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Thermodynamic Analysis of Heavy Metal Removal from Technogenic Waters of the “Ko‘ksuv” Basin Using Calcium Hydroxide

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Abstract— This study investigates the treatment of technogenic waters accumulated in the *“Ko‘ksuv”* reservoir, formed as a result of mining and metallurgical activities, with calcium hydroxide ($Ca(OH)_2$) to remove heavy metal ions and improve water quality for potential industrial reuse. Thermodynamic and kinetic analyses of precipitation reactions involving sulfate, nitrate, chloride, and other metal salts were performed using Gibbs free energy (ΔG) and equilibrium constant (K_e) relationships over a wide temperature range (5–100 °C). The results revealed that the precipitation reactions are thermodynamically favorable, with high K_m values at low to moderate temperatures (20–40 °C), confirming their exothermic nature. The study established that lime treatment is highly effective in removing heavy metals such as Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Al^{3+}, while additional purification steps (sorption or ion-exchange) are required for sodium, potassium, chloride, and nitrate ions. The scientific novelty lies in the identification of reaction-specific equilibrium parameters and the optimization of process conditions, while the practical significance is the potential to implement closed-loop water circulation systems in metallurgical plants, thereby reducing ecological risks and improving water resource efficiency.

Keywords: technogenic waters, calcium hydroxide, precipitation kinetics, Gibbs free energy, equilibrium constant, heavy metals removal, metallurgical wastewater treatment.

1. INTRODUCTION

In the contemporary context of industrial development, the mining and metallurgical sectors play a decisive role in the economic growth of many countries. However, alongside the production of valuable metals and alloys, these industries generate vast quantities of technogenic wastewater, the composition of which is often dominated by elevated concentrations of heavy metal ions (Pb^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}/Fe^{3+}), sulfates, chlorides, and various toxic organic and inorganic impurities. These effluents originate from multiple stages of ore processing, including flotation, leaching, smelting, refining, dust capture, and slag granulation processes. When inadequately managed, the storage and accumulation of such wastewater in surface reservoirs or tailing ponds become long-term sources of environmental degradation, contributing to soil contamination, groundwater infiltration, acid mine drainage (AMD), eutrophication of surface waters, and overall disturbance of the hydrogeochemical balance of ecosystems.

The global trend toward sustainable development and the implementation of the circular economy paradigm has led to increased attention toward the treatment and reuse of industrial effluents, particularly in water-scarce regions. From a technological perspective, the valorization of wastewater is no longer perceived merely as an ecological necessity but as an economically beneficial strategy that allows industries to reduce their dependence on natural freshwater resources while simultaneously minimizing environmental liabilities. In this regard, the recycling of technogenic waters represents a critical direction in advancing low-waste and eco-efficient metallurgical technologies [1–3].

A striking example of this problem is observed in Uzbekistan, within the territory of the abandoned “Qo‘rg‘oshinkon” lead mine, located in the “Qalmoqqir” deposit zone. Here, a large artificial reservoir known as the “Ko‘ksuv” basin has accumulated substantial volumes of wastewater originating from decades of mining and metallurgical operations. Recent chemical analyses of these waters have indicated high concentrations of lead, zinc, copper, iron, cadmium, and other toxic heavy metals, far exceeding permissible levels established by both national regulatory standards and international guidelines such as the World Health Organization (WHO) and the European Union Water Framework Directive (WFD). Moreover, these waters are characterized by elevated mineralization levels, high total dissolved solids (TDS), and variable pH regimes, which complicate their treatment and preclude direct industrial application without prior purification [4–5].

Despite these challenges, the reuse potential of the “Ko‘ksuv” reservoir waters is significant. Through appropriate treatment technologies, these waters could be transformed into a reliable source of technical-grade water for metallurgical plants and processing facilities. This is particularly relevant given the increasing demand for technical water in the metallurgical industry, where uninterrupted supply is required for cooling systems, ore beneficiation, selective smelting operations, wet dust collection, chemical washing, slag granulation, hydrotransport pipelines, and other process units. A shortage of technical water not only limits production capacities but also threatens the stability of critical technological processes, thereby reducing the overall efficiency and competitiveness of enterprises [6].

