



ISSN: 2230-9926

Available online at <http://www.journalijdr.com>

IJDR

International Journal of Development Research

Vol. 15, Issue, 12, pp.69587-69598, December, 2025

<https://doi.org/10.37118/ijdr.30369.12.2025>



REVIEW ARTICLE

OPEN ACCESS

FLUORINE IN COPPER CONCENTRATES: MINERALOGICAL OCCURRENCE, PROCESSING BEHAVIOR, AND ENVIRONMENTAL IMPLICATIONS – A REVIEW

*Antonio Clareti Pereira

Ph.D. in Chemical Engineering Federal University of Minas Gerais (UFMG) – Department of Chemical Engineering Belo Horizonte – MG – Brazil

ARTICLE INFO

Article History:

Received 29th September, 2025

Received in revised form

10th October, 2025

Accepted 24th November, 2025

Published online 30th December, 2025

KeyWords:

Fluorine impurities. Copper concentrates. Hydrometallurgy. Selective leaching. HF volatilization. Environmental impact. Process mitigation strategies. Smelting emissions.

*Corresponding author:

Antonio Clareti Pereira

ABSTRACT

Fluorine is increasingly recognized as a critical impurity in copper concentrates, with significant implications for hydrometallurgical processing, smelting, and environmental management. This review article consolidates and critically evaluates publications from 2014 to 2025, addressing the mineralogical occurrence of fluorine-bearing phases, thermodynamic and kinetic behavior during leaching and thermal treatment, and associated environmental impacts. Fluorite, fluoroapatite, and fluoride-bearing silicates represent the primary mineral sources, exhibiting distinct dissolution and volatilization characteristics. Contractual thresholds imposed by smelters typically range from 0.2 to 0.3% fluorine, requiring proactive mitigation strategies. Blending, selective leaching, controlled calcination, and chemical precipitation are reviewed and compared with respect to effectiveness, limitations, and environmental considerations. Future perspectives highlight the need for standardized analytical methods, advanced process modeling, and integration of fluorine management into circular economy frameworks. Collectively, this review provides a comprehensive foundation for researchers and practitioners aiming to optimize fluorine control in copper production.

Copyright©2025, Antonio Clareti Pereira. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Citation: Antonio Clareti Pereira. 2025. "Fluorine in Copper Concentrates: Mineralogical Occurrence, Processing Behavior, and Environmental Implications – A Review." *International Journal of Development Research*, 15, (12), 69587-69598.

INTRODUCTION

Copper hydrometallurgy plays a pivotal role in ensuring the global supply of refined copper by providing efficient processing routes for low-grade ores, polymetallic concentrates, and recycled materials (1,2). While extensive research has been devoted to the treatment of metallurgical impurities such as arsenic, antimony, and lead (3–5), the issue of fluorine contamination remains relatively underexplored—particularly within hydrometallurgical circuits (6,7). Fluorine can be present in copper ores and concentrates in a variety of mineralogical forms, including fluorite (CaF_2), fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), and fluorine-bearing phyllosilicates such as micas and amphiboles (7,13). Although typically present in trace to minor quantities, these minerals can have disproportionately negative impacts on process performance (5,13,15). During acid or alkaline leaching, fluorine may be partially or fully solubilized, increasing its concentration in pregnant leach solutions (PLS), raffinate streams, and tailings effluents (4,13,19). In thermochemical stages—such as concentrate drying, oxidative roasting, or calcination—fluorine may be released as hydrogen fluoride (HF), posing serious risks to human health, environmental safety, and the integrity of process equipment (14). In response to these concerns, both regulatory frameworks and commercial contracts have increasingly imposed strict limits on fluorine content in copper concentrates. Major smelters and refineries often enforce maximum

allowable levels in the range of 0.2 to 0.3 wt% F, above which financial penalties or outright rejection may occur. This has driven demand for robust detection methods, predictive modeling tools, and practical mitigation strategies across the copper value chain (14,19,20).

