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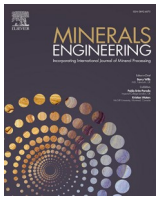

Optimizing heap leaching of complex sulphide ores ($(Fe,Ni)_9S_8$-$CuFeS_2$): A review on dissolution kinetics and process improvement for nickel (Ni) and copper (Cu)

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ABSTRACT

Heap leaching of polymetallic sulphide ores has become a cost-effective and scalable method for recovering base metals such as copper (Cu) and nickel (Ni). However, optimizing metal recovery remains challenging due to mineralogical heterogeneity, electrochemical reactivity, and surface passivation phenomena. This review synthesizes recent advances in understanding dissolution mechanisms in composite sulphidic ores containing pentlandite, chalcopyrite, and associated gangue phases. It emphasizes the need for a geo-metallurgical characterization framework that integrates host-rock composition and microstructural features to predict leach behaviour. The galvanic interactions within mixed pentlandite–chalcopyrite assemblages ($(Fe,Ni)_9S_8$–$CuFeS_2$) are examined, highlighting their distinct behaviour compared to single-mineral systems. Findings reveal that single-mineral phases dissolve through transient intermediate phases, which retard recovery rates. The review also highlights the positive impact of chloride (Cl^-) as a potential additive during leaching or pretreatment. Finally, it promotes emerging computational tools such as machine learning and process automation that can enhance predictive accuracy and operational efficiency.

1. Introduction

Despite the growing demand for Cu and Ni in renewable energy, electric vehicles, and advanced manufacturing (Zhao et al., 2022; Abbas et al., 2024; Zou et al., 2025), their recovery from polymetallic sulphide ores via heap leaching remains particularly challenging due to metallic low grades, complex mineralogy, and the refractory nature of pentlandite ($(Ni,Fe)_9S_8$) and chalcopyrite (CuFeS). Heap technology involve solution-mineral interface interactions and the diffusion of reagents through pore networks to reach mineral grains containing metal values, stacked in a "heap" over an impermeable pad (Fig. 1). This extraction method demonstrates economic advantages and holds great potential toward circular and low carbon economy (Jia et al., 2024), including substantially lower water consumption (0.3–1 ton of water per ton of processed material vs. 2–4 tons typically required in conventional tank leaching systems) (Van Staden and Petersen, 2018; Thenepalli et al., 2019; Surimbayev et al., 2025). However, its application to primary sulphides remains constrained by slow kinetics, low recoveries, and extended leach cycles.

While the process appears simpler at first glance, it becomes complex when considering the numerous interconnected sub-processes involved, including chemical reactions governing metal dissolution, oxidation, precipitation, and various solution-phase reactions. Current heap leaching processes for refractory sulphide ores exhibit markedly low metal recovery rates, necessitating prolonged operational ramp-up phases and extensive empirical process optimization. Cu recovery from chalcocite (Cu_2S) ores reaches only ~ 80% over 8–24 months (Petersen and Dixon 2007), while chalcopyrite ores demand 3-year leach cycles for 60–70% Cu recovery (Giyani et al., 2025). Furthermore, mixed Ni-Cu sulphide ores under heap process achieve merely 50% extraction at Talvivaara (Saari and Riekkola-Vanhanen, 2012). These timescale operational incompatibilities and limitations originate from ore heterogeneity, inadequate mineral exposure, preferential flow paths (Petersen 2016; Lin et al., 2016; Winarko, Liu, et al., 2022; Giyani

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et al., 2025), and critically, passivation phenomena that remain to be addressed in polymetallic systems.

Over the next decade, it is believed that polymetallic ores will increasingly dominate global reserves, with $CuFeS_2$ alone representing approximately 70% of Cu world reserve and expected to account for roughly 25% of low-grade sulphide resources contained in polymetallic ore bodies (Cu/Ni/Zn) (Debernardi and Carlesi, 2013; Owen et al., 2024) developing viable heap leaching systems for composite sulphide ores has become imperative. While previous investigations have focused on optimizing Cu or Ni heap leaching processes individually from their respective sulphide minerals: pentlandite $(Fe,Ni)_9S_8$, and chalcopyrite ($CuFeS_2$), yet no comprehensive synthesis addresses the integrated Ni/Cu co-dissolution dynamics during heap leaching of polymetallic composite sulphide ores. This critical gap is particularly significant given that galvanic interactions, solution chemistry evolution, and passivation behaviour in pentlandite-chalcopyrite assemblages diverge substantially from single-mineral systems, differences that fundamentally alter process design requirements and performance predictions. To gain knowledge and improve heap process from polymetallic, this review assesses the influence of geological settings (gangue mineralogy's) to process design and performances (Ni and Cu recoveries). It further examines the influence of galvanic interactions framework on the dissolution behaviour of poly metallic sulphide minerals. Moreover, this work critically synthesizes mechanistic insights into $CuFeS_2$ passivation within polymetallic contexts. In this regard, pretreatment strategies are reviewed and critically evaluated for their effectiveness in enhancing heap leaching performance particularly Ni and Cu recoveries while substantial attention is directed toward computational contributions and emerging digitalization frameworks for real-time heap monitoring, adaptive leaching control, and predictive process optimization.

2. Review methodology

To ensure transparency and reproducibility, the review methodology was structured into four key steps. First, database selection: relevant literature was retrieved from major scientific indexing platforms recognized for peer-reviewed engineering and mineral-processing research, including Scopus, Web of Science (WoS), ScienceDirect (Elsevier), and SpringerLink. Second, search strategy: targeted keyword combinations were employed to capture studies addressing heap leaching, sulphide mineral dissolution, and the geological context of polymetallic ore systems. Third, inclusion and exclusion criteria: studies were included if they focused on Ni–Cu sulphide heap leaching and excluded if they lacked sufficient methodological or mineralogical detail. Fourth, evaluation of selected studies: each work was assessed for the adequacy of its characterization techniques (XRD, QEMSCAN, SEM-EDS), thermodynamic consistency (Eh–pH stability fields, Pourbaix diagrams), kinetic modelling approaches, leaching mechanisms (electrochemical, chemical, or bioleaching), and practical relevance to industrial heap operations.

The reviewed literature primarily spans the period from the early 2000 s to 2025, with occasional reference to foundational classical studies. This timeframe was deliberately chosen to encompass both historical developments in heap leaching and the emergence of modern approaches that integrate electrochemical modelling, advanced mineralogical characterization, and heap-scale simulation techniques.

3. Ore type description and gangue reactivity

3.1. Ore description

Polymetallic Ni–Cu sulphide deposits, predominantly of magmatic origin, occur across most continents, with major resources in Russia, Australia, Canada, and Southern Africa (Faris et al., 2023). Their formation reflects complex interactions between magmatic processes and subsequent hydrothermal activity, which govern the distribution and texture of sulphide mineralization (Chen et al., 2024). These deposits account for approximately 60% of global nickel reserves (Schulz et al., 2014) and are broadly classified as sulphide-rich (> 5%, typically 20–90%) or sulphide-poor (< 5%) (Song et al., 2011). The principal ore minerals include pyrrhotite, pentlandite, and chalcopyrite, with cobalt, PGMs, and gold commonly recovered as by-products (Barnes and Lightfoot, 2005).

Despite extensive mineralogical characterization, the influence of sulphide textural variations such as pyrrhotite ordering or pentlandite exsolution on leaching behaviour remains underreported in hydrometallurgical studies, even though these micro-scale features significantly affect dissolution kinetics. For example, the Talvivaara deposit in eastern Finland hosts graphitic black schist ore composed of quartz (25%), biotite (38%), graphite (10%), and sulphides (15–25%) distributed across minerals including FeS_2, $(Fe,Ni)_9S_8$, ZnS, $FeNi_2S_4$, and $CuFeS_2$ (Saari and Riekkola-Vanhanen, 2012). Approximately 70% of

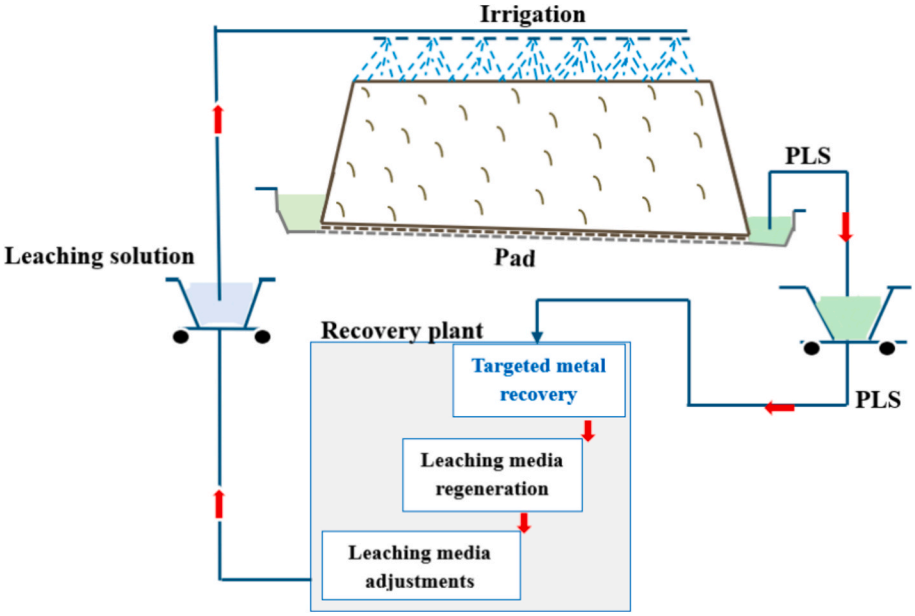

Fig. 1. Schematic of a typical copper sulphide heap leach circuit.

nickel occurs in pentlandite, 21% in $Fe_{1-x}S$, and 8% in pyrite (Svetlov et al., 2017), while Cu is primarily hosted in $CuFeS_2$. The high degree of Ni–Cu sulphide dissemination within a graphite matrix increases effective mineral surface area and promotes high Ni recoveries but also induces strong acid buffering due to the dissolution of biotite, feldspars, and other reactive silicates.

In contrast, the Jinchuan deposit in China is dominated by olivine–serpentine assemblages, comprising olivine (37%), antigorite (30%), chlorite (7%), talc (6%), and tremolite (6%), with minor magnetite (~3%) and chromite (~0.4%) (Qin et al., 2009). While its sulphur content mainly occurs in the form of $Fe_{1-x}S$ (3.3%), $(Fe, Ni)_9S_8$ (~1.6%), $CuFeS_2$ (~0.8%), FeS_2 (~0.5%), and $(Fe, Ni)_3S_4$ (~0.2%). Being an Mg-rich ultramafic matrix, its behaviour under heap leaching conditions differs from the graphitic case of Talvivaara. Notably, the release of Mg^{2+} and Fe^{2+} elevates pH, promotes precipitation of secondary Fe phases, and hinders metal extraction. These mineralogical contrasts directly influence heap performance in terms of dissolution rates, acid consumption, secondary mineral formation, permeability evolution, and overall leaching kinetics yet acid consumption is often reported as a single value without adequate linkage to specific gangue dissolution mechanisms (e.g., serpentinization degree, Mg-bearing mineral breakdown, Fe oxyhydroxide precipitation).

