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Mechanism, kinetics and thermodynamics of nickel, iron, and magnesium hydrochloric acid leaching from laterite ore

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The kinetics of hydrochloric acid leaching of oxidized magnesite–iron nickel ores from the Gornostaevskoye deposit (Eastern Kazakhstan) were investigated. The ore has high contents of Mg (14.25 wt.%), Fe (10.8 wt.%) and Si (24.32 wt.%), with a Ni content of 0.87 wt.%. The optimal process parameters were determined as follows: S:L = 1:4, temperature = 85–90 °C, leaching duration = 120 min, HCl concentration = 18%, and stirring rate = 400 rpm. The extraction rates of Ni, Mg and Fe were 91.03%, 97.88% and 93.04%, respectively. The pregnant leach solution contained 1.98 g L⁻¹ Ni, 35.31 g L⁻¹ Mg and 25.12 g L⁻¹ Fe. Kinetic modeling indicated that the leaching of Ni, Fe, and Mg followed a mixed-control mechanism, with activation energies of 76.07 kJ mol⁻¹ for Ni, 125.45 kJ mol⁻¹ for Fe, and 119.33 kJ mol⁻¹ for Mg, confirming that the chemical reaction was controlled. Thermodynamic analysis revealed that pimelite, nickel silicate hydrate, and antigorite are the most reactive phases under hydrochloric acid leaching, on the basis of their highly negative ΔG values. The established mineral dissolution sequence, namely, pimelite > Ni – silicate hydrate > nepouite > antigorite > lizardite > talc > wüstite > hematite, reflects the combined influence of structural accessibility and thermodynamic favorability.

Keywords Hydrochloric acid leaching (HAL), Nickel, Laterite, Kinetics, Thermodynamics, Mechanism

Recently, the industries of electric vehicles and unmanned aerial vehicles using batteries have been developing rapidly. In particular, lithium-ion batteries (LIBs) with high energy density and long service life have been widely used. Nickel-rich cathode materials (such as nickel–cobalt–manganese (NCM) and nickel–cobalt–aluminum (NCA)) have advantages in terms of service life and thermal stability¹. In addition, modern metallurgy produces a wide variety of nickel-containing alloys, including heat-resistant alloys, corrosion-resistant alloys, and shape memory alloys. In this regard, the demand for processing nickel-containing ores has been steadily increasing². According to the USGS³, the global nickel reserves are more than 350 million tons, of which laterite ores account for 54%, sulfide ores for 35%, manganese nodules on the seabed for 10%, and other for 1%. Currently, most nickel is produced from sulfide ores. The constant reduction in the global reserves of sulfide nickel ores has made the extraction of nickel and other valuable metals from laterite ores attractive.

Nickel ores localized at deep depths in Kazakhstan are characterized by a specific composition and are represented mainly by lateritic deposits. These deposits include the Gornostaevskoye deposit (East Kazakhstan region), Batamshinskoye deposit, and Bugetkolskoye and Nikeltauskoye deposits (West Kazakhstan region). Kazakhstan has sufficient reserves of nickel ores and is among the top 20 countries in terms of nickel reserves⁴. In total, 2% of the world's ore reserves are recorded in the territory of Kazakhstan, while metallurgical processing of lateritic nickel ores in the country is limited.

Industrial production of nickel from lateritic nickel ores is based on pyrometallurgical^{5,6} and hydrometallurgical processes^{7–9}.

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Pyrometallurgy is a suitable method for processing sulfide ores. However, this process is unprofitable because of its considerable energy consumption. Hydrometallurgy is an acceptable option for processing laterite ore because of its lower energy costs and the possibility of simultaneously extracting valuable metals¹⁰. Hydrometallurgical processes such as heap leaching (HL)¹¹, high-pressure acid leaching (HPAL)^{12–14}, and atmospheric acid leaching (AAL)^{15–18} can extract nickel from laterite ore^{15,19}.

Acid leaching of lateritic nickel ore is a complex process, the efficiency of which is affected by the physicochemical properties of the ore and the leaching parameters.

Atmospheric acid leaching methods include primarily sulfuric acid^{20,21}, nitric acid^{10,22,23}, and hydrochloric acid leaching²⁴. To increase the efficiency of leaching, various additives, such as oxidizers, reducing agents, and complexing agents, are used.

The disadvantages of atmospheric leaching with sulfuric acid are longer leaching times, low metal recovery and higher acid consumption²⁵. Similarly, the disadvantage of using HNO_3 as a solvent is that it dissolves iron, which in turn leads to the formation of iron nitrates, which complicate the removal of impurities and can affect the efficiency of subsequent process steps²⁶. The advantages of using HCl as a lixiviant are the easier production of metal chloride solutions containing Ni, Fe and Mg and the possibility of regenerating free hydrochloric acid from its spent solution¹⁰; therefore, hydrochloric acid was chosen as a leaching reagent²⁷ since the ore minerals are completely exposed and impurities such as iron and magnesium are easier to remove from chloride media.

The authors in Ref²⁸ studied the kinetics of laterite leaching with a NH_4Cl – HCl solution; mineral dissolution proceeded in the following order: goethite > serpentine > hematite and magnetite, which is consistent with the results obtained when the extraction of metals into solution was calculated. The activation energies for nickel, cobalt and iron are 4.01 kJ mol^{-1} , 3.43 kJ mol^{-1} and 1.87 kJ mol^{-1} , respectively, which confirms the diffusion-controlled extraction of these metals.

Santos et al.²¹ studied the leaching mechanism at a hydrochloric acid concentration of 8 M and reported that the order of mineral dissolution is as follows: goethite > lizardite > magnetite and hematite. On the basis of the linear Arrhenius equation, the authors calculated the activation energies of metal leaching to be $11.56 \text{ kJ mol}^{-1}$ for nickel, $11.26 \text{ kJ mol}^{-1}$ for cobalt, and $10.77 \text{ kJ mol}^{-1}$ for manganese. Thus, the diffusion regulation stage is internal diffusion, namely, diffusion regulation in a solid film.

Studies on the kinetics of the leaching of laterite ores with sulfuric acid²⁹ have shown that the activation energies are 53.9 kJ mol^{-1} for nickel and 59.4 kJ mol^{-1} for magnesium, which are characteristic of a chemical reaction-controlled process. The similarity of the activation energies for the leaching of nickel and magnesium from the laterite material of saprolite with sulfuric acid means that the nickel in lizardite is weakly bound in the octahedral layer, and almost all of the nickel can be leached simultaneously with magnesium but without complete destruction of the silicate structure.

The problem of involving oxidized nickel ores in metallurgical processing in Kazakhstan remains unsolved. The purpose of this study is to investigate the kinetic patterns of nickel dissolution and the main impurities (iron and magnesium) present during hydrochloric acid leaching of laterite ores in Kazakhstan, namely, the Gornostaevskoye deposit. This work involves laboratory leaching of a sample of oxidized magnesite–ferrous nickel ore with an 18% hydrochloric acid solution under optimal conditions, followed by analysis of the resulting product solution and solid residues. This technique is aimed at determining the ratio of extraction of nickel, magnesium and iron into the solution, as well as developing an effective three-stage countercurrent washing of the silica residue for maximum removal of soluble compounds and improving the environmental friendliness of the process. The obtained kinetic data will be used to identify conditions that promote the selective transition of valuable metals into solution and minimize the dissolution of gangue.

The feature of this study lies in the oxidative–hydrolytic removal of Fe^{3+} from solution using H_2O_2 , followed by controlled precipitation at pH 3.6–3.8 with the addition of MgO . This approach ensures high selectivity: Fe^{3+} is completely precipitated, while Ni^{2+} and Co^{2+} remain in solution. Nickel losses are minimized through controlled precipitation kinetics—stepwise MgO dosing, strict temperature control, and the use of the flocculant Praestol. In contrast to literature reports, where Ni recovery requires higher HCl consumption and prolonged leaching times^{30,31}, the proposed method achieves comparable or superior extraction efficiency with lower acid consumption and a significantly shorter process time of only 2 h.

Methods

Materials

The initial raw material used for the work was oxidized magnesite–iron nickel ore from the Gornostaevskoye deposit in Eastern Kazakhstan. The ore was precrushed to the recommended granulometric fraction of $-2+1 \text{ mm}$. The initial ore is a complex polymineral with a high silica content and considerable amounts of magnesium and iron, requiring the use of an adapted leaching technique for the effective extraction of target components, particularly nickel, magnesium and iron.

Nickel was leached using 37% hydrochloric acid supplied by BSK Company JSC (Russia). The molarity of concentrated HCl solution with a density of 1.18 g cm^{-3} is 11.65 M.

Hydrogen peroxide (H_2O_2 , 37%) and magnesium oxide (MgO) were purchased from Sigma-Aldrich (USA) and used without additional purification. Praestol 2500 (Ashland Inc., USA) was added to the pulp before filtration to improve the filtration properties of iron-containing hydrated sediments and to form the required structure.

All the chemicals were of analytical grade (analytical grade, $\geq 99\%$), which ensured the reproducibility and accuracy of the results. Deionized water with a specific resistance of at least $18.2 \text{ M}\Omega\text{-cm}$ at 20°C was used to prepare all the solutions and conduct the experiments.

Methods

To study the material composition, crushed samples of the material were used, from which polished sections in the form of briquettes were made. Microscopic studies were conducted using an OLYMPUS BX 51 optical microscope. The morphology and elemental composition of the samples were studied using a JEOL JSM-7600F scanning electron microscope (Japan) equipped with an Oxford INCA Energy 350 energy-dispersive analysis system. Shooting was performed at an accelerating voltage of 15 kV and a working distance of 12.0 mm in high vacuum mode (HighVac), with a magnification of 300×.

X-ray fluorescence semiquantitative analysis was performed using an Axios 1 kW X-ray fluorescence wavelength-dispersive spectrometer (PANalytical). The obtained data were processed and interpreted in SuperQ software (Omnian 37).

X-ray phase analysis was performed on a D8 Advance diffractometer (Bruker) using Cu-Kα X-ray radiation at a tube voltage of 40 kV and a current of 40 mA in the two-theta range of 3–90° at a step size of 0.02°. Diffraction patterns were processed, and interplanar distances were calculated in EVA software. Phases were interpreted using the Search/Match program and the PDF-2, rel.2020 (ICDD) database.

The content of elements in the productive solutions was determined via atomic absorption spectroscopy using a Shimadzu AA-7000 spectrometer (Japan). Measurements were performed in a flame/graphite furnace (depending on the element) in accordance with the manufacturer's guidelines. Calibration was performed using standard comparison samples.

Leaching experiments

A 200 g ore sample crushed to the recommended fraction of −2 + 1 mm was used to conduct the acid leaching experiment. This particle size was chosen as optimal in terms of uniform dissolution and ensuring good pulp filterability. Smaller fractions (<0.5 mm) were not used because of the risk of silica gel formation and deterioration of filtration.

The leaching of oxidized magnesian–iron nickel ores with sequential countercurrent three-stage washing was performed under laboratory conditions. The leaching process was performed under the following conditions: S:L = 1:1–1:4, T = 20–90 °C, HCl = 100% stoichiometry, HCl concentration of 6–21 wt.%, and V = 100–500 rpm.

The following leaching conditions are recommended as optimal for subsequent studies: a hydrochloric acid concentration of 18 wt.%, S:L = 1:4, a process temperature of 85–90 °C, and a contact time of 120 min.

