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# The assessment of zinc precipitation from sulfate solutions using magnesium-rich ores

Saeid Karimi [a], Bahram Behnajady [b,*] and Javad Moghaddam [c]

[a] *Department of Metallurgy and Materials Engineering, Hamedan University of Technology, Hamedan, Iran.*
[b] *Research Centre of Advanced Materials, Faculty of Materials Engineering, Sahand University of Technology, Sahand New Town, Iran.*
[c] *Materials and Metallurgical Engineering Department, University of Zanjan, Zanjan, Iran.*

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## ABSTRACT

This study systematically investigates the mechanisms and optimization of zinc precipitation from sulfate solutions using magnesium-containing ores. The dominant reaction pathway leads to the formation of zinc hydroxysulfate ($Zn_5(OH)_6(SO_4)_2$) at moderate pH (4–6.5), as confirmed by a consistent final pH of 6.5 in all experiments. Temperature critically influences reaction kinetics, with 80 °C identified as optimal for maximizing zinc recovery (73.4 %) and ensuring effective magnesium participation in precipitation reactions. Process efficiency is governed by ore dosage, where 100 g/L of magnesium-rich ore yields peak zinc recovery, beyond which marginal improvements occur. Time-dependent studies reveal that 150 minutes represents the practical equilibrium for zinc precipitation at 80 °C, achieving 73.4% recovery with diminishing returns thereafter. Key findings demonstrate that controlled parameters—pH 6.5, 80°C, 150-min reaction time, and optimized ore dosage—collectively enhance zinc recovery while minimizing reagent consumption and energy costs. Under the optimized conditions (T = 80°C, ore dosage = 100 g/l, time = 150 minutes), the magnesium content demonstrated a significant reduction from 7.0 g to 5.1 g, corresponding to an absolute decrease of 1.9 g (27.1% decrement), which clearly indicates effective magnesium participation in the precipitation process, where the combination of elevated temperature and controlled ore dosage synergistically enhanced magnesium removal efficiency while minimizing residual content, ultimately contributing to improved process performance.

**Keywords:** *Zinc precipitation, Basic zinc sulfate, Magnesium-rich ore, Magnesium removal.*

## 1. Introduction

With the increasing global demand for zinc and the depletion of high-grade zinc reserves, low-grade zinc ores have gained significant attention from producers ( Karimi et al., 2017; Ashtari et al., 2025). Zinc oxide deposits may contain minerals, such as smithsonite, hemimorphite, or willemite, while low-grade ores often include gangue minerals like calcite, dolomite, quartz, and iron oxides (Khanmohammadi Hazaveh et al., 2020). Among the soluble impurities in zinc sulfate solutions, magnesium is particularly problematic as it is not removed during the purification stages of the zinc production process, including iron precipitation or hot and cold purification processes. Due to magnesium's higher standard potential compared to zinc, it cannot be deposited on aluminum cathodes during electrowinning (MacKinnon & Brannen, 1991), leading to its accumulation in the solution over time. Increased magnesium concentration raises energy consumption and reduces current efficiency in the electrowinning process. The permissible magnesium concentration in zinc solutions is typically limited to 10-15 g/L, making its removal crucial in zinc production (Mosayebi et al., 2021).

