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Chlorination Routes for Limonitic Nickel Laterites: A Critical Review of Solid-State and Gas-Phase Selective Volatilization

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ABSTRACT

Review Article

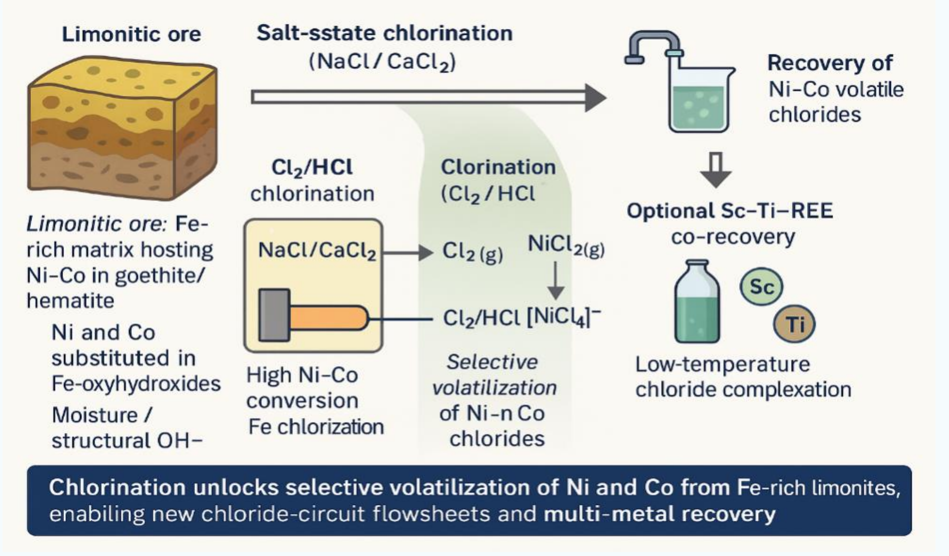
Chlorination has re-emerged as a strategic alternative for processing limonitic nickel laterites, providing selective conversion of Ni and Co into volatile or soluble chlorides under controlled thermal and chemical conditions. Compared to traditional hydrometallurgical and pyrometallurgical methods—such as HPAL, atmospheric leaching, Caron-type processes, and sulfation roasting—chlorination offers unique process windows where nickel and cobalt chlorides are highly stable and tend to volatilize, while iron remains mostly refractory as hematite or decomposes into ferric chloride. This comprehensive review consolidates recent advances in solid-state chlorination (using NaCl, $CaCl_2$, and NH_4Cl), gas-phase chlorination (Cl_2, HCl, and Cl_2/CO mixtures), and emerging chlorohydrometallurgical systems employing ionic liquids and deep eutectic solvents. Special focus is given to (i) The reaction pathways controlling chlorination and volatilization of Ni/Co from goethite–hematite matrices, (ii) The kinetic and mass transfer limitations in mixed-laterite systems, (iii) The effects of mineralogical factors like silica, serpentine, and chromite on chloride conversion, and (iv) Opportunities for integrating processes to recover critical elements such as Sc, Ti, and REEs. The review also assesses the technology readiness, environmental impacts, chloride-circuit regeneration, corrosion challenges, and energy demands compared to established commercial processes. Overall, the synthesis underscores chlorination as a technically promising but underdeveloped pathway, with industrial application depending on advances in reactor design, recycling of chlorinating agents, materials suitability, and multi-metal recovery methods.

Keywords: Selective Chlorination, Limonitic Nickel Laterites, Chloride, Volatilization, Nickel and Cobalt Chlorides, Solid-State Chlorination, Chloro-Hydrometallurgy.

Highlights

- Selective chlorination enables Ni–Co volatilization while suppressing Fe chlorination.
- Solid-state routes (NaCl/$CaCl_2$) and Cl_2/HCl gas-phase pathways are critically compared.
- Mechanistic insights clarify Ni/Co chloride formation, stability, and mass-transfer limits.
- Chlorination integrates with Sc, Ti, and REE recovery from limonitic laterites.
- Key gaps include chloride recycling, corrosion control, and reactor-scale validation.

Graphical abstract



Chlorination unlocks selective volatilization of Ni and Co from Fe-rich limonites, enabiling new chloride-circuit flowsheets and **multi-metal recovery**

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1. Introduction

Nickel laterites make up over 70% of global nickel resources, but their industrial use remains limited due to low nickel grades, complex mineralogy, and high natural moisture content. Limonitic laterites, in particular, are rich in iron oxyhydroxides that contain nickel as finely dispersed substitutions or inclusions, making extraction difficult using conventional pyrometallurgical or hydrometallurgical methods (Fan et al.., 2010; Olanipekun, 2000). Although techniques like high-pressure acid leaching (HPAL), atmospheric leaching, and rotary kiln–electric furnace (RKEF) smelting are standard, each has significant disadvantages—including high acid consumption, high capital costs, impurity sensitivity, and limited selectivity—especially for ores with less than about 1.3 wt.% Ni (Chang et al.., 2012; Ribeiro et al.., 2022).

These constraints have renewed interest in chlorination and chloro-hydrometallurgical methods, which provide a fundamentally different thermochemical approach to extracting nickel. Solid–gas chlorination can convert nickel and cobalt oxides into volatile or water-soluble chlorides, enabling highly selective separation from iron-rich gangue. Early mechanistic studies showed that $NiCl_2$ and $CoCl_2$ readily form at moderate temperatures through reactions with Cl_2 or HCl (Kanungo & Mishra, 1997a; Ilić et al.., 2000a). Later research revealed that alkali and alkaline-earth chlorides, such as NaCl and $CaCl_2$, significantly improve chlorination efficiency by increasing metal mobility and promoting chloride-exchange reactions (Pintowantoro et al.., 2019; Xiao et al.., 2020).

The thermodynamic basis of these transformations is well established: nickel and cobalt chlorides possess significantly higher vapor pressures than iron chlorides under controlled oxygen–chlorine potentials, enabling selective volatilization or dissolution (Varley, 1969; Alvarez & Bohé, 2008). Reactive additives such as $CaCl_2$, $FeCl_3 \cdot 6H_2O$, and mixed chloride reagents further improve chlorination kinetics by disrupting the goethite-dominated structure of limonites, promoting salt–oxide interactions, and lowering the required chlorination temperature (Cui et al.., 2020; Sun et al.., 2019). These effects have been confirmed in both controlled-atmosphere experiments and industrially relevant roasting–segregation configurations (Zhou et al.., 2016; Tian et al.., 2022).

Recently, chlorination has expanded beyond selective volatilization to include segregation roasting, chloride-activated reduction–magnetic separation, and chloro-hydrometallurgical dissolution, greatly increasing the potential processing options for limonitic ores. Pilot- and bench-scale studies show that chloride-assisted roasting boosts metallization rates, improves the magnetic susceptibility of Ni–Fe phases, and aids in downstream upgrading (Ma et al.., 2017; Zheng et al.., 2014). At the same time, advances in HCl regeneration and chloride recycling have made closed-loop operation more practical, overcoming a major historical obstacle to industrial use (CN101306797B, 2011; Peek, 2011).

Chloride chemistry has also intersected with innovations in hydrometallurgy, including ionic liquids, deep eutectic solvents, and hybrid pyro-hydrometallurgical processes that enable selective dissolution of nickel and cobalt while limiting iron extraction (Fan et al.., 2011; Han et al.., 2021). At the same time, improved thermodynamic modeling of chloride-bearing systems is refining reactor design and process control (Senanayake et al.., 2022; Ge et al.., 2022).

Despite these advances, research on chlorination and chloro-hydrometallurgical processing remains fragmented and methodologically inconsistent. Variations in ore composition, particle size distribution, chlorinating atmospheres, reagent dosages, and thermal conditions result in significant differences in chloride formation, stability, and volatilization behavior. Many studies also lack rigorous kinetic treatment, complete mass balances, or integrated assessments of Fe- and Mg-rich by-products. Fundamental questions persist regarding solid-state diffusion pathways, salt–oxide interactions in goethitic matrices, and the stability of intermediate chloride species under industrially relevant conditions.

This heterogeneity highlights the importance of a structured analytical framework that can integrate these otherwise disparate findings. Despite extensive experimental and thermodynamic studies on laterite chlorination, the literature remains fragmented, with limited cross-comparison between solid-state, gas-phase, and chloro-hydrometallurgical routes. In particular, there is a lack of integrated analysis linking thermodynamic stability, volatilization behavior, mineralogical controls, and industrial feasibility. This review addresses this gap by providing a unified framework that critically compares chlorination pathways, evaluates their selectivity and technological readiness, and identifies key limitations and opportunities for industrial deployment.

The goal of this review is to analyze the mechanisms, thermodynamics, kinetics, and engineering strategies behind chlorination and chloro-hydrometallurgical routes for limonitic nickel laterites. It combines insights from selective chlorination, volatilization processes, chloride-activated roasting, and hybrid hydrometallurgical systems. By gathering evidence from over fifty years of research—from early volatilization studies (Yazawa & Kameda, 1967) to recent chloride reagent systems (Barrios et al.., 2022; Li et al.., 2024)—this review offers a strong framework for assessing process performance, selectivity, industrial viability, and future research directions. This manuscript is structured as a critical review, synthesizing thermodynamic, mechanistic, and engineering insights from the published literature rather than presenting new experimental data.

To support this evaluation, the following section explains the methodological approach used in this review, including the search strategy, inclusion and exclusion criteria, and the classification system employed to compare solid–gas chlorination, chloride-activated roasting, and chloro-hydrometallurgical pathways. It also clarifies the analytical parameters used to assess metallurgical performance, selectivity, environmental impacts, and technology readiness levels. This methodological foundation ensures consistent interpretation of the diverse literature and simplifies subsequent analysis of reaction mechanisms, thermodynamic factors, and the potential for industrial implementation (Gaballah & Djona, 1994, 1995; Gaballah et al., 1995).

2. Methodology (Review Strategy and Selection Criteria)

This review employed a structured, multi-stage approach to guarantee thorough and unbiased analysis of chlorination-based processing of limonitic nickel laterites. It was based on three main components standard in high-level review methods: search strategy, inclusion and exclusion criteria, and data extraction categories.

2.1. Search strategy

A systematic search was conducted across Web of Science, Scopus, ScienceDirect, SpringerLink, Wiley Online Library, Google Patents, and Espacenet. The time span covered over fifty years (1964–2024) to include both fundamental thermodynamic research and recent developments. Keywords used included: “nickel laterite chlorination,” “$NiCl_2$ volatilization,” “selective chlorination,” “segregation roasting,” “molten salt chlorination,” “chloride hydrometallurgy,” “HCl/Cl_2 roasting,” “Fe–Ni separation,” “chlorination thermodynamics,” and related variations.

Patent literature was included because of its historically important role in chloride-based processes.

2.2. Inclusion and Exclusion Criteria

Studies were included if they met at least one of the following criteria:

1. Reported chlorination, oxychlorination, or chloride-assisted roasting of limonitic laterites, goethite/hematite systems, or model Ni-bearing oxides.
2. Provided thermodynamic, kinetic, or mechanistic insights on Ni/Co chlorides, Fe chlorides, or chloride–oxide equilibria.
3. Examined molten-salt chlorination (e.g., NaCl, $CaCl_2$), gas-phase chlorination (Cl_2, HCl), segregation roasting, or hybrid chloride–hydrometallurgical systems.
4. Documented volatilization, dissolution, or migration behavior of chloride species.