This review aims to provide a comprehensive and critical synthesis of the scientific and technical literature published between 2014 and 2025 concerning fluorine as an impurity in copper hydrometallurgy. Key topics addressed include:

- The mineralogical occurrence and chemical behavior of fluorine-bearing species. (5,15)
- The thermodynamic and kinetic characteristics governing fluorine dissolution and volatilization. (16,34)
- The environmental implications of fluorine release in aqueous and gaseous forms. (14,43)
- Mitigation strategies, including selective leaching, blending, calcination, and effluent treatment technologies. (27,44)

Furthermore, the review contextualizes these findings within evolving regulatory standards and explores promising future research

directions to reduce fluorine-related impacts in industrial copper production (14).

Mineralogical occurrence and deportment of fluorine: The deportment of fluorine in copper ores is controlled by both mineralogy and degree of liberation. Its distribution creates a dual challenge for processing plants:

- Analytical underestimation – bulk fluorine assays and selective flotation monitoring frequently neglect F bound in apatite, micas, amphiboles, or in cryptic adsorption phases on clays and sulfides. These hidden forms remain below the detection limits of routine methods, leading to discrepancies between predicted and observed F behavior in concentrates (15,16).
- Process-specific risks – each host expresses distinct problems, depending on association and liberation. Fluorite often persists in flotation and dissolves under aggressive leaching (15); fluoroapatite releases both F^- and PO_4^{3-} in acidic solutions, complicating SX circuits (10); phyllosilicates remain stable at ambient conditions but generate HF at $>600\text{ }^\circ\text{C}$ in roasters and smelters (27); and clays & sulfides carry cryptic F by adsorption or inclusions, frequently overlooked in assays yet elevating F load in concentrates (34).

To address these challenges, advanced mineralogical tools such as SEM-EDS mapping, LA-ICP-MS, LIBS, and automated mineralogy (QEMSCAN, MLA) are essential (4). Moreover, geometallurgical models integrating F deportment are required to anticipate penalties, optimize ore blending, and ensure environmental compliance. Table 1 summarizes the main fluorine-bearing phases identified in copper ores and highlights their implications for mineral processing. Fluorite and fluoroapatite are the most frequently reported hosts (4,15). Still, phyllosilicates and fluorine associated with sulfides or clays also play significant roles—often underestimated due to limitations in standard bulk assays (4,10).

The deportment of fluorine in copper ores is strongly controlled by mineralogy and the degree of liberation.

- Fluorite and fluoroapatite are relatively well recognized and, in part, can be accounted for during flotation or leaching. Their behavior is predictable, and fluorite is resistant under neutral conditions but dissolves under aggressive acidic leaching (15).
- Phyllosilicates and cryptic fluorine in sulfides or clays, however, pose far greater challenges. Their low solubility under normal hydrometallurgical conditions and their poor liberation during grinding mean they often pass undetected into concentrates. Upon thermal treatment, these phases release HF, contributing to gas emissions and refractory corrosion in smelters (27). This highlights the limitations of routine bulk assays, which frequently underestimate total F content by focusing only on fluorite. Advanced mineralogical characterization tools, such as SEM-EDS mapping, LA-ICP-MS, and automated mineralogy platforms (QEMSCAN, MLA), have therefore become essential for identifying hidden F deportment (4).
- From a process perspective, strategies such as selective flotation reagents, ore sorting to reject F-rich domains, and thermal pretreatments can mitigate fluorine-related penalties (19). Importantly, geometallurgical models that integrate fluorine mineralogy into ore blending and plant design are critical for ensuring environmental compliance and reducing downstream impacts.

Figure 1 illustrates the main fluorine-bearing phases in copper ores according to their degree of liberation (y-axis) and mineral association (x-axis). Four representative groups are shown: fluorite and fluoroapatite, which are typically coarse and partly liberated gangue phases, and phyllosilicates plus clays & sulfides, which represent cryptic or fine-grained hosts often occurring as inclusions or adsorption phases (2,7,11-13). This framework reinforces that the risk of fluorine is not solely determined by head grade, but also by how F is hosted and liberated. Fluorite and fluoroapatite are coarse,