Two hundred grams of ore was loaded into a laboratory beaker for leaching with 18 wt.% hydrochloric acid. Separately, 400 ml of 18 wt.% HCl solution was prepared. Distilled water was used to dilute the acid. The resulting hydrochloric acid solution was poured into the beaker with the ore. This step achieved the required ratio of S:L = 1:4. The stirrer was set to 400 rpm to ensure uniform mixing. The reaction mass was heated gradually until a temperature of 85–90 °C was reached.

After the set temperature was reached, the leaching process was continued for 120 min with stirring at 400 rpm. Upon completion of the leaching process, saturated productive solution with a volume of approximately 700 ml and Ni, Mg, and Fe concentrations of 1.98 g L^{−1}, 35.31 g L^{−1}, and 25.12 g L^{−1}, respectively, were drained. Ni (91.03%), Mg (97.88%), and Fe (93.04%) were extracted into the solution. The degree of extraction is calculated on the basis of the content of the element in the solution (g L^{−1}), the total volume of the solution and the initial content of the given element in the ore sample.

Next, three-stage washing of the resulting silica cake was performed, with decantation of the washing solution and filtration at the last stage. The washing water from the first stage was sent to prepare the leaching solution. The full use of recycled washing water in the technological cycle allows for highly environmentally friendly production. After being washed and filtered, the cake contained 38.5% moisture. The silica cake was dried at 105 °C for 2 h.

After the leaching process, the productive solution was drained and sent for further purification, and the silica cake was thoroughly washed sequentially by a countercurrent three-stage wash. The first wash was performed with clean water, and subsequent washes were performed with the wash water of the previous cycle. Wash water 1 with a Mg content of 8.3 g L^{−1} was completely used to prepare the leaching solution. Wash water 2 was used to wash 1, wash water 3 was used to wash 2, and the remainder of wash 3 was used with the addition of clean water under the conditions of S:L = 1:1 for wash 3. After being washed 3 times, the resulting solution with silica cake was filtered via a vacuum filter. The filtrate was drained, and the wet silica cake was unloaded and dried.

All leaching experiments were conducted in triplicate and the average values were used to calculate metal leaching degrees (%) and kinetic parameters.

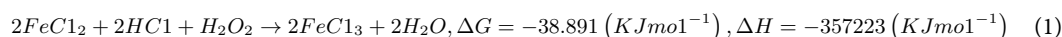
The basic flow chart of the leaching and precipitation stage is shown in Fig. 1.

Study of hydrolytic precipitation of iron from a productive solution containing nickel and magnesium

The hydrolytic precipitation process was conducted to study the possibility of the selective removal of iron(III) ions by using activating reagents.

The object of the study was a productive solution of the following composition: 1.98 g L^{−1} of Ni, 25.12 g L^{−1} of Fe, and 35.31 g L^{−1} of Mg. The iron-containing cake in wet form after filtration and dry form after dehydration is shown in Fig. 2.

To convert divalent iron (Fe²⁺) into the trivalent form (Fe³⁺), an oxidizing agent, hydrogen peroxide (H₂O₂), was used according to the following reaction:



Further precipitation of iron was accomplished by adding magnesium oxide (MgO), which ensured the hydrolysis of Fe³⁺ ions with the formation of poorly soluble iron(III) hydroxide:

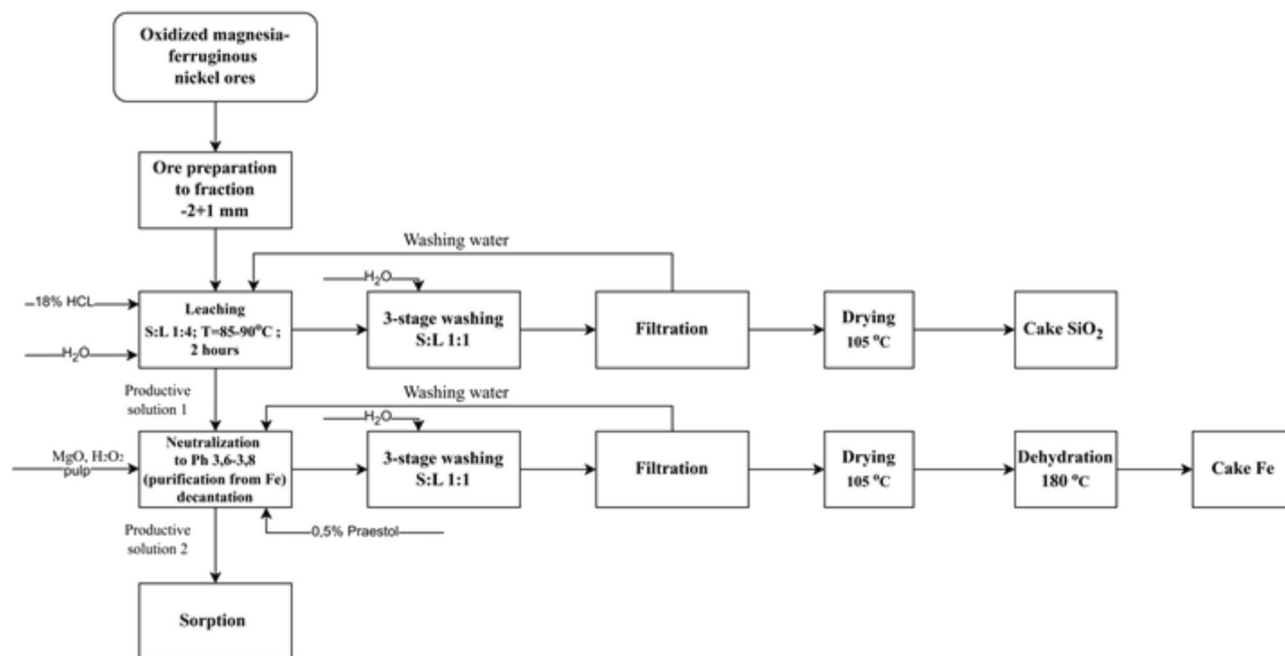
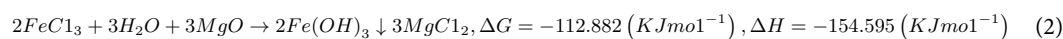


Fig. 1. Principal flow chart of the leaching process.



Fig. 2. Iron-containing cake: (a) wet and (b) dry.



MgO performs a dual function: it creates a weakly basic environment for hydrolysis and binds the resulting chlorine ions as the soluble salt MgCl_2 . The process was conducted at a temperature of 70 °C and a contact time of 20 min. MgO performs a dual function: it creates a weakly basic environment for hydrolysis and binds the resulting chlorine ions as the soluble salt MgCl_2 ^{30,31}. A two-stage iron removal process (oxidative → hydrolytic) was developed to optimize acid consumption, chloride regeneration, and nickel recovery. In the first stage, dissolved $\text{Fe}(\text{II})$ was oxidized to $\text{Fe}(\text{III})$ with H_2O_2 at 70 °C, thereby minimizing additional acid demand. In the second stage, neutralization with MgO increased the pH to 3.6–3.8, leading to complete precipitation of Fe^{3+} as $\text{Fe}(\text{OH})_3$. Notably, the neutralizing agent (MgO) does not introduce foreign ions but converts into soluble MgCl_2 , thus maintaining the chloride balance in the system and enabling efficient chloride regeneration.

The selectivity of Fe precipitation relative to Ni was confirmed: at pH 3.6–3.8, Ni^{2+} remained in solution, whereas significant nickel precipitation was observed only at pH ≈ 8–9. Nickel losses were primarily attributed to surface adsorption on freshly formed $\text{Fe}(\text{OH})_3$ and, to a lesser extent, to substitution at defect sites of amorphous Fe hydroxides formed during rapid precipitation. These losses were mitigated through gradual MgO dosing, strict temperature control, and the addition of a flocculant (Praestol), which facilitated agglomeration and improved solid–liquid separation.

Chemical composition and SEM of obtained iron-containing is presented in Appendix A.

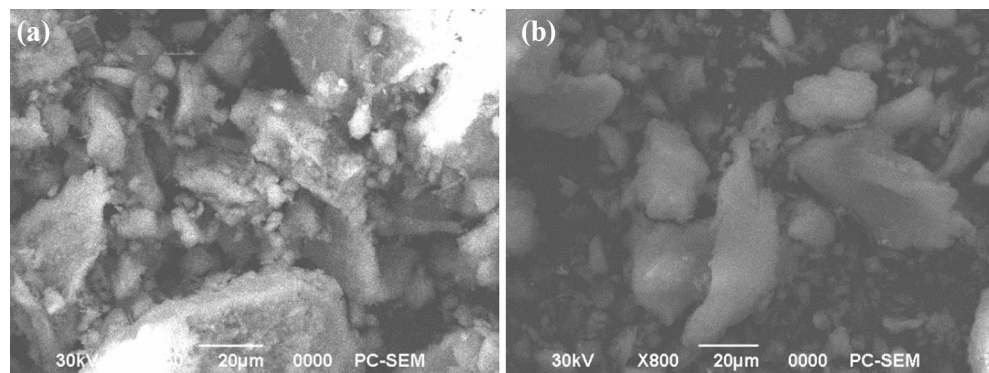


Fig. 3. SEM images of (a) original laterite ore and (b) laterite ore samples after leaching.

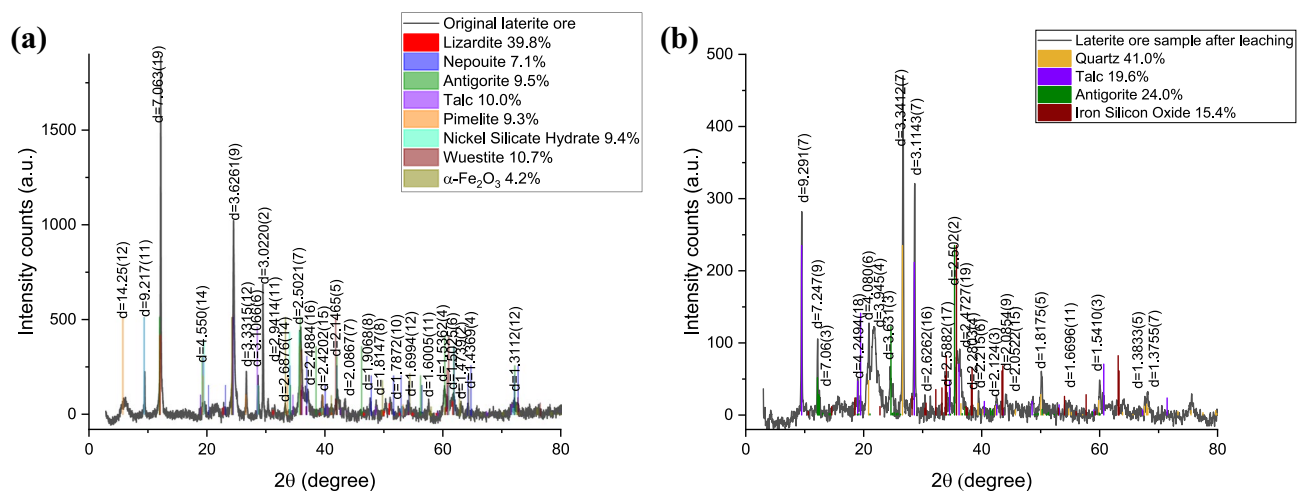


Fig. 4. X-ray diffraction patterns of (a) initial laterite ore and (b) laterite ore samples after leaching.