It is evident that variability in host-rock composition, hydrothermal overprinting, and microstructural characteristics exerts a direct influence on leaching behaviour. Consequently, geological context must be integrated into predictive models of metallurgical heap performance. Furthermore, greater consideration of mineralogical heterogeneity both between and within deposits is essential to improve leaching models and avoid overgeneralization of metallurgical outcomes. Subsequently, gangue mineral interactions and their role in controlling acid consumption, secondary phase formation, and overall heap leaching efficiency should be established.

3.2. Gangue mineral interactions

Beyond the presence of targeted sulphide minerals, the overall ore complexity exerts a critical influence on metal recovery during heap leaching (Thomas, 2021). In many low-grade deposits, gangue or barren minerals constitute more than 95% of the ore matrix (Owen et al., 2024), frequently interacting with the lixiviant and releasing gangue-derived cations that accumulate in the pregnant leach solution (PLS), altering its chemical speciation, pH, and redox potential. Heap operations treating porphyry-type ores containing nickeliferous $(Fe,Ni)_9S_8$ and $CuFeS_2$ are therefore commonly characterized by high acid consumption, driven by mineralogical composition, leach solution pH, and particle size distribution (Free, 2010). Dissolution of reactive gangue phases further promotes precipitation of secondary minerals such as jarosite, goethite, and gypsum, which passivate unreacted sulphide surfaces, hinder metal recovery, extend leaching cycles, and reduce heap permeability (Tuovinen et al., 2016).

Ni–Cu sulphide ores typically contain quartz, K-feldspar, biotite, muscovite (sericite), chlorite, anhydrite, epidote, and magnetite as major gangue minerals, along with minor phases such as rutile, apatite, and titanite (Chetty, 2018). Collectively, these minerals strongly influence the overall dissolution behaviour of the ore (Rezvani et al., 2024). Understanding the dissolution mechanisms of these diverse mineral phases is essential for designing, optimizing, and intensifying Ni/Cu recovery under heap-leaching operations.

The influence of gangue minerals on heap performance has been widely studied, and various researchers have proposed dissolution or solubility sequences for common gangue phases. For example, Snäll and Liljefors ((Snäll and Liljefors, 2000) examined the dissolution of gangue minerals in strongly acidic media (HCl, HNO_3, and aqua regia) and established the following reactivity sequence, from most to least soluble: calcite > biotite > chlorite > sphene > ilmenite > epidote > hornblende > muscovite > plagioclase > microcline > rutile > anatase. Although informative, these experimental conditions do not fully reflect true heap-leaching environments. Under more representative geo-metallurgical conditions, Thomas (Thomas, 2021) reported that biotite, chlorite, orthoclase, and iron oxides/carbonates are the dominant acid-consuming phases, indicating acid attack as the primary dissolution pathway. In contrast, sulphide mineral dissolution is more complex, governed by electrochemical properties, lattice structure, and chemical environment, and may yield elemental sulphur (S^0) or aqueous sulphur species (Zhang et al., 2020). Early research by Forward and Veltman (1961) proposed a dissolution reactivity sequence for multi-metal sulphide systems in sulphuric acid (H_2SO_4–O_2), as follows: pyrrhotite > galena > sphalerite > pyrite > argentite.

Under heap-leaching operations, gangue interactions are primarily manifested through changes in solution pH, where both the rate and magnitude of pH evolution are strongly influenced by gangue abundance and mineralogical characteristics. Gangue dissolution alters leach solution chemistry, affects the Fe^{2+}/Fe^{3+} redox balance and can promote secondary phases precipitation due to cation accumulation (Na^+, Ca^{2+}, K^+), ultimately reducing heap permeability (Hidalgo et al., 2020). In general, silicate minerals consume protons, causing pH to rise (Ansah et al., 2023). For instance, Qin et al. (Qin et al., 2009) reported that extensive dissolution of olivine, chlorite, and antigorite at MgO contents of 30–35% resulted in substantial release of Mg^{2+} and Fe^{2+}, increasing pH from ~0.5 to ~5.5. Similar pH increases were observed by Ke and Li (Ke and Li, 2006), which consequently limited Ni and Cu extractions to only about 5%.

Gangue dissolution behaviour also varies according to mineral chemistry, particularly elemental ratios. Differences in Mg, Fe, and Si content influence dissolution pathways, with Fe-rich chlorite exhibiting faster cation release than Mg-rich varieties (Liao et al., 2021). Elevated Al/Si ratios (~2:3) favour the formation of amorphous gels that obstruct percolation and lead to heap blinding (Toro et al., 2021). Muscovite, by contrast, shows limited dissolution due to strong Al–O bonding, whereas biotite dissolves more readily owing to weaker Mg–O and Fe–O bonds (Chetty, 2018; Rosemann et al., 2025).

These findings emphasize the importance of detailed characterization of gangue mineralogy, elemental compositions and ratios, and textural attributes, as these factors strongly influence acid consumption, secondary mineral precipitation, and overall heap performance, as summarized in Table 1. Pre-treatment strategies aimed at removing or neutralizing highly reactive gangue phases have been proposed to mitigate these challenges, since gangue-derived dissolution products can hinder metal recovery and complicate reagent management (Lu, Dreisinger, and West-Sells, 2017a; Sun et al., 2020a). Although significant efforts have been made to characterize ore bodies, gangue interactions during heap leaching remain oversimplified in many studies. There is a clear need for a comprehensive geo-metallurgical framework that integrates gangue mineralogy, sulphide texture (e.g., massive vs. disseminated), and alteration intensity to more reliably predict heap-scale behaviour (see Table 2).

3.3. Leaching agent selection

A successful leaching process depends not only on the reactivity of the lixiviant but also on its selectivity toward the targeted metal values and its compatibility with downstream separation processes (Maltrana and Morales, 2023; Pramanik et al., 2024). The choice of counter–ion is central: it can either enhance the mobility of target metals or promote unwanted secondary phase formation. Laboratory and pilot programs have evaluated a range of lixiviants for Ni–Cu sulphides, including sulphuric acid (H_2SO_4), hydrochloric/chloride systems (HCl, Cl^- media), nitric acid (HNO_3), ammoniacal/ammonium systems, and emerging organic/green lixiviants such as glycine (amino acid).

Sulphuric acid (H_2SO_4) remains widely used in industry due to its low cost, established (Sun et al., 2025) handling practices, and compatibility with downstream solvent extraction (SX), delivering

Table 1
Gangue reactivity on heap performance (Ni/Cu recovery).

Gangue type	Content (%)	Effect on dissolution	Observation/ mechanism	Effect on Cu/ Ni
Lizardite (MgO) Carbonates	≈ 64 ≈ 2.1	Cations release (Ca & Mg)	Acid consumption at low pH (pH ≤ 3) gypsum and jarosite precipitation (Sracek et al., 2024a)	Ni Inversely proportional to acidity Hinders Ni recovery Restrict Cu dissolution
Olivine	≈ 95	Cations release (Mg/ Fe) Si gel formation	Acid attack/ consumption, silicate gel-formation & Fe precipitation: goethite/ magnetite/ hematite	Cu and Ni trapped inside the silica gel.
Chlorite	35 ≈ 50	Cations release (Al > Mg > Fe > Si) (Brandt et al., 2003)	Acid consumption silica gel and jarosite precipitation (Rosemann et al., 2025)	Precipitates on unreacted core. Hinders further dissolution
Pyrrhotite	10 ~ 90	High release of ferrous iron (Fe^{2+}) Consume oxidant and change Eh (Rezvani et al., 2024)	Acid and oxidant (O_2 & Fe^{3+}) consumption. Iron compounds precipitates (jarosite). (Faris et al., 2023)	Precipitates on unreacted core. Hinders further dissolution
Carbonates Siderite	10 ~ 90	Release of cations (Na^+, K^+, Fe^{3+}) depending on carbonates content	Acid consumption and jarosite and gypsum formation/ precipitation	Precipitates on unreacted core. Hinders further dissolution
Anorthite/ Feldspar/ Silicate	≈ 50 ≈ 16 ≈ 95	Release of Ca, Al, Mg & Si	Acid attack and consumption Silicate gel	Requires heap conditioning encases ore particles

Anorthite: $CaAl_2Si_2O_8$; Jarosite: $MFe_3(SO_4)_2(OH)_6$, where M = Na^+, H_3O^+, K^+, Ag^+, NH_4^+; Olivine: $(Mg,Fe)_2SiO_4$; Pyrrhotite: $(Fe_{1-x}S)$.

acceptable kinetics for many Ni and Cu systems especially laterites and some secondary sulphides (Echeverry-Vargas et al., 2023). However, sulphate media frequently generate secondary sulphate and basic salts (e.g., jarosite, gypsum, basic sulphates) that can induce surface passivation and pore clogging, and they are prone to high acid consumption in the presence of Mg- and Ca-bearing gangue. This balance of cost, familiarity, and SX/EW compatibility explains the industrial dominance of H_2SO_4 despite its drawbacks for ores with high concentrations of acid-consuming gangue such as dolomite (Sracek et al., 2024b).

By contrast, chloride media (HCl/Cl^-) often exhibit faster kinetics and stronger complexation of Cu and Ni, which makes it an attractive lixiviant. Cl^- commonly facilitates the formation of a more porous elemental sulphur (S^0) reaction product, improving recovery efficiency (Sun et al., 2020). The faster kinetics reported in the literature are also linked to the smaller ionic size and monovalent nature of Cl^- relative to the larger, divalent SO_4^{2-} (Ghaderi et al., 2024). In addition, chloro–complexes of Cu are typically more stable than those of Ni (Cu > Ni), supporting enhanced Cu recovery relative to Ni in Cl^- media (Torres et al., 2020; Ke et al., 2024). Despite these advantages, chloride systems face practical constraints: corrosivity, potential Cl_2 evolution, and impacts on SX/EW, which demand more resistant (and expensive) materials of construction and impose siting restrictions (Bobadilla-Fazzini et al., 2017; Kobayashi et al., 2018). Notably, improved process controls and additional SX stages can minimize chloride transfer into EW, and chloride systems have gained prominence in heap operations particularly in Chile (Jumbo-Pacheco et al., 2025).

Nitric acid (HNO_3) is an effective lixiviant that serves as both a counter-ion and an oxidant (with NO_3^- reduced to NO/NO_2 under acidic conditions). Although relatively costly, its oxidative nature accelerates the dissolution of Ni and Cu sulphides and reduces sulphur passivation, whereas H_2SO_4 systems generally require an external oxidant for primary.

