Thermodynamic assessment of hydrometallurgical alternatives for nickel recovery in Colombia toward cleaner production

Evaluación termodinámica de alternativas hidrometalúrgicas para la recuperación de níquel en Colombia hacia una producción más limpia

Avaliação termodinâmica de alternativas hidrometalúrgicas para a recuperação de níquel na Colômbia visando uma produção mais limpa

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Abstract

Introduction: This article is the result of the review and research entitled "Aqueous Extraction of Nickel from Low-Grade Laterites Using Alternative Leaching Agents", conducted during 2025 at the Universidad Pedagógica y Tecnológica de Colombia.

Problem: The increasing demand for nickel has intensified the exploitation of lateritic deposits, which constitute a significant proportion of global reserves. However, the low nickel grades and the presence of impurities such as Fe, Mg, and Si complicate the extraction and purification processes. In Colombia, nickel production still relies predominantly on energy-intensive pyrometallurgical routes, which involve considerable operational costs and environmental impacts, highlighting the need to explore alternative and more sustainable processing approaches.

Objective: To analyze the characteristics of laterite processing for nickel extraction and assess hydrometallurgical alternatives to the pyrometallurgical process currently used in Colombia.

Methodology: A literature review was conducted on laterite processing technologies, describing the current process applied in Colombia and comparing it with hydrometallurgical routes reported in the literature.

Results: The review indicates that hydrometallurgical processes can be viable alternatives for low-grade laterites, enabling significant nickel recovery with lower energy consumption, reduced reagent use, and fewer atmospheric emissions.

Conclusions: Hydrometallurgical routes represent a promising option to diversify laterite processing in Colombia, particularly for low-grade ores, due to their potential operational and environmental advantages over conventional pyrometallurgical methods.

Originality: This study integrates an analysis of the current nickel extraction process in Colombia and contrasts it with potential hydrometallurgical alternatives suitable for the national context.

Limitations: The analysis is based mainly on bibliographic information and a preliminary assessment; therefore, further experimental and technical studies are required to confirm the feasibility of the proposed alternatives.

Keywords: Nickel recovery, lateritic ores, hydrometallurgy, clean production.

Resumen

Introducción: Este artículo es resultado de la revisión e investigación titulada "Extracción acuosa de níquel desde lateritas de baja ley utilizando agentes lixiviantes alternativos", desarrollada durante el año 2025 en la Universidad Pedagógica y Tecnológica de Colombia.

Problema: La creciente demanda de níquel ha intensificado la explotación de depósitos lateríticos, los cuales constituyen una proporción significativa de las reservas mundiales. Sin embargo, las bajas leyes de níquel y la presencia de impurezas como Fe, Mg y Si dificultan los procesos de extracción y purificación. En Colombia, la producción de níquel aún depende predominantemente de rutas pirometalúrgicas intensivas en energía, las cuales implican altos costos operativos y significativos impactos ambientales, lo que resalta la necesidad de explorar enfoques de procesamiento alternativos y más sostenibles.

Objetivo: Analizar las características del procesamiento de lateritas para la extracción de níquel y evaluar alternativas hidrometalúrgicas al proceso pirometalúrgico actualmente utilizado en Colombia.

Metodología: Se realizó una revisión de la literatura sobre tecnologías de procesamiento de lateritas, describiendo el proceso actual aplicado en Colombia y comparándolo con rutas hidrometalúrgicas reportadas en la literatura.

Resultados: La revisión indica que los procesos hidrometalúrgicos pueden constituir alternativas viables para lateritas de baja ley, permitiendo recuperaciones significativas de níquel con menor consumo energético, menor uso de reactivos y menores emisiones atmosféricas.

Conclusiones: Las rutas hidrometalúrgicas representan una opción prometedora para diversificar el procesamiento de lateritas en Colombia, particularmente para minerales de baja ley, debido a sus potenciales ventajas operativas y ambientales frente a los métodos pirometalúrgicos convencionales.

Originalidad: Este estudio integra un análisis del proceso actual de extracción de níquel en Colombia y lo contrasta con posibles alternativas hidrometalúrgicas adecuadas para el contexto nacional.

Limitaciones: El análisis se basa principalmente en información bibliográfica y en una evaluación preliminar; por lo tanto, se requieren estudios experimentales y técnicos adicionales para confirmar la viabilidad de las alternativas propuestas.

Palabras clave: Recuperación de níquel, minerales lateríticos, hidrometalurgia, producción más limpia.

Resumo

Introdução: Este artigo é resultado da revisão e pesquisa intitulada "Extração Aquosa de Níquel de Lateritas de Baixo Teor Utilizando Agentes de Lixiviação Alternativos", realizada em 2025 na Universidade Pedagógica e Tecnológica da Colômbia.

Problema: A crescente demanda por níquel intensificou a exploração de depósitos lateríticos, que constituem uma parcela significativa das reservas globais. No entanto, os baixos teores de níquel e a presença de impurezas como Fe, Mg e Si complicam os processos de extração e purificação. Na Colômbia, a produção de níquel ainda depende predominantemente de rotas pirometalúrgicas de alto consumo energético, que envolvem custos operacionais consideráveis e impactos ambientais, evidenciando a necessidade de explorar abordagens de processamento alternativas e mais sustentáveis.

Objetivo: Analisar as características do processamento de lateritas para extração de níquel e avaliar alternativas hidrometalúrgicas ao processo pirometalúrgico atualmente utilizado na Colômbia. Metodologia: Foi realizada uma revisão da literatura sobre tecnologias de processamento de laterita, descrevendo o processo atualmente aplicado na Colômbia e comparando-o com rotas hidrometalúrgicas relatadas na literatura.

Resultados: A revisão indica que os processos hidrometalúrgicos podem ser alternativas viáveis para lateritas de baixo teor, possibilitando uma recuperação significativa de níquel com menor consumo de energia, uso de reagentes e redução das emissões atmosféricas.

Conclusões: As rotas hidrometalúrgicas representam uma opção promissora para diversificar o processamento de laterita na Colômbia, particularmente para minérios de baixo teor, devido às suas potenciais vantagens operacionais e ambientais em relação aos métodos pirometalúrgicos convencionais.

Originalidade: Este estudo integra uma análise do processo atual de extração de níquel na Colômbia e o contrasta com potenciais alternativas hidrometalúrgicas adequadas ao contexto nacional.

Limitações: A análise baseia-se principalmente em informações bibliográficas e em uma avaliação preliminar; portanto, são necessários mais estudos experimentais e técnicos para confirmar a viabilidade das alternativas propostas.