Thus, this study demonstrated the efficiency of the scheme for oxidative–hydrolytic removal of iron from solutions containing nickel and magnesium. The thermal probability of the reactions was confirmed by the negative values of ΔG and ΔH .

Results and discussion

Characteristics of the samples

The object of the study was oxidized magnesian–ferrous nickel ore from the Gornostaevskoye deposit, Eastern Kazakhstan. The ore has the following main components (in wt. %): 0.87% Ni, 10.8% Fe, 14.25% Mg, 24.32% Si, 0.07% Co, 1.73% Ca, 0.24% Cr, 0.17% Mn, and 47.5% O.

The ore has a high silica content, which is typical for oxidized nickel ores. A considerable proportion of magnesium and iron indicates the predominance of magnesian–ferrous minerals in the mineral matrix. The relatively low nickel content requires intensification of the leaching process to increase its extraction.

Scanning electron microscopy (SEM) was used to study the surface morphology of the powder samples. The presented micrographs (Fig. 3) show particles of different shapes and sizes, indicating the heterogeneity of the material under study. Individual particles have noticeable porosity, which may be due to natural crystalline anisotropy.

The mineralogical composition of oxidized nickel ores of the Gornostaevskoye deposit (Fig. 4) is 39.8% lizardite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, 7.1% nepouite $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$, 9.5% antigorite $\text{Mg}_{48}\text{Si}_{34}\text{O}_{85}(\text{OH})_{62}$, 10.0% talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, 9.3% pimelite $(\text{Ni,Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, 9.4% nickel silicate hydrate $(\text{Ni,Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, 10.7% wustite FeO , and 4.2% hematite $\alpha\text{-Fe}_2\text{O}_3$. Chemical composition and SEM of siliceous cake after leaching is presented in Appendix B.

Lizardite is a magnesium-containing phyllosilicate (a mineral of the serpentine group) with hydroxyl groups. Under nickel ore conditions, magnesium in the lizardite structure can be partially replaced by nickel, resulting in the formation of a continuous series of mixed components up to the nickel end member, nepouite. Nepouite is a nickel-containing mineral of the serpentine group (analog of lizardite) with a bright green color³². Antigorite is a plate phyllosilicate of the serpentine group and is characterized by a layered structure. The ideal formula contains magnesium, but a considerable portion of Mg is usually replaced by divalent iron, which is reflected by

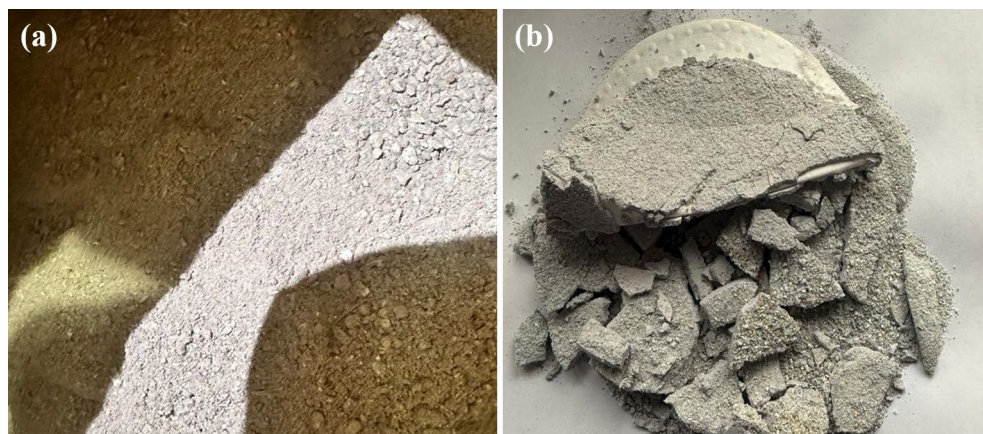


Fig. 5. (a) Original ore of fraction $-2 + 1$ mm; (b) cake after leaching, dried at $105\text{ }^{\circ}\text{C}$ (a).

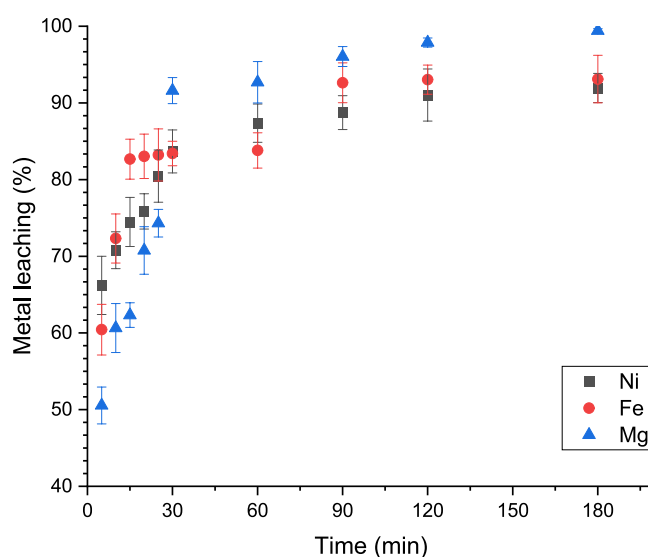


Fig. 6. Effect of time on Ni, Fe, and Mg leaching from laterite ore (S:L = 1:4, $t = 85\text{ }^{\circ}\text{C}$, $C(\text{HCl}) = 18\text{ wt.}\%$, 400 rpm).

the entry $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$. In addition, impurities of other cations are possible: in the antigorite lattice, Mg^{2+} is partially isomorphically replaced by Fe^{2+} , Mn^{2+} , Ca^{2+} and even Ni^{2+} (in the presence of nickel in the rock) and Si^{4+} by Al^{3+} or Fe^{3+} . Thus, the composition of antigorite varies within certain limits, although the basic formula remains the same as that of serpentine³³. Talc is a 2:1 layered silicate (trioctahedral phyllosilicate) with the ideal formula of hydrated magnesium silicate³⁴. Pimelite is a nickel–dynamic clay mineral (hydrous phyllosilicate) belonging to the smectite group. Its formula is similar to that of trioctahedral talc but with a dominance of Ni and the presence of water molecules in the interlayer spaces. Nickel silicate hydrates are mixtures of various Ni-containing magnesium hydrosilicates formed in the weathering zone of ultramafic rocks. The name garnierite is often used to describe these green nickel silicates³⁵. The formula $(\text{Ni,Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$ indicates a similarity to serpentine: nickel replaces magnesium in the layer structure 1:1.

After leaching of the initial ore (Fig. 5a), dissolution of the phases of lizardite, nepouite, pimelite, nickel silicate hydrate, and wustite is observed. The residue after leaching (Fig. 5b) has the following composition: 41.0% quartz, 24.0% antigorite, 19.6% talc, and 15.4% iron silicone oxide. The elemental mass balance between solution and residue is in Appendix C.

Dissolution process optimization

Effect of time

The effects of time on the leaching efficiency of nickel (Ni), iron (Fe), and magnesium (Mg) from laterite ore were investigated in the range of 0–180 min at a solid-to-liquid ratio of 1:4, a temperature of $85\text{ }^{\circ}\text{C}$, a HCl concentration of 18%, and a stirring speed of 400 rpm. The results are shown in Fig. 6. The leaching efficiencies of all three metals increased considerably within the first 60 min, after which the dissolution rates gradually leveled

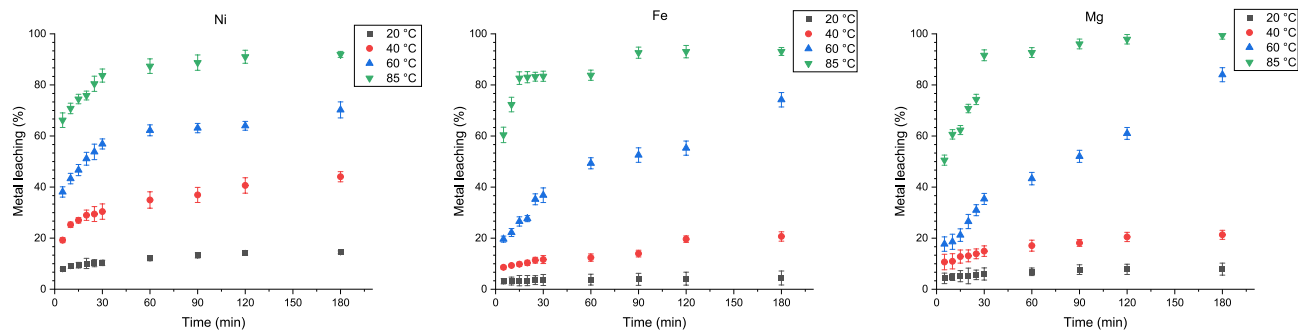


Fig. 7. Effect of temperature on Ni, Fe, and Mg leaching from laterite (S:L = 1:4, τ = 120 min, C(HCl) = 18 wt.%, 400 rpm).

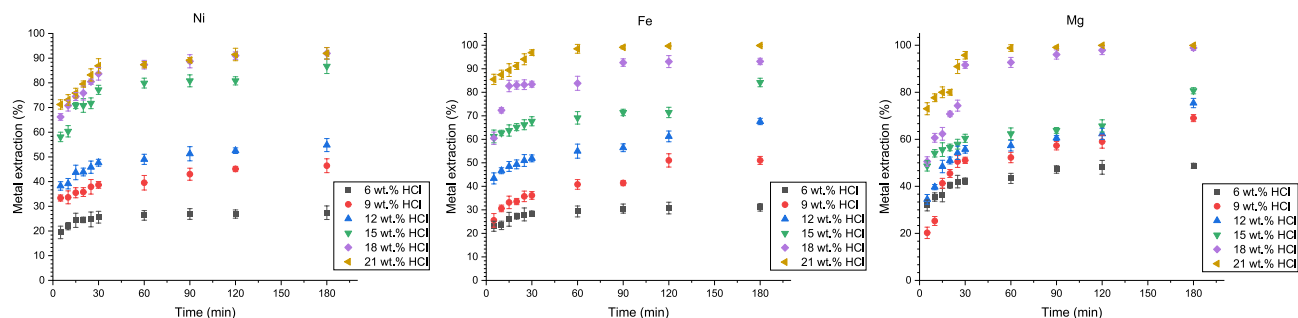


Fig. 8. Effect of acid concentration on Ni, Fe, and Mg leaching from laterite (S:L = 1:4, τ = 120 min, t = 85 °C, 400 rpm).

off. Magnesium demonstrated the highest leaching efficiency, reaching nearly 99% at 120 min. The maximum recoveries of nickel and iron were slightly lower, approximately 92% and 94%, respectively. On the basis of the stabilization of the leaching curves, the equilibrium leaching time was determined to be 120 min, which was selected as the optimum duration for subsequent experiments.

Effect of temperature

The effects of temperature on the leaching efficiency of nickel (Ni), iron (Fe), and magnesium (Mg) from laterite ore were studied at four temperatures: 20, 40, 60, and 85 °C. The experiments were conducted at a constant leaching time of 120 min, using an HCl concentration of 18 wt.%, a solid-to-liquid ratio of 1:4, and a stirring speed of 400 rpm. The results, shown in Fig. 7, indicate that temperature had a considerable influence on metal dissolution. For all three metals, an increase in temperature substantially increased the leaching efficiency.

At 85 °C, the maximum leaching efficiency was greater than 90% for Ni and Fe and nearly 99% for Mg. At lower temperatures (20–60 °C), the extraction rates were considerably lower, especially for Fe and Mg, whose extraction rates remained below 50% at 60 °C. On the basis of these results, 85 °C was selected as the optimum leaching temperature for further experiments, as it provided the highest recovery rates for all target metals.