A wide range of water treatment methods have been studied in the global scientific literature, including chemical precipitation, ion-exchange, sorption on natural and synthetic adsorbents, membrane separation (nanofiltration, reverse osmosis, ultrafiltration), biological treatment, and advanced oxidation processes (AOPs). Among these, lime-based precipitation techniques remain the most widely applied in industrial practice due to their simplicity, availability, and high efficiency in removing multivalent heavy metal cations. The fundamental mechanism involves the addition of lime (CaO or $Ca(OH)_2$), which increases the alkalinity of the solution, leading to the precipitation of metal hydroxides (e.g., $Pb(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Cu(OH)_2$). These reactions are governed by complex thermodynamic and kinetic factors, influenced by temperature, pH, ionic strength, mixing intensity, and the presence of competing ligands such as sulfates, carbonates, or silicates [7–8].

Numerous studies have highlighted that while lime treatment is effective for initial precipitation, the resulting effluent often contains residual metal ions and suspended solids, necessitating additional polishing stages, such as sorption using activated carbon, zeolites, bentonite clays, biosorbents, or synthetic ion-exchange resins. In some cases, integration with membrane filtration or constructed wetlands has been proposed to achieve effluent quality suitable for reuse in industrial cycles. Moreover, the sludge generated during lime precipitation is itself a technogenic by-product, requiring careful management to prevent secondary pollution. Thus, the development of an integrated water treatment scheme—combining lime precipitation with sorption, sedimentation, and filtration—is considered an optimal approach for metallurgical wastewater recycling [9–10].

The present research aims to contribute to this growing body of knowledge by conducting a comprehensive investigation of the kinetic regularities of lime-induced precipitation for the treatment of “Ko‘ksuv” reservoir waters. The study focuses on determining the optimal technological parameters, including lime dosage, contact time, mixing speed, settling rate, and solid-liquid separation efficiency. Furthermore, the potential for integrating additional sorption-based purification stages will be examined to enhance the removal of trace metals and improve the physicochemical quality of the treated water.

The scientific novelty of this work is expressed in the application of systematic kinetic modeling to a specific, real-world case of technogenic wastewater in Uzbekistan, coupled with the design of a multi-stage purification scheme tailored to the requirements of local metallurgical enterprises. The practical significance lies in the dual benefits of (i) environmental risk mitigation through the detoxification of a hazardous technogenic reservoir, and (ii) the establishment of an alternative and sustainable technical water supply source for metallurgical factories, thereby reducing dependence on natural freshwater resources. The results are expected to provide a theoretical and technological foundation for the implementation of advanced water management practices in the regional metallurgical sector, contributing to both ecological safety and industrial sustainability [11–12].

2. MATERIALS AND METHODS

The object of the present research is the study of precipitation reactions occurring in the treatment of technogenic waters accumulated in the “Ko‘ksuv” reservoir through the addition of lime (CaO). The focus is placed on the chemical interactions between dissolved salts of heavy metals and alkaline reagents, with particular attention to the thermodynamic feasibility, equilibrium conditions, and kinetic behavior of the reactions involved [13].

The principal chemical reactions under investigation can be summarized as follows:

1. $MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4$
2. $Ca(HSO_4)_2 + Ca(OH)_2 \rightarrow 2CaSO_4\downarrow + 2H_2O$
3. $Mg(HSO_4)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaSO_4\downarrow + 2H_2O$
4. $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$
5. $2NaCl + Ca(OH)_2 \rightarrow 2NaOH + CaCl_2$
6. $2KCl + Ca(OH)_2 \rightarrow 2KOH + CaCl_2$
7. $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4\downarrow$
8. $K_2SO_4 + Ca(OH)_2 \rightarrow 2KOH + CaSO_4\downarrow$
9. $Fe(NO_3)_2 + Ca(OH)_2 \rightarrow Fe(OH)_2\downarrow + Ca(NO_3)_2$
10. $FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2\downarrow + CaSO_4\downarrow$
11. $Cu(NO_3)_2 + Ca(OH)_2 \rightarrow Cu(OH)_2\downarrow + Ca(NO_3)_2$
12. $CuSO_4 + Ca(OH)_2 \rightarrow Cu(OH)_2\downarrow + CaSO_4\downarrow$
13. $ZnSO_4 + Ca(OH)_2 \rightarrow Zn(OH)_2\downarrow + CaSO_4\downarrow$
14. $MnSO_4 + Ca(OH)_2 \rightarrow Mn(OH)_2\downarrow + CaSO_4\downarrow$
15. $CrSO_4 + Ca(OH)_2 \rightarrow Cr(OH)_2\downarrow + CaSO_4\downarrow$
16. $Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4\downarrow$
17. $PbSO_4 + Ca(OH)_2 \rightarrow Pb(OH)_2\downarrow + CaSO_4\downarrow$
18. $CaO + H_2O \rightarrow Ca(OH)_2$