Beyond inorganic acids, salts systems (e.g., ammonium salt solutions) have demonstrated comparable performance to chloride-based methods for non-ferrous metal recovery (Ma et al., 2021), but they often suffer significant ammonia losses (≈5–20% of initial NH_3), which hinders commercial-scale heap implementation for chalcopyrite. Ammonium carbonate has shown up to ~12% higher recoveries than chlorides (Sun et al., 2025), though results are largely limited to sealed, agitated tests. The efficiency of ammonia systems ($NH_3/(NH_4)_2CO_3/(NH_4)_2SO_4$) appears strongly dependent on ore texture and dissemination; for example, poor heap-scale Cu recovery has been observed where Cu phases are highly disseminated within non-reactive silicate gangue (Owen et al., 2024). Biological agents (bioleaching microbes) and emerging green solvents (ionic liquids, deep eutectic solvents) are receiving increased attention for their potential selectivity and lower environmental footprint, but industrial adoption is constrained by cost, recovery efficiency, and scalability (Binnemans and Jones, 2023). Among organic lixiviants, glycine-based processes are particularly promising as an environmentally responsible alternative to traditional hydrometallurgy while retaining technical and economic viability (Li et al., 2023; Safari et al., 2024). Under heap-like conditions, Ni recovery has been reported with 83.5% Ni extraction at room temperature and minimal Fe/Mg co-dissolution (Eksteen et al., 2020). For Cu, fast kinetics (≈ 78% in 6 h) have been obtained for secondary sulphides (Cu_2S) at finer particle sizes (Li et al., 2023). In contrast, refractory chalcopyrite ($CuFeS_2$) typically requires more aggressive conditions—tight DO control, ultrafine grinding, and elevated temperatures (Khezri et al., 2021) which may not translate to heap operations. Even so, employing glycine with a mild oxidant has improved overall recoveries while reducing gangue co-dissolution, aligning with the Sustainable Leachate Recovery (SLR) framework's dual mandate of high metallurgical efficiency and lower environmental footprint for 21st-century copper operations (León et al., 2025).

4. Polymetallic sulphidic mineral heterogeneity and metal recovery

The leaching behaviour of polymetallic sulphide minerals has been studied under both biotic and abiotic conditions. The former involves microorganisms (bacteria or archaea) that promote or accelerate metal release into solution, while the latter refers strictly to pure chemical dissolution systems occurring through chemical or electrochemical phenomena such as acid attack, complexation, and oxidation. A preferential dissolution order has been reported for polymetallic mineral leaching and appears to be governed by the composition and surface heterogeneity of the ore assemblage (Chanturiya et al., 2022). Arpalahti and Lundström (Arpalahti and Lundström, 2018) further suggested that alabandite (MnS), when present in an ore body, is likely to dissolve first due to its lower nobility compared with other base metal sulphides such as pyrrhotite ($Fe_{1-x}S$), sphalerite (ZnS), galena (PbS), millerite (NiS), Cu-sulphides, chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and arsenopyrite (FeAsS). The electrochemical potential range of certain sulphide minerals and their relative refractory attributes, plotted against the standard calomel electrode (SCE), is illustrated in Fig. 2.

According to rest potential theory, when minerals with dissimilar rest potentials are in direct contact, galvanic interactions are expected. In such systems, the lower-potential phase acts as the anode and preferentially dissolves, whereas the higher-potential mineral is cathodically protected (Cruz et al., 2005, Santos et al., 2006; Yang et al., 2018).

Table 2
Comparative assessment of common lixiviants for Ni–Cu sulphide leaching.

Lixiviant	Strengths	Weaknesses / Cost Constraints	Major Research Gaps
H_2SO_4	Low cost, compatible with SX–EW. Effective for secondary sulphides and serpentine-rich ores.	Acid consumption (Ca/Mg) Low heap permeability (gypsum) Long leach times increase labour/ energy costs. Formation jarosite, gypsum cause passivation.	Limited heap-scale studies linking mineralogy acid consumption metal recovery.
HCl/Cl^-	Fast dissolution kinetics of Cu and Ni Less sulphur passivation than in sulphate media.	Expensive vessel materials. Cl_2 off-gas risk Environmental constraints.	Almost no true heap-scale chloride leaching trials at coarse particle size.
HNO_3	Decomposition of sulphide matrix. Strong oxidation, rapid kinetics. Minimizes sulphur passivation	High reagent price. Requires high grade / concentrate material Poor suitability for open heaps due to gas losses	No heap leach demonstrations exist. Very few techno-economic analyses considering NO_x capture
(NH_3, $(NH_4)_2SO_4$, NH_4Cl	High selectivity for Cu/Ni. Non-acidic limited gangue dissolution.	Complex equilibrium behaviour poorly understood. NH_3 losses in open heaps high operating cost	No ammoniacal heap leach data at realistic percolation/temperature. Lack of NH_3-loss quantification under field conditions.
Glycine (amino-acid systems)	Environmentally benign Good selectivity and fast kinetics for some sulphides under agitation Recyclable under controlled pH	$CuFeS_2$ slow dissolution without high T, O_2, agitation. Reagent loss pathways in heaps unknown. Only in lab reactors not at heap scale	No field or pilot heap trials. Behaviour at coarse size, low T, & interaction with Fe-rich does not establish.

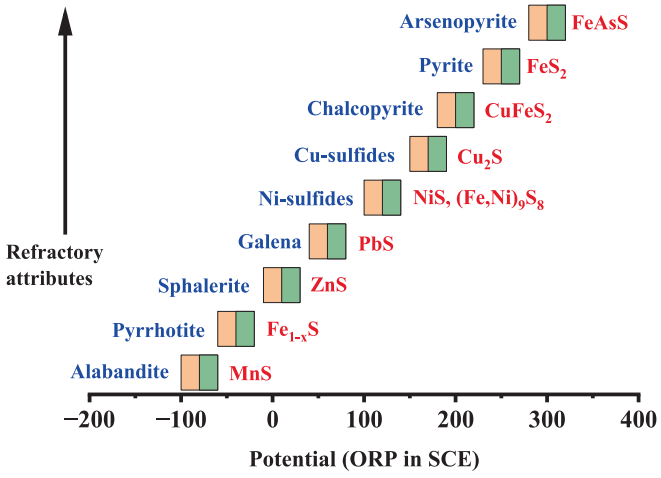

Fig. 2. Leaching potential of sulphide minerals.

However, this thermodynamic prediction oversimplifies the kinetic complexity observed in practice. $(Fe,Ni)_9S_8$ (anode) should dissolve preferentially over $CuFeS_2$ (cathode) in $(Fe,Ni)_9S_8$-$CuFeS_2$ assemblages, experimental evidence (Table 3) reveals that $(Fe,Ni)_9S_8$ dissolution rates in mixed ores are often lower than in pure systems suggesting the galvanic cathode ($CuFeS_2$) provides insufficient surface area to support rapid $(Fe,Ni)_9S_8$ oxidation. Moreover, Cu dissolution from the cathode ($CuFeS_2$), although slower than anode $(Fe,Ni)_9S_8$, still occurs simultaneously rather than being completely suppressed, indicating localized electrochemical cells or solution-phase oxidation pathways that bypass galvanic protection. The critical questions remain: What determines the mixed potential in polymetallic heaps where mineral contacts vary spatially? How does this influence the dominant rate-controlling mechanism? What are the optimum parameters to enhance the co-dissolution of Ni and Cu from $(Fe,Ni)_9S_8$-$CuFeS_8$ assemblages?

$(Fe,Ni)_9S_8$ and $CuFeS_2$ are recognized as refractory phases to dissolution, and considerable experimental effort has been devoted to the extraction of their metallic values (Ni, and Cu) (Balaz et al., 2000; Karppinen et al., 2024). In biotic environments, researchers have consistently observed prompt Ni solubilization from $(Fe,Ni)_9S_8$ as opposed to sluggish Cu extraction from $CuFeS_2$ (Halinen et al., 2009; Qin et al., 2009; Bhatti et al., 2012; Zhihong et al., 2016; Hubau et al., 2020; Goryachev et al., 2022; Hubau et al., 2020; Latyuk et al., 2024; Alajoki et al., 2024; Surimbayev et al., 2025). These studies have identified that metal recovery is pH-dependent. Halinen et al (Halinen et al., 2009) reported maximum yields of 59% and 16% for Ni and Cu, respectively, at pH 1.5, compared to 15% and 5% at pH 3 within a period of 140 days. The solution redox potential was dictated by pH values, with black schist dissolution favoured at 515–518 mV. Ferric iron (Fe^{3+}) concentrations were higher at lower pH values. The authors further observed clogging issues from pH 2 onwards and characterized solid residues for mineralogical composition (XRD) and morphology (SEM). The analysis revealed $Fe_{1-x}S$, FeS_2, $CuFeS_2$, and $FeNi_2S_4$ as the main sulphides, whereas jarosite and goethite formations were attributed to precipitates.

Under similar conditions (140 days, pH 1.5), Hubau et al. (Hubau et al., 2020) also reported rapid release of Ni (55%) and Cu (10%) within 2 days, followed by a rise in Eh value from 550 to 850 mV. The initial rapid dissolution was attributed to the leaching of metallic salts, whereas the rising Eh was accompanied by further withdrawal of Ni (35%) from $Fe_{1-x}S$ and $FeNi_2S_4$. The sluggish Cu dissolution from $CuFeS_2$ was found to be temperature-dependent, reaching a maximum of 50% at 55 °C after 14 days due to the recalcitrant nature of chalcopyrite. Again, significant jarosite precipitation was observed in the leached residues. Latyuk et al. (Latyuk et al., 2024) recorded much lower yields up to up to 35% and 10% for Ni and Cu. They observed an increase solution potential from m 540 to 930 mV. Similarly to previous investigation jarosite formation was identified present in leached residues.

Similar observations are also encountered in commercial processing of mixed $(Fe,Ni)_9S_8$-$CuFeS_2$ and includes the Talvivaara heap bioleaching operation (Finland) and the Jinchuan Group Ltd. (JNMC: China) treatment approach. The former process employs H_2SO_4 (PSD: 8 mm & T: 20 °C) as the main lixiviant agent and achieves 85% Ni recoveries. However, Cu yields remain relatively lower at 50% over a 14-month leaching period, due to the formation of secondary phases and their eventual precipitation in form of CuS, $CaSO_4$-xH_2O, (FeO(OH) and jarosite (Riekkola-Vanhanen, 2013; Faris et al., 2023). Similarly, JNMC applies an acid pre-leaching process followed by a bioleaching process in an acidic environment (pH 1.7–2.2, PSD < 10 mm, temperature ~

Table 3
Ni and Cu recoveries from mixed polymetallic sulphide ores dissolution.