Studies were excluded if they:

- Focused solely on saprolitic ores, sulfide concentrates, or non-chloride processing methods;
- Lacked extractable experimental, thermodynamic, or mechanistic data.
- Addressed catalytic or organic chlorination not related to metallurgical systems.ems.

2.3. Data Extraction and Normalization

From each selected source, the following variables were systematically extracted:

- Ore characteristics (mineralogy, Fe/Ni ratio, goethite–hematite distribution).
- Chlorinating agents and atmospheres (Cl_2, HCl, NaCl, $CaCl_2$, $FeCl_3{\cdot}6H_2O$, mixed salts).
- Operating parameters (T, pO_2/pCl_2, heating profiles, residence time).

- Mechanistic observations (phase evolution, Ni/Co chloride stability, Fe behavior).
- Performance metrics (Ni/Co volatilization %, extraction %, selectivity).
- Reactor type / process configuration.
- Post-chlorination treatment (condensation, dissolution, reduction).

These categories allowed cross-comparison despite the significant methodological diversity of published studies.

Full normalization procedures, parameter scaling, and extended methodology are included in the Supplementary Material.

2.4. Methodological Limitations

Several limitations inherent in the available literature were also considered when analyzing and comparing results across studies. A common issue is the incomplete reporting of chlorination atmospheres, especially regarding the fugacities of Cl_2 and HCl. This lack of detail hampers accurate reconstruction of oxygen–chlorine potentials and can lead to ambiguous mechanistic interpretations. Kinetic data are often limited or oversimplified despite the inherently complex multiphase reactions occurring in goethite- and hematite-rich matrices, which restricts the development of robust kinetic models. Significant differences in ore mineralogy, moisture-loss pathways, and structural transformations during heating further complicate direct comparisons between studies. Additionally, variations in sample preparation, reactor configuration, heating profiles, and gas-flow control introduce further uncertainties that impact reproducibility and comparability. Finally, despite decades of laboratory-scale research, large-scale or continuous demonstration studies remain rare, making it challenging to assess operational feasibility or industrial readiness. These limitations are acknowledged throughout the review and discussed where they directly influence mechanistic interpretation, performance evaluation, or process design. Having established the methodological constraints and the framework for interpreting diverse datasets, the review now turns to the fundamental thermodynamic principles that govern chlorination behavior. A thorough understanding of metal chloride stability, vapor pressures, and oxygen–chlorine potentials is essential before evaluating reaction pathways or process performance, and therefore forms the basis of Section 3.

3. Thermodynamic Foundations

Understanding the thermodynamic behavior of metal chlorides is crucial for analyzing chlorination pathways in limonitic nickel laterites. The formation, stability, and volatility of chloride species—especially $NiCl_2$ and $CoCl_2$—are influenced by oxygen–chlorine potentials, temperature, and the chemical environment created by solid or gaseous chlorinating agents (Kanungo & Mishra, 1997; Fan et al.., 2011; Peng et al.., 2018). These thermodynamic factors determine whether nickel and cobalt remain in solid form, form stable, non-volatile chlorides, or form volatile species that allow selective separation from the iron-rich matrix typical of limonitic ores (Mishra & Rao, 1989; Senanayake & Zhang, 2015). This section offers an analytical basis for the reaction mechanisms and process behaviors discussed in later sections.

3.1. Stability of Metal Chlorides in Chlorine–Oxygen Atmospheres

In oxidizing–chlorinating environments, metal oxides can undergo replacement reactions with Cl_2 or HCl to form respective chlorides. The spontaneity of these reactions is determined by the Gibbs free energy change ($\Delta G°$), which generally becomes more negative with increasing temperature for many late-transition-metal chlorides (Motzfeld, 1964; Senanayake & Zhang, 2015). Nickel and cobalt oxides easily react to produce $NiCl_2$ and $CoCl_2$ at moderate temperatures (around 400–800 °C), while iron oxides need much higher chlorine potentials to fully convert to $FeCl_2$ or $FeCl_3$ (Kanungo & Mishra, 1997; Peng et al.., 2018).

This difference in chloride stability is key to selective chlorination. Thermodynamic calculations and predominance diagrams for the Ni–Cl–O and Co–Cl–O systems show large stability ranges for $NiCl_2$ and $CoCl_2$ under conditions where iron mainly exists as Fe_2O_3, Fe_3O_4, or FeO (Yazawa & Kameda, 1967; Varley, 1969; Senanayake et al.., 2022). As a result, selective chlorination becomes possible when the process operates within a narrow range where nickel and cobalt chlorides are stable but iron chlorides are not, a fact confirmed in both model-oxide systems and actual laterites (Paredes et al.., 2012; Padilla et al.., 2013; Fan et al.., 2010).

To visually reinforce the stability relationships discussed above, Figure 1 shows the predominance fields of chloride and oxide species for the Ni–Cl–O and Fe–Cl–O systems under chlorinating–oxidizing conditions. These diagrams quickly demonstrate why $NiCl_2$ and $CoCl_2$ can be stabilized within moderate pCl_2–pO_2 ranges, while iron remains mainly in oxide form unless exposed to much higher chlorine potentials. This thermodynamic difference is the key reason for the selective chlorination of limonitic laterites.

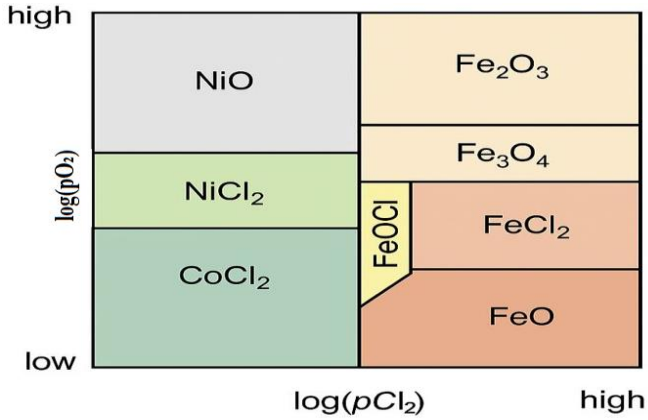

Figure 1. Predominance diagrams for the Ni–Cl–O and Fe–Cl–O systems showing the stability fields of major chloride and oxide species as a function of log (pCl_2) and log (pO_2). Adapted from Motzfeld (1964), Yazawa & Kameda (1967), Senanayake & Zhang (2015), and Senanayake et al.. (2022).

From a comparative perspective, thermodynamics alone does not differentiate the industrial attractiveness of solid-state versus gas-phase chlorination. While both routes exploit the stability of $NiCl_2$, gas-phase systems offer superior selectivity through controlled volatilization. In contrast, molten-salt-assisted solid-state routes benefit from lower chlorine partial pressures and simpler reactor configurations. These distinctions become critical when evaluating scalability, corrosion risks, and reagent recycling strategies.

Taken together, these dominance fields define the thermodynamic limits within which selective chlorination becomes possible. However, chloride stability alone does not ensure efficient separation: the ability of $NiCl_2$ and $CoCl_2$ to volatilize during roasting is equally crucial. The next subsection thus explores the vapor-pressure behavior and volatilization kinetics of key metal chlorides, showing how thermodynamic stability translates into practical transport and separation during roasting.

3.2. Volatilization Behavior and Vapor Pressure Constraints

A key advantage of chlorination for Ni/Co extraction is the volatility of the resulting chlorides. Both $NiCl_2$ and $CoCl_2$ have high vapor pressures at temperatures relevant to roasting, allowing their removal from the ore as gases or condensable aerosols (Motzfeld, 1964; Mishra & Rao, 1989). In contrast, iron chlorides either need higher chlorine potentials to form or decompose before they can volatilize under the same conditions, which limits their transport in selective chlorination processes (Varley, 1969; Alvarez & Bohé, 2008). Consequently, volatilization strongly influences selectivity in chloride volatilization and segregation roasting flowsheets (Mishra & Rao, 1989; Ge et al.., 2022).

The vapor pressure of $NiCl_2$ rises logarithmically with temperature, allowing meaningful industrial transport above roughly 800 °C; $CoCl_2$ behaves similarly but with slightly higher volatility (Motzfeld, 1964; Senanayake & Zhang, 2015). Maintaining proper pCl_2/pO_2 ratios ensures chlorides remain in the vapor phase rather than forming oxychlorides or reverting to oxides, as shown in fundamental thermogravimetric studies and applied roasting experiments (Titi-Manyaka & Iwasaki, 1976; Wang et al.., 2009; Chepushtanova et al.., 2025). This thermodynamic behavior underpins volatilization-based purification methods and segregation roasting flowsheets, where metal chlorides migrate toward reductants or metallic iron particles (Hoover, 1975; Xu et al.., 2017).

To contextualize the volatilization behavior discussed above, the key thermodynamic parameters governing the stability and vapor transport of major metal chlorides are summarized in Table 1.

Table 1. Thermodynamic Properties of Key Metal Chlorides Relevant to Laterite Chlorination. Adapted from *Motzfeld (1964), Yazawa & Kameda (1967), Senanayake & Zhang (2015).*

Metal Chloride	Approx. Formation Temperature Range	ΔG° of Chloriation (kJ/mol)	Vapor Pressure at 800 °C	Thermodynamic Stability (Relative)
$CoCl_2$	Forms readily at 350–750 °C	–75 / –82 / –90 (400/600/800 °C)	~10^{-1}–10^{0} atm	Very high
$NiCl_2$	Forms readily at 400–800 °C	–65 / –72 / –85 (400/600/800 °C)	~10^{-2}–10^{-1} atm	High
$FeCl_2$	Requires elevated pCl_2; unstable above ~700 °C unless strongly chlorinating	–25 / –30 / –35 (400/600/800 °C)	~10^{-4} atm	Low
$FeCl_3$	Forms at low temperatures but decomposes above ~450–500 °C; unstable at roasting conditions	–110 / –118 / decomposes	Decomposes before significant vaporization	Very low at roasting conditions

These contrasting stability fields and vapor pressures explain why $NiCl_2$ and $CoCl_2$ vaporize efficiently at temperatures above ~800 °C, whereas iron chlorides either stay non-volatile ($FeCl_2$) or decompose during roasting ($FeCl_3$).l_3).

3.3. Influence of Oxygen–Chlorine Potential

The oxygen–chlorine potential (pO_2–pCl_2 balance) is one of the most important thermodynamic parameters in chlorination metallurgy. High pCl_2 encourages chloride formation but also increases corrosion risks and may unintentionally chlorinate iron, reducing selectivity; high pO_2 reduces chloride volatilization by stabilizing oxides or oxychlorides (Rojas et al.., 2017; Peng et al.., 2018). Optimal selectivity for Ni and Co occurs in intermediate conditions where $NiCl_2$ and $CoCl_2$ are stable, $FeCl_2/FeCl_3$ are thermodynamically unfavorable, and oxychloride formation is minimized (Senanayake & Zhang, 2015; Senanayake et al.., 2022).