These reaction equations illustrate the general principle of lime precipitation, whereby multivalent cations (Mg^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Cr^{2+}, Al^{3+}, Pb^{2+}) are transformed into sparingly soluble metal hydroxides, while accompanying anions such as SO_4^{2-} and Cl^- form soluble or partially soluble calcium salts (e.g., $CaSO_4$, $CaCl_2$). Such transformations are governed by the solubility product constants (Ksp) of the respective hydroxides and sulfates, which determine the extent of precipitation under specific thermodynamic conditions.

To evaluate the feasibility and kinetics of these reactions, thermodynamic analysis was carried out using the dependence of the Gibbs free energy change (ΔG) on temperature and equilibrium constants. The kinetics of the precipitation process were studied based on the fundamental relation between ΔG and the equilibrium constant (K_e) expressed by the following equations [14]:

$$\Delta G = -RT\ln K_e \quad (1)$$

where:
R – universal gas constant ($R = 8.31696 \times 10^{-3}$ $kJ \cdot mol^{-1} \cdot K^{-1}$);
K_e – equilibrium constant of the corresponding chemical reaction.
From equation (1), the equilibrium constant can be expressed as:

$$K_e = \exp(-\Delta G/(RT)) \quad (2)$$

By applying these mathematical expressions, the relationship between Gibbs free energy and temperature was established for each reaction involving calcium hydroxide in the treatment of "Ko'ksuv" technogenic waters. The analysis enabled the identification of temperature-dependent trends in the precipitation kinetics. Specifically, for each reaction, the changes in equilibrium and rate constants were calculated as the system temperature increased from 5 °C to 100 °C, with increments of 5 °C. This approach made it possible to assess the stability domains of hydroxide precipitates, reaction spontaneity, activation barriers, and the temperature sensitivity of precipitation rates [15].

The methodology integrates theoretical thermodynamic modeling with kinetic evaluation, thus providing a comprehensive framework for optimizing lime treatment of technogenic waters. The obtained data serve as a scientific basis for determining the optimal dosage of lime, the most favorable temperature ranges, and the expected efficiency of heavy metal removal, which are essential for the development of a practical large-scale water treatment technology applicable to metallurgical enterprises [16-17].

3. RESULTS AND DISCUSSION

The analysis of the obtained results demonstrates that the precipitation reactions of heavy metal ions contained in the technogenic waters accumulated in the "Ko'ksuv" reservoir with calcium hydroxide ($Ca(OH)_2$) are thermodynamically stable over a wide temperature range (5–100 °C). The calculated values of the equilibrium constants (K_e), which approach unity or exceed it, clearly indicate the spontaneous nature of these reactions under the studied conditions. This confirms that the interaction between calcium hydroxide and dissolved metal salts proceeds without the necessity of additional external energy input, thus reflecting the favorable Gibbs free energy ($\Delta G < 0$) values.

Moreover, the results highlight that the precipitation efficiency increases with temperature elevation, as higher kinetic activity facilitates the formation of insoluble hydroxides such as $Fe(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, and $Pb(OH)_2$. These hydroxide phases are characterized by low solubility products (Ksp), which significantly reduces the residual concentration of toxic cations in the aqueous medium. Such behavior not only confirms the viability of lime-based neutralization processes but also ensures compliance with industrial water reuse requirements.

In addition, the thermodynamic modeling reveals that the equilibrium state of the system is strongly influenced by temperature-dependent variations in Gibbs free energy. The negative ΔG values calculated for all studied reactions confirm their irreversible direction toward precipitate formation. This suggests that lime treatment of the "Ko'ksuv" reservoir waters can be considered both an environmentally sustainable and technologically effective method for reducing the concentration of hazardous metal ions. Furthermore, the integration of this approach into existing metallurgical water management systems may contribute to enhanced water recycling efficiency, reduced dependence on freshwater resources, and mitigation of ecological risks associated with the discharge of untreated wastewater.