Media pH/Molarity	Environment Bio/ Chemical	T °C	Conditions Eh /Fe^{3+}/Cl^- /NO_2	Recovery (%) Ni	Cu	Time hours/days/months	References/ Researchers
H_2SO_4 pH = 1.8	Bio	20	———	85	50	14 months	(Riekkola-Vanhanen 2013) (Faris et al., 2023)
H_2SO_4 pH = 1.5	Bio	45	540 ~ 930	35	10	140 days	(Latyuk et al., 2024)
H_2SO_4 pH = 1.5	Bio	30	400 ~ 800	70	14	40 days	(Latyuk et al., 2022)
		40		72	34		
H_2SO_4 pH = 1.5	Bio	55	550 ~ 850	90	50	140 days	(Hubau et al., 2020)
H_2SO_4 pH = 1.9	Bio	19	488 ~ 608	23	13	80 days	(Surimbayev et al., 2025)
H_2SO_4 pH = 1.5	Bio	25	515 ~ 580	59	16	140 days	(Halinen et al., 2009)
H_2SO_4 pH = 1.7	Bio	21	321 ~ 570	85	33	80 days	(Qin et al., 2009)
H_2SO_4 pH = 1.5	Bio	22	300 ~ 400	90	< 30	30 days	(Bhatti et al., 2012)
H_2SO4 10 g/L	Bio	25	Fe^{3+} (15 g/L)	89	67	100 days	(Zhihong et al., 2016)
H_2SO_4 1 M	Chemical	90	Fe^{3+} (30 g/L) Cl (20 g/L)	70	87	8 h	(Heikola et al., 2024)
H_2SO_4 0.5%	Chemical	19	NO_2^- (2 g/L)	70	16	40 days	(Goryachev et al., 2022)
H_2SO_4 1 M	chemical	80	300–580 $CuCl_2$	63	37	6 h	(Alajoki et al., 2024)

21 °C). Over 350 days (including 80 days of acid leaching and 270 days of bioleaching), recoveries of 84.6% Ni, and only 32.6% Cu were obtained (Qin et al., 2009). It is believed that high level of multi-metals ions (Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Fe^{2+}/Fe^{3+}) in solution had an inhibitory effect upon further metal release and the negatively impact microbial activity (Cabrera et al., 2005; Qin et al., 2009). Rosemann et al, (Rosemann et al., 2025) highlighted that the accumulation of gangue components can interfere with the leaching system by affecting acid consumption, and the pH, Eh/redox, and solution elemental compositions of the lixiviant. These changes can also lead to mineral precipitation diminishing heap porosity.

Under abiotic conditions, heap operations typically exhibit lower redox potential (ORP), primarily due to the accumulation of ferrous ions (Fe^{2+}) and their slow oxidation to Fe^{3+} in the presence of O_2, particularly in the absence of oxidizing bacteria (Bhatti et al., 2012; Huang et al., 2018; Hubau et al., 2020). Bhatti et al, (Bhatti et al., 2012) investigated a mixed sulphide composite in H_2SO_4 (pH 1.5, T: 22 ± 2 °C, Eh: 300–400 mV (Ag/AgCl)) while also assessing the influence of added Fe^{2+} and Fe^{3+} over a 30-day leach period. They observed that Fe^{2+} accumulation had little effect on ORP, whereas Fe^{3+} addition promoted additional mineral dissolution, achieving nearly complete Ni extraction (> 85%) with poor Cu recovery (< 30%). Analysis of leached residues revealed the formation of gypsum, jarosite, and S^0, which may mask reactive surfaces of sulphide minerals.

Similarly, Karppinen et al (Karppinen et al., 2024) assessed the effect of Fe^{3+} (0.05–0.3 M) as a supplementary oxidant at varying sulphuric acid concentrations (H_2SO_4: 0.5–1 M) for the dissolution of a composite sulphidic ore at constant temperature (90 °C). The authors observed an improvement in Cu extraction rate, reaching an optimum value of 24.9%, confirming the benefit of oxidant presence for Cu extraction. Although improved, Cu recovery remained poor and was attributed to $CuFeS_2$ passivation, where jarosite and elemental sulphur (S^0) were identified as the main passivating species (Bhatti et al., 2012; Garg et al., 2017). In contrast, Ni displayed appreciable solubility over a broader pH window than Cu, highlighting the importance of relatively low pH values for Cu dissolution from $CuFeS_2$.

To shorten leaching times and improve metal recovery, various leaching additives have been explored, with chloride (Cl^-) media emerging as one of the most promising options due to its strong potential for industrial application. Velásquez-Yévenes et al. (Velásquez-Yévenes et al., 2018) demonstrated the positive influence of Cl^- on the dissolution of refractory sulphides, particularly chalcopyrite ($CuFeS_2$). More recently, Heikola et al. (Heikola et al., 2024), evaluated the effect of chloride (as NaCl) addition during the chemical leaching of mixed pentlandite–chalcopyrite ores in H_2SO_4 and H_2SO_4–$Fe_2(SO_4)_3$ media (Eh: 490–540 mV). Their results showed poor recoveries in H_2SO_4 (Cu: 0%, Ni: 13%), whereas the addition of Fe^{3+} significantly improved dissolution (Cu: 45%, Ni: 45%). Remarkably, introducing chloride (5–20 g/L) further enhanced leaching performance, achieving up to 100% Cu and 92% Ni recovery after 24 h. The solid residues consisted mainly of natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) a high-temperature-dependent phase along with nickel sulphate hexahydrate ((Ni,Mg,Fe)$SO_4{\cdot}6H_2O$), pentlandite, and S^0. The exceptionally high metal recoveries display chloride's ability to disrupt passivating layers and accelerate reaction kinetics.

Apart from the leaching environment (biotic or abiotic) and operating parameters (Eh, temperature, and additives), metal recovery is strongly influenced by mineralogical factors such as mineral distribution, degree of dissemination, the presence of soluble metal salts, and resistant phases including pyrite, arsenopyrite, and pyrrhotite (Bailey and Hansford, 1993). Bhatti et al. (Bhatti et al., 2012) investigated flask-scale leaching of black shale at fine particle sizes (≤ 59 μm) in H_2SO_4 (pH 1.5–3.5; ORP 250–600 mV; T = 21 °C). Their results showed that Ni dissolved much more rapidly (> 90%) than Cu (< 30%), with optimal Ni solubilization occurring at pH 1.5–2.3. The enhanced Ni recovery cannot be attributed solely to the increased surface area; it primarily relates to mineral liberation and the relative proportion of exposed pentlandite. In disseminated ores where pentlandite occurs as fine inclusions within silicate or other sulphide matrices, coarse particles may leave significant mineral unexposed, creating geometrical barriers independent of chemical kinetics. This distinction is critical for interpreting apparent "kinetic" improvements that may reflect liberation effects with known challenges in processing disseminated sulphide ores with low degrees of liberation (Maurice and Hawk, 1999).

In contrast, long-abandoned process tailings (historical tailings) often contain easily soluble metallic salts of Ni and Cu (Hubau et al., 2020). Alajoki et al (Alajoki et al., 2024) reported that 37% of Ni was water-soluble under mild conditions (pH 3.7, 80 °C, 300–580 mV). Higher Ni dissolution was observed in acidic conditions (1 M H_2SO_4), while the addition of an oxidant ($CuCl_2$) further increased Ni and Cu

extraction to 63% and 37%, respectively. These findings support the enhancing effect of chloride on the dissolution of Ni–Cu–S minerals. The relatively low metal recoveries observed in this study may be attributed to the lower acid concentration.

Despite the industrialization of heap process worldwide, there are still numerous challenges (low recoveries, long extraction times) associated with its development and implementation. Optimization of heap process requires an understanding of ore geological attributes, interactions between physical, chemical, and biological processes within the heap. The need therefore rises to revisit recent literature on individual mineral phase (((Fe,Ni)$_9$S$_8$)-CuFeS$_2$) dissolution chemistry, mechanism, passivating conditions and leaching additive. It has become evident that effective heap operations require stringent control of redox potential (ORP) and pH. Biotic systems often operate at relatively high ORP values (~0.65–0.70 V vs SHE), which are favourable for Fe^{2+}/Fe^{3+} cycling, are less conducive to sustain CuFeS$_2$ dissolution (Watling, 2006). A narrow critical potential window has been identified in which Cu extraction is maximized, while excessively oxidizing conditions trigger passivation through the formation of refractory surface layers (Córdoba et al., 2008a). Unlike Ni, which dissolves across a broader pH range (Wakeman et al., 2008), Cu dissolution requires controlled acidity (pH < 2) for optimal kinetics (Bhatti et al., 2012; Karppinen et al., 2024; Heikola et al., 2024). Furthermore, the detection of secondary phases: (Fe,Ni)$_2$S$_4$ (Halinen et al., 2009) and CuS in residues (Riekkola-Vanhanen, 2013; Faris et al., 2023) suggests that dissolution each primary phase (pentlandite and chalcopyrite) proceed through transient intermediate phases that can retard overall metal-recovery kinetics. To that, the accumulation/ precipitation of inhibitory elements in complex ores matrix can hinder metal extraction efficiency. Suggesting, consideration for mineral liberation and pretreatment strategies to improve the overall efficiency of heap operations.

4.1. Pentlandite dissolution mechanism

(Fe,Ni)$_9$S$_8$ dissolution is an electrochemical process (Lu, Jeffrey, Zhu, et al., 2000a), its dissolution process has been well discussed with the aid of the Pourbaix diagram (Eh–pH (Fig. 1)), which simultaneously describes the redox potential and pH behaviour during the dissolution. It is usually employed to understand the mineral's aqueous stability under a specific Eh and pH condition (Qi, 2021; Kolela J. Nyembwe et al., 2022). Oxidative and acidic conditions are necessary for Ni^{2+} withdrawal from the (FeNi)$_9$S$_8$ phase (Fig. 3) whereby acidity level and oxidant weaken the M-S bond and oxidise sulphide products (S^{2-} and S_n^{2-}), respectively (Droppert and Shang, 1995; Sun et al., 2020b). The mechanism of Fe^{3+} leaching is primarily a chemical process (Eqs. (1) and (2)), the role of the microorganisms being to produce the Fe^{3+} (Eq. (3)) with sulphur S^0 and/or SO_4^{2-} as products. Yang et al. (Yang et al., 2008) highlighted that S^0/SO_4^{2-} formation (Eqs. (1) and (2)) is determined by the type of sulphides. For instance, ((Fe,Ni)$_9$S$_8$) and CuFeS$_2$ lead to S^o formation (Eq. (2)). In contrast, other sulphide including FeS$_2$, NiS, MoS$_2$, and WS$_2$, promote SO_4^{2-} formation and cause a decrease in the pH value.

$$MS_{(s)} + 8Fe^{3+}_{(aq)} + 4H_2O_{(l)} \rightarrow 8Fe^{2+}_{(aq)} + M^{2+}_{(aq)} + 8H^{+}_{(aq)} + SO^{2-}_{4(aq)} \quad (1)$$

$$MS_{(s)} + 8Fe^{3+}_{(aq)} \rightarrow M^{2+}_{(aq)} + S_{(s)} + 8Fe^{2+}_{(aq)} \quad (2)$$

$$4Fe^{2+}_{(aq)} + O_2 + 4H^{+}_{(aq)} \xrightarrow{Bacteria} 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \quad (3)$$

(whereby M represents the total metallic portion.).