In practical systems, this balance is affected by reagent type (Cl_2, HCl, $CaCl_2$, $FeCl_3 \cdot 6H_2O$), gas flow rate, sample porosity, heating rate, and catalytic effects from ore components such as hematite or silica (Han et al.., 2021;

Roca et al.., 2016). The dynamic changes of pCl_2 and pO_2 during roasting mean that achieving stable selectivity often requires carefully controlled addition of chloride donors and, in some systems, buffering with inert gases or oxygen bleed streams (Adam & Iwasaki, 1984; Ge et al.., 2022). These limitations are especially noticeable in laterite and nickel-concentrate systems, where multiphase transformations and the gradual dehydroxylation of goethite alter the local chemical environment as temperature rises (Mukherjee, 1985; Li et al.., 2016).

The relative thermodynamic stability of chloride and oxide species can be visualized by comparing the standard Gibbs free energies of formation (ΔGf°) for each class of compounds. Figure 2 maps ΔGf°(chloride) against ΔGf°(oxide), providing a clear thermodynamic basis for understanding why certain metals—including Ni and Co—chlorinate readily under moderate pCl_2/pO_2 ratios, while others remain predominantly in oxide form.

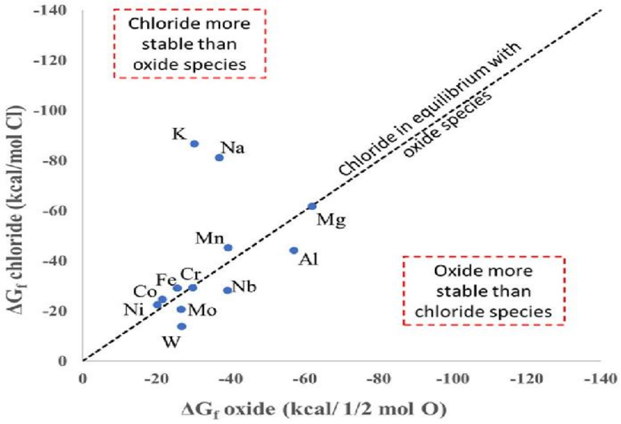

Figure 2. Stability Map of Metal Oxides vs. Metal Chlorides. Adapted from Motzfeld (1964).

3.4. Role of Solid Chloride Additives (NaCl, $CaCl_2$, $FeCl_3 \cdot 6H_2O$)

Solid chloride reagents enable alternative chlorination pathways by modifying local chemical potentials and introducing solid–solid and solid–liquid diffusion mechanisms. NaCl and $CaCl_2$ can form transient eutectic or molten-salt phases at elevated temperatures, which enhance ionic mobility and allow the formation of $NiCl_2$ even when gaseous chlorine is absent or minimal (Padilla et al.., 2013; Segura et al.., 2013). Selective chlorination of limonitic and saprolitic laterites using NaCl, $CaCl_2$, or mixed salts has shown that these additives significantly lower the temperature needed for chloride formation and improve Ni/Co extraction efficiency (Paredes et al.., 2012; Lin et al.., 2019; Ma et al.., 2021).

$CaCl_2$, in particular, acts as an effective chlorinating agent for Co and Ni oxides while only weakly affecting iron oxides at moderate temperatures—further enhancing selectivity in both laterite and model-oxide systems (Han et al.., 2023; Pintowantoro et al.., 2019; Zhou et al.., 2016). $FeCl_3 \cdot 6H_2O$ behaves differently, serving as both a chlorinating and oxidizing agent: upon decomposition, it releases $FeCl_3$ vapor and HCl, creating localized high-pCl_2 environments that promote rapid chlorination of Ni-bearing phases (Liu et al.., 2022; Cui et al.., 2020). These effects are especially significant in segregation roasting and Fe-assisted systems, where chloride migration and interparticle reactions influence metal upgrading efficiency (Stopić et al.., 2002; Krstev et al.., 1988; Ilić et al.., 1997).

3.5. Implications for Process Design

The thermodynamic principles discussed earlier directly influence how you select operating parameters for chlorination-based processing. Temperature ranges should be chosen to maximize $NiCl_2$ and $CoCl_2$ formation while minimizing the volatility or formation of iron chlorides (Fan et al.., 2010; Chang et al.., 2012; Li et al.., 2016). Gas compositions need to be controlled to maintain favorable pCl_2/pO_2 ratios that promote selective chlorination and volatilization without excessive formation of Fe chlorides or oxychlorides (Peng et al.., 2018; Senanayake & Zhang, 2015). The choice and amount of solid or gaseous chlorinating agents should reflect both the ore mineralogy and the intended chlorination mechanism—whether volatilization, segregation, or dissolution—an aspect often emphasized in pilot-scale studies combining chloride roasting with reduction and magnetic separation (Liu et al.., 2010; Ma et al.., 2017; Zhou et al.., 2016; Zheng et al.., 2014).

Thermodynamic constraints also guide engineering decisions such as reactor design, corrosion mitigation strategies, off-gas handling, and HCl regeneration (Norgate et al.., 2011; Peek, 2011; Jena & Brocchi, 1997). The ability to predict chloride stability fields and volatilization behavior allows for more accurate modeling of industrial roasting and chlorination reactors, enhancing both selectivity and energy efficiency while clarifying the trade-offs between chloride-based flowsheets and traditional laterite processing methods (Ribeiro et al.., 2022; Rinne et al.., 2025).

Despite the solid thermodynamic foundation outlined here, significant gaps and uncertainties still limit the predictive capability of current models for chlorination-based processing of limonitic laterites. Much of the available thermodynamic data for metal chlorides comes from simplified systems or high-temperature measurements on pure compounds, whereas real laterites involve complex, multiphase matrices with goethite–hematite intergrowths, silica-rich gangue, and Mg-bearing phases that can affect local activities and reaction pathways. Activity models and predominance diagrams often overlook the effects of molten salt phases, transient eutectics, and solid–liquid interfaces created by NaCl, $CaCl_2$, or $FeCl_3 \cdot 6H_2O$, even though these features demonstrably influence chlorination kinetics and selectivity. Additionally, only a few studies incorporate detailed thermodynamic analysis with in situ measurements of gas composition, phase evolution, or vapor transport, making it difficult to validate pCl_2–pO_2 control strategies under real conditions. Consequently, thermodynamic assessments are often used retrospectively to explain experimental results rather than prospectively to define operating ranges and reactor designs. Overcoming these limitations—by improving databases, integrating thermo–kinetic modeling, and employing in situ characterization—is essential for translating chloride thermodynamics into reliable, industrial-scale process designs. Taken together, these thermodynamic principles set the boundary conditions for the selective chlorination of limonitic nickel laterites, defining the temperature ranges, chloride potentials, and stability fields that govern the formation and volatilization of $NiCl_2$ and $CoCl_2$. However, thermodynamics alone cannot fully explain the behavior observed in practical systems, where reaction pathways are heavily influenced by mineralogical heterogeneity, heat- and mass-transfer constraints, molten-salt formation, and solid–gas diffusion barriers. To understand how these factors interact to produce the chlorination patterns reported in the literature—whether through volatilization, segregation, or chloride-assisted reduction—it is necessary to analyze the underlying reaction mechanisms and phase-evolution sequences under actual roasting conditions. The following section builds on the thermodynamic foundation provided here by examining the mechanistic pathways, intermediate species, and solid-state transformations that determine chlorination efficiency and selectivity in limonitic laterite systems.

4. Chlorination-Based Processing Routes for Nickel in Limonitic Laterites

Chlorination has re-emerged as a selective and energy-efficient method for upgrading limonitic laterites, which are mainly composed of goethite, hematite, silica-rich gangue, and ultrafine Ni-bearing phases dispersed within Fe-oxyhydroxide matrices. Several studies have shown that transforming NiO into $NiCl_2$ under controlled pCl_2–pO_2–T conditions offers a powerful way to separate nickel from iron-rich structures that are otherwise resistant to reductive or acid-based processing (Mishra & Rao, 1989; Kanungo & Mishra, 1997; Senanayake & Zhang, 2015).

To help visualize the thermodynamic basis for selective nickel chlorination, Figure 4 shows predominance diagrams for the Ni–Cl–O and Fe–Cl–O systems. These diagrams clearly demonstrate that $NiCl_2$ becomes stable at moderately low pO_2 and high pCl_2, while Fe tends to stay in oxide form across nearly all chlorination conditions relevant to laterite processing. This contrasting thermodynamic behavior underpins the fundamental selectivity used in all chlorination-based upgrading methods.

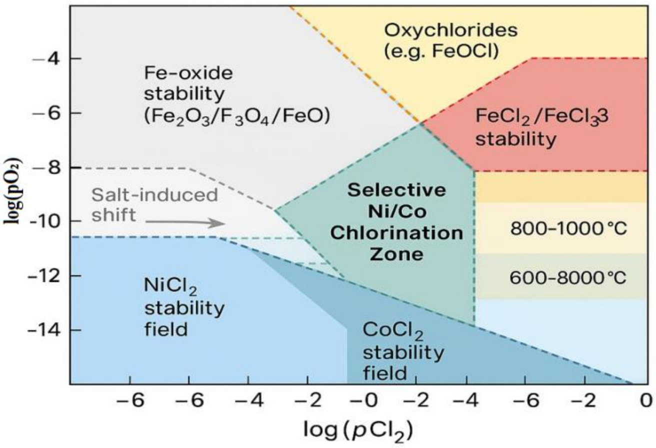

Figure 3. redominance diagrams for the (a) Ni–Cl–O and (b) Fe–Cl–O systems, plotted as $\log(pCl_2)$ vs. $\log(pO_2)$.Adapted from Yazawa & Kameda (1967); Varley (1969); Mishra & Rao (1989); Fan et al.. (2010); Peng et al.. (2018).

The thermodynamic preference for chloride formation—confirmed through predominance diagrams and ΔG° evaluations for the Ni–Cl–O system—indicates that $NiCl_2$ becomes stable and, above approximately 750–800 °C, sufficiently volatile to enable migration, condensation, or chlorination-assisted segregation, while iron mainly remains in oxide form (Yazawa & Kameda, 1967; Varley, 1969; Fan et al.., 2010; Peng et al.., 2018). This difference in chloride stability and volatility underpins the whole rationale for chlorination-based processing methods.

To quantitatively support the thermodynamic trends discussed above, Table 2 summarizes key Gibbs free energies of formation and vapor-pressure data for major metal chlorides relevant to limonitic laterites. These values emphasize the strong stability and volatility of $NiCl_2$ (and $CoCl_2$) compared to Fe chlorides, reinforcing the fundamental basis for selective nickel chlorination.

Table 2. Thermodynamic Properties of Key Metal Chlorides Relevant to Limonite Chlorination. Adapted from Motzfeld (1964), Mishra & Rao (1989), Fan et al.. (2010), and Peng et al.. (2018).

