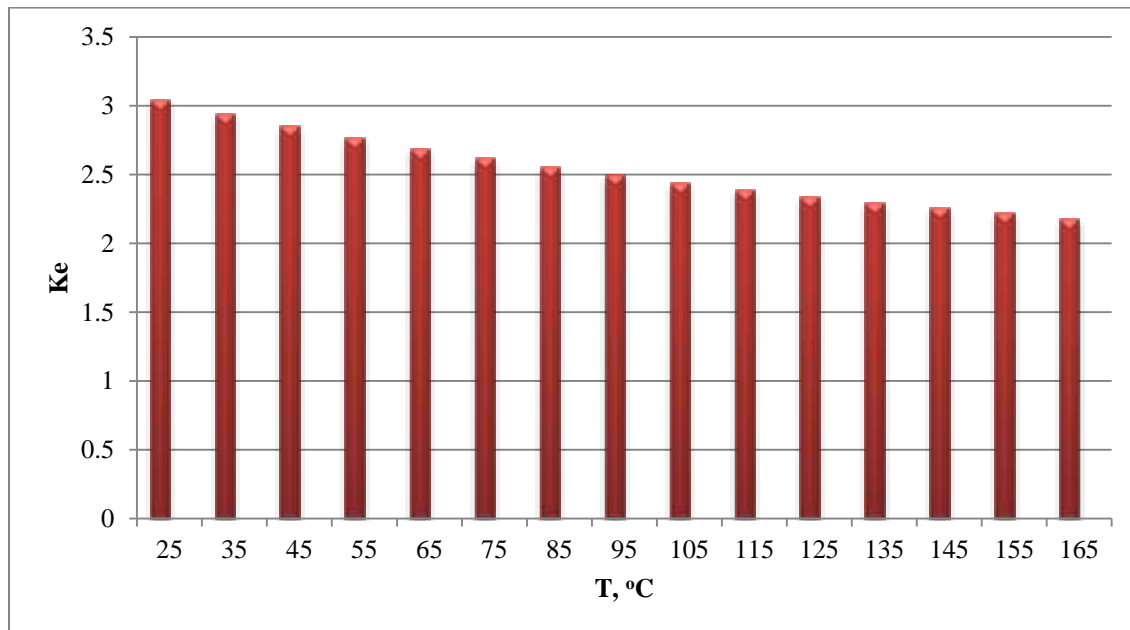


Fig.3. The fluctuation of the equilibrium constant throughout the reduction process of zinc ferrite with citric acid, as a function of temperature.

The outcomes of the thermodynamic and kinetic analyses pertaining to the reduction of zinc ferrite with citric acid reveal a noteworthy trend: an escalation in temperature corresponds to an augmented probability of the reaction transpiring, yet concurrently, the equilibrium constant diminishes. This phenomenon is ascribed to the exothermic nature of the leaching process. Beyond 65°C, elevating the temperature adversely impacts the equilibrium constant and results in a deceleration of the chemical reaction rate.

The significance of investigating this process lies in the subsequent electrolytic separation of the zinc sulfate formed during the reaction. Prior to this separation, it is imperative to purify the solution from extraneous elements. Moreover, through the dissolution of iron and zinc within the remaining solids from the leaching of Zinc plant cakes, the concentration of noble metals increases, attaining levels conducive to efficient production. The extraction of these valuable metals through leaching introduces a waste-free technology paradigm, concurrently heightening environmental protection measures.

In the course of the investigation, the research utilized the zinc cakes sourced from the Zinc Plant of “Almalyk MMC” JSC. Given the substantial dimensions of the initial zinc cake, a porcelain mortar was employed for the purpose of crushing. Following the grinding process, granulometric analysis indicated that the particle size of the zinc cake was reduced to dimensions below 100 µm. The outcomes of the comparative granulometric analysis are visually presented in Figure 4.

