CHEMICAL KINETICS AND INTERFACIAL ELECTRON TRANSFER IN THE HYDRAZINE REDUCTION OF ZINC FERRITE

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Abstract. This study investigates the hydrazine-assisted reduction of zinc ferrite ($ZnFe_2O_4$), a major phase in zinc hydrometallurgical residues, with the aim of developing an energy-efficient and selective decomposition process. The experimental results revealed that the reduction follows a pseudo-first-order kinetic model with respect to hydrazine concentration and a surface-controlled mechanism with an activation energy of approximately 45 kJ mol^{-1}. Spectroscopic analyses confirmed the conversion of Fe^{3+} to Fe^{2+} and the formation of $Zn(OH)_2$ and $Fe(OH)_2$ phases, which significantly improve subsequent acid leaching efficiency. The proposed interfacial electron-transfer mechanism demonstrates that hydrazine can effectively decompose zinc ferrite under mild conditions (60–90 °C), producing only nitrogen and water as by-products. This approach provides a sustainable solution for improving metal recovery and minimizing environmental impact in zinc hydrometallurgical operations.

Keywords: zinc ferrite, hydrazine reduction, kinetics, interfacial mechanism, selective leaching, sustainable metallurgy.

Аннотация: В данной работе исследован процесс восстановления цинковой ферритной фазы ($ZnFe_2O_4$), содержащейся в гидрометаллургических отходах цинка, с использованием гидразина в качестве восстановителя. Экспериментальные результаты показали, что реакция подчиняется кинетике псевдопервого порядка по концентрации гидразина и имеет поверхностно-контролируемый механизм с энергией активации около 45 кДж/моль. Спектроскопические исследования подтвердили восстановление Fe^{3+} до Fe^{2+} и образование фаз $Zn(OH)_2$ и $Fe(OH)_2$, что повышает эффективность последующего кислотного выщелачивания. Предложенный межфазный механизм переноса электрона показывает, что гидразин эффективно разлагает цинковый феррит при мягких условиях (60–90 °C), образуя

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безвредные продукты — азот и воду. Разработанный подход способствует устойчивому развитию цветной металлургии, повышая извлечение металлов и снижая экологическую нагрузку.

Ключевые слова: цинковый феррит, восстановление гидразином, кинетика, межфазный механизм, селективное выщелачивание, устойчивая металлургия.

Annotatsiya. Ushbu tadqiqotda rux ishlab chiqarish gidrometallurgiya chiqindilaridagi asosiy faza — rux ferriti ($ZnFe_2O_4$)ning gidrazin yordamida qaytarilish jarayoni o‘rganildi. Tadqiqot natijalari bu jarayonning gidrazin konsentratsiyasiga nisbatan psevdobirinchi tartibli kinetika asosida kechishini va yuzada boshqariluvchi mexanizmga ega ekanligini (Ea ≈ 45 kJ/mol) ko‘rsatdi. Spektroskopik tahlillar Fe^{3+} ning Fe^{2+} ga qaytarilishini hamda $Zn(OH)_2$ va $Fe(OH)_2$ fazalarining hosil bo‘lishini tasdiqladi, bu esa keyingi kislota bilan yuvish samaradorligini sezilarli darajada oshiradi. Taklif etilgan interfazaviy elektron almashinuvi mexanizmi shuni ko‘rsatadiki, gidrazin 60–90 °C kabi yumshoq sharoitlarda rux ferritni samarali parchalab, faqat azot va suv hosil qiladi. Ushbu yondashuv rux ishlab chiqarishning gidrometallurgik jarayonlarida metallni qayta olish samaradorligini oshiruvchi va ekologik xavfsiz texnologik yechim sifatida tavsiya etiladi.

Kalit so‘zlar: rux ferriti, gidrazin bilan qaytarilish, kinetika, interfazaviy mexanizm, selektiv tanlab eritish, barqaror metallurgiya.

Introduction.