From the diagram (Fig. 3), it could be seen that Ni dissolution is strongly influenced by acidity level and redox potential. Effective Ni leaching occurs across a pH range of < 1.5 to ~3.0 and is favoured at potentials between 300 to 600 mV (Fig. 3), conditions that are consistent with current industrial operations. Despite these, heap leaching is often kinetically slow and incomplete, as reported in several studies

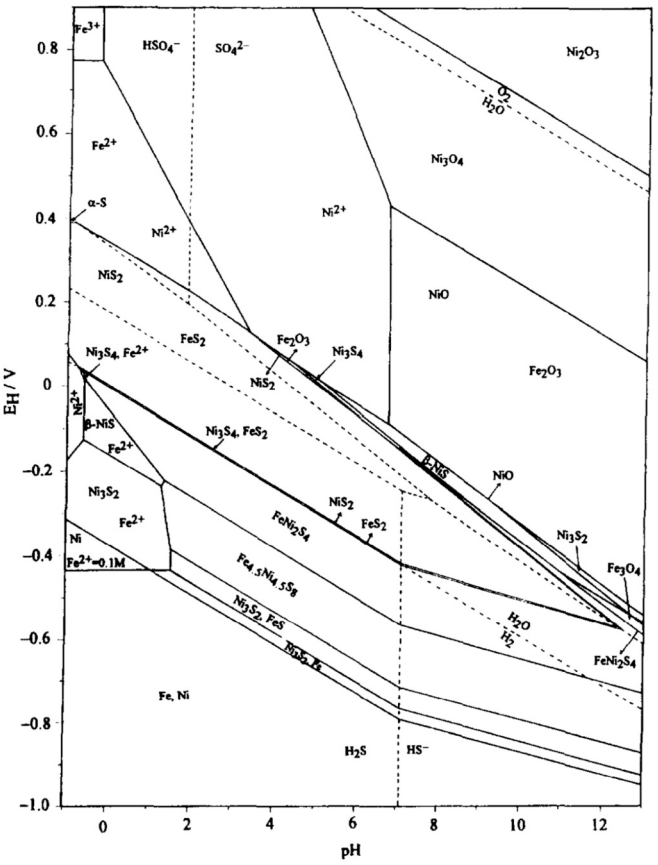

Fig. 3. Eh-pH diagram for Fe-Ni-S aqueous system at 298 K. Activities of aqueous sulphur (S), iron (Fe), and nickel (Ni) species = 0.1 mol/dm^{-3}. (reproduced from Warner et al., 1996 (Warner et al., 1996).

(Riekkola-Vanhanen, 2013; Faris et al., 2023; Surimbayev et al., 2025). Fig. 3 further indicates that Ni release from (Fe,Ni)$_9$S$_8$ may proceed through the formation of intermediate secondary solid phases, which can impede further dissolution by passivating the mineral surface. Therefore, it is worthwhile to review the dissolution mechanism of (Fe,Ni)$_9$S$_8$ in more detail and to assess the stability and transformation behaviour of these secondary or transient phases, as they may represent key kinetic barriers to complete nickel extraction.

A metal-deficient structure of the (Fe,Ni)$_9$S$_8$ mineral, formed through solid-state transformation, has been reported in the literature (Sun et al., 2020; Thornber, 1975). This structural change ($Fe_{4.5-y}Ni_{4.5-x}S_{8-z}$) is attributed to the non-uniform release of Ni and Fe (Eq. (1)) during dissolution of the sulphide lattice, leading to a compositional imbalance (Thornber, 1975; Lu, Jeffrey, Zhu, et al., 2000b) and can include violarite (Legrand et al., 2005; Xia, 2009) and millerite (Tenailleau et al., 2006; Arpalahti, 2021; Khodadadmahmoudi et al., 2022), which were ORP dependent. For example, under electrochemical measurements, Li and colleagues (2012), studied the decomposition of (Fe,Ni)$_9$S$_8$ and revealed the occurrence of Fe-Ni deficient phase ($Fe_{4.5-y}Ni_{4.5-x}S_{8-z}$) at low surface potential (ORP < −0.2 V (vs SCE)) whereas at a potential range between −0.2 and 0.2 (vs SCE) Ni led to the formation of unstable $Fe_3Ni_3S_4$, $FeNi_2S_4$ and S^0 on the mineral surface. At higher potentials above ≥ 0.2, complete Ni dissolution was reported, promoted by the high oxidation rate of Fe^{2+} (dissolved) to Fe^{3+}. This agrees with Warner et al. (1992) who imposed high potential (0.8 V vs SCE at 293–343 K) conditions and observed complete Ni release accompanied by amorphous S, which can contribute to the to surface passivation.

Cl^- has been reported to positively affect dissolution and recovery (Mends et al., 2025). It was reported that Cl^- ions allow a porous sulphur layer to be formed on the mineral surface, facilitating reagent diffusion

and, consequently, higher solubility of the metal (Schueler et al., 2021). Moreover, previous reports by (Watling, 2006; Byrne et al., 2010) suggested that Cl^- in sulphate systems changes the solution speciation, as the metals can form metal-chloride complexes, which may contribute to the leaching rate. Lu et al (Lu, Jeffrey, Zhu, et al., 2000a) reported a morphological change on S^0 by Cl^- in $Fe_2(SO_4)_3$ which led to 96% Ni extraction.

The thermodynamic predictions (Eqs. (4)–(8)) agree with previous dissolution test residue characterisation. Elemental S^0 and Fe-Ni deficient phases are formed during $(Fe,Ni)_9S_8$ dissolution. The predictions further revealed that although violerite $FeNi_2S_4$ (Eq. (4)) and NiS (Eq. (5)) are both potential intermediate phases as identified in the literature (Tenailleau et al., 2006, Arpalahti, 2021; Khodadadmahmoudi et al., 2022), NiS formation is more favorable (Eq. (7)) than $FeNi_2S_4$ (Eq4). Nonetheless, its occurrence with pyrrhotite appeared not feasible (Eq5). On the other hand, $Fe_{1-x}S$, although soluble (Eq. (8)), this phase displayed retarding effect upon Ni leaching once formed (Eq. (4) vs Eq. (7)). This appears to contradict the earlier investigation by Arpalahti & Lundström (2018) who propose a relatively instantaneous dissolution of $Fe_{1-x}S$ as summarised in Fig. 3. However, literature reported that Ni recovery appeared to be crystal structure dependent. For instance, Khodadadmahmoudi et al. (Khodadadmahmoudi et al., 2022) compared Ni dissolution from two pyrrhotite samples, different in crystal structures, mainly hexagonal and monoclinic. Their study revealed a relatively complete Ni recovery (95%) from the hexagonal phase, where a maximum of 67% was achieved from monoclinic samples. The retarding effect, as identified in thermodynamic predictions, suggests that the $Fe_{1-x}S$ intermediate phase formed possesses a monoclinic structure.

Ni dissolution via Intermediate phase formation:

$$Fe_5Ni_4S_{8(s)} + Fe_2(SO_4)_{3(aq)} + H_2SO_{4(aq)} \rightarrow Fe_{0.875}S_{(s)} + FeNi_2S_{4(s)} + 5.125FeSO4(aq) + 2NiSO_{4(aq)} + 2S^0_{(s)} + 3H_2O_{(l)}\ \Delta G = -4879\ kJ \quad (4)$$

$$Fe_5Ni_4S_{8(aq)} + 4Fe_2(SO_4)_{3(aq)} + 4H_2SO_{4(aq)} \rightarrow Fe_{0.875}S_{(s)} + 4\ NiS_{(s)} + 5.125FeSO_{4(aq)} + 2NiSO_{4(aq)} + 2S^0_{(aq)} + 3H_2O_{(l)}\Delta G = +1813\ kJ \quad (5)$$

$$Fe_5Ni_4S_{8(aq)} + Fe_2(SO_4)_{3(aq)} + H_2SO_{4(aq)} \rightarrow FeNi_2S_{4(s)} + 5.125FeSO_{4(aq)} + 2NiSO_{4(aq)} + 2S^0_{(aq)} + 3H_2O_{(l)}\ \Delta G = -3387\ kJ \quad (6)$$

$$Fe_5Ni_4S_{8(aq)} + 4Fe_2(SO_4)_{3(aq)} + 4H_2SO_{4(aq)} \rightarrow 2NiS_{(s)} + 13FeSO_{4(aq)} + 2NiSO_{4(aq)} + 7S^0_{(aq)} + 4H_2O_{(l)}\Delta G = -6392\ kJ \quad (7)$$

Intermediate phase dissolution formation:

$$Fe_{0.875}S_{(s)} + Fe_2(SO_4)_{3(aq)} + H_2SO_{4(aq)} \rightarrow 21FeSO_{4(aq)} + 7S^0_{(s)} + 7H_2O_{(l)}\Delta G = -4.77\ kJ \quad (8)$$

4.2. Chalcopyrite dissolution mechanism

Similarly to the $(Fe,Ni)_9S_8$, $CuFeS_2$ dissolution is an electrochemical process, and its stability diagram (Fig. 4) shows that efficient Cu dissolution is likely to occur at a potential range between 0.45 and 0.85 vs (SHE) (Tshilombo, 2004; Nicol, 2022). These conditions are similar to those applied in under heap conditions (0.3 to 0.7 vs (SHE)). However, Cu dissolution from its composite ore sulphide ($(Fe,Ni)_9S_8$-$CuFeS_2$ (Table 3)) is characterised by slow kinetics and low recoveries (40%) under both biotic and abiotic environments. Hence, the need arises to review and better understand the $CuFeS_2$ dissolution mechanism for

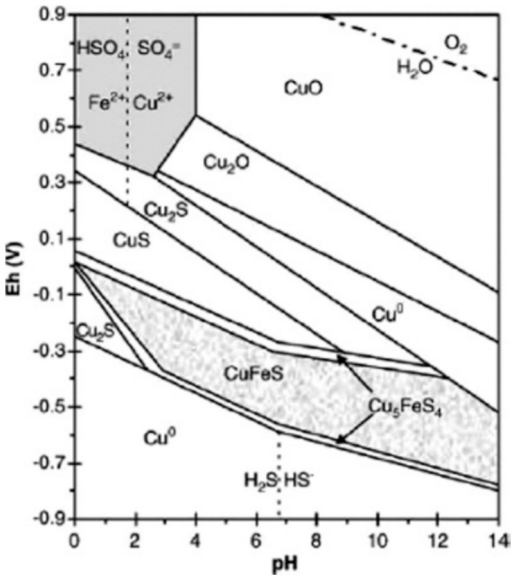

Fig. 4. Pourbaix diagram of Cu-Fe-S-H_2O system at 25 °C (reproduced from Debernardi and Carlesi, 2013).

successful industrial hydrometallurgical leaching implementation (Li et al., 2013). The primary Cu dissolution route development uses the oxidative decomposition of chalcopyrite (Dreisinger and Abed, 2002; Liang et al., 2011; Li et al., 2013). The hydro-metallurgical processing of chalcopyrite typically employs oxidants such as Fe^{3+}, $Cr_2O_7^{2-}$, and H_2O_2. Among these, Fe^{3+} is considered cost-effective, recyclable, and advantageous as it does not introduce miscellaneous ions (Watling 2013) (Zhang et al., 2024). Cu dissolution from the $CuFeS_2$ mineral has been reported to proceed by the formation of rich copper sulphide intermediate phases (Eq9 to Eq14) (Yévenes et al., 2010; Nyembwe et al., 2021) mainly due to its preferential Fe withdrawal from $CuFeS_2$ (Liu et al., 2024) leaving a Fe-deficient structure as a result of the greater exothermicity of oxidation on the Fe site than that on the Cu within the $CuFeS_2$ lattice structure (Yang et al., 2019).