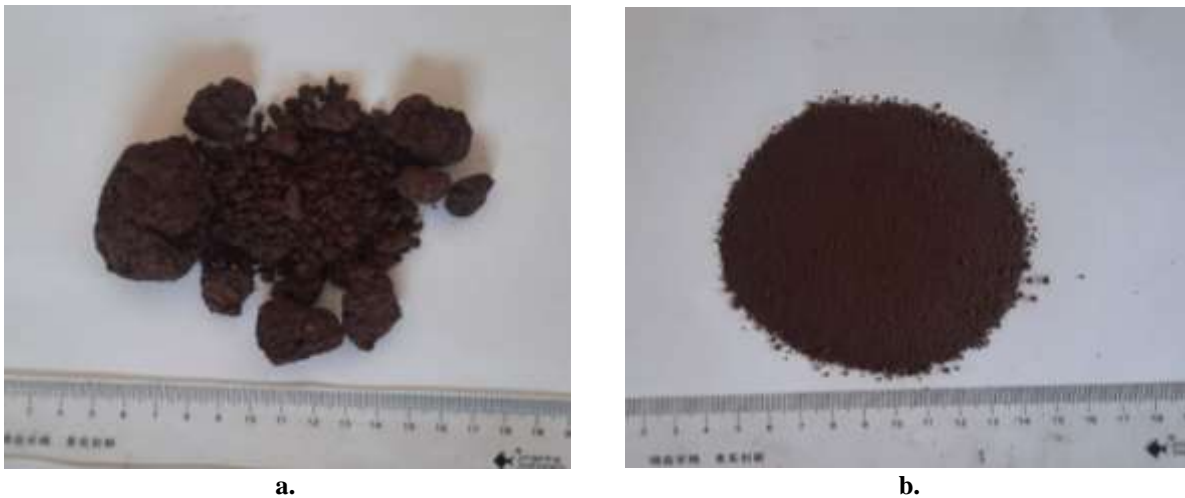


Fig.4. Zinc cake selected for research: a-size before crushing; b- size after crushing

A series of 20 g samples were meticulously weighed from the finely ground zinc cake specimen. Each sample was then placed in a flat-bottomed flask, and 100 ml of water was introduced. Upon thorough agitation, the mixture of cake and water separated into distinct sediment and aqueous fractions within a brief interval of 5 minutes. Notably, the experiment revealed that the zinc cake materials exhibited negligible solubility in water, and particles of cake, with sizes smaller than 100 µm, effectively settled to the bottom of the container within the aforementioned timeframe. The objective underlying the determination of the sedimentation rate of diverse cake particles, all smaller than 100 µm, was to ascertain the duration of particle interaction with sulfuric acid during the exposure of the suspension to an acidic environment. In a subsequent experimental iteration, 10 g of citric acid was introduced to the cake and water mixture from the preceding experiment, followed by thorough agitation. The suspension required approximately 10 minutes to settle, indicating a diminished settling rate of zinc cake particles smaller than 100 µm when the solution medium exhibited an acidic index.

Following the cooling of the amalgamated mixture comprising zinc cake, water, and citric acid, it was observed that no discernible chemical alterations transpired within the solution. To delve into the process of reductive leaching, solutions of sulfuric acid with varying concentrations were subsequently introduced into the aforementioned suspension. Upon exposure to diverse concentrations of sulfuric and citric acids, a discernable reduction in the mass of the residual zinc cake ensued. The outcomes of these research endeavours are succinctly presented in Table 1.

The tabulated values in Table 1 illustrate a notable augmentation in the solubility of zinc cake with an increase in the concentrations of both sulfuric and citric acids. Notably, a series of experiments conducted with varying concentrations of acids revealed a substantial reduction in the mass of the zinc cake, particularly evident when the ratio of sulfuric to citric acid concentrations was maintained at 28.7:4. This observation is distinctly portrayed in the graphical representation featured in Figure 5.