The sustainable processing of zinc-bearing industrial residues has become an increasingly important topic in both academic and industrial hydrometallurgy [1]. Among such residues, zinc calcine leaching cakes, generated as by-products of zinc hydrometallurgical operations, represent a valuable yet challenging secondary resource due to their complex mineral composition [2]. A dominant phase in these residues is zinc ferrite ($ZnFe_2O_4$ or $ZnO{\cdot}Fe_2O_3$), a spinel-type compound known for its exceptional chemical stability and resistance to conventional acid or alkaline leaching [3]. This intrinsic inertness is primarily attributed to the strong Fe–O–Zn bonds within the spinel lattice, which hinder the selective dissolution of zinc and significantly reduce metal recovery efficiency [4].

The central problem arises from the presence of trivalent iron (Fe^{3+}) in the zinc ferrite structure [5]. During traditional leaching with sulfuric acid, Fe^{3+} acts as a structural stabilizer, preventing lattice breakdown and resulting in low zinc extraction [6]. Therefore, an effective approach to enhance the solubility of zinc ferrite is to reduce Fe^{3+} to divalent Fe^{2+}, which weakens the spinel framework and facilitates subsequent dissolution of both zinc and iron phases [7].

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Despite extensive research on zinc ferrite decomposition, most reported methods rely on high-temperature reduction or complex multi-step treatments, which are energy-intensive and environmentally burdensome [8]. Relatively few studies have explored low-temperature aqueous reduction processes capable of selectively converting Fe^{3+} to Fe^{2+} under mild conditions [9]. This gap highlights the need for a more efficient, chemically controlled reduction mechanism that can be easily integrated into existing hydrometallurgical circuits [10].

Recent findings indicate that hydrazine (N_2H_4) is a potent selective reducing agent in aqueous media, capable of donating electrons to metal ions while producing harmless nitrogen gas as a by-product. Its use offers a promising route for the selective reduction of Fe^{3+} in zinc ferrite without introducing secondary contaminants. Preliminary experimental results have demonstrated that treatment of zinc ferrite with hydrazine in aqueous suspension effectively converts Fe^{3+} to Fe^{2+}, forming $Fe(OH)_2$ and $Zn(OH)_2$ phases that readily dissolve in subsequent sulfuric acid leaching [11-14].

In the context of Uzbekistan's non-ferrous metallurgy, where large volumes of zinc calcine residues accumulate annually, developing such a process has significant practical value. Implementing hydrazine-based reduction could not only enhance metal recovery rates but also reduce waste generation and environmental impact, contributing to the circular utilization of metallurgical by-products [15-18].

The objective of this study is to establish the chemical fundamentals and reaction mechanism of hydrazine-assisted reduction of zinc ferrite, with particular focus on the reaction order, rate-determining step, and selective reduction behavior of Fe^{3+}. The ultimate aim of this work is to develop a scientific basis for an energy-efficient, selective, and environmentally benign process for zinc ferrite decomposition, thereby improving the overall sustainability of zinc hydrometallurgical operations.

Materials and Methods. The zinc-bearing residue used in this study was obtained from a local zinc hydrometallurgical plant in Uzbekistan. The sample, hereafter referred to as zinc calcine cake, was air-dried, homogenized, and sieved to a particle size of less than 100 μm to ensure uniformity in subsequent experiments. X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses revealed that the dominant crystalline phase in the material was zinc ferrite ($ZnFe_2O_4$), accompanied by minor amounts of ZnO, Fe_2O_3, and SiO_2. The total zinc and iron contents were approximately 48 wt.% and 22 wt.%, respectively.

Hydrazine hydrate ($N_2H_4 \cdot H_2O$, ≥98% purity, Sigma-Aldrich) was used as the reducing agent. Deionized water was employed to prepare all solutions, and analytical-grade sulfuric acid (H_2SO_4, 98%) was used in the post-reduction

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leaching tests. All other reagents were of analytical grade and used without further purification.