$$5CuFeS_{2(s)} + 4Fe_2(SO_4)_{3(aq)} \rightarrow Cu_5FeS_{4(s)} + 12FeSO_{4(aq)} + 6S^0_{(s)}\Delta G = -284.5\ kj \quad (9)$$

$$2CuFeS_{2(s)} + 2Fe_2(SO_4)_{3(aq)} \rightarrow Cu_2S_{(s)} + 6FeSO_{4(aq)} + 3\ S^0_{(s)}\Delta G = -125,52\ kj \quad (10)$$

$$CuFeS_{2(s)} + Fe_2(SO_4)_{3(aq)} \rightarrow CuS_{(s)} + 3FeSO_{4(aq)} + S^0_{(s)}\Delta G = -75,3\ kj \quad (11)$$

$$Cu_5FeS_{4(s)} + 2Fe_2(SO_4)_{3(aq)} \rightarrow 4CuS_{(s)} + 5FeSO_{4(aq)} + CuSO_{4(aq)}\Delta G = -92,048\ kj \quad (12)$$

$$Cu_2S_{(s)} + Fe_2(SO_4)_{3(aq)} \rightarrow CuS_{(s)} + 2FeSO_{4(aq)} + CuSO_{4(aq)}\Delta G = -16,7\ kj \quad (13)$$

$$CuS_{(s)} + Fe_2(SO_4)_{3(aq)} \rightarrow S^\circ_{(s)} + 2FeSO_{4(aq)} + CuSO_{4(aq)}\Delta G = +8.4\ kj \quad (14)$$

The literature attributes the slow kinetics and incomplete dissolution to the formation of a passivation layer on the mineral surface, of which the nature remains controversial (Yévenes et al., 2010, Liang et al., 2011, Li et al., 2013, Nyembwe et al., 2021, Liu et al., 2024, Shangguan et al., 2024). Various passivating candidates are observed and reported

through electrochemical analysis and solid leachate residue analysis. These include metal-deficient sulphides (Wang et al., 2021), jarosite, S^0 (Zhang et al., 2023), and iron-oxyhydroxide as the main candidates. Recently, Zhao et al (2019) reviewed previous works on $CuFeS_2$ dissolution. Their survey reported that potential passivating species mainly consist of polysulphide (S^{2-}), S^0, and insoluble Fe compounds sulphate (SO_4^{2-}). Their conclusions were supported by other studies, confirming the formation of both elemental sulphur and copper-rich polysulphide $Cu_{1-x}S$ (Bai et al., 2022). Some of these phases thermodynamically displayed a retarding effect once formed, mainly for chalcocite (Eq13) and covellite (Eq14) (Nyembwe et al., 2022). In addition to that, these phases are typically characterized by low electrical conductivity and high copper content. Furthermore, Wang et al (Wang et al., 2021) observed that such passivating layers enclose the unreacted $CuFeS_2$ core, significantly hindering further copper dissolution.

Under electrochemical study, Ren et al (Ren et al., 2022) proposed a three-step synergistic mechanism strongly dependent on redox potential (Eh). They observed that dielectric breakdown occurs at a minimum potential of 0.7 V vs. Ag/AgCl (Eh $\leq$ 0.7 V), favouring rapid electron transfer and enhancing dissolution kinetics. Within the potential range of 0.50–0.70 V, preferential dissolution of Fe over Cu was reported, whereas at lower potentials (Eh < 0.5 V), strong passivation characterized by sluggish kinetics was observed. Across all conditions, the formation of a Cu-rich, Fe-deficient phase with covellite-like properties (CuS) was identified. Although the recurrent appearance of this Cu-rich, Fe-deficient phase supports polysulfide formation previously, noted by O'Connor & Eksteen (O'Connor and Eksteen, 2020) and which could relate to the different secondary phases (Eq. (9) – Eq. (13)), this mechanism presents a paradox for $CuFeS_2$ dissolution. Bio-heap leaching, which typically operates at Eh values equal to or greater than 0.7 V vs. Ag/AgCl, should theoretically reach dielectric breakdown (Table 3), thereby promoting rapid electron transfer and enhancing Cu dissolution; in practice, however, it often results in passivation. This discrepancy may be partly explained by excess Fe^{3+}, which can hinder Cu dissolution through the precipitation of FeOOH and $KFe_3(SO_4)_2(OH)_6$.

In contrast, for chemical heap leaching, the proposed mechanism conflicts with the critical potential range ($\approx$ 380–480 mV vs. Ag/AgCl) reported in the literature by Nicol, Lázaro, & Parker (Nicol, Lázaro, and Parker 2002), Sandström, Shchukarev, & Paul (Sandström et al., 2005). and Zao et al (Zhao et al., 2017) where $CuFeS_2$ dissolution is maximized. Reviewing the influence of redox potential on chalcopyrite leaching, Tian et al (Tian et al., 2021) emphasized that Eh is a critical controlling factor in both bioleaching and abiotic systems, further suggesting that the choice of potential should be guided by the mineral's electronic structure and invoking band theory as part of their framework for understanding how Eh governs dissolution.

Under kinetic study of finely ground mineral, several strategies have been explored to improve chalcopyrite ($CuFeS_2$) dissolution, often assessed through activation energy (Ea) and reaction order to support the dissolution mechanism. These approaches include oxidant-based systems O_3 (Barton and Hiskey, 2022) (Zhang et al.). 20 additive incorporation such as Cl (Lu, Jeffrey, and Lawson 2000) (Yévenes et al., 2010), Ag (Abdollahi et al., 2015; Etschmann et al., 2025) ammonia solution (Ma et al., 2021; Sun et al., 2025), pyrite addition (Dixon, Mayne, and Baxter 2008) were studied. While physico-chemical alteration has been evaluated through mechanical activation (SUN et al., 2025). Despite variations in experimental conditions, most studies report enhanced copper recovery.

Oxidants strength plays a critical role in Cu overall leaching kinetics. To that, Zhang et al (Zhang et al., 2024) highlighted Fe^{3+} alone has limited oxidation potential to overcome the passivation layer that forms on chalcopyrite. To address this, Zhang et al (Zhang et al., 2024) combined ultrasound with an O_3–H_2SO_4 system (2 M H_2SO_4, L/S = 8:1, O = 8 L/h), achieving 56% copper recovery within 5 h. Residue analysis revealed unreacted $CuFeS_2$ along with $CaSO_4$ and SiO_2. The apparent activation energy was 15 kJ·mol^{-1}, indicating that dissolution was controlled by a combination of chemical reaction and mass diffusion.

In acidified ferric sulphate (H_2SO_4 + Fe^{3+}) as the primary media, Cl addition has positive Cu dissolution efficiency. Yévenes et al. (Yévenes et al., 2010) reported that chloride ions (Cl^-) enhance $CuFeS_2$ leaching by promoting the oxidation of Cu(I) and Fe(II). In H_2SO_4–$Fe_2(SO_4)_3$ + NaCl media, an Ea of 72 kJ·mol^{-1} was observed at Eh = 580–600 mV vs SHE ($\approx$ 383–403 mV Ag/AgCl) and temperatures of 25–75 °C, suggesting a surface-controlled electrochemical process. Solid residues contained Cu-rich sulphides without Fe precipitation. Lu et al. (Lu, Jeffrey, and Lawson 2000) further noted the formation of a porous elemental sulphur (S°) layer, which facilitates electron transfer and contributes to high recoveries—up to 90% at 80–100 °C (Ruiz et al., 2011). Heap leaching studies by Jumbo-Pacheco et al. (Jumbo-Pacheco et al., 2025) under conditions of H_2SO_4 (50 g/L), Fe^{3+} (5 g/L), and T = 30 °C showed that increasing NaCl concentration (0–4 M) improved recoveries from 30.10% to 44.12%. BET analysis indicated increased porosity, suggesting diffusion-controlled dissolution.

Silver (Ag^+), introduced via AgCl or $AgNO_3$, acts as a catalyst by disrupting surface passivation and accelerating $CuFeS_2$ dissolution. For instance, Etschmann et al. (Etschmann et al., 2025) achieved 73% Cu recovery in H_2SO_4–$Fe_2(SO_4)_3$ at Eh = 500 mV vs Ag/AgCl, with ~ 1 ppm Ag at 70 °C over four days. Residues were highly porous and contained variable Cu–S phases alongside jarosite. Córdoba et al. (Córdoba et al., 2008b) compared dissolution with and without Ag_2SO_4 in similar media (pH $\approx$ 1.8, Eh = 300–600 mV Ag/AgCl, T = 35–68 °C) and observed improved Cu recovery due to increased surface reactivity. Activation energy decreased from 130.7 kJ·mol^{-1} (without Ag) to 29.25 kJ·mol^{-1} with Ag, indicating a mixed control mechanism involving electrochemical, chemical, and diffusion processes.

Iodide addition has also been reported to enhance $CuFeS_2$ dissolution. Iodide (I^-) is oxidized by ferric ions to diiodine (I_2), a strong oxidant that promotes Cu and Fe release, while I_2 is continuously regenerated by ferric ions under constant potential (Winarko et al., 2022). Heap leaching studies at Eh = 669–769 mV/SHE, iodide concentrations of 50–200 mg/L, ferric = 5 g/L, and T = 25–45 °C showed accelerated Cu extraction with increasing potential and iodide concentration. Complete dissolution was achieved at 769 mV at room temperature. Kinetic modelling indicated Eh and I_2 dependence with reaction orders of 0.32 and 1.17, respectively, and Ea = 43.1 kJ·mol^{-1}, consistent with surface-controlled chemical reactions (Winarko, Dreisinger, et al., 2022). Process additives have also been evaluated to tackle operational challenges in heap leaching. For instance, to reduce acid consumption, Ma et al. (Ma et al., 2021) investigated ammonium chloride solutions (pH $\approx$ 8.5) with varying Cu(II) concentrations (0–3 g/L as $CuCl_2$), achieving > 80% recovery under atmospheric conditions after 30 days. Surfactant addition also improved dissolution by reducing interfacial tension and enhancing heap permeability for that ethylene glycol and polyvinyl pyrrolidone (PVP) were effective (Ruiz-Sánchez and Lapidus 2022) (Zhang et al., 2023). Bai et al. (Bai et al., 2022) reported accelerated rates and ~ 80% recovery with calcium lignosulphonate in O_2-enriched H_2SO_4.

Mechanical activation and microwave-assisted leaching significantly improve dissolution (Bai et al., 2022). Sun et al. (SUN et al., 2025) compared ammonia salts (NH_4Cl, $(NH_4)_2SO_4$, and $(NH_4)_2CO_3$) and observed linear kinetics with $(NH_4)_2CO_3$, while others showed slower rates. Porous Fe precipitates (hematite, ferrihydrite) formed, creating diffusion barriers. Under these conditions, dissolution was controlled by product-layer diffusion with Ea $\approx$ 10.18 kJ·mol^{-1}. Microwave-assisted leaching and mechanical activation (grinding $CuFeS_2$ with $Fe_2(SO_4)_3$) achieved 90–98% Cu recovery within 3 h due to internal stress and solid-state transformations. Pyrite addition also acted as an effective catalyst, enabling complete dissolution at Eh = 470 mV and T = 80 °C (Dixon et al., 2008; Nazari et al., 2011). Its positive effect in the mixture with $CuFeS_2$ can be explained by the formation of an electrochemical bond between the minerals (Karimov et al., 2025).