Current pretreatment methods for zinc concentrate include dilute sulfuric acid leaching, magnesium fluoride precipitation (Booster et al., 2000; Georgalli et al., 2008), lime neutralization (Matthew et al., 1980; Sharma, 1990), solvent extraction (Cheng et al., 2010; Abutalebi et al., 2019), and freezing crystallization (Jin et al., 2023). During dilute sulfuric acid leaching of zinc concentrate, magnesium oxide (MgO) and magnesium carbonate ($MgCO_3$) dissolve along with zinc oxide (ZnO) and zinc carbonate ($ZnCO_3$), resulting in zinc losses. In fluoride precipitation, fluoride ions act as ligands, reacting with magnesium to form low-solubility magnesium fluoride ($MgF_2$), which is removed as a precipitate (Jin et al., 2023). However, increased fluoride concentration can cause zinc sheets to stick to aluminum cathodes, reducing their effectiveness. The lime neutralization method exploits the difference in hydrolysis pH between zinc and magnesium, adjusting the pH to 10-11 using calcium hydroxide ($Ca(OH)_2$). This process consumes significant amounts of lime and produces gypsum as a byproduct, requiring further treatment (Heimala, 1981). Solvent extraction is effective for separating specific metals from polymetallic solutions, but residual organic phases in the aqueous phase and high chemical costs limit its application (Haghighi et al., 2015). The high energy consumption of freezing crystallization has prevented its industrial adoption. Currently, lime neutralization at pH 10-11 remains the primary industrial method for magnesium removal.

This study investigates the feasibility of precipitating zinc from sulfate solutions using magnesium-rich soil, aiming to separate magnesium from zinc through a displacement precipitation reaction where magnesium enters the solution while zinc is incorporated into the final precipitate. The research focuses on optimizing key parameters, such as temperature, reaction time, and the quantity of magnesium-rich soil to achieve efficient separation.

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* Corresponding author. *E-mail address:* b_behnajady@sut.ac.ir (B. Behnajady).

## 2. Material and methods

### *2.1. Material*

The main experimental material was a magnesium-rich zinc concentrate containing approximately 11.7% zinc and 7.1% magnesium. The zinc sulfate solution used had concentrations of 21.4 g/L of zinc and 9.2 g/L of magnesium. Both the concentrate and the solution were provided by Zanjan Zinc Khales Sazan Industries Company (ZZKICo) in Zanjan, Iran.

### *2.2. Experimental procedure*

In this study, the precipitation of zinc from a one-liter zinc sulfate solution was investigated using magnesium-rich ore as a precipitant. The key parameters evaluated included temperature (ranging from 65 to 85 °C), reaction time (ranging from 30 to 180 minutes), and ore dosage (between 50 and 150 g/L). The process began by heating the zinc sulfate solution to the target temperature, followed by the controlled addition of a predetermined amount of ore. The solution was continuously stirred at 1000 rpm using a mechanical stirrer to ensure uniform mixing and enhance the precipitation process.

All experiments were conducted in a 2-liter beaker, with temperature precisely controlled to maintain accuracy within ±1 °C. Once the reaction was complete, the entire mixture was subjected to solid-liquid separation using vacuum filtration, ensuring effective removal of the precipitated solids. The collected precipitates were then dried in an oven at 110 °C for 24 h to remove residual moisture, preserving their composition for further analysis.

$$R_{Zn\ \ Prec,} = \frac{Zn_{prec,} \times m_{prec,} - Zn_{ore} \times m_{ore}}{Zn_{ore} \times m_{ore}} \times 100 \tag{1}$$

In this equation, $Zn_{prec.}$ represents the zinc grade in the final precipitates (in %), $m_{prec.}$ denotes the weight of the final precipitates (in g), $Zn_{ore}$ refers to the zinc grade in the initial material (in %), and $m_{ore}$ indicates the weight of the initial material (in g).

## 3. Results and discussion

### *3.1. Proposed precipitation reactions*

To determine the mechanism of zinc precipitation during the process of adding magnesium-containing ore, the possible reactions can be considered as follows. The formation of zinc hydroxysulfate ($Zn_5(OH)_6(SO_4)_2$) is formed via reaction (2), where carbonate hydrolysis releases $OH^-$ ions to precipitate zinc while evolving $CO_2$ gas and leaving soluble $MgSO_4$ in solution. The direct precipitation of zinc hydroxide ($Zn(OH)_2$) occurs under higher pH conditions, as shown in reaction (3). The dominant product (hydroxysulfate vs. hydroxide) depends on pH, with hydroxysulfate favored at moderate pH (4–6) and hydroxide at higher pH (>7). Since all experiments reached an identical final pH of 6.5, the data confirmed zinc hydroxysulfate as the prevailing reaction phase. In addition, temperature plays a critical role by accelerating kinetics and promoting hydroxysulfate formation based on the measured pH in the final solution.