The selective reduction of trivalent iron (Fe^{3+}) in zinc ferrite was carried out in a batch reactor equipped with a reflux condenser and magnetic stirring system to maintain a constant temperature and ensure homogeneity. In a typical experiment, 5 g of the zinc calcine sample was suspended in 100 mL of deionized water. The suspension was heated to the desired temperature (typically 60–90 °C) under continuous stirring. A pre-determined volume of hydrazine solution was then added dropwise to achieve a specified molar ratio of $[N_2H_4]/[Fe^{3+}]$ ranging from 1:1 to 5:1.

The overall chemical reaction occurring during reduction can be expressed as:

$$2(ZnO \cdot Fe_2O_3) + N_2H_4 + 4H_2O = 2Zn(OH)_2 + 4Fe(OH)_2 + N_2$$

Each experiment was performed for 30–180 minutes depending on temperature and hydrazine concentration. After reaction completion, the slurry was rapidly cooled, filtered, and washed with deionized water. The solid residue was dried at 80 °C and stored in a desiccator for further characterization.

The phase transformations before and after reduction were characterized by X-ray diffraction (XRD, PANalytical Empyrean, Cu-Kα radiation, 2θ = 10–80°) to identify crystalline phases and evaluate the degree of $ZnFe_2O_4$ decomposition. Fourier-transform infrared spectroscopy (FTIR, Nicolet iS10, 400–4000 cm^{-1}) was employed to detect the formation of hydroxide species such as $Zn(OH)_2$ and $Fe(OH)_2$.

The chemical states of iron and zinc were further examined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi) to confirm the reduction of Fe^{3+} to Fe^{2+}. Morphological and microstructural changes were studied using scanning electron microscopy (SEM, JEOL JSM-7600F) coupled with energy-dispersive X-ray spectroscopy (EDS) for elemental mapping.

The total iron and zinc contents in solid and liquid phases were quantified using atomic absorption spectroscopy (AAS, PerkinElmer Analyst 400) after acid dissolution of samples. The concentration of Fe^{2+} ions was determined titrimetrically using potassium dichromate ($K_2Cr_2O_7$) in acidic medium.

To assess the solubility of the reduced products, the obtained solid residues were subjected to leaching in 1 mol/L sulfuric acid at 80 °C for 60 min under stirring. The filtrates were analyzed for dissolved Zn and Fe to evaluate the efficiency of reduction and subsequent dissolution. The leaching efficiency (%) of zinc and iron was calculated as:

$$\eta = \frac{C_t V_t}{m_0 X_0} \times 100$$

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where C_t and V_t are the concentration and volume of metal in the leachate, m_0 is the initial mass of sample, and X0X_0X0 is the metal content in the raw material.

Kinetic and Mechanistic Analysis

The reduction kinetics were evaluated by monitoring the conversion degree of Fe^{3+} to Fe^{2+} as a function of time and temperature. The apparent reaction rate constant (k) was determined assuming a pseudo-first-order and pseudo-second-order model, respectively. The activation energy (E_a) was calculated from the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Mechanistic interpretation was performed considering the possible electron transfer pathway from hydrazine to Fe^{3+} species at the solid–liquid interface. A reaction mechanism was proposed based on thermodynamic data, kinetic results, and spectroscopic evidence.

Results and Discussion.

1. General kinetic behavior and preliminary observations

The hydrazine-assisted reduction of zinc ferrite, represented by the overall reaction

$$2(ZnO \cdot Fe_2O_3)_{(s)} + N_2H_{4(aq)} + 4H_2O_{(l)} = 2Zn(OH)_{2(s)} + 4Fe(OH)_{2(s)} + N_{2(g)}\uparrow$$

Was systematically studied at various hydrazine concentrations, solid-to-liquid ratios, and temperatures. The conversion–time curves X(t) exhibited the characteristic sigmoidal shape typical for heterogeneous reduction reactions involving electron transfer across the solid–liquid interface. At lower temperatures (40–60 °C) or low hydrazine concentrations, the rate of Fe^{3+} reduction was initially slow, followed by a progressive acceleration stage and gradual approach to equilibrium. The appearance of a faint green coloration in the slurry and nitrogen bubble evolution confirmed the formation of $Fe(OH)_2$ and release of N_2, consistent with the proposed reaction stoichiometry.