Palavras-chave: Recuperação de níquel, minérios lateríticos, hidrometalurgia, produção limpa.

1. INTRODUCTION

Nickel is a metal valued for its importance and wide range of applications due to its malleability, hardness, and ductility [1]. Although its production was traditionally limited to the extraction of sulfide minerals, the potential depletion of these reserves has led to the increasing use of nickeliferous laterite minerals to meet the growing demand for the metal. However, the nickel content in laterites rarely exceeds 6%. It is estimated that these deposits account for approximately 73% of global reserves and supply around 42% of the world's nickel production [2], [3], [4], [5], [6]. The recovery of nickel from these minerals is particularly challenging due to their low grade and the presence of other elements such as magnesium, iron, and silicon [3], [7]. The choice of metallurgical processing routes depends largely on the ore grade: pyrometallurgical processes are generally applied to high-grade ores, while hydrometallurgical methods are preferred for low-grade materials.

In Colombia, nickel production is derived from a single operation based on pyrometallurgical routes that process lateritic minerals with significant chemical and mineralogical variability [8]. However, Idrovo [9] reported that these operations involve high energy consumption of electricity, gas, and coal, in addition to causing serious health and environmental impacts due to elevated atmospheric emissions. Although pyrometallurgical routes are not the most suitable option for treating low-grade ores, Colombia currently does not employ alternative methods for laterite processing.

The objective of this document is to present a bibliographic review and preliminary assessment of the general characteristics of laterite treatment for nickel extraction. The current process used in Colombia is described, along with its associated impacts, despite its importance and benefits for the country's mining and economic sector. In addition, the study presents and compares different hydrometallurgical methods currently available as potential and attractive alternatives to the traditional process employed in Colombia for metal recovery from laterite ores. These aqueous extraction routes are capable of producing significant amounts of nickel while offering environmental advantages, including lower energy and reagent consumption, reduced gas emissions, and fewer public health risks.

2. METHODOLOGY

The methodology of this study was based on a systematic and critical review of the scientific and technical literature related to nickel extraction from lateritic ores. The

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selected studies were analyzed and classified according to geological setting, mineralogical composition, and processing routes.

3. RESULTS

3.1. Colombian deposits of nickel laterite

Lateritic soils exploited for nickel extraction are derived from ultramafic rocks of Cretaceous age, where metal enrichment occurs during the weathering process. Laterites are commonly classified as limonite or saprolite, depending on their chemical composition, with nickel content generally increasing with deposit depth. The limonite and saprolite zones, along with their transition layer, represent the areas with the highest potential for nickel extraction due to their metallic content (Table 1). In contrast, the uppermost layer and the base of the deposit, composed mainly of hematite and unweathered rock, contain the lowest nickel concentrations.

Table 1. Typical profile of a nickel laterite [5]. Source: Authors

	Metallic content			
Zones	**Ni**	**Co**	**Fe**	**Mg**
Uppermost layer and the deposit base	< 0.8	< 0.1	>50	< 0.5
Limonite	0.8 to 1.5	0.1 to 0.2	40 to 50	0.5 to 5
Transition	1.5 to 4	0.02 to 0.1	10 to 25	15 to 35
Saprolite	1.8 to 3	0.02 to 0.1	10 to 25	15 to 35

Source: own work

In Colombia, three saprolitic nickel deposits have been identified in the department of Córdoba: Cerro Matoso, Planeta Rica, and Uré. Among these, Cerro Matoso contains the largest measured reserves and is the only deposit that has been economically evaluated and is currently in operation [10]. Although no new deposits have been formally explored in the country, the Colombian Geological Survey has reported prospects and occurrences with potential for lateritic deposits in the Western Cordillera, particularly in Ituango, Morro Pelón, and Medellín, in the department of Antioquia [11].

Colombian lateritic minerals are classified according to their contents of magnesium oxide (MgO), iron (Fe), silica (SiO_2), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}). Concentrations of 15% to 25% MgO are associated with the highest nickel grades [12]. In laterites, nickel commonly occurs with cobalt (Co) in oxide phases formed at the

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surface of the deposits. Although these deposits are typically low grade (1.0–1.6% Ni, maximum), they are extensive and therefore contribute significantly to global nickel production. However, the treatment of laterites is technically complex and requires substantial capital investment [10], [13].

According to the XRD analysis, Colombian lateritic mineral is mainly composed of magnesium silicates in the form of nepouite [$Mg_3Si_2O_5(OH)_4$], iron as goethite [FeO(OH)], and silica as quartz [SiO_2] (Figure 1).

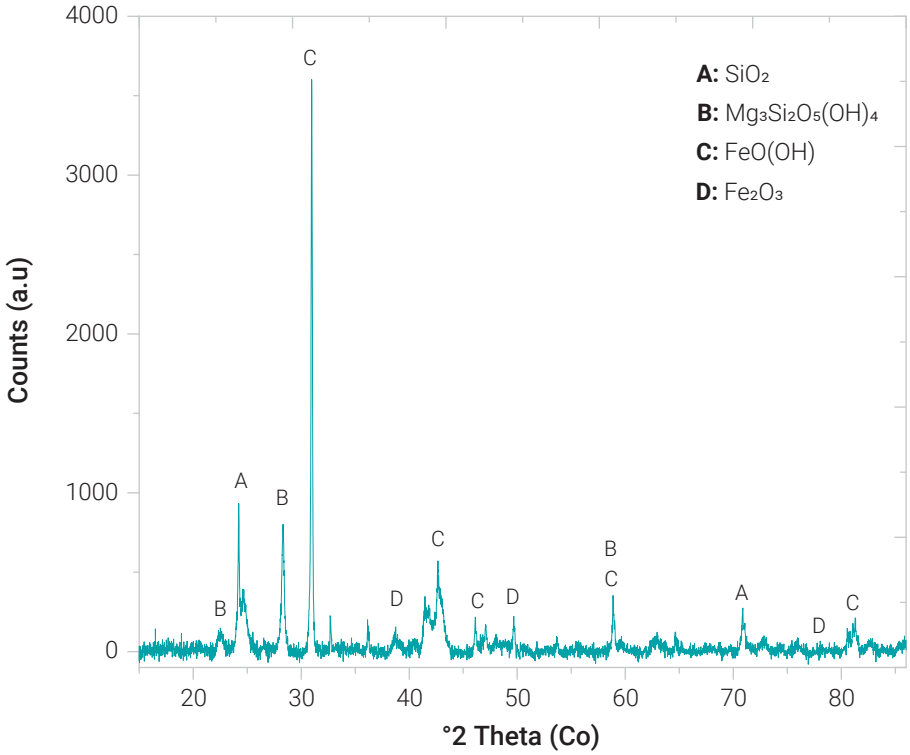

Figure 1. XRD pattern of a Colombian lateritic study sample.
Source: own work

There is no evidence for the existence of a single nickel phase, as several authors have reported that the metal is most commonly associated with iron oxides [14], while in other cases it is linked to silicate structures [15].