Species	ΔG°f (400 °C) (kJ/mol)	ΔG°f (600 °C) (kJ/mol)	ΔG°f (800 °C) (kJ/mol)	Vapor pressure at 800–900 °C	Notes on stability
$NiCl_2$(s/g)	–260 to –290	–220 to –250	–180 to –210	10^{-2} to 10^{-1} atm (high volatility)	Highly stable at moderate pCl_2; volatilizes above ~750–800 °C
$CoCl_2$(s/g)	–300 to –330	–260 to –290	–220 to –250	~10^{-1} atm (very high volatility)	More volatile than $NiCl_2$; co-migrates with $NiCl_2$ during roasting
$FeCl_2$(s)	–180 to –200	–150 to –170	–120 to –140	<10^{-6} atm (negligible)	Thermodynamically unstable in typical roasting pO_2; decomposes back to oxides
$FeCl_3$(s)	–250 to –270	–210 to –230	–170 to –200	Not volatile; decomposes	Converts to Fe_2O_3/Fe_3O_4 above ~500–600 °C; unstable in most chlorination windows

Experimental work on both model oxides and natural laterites has confirmed that selective nickel chlorination can be achieved through a combination of salt-assisted reactions (NaCl, $CaCl_2$), direct gas-phase chlorination (Cl_2, HCl), and hybrid pathways involving molten chloride intermediates—approaches that significantly enhance Ni mobility while reducing Fe chlorination (Paredes et al.., 2012; Padilla et al.., 2013; Segura et al.., 2013; Lin et al.., 2019; Ma et al.., 2021). In particular, the presence of transient molten-salt phases or in situ formation of reactive chlorinating species has been identified as a key factor influencing $NiCl_2$ production and volatilization efficiency (Han et al.., 2023; Liu et al.., 2022; Cui et al.., 2020).

Together, these thermodynamic and mechanistic insights lay the groundwork for the chlorination methods described in the following sections—ranging from solid-state chlorination to gas-phase volatilization and low-temperature chloro-hydrometallurgical dissolution—each taking advantage of the selective stability of $NiCl_2$ over Fe chlorides to upgrade nickel from limonitic ores.

4.1. Thermodynamic Basis for Selective Nickel Chlorination

Chlorination reactions in limonites follow trends dictated by the interplay of temperature, chloride potential, and oxide stability:

- $NiCl_2$ formation is strongly favored between 350–750 °C at moderate pCl_2, with $\Delta G°$ values significantly more negative than those of Fe chlorides (Kanungo & Mishra, 1997; Senanayake & Zhang, 2015).
- Fe chlorination is limited because $FeCl_3$ easily decomposes into Fe_2O_3 at temperatures above approximately 500–600 °C, which restricts volatilization (Varley, 1969; Peng et al.., 2018; Sahu et al.., 2005).
- The hydrolysis of $NiCl_2$ is a key concern in poorly dehydrated ores, requiring controlled dehydroxylation of goethite to prevent the re-formation of NiO (Mishra & Rao, 1989).

These conditions create a selective volatilization window where $NiCl_2$ is mobile while Fe remains immobilized, a behavior repeatedly confirmed in experimental roasting and TGA studies (Titi-Manyaka & Iwasaki, 1976; Wang et al.., 2009; Chepushtanova et al.., 2025).

4.2. Chlorination Routes Applied Directly to Nickel in Limonitic Ores

Three broad process families have been developed:

- Solid-state chlorination (NaCl, $CaCl_2$, NH_4Cl, $FeCl_3{\cdot}6H_2O$).

Figure 5 summarizes the three main chlorination methods used for limonitic laterites, showing their operating temperature ranges, key reagents, main nickel-bearing products, and typical recovery rates. This comparison helps provide context for the mechanistic discussion in the following subsections.

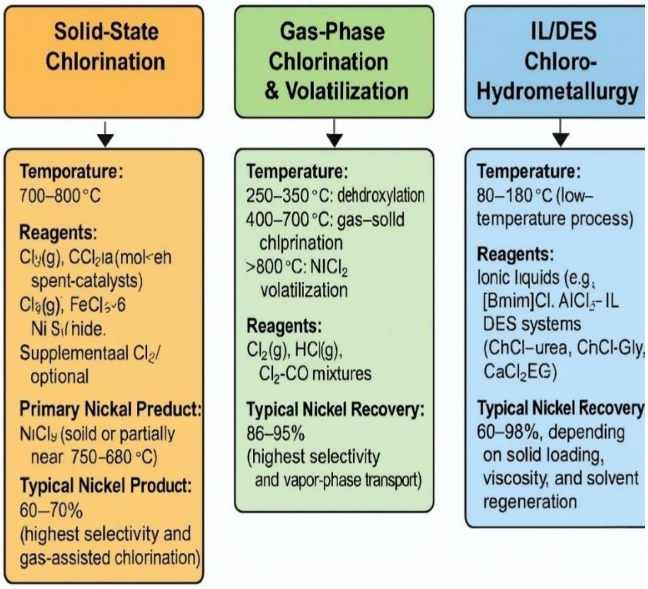

Figure 4. Solid-State vs. Gas-Phase vs. Chloro-Hydrometallurgy. Adapted from Mishra & Rao (1989); Kanungo & Mishra (1997); Paredes et al.. (2012); Segura et al.. (2013); Lin et al.. (2019); Roca et al.. (2016).

- Gas-phase chlorination and volatilization (Cl_2, HCl, Cl_2–CO mixtures).
- Chloro-hydrometallurgical dissolution using ionic liquids (ILs) or deep eutectic solvents (DES).

Each approach leverages different aspects of $NiCl_2$ stability, mobility, or solubility.

4.3. Solid-State Chlorination (NaCl / $CaCl_2$ / HCl / Cl_2)

Solid-state chlorination plays a key role in the targeted upgrading of nickel from limonitic laterites. Experimental research has shown that systems containing NaCl or $CaCl_2$ form eutectic or molten-salt films at 500–650 °C, thereby greatly improving ionic mobility and diffusion-controlled reactions (Padilla et al.., 2013; Segura et al.., 2013). The creation of these temporary molten phases encourages:

- Rapid conversion of **NiO** and Ni-bearing silicates into **$NiCl_2$**.
- Stabilization of iron as **Fe_2O_3/Fe_3O_4**, thereby preventing undesirable Fe chlorination.
- Reduced activation energy compared with purely gas–solid chlorination routes.

Gas-assisted chlorination with Cl_2 or HCl enhances selectivity and reaction rates. As shown in traditional oxide-model studies (Kanungo & Mishra, 1997; Fan et al.., 2011; Peng et al.., 2018), gas–solid reactions occur quickly after the ore is dehydroxylated, allowing efficient $NiCl_2$ formation while Fe stays largely inactive under moderate pCl_2–pO_2 conditions.

Volatility and Selectivity

A key benefit of solid-state and hybrid chlorination is the favorable volatility profile of nickel and cobalt chlorides. $NiCl_2$ and $CoCl_2$ show significantly higher vapor pressures throughout the roasting temperature range compared to $FeCl_2$ and $FeCl_3$ (Motzfeld, 1964; Mishra & Rao, 1989). This difference ensures:

- Efficient volatilization and downstream recovery of Ni and Co.
- Minimal Fe entrainment in the vapor phase, reinforcing overall process selectivity.

Performance on Natural Limonites

Pilot-scale and laboratory experiments indicate that 85–95% of nickel can be volatilized or extracted when limonites are processed with optimized $NaCl/CaCl_2$–Cl_2 systems (Paredes et al.., 2012; Lin et al.., 2019; Ma et al.., 2021). These high extraction efficiencies highlight the combined effects of molten-salt transport, gas–solid chlorination, and the selective volatilization of $NiCl_2$.

To illustrate the temperature dependence of selective nickel chlorination, Figure 6 displays the typical Ni extraction profile observed in $NaCl/CaCl_2$–Cl_2 systems. The sigmoidal shape indicates the combined effects of dehydroxylation, molten-salt film formation, gas–solid chlorination, and the start of $NiCl_2$ volatilization at higher temperatures.

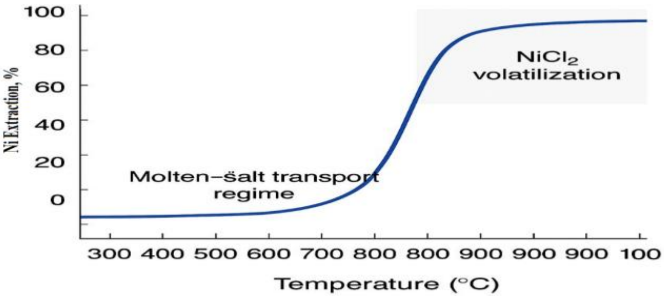

Figure 5. Temperature-dependent Ni extraction in $NaCl/CaCl_2$–Cl_2 chlorination systems. Adapted from Paredes et al.. (2012); Segura et al.. (2013); Lin et al.. (2019); Ma et al.. (2021).

Limitations

Despite its advantages, solid-state chlorination presents operational challenges:

- **Chloride-induced corrosion**, particularly in reactor linings and off-gas components (Ge et al.., 2022).
- Stringent requirements for **moisture and CO_2 control**, due to hydrolysis risks and carbonate formation.
- Potential **co-volatilization of minor elements** such as Cr or Al in ores with specific mineralogical compositions.

These limitations highlight the need for precise temperature regulation, durable construction materials, and customized reagent dosing strategies in industrial settings.

Operational limitations in chlorination-based processes are heavily affected by corrosion issues, degradation of reactor materials, and gas–solid compatibility at high temperatures. Table 3 outlines the main material challenges identified in laboratory and pilot-scale studies, along with recommended mitigation strategies.

Table 3. Corrosion and Operational Challenges in Chlorination Processes. Adapted from Peng et al.. (2018); Ge et al.. (2022); Mishra & Rao (1989); Varley (1969).

Material	Corrosion / Degradation Mechanism	Critical Temperature Range	Mitigation Strategy
Stainless steel (304/316)	Cl_2-induced stress cracking and pitting; rapid loss of mechanical integrity	< 400 °C in Cl_2/HCl environments	Replace with SiC, high-nickel alloys, or ceramic components; avoid direct halogen exposure
Al_2O_3 refractories (standard bricks)	Pitting and chemical attack by molten or vapor-phase chlorides (NaCl, $CaCl_2$, $FeCl_x$)	600–900 °C	Use dense alumina linings, Al_2O_3–SiC composites, or high-purity (>99%) corundum blocks
Graphite and carbon-based components	Oxidation by Cl_2 and chlorinated species leading to rapid mass loss	> 500 °C	Maintain reducing atmosphere or N_2 purge; avoid graphite in oxidizing/chlorinating zones
Nickel-based alloys (Inconel, Hastelloy)	Halogen embrittlement; intergranular attack under $pCl_2 > 10^{-3}$ atm	500–800 °C	Use protective ceramic coatings; limit mechanical stress; operate under controlled pO_2
Silicon carbide (SiC)	Slow volatilization via $SiCl_4$ formation under high pCl_2	> 900 °C	Maintain moderate chloride potential; use SiC with oxide-forming surface layers
Quartz tubes / SiO_2 components	Rapid conversion to volatile $SiCl_4$; catastrophic structural loss	> 400 °C	Avoid SiO_2 entirely in high-chlorine environments; replace with Al_2O_3 or SiC
Mild steel / carbon steel	Uniform corrosion in presence of HCl(g) and chlorinated condensates	200–500 °C	Use corrosion-resistant linings; avoid HCl condensation regions

4.4. Gas-Phase Chlorination & $NiCl_2$ Volatilization

Gas-phase chlorination is the most selective and thermodynamically controlled method for upgrading nickel from limonitic laterites. This technique allows for continuous chlorination, volatilization, and condensation of $NiCl_2$, effectively utilizing the stability fields and vapor-pressure properties outlined in classical and modern research (Motzfeld, 1964; Mishra & Rao, 1989; Peng et al.., 2018).

Process Steps

Gas-phase chlorination flowcharts usually follow a multi-step thermal process:

Dehydroxylation of limonite (250–350 °C):

- Removing structural water from goethite and related phases prevents hydrolysis of $NiCl_2$ and ensures clean gas–solid reaction interfaces.