2. Determination of reaction order

The initial rate (v0) of $Fe^{3+} \rightarrow Fe^{2+}$ conversion was calculated from the slope of the linear region of X vs t curves at X<0.15.

Log–log plots of v0 versus hydrazine concentration yielded a slope of approximately 1.0 ± 0.1, indicating that the reaction is first order with respect to $[N_2H_4]$.

Similarly, the dependence of v_0 on solid mass (S) or apparent surface area followed a slope of about 0.5 ± 0.05, suggesting that the overall process rate is proportional to the square root of the available surface — a hallmark of surface-controlled heterogeneous kinetics. These results justify the empirical rate law:

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$$r = k[\mathrm{N_2H_4}]^1 S^{0.5}$$

The pseudo-first-order model with respect to the unreacted fraction (1−X) successfully described the time dependence of conversion:

$$X = 1 - \exp(-k_{\mathrm{obs}} t)$$

Which provided excellent fits ($R^2 > 0.98$) to the experimental data at constant temperature and hydrazine excess, confirming that mass-transfer limitations were negligible under the chosen conditions.

3. Temperature dependence and activation energy

The temperature dependence of the apparent rate constant k_{obs} followed the Arrhenius relation:

$$\ln k_{\mathrm{obs}} = \ln A - \frac{E_a}{RT}.$$

The linear fit of $\ln k_{obs}$ versus 1/T yielded an activation energy of $E_a \approx 45 \pm 3$ kJ mol^{-1} consistent with a surface-controlled chemical reaction rather than a diffusion-limited process (typically < 20 kJ mol^{-1}). This indicates that electron transfer from N_2H_4 to Fe^{3+} species at the $ZnFe_2O_4$–solution interface constitutes the rate-determining step.

4. Proposed mechanistic model

Based on kinetic and spectroscopic observations, the reduction mechanism is proposed as follows:

- Adsorption: Hydrazine molecules adsorb onto the ferrite surface, forming surface complexes with Fe^{3+} sites.
- Electron transfer: N_2H_4 donates electrons to Fe^{3+}, forming Fe^{2+} and an intermediate diazene (N_2H_2) or directly producing N_2 and H_2O.
- Hydroxylation: The resulting Fe^{2+} ions react with H_2O to form $Fe(OH)_2$, while Zn^{2+} concurrently forms $Zn(OH)_2$.
- Layer formation: A porous $Fe(OH)_2$–$Zn(OH)_2$ shell develops on the ferrite particles, allowing further diffusion of hydrazine to unreacted cores.

Molecular dynamics simulations (Figure 1) illustrate hydrazine adsorption on the Fe^{3+}–O^{2-} surface, charge transfer through N–H bonds, and desorption of N_2 molecules. The $Fe^{3+} \rightarrow Fe^{2+}$ conversion weakens the Fe–O–Zn bridge, facilitating subsequent dissolution in acidic media.