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3.2. Extraction Methods

3.2.1. Pyrometallurgical Route – Conventional

The pyrometallurgical route is generally applied to hydrated silicate deposits, which contain the highest nickel grades among lateritic ores [16]. This route typically involves drying, calcination, reduction, smelting, and refining to produce ferronickel or a matte with low iron content (Figure 2). However, it has been reported that pretreatment significantly affects the reducibility of these minerals [17].

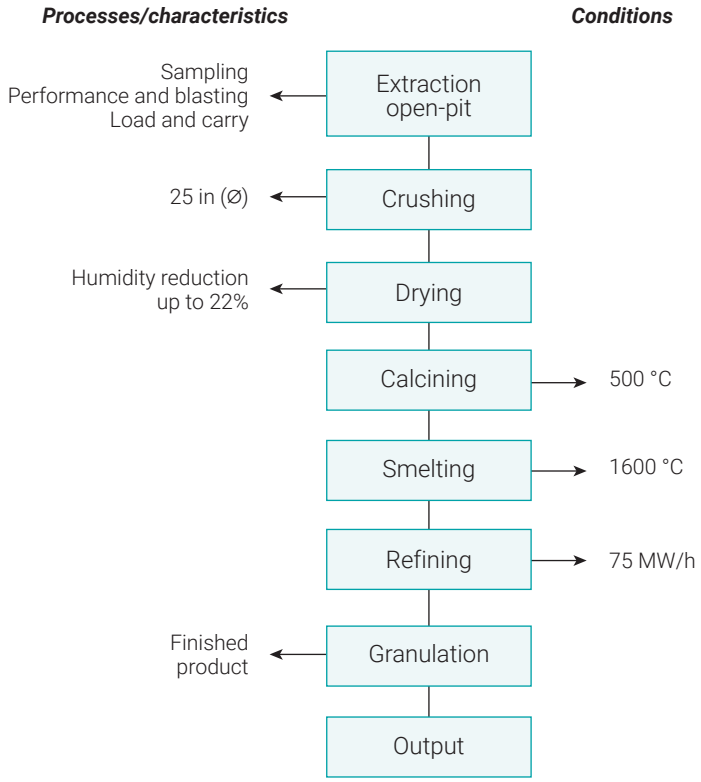

Figure 2. Industrial mining process for the ferronickel production in Colombia.
Source: own work

In Colombia, ore is extracted by open-pit mining and stockpiled according to quality and nickel grade. After crushing, the particle size is standardized, and the material is processed in the smelting plant, which produces high-purity ferronickel granules (37.5% Ni) with low carbon content [10]. Lateritic ores cannot be smelted to pure metallic nickel because of their high iron content and the strong affinity of iron for oxygen. As a result, FeO is reduced almost as readily as NiO during calcination.

Ferronickel production from lateritic minerals is achieved through the sequential reduction of nickel and iron oxides across four main stages:

- Drying and storage of partially dried ore (rotary kiln).
- Calcination (calciner furnaces 1 and 2).
- Smelting (electric furnaces 1 and 2).
- Refining, followed by finished product management.

The overall process enables ferronickel production due to the relatively easy reduction of nickel and iron oxides under pyrometallurgical conditions.

$$C + NiO \rightarrow CO + Ni \quad (1)$$

$$C + FeO \rightarrow CO + Fe \quad (2)$$

The origin of special apparatus, reagents, and biological materials used should be specified. Reagents commonly available in laboratories and preparations described in standard textbooks should not be listed. Experimental methods must be described with sufficient detail to allow replication of the experiments without ambiguity. Procedural details that are common knowledge in the field may be omitted. Brief highlights of previously published procedures may be included, with full details left to the cited literature. Statistical design and methods should also be described in this section.

In the pyrometallurgical process, the addition of carbon promotes the formation of carbon monoxide, which reduces NiO and FeO. However, oxides of aluminum, magnesium, silicon, and chromium form stronger bonds, making their reduction to metallic elements more difficult. As a result, ferronickel often contains residual amounts of silicon and chromium in its composition.

For the production process to remain economically viable, current smelters must meet strict criteria regarding Ni, Fe–Ni, and Ni–Co grades, as well as SiO_2/MgO ratios; otherwise, recoveries of the target metal cannot be achieved. During operation, the presence of cobalt concentrations equal to or greater than 0.5% and slag overheating above 100 °C can cause serious operational issues, including damage to the furnace refractory [5].

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3.2.1.1. Process disadvantages

Several disadvantages are associated with this extraction method, including the generation and accumulation of more than 1000 tons of slag with limited social and industrial applications [18], SO_2 emissions, the processing of bush ore, high costs related to coke consumption (in the case of shaft furnaces), and the elevated energy demand per ton of metal produced, since all process reactions are highly endothermic.

From a technical perspective, energy input is required to calcine the laterite, as evidenced by the thermogravimetric analysis (TGA, Figure 3).