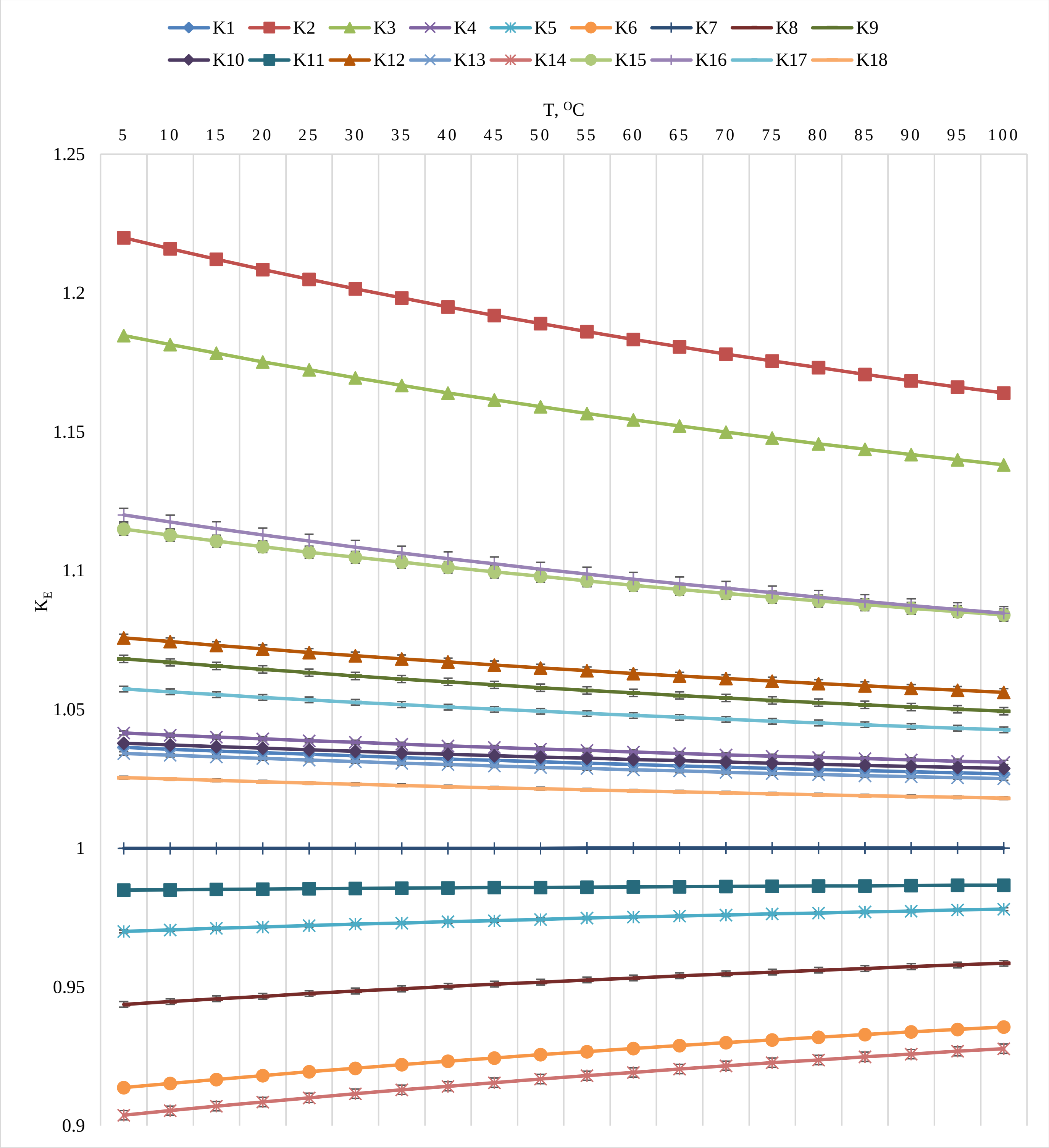

Fig. 1. Temperature dependence of the equilibrium constants of the precipitation and displacement reactions resulting from neutralization with calcium hydroxide (5–100 °C)