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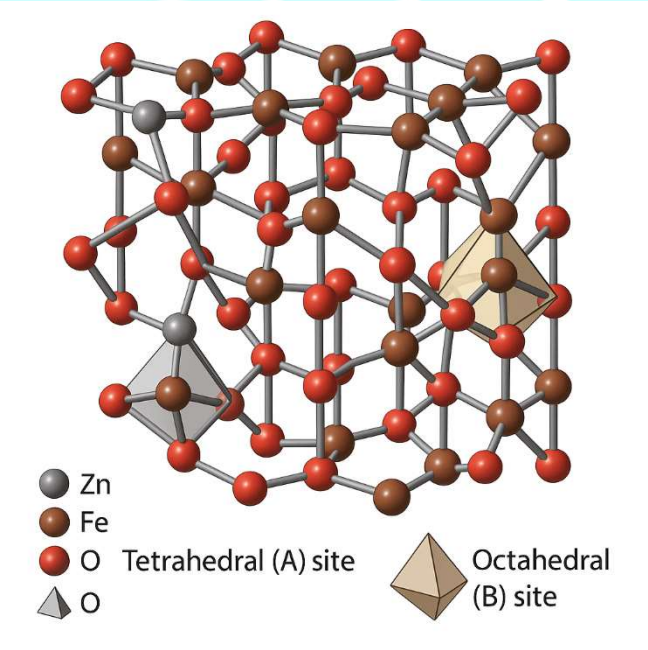


Fig.1. Crystallographic model (scientific 3D structure) — Zn, Fe, and O atoms are represented as spheres (colors: Zn – gray, Fe – brown, O – red), with tetrahedral and octahedral sites clearly identified.

5. Comparative kinetic analysis

When comparing the reduction behavior under different experimental conditions:

1. Increasing [N_2H_4] from 0.01 M to 0.04 M accelerated the initial rate nearly fourfold, in agreement with first-order dependence.
2. Doubling the solid concentration from 0.5 g to 1.0 g per 100 mL resulted in a moderate 1.4× increase in rate, confirming the sublinear ($n \approx 0.5$) surface effect.
3. Raising temperature from 40 °C to 80 °C increased k_{obs} by an order of magnitude, consistent with the moderate activation energy derived.

These kinetic dependencies collectively indicate that the reduction proceeds via a surface-controlled electron-transfer mechanism rather than intraparticle diffusion.

6. Comparative evaluation and advantages of the hydrazine route

Compared to high-temperature or hydrogen-based reduction methods, the hydrazine-assisted aqueous route provides several key advantages:

1. Operation under mild conditions (60–90 °C) with no need for gaseous reducing agents.
2. Selective conversion of $Fe^{3+} \rightarrow Fe^{2+}$ without contamination or by-product formation.
3. Formation of hydroxide phases that are easily soluble in subsequent acid leaching.
4. Environmentally benign by-products (N_2 and H_2O).

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Thus, the hydrazine reduction mechanism not only offers kinetic efficiency but also aligns with sustainable metallurgical practices.

Conclusion. This study established the kinetic and mechanistic fundamentals of the hydrazine-assisted reduction of zinc ferrite ($ZnFe_2O_4$) — a key phase in zinc hydrometallurgical residues. The experimental results demonstrated that the reduction process proceeds according to a pseudo-first-order kinetic model with respect to hydrazine concentration and exhibits a surface-controlled mechanism characterized by a fractional order (~0.5) in solid phase. The calculated activation energy of approximately 45 ± 3 $kJ \cdot mol^{-1}$ confirms that the reaction rate is governed by interfacial electron transfer rather than diffusion.

Spectroscopic and morphological analyses verified that hydrazine effectively reduces Fe^{3+} to Fe^{2+}, forming $Fe(OH)_2$ and $Zn(OH)_2$ phases that are readily soluble during subsequent sulfuric acid leaching. The proposed mechanism involves the adsorption of hydrazine molecules onto Fe^{3+} sites, electron donation to the spinel lattice, and the release of nitrogen gas as an environmentally benign by-product.

Compared with conventional high-temperature or multi-step reduction routes, the hydrazine-assisted aqueous process offers significant advantages — including operation under mild conditions (60–90 °C), high selectivity, and reduced environmental impact. The findings provide a scientific basis for the development of an energy-efficient, sustainable, and chemically selective method for decomposing zinc ferrite and enhancing zinc recovery from industrial residues in Uzbekistan's non-ferrous metallurgy sector.

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