$$5ZnSO_{4(aq)} + 3MgCO_{3(s)} + 3H_2O_{(aq)} \rightarrow Zn_5(OH)_6(SO_4)_{2(s)} + 3MgSO_{4(aq)} + 3CO_{2(g)} \tag{2}$$

$$ZnSO_{4(aq)} + MgCO_{3(s)} + H_2O_{(aq)} \rightarrow Zn(OH)_{2_{(s)}} + MgSO_{4(aq)} + CO_{2(g)} \tag{3}$$

If calcium is present in the ore, the zinc precipitation reaction can also proceed as follows. In industrial zinc recovery processes, the precipitation reaction using calcium carbonate ($CaCO_3$) proceeds primarily through the formation of zinc hydroxysulfate under moderately acidic to neutral conditions (pH ~4-6.5), as described by reaction (4). This pathway is industrially preferred due to the stability and filterability of the hydroxysulfate precipitate, though it generates $CaSO_4$ (gypsum) as a byproduct, which requires management to prevent equipment scaling. The process is typically conducted at elevated temperatures (70-80 °C) to enhance reaction kinetics, with the $CO_2$ off-gas necessitating proper handling. The consistent final pH of 6.5 in these experiments confirmed the dominance of hydroxysulfate formation, as this pH range optimally suppressed competing zinc hydroxide ($Zn(OH)_2$) precipitation while maximizing zinc recovery efficiency, in agreement with established hydrometallurgical practices (Dutrizac, 2002). The carbonate-to-zinc stoichiometry (3:5 ratio) was carefully controlled to ensure complete zinc precipitation while minimizing excessed reagent consumption.

$$5ZnSO_{4(aq)} + 3CaCO_{3(s)} + 3H_2O_{(aq)} \rightarrow Zn_5(OH)_6(SO_4)_{2(s)} + 3CaSO_{4(s)} + 3CO_{2(g)} \tag{4}$$

$$ZnSO_{4(aq)} + CaCO_{3(s)} + H_2O_{(aq)} \rightarrow Zn(OH)_{2_{(s)}} + CaSO_{4(s)} + CO_{2(g)} \tag{5}$$

Fig. 1 illustrates the relationship between zinc precipitation recovery (%) and the amount of magnesium-rich ore (g) used in the process at 75 °C for 150 minutes, highlighting the impact of ore dosage on zinc removal efficiency. As the ore dosage increased from 50 to 150 g/L, a significant improvement in zinc precipitation recovery was observed, emphasizing the role of ore quantity in facilitating the reaction. At 50 g/L of ore dosage, the recovery rate was relatively low at 28.6 %, indicating that the available reactive components are insufficient for effective zinc precipitation. As the ore addition increased to 100 g/L, the recovery rate improved notably to 55.8 %, demonstrating a more favorable condition for precipitation, likely due to better interaction between zinc ions and the active sites of the ore. The highest recovery of 62.6 % was recorded at 150 g/L of ore dosage, suggesting that this dosage provides an optimal balance of reactants, maximizing zinc removal while ensuring efficient resource utilization. However, beyond this point, further increasing the ore dosage may not result in a significant improvement in recovery efficiency and could lead to excessive material consumption, making the process less economical.