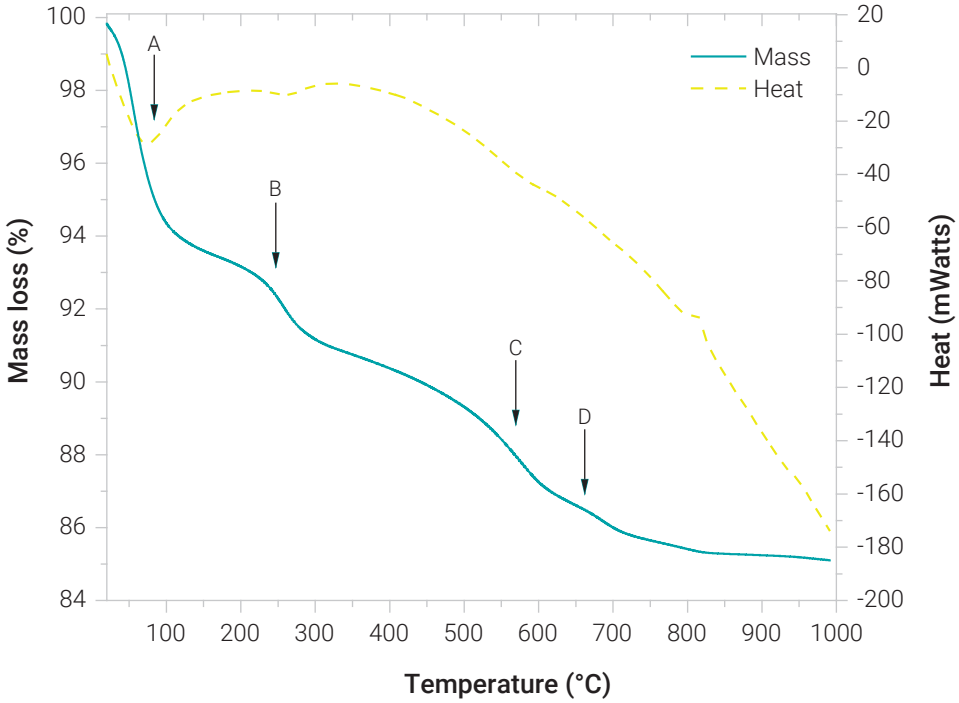

Figure 3. TGA / DSC of a Colombian lateritic study sample.
Source: own work

The main temperature ranges associated with mass loss are as follows: A – dehydration (~100 °C); B – decomposition of goethite (~250 °C); C – onset of NiO formation (~550 °C); and D – complete conversion to NiO (~650 °C). These transformations are consistent with expectations derived from a predominance-area diagram (Figure 4), where the stability of NiO is observed at temperatures above 100 °C.

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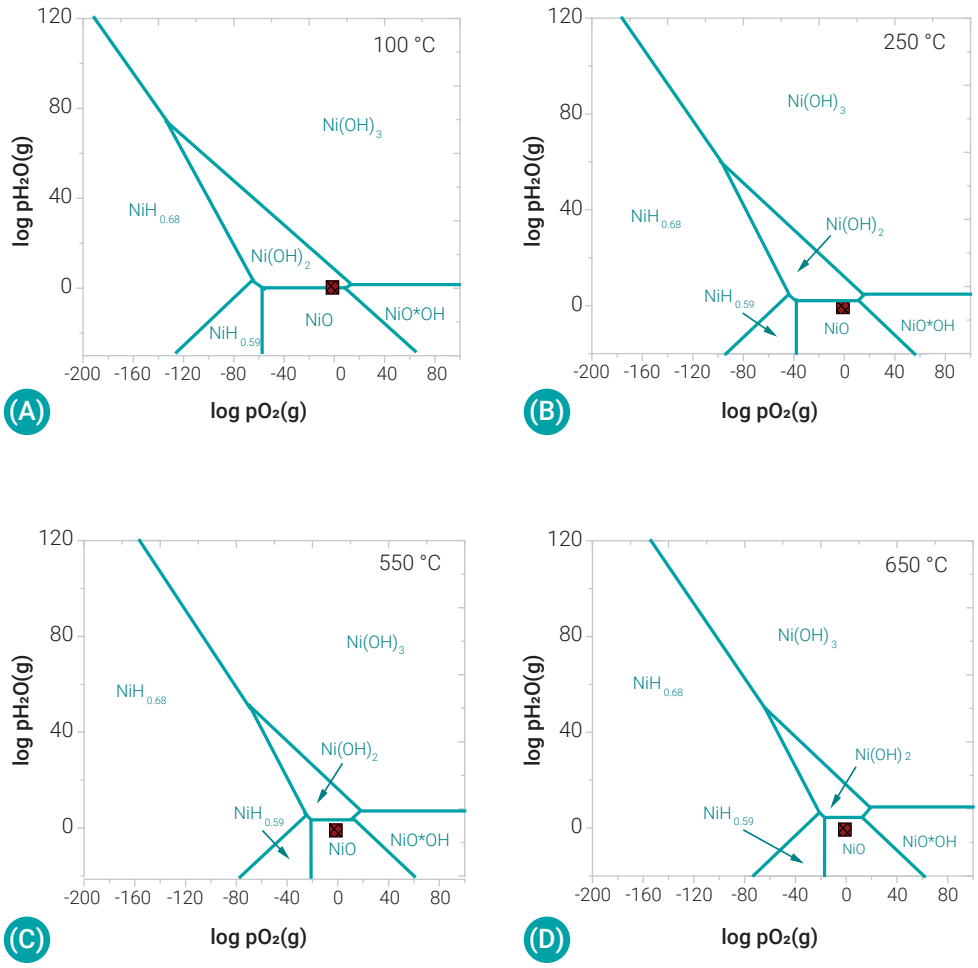

Figure 4. Phase stability diagram for Ni. Conditions: Pressure of O2 = 0.21 atm and H2O = 1 atm; Temperature: A) 100°C, B) 250°C, C) 550°C and D) 650°C.
Designed with HSC 5.1 software and adapted by authors.

Thermodynamically, the NiO phase does not exhibit significant changes with increasing temperature; however, heat treatment modifies the mineral matrix, thereby affecting other metallic compounds. For instance, iron occurs as ferric oxyhydroxide at ~100 °C (Figure 5.A), but undergoes thermal decomposition above 250 °C, forming iron oxides (Figures 5.B, 5.C, and 5.D), characterized by the complete removal of OH^- groups.