Effect of acid concentration

The effects of hydrochloric acid concentration on the leaching of nickel (Ni), iron (Fe), and magnesium (Mg) from laterite ore were investigated over the range of 6–21 wt.% HCl. The experiments were performed at a fixed leaching time of 120 min, a temperature of 85 °C, a solid-to-liquid ratio of 1:4, and a stirring speed of 400 rpm. The results are presented in Fig. 8.

Increasing the acid concentration led to a considerable improvement in the extraction efficiency of all three metals. At lower concentrations (6–12 wt.% HCl), metal recovery was relatively low, particularly for Fe and Mg, with extraction efficiencies less than 60%. As the acid concentration increased to 15 wt.% and 18 wt.%, the metal recovery improved markedly. The maximum leaching efficiencies were achieved at 18 wt.% HCl, yielding approximately 92% for Ni, 94% for Fe, and 99% for Mg.

A further increase to 21 wt.% HCl resulted in only a slight improvement or even a plateau of recovery, indicating diminishing returns. Therefore, 18 wt.% HCl was selected as the optimum acid concentration for subsequent experiments, balancing high metal recovery and efficient acid usage.

Effect of the solid-to-liquid ratio

The effects of the solid-to-liquid ratio (S:L) on the leaching efficiency of nickel (Ni), iron (Fe), and magnesium (Mg) from laterite ore were studied at four ratios: 1:2, 1:3, 1:4, and 1:5. The experiments were performed under

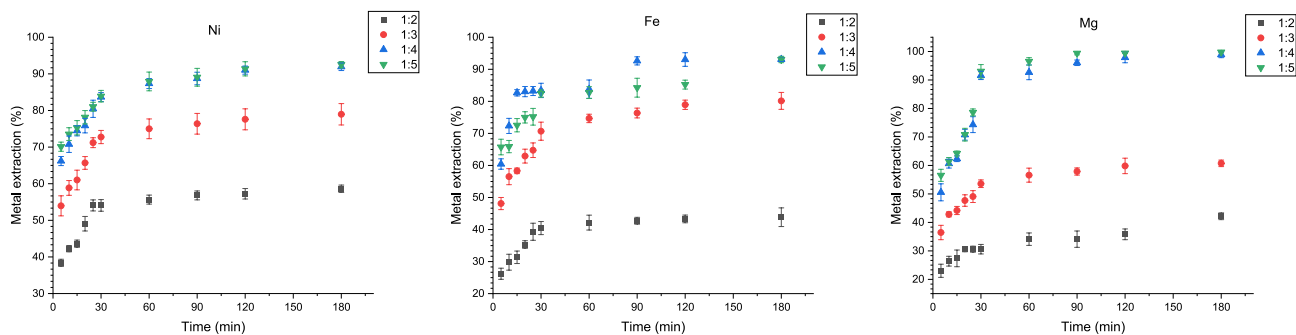


Fig. 9. Effect of the solid-to-liquid ratio on Ni, Fe, and Mg leaching from laterite ore (400 rpm, $\tau = 120$ min, $t = 85^\circ\text{C}$, 18 wt.% HCl).

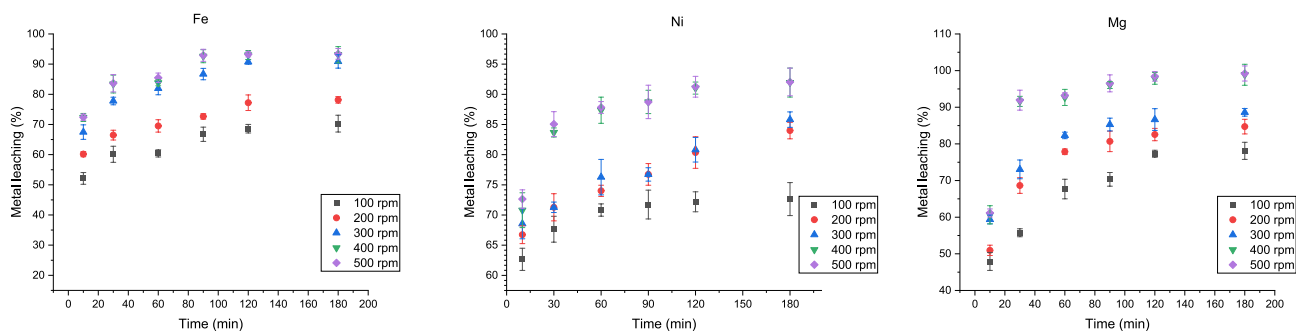


Fig. 10. Effect of stirring speed on Ni, Fe, and Mg leaching from laterite (S:L = 1:4, $\tau = 120$ min, $t = 85^\circ\text{C}$, 18 wt.% HCl).

constant conditions: a stirring speed of 400 rpm, a leaching time of 120 min, a temperature of 85°C , and a HCl concentration of 18 wt.%. The results are shown in Fig. 9.

As S:L increased from 1:2 to 1:4, a notable increase in metal extraction was observed. This effect is attributed to the increased availability of acid per unit mass of solid, which enhances the leaching kinetics. The highest recoveries for all three metals (approximately 92% for Ni, 94% for Fe, and nearly 99% for Mg) were achieved at an S:L of 1:4. Increasing the ratio further to 1:5 resulted in only marginal gains or plateaus in the extraction efficiency, while a larger volume of acid solution was needed.

On the basis of these results, a solid-to-liquid ratio of 1:4 was determined to be optimal, providing efficient leaching performance with reasonable acid consumption.

Effect of stirring speed

The effects of stirring speed on the leaching efficiency of Ni, Fe, and Mg from laterite ore were studied at five speeds: 100, 200, 300, 400, and 500 rpm. The experiments were conducted under fixed conditions: a solid-to-liquid ratio of 1:4, a temperature of 85°C , a leaching time of 120 min, and a HCl concentration of 18 wt.%. The results are shown in Fig. 10.

The leaching efficiency of the metals increased with the stirring speed, particularly between 100 and 400 rpm. The dissolution rate considerably increased up to 400 rpm, reaching a maximum Ni extraction of approximately 92%. A further increase to 500 rpm did not result in a notable improvement, indicating that mass transfer limitations were minimized at 400 rpm.

Therefore, 400 rpm was selected as the optimum stirring speed for subsequent experiments, as it ensured efficient mixing and high nickel recovery without unnecessary energy consumption.

Leaching under optimal conditions

Under the optimum leaching conditions (Fig. 11), a solid-to-liquid ratio of 1:4, a HCl concentration of 18 wt.%, a temperature of 85°C , a stirring speed of 400 rpm, and a leaching time of 120 min, the maximum extraction efficiencies for nickel, iron, and magnesium from laterite ore were achieved. Nickel leaching reached 92.3%, iron leaching reached 93.7%, and magnesium leaching reached 98.9%. These results confirm that the selected conditions are highly effective for the simultaneous recovery of all three metals.

In this work, it can be concluded that applying an HCl concentration of 18 wt.%, a solid-to-liquid ratio of 1:4, a leaching time of 120 min, a temperature of 85°C , and a stirring speed of 400 rpm ensures optimal dissolution of Ni, Fe, and Mg from laterite ore.

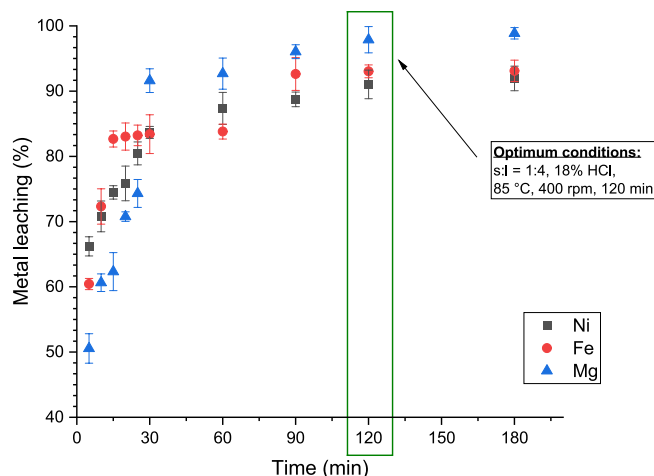


Fig. 11. Leaching of Ni, Fe, and Mg from laterite ore under optimal conditions (S:L = 1:4, 18 wt.% HCl, $t = 85^\circ\text{C}$, 400 rpm, $\tau = 120$ min).

Kinetic analysis

Shrinking core model and Arrhenius equation

The application of various kinetic models for the leaching process allows us to obtain data on the mechanism of the hydrometallurgical process, as well as to obtain equations for modeling and predicting changes in the concentrations of extractable metals from the ore, which can serve as an economically more advantageous alternative to conducting multiple experiments.

The most commonly used model for studying the kinetics of leaching is the *shrinking core model*³⁶, which can be represented as the following Eqs. (3)–(6) that describe processes with different rate-limiting stages:

$$x = kt \quad (3)$$

$$1 - (1 - x)^{1/3} = kt \quad (4)$$

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kt \quad (5)$$

$$(1 - x)^{-1/3} - 1 + \left(\frac{1}{3}\right)(1 - x) = kt \quad (6)$$

Equation (3) is applicable to a film diffusion-controlled process; Eq. (4) represents a chemical reaction-controlled process; Eq. (5) represents a product layer diffusion-controlled process; and Eq. (6) represents a mixed-controlled process (a combination of film diffusion and chemical reaction).

The fitting was performed using 10 data points corresponding to the initial to intermediate leaching stages ($t = 5$ –180 min), where kinetic control is most evident. The number of data points (n) and the selected fitting range were consistent across all models to ensure comparability. As shown in Fig. 12, Eq. (6), which describes processes occurring in a mixed regime, where the diffusion rate through a liquid film is comparable to the reaction rate, best describes the leaching of all three metals; i.e., for Ni, Fe and Mg from the ore, R^2 is equal to 0.92, 0.83, and 0.98, respectively. On the basis of Eq. (6), the apparent rate constants of the leaching process at different temperatures were calculated. On the basis of the Arrhenius equation (Eq. (7)) and the graph of $\ln K$ vs. $1/T$, $E_a = R \cdot \text{slope}$. The activation energies of the process were determined as follows:

$$k = Ae^{\frac{-E_a}{RT}} \quad (7)$$

where k is the reaction rate constant (min^{-1}), A is the exponential factor, E_a is the activation energy, R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T represents the leaching temperature (Kelvin).

The results are presented in Table 1 and Fig. 13. As shown in Table 1, the calculated activation energies were $76.06 \text{ kJ mol}^{-1}$ for nickel, $125.45 \text{ kJ mol}^{-1}$ for iron, and $119.33 \text{ kJ mol}^{-1}$ for magnesium. E_a for all three metals was $>40 \text{ kJ mol}^{-1}$, which means that the process is controlled by a chemical reaction³⁷, which also confirms the results obtained via the shrinking core model (SCM).

Application of order-based kinetic models for leaching process evaluation

Among the commonly used kinetic modeling approaches, pseudohomogeneous reaction order models, including zero-, half-, first-, and second-order models, provide a simple yet effective framework to characterize the rate behavior of solid–liquid reactions^{38–40}.