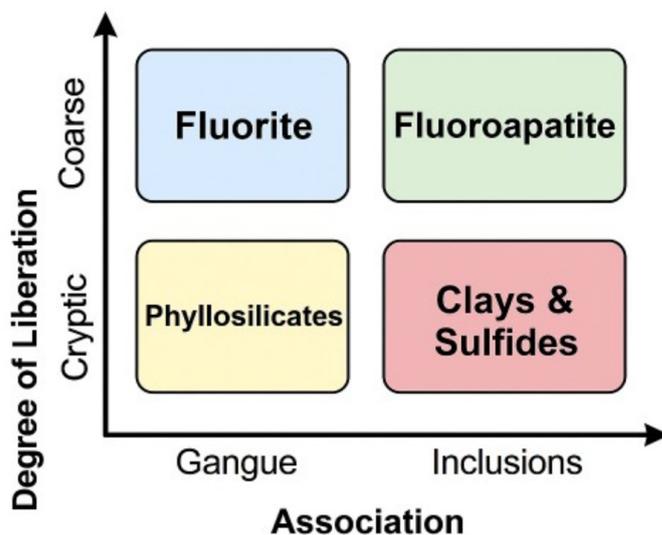


Figure 1. Fluorine-bearing phases in copper ores. Elaborated by the authors

partly liberated gangue phases (2,7), whereas phyllosilicates and clays/sulfides represent cryptic inclusions and adsorption phases (13,25).

- Fluorite: identifiable but persistent in flotation; dissolves under firm acidity (2,19).
- Fluoroapatite: moderately liberated; releases F^- and PO_4^{3-} affecting SX (7,19).
- Phyllosilicates: poorly liberated; generate HF under thermal processing (13).
- Clays & sulfides: cryptic; elevate F burden in concentrates (25).

Overall, fluorine management requires integrating mineralogical data into geometallurgical strategies to predict F deportment across beneficiation, hydrometallurgy, and pyrometallurgy (17-19). Beyond qualitative occurrence, differences in processing-relevant features can be contrasted using a radar diagram (Figure 2). Here, fluorite shows the highest F content and detectability by ore sorting, though it is chemically inert under mild leaching. Fluoroapatite exhibits high acid solubility but moderate F content, complicating SX by releasing phosphate. Phyllosilicates and F-bearing sulfides are the most problematic: although often underreported, they are associated with copper-bearing phases and have the potential to release HF during roasting or smelting, posing both environmental and metallurgical risks (19-21).

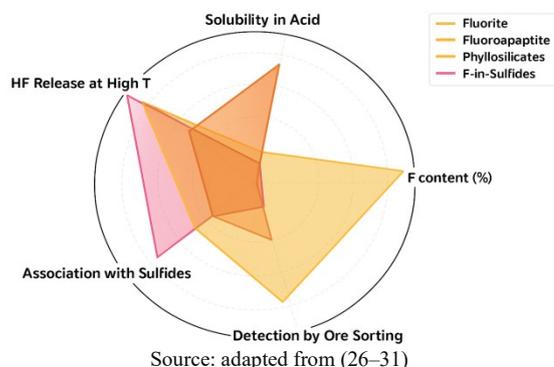


Figure 2. Comparative radar plot of fluorine-bearing minerals

The behavior of fluoride in aqueous systems is strongly dependent on pH, ionic strength, and temperature. Speciation diagrams typically show fluoride as free F^- at alkaline conditions. In contrast, in acidic media, it forms HF and HF_2^- complexes, with the stability domains shifting with activity coefficients and solution composition. (31,26). To move beyond qualitative descriptions, thermodynamic modeling

tools provide quantitative insight into fluoride speciation and phase equilibria. Programs such as PHREEQC enable the simulation of aqueous complexation, mineral solubility, and adsorption processes, making it widely applied in the geochemical modeling of fluoride in mine effluents and groundwater systems (67). On the metallurgical side, HSC Chemistry (69) enables multi-phase equilibrium calculations across gas–liquid–solid systems, which are particularly relevant for predicting fluoride volatilization and HF release during roasting and smelting operations (35). Critical perspective: Integrating these modeling platforms into fluorine studies enhances predictive capacity by coupling mineralogical occurrence with aqueous chemistry. This combined approach supports both environmental monitoring (e.g., tailings seepage) and process optimization (e.g., slag chemistry, off-gas control).