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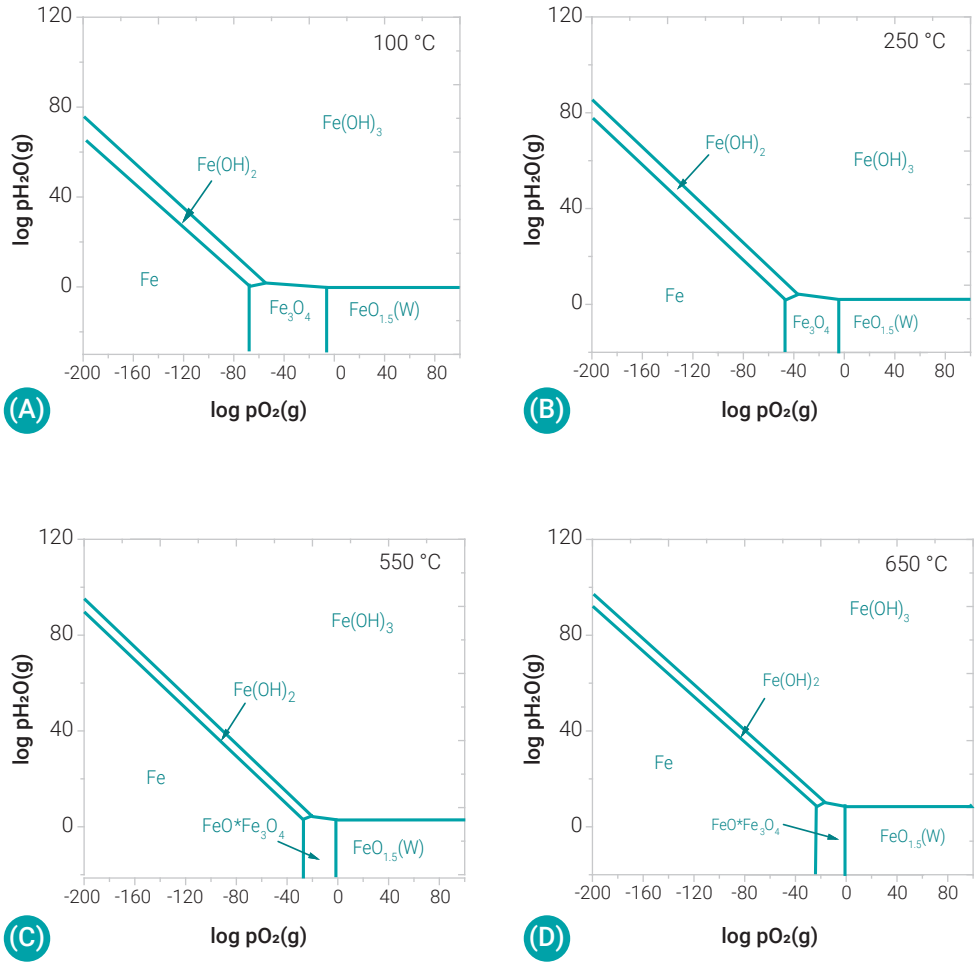

Figure 5. Phase stability diagram for Fe. Conditions: Pressure of O2 = 0.21 atm and H2O = 1 atm; Temperature: A) 100°C, B) 250°C, C) 550°C and D) 650°C.
Designed with HSC 5.1 software and adapted by authors

Nickel and iron oxides can be readily reduced to metallic ferronickel. Nevertheless, current technological demands require nickel in its pure form rather than as an iron alloy, particularly for applications in energy storage and batteries. Nickel is highly attractive in this context because it is relatively easy to synthesize and exhibits both high capacity and energy density.

The production of ferronickel through pyrometallurgical routes has been advantageous for the Colombian industrial sector, since there are no alternative processes currently in operation in the country for laterite treatment. However, this conventional route becomes economically inefficient when the objective is to obtain pure metallic nickel, due to the high cost per gram of Ni produced [19].

Consequently, research efforts have focused on the development of alternative laterite treatment methods, particularly hydrometallurgical processes, which allow for the recovery of metallic nickel with lower energy and fuel consumption and reduced atmospheric emissions.

3.2.2. Hydrometallurgical Route

Due to the limitations of pyrometallurgical processes and the decreasing availability of higher-grade saprolitic deposits, alternative technologies have been developed to process the abundant low-grade laterites through hydrometallurgical routes, which involve heterogeneous solid–aqueous systems. These methods yield high-quality nickel products by employing leaching techniques that have already been extensively studied, such as high-pressure acid leaching (HPAL), atmospheric acid leaching (AL), and heap leaching (HL). The efficiency of these processes, both in terms of nickel recovery and reagent consumption, is strongly influenced by the mineralogical associations within the ore, which determine the leachability of the metal [5].

3.2.2.1. High pressure acid leaching process HPAL

The operation of the process begins with the extraction and crushing of the laterite ore (Figure 6).

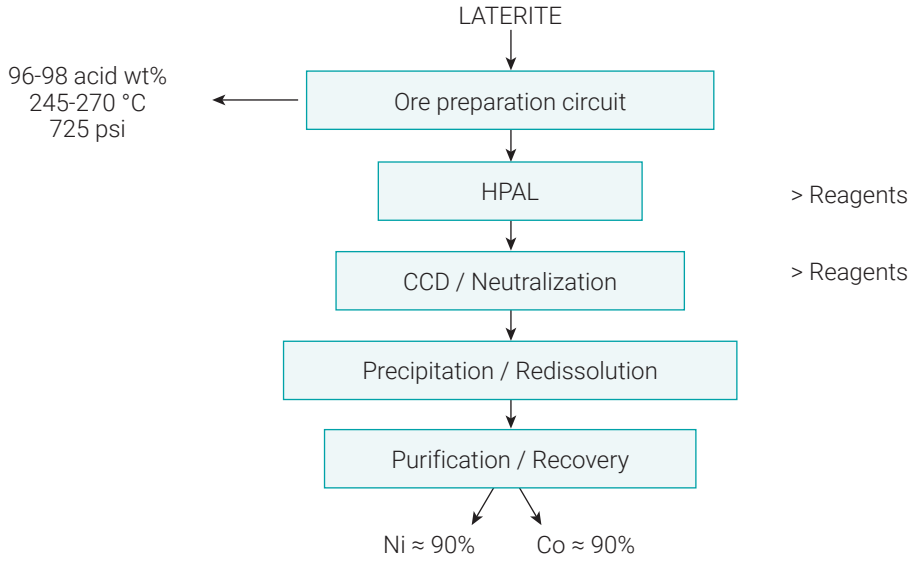

Figure 6. Conceptual flow diagram for laterite treatment through the HPAL process
Source: Authors

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HPAL processes are typically applied to limonitic ores with low magnesium content (Mg < 4%) and fine particle size, which are mixed with water to form a slurry. This slurry is preheated and fed into lined autoclaves, where it reacts with acidic solutions—predominantly sulfuric acid, but also chloride and nitrate media—under conditions of elevated temperature (245–270 °C) and high pressure (approximately 50 bar or 725 psi). Under these conditions, the oxides of metallic elements such as Ni and Co are decomposed and react with sulfuric acid, enabling their dissolution into the leach liquor as soluble sulfates.

$$Me_2On(s) + 2nH^+ \rightarrow 2Me^{n+} + nH_2O \quad (3)$$

Where Me: nickel, cobalt or manganese, n: metal ionic compound

When the suspension is washed and separated after leaving the high-pressure and high-temperature environment of the autoclave, nickel and cobalt are recovered from the liquid fraction. The suspension is neutralized and subjected to counter-current decantation (CCD). Impurities such as iron, aluminum, and silicon are removed, and nickel and cobalt are precipitated as sulfides or hydroxides, or removed directly by solvent extraction (organophosphate extractants, amines, phosphorous acids, D2EHPA, LIX 63, Cyanex 302) to produce electro-nickel, nickel oxide, or nickel briquettes [5], [20]. Sometimes, limestone slurry is used as a neutralizer, and air is introduced into the solution to oxidize ferrous elements. The pH value of the solutions is controlled at 3–5 in two stages to achieve hydrolytic precipitation and the removal of iron, aluminum, and silicon dioxide, thus:

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \quad (4)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe(SO_4) + 2H_2O \quad (5)$$

$$M2(SO_4)_3 + 4H_2O \rightarrow 2MO(OH) + 3\ H_2SO_4 \quad (6)$$

$$M2(SO_4)_3 + 6H_2O \rightarrow 2MO(OH)_3 + 3\ H_2SO_4 \quad (7)$$

$$nH_2SiO_4 \rightarrow (SiO_2)_n + 2nH_2O \quad (8)$$

Where M: aluminum and iron

An optional stage of purification and separation may be incorporated, which involves the redissolution of precipitated solids (if formed), followed by purification through solvent extraction or selective precipitation. The final recovery of nickel can then be achieved either by electrodeposition, hydrogen reduction, or by producing nickel oxide through pyrohydrolysis of the purified intermediate solution [6]. HPAL processes have the advantage of enabling the rapid treatment of nickeliferous laterites; however, they also present significant operational challenges. Among the most critical are corrosion, autoclave level control, and the complexity of operation and maintenance procedures, all of which arise from the combination of high pressures, elevated temperatures, and strongly acidic conditions [21].

3.2.2.2. Atmospheric acid leaching process AL and heap leaching HL

Atmospheric acid leaching (AL) can achieve nickel extraction efficiencies of 98–99% under atmospheric pressure and temperatures of 90–95 °C [22], provided that key variables such as particle size and pulp density are carefully controlled [1]. Nevertheless, its main drawbacks include slower leaching kinetics, excessive acid consumption (up to 8 M), and low nickel selectivity, given the strong linear correlation between Ni and Fe dissolution [23], [24]. In oxide-type deposits, nickel is often isomorphically substituted within goethite, a mineral that is difficult to dissolve under conditions of high oxidation–reduction potential, thereby limiting Ni recovery. To overcome this, strategies such as extended leaching time or higher temperatures, controlled redox conditions, addition of salts, and mineral sulphation have been investigated [24], [25]. Finally, heap leaching (HL) projects have shown greater economic stability, offering substantially lower capital costs compared to alternative hydrometallurgical routes, which, as discussed, face persistent technical and commercial challenges [26].

3.2.2.3. Hydro-pyro integration in nickel laterite processing

Nickel production from laterites remains costly and complex due to their diverse mineralogy, heterogeneous composition, and low Ni grades [27]. Consequently, research continues to focus on optimizing production by integrating pyro- and hydrometallurgical

methods with alternative pretreatment techniques. For example, Guo et al. [28] reported that alkaline roasting of limonitic ore with Na_2CO_3 at 700 °C (NaOH/ore mass ratio of 1.2 for 150 min) removed Cr and Al, enabling subsequent pressurized acid leaching (80 °C, 261 psi) and achieving a 17.56% increase in Ni recovery, with a final extraction of 97.52%. Similarly, thermal pretreatment of garnieritic minerals under argon at 400–1000 °C enhanced porosity and surface area, improving Ni release. Phase transformations were observed: chlorite converted to forsterite and enstatite at 700–800 °C, with recrystallization occurring between 800 and 850 °C, while talc transformed to forsterite and enstatite at ~1000 °C. However, above 700 °C, ore sintering reduced porosity and surface area [7]. Additionally, Kim et al. [3] demonstrated that pre-calcination at 500 °C for 1 h modified the crystalline and magnetic properties of laterite, facilitating subsequent recovery via wet magnetic separation. Their results highlighted the importance of controlling (i) calcination temperature, (ii) pulp density, and (iii) applied magnetic field strength. Under optimal conditions, magnetic separation recovered 48% of Ni, increasing the Ni grade in the concentrate from 1.5% to 2.9%.

3.2.2.4. Laterite bioleaching

Biological leaching has emerged as a promising approach for the treatment of low-grade minerals, relying on microorganisms and their metabolic products, primarily acidophilic chemolithoautotrophic bacteria. Its main advantages are its ecological nature, operational simplicity, and relatively low energy and operating costs [29], [30]. Bioleaching experiments have been performed under both aerobic and anaerobic conditions, with pH identified as a critical factor for nickel solubilization. High bacterial activity at low pH values (0.8–1.7) enhances metal recovery [31]. However, a significant limitation of the process is that it does not promote the reductive dissolution of goethite, the mineral phase that contains the highest proportion of nickel in laterites [32]. Other variables strongly influencing Ni recovery include pulp density, temperature (80–95 °C), particle size (surface area), and the type of substrate, commonly sulfur [33], [34], [35], [36].

The application of microorganisms is primarily related to their capacity to generate hydroxycarboxylic acids and other organic metabolites in the culture medium. These compounds facilitate nickel solubilization through proton complexation/chelation and the subsequent formation of Ni–organic complexes. This mechanism increases the apparent solubility of the metal by reducing its free activity in solution. Nevertheless, despite these advantages, the bioleaching of non-sulfide minerals has not yet been commercialized due to limitations such as long residence times and relatively low extraction yields [37], [38].

3.2.2.5. Leaching with organic solutions

As previously discussed, several studies have investigated alternative approaches for the exploitation of laterite resources, including leaching with sulfuric acid, chloride media, and biotechnological routes [39], [40], [41]. Although these methods have yielded favorable results, they also present limitations: leaching tends to be non-selective, operating conditions are often harsh, and many reagents are toxic or corrosive, generating effluents that, if not properly treated, represent significant environmental liabilities (Astuti et al., 2016).

Among inorganic reagents, sulfuric acid remains the most widely applied due to its efficiency, availability, and relatively low cost. Nonetheless, hydrochloric and nitric acids have gained increasing attention since, unlike sulfuric acid, they can be recycled [42]. However, their application continues to pose environmental challenges when effluent treatment is inadequate.

Recent research has thus shifted toward the evaluation of organic acids as alternative leaching agents in hydrometallurgical processes. These compounds promote metal dissolution through proton release, acceleration of ion exchange, and the formation of soluble metal–organic complexes, thereby enhancing mineral solubilization [43]. Comparative studies on lateritic ores have shown that citric and oxalic acids exhibit distinct behaviors compared with inorganic acids. While oxalic acid can contribute to the dissolution of both goethite and serpentine phases, citric acid is ineffective at solubilizing nickel from oxides such as goethite [42], [43], [44]. Nevertheless, citric acid is particularly effective in dissolving nickel from silicate minerals, notably serpentine, which underscores its potential suitability for Colombian laterites, where silicate phases predominate [5].