These models assume that the leaching rate depends on the concentration or fraction of the unreacted solid and are widely used because of their clear mathematical form, ease of linearization, and capacity to describe

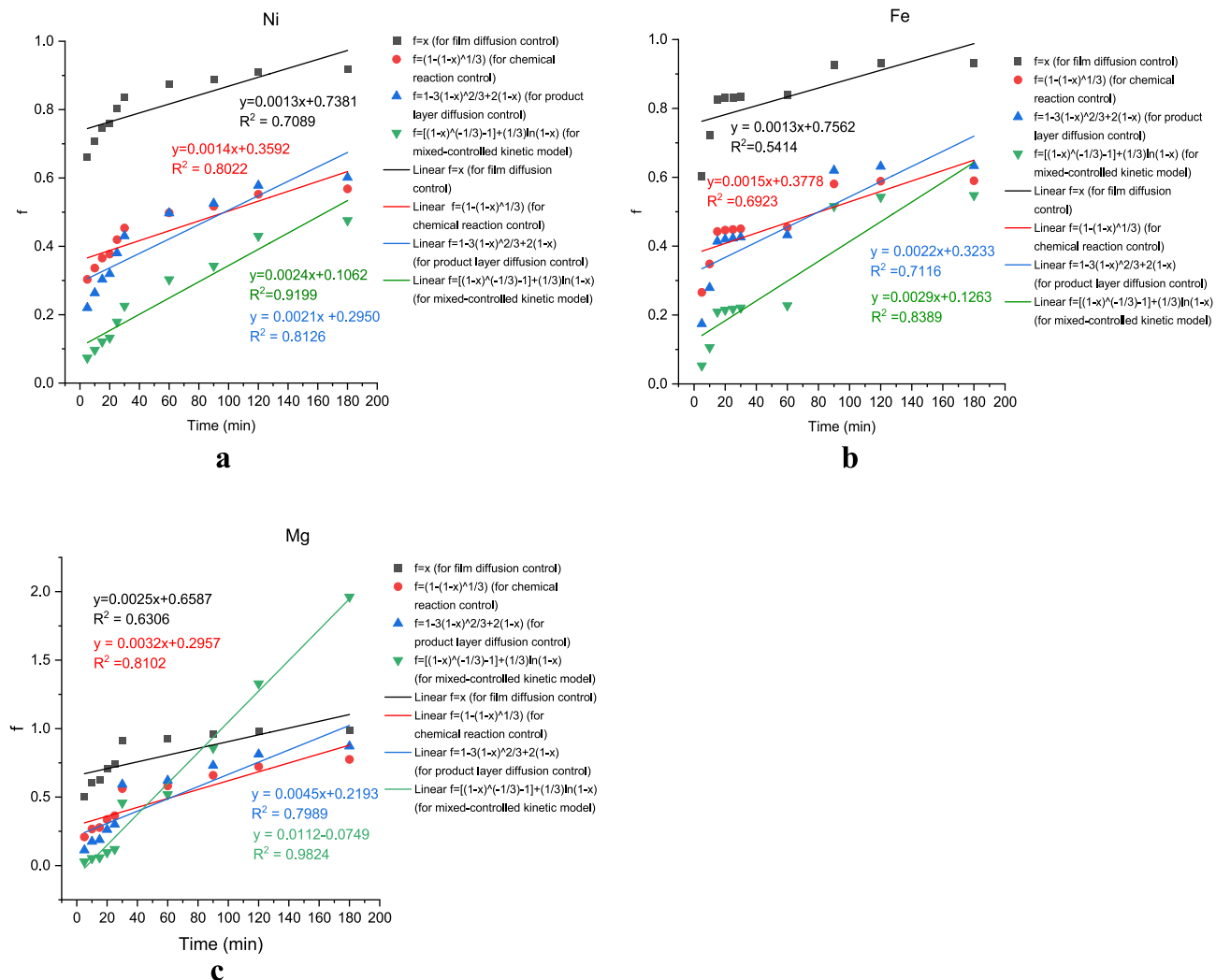


Fig. 12. Determination of the rate-controlling factor of dissolution of nickel (a), iron (b) and magnesium (c) for the data presented in Fig. 6 (using mean values of Metal leaching (%)).

t, °C	Apparent rate constants k determined from Eq. (4)		
	Ni	Fe	Mg
20	6×10^{-6}	3×10^{-7}	2×10^{-6}
40	9×10^{-5}	2×10^{-5}	2×10^{-5}
60	0.0004	0.0006	0.0011
85	0.0024	0.0029	0.0112
E _a , kJ mol ⁻¹	76.07	125.45	119.33

Table 1. Apparent rate constants k determined from Eq. (4) and activation energies determined from the lnK vs. 1/T Arrhenius plot.

basic kinetic regimes. In the present study, these models were applied to experimental leaching data for nickel (Ni), iron (Fe), and magnesium (Mg) extracted from lateritic ore under optimized hydrochloric acid conditions.

The kinetic expressions vary depending on the reaction order and can be expressed in the following forms (Eqs. (8)–(11)):

The zero-order pseudohomogeneous model assumes a constant leaching rate, independent of the concentration of unreacted material. It is typically applicable when the reagent is present in large excess or when surface reaction sites are quickly replenished.

$$X = kt \quad (8)$$

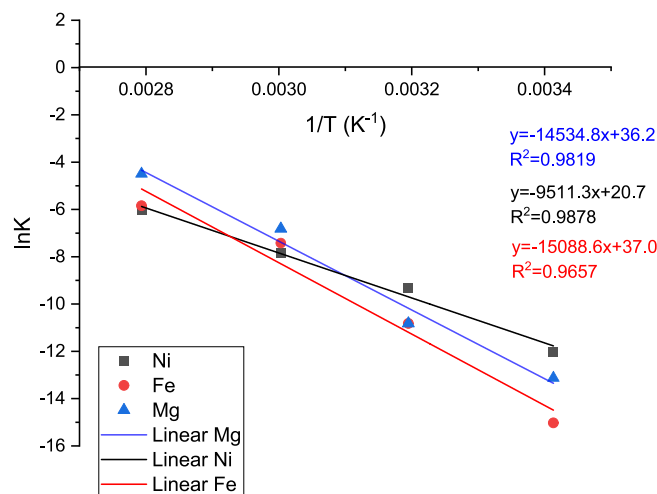


Fig. 13. Arrhenius plot for determining E_a (for data presented in Fig. 6 (using mean values of Metal leaching (%))).

Model	R^2		
	Ni	Fe	Mg
Zero-order	0.7090	0.5414	0.6306
Half-order	0.6927	0.5128	0.6080
First-order	0.8449	0.7530	0.9056
Second-order	0.9418	0.8466	0.9475

Table 2. Correlation coefficients of linear fitting data from Fig. 6 to pseudohomogeneous models.

In the half-order pseudohomogeneous model, the rate is proportional to the square root of the unreacted fraction. This type of behavior may occur in systems where the reaction proceeds via diffusion to a few surface sites.

$$(1 - X)^{1/2} = kt \quad (9)$$

The first-order pseudohomogeneous model assumes that the rate of reaction is directly proportional to the remaining unreacted material. This model is one of the most frequently used kinetic models in leaching studies and is suitable for cases where surface chemical reactions are rate controlled.

$$\ln(1 - X) = kt \quad (10)$$

In the second-order pseudohomogeneous model, the rate is assumed to be proportional to the square of the unreacted fraction. This model may be appropriate when the leaching rate increases significantly with increasing surface area.

$$\frac{1}{(1 - X)} = kt \quad (11)$$

The results of fitting the experimental data to Eqs. (8)–(11) are shown in Table 2.

As shown in Table 2, the pseudo-second-order model best describes the leaching of all three metals, with R^2 values of 0.94, 0.85 and 0.95 for Ni, Fe and Mg, respectively. A graphical representation of fitting the experimental data to the second-order pseudohomogeneous model is shown in Fig. 14.

The applicability of the pseudo-second-order model to acid leaching of multi-phase solids is justified by its underlying assumption of surface-controlled reactions involving chemical interactions between protons and reactive sites. Similar to sorption systems, the leaching of nickel, iron, and magnesium from laterite ore occurs via proton exchange mechanisms that are governed by valence forces, consistent with previous reports on heterogeneous dissolution kinetics (Ho & McKay, 1999)⁴¹.

Hixson and Crowell model

The Hixson–Crowell model⁴² describes the dissolution rate of solid particles by accounting for changes in surface area as a function of particle size reduction. It is assumed that the mass of the solid decreases uniformly

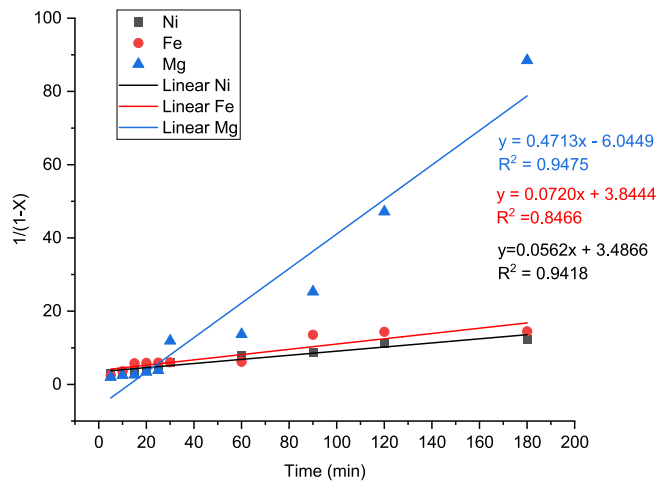


Fig. 14. Second-order kinetic model fitting to the data presented in Fig. 6 (using mean values of Metal leaching (%)).

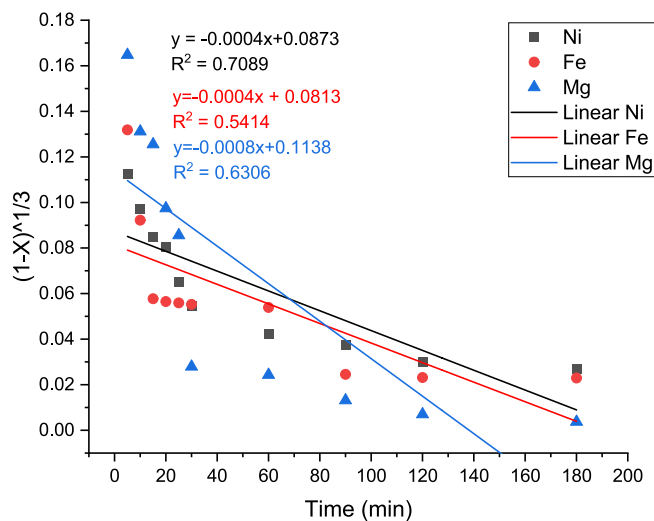


Fig. 15. Hixson and Crowell kinetic model fitting for the data presented in Fig. 6 (using mean values of Metal leaching (%)).

with time and that the surface area of the particle decreases proportionally to the cube root of its volume. The model is mathematically represented by Eq. (12):

$$C_t^{1/3} = C_0^{1/3} - Kt \quad (12)$$

where C_t (%) is the amount of dissolved element at time t , C_0 (%) is the initial amount of the element in the solid phase, and K is the Hixson–Crowell constant reflecting the rate of surface–volume-controlled dissolution.

To evaluate the applicability of this model to the leaching system, the experimental data were plotted as the cube root of the remaining solid fraction versus time (Fig. 15). A linear correlation indicates that the dissolution process is significantly influenced by the reduction in particle size and surface area during leaching. Conversely, the absence of a linear relationship implies that the surface area variation does not predominantly govern the rate of dissolution under the studied conditions. Figure 14 shows low R^2 values for all three metals, indicating that the leaching rate is not primarily controlled by particle size reduction or surface area changes. This finding suggests that the process is governed by surface chemical reactions or diffusion mechanisms rather than geometric shrinkage.