Gas–solid chlorination (400–700 °C):

- Introducing Cl_2 or HCl quickly transforms NiO and Ni-bearing silicates into $NiCl_2$, following kinetic patterns previously identified in oxide-model systems (Kanungo & Mishra, 1997; Fan et al.., 2011; Peng et al.., 2018).

Volatilization (>800 °C):

- Once formed, $NiCl_2$ reaches enough vapor pressure—consistent with the log P–1/T behavior reported by Motzfeld (1964)—to vaporize and move through the reactor or gas stream.

Condensation:

- $NiCl_2$ vapors are collected in controlled cooling columns, creating a purified chloride fraction suitable for downstream hydrometallurgical processing.

Cl_2 regeneration:

- HCl produced during roasting or condensation is oxidized back to Cl_2, usually through Deacon-type reactions, allowing for partial or complete closure of the chlorine loop.

Selectivity Basis

The inherent selectivity of this route arises from the limited stability and very low vapor pressure of Fe chlorides within the operating pCl_2–pO_2–T regime.

Studies show that $FeCl_2$ and $FeCl_3$ are either thermodynamically unstable or non-volatile during roasting temperatures, ensuring effective nickel–iron separation.

Advantages

Gas-phase chlorination offers several key benefits:

- High-purity $NiCl_2$ production with minimal entrainment of Fe and gangue elements.
- Very low solid residue production because most Ni and Co vaporize.
- Direct compatibility with hydrometallurgical recovery, including aqueous dissolution of $NiCl_2$ and electrochemical methods.

Challenges

The method also poses significant engineering and operational challenges:

- Severe corrosion risks necessitate the use of advanced refractories and halogen-resistant alloys in reactor design.
- Complex halogen-handling infrastructure, including gas-tight seals, scrubbers, condensers, and Cl_2 regeneration units.
- Safety considerations related to high-temperature chlorine environments.nts.

4.5. Chloro-Hydrometallurgical Routes for Nickel (ILs and DES)

Although still less developed industrially, ionic liquids (ILs) and deep eutectic solvents (DES) have attracted interest as alternative chlorination and dissolution agents for extracting nickel from limonitic laterites at low temperatures with high selectivity over iron. Their effectiveness stems from the chloride-rich liquid phases' ability to stabilize Ni in chloro-complex form while minimizing Fe dissolution—an outcome consistent with findings from chloride thermodynamics and solid-state chlorination studies (Roca et al.., 2016; Stopić et al.., 2002; Ge et al.., 2022).

4.5.1. Ionic Liquids (ILs)

In chloride-based IL systems—such as [Bmim]Cl, $AlCl_3$–IL mixtures, and structurally related molten-salt analogues—nickel forms stable tetrahedral complexes.$[NiCl_4]^{2-}$

The molecular structure of the tetrachloronickelate(II) complex is depicted in Figure 7. This tetrahedral Ni–Cl coordination environment is typical of chloride-rich ionic liquids and is key in stabilizing Ni in solution while preventing iron dissolution.

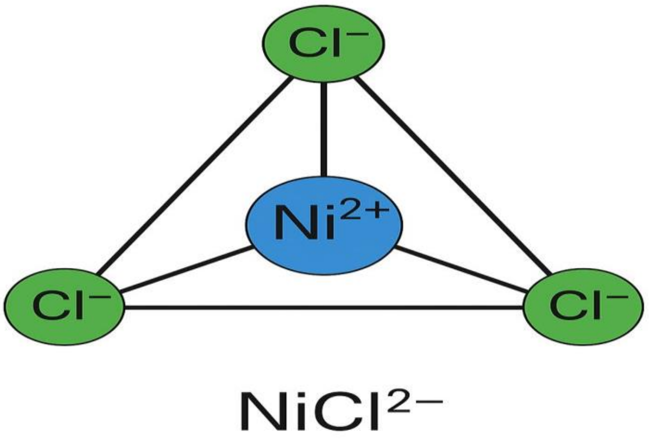

Figure 6. Schematic representation of the $[NiCl_4]^{2-}$ complex, showing the tetrahedral coordination of Ni^{2+} by four chloride ligands in ionic-liquid media. Adapted from Stopić et al.. (2002); Roca et al.. (2016); Ge et al.. (2022).

This coordination environment facilitates efficient solubilization of Ni even at mild temperatures (80–180 °C). In contrast, iron usually polymerizes into oxide–chloride networks or Fe-rich gels that have very limited solubility, leading to Ni/Fe separation efficiencies exceeding 95% (Stopić et al.., 2002; Roca et al.., 2016).

These systems also prevent $NiCl_2$ volatilization, which is an important advantage when working with low-grade limonites where maximizing Ni retention is crucial.

Key Advantages:

- High selectivity for Ni over Fe, Al, and Cr.
- Operation at moderate temperatures, reducing energy demand.
- Minimal volatilization or chloride loss.

Main Limitations:

- Elevated cost and long-term stability issues of ILs.
- High viscosity, which limits solid loading and increases reaction time.
- Regeneration/recycling complexity, particularly in chloride-rich IL systems.

4.5.2. Deep Eutectic Solvents (DES)

DES systems—including ChCl–urea, ChCl–ethylene glycol (EG), and ChCl–$CaCl_2$—have become more affordable and environmentally friendly options compared to ILs. In these solvents, the in situ formation of active chloride species and strong hydrogen-bonding environments help dissolve Ni from limonite after mild pre-activation or roasting (Roca et al.., 2016; Ge et al.., 2022).

Advantages:

- Lower cost compared to ILs and traditional hydrometallurgical reagents.
- Designing green solvents with low toxicity and biodegradability.
- Possible integration with nickel electrowinning due to the stability of chloride-based complexation.

Challenges:

- High moisture sensitivity affects chloride activity and solvent structure.
- Slower kinetics when processing raw limonitic ores without pre-treatment.
- Limited evidence for scale-up, with almost no pilot-scale demonstrations documented in the literature.

4.6. Recovery of Companion Metals During Nickel Chlorination

Although chlorination primarily targets nickel upgrading, the thermochemical environment created during roasting also affects the behavior of several related elements. Selective chloride formation, differences in volatility, and solubility all determine which species become vapor, dissolve in chloride-rich solutions, or stay in the solid residue.

The chlorination environment not only affects nickel behavior but also significantly affects the volatilization, solubility, and partitioning of associated metals in limonitic laterites. Table 4 summarizes the thermodynamic tendencies of Co, Sc, and Fe under typical pCl_2–pO_2–T conditions, offering a comparative basis for understanding their recovery processes during nickel chlorination.

Table 4. Behavior of Companion Metals (Co, Sc, Fe) During Chlorination of Limonitic Laterites. Adapted from Mishra & Rao (1989); Paredes et al.. (2012); Roca et al.. (2016); Peng et al.. (2018).

Element	Chloride Formed	Volatility	Solubility in Aqueous / IL / DES Media	Recovery Route
Ni	$NiCl_2$	High (volatile above ~750–800 °C)	Moderate	Vapor-phase transport + leaching of condensed $NiCl_2$
Co	$CoCl_2$	Very high (volatilizes more readily than $NiCl_2$)	Moderate	Vapor-phase transport; co-condensation with $NiCl_2$
Sc	$ScCl_3$	Low (non-volatile under roasting conditions)	Very high in chloride-rich solutions	Selective leaching of roasted residue or IL/DES dissolution
Fe	$FeCl_2$ / $FeCl_3$ (unstable)	Very low; $FeCl_3$ decomposes, $FeCl_2$ non-volatile	Low	Remains in solid oxide form (Fe_2O_3 / Fe_3O_4)

Cobalt

Cobalt closely follows the chlorination behavior of nickel. Studies consistently show that CoO easily converts to $CoCl_2$ under the same pCl_2–pO_2–T conditions used for Ni chlorination (Motzfeld, 1964; Mishra & Rao, 1989; Senanayake & Zhang, 2015).

Since $CoCl_2$ is somewhat more volatile than $NiCl_2$, cobalt is effectively transported during volatilization or segregation roasting processes. In well-optimized systems, Ni and Co often co-migrate as mixed chloride vapors, aiding their combined downstream recovery.

Scandium

Scandium, often contained within goethite–hematite matrices, is partly released during the dehydroxylation and breakdown of Fe oxyhydroxides. Under chlorinating conditions, Sc forms $ScCl_3$, a chloride that, while not volatile during roasting, has high solubility in aqueous and ionic-liquid environments (Paredes et al.., 2012; Roca et al.., 2016).

As a result, Sc can be recovered through selective leaching of roasted residues or by direct extraction in IL/DES media, providing a potentially valuable by-product stream.

Iron

Iron plays a crucial role in maintaining selectivity. During the typical chlorination process for Ni upgrading, Fe mainly exists as Fe_2O_3, Fe_3O_4, or partially reduced FeO because $FeCl_2$ and $FeCl_3$ are thermodynamically unstable or non-volatile across the operational temperature range (Varley, 1969; Peng et al.., 2018).

This preferential retention of iron in solid form is crucial to prevent contamination of Ni/Co chloride vapors and to ensure the overall efficiency of the chlorination process.

4.7. Comparative Assessment of Chlorination Routes for Nickel

Table 5 offers a comparison of the main chlorination methods used for nickel recovery from limonitic laterites. The analysis highlights the operating temperature ranges, the extent to which each method selectively favors Ni over Fe, and the key strengths and weaknesses of each approach. Together, these methods demonstrate the trade-offs between high-temperature volatilization and emerging low-temperature chloro-hydrometallurgical systems.

Table 5. Comparative assessment of major chlorination routes for nickel recovery from limonitic laterites. Adapted from: Mishra & Rao (1989); Kanungo & Mishra (1997); Segura et al.. (2013); Padilla et al.. (2013); Paredes et al.. (2012); Lin et al.. (2019); Ma et al.. (2021); Roca et al.. (2016); Ge et al.. (2022).

Route	T (°C)	Nickel Selectivity	Strengths	Weaknesses
Solid-state chlorination	450–900	High	Low-cost, scalable, works for low-grade limonite	Sensitive to moisture; corrosion
Gas-phase chlorination	400–950	Very High	Best pathway for selective $NiCl_2$ volatilization	Cl-handling complexity
IL chloro-hydrometallurgy	80–180	Very High	Green, low-temperature	Solvent cost & regeneration
DES chloro-hydrometallurgy	90–150	High	Low cost, benign	Slower kinetics

4.8. Outlook for Nickel Chlorination in Limonitic Laterites

Future progress in chloride-based processing of limonitic laterites will rely on bridging the gap between laboratory-scale demonstrations and industrial feasibility. Several key research directions have emerged from recent thermodynamic, kinetic, and process studies (Mishra & Rao, 1989; Kanungo & Mishra, 1997; Senanayake & Zhang, 2015; Peng et al.., 2018; Ge et al.., 2022):

Pilot-scale validation of gas-phase $NiCl_2$ volatilization systems.

- Although small-scale experiments have shown high selectivity for Ni volatilization (Motzfeld, 1964; Paredes et al.., 2012; Lin et al.., 2019; Ma et al.., 2021), continuous operation with controlled pCl_2–pO_2, vapor transport, and staged condensation remains largely untested at capacities relevant to industry.

Development of chloride-resistant reactor materials.