$CuFeS_2$ passivation and dissolution are strongly influenced by redox

conditions and chemical environment. Residual Cu–S phases indicate that chalcopyrite oxidation proceeds through transitional intermediates. Activation energy varies widely—from surface-controlled to mixed-control regimes and offers limited mechanistic insight (Crundwell, 2013). This variability suggests that external conditions, rather than intrinsic stability, govern chalcopyrite's refractory behaviour, making reaction order a more meaningful kinetic parameter. Dissolution is most effectively improved by additives that suppress passivation, with chloride (Cl^-) consistently emerging as one of the most practical and efficient options in both heap (biotic and abiotic) and stirred-tank leaching systems.

5. Mineral pretreatments strategies improving heap leaching efficiencies

Pretreatment strategies are increasingly employed to overcome the refractory nature of sulphide ores by enhancing mineral dissolution efficiency, improving leaching kinetics, and significantly reducing overall processing times (Lu, Dreisinger, and West-Sells, 2017b; Quezada et al., 2020; Larrabure et al., 2023). The primary objective of pretreatment is to modify or disrupt the mineral's crystal lattice and surface structure, thereby exposing encapsulated or passivated metal values and making them more accessible to leaching reagents (Barbouchi et al., 2025). These approaches can be implemented as a dedicated stage prior to leaching or integrated into heap leaching operations (Neira et al., 2021), where they have consistently improved metal recovery from polymetallic sulphides. Reported methods include operational techniques such as agglomeration, acid-salt curing, and microbial pretreatment (bio-oxidation).

5.1. Agglomeration

The technique involves particle size enlargement, usually dictated by mineral attributes including the physical, chemical, and mineralogical characteristics (Bouffard, 2007; Nosrati et al., 2014a). Performed for fine (less than 10 μm) removal, it relies on adhesion by attractive surface forces and/or binder addition and increases heap permeability (Kawatra et al., 2004; Dhawan et al., 2013a) (Ghorbani et al., 2016). The literature highlighted the need for a binding agent for materials with a particle size of less than 75 μm. Furthermore, in addition to cost effectiveness and stability (Kawatra et al., 2004), the binding agent should withstand the acidic environment (pH ~ 2) and should not interfere with the leaching chemistry during irrigation or the subsequent processes for metal recovery (Kodali et al., 2011; Dhawan et al., 2013).

Under commercial heap leaching of Cu and Ni from polymetallic sulphide, $H_2SO_4 + H_2O$ is frequently used as a agglomerating binder. Its reaction with gangue mineral positively impacts metal dissolution by rendering gangue related phase amorphous and by inhibiting silica dissolution (Kodali et al., 2011). A curing period, initiating partial mineral dissolution, improves acid penetration, and stabilizes the agglomerates is usually optimised according to ores mineralogy (Lu et al., 2017; Cerda et al., 2018). It was reported that longer curing time allow intensifies reactions to occur, facilitating metal values (Ni/Cu) release during leaching (Quezada et al., 2020) and inhibits the dissolution of aluminium–silicate minerals (acid consumers) (Dhawan et al., 2013a). To that, Nosrati and colleagues (Nosrati et al., 2014b) investigated the impact of agglomeration on nickel dissolution from low-grade lateritic ores using sulphuric acid leaching (200 g/L H_2SO_4). Their investigation revealed that un-agglomerated ores exhibited poor Ni recovery due to clogging issues. In contrast, agglomeration with 30% w/w H_2SO_4 followed by acid curing for 48 h at room temperature significantly enhanced performance. The agglomerated ores achieved approximately 90% Ni recovery within 100 days of column leaching, underscoring the critical role of agglomeration and curing in improving leach efficiency.

The overall heap performance has also been reported to improve through Cl^- addition at the agglomeration stage. Velásquez-Yévenes (Velásquez-Yévenes et al., 2018) used $H_2SO_4 + H_2O$ at a moisture content of 10% and agglomerated low $CuFeS_2$. The authors further incorporated Cl^- (NaCl) and observed an improved Cu rate and recovery, reaching up to 60% in 20 days of leaching. Quezada (Quezada et al., 2021) achieved Cu 94% extraction from $CuFeS_2$ was when after agglomeration process with 50 g/L of Cl^- (NaCl-H_2SO_4) and curing at 90ºC (15 days) and leaching with 0.2 M of H_2SO_4 (90 °C). Other studies have used seawater as binder and source of Cl during agglomeration. Quezada et al. (Quezada et al., 2018) for instance, compared the efficiency of seawater and discarded brines with Cl- concentrations of 20 and 32 g/L respectively. A recovery of 68 and 72% Cu was obtained from 50-day curing using the different solutions. Industrial application of Cl through agglomeration stage has been reported by Jumbo-Pacheco et al., et al. (Jumbo-Pacheco et al., 2025) who reported its addition in form of NaCl or CaCl2, but the acidic conditions are established adding sulfuric acid to overcome refractory CuFeS2 during heap process.

5.2. Bio-oxidation

Biological oxidation involves inoculating crushed or agglomerated sulphide ore with iron- and sulphur-oxidizing bacteria (e.g., Acidithiobacillus ferrooxidans), which catalyse oxidative breakdown of minerals such as pentlandite and chalcopyrite. Zhihong et al. (Zhihong et al., 2016), reported that this approach reduces chemical consumption in treating low-grade Cu–Ni ores, improving process economics. Bailey and Hansford (Bailey and Hansford, 1993) identified *Thiobacillus ferrooxidans*, T. thiooxidans, and Leptospirillum ferrooxidans as the most common species used. These microorganisms attach to mineral surfaces (up to 80–90%; (Vera et al., 2022)), directly oxidizing sulphidic minerals using Fe and S as energy sources, while unattached bacteria oxidize ferrous iron to ferric, which further attacks the ore an indirect oxidation pathway.

Yanishevskya et al. (Yanishevskya et al., 2021) demonstrated that iron-oxidizing microorganisms dissolve natural and anthropogenic Cu–Ni sulphides, though recoveries were modest (Ni: 22.5% and 16.5%; Cu: 12.7% and 7.5%). The study highlighted mineralogical effects on dissolution and confirmed bacterial activity at low pH (1.8–2.3) and high metal concentrations. Similarly, Zhihong et al. (Zhihong et al., 2016), reported microbial pretreatment of Ni–Cu sulphides (Ni: 0.32%, Cu: 0.11%, Fe: 14.2%) reduced acid consumption by 5–15% and improved Ni and Cu extraction by 6.3–19.5% and 5.8–24.2%, respectively.

Both pretreatment strategies have proven effective in heap leaching by reducing acid consumption and enhancing dissolution of metal values from refractory phases (Table 4). However, agglomeration with chloride addition has so far been applied primarily to single-phase $CuFeS_2$ systems. In contrast, bio-oxidation remains dominant for Ni/Cu sulphides, with pilot- and demonstration-scale trials conducted in heaps and agitated tanks in Australia, China, Finland, and South Africa in recent years (Watling, 2008), though copper extraction remains relatively low. Further research into synergistic pretreatment approaches could significantly enhance copper recovery during heap operations involving Ni–Cu sulphide ores.

6. Computer contribution to heap leaching technology

6.1. Physical and geochemical computational model

Under heap leaching conditions, the selective dissolution of metals depends largely on the interaction between the leaching solution and ore particles. Consequently, the flow behaviour of the leaching agent is one of the most critical factors influencing process efficiency, as it directly affects extraction kinetics and overall recovery (Chaitanya and Gupta, 2023). Yin et al (Yin et al., 2013) reported that under heap leaching conditions, solution flow follows two distinct regimes: saturated and unsaturated flow. Each determined by Darcy's law and the

Table 4
Pretreatment strategies for heap leaching.

Mineral/Ore type	Pretreatment	Binder / Agent	Recovery (%Cu)	Recovery (%Ni)	Curing Conditions
Ni–Cu sulphides	Bio-oxidation	A. ferrooxidans	24.2	19.5	——
		Oxidising bacteria	12.7	22.5	——
		Oxidising bacteria	50	85	——
$CuFeS_2$	Agglomeration	H_2SO_4 + NaCl (50 g/L Cl^-)	94	—	15 days (90 °C)
		Seawater (20 g/L Cl^-)	68	—	50 days
Brine (32 g/L Cl^-)	72	—			

Brooks–Corey capillary pressure model respectively. Inadequate regime flows can lead to operational challenges such as non-uniform percolation, prolonged extraction times, and in severe cases heap instabilities or failure and poor metal values extraction (Odidi et al., 2024). To address these challenges, heap leaching instrumentations continues to develop in order to reach the required level automated system control and stable operation. Computer-based simulations have become essential tools for analysing heap hydrodynamics, predicting system behaviour, and optimizing operating strategies.

Over the past decades, significant progress has been made in developing numerical models for heap leaching. Early models were limited to a narrow set of phenomena due to computational constraints. McBride, Cross, and Gebhardt (McBride, Cross, and Gebhardt, 2012) outlined the historical evolution of heap leach modelling, noting the introduction of the shrinking-core model in the 1970 s as a key milestone. More recently, computational fluid dynamics (CFD) has enabled detailed investigation of multiphase flow and heat transport within heaps. Models have since been developed in one-, two-, and three-dimensional frameworks, each with unique features and assumptions (Bennett et al., 2006). For instance, one-dimension models (1D) are useful for studying dissolution kinetics under simplified, uniform heap structures. Using it (1D), Dixon & Hendrix (Dixon and Hendrix, 1993) demonstrated that particle size strongly influences diffusion-controlled leaching. Two-dimension models on the other hand, allow for the analysis of hydrodynamic behaviour, preferential flow, channelling, and heat transfer (Bouffard and Dixon, 2001; Yang et al., 2011). Lastly, the three-dimension framework captures the full spatial complexity of heaps while improving the realism of simulations. These models are often parameterized against experimental data and validated across a wide range of conditions (Wu et al., 2007, Liuet al., 2015; McBride et al., 2018).

Beyond physics-based models, artificial neural networks (ANNs) have emerged as complementary tools for simulating and predicting heap leach performance (Golmohammadi et al., 2013). ANNs are machine learning architectures inspired by the structure of the human brain, consisting of interconnected computational units (neurons) organized into input, hidden, and output layers (Leiva et al., 2017). Each neuron receives weighted input, applies an activation function, and transmits signals forward through the network (Fig. 5). In heap leaching, ANNs offer advantages in handling nonlinear and multivariable systems, enabling improved prediction of extraction rates, optimization of operating parameters, and reduction of production costs. Their adaptability makes them particularly valuable for modern heap operations, where ore variability, environmental constraints, and operational complexities demand more flexible predictive tools (Chehreh Chelgani and Jorjani, 2009).