Table 1. Variation of residual cake mass obtained after reductive leaching of zinc cake at different concentrations of citric and sulfuric acids

№	Sulfuric acid concentration, %	Concentration of citric acid, %	Residual cake mass, g	The degree of weight loss of the residual cake mass, %
1	17.1	1	11.1	44.5
2	22.3	2	9.4	53
3	25.5	3	5.9	70.5
4	28.7	4	2.8	86
5	30.2	5	2.5	87.5
6	34.6	6	2.1	89.5
7	39.8	7	1.8	91

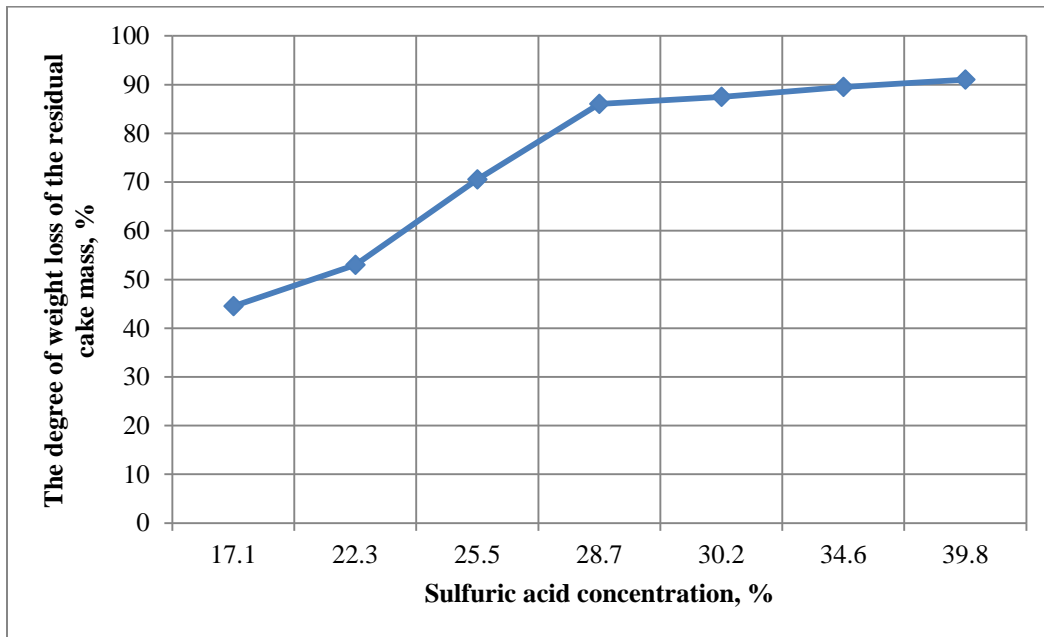


Fig.5. Changes in zinc cake mass with increasing acid concentration



Fig.6. Filtrate solution obtained after zinc cake reductive leaching

Subsequent to the reductive leaching of the zinc cake in the presence of citric acid, the resultant mixture underwent a cooling process followed by filtration. The filtrate solution exhibited a transparent green hue, attributable to the presence of divalent iron ions (Fe^{2+}). Conversely, zinc ions did not impart a distinctive color to the solution as they are inherently colorless. The presence of divalent iron ions in the solution signifies the successful accomplishment of the intended objective in the reductive leaching process. In the exploration of the thermodynamic facets of the reductive leaching of zinc ferrite in the presence of citric acid, it was ascertained

that the optimal temperature for the intended progression of the process was 65 °C. Concurrently, several studies were conducted to evaluate the impact of varying solution mixing intensities at this temperature on the equilibrium constant and reaction yield of the reductive leaching reaction. The outcomes of these research investigations are systematically presented in Table 2.

Upon scrutiny of the data outlined in Table 2 and Figure 7, it is evident that an escalation in the stirring speed of the solution at 65 °C correlates with an increase in the solubility of zinc cake.