Gompertz model

The Gompertz model is an empirical sigmoidal equation commonly used to describe processes with an initial lag phase, a rapid growth stage, and a final deceleration. The linear equation of the model is expressed as follows:

$$\ln \left[-\ln \left(\frac{C_t}{C_{max}} \right) \right] = \ln \alpha + \beta \log t \quad (13)$$

where C_t represents the amount of leached element at time t ; C_{max} is the maximum dissolution; α is the undissolved proportion at time $t = 1$ and described as the location or scale parameter; and β is the leaching rate per unit time, described as the shape parameter⁴³.

A good fit to the Gompertz model indicates that the leaching process proceeded in a sigmoidal manner, suggesting a multistage mechanism involving induction, surface activation, and saturation. Conversely, poor agreement implies that the leaching reaction lacks such transitional phases and may follow simpler kinetics⁴⁴.

The fitting of the experimental leaching data to the Gompertz kinetic model is shown in Fig. 16. The linear regression yielded high R^2 values for Ni (0.8893) and Mg (0.8971), indicating a good fit and suggesting sigmoidal leaching behavior with distinct kinetic phases. In contrast, the fit for Fe was less satisfactory ($R^2 = 0.7284$), implying a more irregular or simplified dissolution mechanism. These results support the applicability of the Gompertz model for Ni and Mg, which are likely to undergo surface activation and saturation-controlled dissolution, whereas Fe exhibits a different leaching pathway.

The Gompertz model parameters α and β , which are calculated for nickel and magnesium leaching, provide valuable insight into the kinetics and mechanism of the dissolution process under acidic conditions^{45,46}.

For nickel, the values $\alpha = 2.86$ and $\beta = -2.37$ suggest a short induction period followed by a moderately rapid leaching phase. The relatively low α indicates that the leaching of nickel begins quickly, likely because of the immediate availability of reactive nickel-bearing phases and minimal surface passivation. This behavior implies that nickel dissolution is surface controlled with good accessibility to protons in the early stages.

In contrast, magnesium has $\alpha = 8.53$ and $\beta = -2.81$, indicating a pronounced induction phase despite a slightly faster rate in the active stage. The high α value reflects a delayed onset of dissolution, possibly due to surface barriers such as passivation layers, slower activation of magnesium-rich phases, or structural constraints within the ore matrix. This finding suggests that although the dissolution of magnesium eventually accelerates, it requires an initial transformation or exposure of reactive sites before it becomes kinetically significant.

In summary, despite similar values of β , the leaching behaviors differ: nickel undergoes rapid and early dissolution, whereas magnesium experiences a lag period before accelerating, highlighting the importance of induction effects in multicomponent systems.

Avrami model

The Avrami model⁴⁷ is widely applied to describe nucleation and growth processes and has been adapted for leaching kinetics to represent complex, time-dependent mechanisms. It is assumed that the leaching reaction may proceed via phase boundary advancement, nucleation, or structural transformation. The model is expressed in its linearized form as Eq. (14):

$$\ln [-\ln(1 - X)] = n \ln(t) + \ln(k) \quad (14)$$

where X is the fractional conversion (leaching extent), t is time, k is the rate constant, and n is the Avrami exponent that provides mechanistic insight (e.g., values of n close to 1 suggest linear growth, whereas values considerably different from 1 may imply nucleation, diffusion, or a combination of processes).

The linearized Avrami plots for the leaching of Ni, Fe, and Mg at 85 °C are shown in Fig. 17. The regression lines and corresponding R^2 values demonstrate an excellent fit for all three metals, with $R^2 = 0.9789$ for Ni, $R^2 = 0.8866$ for Fe, and $R^2 = 0.9462$ for Mg.

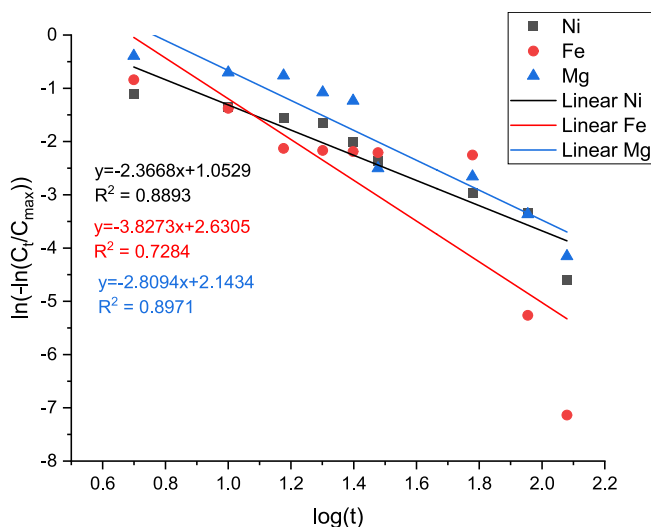


Fig. 16. Gompertz kinetic model fitting for the data presented in Fig. 6 (using mean values of Metal leaching (%)).

The calculated Avrami exponents (n) were 0.25 for Ni, 0.27 for Fe, and 0.56 for Mg. These relatively low n values suggest that the leaching mechanism is likely not dominated by progressive nucleation or uniform phase growth^{48,49}. Instead, the values imply irregular surface-controlled dissolution, possibly influenced by structural heterogeneity, surface passivation, or variable reaction sites within the ore particles. The stronger linearity for Ni and Mg also supports the applicability of Avrami kinetics to systems with a complex but consistent reaction front, whereas the more scattered data for Fe may reflect a less uniform mechanism.

Elovich model

The Elovich model⁵⁰ is frequently applied to describe heterogeneous chemisorption processes and systems with variable activation energies of surface reactions. It is assumed that the rate of reaction decreases exponentially with increasing conversion because of surface site saturation or energetic heterogeneity. The linearized Elovich equation is expressed as Eq. (15):

$$X = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (15)$$

where X represents the leached fraction at time t , α represents the initial leaching rate (when $t \rightarrow 0$), and β is related to the desorption or activation energy and describes the rate at which the surface becomes less reactive.

The Elovich model fitting for nickel, iron, and magnesium leaching at 85 °C using the linear form X versus $\ln(t)$ is shown in Fig. 18. The results show excellent linear correlation for Ni ($R^2 = 0.9829$) and Mg ($R^2 = 0.9059$), whereas Fe has a moderately good fit ($R^2 = 0.8404$). These correlations support the applicability of the Elovich model, especially for Ni and Mg.

The values of α and β obtained from the plots are as follows (Table 3):

The low α values for Ni and Fe indicate a slow initial leaching rate, possibly because of the need for surface activation or penetration of the leaching agent through a passive layer. In contrast, the higher α value for Mg suggests faster initial dissolution, which may be attributed to better exposure or higher reactivity of magnesium-bearing phases^{51,52}.

With respect to β , the higher values for Ni and Fe imply a greater decrease in the reaction rate over time, which is consistent with surface deactivation or limited reactive sites. The lower β for Mg indicates more sustained leaching activity, potentially because of higher accessibility and lower surface heterogeneity.

Thermodynamic analysis

Thermodynamic calculations allow prediction of the energetic feasibility and stability of phases involved in leaching processes, as well as determination of the optimal conditions for the selective extraction of target components from multicomponent ores. In this study, changes in the standard Gibbs energy (ΔG) and enthalpy (ΔH) were calculated for the leaching reactions of various silicate and oxide minerals typical of nickel-containing ores using the HSC Chemistry 10.0 program.

The lowest values of ΔG and ΔH (Table 4), indicating the highest thermodynamic favorability, were obtained for antigorite ($\text{Mg}_{48}\text{Si}_{34}\text{O}_{85}(\text{OH})_{62}$), for which ΔG was $-3887.07 \text{ kJ mol}^{-1}$ and ΔH was $-4642.55 \text{ kJ mol}^{-1}$. Nickel silicates also showed high solubility: pimelite ($\text{Ni}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) with $\Delta G = -3302.6 \text{ kJ mol}^{-1}$ and $\Delta H = -3321.5 \text{ kJ mol}^{-1}$; and nickel silicate hydrate ($\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) with $\Delta G = -757.6 \text{ kJ mol}^{-1}$ and $\Delta H = -749.5 \text{ kJ mol}^{-1}$. The nepouite form of nickel silicate ($\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$) also has considerable negative thermodynamic characteristics: $\Delta G = -720.5 \text{ kJ mol}^{-1}$ and $\Delta H = -688.7 \text{ kJ mol}^{-1}$. Moreover, lizardite, a magnesium-containing phyllosilicate widespread in nickel ores, tended to dissolve less readily ($\Delta G = -250.7 \text{ kJ}$

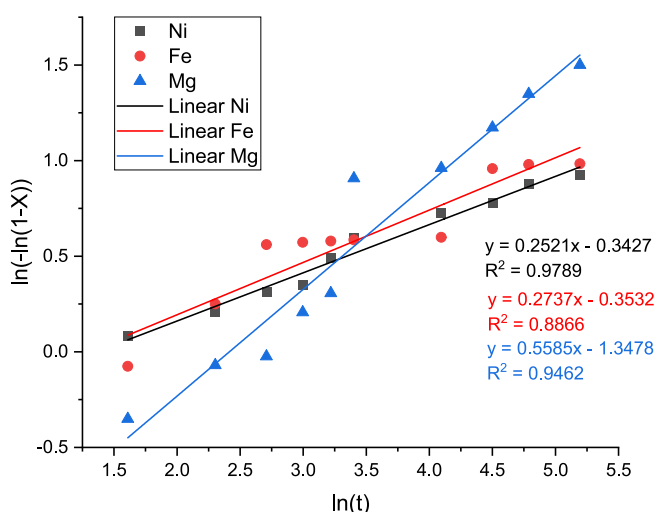


Fig. 17. Avrami kinetic model fitting for the data presented in Fig. 6 (using mean values of Metal leaching (%)).

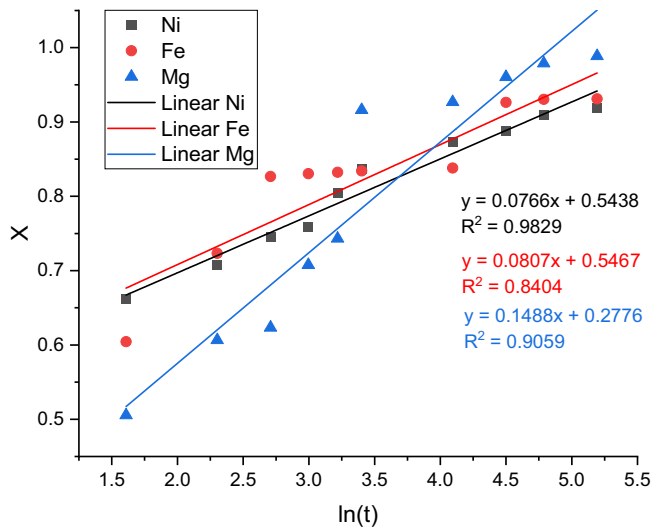


Fig. 18. Elovich kinetic model fitting for the data presented in Fig. 6 (using mean values of Metal leaching (%)).

Metal	α	β
Ni	0.0882	13.05
Fe	0.0935	12.39
Mg	0.2543	6.72

Table 3. α and β values calculated from Elovich model fitting.