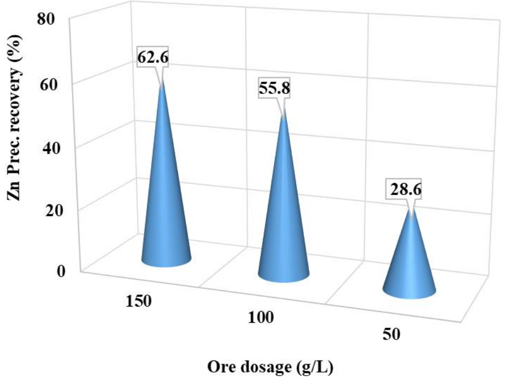

**Fig. 1.** The effect of magnesium-rich ore addition on zinc precipitation recovery at conditions of 75 °C for 150 minutes.

Table 1 presents the magnesium content measured before and after the zinc precipitation reaction conducted at 75°C for 150 minutes using various amounts of magnesium-bearing ores. The experimental results demonstrate that the amount of added ore has a direct impact on magnesium behavior in the precipitation process. In the 150 g/L treatment, the slight increase in magnesium after precipitation (from 10.5 to 12 g) indicates that the excessive ore quantity prevented effective magnesium participation in zinc precipitation reactions. Conversely, when the ore amount was reduced to 100 and 50 g/L, significant decreases in magnesium were observed (from 7 to 5.7 g and from 3.5 to 2.4 g, respectively), demonstrating more active magnesium involvement in precipitation reactions at lower ore quantities. This pattern suggests that for optimal magnesium removal from waste, controlled and reduced amounts of ore should be used to create favorable conditions for magnesium reactivity, while ensuring sufficient time for reaction completion. These findings can be applied to the design of industrial processes for managing magnesium-containing waste.

**Table 1.** Magnesium content before and after the zinc precipitation process using various magnesium-bearing ores.

| Ore dosage (g/L) | Before (g) | After (g) |
|---|---|---|
| 150 | 10.5 | 12.0 |
| 100 | 7 | 5.7 |
| 50 | 3.5 | 2.4 |

Fig. 2 illustrates the effect of temperature on zinc precipitation recovery (%) within the range of 65 to 85 °C, under the reaction conditions of 150 minutes and 100 g/L of magnesium-rich ore. As the temperature increased, zinc precipitation recovery improved significantly, highlighting the positive influence of temperature on the reaction kinetics and precipitation efficiency. At 65 °C, the recovery was relatively low at 18.2%, suggesting insufficient thermal energy to drive the reaction effectively. Increasing the temperature to 70 °C slightly enhanced recovery to 23.7%, but a more substantial improvement is observed at 75 °C, where recovery reaches 55.8 %. The highest recovery rates are achieved at 80 °C (73.4 %) and 85 °C (75.6 %), with only a minor difference of 2.2 % between them. This suggests that 80 °C is the optimum temperature, as further increasing it to 85 °C does not provide a significant improvement in zinc removal while leading to higher energy consumption. Thus, 80°C offers the best balance between efficiency and energy use for maximizing zinc precipitation recovery.

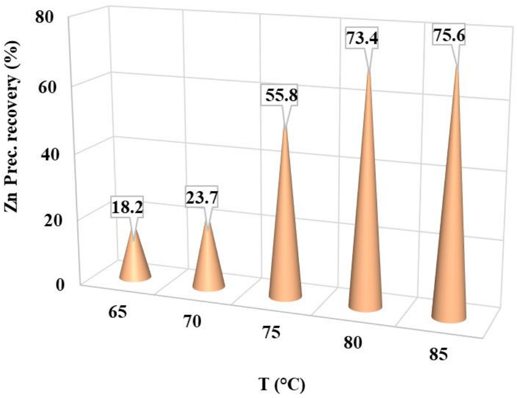

**Fig. 2.** The effect of temperature on zinc precipitation recovery at conditions of 100 g/L magnesium-rich ore for 150 minutes.