- The high corrosivity of Cl_2/HCl at roasting temperatures (Ge et al.., 2022) necessitates improved refractories and ceramics—such as dense Al_2O_3 linings and SiC-based components—to enhance reactor lifetime and reduce operational downtime.

Integration of hybrid chloride flow sheets.

- Coupling chlorination, $NiCl_2$ volatilization and condensation, dissolution in aqueous or IL/DES media, and final electrowinning provides a modular pathway from ore to metal. Studies of $NiCl_2$ solubility and chloro-complex stability (Stopić et al.., 2002; Roca et al.., 2016) support the viability of such integrated processes.

Valorization of companion metals (Co, Sc).

- Because cobalt forms volatile $CoCl_2$ under similar conditions (Mishra & Rao, 1989; Senanayake & Zhang, 2015) and scandium forms soluble $ScCl_3$ in chloride-rich leachates (Paredes et al.., 2012; Roca et al.., 2016), coordinated recovery strategies may greatly enhance process economics.

Life-cycle and techno-economic assessments relative to HPAL and reductive roasting.

- Comparative evaluation of reagent use, energy demand, residue stability, and emissions is essential for defining the industrial role of chlorination, especially considering the environmental constraints emphasized in recent roasting and chlorination studies (Peng et al.., 2018; Ge et al.., 2022).

Taken together, these research directions suggest that chlorination has strong potential as a selective, modular, and resource-efficient method for treating limonitic laterites. However, achieving industrial success will depend on coordinated progress in reactor design, corrosion management, integrated flowsheet development, and independent pilot-scale validation.

Section 4 offers a clear and well-organized overview of chlorination routes for nickel, but several aspects could be enhanced to boost technical detail and industrial relevance. The discussion of solid-state, gas-phase, and IL/DES processes is thorough, yet factors like kinetics, morphological changes, and mineralogical controls— which are essential for selective Ni chlorination—are addressed only briefly. The description of selectivity mechanisms is included, but the differences between molten-salt effects, pCl_2–pO_2 control, and chloro-complex stability could be more clearly explained.

The section would also benefit from a clearer comparison of technology readiness levels, since IL/DES systems remain in early stages while gas-phase chlorination lacks pilot-scale demonstrations. Environmental and engineering constraints—particularly chlorine handling, off-gas scrubbing, and corrosion—should be more explicitly acknowledged. Finally, companion metal recovery (Co, Sc) is well introduced but could be expanded to address impurity risks and downstream separation challenges.

Overall, the section is solid but can be improved by including process diagrams, vapor-pressure visuals, a TRL table, and a brief techno-economic overview to better link chlorination chemistry with industrial feasibility.

When compared to established laterite-processing methods such as HPAL, the Caron process, and sulfation roasting, chlorination offers a unique set of advantages and limitations. Its main strengths include better Ni/Co selectivity over Fe, opportunities for co-recovery of valuable elements, lower energy requirements than reduction roasting, and the ability to operate with more compact and modular flowsheets. However, chlorination also faces practical challenges—most notably handling highly corrosive chloride gases, the need for precise dehydration and control of pCl_2–pO_2, and the relatively low technology readiness level of emerging IL/DES-based routes.

These differences set the stage for the next section, which compares chlorination with other nickel-extraction strategies in terms of efficiency, scalability, environmental impact, and economic potential.

5. Comparison with Other Processing Routes

Building on the thermodynamic and mechanistic principles outlined in the previous sections, it is helpful to compare chlorination-based strategies with established laterite-processing technologies. Compared to HPAL, Caron, and sulfation roasting, chlorination offers several structural advantages. First, this method provides greater inherent selectivity for Ni and Co over Fe since chloride stability fields favor the formation and volatilization of $NiCl_2$ and $CoCl_2$ under conditions where iron remains largely oxidic (Mishra & Rao, 1989; Senanayake & Zhang, 2015; Peng et al.., 2018). Chlorination routes also create opportunities for co-recovery of high-value elements such as Sc and REEs, which are often mobilized alongside Ni/Co in chloride-bearing systems, as seen in molten-salt and Cl_2/HCl roasting studies (Hoover, 1975; Xu et al.., 2017; Ge et al.., 2022). In terms of energy use, chloride-assisted volatilization or segregation roasting can require lower overall thermal input than traditional reduction roasting, primarily when molten-salt pathways involving NaCl, $CaCl_2$, or mixed chlorides are used (Padilla et al.., 2013; Lin et al.., 2019; Ma et al.., 2021). Additionally, chlorination processes can support more compact flowsheets, particularly when volatilized chlorides are condensed and directly fed into hydrometallurgical dissolution or electrowinning steps (Fan et al.., 2010; Norgate et al.., 2011).

These advantages, however, are tempered by several practical constraints. The most notable challenges are operational: handling corrosive chlorinating gases (Cl_2, HCl), which requires robust reactor designs and corrosion-resistant linings (Chen et al.., 2020; Peek, 2011); maintaining precise dehydration control to prevent oxychloride formation, especially in goethite-rich laterites (Mukherjee, 1985; Li et al.., 2016); and managing materials limitations to sustain stable pCl_2/pO_2 conditions during roasting (Rojas et al.., 2017; Han et al.., 2021). Emerging ionic liquid (IL) and deep eutectic solvent (DES) chlorometallurgical systems provide safer, low-temperature options by reducing gas-phase chlorine needs (Liu et al.., 2012), but their technology readiness level remains modest, with only limited pilot-scale demonstrations reported (Rinne et al.., 2025). Therefore, although chlorination is advantageous thermodynamically and mechanistically, its industrial application must balance selectivity benefits against engineering complexity, safety risks, and long-term durability of process materials.

To consolidate the comparative analysis across major laterite-processing technologies, Table 6 summarizes the operational principles, thermal requirements, selectivity profiles, energy consumption, flowsheet complexity, and co-recovery potential of the primary extraction methods. By presenting chlorination, HPAL, the Caro process, and sulfation roasting within a single framework, the table highlights the distinct thermodynamic and engineering trade-offs for each approach. This comparative view clarifies where chlorination provides better Ni/Co selectivity and multi-metal recovery, and where traditional hydrometallurgical or reductive methods maintain advantages in process simplicity or maturity.

Table 6. Comparative Performance of Chlorination vs. Established Laterite-Processing Routes. Adapted from Mishra & Rao (1989); Norgate et al.. (2011); Senanayake & Zhang (2015); Peng et al.. (2018); Padilla et al.. (2013); Ge et al.. (2022).

Processing Route	Operating Principle	Temperature Range	Ni/Co Selectivity vs Fe	Energy Demand	Complexity	Co-/Sc-Recovery Potential
Chlorination (solid-state / gas-phase)	Chloride formation + volatilization or dissolution	450–950°C	Very high ($NiCl_2$ stable while Fe remains oxidic)	Low–moderate	High (Cl_2/HCl handling)	High (Co, Sc mobilized as chlorides)
HPAL	Acid pressure leaching	240–270°C	Moderate	High (steam generation)	High	Moderate (Sc sometimes co-leaches)
Caron Process	Reduction → ammonia leaching	700–850°C + leaching	Low	High	Very high	Low
Sulfation Roasting	Metal sulfate formation	400–700°C	Moderate	Moderate	Moderate	Low–moderate

Section 5 offers a clear qualitative comparison between chlorination and traditional laterite-processing methods, effectively connecting the thermodynamic benefits of Ni/Co chloride stability and volatility to process selectivity and flowsheet simplification. The discussion accurately emphasizes opportunities for co-recovery of multiple metals and the potential for reduced thermal input compared to reduction roasting.

However, several aspects could be improved. The comparison remains primarily qualitative; adding details like approximate operating temperatures, reagent requirements, or energy ranges would better differentiate HPAL, Caron, and sulfation roasting. The discussion of environmental and residue-management issues could also be more balanced, especially regarding chloride-rich residues versus sulfate-rich HPAL tailings. Mentioning chlorination's low water demand and potential trade-offs in CO_2 footprint is also important. Additionally, differences in capital costs and TRL levels deserve a more detailed discussion, particularly considering the limited scale-up of IL/DES systems.

To improve clarity, a brief comparative table or a small diagram showing the operating window would help readers visualize the differences in process space across technologies.

Because these advantages and disadvantages extend beyond metallurgical performance, a thorough evaluation should include the environmental, safety, and economic impacts of chloride-assisted laterite processing.

Overall, chlorination occupies a distinct process niche where thermodynamic selectivity compensates for increased engineering complexity, making it particularly attractive for low-grade limonitic ores and multi-metal recovery scenarios rather than bulk nickel production alone.

6. Environmental, Safety, and Economic Considerations

To illustrate how environmental responsibilities differ between chloride- and sulfate-based processing methods, Figure 7 presents a side-by-side schematic comparing the primary waste streams and reagent management requirements of chlorination and HPAL/sulfate systems. The graphic shows that chlorination significantly reduces solid tailings production but shifts the operational burden toward gas-phase handling and reagent regeneration. In contrast, HPAL generates large volumes of sulfate-rich residues, with lower gaseous emissions but fewer opportunities for reagent recycling. This visual comparison clarifies the trade-offs discussed in Section 6. Unlike conventional hydrometallurgical routes, chlorination-based processes shift environmental and safety challenges from liquid waste management to gas-phase control, corrosion mitigation, and chlorine handling, requiring fundamentally different engineering and regulatory approaches.

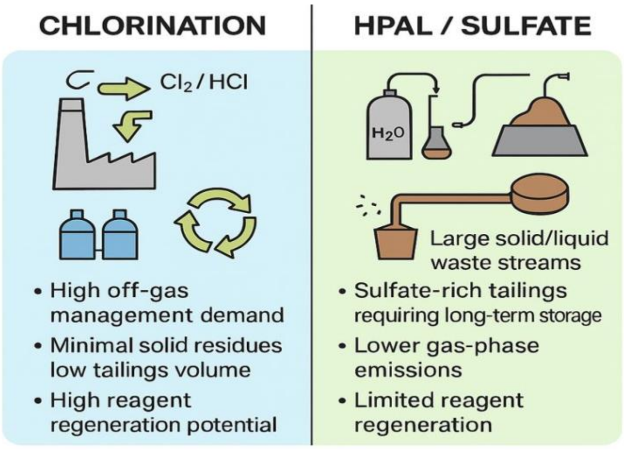

Figure 7. Environmental Burden Shift in Chlorination vs. Hydrometallurgy. Adapted from Mishra & Rao (1989); Norgate et al.. (2011); Senanayake & Zhang (2015); Ge et al.. (2022).

6.1. Environmental Aspects

Chlorination-based flowsheets can significantly decrease solid tailings volumes, especially in volatilization-driven processes where Ni and Co are transported as vapor-phase chlorides rather than staying in the solid residue (Mishra & Rao, 1989; Senanayake & Zhang, 2015). However, the environmental impact shifts toward chlorine production, handling, and scrubbing, as well as managing chloride-rich residues that may need stabilization or controlled neutralization (Wang et al.., 2009; Ge et al.., 2022). The choice of chlorinating reagent—whether Cl_2/HCl gas mixtures, $CaCl_2$, or $FeCl_3·6H_2O$—strongly affects off-gas composition and the design of scrubbing and regeneration units (Rojas et al.., 2017; Cui et al.., 2020).