Probable reaction sequence	Reaction	ΔG , kJ mol ⁻¹	ΔH , kJ mol ⁻¹
1	$Mg_{48}Si_{34}O_{85}(OH)_{62}(\text{antigorite}) + 96HCl = 48MgCl_2 + 34SiO_2 + 79H_2O$	-3887.1	-4642.6
2	$Ni_4Si_6O_{15}(OH)_2 \cdot 6H_2O(\text{pimelite}) + 8HCl = 4NiCl_2 + 6SiO_2 + 9H_2O$	-3302.6	-3321.5
3	$Ni_3Si_2O_5(OH)_4 \cdot 2H_2O(\text{nickel silicate hydrate}) + 6HCl = 3NiCl_2 + 2SiO_2 + 6H_2O$	-757.6	-749.5
4	$Ni_3Si_2O_5(OH)_4(\text{nepouite}) + 6HCl = 3NiCl_2 + 2SiO_2 + 5H_2O$	-720.5	-688.7
5	$Mg_3Si_2O_5(OH)_4(\text{lizardite}) + 6HCl = 2SiO_2 + 3MgCl_2 + 5H_2O$	-250.7	-296.6
6	$Mg_3Si_4O_{10}(OH)_2(\text{talc}) + 6HCl = 3MgCl_2 + 4SiO_2 + 4H_2O$	-216.1	-279.9
7	$FeO(\text{wüstite}) + 2HCl = FeCl_2 + H_2O$	-44.3	-15.6
8	$Fe_2O_3(\text{hematite}) + 6HCl = 2FeCl_3 + 3H_2O$	-15.5	-116.8

Table 4. Reactions used for thermodynamic calculations and their parameters (ΔG , ΔH).

mol⁻¹; $\Delta H = -296.5$ kJ mol⁻¹), as did its amorphous analog talc $MgSi_4O_{10}(OH)_2$ ($\Delta G = -216.1$ kJ mol⁻¹; $\Delta H = -279.9$ kJ mol⁻¹). Iron oxides were the least favorable for leaching: for FeO (wüstite) and Fe₂O₃ (gematite), the ΔG values were -44.3 kJ mol⁻¹ and -15.5 kJ mol⁻¹, respectively.

To assess the stable phases of the components involved in the coprocessing of magnesium-containing and iron–nickel ores, diagrams of the potential–acid stability (Eh–pH) of the Ni–Mg–Fe–Cl system (Fig. 19) were constructed at a temperature of 85 °C, a pressure of 1 bar and the following component molalities: Fe – 0.448 m, Ni – 0.0337 m, Mg – 1.44 m, and Cl – 5.36 m. The diagrams cover the pH range of 0 to 14 and the Eh potentials from -2 to +2 V, including the water stability boundaries indicated by the dotted lines (H₂/H⁺ and O₂/H₂O).

In the nickel system (Fig. 19a) in a reducing environment (Eh < -0.4 V), the stable phase is the intermetallic compound NiH_{0.68}, covering a wide pH range of 0–14. With an increase in potential from -1.2 to -0.5 V and a pH of 4–14, a region of stability of metallic nickel (Ni⁰) is formed, which is replaced with further oxidation at pH 8.8–14 by the Ni(OH)₂ phases and, at high Eh values (> 1.0 V), by NiO·OH and Ni₂O(OH)(⁺³). In a weakly basic and moderately oxidizing environment, the Fe₂NiO₄ spinel is stable, indicating the possibility of the formation of mixed oxide phases.

For magnesium (Fig. 19b) under reducing conditions (Eh < -1.2 V), the stable phase is the hydride MgH₂. When a neutral and alkaline environment (pH 7–13) with Eh < 0.7 V is reached, the stable form becomes Mg(OH)₂, and at high potentials, MgO₂. In acidic solutions (pH 1–6.8), the MgCl⁺ complex is formed, indicating that magnesium can form soluble chloride compounds in the presence of Cl⁻. At pH values from 0 to 6.8, Mg⁺²

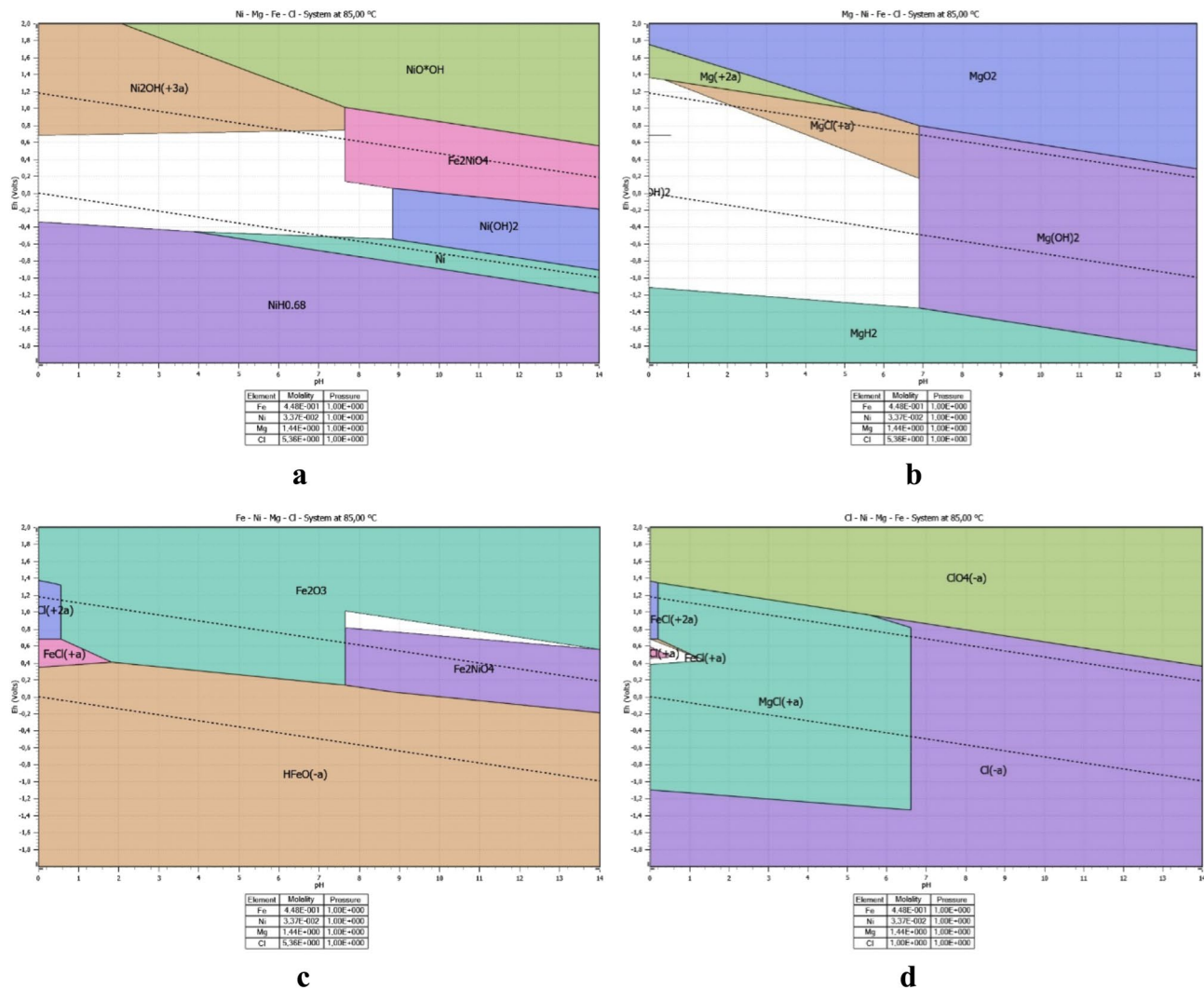


Fig. 19. Eh-pH diagrams for the system Ni-Mg-Fe-Cl ($t = 85\text{ }^{\circ}\text{C}$, $p = 1\text{ bar}$, molality of components: Fe – 0,448 m, Ni – 0,0337 m, Mg – 1,44 m, and Cl – 5,36 m): (a) for Ni compounds; (b) for Mg compounds; (c) for Fe compounds; and (d) for Cl compounds.

and MgCl^+ are in equilibrium with MgH_2 . Above pH 7, only magnesium hydroxide exists in solution as the dominant form of magnesium, whereas at lower pH values close to 7 or less than 5, free magnesium ions and the MgCl^+ complex are present.

The iron diagram (Fig. 19c) reflects the stability of the Fe_2O_3 oxide phase at high potentials ($E_h > 1.0\text{ V}$) and at $\text{pH} > 4$. In the range of E_h of 0.6–1.0 V and $\text{pH} < 7.6$, the stability of the Fe_2NiO_4 spinel is observed, similar to the nickel diagram. With decreasing potential ($E_h < 0\text{ V}$), the soluble form of HFeO^- becomes stable. In an acidic medium ($\text{pH} < 4$) and oxidizing conditions, complex ions FeCl^+ and Cl^{2+} are formed, which are characteristic of soluble iron(II) and iron(III).

Analysis of the chlorine diagram (Fig. 19d) reveals that at $E_h > 1.4\text{ V}$, the stable form is perchlorate ClO_4^- , whereas at low potentials, Cl^- ions dominate. In an acidic and weakly oxidizing environment ($\text{pH} 1\text{--}6$, $E_h 0\text{--}1\text{ V}$), complex ions FeCl^+ and MgCl^+ are observed, as well as a slight presence of Cl^+ , which indicates the active participation of Cl^- in complex formation.

Thus, the constructed diagrams allow us to identify the ranges of thermodynamic stability of individual and mixed phases under conditions close to technological ones. Of greatest interest are the regions with stable deposits of $\text{Ni}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ and Fe_2NiO_4 at $\text{pH} 8\text{--}11$ and $E_h 0.3\text{--}0.8\text{ V}$, which can be used for targeted precipitation and the selective isolation of components during the hydrometallurgical processing of multicomponent solutions.

Leaching mechanism

Understanding the leaching mechanism is key for developing efficient and sustainable hydrometallurgical technologies. Determining the rate-limiting stage allows not only accurate interpretation of experimental data but also optimization of the process parameters to improve the recovery of target metals. In the case of laterite

ores containing nickel (Ni), iron (Fe) and magnesium (Mg), the dissolution process is complex because of the multicomponent composition and differences in the crystal chemistry of the phases.

The kinetic analysis was performed via an integrated approach using various models, namely, the shrinking core model (SCM), pseudohomogeneous models of different orders, and the empirical models of Elovich, Avrami and Gompertz, which allowed for a comprehensive assessment of the leaching mechanism. Equation (6), which describes the mixed regime (simultaneous influence of diffusion through the liquid film and chemical reaction at the phase boundary), agrees best with the experimental data for all three metals: $R^2 = 0.92$ for Ni, 0.83 for Fe and 0.98 for Mg. This finding indicates that neither mechanism is the only limiting link and that the contribution of both must be considered. It is assumed that the chemical reaction predominates in the early stages of the process, whereas the diffusion resistance increasingly plays a role in later stages.

The calculated activation energy (E_a) values were $76.07 \text{ kJ mol}^{-1}$ for Ni, $125.45 \text{ kJ mol}^{-1}$ for Fe and $119.33 \text{ kJ mol}^{-1}$ for Mg, which considerably exceed the threshold value of 40 kJ mol^{-1} , which is typical for reactions limited by the chemical stage³⁷. These data verify the dominance of the chemical reaction as the rate-limiting stage of leaching under the studied conditions.