Finally, the application of predominance (Pourbaix) diagrams provides a valuable thermodynamic framework to analyze these processes, since they enable the identification of favorable pH and redox potential conditions for the stability and solubility of nickel species, thus supporting the rational selection of leaching agents and operational parameters.

3.3. Preliminary test

3.3.1. Thermodynamic study

Studies performed with Colombian laterite (deposit of unspecified location) have shown that leaching systems employing citric, oxalic, nitric, hydrochloric, and sulfuric acids present favorable thermodynamic conditions for the stabilization of nickel compounds (Figure 7).

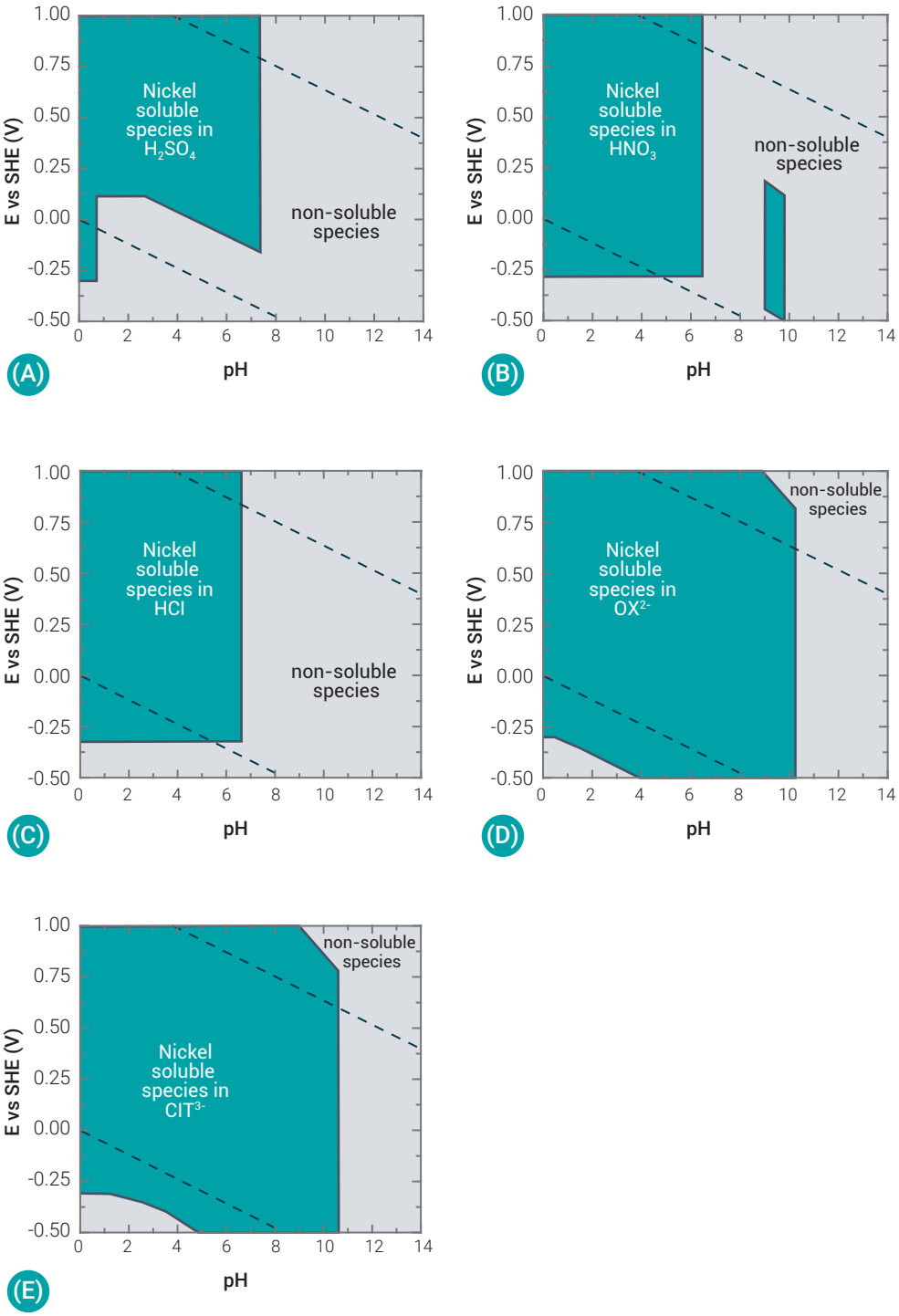

Figure 7. Simplified stability diagrams for Ni (0.0073 M) and SO42-(A), NO-3(B), Cl-(C), Ox (D), Cit (E), (0.5 M).
Designed with MEDUSA® software, with information from the NIST database (Database 46 - Vers. 8.0) [45], [46], [47] and adapted by authors.

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Based on the reaction energies between nickel and each leaching agent, the system evolves toward its most stable energy state under acidic conditions (Appendix).

In the case of sulfuric acid, the stability domain of $NiSO_4$ is defined within a pH range of 0–7.4 (Figure 7A) and at potentials higher than –300 mV, under typical leaching conditions (pH < 1).

A similar thermodynamic evaluation carried out for nickel in the presence of NO_3^- and Cl^- ions (Figures 7B and 7C) indicates that stability is constrained to pH values below 6.5, with nickel predominating in ionic forms such as Ni^{2+} (nitrate medium) and $NiCl_2$ (chloride medium). Although nitric acid systems can thermodynamically yield the $Ni(NH_3)_5^{2+}$ species at pH 9–10 and potentials below 250 mV, the required pH adjustment results in neutralization of the reagent and introduces the risk of violent reactions when combined with alkaline substances.

In contrast, citric and oxalic acids exhibit broader thermodynamic flexibility (Figures 7D and 7E), with stability domains spanning a wider pH range (1–10) and potential window. This makes them particularly attractive as alternative lixiviants, as they can sustain soluble nickel–organic complexes under more moderate operating conditions.

Overall, regardless of the reagent employed, both pH and redox potential must be carefully controlled in tandem to ensure operation within the ionic stability domain and thereby favor the formation of soluble complexes that enable efficient nickel extraction.

3.3.2. Preliminary results

This manuscript presents a thermodynamic study of alternative routes to the traditional process for the treatment of laterites in Colombia. The authors are currently conducting laboratory-scale tests to evaluate the kinetics of these alternative pathways. Accordingly, Figure 8 shows the preliminary extractions obtained with different reagents.