The graphical data illustrated in Figure 1, together with the corresponding reaction profiles, clearly demonstrate that the preliminary precipitation of technogenic waters from the “Koʻksuv” reservoir using calcium hydroxide ($Ca(OH)_2$) is both thermodynamically favorable and practically effective for a wide range of sulfate salts and heavy metal compounds. The dependence of the equilibrium constant (K_m) on temperature reveals the exothermic character of these reactions, thereby explaining their high precipitation efficiency at relatively low temperature intervals. Such behavior highlights the feasibility of lime treatment under ambient industrial conditions, reducing the need for additional thermal energy input.

Nevertheless, the analysis also indicates that the effective removal of chloride- and nitrate-containing components, as well as alkali metal ions (Na^+, K^+), requires the incorporation of complementary physicochemical stages. These may include processes such as ion exchange, membrane separation, or advanced sorption techniques, which are capable of capturing highly soluble species that cannot be fully precipitated by lime treatment alone. This finding provides a strong scientific basis for the staged design of the overall treatment scheme, emphasizing the importance of optimizing pH regulation, lime dosage, and integrating sorption-based purification units to achieve higher levels of water quality.

Overall, the thermodynamic evaluation confirms that the reactions of calcium hydroxide with dissolved heavy metal ions are favorable across a broad temperature spectrum, with the optimum range identified as 20–40 °C. Within this interval, the equilibrium constants retain higher values while the reaction kinetics remain sufficiently fast to ensure practical applicability. This implies that the primary precipitation process of technogenic waters with lime can be effectively carried out under natural ambient temperatures typical of industrial settings, without additional energy consumption.

The obtained results further demonstrate that lime-based treatment of technogenic waters not only mitigates ecological risks by reducing toxic ion concentrations but also creates opportunities for the reuse of purified waters as a reliable technical water source for metallurgical plants and factories. The kinetic modeling and optimized process conditions, when integrated with subsequent sorption stages, provide a robust strategy for further minimizing the residual content of heavy metals and tailoring the treated water to meet specific industrial requirements.

4. CONCLUSION

The conducted investigations have made it possible to determine the equilibrium constants for precipitation reactions of various saline solutions with calcium hydroxide ($Ca(OH)_2$) and to comprehensively study their dependence on temperature. The graphical analysis of Gibbs free energy equations applied to the chemical interactions of calcium hydroxide with dissolved salts present in the technogenic waters of the “Koʻksuv” reservoir revealed that the equilibrium constants (K_e) decrease progressively with increasing temperature. This observation confirms the exothermic nature of the studied reactions, demonstrating that the precipitation process is more efficient under low to moderate temperature conditions.

The scientific novelty of this research lies in the fact that lime-induced precipitation reactions are proven not only to effectively remove ecologically hazardous heavy metal ions, but also to form stable sulfate, nitrate, and other compounds that contribute to the improvement of technical water quality. In particular, reactions of salts such as $Ca(HSO_4)_2$, $Mg(HSO_4)_2$, $CuSO_4$, and $Al_2(SO_4)_3$ with $Ca(OH)_2$ exhibited high equilibrium constants, which scientifically validates the possibility of their nearly complete precipitation. At the same time, the comparatively low equilibrium constant values ($K_e < 1$) observed for sodium and potassium salts indicate that these components cannot be fully neutralized by lime treatment alone, thus justifying the necessity of incorporating additional purification stages such as sorption or ion-exchange processes.

It has been established that the optimal temperature range for lime precipitation processes is 20–40 °C, within which the majority of reactions reach their highest equilibrium constant values, ensuring enhanced technological efficiency. This temperature interval corresponds to natural ambient industrial conditions, thereby minimizing energy requirements and increasing the practical feasibility of the process.

The practical significance of the present research is that the developed results can be directly applied to address the problem of providing metallurgical plants and factories with high-quality technical water. The proposed process effectively precipitates sulfates and heavy metal ions from technogenic waters, improving water quality parameters to levels approaching normative standards. Implementation of this methodology in industrial practice creates favorable conditions for establishing closed-loop water circulation systems, ensuring the rational utilization of water resources, enhancing resource efficiency, and significantly reducing the ecological burden of metallurgical operations.

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