Despite these challenges, chloride circuits can produce less net waste than sulfate-bearing systems like HPAL when reagent recycling and HCl/Cl_2 regeneration loops are used (Norgate et al.., 2011). Properly managed chloride processes therefore enable chlorination routes to have a more favorable environmental impact compared to traditional hydrometallurgical methods.

To contextualize the benefits and limitations of chlorination within the larger framework of laterite-processing technologies, Table 6 provides a side-by-side comparison of chloride-based routes, HPAL/sulfate systems, and Caron/reduction-roasting processes. The comparison emphasizes critical operational aspects—including solid waste production, off-gas load, reagent regeneration potential, corrosion and safety issues, energy demands, and multi-metal recovery potential—enabling a structured assessment of where chlorination offers competitive advantages and where engineering or safety challenges remain. This table acts as a decision-support overview to determine which processing environments are most suitable for chlorination-focused flowsheets.

Table 7. Key Environmental, Safety, and Economic Implications of Chlorination Routes. Adapted from Mishra & Rao (1989); Norgate et al.. (2011); Senanayake & Zhang (2015); Peng et al.. (2018); Padilla et al.. (2013); Ge et al.. (2022).

Dimension	Chlorination Routes	HPAL / Sulfate Systems	Caron / Reduction Roasting
Solid Waste Generation	Low (volatile chlorides reduce tailings)	High (large sulfate residues)	Moderate–high
Off-Gas Burden	High Cl_2/HCl load; requires scrubbing & regeneration	Moderate SO_2/H_2SO_4 handling	Low–moderate
Reagent Regeneration Potential	High (Cl_2/HCl closed-loop possible)	Limited (acid losses significant)	Moderate
Corrosion Risk	High (chlorides, pCl_2 spikes)	Moderate	Low–moderate
Safety Level	Dependent on Cl_2 management; IL/DES improves	High-pressure risks	High-temperature risks
Energy Demand	Low–moderate (molten-salt assistance)	High (steam + autoclave)	High (reduction furnace)
Multi-Metal Recovery (Sc, REE)	Strong potential	Limited	Very limited
Economic Potential	High when Cl_2 recycled + Co/Sc recovered	High CAPEX/OPEX	Moderate, declining globally

6.2. Safety Considerations

To clarify the unique environmental and safety issues associated with chlorination-based processing compared to traditional laterite methods, Table 7 presents a comparative schematic of the environmental burden pathways for chlorination, HPAL, and Caron processes. Instead of measuring emissions or residues, the diagram illustrates how each method distributes environmental and safety burdens across gas-handling, solid-waste management, and effluent-treatment systems. This comparison helps explain why chlorination processes require strict gas-phase control, whereas conventional methods mainly pose risks in solid and liquid waste streams.

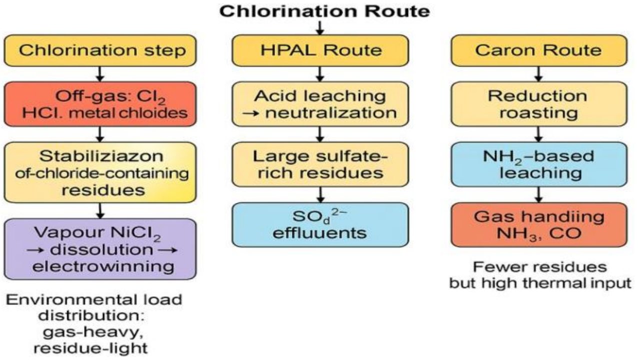

Figure 8. Environmental and Safety Burden Paths in Ni Laterite Processing. Adapted from Mishra and Rao (1989), Varley (1969), Norgate et al.. (2011), and Senanayake et al.. (2022).

Safety performance in chlorination metallurgy mainly depends on controlling corrosion and managing gas-phase hazards. Using Cl_2 and HCl requires corrosion-resistant materials (e.g., Al_2O_3 linings, SiC ceramics), high-quality sealing, continuous leak detection, and strong gas-scrubbing systems (Peek, 2011; Chen et al.., 2020). Local pCl_2 spikes caused by $CaCl_2$ or $FeCl_3·6H_2O$ decomposition can increase corrosion risks and demand specially designed reactors (Han et al.., 2023; Liu et al.., 2022).

Emerging ionic liquid (IL) and deep eutectic solvent (DES) systems largely eliminate gas-phase chlorine, enhancing operational safety by allowing chlorination and dissolution at lower temperatures (Liu et al.., 2012). However, these systems introduce their own limitations, especially concerning solvent degradation, recyclability, and impurity accumulation.

6.3. Economic Drivers

The economic feasibility of chlorination hinges on several interacting factors. First, Ni/Co market prices directly determine the value of vapor-phase or segregated products and strongly influence the competitiveness of chloride roasting relative to HPAL or Caron (Norgate et al.., 2011). Second, chlorination creates opportunities for co-recovery of Sc and REEs—elements known to be mobilized in chloride systems—which can significantly improve project economics (Fan et al.., 2010; Paredes et al.., 2012).

A third critical factor is the degree to which chlorinating agents can be regenerated. Closed-loop recycling of Cl_2 or HCl—via, for example, Deacon-type oxidation—reduces reagent consumption and mitigates environmental impact (Peek, 2011). Finally, energy consumption is sensitive to whether the process leverages molten-salt phases or gas-recycle configurations, both of which can reduce thermal demand compared with reduction roasting (Padilla et al.., 2013; Lin et al.., 2019).

When multi-metal recovery is achieved and reagent recycling is optimized, chlorination flowsheets can attain favorable operating costs and, in some scenarios, outperform established hydrometallurgical routes.

Section 6 offers a well-balanced and technically sound evaluation of the environmental, safety, and economic aspects of chlorination-based laterite processing. It correctly acknowledges that while chlorination can reduce solid waste production and allow for reagent recycling, it shifts environmental and operational responsibilities to chlorine handling, corrosion management, and off-gas treatment systems. The discussion accurately emphasizes the dual role of chloride chemistry as both a way to improve efficiency and a safety concern.

Nevertheless, the analysis remains mostly qualitative. Greater clarity could be achieved by including comparisons with HPAL or Caron routes regarding water use, residue stability, and capital requirements for gas-handling systems. The economic discussion correctly emphasizes Ni/Co prices, by-product recovery, and reagent regeneration as key factors, but would benefit from explicitly addressing the cost sensitivity to chlorine supply and solvent management in IL/DES systems. Overall

Given these operational and economic considerations, it is essential to evaluate how chlorination technologies may evolve and how they can be integrated with emerging hydrometallurgical and electrochemical processes.

7. Future Trends and Hybrid Flowsheets

To contextualize the emerging role of chlorination within next-generation laterite processing, Figure 8 presents a conceptual architecture of future chlorination-based flowsheets. Rather than being treated as a standalone extraction step, chlorination is increasingly envisioned as a modular core that can be integrated with complementary technologies to enhance selectivity, safety, and resource efficiency. The graphical concept highlights how thermochemically driven $NiCl_2$ and $CoCl_2$ formation can interface with advanced dissolution media, selective oxidation strategies, and continuous hybrid reactors, enabling flexible and circular processing routes tailored to complex limonitic ores.

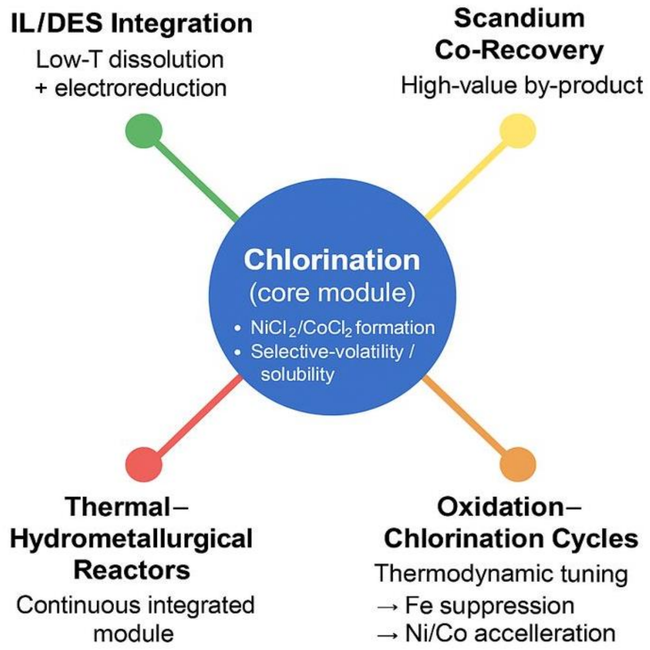

Figure 9. Adapted from concepts discussed in Senanayake & Zhang (2015), Norgate et al.. (2011), Han et al.. (2021), Ge et al.. (2022).

Chlorination is increasingly seen not as a standalone technology but as a modular step within broader, integrated flowsheets that combine thermochemical selectivity with advanced hydrometallurgical or electrochemical recovery processes. Several promising hybrid pathways are emerging due to recent advances in chloride chemistry, solvent systems, and reactor design.

One of the most actively researched concepts is combining chlorination with ionic liquid (IL) or deep eutectic solvent (DES) leaching, followed by electroreduction. In these methods, chlorination turns Ni and Co into easily soluble chloride forms, which can then be selectively dissolved in non-aqueous media at low temperatures and directly recovered as metals in compact electrochemical cells (Liu et al.., 2012; Han et al.., 2021; Rinne et al.., 2025). This method reduces gas-phase chlorine handling downstream while allowing closed-loop solvent and chloride recycling.

To contextualize the emerging hybrid pathways discussed earlier, Table 6 offers a comparative overview of the main chlorination-based integration strategies currently under development. The table summarizes how each approach combines thermochemical chlorination with non-aqueous leaching, cyclic oxidation, scandium co-recovery, or integrated reactor concepts, emphasizing their core mechanisms, operational strengths, and remaining technological challenges. This comparison clarifies which hybrid configurations show the greatest potential for industrial deployment and which are still in early research stages.

Table 8. Emerging Hybrid Chlorination-Based Processing Routes for Ni Laterites. Adapted from Mishra & Rao (1989); Senanayake & Zhang (2015); Peng et al.. (2018); Fan et al.. (2010); Padilla et al.. (2013); Liu et al.. (2012); Rinne et al.. (2025).

Hybrid Route	Core Integration	Key Advantages	Limitations / Challenges
Chlorination → IL/DES Leaching → Electroreduction	Gas-phase or molten-salt chlorination feeding non-aqueous dissolution and direct Ni/Co electroreduction	High selectivity; minimal gas-phase Cl_2 downstream; solvent recycling	IL/DES cost, viscosity, regeneration
Chlorination-Assisted Scandium Recovery	Sc mobilization under controlled chlorination, recovered from residues or chloride-rich leachates	High-value co-product; improves economics	Sensitive to ore mineralogy; partial Sc mobility
Selective Oxidation–Chlorination Cycles	Fe stabilized as Fe_2O_3/Fe_3O_4, Ni/Co selectively chlorinated in cycles	Suppresses Fe chlorination; enhances Ni/Co selectivity	Requires precise pCl_2–pO_2 control
Thermal–Hydrometallurgical Hybrid Reactors	Molten-salt chlorination coupled directly with non-aqueous lixiviants	Near-continuous operation; reduced residue; integrated Cl regeneration	Complex reactor design; limited pilot data

To complement the comparative insights in Table 6, Figure 9 illustrates the relative technology readiness level (TRL) of each hybrid route against its degree of process integration. This two-dimensional framework shows how emerging chlorination-based flowsheets occupy different innovation spaces: some are already supported by strong pilot data but need moderate integration, while others reach deeper thermochemical–hydrometallurgical coupling but remain at early experimental stages. The diagram clarifies development priorities and the likely order of industrial adoption.