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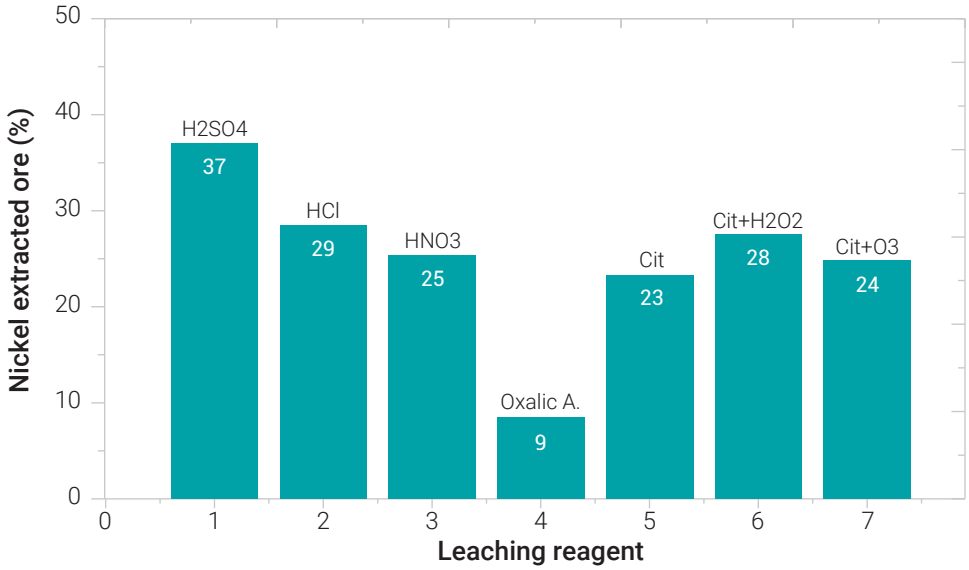

Figure 8. Metal extraction by agitation leaching, conditions: 500 rpm, atmospheric pressure, 25 °C, particle size 63 µm, 30 h.
Source: Authors

Based on the preceding thermodynamic study, two organic agents (citric and oxalic acids) were selected, and their performance was compared with that of conventional inorganic solutions (HCl, HNO_3, and H_2SO_4). Experimentally, the oxidation potential measured for each leaching agent was within the favorable range for nickel dissolution (660–945 mV) under acidic conditions, referenced to the standard hydrogen electrode (SHE). Under such conditions, the general mechanism can be summarized as the oxidation of metallic nickel to its ionic form, followed by complexation with leaching-agent ions in sufficient concentration to form soluble species.

Among the inorganic reagents, the SO_4^{2-} ion from sulfuric acid exhibited the strongest complexing capacity with Ni^{2+}. However, the difference in extraction yields compared to citric acid was not substantial. Therefore, citric acid solutions are promising, as they not only display selectivity for specific metals depending on pH [48], but also pose no significant environmental risk and can be reused over several leaching/electrowinning cycles without significant loss of efficiency [39].

In contrast, although oxalic acid shows similar thermodynamic potential to citric acid for soluble species formation, its extraction efficiency was the lowest. This behavior is attributed to the higher stability of iron oxalates. Considering that iron is one of the predominant elements in lateritic ores (Figure 1), oxalate precipitation occurs after nickel dissolution, limiting overall recovery.

To address this, leaching systems combining citric acid with oxidizing agents such as ozone and hydrogen peroxide have been investigated to enhance nickel extraction. The main challenge, however, as reported by Astuti et al. [42] and confirmed in the authors' ongoing work, lies in the slow kinetics of the process, which necessitates further studies aimed at accelerating the formation of nickel complexes.

A comprehensive thermodynamic, kinetic, and phenomenological analysis establishing the conditions and favorable pathways for the extraction process is currently under preparation by the authors for publication.

4. CONCLUSIONS

The nickel mined in Colombia originates from low-grade lateritic soils and is currently treated using pyrometallurgical processes. However, the development of alternative processing techniques is necessary to obtain higher-purity nickel. Pyrometallurgy presents significant drawbacks, including the accumulation of large volumes of slag, high operating costs, and the emission of toxic gases such as SO_2. These limitations highlight the relevance of exploring hydrometallurgical routes for nickel extraction. In this context, the mineralogical composition of the laterites becomes a decisive factor, as it strongly influences the performance of leaching processes and the dissolution rate of the metal when exposed to different acid solutions.

While nickel has traditionally been used in the steel industry, mainly as ferronickel, its role in the production of energy storage systems (e.g., batteries) has dramatically increased its strategic importance. This shift adds complexity to its processing but also provides much higher added value for the metal.

Given these factors, urgent research is required to demonstrate to the industrial sector that hydrometallurgical alternatives can be both technically viable and less environmentally damaging. These processes offer advantages such as reduced emissions, potentially higher selectivity, and improved recovery efficiencies. The authors are actively working on these approaches, and the corresponding results are already in the process of publication.

Furthermore, balancing environmental impacts on surrounding communities (Idrovo, 2018) with the economic profitability of production and the advancement of novel processing methodologies requires robust collaboration. It is therefore essential to foster R&D projects that bridge the productive sector and academia, ensuring innovation while addressing environmental and social challenges.

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Appendix 1

Appendix 1. Thermochemical data for the reaction product of Nickel leaching (NIST, 2004; Eriksson, 1979; Puigdomenech, 2004)

Reaction	ΔG (kJ/mol)
$Ni^{2+} + 2SO_4^{2-} \rightarrow Ni(SO4)_2^{2-}$	-5,820
$Ni^{2+} + SO_4^{2-} \rightarrow NiSO_4$	-13,066
$Ni^{2+} + Cl^- \rightarrow NiCl^+$	-2,282
$Ni^{2+} + 2Cl^- \rightarrow NiCl_2$	-5,478
$Ni^{2+} + Ox^{2-} \rightarrow Ni(Ox)$	-29,442
$Ni^{2+} + 9H^+ + NO_3^- + 8e^- \rightarrow NiNH_3^{+2}$	-641,908
$Ni^{2+} + 2Ox^{2-} \rightarrow Ni(Ox)_2^{2-}$	-48,386
$Ni^{2+} + Cit^{3-} \rightarrow Ni(cit)^-$	-39,427
$Ni^{2+} + 2Cit^{3-} \rightarrow Ni(cit)_2^{4-}$	-52,779
$Ni^{2+} + 2H^+ + Cit^{3-} \rightarrow Ni(H_2cit)^+$	-75,945
$Ni^{2+} + H^+ + Cit^{3-} \rightarrow Ni(Hcit)$	-61,509
$Ni^{2+} + H^+ + 2Cit^{3-} \rightarrow Ni(Hcit)(cit)^{3-}$	-87,813

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