Table 2. Results of reductive leaching rate acceleration studies

No	Mixing speed of the solution, rpm.	Dissolution rate of zinc cake, %
1	35	41.9
2	40	53.3
3	45	62.1
4	50	79.8
5	55	86.2
6	60	88.1
7	65	90.3
8	70	89.5
9	75	87.4
10	80	85.6

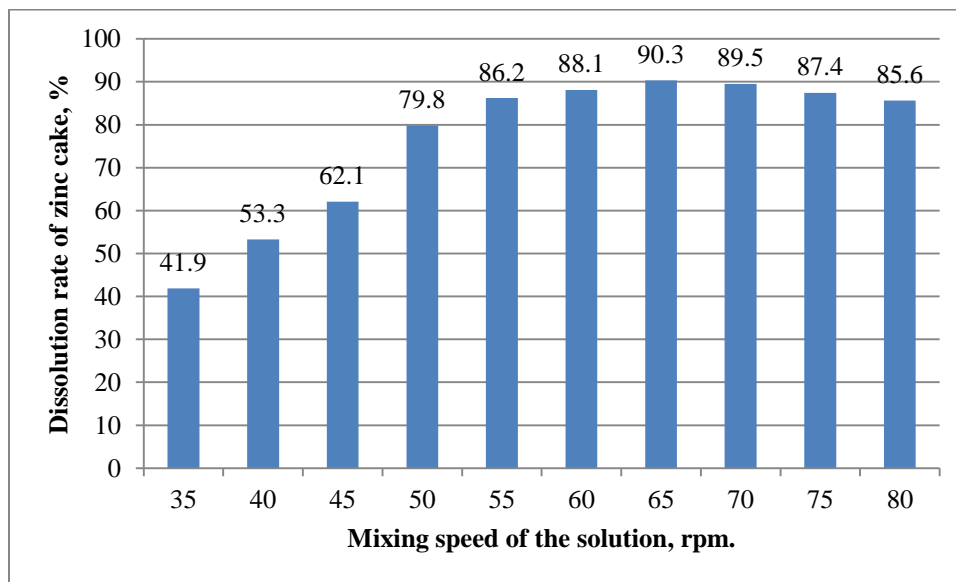


Fig.7. The relationship between the increase in the rate of mixing of the solution and the degree of dissolution rate of the zinc cake

Upon reaching a stirring speed of 65 revolutions per minute, the solubility of zinc cake peaked at 90.3%. Further increments in stirring speed did not yield a substantial increase in solubility; instead, there was a discernible decline. This observed trend can be attributed to the fact that beyond 65 rpm, the increased stirring speed leads to a flow rate of zinc cake particles and solvent acids that aligns with a laminar state. In this laminar regime, the probability of collision between zinc cake components and solvent reagent molecules diminishes. Consequently, the efficiency of the reductive leaching reaction of zinc cake in a sulfuric acid medium experiences a reduction, resulting in a decline in reaction productivity.

4. CONCLUSION

Based on the outcomes of the investigation aimed at enhancing the technology for leaching zinc cakes at “Almalyk MMC” JSC, the following conclusions are presented:

1. Post-leaching of zinc cinder concentrates in zinc production results in the generation of a significant quantity of waste cake comprising insoluble oxidized compounds. Chemical analysis of this waste material revealed a substantial content of oxidized zinc compounds, predominantly in the form of zinc ferrite ($ZnFe_2O_4$).

2. To facilitate the extraction of zinc from the zinc cake, a reductive leaching method was employed, transforming the material from an insoluble to a soluble form. Citric acid, a water-soluble local reducing agent, was utilized, along with a sulfuric acid solution as the solvent. The dissolution rate of zinc cake reached 86% when the concentration ratio of sulfuric to citric acids was maintained at 28.7:4 during the reductive leaching process. This refined technology aims to enhance the efficiency of hydrometallurgical processing of zinc cakes.

3. Thermodynamic analysis indicated that the limiting stage among the chemical reactions in the system of zinc ferrite, citric acid, and sulfuric acid involves the mutual chemical interaction of zinc ferrite and citric acid. The optimum temperature for the complete reaction of zinc ferrite with citric acid was determined to be 338 K (65 °C). Kinetic studies further affirmed that the equilibrium constants of the leaching reactions of zinc and iron oxides in sulfuric acid, resulting from the reduction of zinc ferrite at the same temperature, exhibit high values.

4. Quantitative analysis of the obtained solution and secondary residual cake provided insights into the solubility level of the zinc cake.