Table 2 shows the magnesium content measured before and after the zinc precipitation reaction conducted with 100 g/L magnesium-bearing ore for 150 minutes at various temperatures. The results investigating the temperature effect on the zinc precipitation process demonstrated that temperature variations significantly influence magnesium behavior in the system. At lower temperatures (65 and 70 °C), the slight increase in magnesium to 7.4 and 7.5 g, respectively, indicates that magnesium did not effectively participate in precipitation reactions. When the temperature reached 75 °C, a noticeable decrease in magnesium to 5.7 g revealed the beginning of magnesium's effective participation in precipitation mechanisms. At 80 and 85 °C, the stabilization of magnesium content at 5.1 g demonstrated maximum effective participation of magnesium in the reactions, where magnesium either fully incorporated into the precipitate structure or forms stable compounds. These observations emphasized that maintaining 80 °C was essential for achieving optimal and effective magnesium participation in the precipitation process, as this temperature simultaneously maximized removal efficiency and prevented incomplete magnesium involvement. The current findings are fully consistent with known mechanisms in mineral compound precipitation studies.

Fig. 3 shows zinc precipitation recovery (%) over time (30 to 180 minutes) at a constant temperature of 80 °C with an ore mass of 100 g/L. Initially, the recovery increased rapidly, reaching approximately 27.9 % at 30 minutes, indicating a fast precipitation rate due to favorable kinetic conditions at the elevated temperature. As time progresses, the recovery continued to rise but at a slower pace, reaching 45.4 % at 60 minutes, 53.7 % at 90 minutes, and 68.9 % at 120 minutes, suggesting a gradual approach towards equilibrium. By 150 and 180 minutes, the recovery plateaus at around 73.4 % and 74.6 %, respectively, indicated that most of the recoverable zinc had been precipitated, and further time yielded diminishing returns. The 150 minutes mark emerged as the optimum precipitation time for zinc recovery, achieving 73.4% efficiency, a near-maximum yield with minimal further gains beyond this point. At 80°C, the reaction kinetics were initially rapid, but by 150 minutes, the system approacheed practical equilibrium, where additional time (e.g., 180 minutes, 74.6%) only marginally improved recovery (just 1.2% higher) at the cost of extended processing. This plateau suggested that most accessible zinc had already been precipitated, and further retention is economically unjustified due to diminishing returns. Thus, 150 minutes strikes the best balance between recovery efficiency and operational practicality, optimizing both energy use and throughput in industrial applications.

**Table 2.** Magnesium content before and after the zinc precipitation process using various temperatures.

| Temperature (°C) | Before (g) | After (g) |
|---|---|---|
| 65 | 7 | 7.4 |
| 70 | 7 | 7.5 |
| 75 | 7 | 5.7 |
| 80 | 7 | 5.1 |
| 85 | 7 | 5.1 |

Fig. 3 shows zinc precipitation recovery (%) over time (30 to 180 minutes) at a constant temperature of 80 °C with an ore mass of 100 g/L. Initially, the recovery increased rapidly, reaching approximately 27.9 % at 30 minutes, indicating a fast precipitation rate due to favorable kinetic conditions at the elevated temperature. As time progresses, the recovery continued to rise but at a slower pace, reaching 45.4 % at 60 minutes, 53.7 % at 90 minutes, and 68.9 % at 120 minutes, suggesting a gradual approach towards equilibrium. By 150 and 180 minutes, the recovery plateaus at around 73.4 % and 74.6 %, respectively, indicated that most of the recoverable zinc had been precipitated, and further time yielded diminishing returns. The 150 minutes mark emerged as the optimum precipitation time for zinc recovery, achieving 73.4% efficiency, a near-maximum yield with minimal further gains beyond this point. At 80°C, the reaction kinetics were initially rapid, but by 150 minutes, the system approacheed practical equilibrium, where additional time (e.g., 180 minutes, 74.6%) only marginally improved recovery (just 1.2% higher) at the cost of extended processing. This plateau suggested that most accessible zinc had already been precipitated, and further retention is economically unjustified due to diminishing returns. Thus, 150 minutes strikes the best balance between recovery efficiency and operational practicality, optimizing both energy use and throughput in industrial applications.