Among the models of different orders, the pseudo-second-order model showed the best fit to the experimental data: $R^2 = 0.94$ for Ni, 0.85 for Fe and 0.95 for Mg. This outcome confirms that the leaching rate is determined by the interaction of acid ions with active sites on the particle surface and that the reaction itself probably proceeds via a bimolecular mechanism or involves two types of active sites. The Gompertz model revealed a sigmoidal kinetic pattern for Ni and Mg, suggesting an induction period, a rapid dissolution stage, and a final slowdown. On the basis of the calculated parameters, it was found that nickel ($\alpha = 2.86$; $\beta = -2.37$) is characterized by a short induction phase and rapid initial dissolution, whereas magnesium ($\alpha = 8.53$; $\beta = -2.81$) exhibits a delay in reaction because of surface or structural barriers. These results emphasize the importance of the α parameter as an indicator of the induction effect: nickel begins to leach immediately, whereas magnesium requires preliminary surface activation. For Fe, less pronounced agreement is observed, which may be due to more complex mineral associations or competing reactions.

The Avrami model, traditionally used to describe the growth and nucleation processes, also agrees well with the experimental data for Ni and Mg. The calculated values of the n parameter ($n < 1$) indicate an irregular or interface-limited mechanism, which may be due to the heterogeneous structure of the particles or different accessibilities of the reactive phases.

The Gompertz and Avrami models gave somewhat different values of the α parameter for magnesium, which is explained by the different physical and mathematical natures of these models. The Gompertz model, which describes sigmoidal kinetics, emphasizes the presence of a pronounced induction stage before active leaching⁴⁴, whereas the Avrami model indicates a high initial rate of the process⁴⁸, which may be due to the high availability of magnesium-containing phases. These differences are not contradictory but complement each other, emphasizing the multistage and complex nature of the leaching mechanism, including surface activation and structural transformations in the solid phase.

The Elovich model demonstrated a high degree of agreement with the experimental results for Ni and Mg and was satisfactory for Fe, indicating surface heterogeneity and a decrease in reactivity as the process proceeded. The parameters α and β allowed us to identify differences in the initial leaching rate and the nature of surface passivation. Thus, on the basis of all the results obtained, a brief summary of the leaching mechanisms for each metal separately is shown in Fig. 20.

The most likely sources of nickel in the ore are the phases of pimelite ($\text{Ni}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and hydrated nickel silicate ($\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$). On the basis of the ΔG values (-3302.6 and $-757.6 \text{ kJ mol}^{-1}$, respectively), the leaching reactions are thermodynamically favorable, with pimelite expected to react first (Table 4). Kinetic analysis (pseudosecond order, Gompertz model, and SCM) revealed a short induction period and a rapid onset, confirming the presence of readily accessible phases. Thus, Ni leaching is controlled by a chemical reaction, especially in the early stages, involving rapidly soluble silicate compounds. The prevailing rate of nickel leaching is also evidenced by the lowest value of activation energy (Table 1) compared with magnesium and iron.

Notably, lizardite can also act as a source of nickel. The authors of⁵³ reported that the reaction of sulfuric acid in the sulfation–roasting–leaching process with serpentines, particularly lizardite, is more thermodynamically probable than that with phyllosilicates (goethite). In our case, under the conditions of ore containing a large amount of lizardite (Fig. 4), hydrochloric acid leaching is also effective for extracting nickel from laterite ores.

The main carriers of Mg are antigorite ($\text{Mg}_{48}\text{Si}_{34}\text{O}_{85}(\text{OH})_{62}$), talc and lizardite. The reaction with antigorite has the most negative ΔG ($-3887.07 \text{ kJ mol}^{-1}$), indicating a high thermodynamic probability (order 1 in Table 4). However, the high enthalpy (ΔH) and high α value according to the Gompertz model indicate the presence of a considerable induction period. This induction period occurs possibly because, under the conditions of a real multicomponent system—laterite ore, antigorite is less accessible because of its structure and requires preliminary destruction or activation. Thus, Mg is leached more slowly during the initial stages, despite the high thermodynamic possibility, which is confirmed by structural barriers and the combined mechanism (SCM).

Fe is probably present as wustite (FeO) and hematite (Fe_2O_3). Thermodynamically, both reactions are less favorable ($\Delta G = -44.34$ and $-15.53 \text{ kJ mol}^{-1}$), which explains the low rate and R^2 according to the Gompertz model. Leaching kinetics indicate a slow and irregular process, with probable surface and structural limitations. Iron is leached slowly, primarily because of the low reactivity of the phases and passive surfaces. Additionally, the iron leaching process has the highest activation energy value— 125 kJ mol^{-1} (Table 1), which may also indirectly indicate a low process rate compared with that of nickel and magnesium.

Thus, the order of reactions under conditions of real multicomponent laterite ore of the Gornostaevskoye deposit most likely corresponds to that shown in Fig. 20. If we divide the abovementioned minerals into subgroups, we can see that under conditions of hydrochloric leaching, the order of dissolution is as follows: phyllosilicates (pimelite, nickel silicate hydrate) > serpentines (nepouite, antigorite, lizardite, talc) > iron oxides

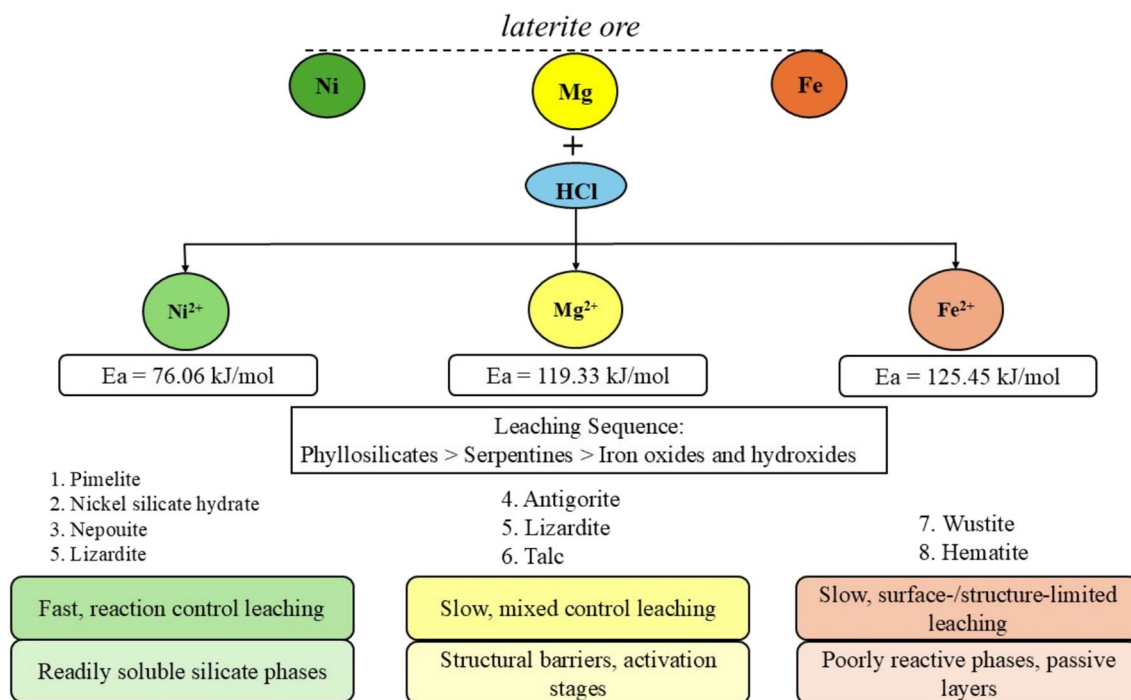


Fig. 20. Hydrochloric leaching mechanism of Ni, Mg, and Fe from Gornostaevskoe deposit laterite ore.

and hydroxides (wüstite, hematite). The authors of²⁸ leached laterite ore with a NH_4Cl –HCl solution and obtained a similar order: goethite > serpentine > magnetite and hematite.

Conclusion

This study presents a comprehensive investigation into the hydrochloric acid leaching behavior of oxidized laterite ore from the Gornostaevskoe deposit in East Kazakhstan, with a focus on the dissolution mechanisms, kinetics, thermodynamics, and mineral transformation pathways of nickel, magnesium, and iron-bearing phases.

Under the optimized leaching conditions, i.e., 18% HCl, a solid-to-liquid ratio of 1:4, a temperature of 85 °C, a leaching duration of 120 min, and a stirring speed of 400 rpm, high metal extraction efficiencies were achieved: 92.3% for nickel, 98.9% for magnesium, and 93.7% for iron. These values highlight the suitability of hydrochloric acid as a leaching reagent for complex multicomponent laterite ores, enabling efficient metal recovery while offering the advantages of chloride system regeneration and improved impurity removal.

Kinetic modeling using the shrinking core model (SCM) revealed that the dissolution process is controlled by a mixed mechanism combining surface chemical reactions and diffusion through the product layer. The calculated activation energies—76.07 kJ mol^{−1} for Ni, 125.45 kJ mol^{−1} for Fe, and 119.33 kJ mol^{−1} for Mg—further confirm that the overall leaching kinetics are predominantly chemically controlled, especially in the early stages of the reaction.

The application of various kinetic models, including pseudo-second-order, Gompertz, Avrami, and Elovich, provided deeper mechanistic insights. The pseudo-second-order model yielded the highest correlation coefficients ($R^2 > 0.94$ for Ni and Mg), suggesting that the leaching rate is closely related to the interaction between acid protons and reactive mineral surfaces. The Gompertz model indicated a sigmoidal leaching behavior for Ni and Mg, with nickel showing an immediate onset of dissolution and magnesium exhibiting a pronounced induction phase because of surface or structural barriers. In contrast, iron displayed irregular kinetic behavior, likely associated with its presence in less reactive oxide phases such as hematite and wüstite.

Thermodynamic modeling supported the experimental findings by identifying the most energetically favorable reactions. Among all the studied minerals, antigorite exhibited the most negative Gibbs free energy ($\Delta G = -3887.1$ kJ mol^{−1}), followed by pimelite and nickel silicate hydrate, indicating their high leaching potential under acidic conditions. Eh–pH stability diagrams confirmed the formation of soluble chloride complexes in acidic environments and suggested favorable zones for the selective precipitation of $\text{Ni}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, and Fe_2NiO_4 under controlled pH and redox conditions.

The sequence of mineral dissolution was determined on the basis of a combined assessment of thermodynamic parameters (ΔG , ΔH), mineralogical composition, and experimental leaching kinetics. The following order of reactivity was established:

Pimelite → Nickel silicate hydrate → Nepouite → Antigorite → Lizardite → Talc → Wüstite → Hematite.

This dissolution sequence reflects the relative thermodynamic favorability and the kinetic accessibility of the mineral phases. The initial rapid leaching of Ni and Mg is attributed to the decomposition of highly reactive nickel and magnesium phyllosilicates (pimelite and hydrated garnierite-type silicates), whereas the slower, late-stage leaching of Fe corresponds to the breakdown of more inert iron oxides.

In conclusion, the integrated approach combining mineralogical characterization, leaching experiments, kinetic modeling, and thermodynamic simulation provides a robust framework for understanding and optimizing the acid leaching behavior of laterite ores. The insights obtained in this study are directly applicable to the design of hydrometallurgical processes for the efficient and selective recovery of valuable metals from complex nickel-bearing laterites.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper. Should any raw data files be needed in another format, they are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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