5. To enhance the efficiency of hydrometallurgical processing of zinc cake at the optimal temperature, the impact of intensive solution stirring indicators was investigated. At 65 °C, the maximum dissolution rate of zinc cake (90.3%) was achieved with a stirring speed ranging from 55 to 65 times per minute. This finding suggests that the proposed improvement method, when implemented on an industrial scale, has the potential to increase the productivity of zinc production.

REFERENCES

- [1] Hojiyev Sh.T. Mahalliy ikkilamchi hosil bo'lgan texnogen chiqindilardan foydalanish asosida mis ishlab chiqarish shlaklarini qayta ishlash texnologiyasini takomillashtirish: t.f.f.d. (PhD) dissertatsiyasi avtoreferati. – Toshkent: 2022. 46 b.
- [2] Yusupxodjayev A.A., Hojiyev Sh.T., Ochilidiyev Q.T. Gidrometallurgiya jarayonlari nazariyasi: darslik. – Toshkent: “Lesson press” nashriyoti, 2022. – 258 b. ISBN 978-9943-8648-8-7
- [3] M. Deniz Turan, Shoeleh Assemi, Rashid K. Nadirov, Galymzhan A. Karamyrzayev, Omirserik Baigenzhenov, Norman Toro. “Selective Hydrochloric Acid Leaching of Zinc, Lead and Silver from Mechanically Activated Zinc Plant Residue” <http://dx.doi.org/10.3103/S1067821222050108>
- [4] Ali Reza Eivazi Hollagh, Eskandar Keshavarz Alamdari, Davooud Moradkhani, Ali Akbar Salardini. “Kinetic analysis of isothermal leaching of zinc from zinc plant residue” <http://dx.doi.org/10.4236/ijnm.2013.21002>
- [5] Hana Rigoulet, Jaromír Drápala, Silvie Brožová, Šárka Langová, Jiřina Vontorová, Jitka Malcharcziková, Nikola Němcová, Václav Nėtek, Jaroslav Kubáč, Dominik Janáček. “Possibilities of zinc extraction from galvanic sludge by means of leaching in sodium hydroxide and following electrolysis”
- [6] Mahmut Sami Alkan, Aydın Rusen, and Mehmet Ali Topcu. “Recovery of Lead and Zinc from Complex Industrial Waste of Zinc Process with Ammonium Acetate”
- [7] Asadollahfardi, G., Yazdani, M., Sarmadi, M.S., Khodadadi Darban, A. Evaluation of Enhanced Electrokinetic Remediation of Arsenic from Cold Filter Cake: Zinc-Leaching Sediment (2022) Journal of Environmental Engineering (United States), 148 (12), art. no. 04022079.
- [8] Yusupkhodzhaev A.A., Khozhiev Sh.T., Akramov I.I.A. Use of non-traditional reducing agents to expand the resource base of OJSC Uzmetkombinat // Chernye Metally, Volume 2021, Issue 4. P. 4 – 8.
- [9] Khojiev Sh.T., Saidova M.S., Mirzajonova S.B., Ibrokhimov H.X., Ismatov Sh.O'. Development of Technology for Processing Zinc Cakes Based on the Use of Petroleum Coke // International Journal of Academic Engineering Research, 6(6), 2022. P. 23-28.
- [10] Khojiev Sh.T., Saidova M.S., O'rinboyev M.J. Modern Methods of Coating Zinc and Chromate Shells on the Surface of Structural Materials // International Journal of Engineering and Information System, 6(6), 2022. P. 1-6.
- [11] Toshpulatov D.D., Khojiev Sh.T., Berdiyarov B.T., Jorayeva A.J., Kholmominova S.F. Thermodynamic Analysis Of Chalcopyrite Oxidation-Reduction Process // International Journal of Engineering and Information System, 6(6), 2022. P. 96-101.
- [12] Toshpulatov D.D., Khojiev Sh.T., Berdiyarov B.T., Kholmominova S.F. Technological analysis of the process of metals recovery of large dust from the converter using metallurgical methods // International Journal of Engineering and Information System, 6(7), 2022. P. 67-71.