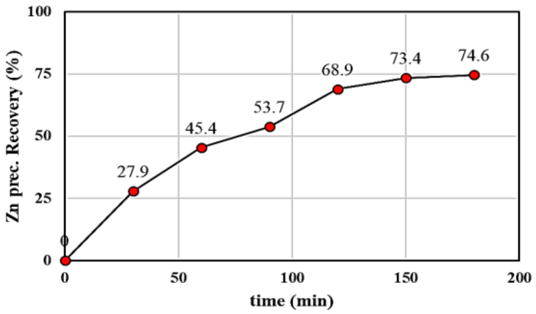

**Fig. 3.** The effect of time on zinc precipitation recovery at a condition of 100 g/L magnesium-rich ore at 80 °C.

Zinc precipitation from sulfate solutions employs various agents under optimized conditions, with patented methods enhancing selectivity and efficiency. Lime ($Ca(OH)_2$) or hydrated lime was another widely used agent, particularly for precipitating zinc as zinc oxide

(ZnO) and simultaneously forming gypsum ($CaSO_4$) as a byproduct. This process operateed optimally at pH 6.5–7.5 and temperatures between 70–95°C. The resulting ZnO particles were typically fine (<30 μm), while gypsum crystals were larger, enabling efficient separation by filtration or sedimentation (Habashi, 1997). Lime is cost-effective and suitable for large-scale operations, though precise pH control is necessary to prevent excessive zinc coprecipitation (Voigtm, 2012). This method minimizes magnesium coprecipitation and allows gypsum recycling. Basic zinc sulfate formation was achieved at lower pH (5.5–6.5) and temperatures ≤95 °C using calcium-based agents, producing distinct gypsum and zinc sulfate particles separable via granulometric sizing (Choi, 2014). Limestone ($CaCO_3$) can also be used to precipitate zinc, forming zinc carbonate ($ZnCO_3$) at pH 4.5–6.5 and elevated temperatures (~90°C). However, limestone reacts more slowly than lime, so excess reagent is often required, and unreacted material is typically recycled. This method is less common industrially due to kinetic limitations, but may be chosen where carbonate byproducts are desired or where lime is not readily available (Gupta & T. K. Mukherjee, 1990). In summary, the selection of a precipitation agent for zinc sulfate solutions depends on the specific impurities present, desired selectivity, operational costs, and downstream processing requirements. Each method offers distinct advantages and trade-offs, and process optimization is essential to maximize zinc recovery and solution purity. If a low-cost agent can be effectively utilized for zinc precipitation while improving economic efficiency, its continued use and potential replacement of conventional methods could become viable.

## 4. Conclusions

In conclusion, this study systematically investigated the mechanisms and optimization of zinc precipitation from sulfate solutions using magnesium-containing ores, demonstrating that the dominant reaction pathway leads to the formation of zinc hydroxysulfate ($Zn_5(OH)_6(SO_4)_2$) under moderate pH conditions, as evidenced by the consistent final pH of 6.5 across all experiments. The research identified 80 °C as the optimal temperature for maximizing zinc recovery and ensuring effective magnesium participation, while an ore dosage of 100 g/L provided peak zinc recovery with minimal marginal gains beyond this point. Time-dependent analysis revealed that 150 minutes represents the practical equilibrium for zinc precipitation at 80 °C, achieving 73.4 % recovery before diminishing returns set in. Notably, under these optimized conditions (80 °C, 100 g/L ore dosage, 150 minutes), magnesium content decreased significantly from 7.0 to 5.1 g (a 27.1 % reduction), highlighting the synergistic effect of temperature and ore dosage in enhancing magnesium removal efficiency and minimizing residual content. These findings collectively established that controlled parameters, pH 6.5, 80 °C reaction temperature, 150 minutes, and 100 g/L ore dosage work in concert to optimize zinc recovery while reducing reagent consumption and energy costs, providing valuable insights for industrial-scale hydrometallurgical applications.

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