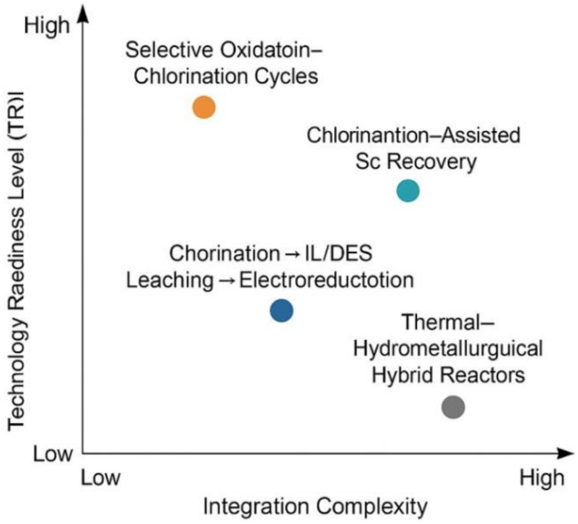

Figure 10. Technology Readiness versus Integration Complexity for emerging hybrid chlorination flowsheets applied to Ni laterite. adapted from Liu et al.. (2012); Padilla et al.. (2013); Senanayake & Zhang (2015); Peng et al.. (2018); Rinne et al.. (2025); Li et al.. (2024).

Another significant emerging method is chlorination-assisted scandium extraction, especially relevant for limonitic laterites where Sc is concentrated within Fe–Mn oxyhydroxide matrices. Several studies have demonstrated that Sc can be mobilized alongside Ni and Co under controlled chlorinating conditions, allowing its recovery either from volatilization residues or from chloride-rich leachates (Fan et al.., 2010; Paredes et al.., 2012; Ge et al.., 2022). Given the high market value of Sc, even modest recoveries can greatly improve process economics.

Selective oxidation–chlorination cycles are also gaining interest as a method to improve separation efficiency. In these systems, iron is intentionally stabilized as Fe_2O_3 or Fe_3O_4 through controlled oxidation, while Ni and Co are subsequently converted to chlorides under moderate pCl_2–pO_2 conditions. These cyclic processes exploit the different thermodynamic behaviors of Fe and Ni/Co chlorides to prevent iron chlorination while allowing high mobility of Ni/Co (Senanayake & Zhang, 2015; Peng et al.., 2018; Senanayake et al.., 2022).

Finally, advances in reactor engineering are enabling thermal–hydrometallurgical hybrid reactors, where molten-salt chlorination is directly combined with non-aqueous lixiviants or chloride-rich dissolution stages. These concepts aim to achieve near-continuous operation, high reagent efficiency, and minimal solid waste production by integrating chlorination, dissolution, and regeneration steps within a single, unified unit (Padilla et al.., 2013; Peek, 2011; Li et al.., 2024).

As pilot- and demonstration-scale data continue to increase, these hybrid strategies are expected to become a crucial part of future laterite processing, offering practical ways to balance high selectivity, safety, and reagent reuse—key factors for the industrial adoption of chloride-based nickel extraction methods.

Section 7 effectively presents chlorination as a flexible, enabling technology within integrated and modular flowsheets, rather than as a standalone processing route. The discussion appropriately highlights emerging synergies between chlorination, IL/DES-based dissolution, and electrochemical recovery, reflecting current research trends toward lower-temperature, closed-loop, and potentially zero-waste systems. The focus on scandium co-recovery and selective oxidation–chlorination cycles is especially relevant, as these strategies directly address the economic and selectivity limitations of traditional laterite processing.

Nonetheless, most of the proposed hybrid pathways remain in the early stages of technological development. Experimental validation primarily involves laboratory or bench-scale studies, and few reports provide data on continuous operation, solvent lifetime, or integrated mass and energy balances. Additionally, while hybrid concepts offer potential for improved safety and reagent circularity, they may also introduce new complexities related to solvent stability, impurity buildup, and process control. Future research should focus on scale-up studies, techno-economic evaluations, and long-term testing to identify hybrid solutions that are broadly applicable rather than niche or ore-specific.

Taken together, these developments indicate that chloride-based processing is transitioning from experimental metallurgy toward a flexible, industrially relevant platform. The final section synthesizes the overarching lessons and prospects.

8. Research Gaps and Future Outlook (Short Version, with References)

Although chlorination routes show strong thermodynamic selectivity for Ni and Co, several critical gaps still limit their industrial deployment. Prior studies have demonstrated promising mechanisms (Mishra & Rao, 1989; Senanayake & Zhang, 2015; Peng et al.., 2018), but key uncertainties remain.

8.1. Research Gaps

Mechanistic Gaps

- Reaction pathways—direct versus indirect chlorination and oxychloride intermediates—still lack full understanding, despite progress in molten-salt and gas-phase research (Padilla et al.., 2013; Lin et al.., 2019; Ma et al.., 2021).
- Limited understanding at the micro-scale of how mineralogy and porosity affect Ni/Co mobility during chlorination and volatilization (Fan et al.., 2010; Paredes et al.., 2012).
- Few in situ experimental datasets are available for gas diffusion, volatilization fronts, and transient chloride phases under controlled pCl_2–pO_2 conditions.

Thermodynamic Gaps

- Multi-component chloride stability for Fe–Mn–Cr–Al–Si systems remains poorly understood, despite foundational vapor-pressure research (Motzfeld, 1964; Mishra & Rao, 1989).
- Hydration-driven changes in pCl_2–pO_2 stability fields for goethite-rich laterites are understudied (Mukherjee, 1985; Li et al.., 2016).
- Sparse modeling of coupled volatilization behavior of Ni, Co, Sc in real ore matrices.

Engineering & Scale-Up Gaps

- Corrosion-resistant reactors and refractory materials have not yet been validated for long-term chloride cycling, even though recent studies highlight severe corrosion spikes caused by chloride decomposition (Ge et al.., 2022; Peek, 2011; Han et al.., 2023).
- Insufficient pilot-scale data on heat and mass transfer, gas handling, solvent recycling, and continuous condensation of volatile chlorides (Rinne et al.., 2025).
- Integration of HCl/Cl_2 regeneration loops remains at the conceptual or bench scale (Norgate et al.., 2011).

Technology Readiness Gaps

- Most chlorination methods—solid-state, gas-phase, IL/DES systems—still operate at TRL 2–4, with only a few demonstration projects (Liu et al.., 2012; Rinne et al.., 2025).
- No continuous pilot (>500 h) has yet validated stability under variable feed composition or demonstrated closed-loop reagent management.

8.2. Industrial Priorities

To advance chlorination toward commercial viability, research should focus on:e:

1. Reactor and materials engineering for high-pCl_2 chloride environments (Peek, 2011; Chen et al.., 2020).
2. Integration of robust Cl_2/HCl regeneration cycles, enabling reagent circularity (Norgate et al.., 2011).
3. Predictive multi-physics modelling combining kinetics, thermodynamics, and volatilization (Senanayake & Zhang, 2015; Peng et al.., 2018).
4. Validation of hybrid flowsheets, including IL/DES electroreduction and oxidation–chlorination cycles (Liu et al., 2012; Rinne et al.., 2025).
5. Systematic evaluation of Co and Sc co-recovery, which is increasingly shown to improve economic viability (Fan et al.., 2010; Paredes et al.., 2012; Ge et al.., 2022).
6. Environmental and safety frameworks specifically tailored to chloride-rich operations and corrosion risks (Peek, 2011; Ge et al.., 2022).

8.3. Outlook

Chlorination offers a compelling, highly selective method for extracting Ni and Co from limonitic laterites, with proven potential for co-recovery of Sc and REE (Fan et al.., 2010; Ge et al.., 2022). However, widespread industrial use depends on linking mechanistic understanding with scalable engineering, developing corrosion-resistant designs, and operating continuous pilot units capable of demonstrating stable reagent recycling and environmental management. Hybrid chlorination–hydrometallurgical flowsheets (Liu et al.., 2012; Rinne et al.., 2025) are expected to lead the next generation of laterite processing technologies.

9. Conclusions

This critical review has examined chlorination-based processing routes for limonitic nickel laterites, integrating thermodynamic principles, reaction mechanisms, and engineering considerations across solid-state, gas-phase, and chloro-hydrometallurgical systems. The analysis confirms that the fundamental selectivity of these routes arises from the markedly higher thermodynamic stability and volatility of $NiCl_2$ and $CoCl_2$ relative to iron chlorides under controlled pCl_2–pO_2–T conditions. This intrinsic chemical contrast enables effective nickel and cobalt separation from iron-rich limonitic matrices that are otherwise resistant to conventional hydrometallurgical and pyrometallurgical treatments.

From a comparative perspective, gas-phase chlorination offers the highest selectivity and product purity through controlled volatilization and condensation of $NiCl_2$, albeit at the cost of increased engineering complexity, corrosion risk, and stringent gas-handling requirements. Solid-state chlorination using NaCl, $CaCl_2$, or mixed chloride systems provides a more operationally flexible alternative, leveraging molten-salt-assisted transport to enhance nickel mobility while suppressing iron chlorination. Emerging chloro-hydrometallurgical routes based on ionic liquids and deep eutectic solvents demonstrate exceptional selectivity at low temperatures and improved safety profiles, although their technology readiness remains limited by solvent cost, viscosity, and recycling challenges.

Beyond nickel recovery alone, chlorination routes present distinct opportunities for the co-recovery of companion metals such as cobalt and scandium. The preferential volatilization of $CoCl_2$ alongside $NiCl_2$ and the high solubility of $ScCl_3$ in chloride-rich leachates offer pathways for multi-metal valorization that can significantly improve process economics, particularly for low-grade limonitic ores. These advantages differentiate chlorination-based flowsheets from established laterite-processing technologies such as HPAL, the Caron process, and sulfation roasting, where selectivity and by-product recovery are more limited.

Nevertheless, the industrial implementation of chlorination remains constrained by several unresolved challenges. Key limitations include chloride-induced corrosion, the need for precise dehydration and pCl_2–pO_2 control, incomplete understanding of molten-salt-mediated reaction pathways, and the scarcity of continuous pilot-scale demonstrations. Environmental benefits linked to reduced solid tailings and reagent recycling must be balanced against the operational risks associated with chlorine handling and off-gas management.

Future research should prioritize (i) Pilot-scale validation of gas-phase and molten-salt chlorination reactors, (ii) Development of durable, chloride-resistant materials for high-temperature operation, (iii) Integration of chlorination with non-aqueous dissolution and electrochemical recovery to minimize gas-phase chlorine circulation, and (iv) Systematic techno-economic and life-cycle assessments benchmarked against HPAL and reduction-based routes. Addressing these issues is essential to move chlorination from a thermodynamically attractive concept toward a robust and industrially viable processing option.

Overall, chlorination-based metallurgy should be viewed not as a universal replacement for existing laterite-processing technologies, but as a selective, modular, and potentially transformative pathway for upgrading limonitic nickel ores—particularly where enhanced selectivity, multi-metal recovery, and flexible flowsheet integration are required.

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