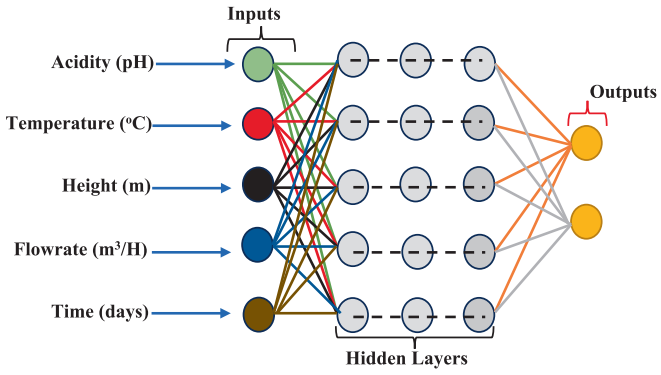

Fig. 5. Four layers ANN training prediction for metal recovery efficiency (structure (5–15-2):5: inputs, 15 neurons in hidden layers and 2 outputs).

6.2. *Artificial neural networks*

Several studies have demonstrated ANN's applicability with experimental dataset to model and optimise metal recovery (Table 5). Milivojevic (2012) applied ANN to high-pressure leaching experimental dataset of nickel (Ni), predicting recovery rates between 93 and 95% under conditions of 240 °C, L/S ratio of 0.35–0.4, and a 30-minute reaction time. Under stirred tank experiments, Kasongo et al. (2021) reported recoveries predictions of 98.98% Cu and 98.43% Co over 3 h dissolution from oxidized Cu–Co ore using 100 g/L H_2SO_4 with $Na_2S_2O_5$ additives. Mathaba and Banza (2024) employed ANN with backpropagation to model dissolution of oxidized Cu–Co ore in sulphuric acid, achieving 97.5% Cu and 95.4% Co recovery within 2 h under optimal laboratory conditions (100 g/L H_2SO_4, 55 °C, 1:40 S/L ratio, 300 rpm). Similarly, Mbuya and Mulaba (2023) integrated Response Surface Methodology (RSM) with ANN for Cu–Co siliceous ore, attaining recoveries of 93.46% Cu and 89.43% Co over 2 h dissolution at 15% solid–liquid ratio in a media having a pH value of 1.55 at 50 °C with 6 g/L of Fe^{2+} for ore size less than 95 μm.

Compared to stirred systems, heap leaching under column assessment introduces distinct mass transfer and flow constraints that require tailored modelling approaches. For example, Hoseinian et al. (Hoseinian et al., 2017) studied column leaching of oxidized copper ores with H_2SO_4 and found that recovery correlated positively with acid flow rate and leaching time, but negatively with column height. To enhance prediction accuracy, they applied both standard ANN (backpropagation) and a hybrid Genetic Algorithm–ANN (GANN). The GANN model outperformed standard ANN, showing lower mean squared error and higher correlation coefficients, underscoring the potential of hybrid approaches to capture the complex, nonlinear, and time-dependent behaviour of column leaching systems. On the other hand, Flores et al (2020) compared machine learning algorithms for classifying copper recovery quality prediction in a heap leaching process random forest (RF), support vector machine (SVM) and ANN using industrial and pilot Cu data. Their comparison showed that RF method was useful for identifying the predictive variables influence class values in the prediction. ANN was confirmed as the best method predictive method to tackle this complex data.

It has become evident that the use of ANN enables recovery forecasting, process optimization, improve operational efficiency and can be applied in conjunction with both laboratory and industrial process data. Both experimental assessments (tank and column) leaching studies provide a strong foundation for extending ANN and hybrid modelling approaches to heap leaching of polymetallic sulphide ores. Since both experimental assessments are widely used as controlled, indoor analogues for heap leaching (Xu et al., 2024). While stirred tanks primarily

Table 5
Computer simulation studies with corresponding performances.

Ore type Metal of interest	Type of Simulation	Data Type	Parameters assessed	Structure & Method	Performance	References
Ore Rudjinci Ni: 1.13 Co: 0.06	ANN	Laboratory high pressure leaching (230–250 °C)	pH, T: 230–250 (°C) t: 0.5—1 h L/S: 0.24—0.40 Agitation: 250–1500 (rpm)	Back propagation 4-9-1	93–95%	(Milivojevic et al., 2012)
Oxidized Cu-Co SiO_2 gangue Cu: 1.64 Co: 0.24	RSN ANN	Laboratory stirred tank	pH: 1.5–1.8 S/L: 20–40 (%) PSD: −75, −53 μm t: 1–2 (h) Fe^{2+}: 2–4 (g/L) T: 30–60 (°C)	Back propagation 4-7-1	93.46% Cu 89.43% Co	(Mbuya and Mulaba-Bafubiandi 2023)
SCM Franke ore Cu carbonate ore	ANN	Industrial heap leaching agglomerate	PSD ≤ 13 mm, m^3/h, pH, height, % Cu, % CO_3, L/S & t	Back propagation 8-12-15-1	Cu: > 95	(Flores et al., 2020)
Cu-Co oxide ore Cu: 3.52, Co: 0.94%	ANN	Laboratory stirred tank (100 μm)	Acidity: 30–100 g/L S/L: 5–20 (g/mL) T: 25–55 (°C) Agitation: 100–300 (rpm)	Back propagation 5-10-2-2	Cu: 97.5 Co: 95.4	(Mathaba and Banza 2024)
Cu-Co oxide ore Cu: 2.4, Co: 0.8%	ANN	Laboratory stirred tank (150 μm)	Acidity: 20–100 g/L S/L: 10–30 (%) T: 25–65 $Na_2S_2O_5$: 2–10 (g) t: 1–3 (h)	Back propagation 5-15-2-2	Cu: 94.9 Co: 98.4	(Kasongo et al., 2021)
Copper oxide agglomerated 30% H_2SO_4	ANN GANN	Laboratory column	PSD: ≤ 25.4 – ≤ 50.8 M3/h: 0.48—-58.17 (kg/t) t: 3 – 78 days Height: 2 – 6 (m)	Back propagation 4-22-16-15-1 4-15-10-1	GANN > ANN Cu > 95%	(HOSEINIAN et al., 2017)

elucidate ore leaching behaviour and dissolution kinetics, column tests are consistently selected to simulate the hydrodynamic and mass transfer conditions of heaps, serving as essential tools for process optimization prior to scale-up (Larrabure et al., 2024). Heap systems, however, introduce additional complexities including mineralogical heterogeneity, solution channelling, variable aeration, and prolonged reaction times that demand robust, adaptive models capable of integrating electrochemical, mineralogical, thermodynamic, and kinetic parameters. Leveraging such machine learning frameworks could substantially enhance predictive accuracy and operational optimization in large-scale Cu–Ni heap leaching operations.

6.3. Recent advances in digitalization and automation

The mining industry is undergoing a digital transformation, increasingly adopting advanced automation technologies to enhance production, efficiency, and sustainability. By integrating artificial intelligence (AI), machine learning (ML), deep learning (DL), Internet of Things (IoT), multi-modal sensing, and next-generation wireless systems, mining operations are becoming intelligent environments capable of executing complex tasks with minimal human intervention (Obosu and Frimpong, 2025). These innovations are particularly valuable in heap leaching, where optimization relies on accurate parameter determination and continuous monitoring since process recovery often much lower than predicted from column tests (Jia et al., 2024), largely due to the inherent complexity of heap leaching, which involves simultaneous physical, chemical, hydrological, geochemical, and biological interactions. Additional challenges arise from limited information about the internal state of the heap, including the distribution of substances within its inner layers (Groznov, 2015). Given that heap leaching is a continuous process, real-time monitoring becomes essential for improving recovery and supporting informed decision-making. In this context, IoT and sensor networks play a pivotal role in modern process control systems, enabling automation, enhancing productivity, and facilitating data-driven decisions (Pandey et al., 2025). Furthermore, digitalization strategies—such as integrated data platforms, advanced analytics, and remote sensing—combined with computer vision techniques allow for systematic monitoring and resolution of technical challenges, providing high-quality data on parameters like temperature, humidity, oxygen content, and pH (Aziz et al., 2020).

Maintaining unsaturated flow conditions is essential for ensuring the geotechnical stability of the heap (Slupsky and McIsaac, 2022). Adequate flow enables leaching within an economically viable timeframe, while uniform distribution ensures that all ore is thoroughly leached and prevents internal saturation, which could lead to liquefaction and potential local or general collapse of the pile. To achieve this, sensor networks collect data and transmit it to cloud servers, where it is analysed and made accessible through web applications for process control and yield optimization. For example, Daud et al. (Daud et al., 2021) presents demonstrated the use of temperature measurements and thermal analysis to identify and manage oversaturated zones within the heap at El Soldado mine in Chile, improving irrigation strategies and metal recovery. Similarly, Tang and Esmaeili (Tang and Esmaeili, 2021) implemented thermal infrared sensors to generate surface moisture maps and monitor reagent distribution during heap leach operations at El Gallo mine in Mexico. In addition, oxygen levels—critical for aeration and the health of bacteria involved in mineral dissolution—are monitored using OXYBase sensors deployed by Canary Systems, supporting a fully automated heap leaching process (Fiscor, 2023). These developments collectively contribute to smarter, safer, and more efficient mining operations.

7. Conclusion

Heap leaching of polymetallic sulphide ores, containing Ni and Cu, offers a promising yet challenging route for sustainable metal extraction, constrained by low recoveries and prolonged leaching cycles. This review emphasizes the need for a geo-metallurgical characterization framework that integrates host-rock composition, hydrothermal alteration, and microstructural features such as elemental ratios and accessory sulphide phases (e.g., $Fe_{1-x}S$) to predict leach behaviour. Co-dissolution of Ni and Cu suggests galvanic interactions, where $CuFeS_2$ acts as a cathode, provide insufficient surface area to accelerate pentlandite $(Fe,Ni)_9S_8$ oxidation, while transient intermediate phases often retard dissolution. Biotic environments with high Eh restrict Cu dissolution compared to abiotic systems. Solution chemistry is critical: Ni

dissolves across a broad pH (1–4) range and up to ~800 mV (Ag/AgCl), whereas Cu requires low pH (< 2) and elevated Eh, though optimal potentials for $CuFeS_2$ remain controversial. Chloride addition enhances dissolution of both metals, making it a candidate additive for leaching or pretreatment. Understanding these mechanisms enables predictive heap design through ore geology, oxidant selection, and bioleaching integration. Emerging computational tools, including machine learning and process automation, can improve predictive accuracy and operational efficiency. Future research should focus on real-time monitoring of redox dynamics, mitigating secondary mineral passivation, and developing selective lixiviants that exploit galvanic synergies, aligning with the broader goal of sustainable hydrometallurgy.

CRediT authorship contribution statement

Joseph Kolela Nyembwe: Writing – review & editing, Writing – original draft, Conceptualization. **Christian Ekberg:** Writing – review & editing, Writing – original draft, Conceptualization, Writing – original draft, Writing – review & editing, Supervision. **Ilyes Mahti:** Writing – review & editing. **Martina Petranikova:** Writing – review & editing. **Fei Wang:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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