Thermodynamic behavior and leaching of fluorine: The mobilization of fluorine in copper processing is strongly controlled by thermodynamic conditions, particularly pH, temperature, and redox environment. Under most operational regimes, fluorine remains relatively immobile; however, extreme acid conditions and high-temperature processing can lead to significant release, either as dissolved species in pregnant leach solutions (PLS) or as volatile HF in roasters and smelters. (23-28). Table 2. Summarizes key fluorine-related reactions and behaviors under different processing conditions commonly encountered in copper metallurgy. It links the thermodynamic environment to the fate of fluorine, outlining both chemical transformations and practical process implications. This overview demonstrates that substantial fluorine mobilization occurs only under extreme acid-leaching or thermal-processing conditions. In hydrometallurgy, fluoroapatite is moderately reactive in strong sulfuric acid, releasing fluoride and phosphate, while fluorite remains largely unreactive unless exposed to very low pH and high temperature (23,76). In alkaline or mixed leaching systems, phyllosilicates exhibit very slow dissolution, but their contribution becomes relevant in long-term heap or in-situ leaching (26). In aqueous circuits, fluoride speciation is highly sensitive to pH: HF dominates under acidic conditions ($\text{pH} < 2$), free F^- is stable in near-neutral systems, and metal–fluoride complexes prevail in alkaline solutions (31,26). This directly affects solvent extraction efficiency and effluent treatment strategies, as fluoride can interfere with phase separation and must be removed by precipitation or ion exchange. During pyrometallurgy, the decomposition of fluorite and phyllosilicates above 700–800 °C produces HF, leading to corrosion of furnace linings and gas ducts, and necessitating efficient scrubbing systems (23,58–60). Finally, thermodynamic modeling tools—notably PHREEQC, HSC Chemistry, and FactSage—are indispensable for predicting fluoride solubility, speciation, and volatilization. Their use enables proactive process design and helps ensure both metallurgical performance and environmental compliance (28,35,37). Figure 3 shows qualitative comparison of fluoride release from major F-bearing minerals (fluorite, fluoroapatite, biotite, muscovite) under acidic leaching, alkaline leaching, and high-temperature processing ($>700^\circ\text{C}$). Fluorite is highly resistant to leaching but susceptible to thermal volatilization, while phyllosilicates tend to release F mainly during heating.

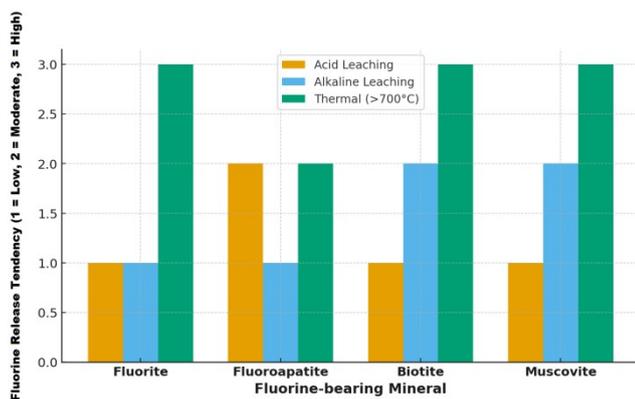


Figure 3. Relative solubility of fluorine-bearing minerals under different conditions. Source: Elaborated by the authors

The comparative solubility profile highlights the contrasting behaviors of fluorine-bearing minerals under different processing conditions.

Fluorite (CaF_2): Exhibits high thermal volatility, releasing HF at elevated temperatures ($>700^\circ\text{C}$), which represents a significant risk during drying, roasting, and smelting operations. However, under acid or alkaline leaching, fluorite remains stable mainly, requiring extreme acidity ($\text{pH} < 1$) and high temperature ($>80^\circ\text{C}$) for significant dissolution (23-25).

Fluoroapatite: Shows moderate solubility in acidic environments, especially in sulfuric acid, releasing both fluoride (F^-) and phosphate (PO_4^{3-}) ions. This behavior makes fluoroapatite a key contributor to fluoride accumulation in hydrometallurgical circuits and a challenge for solvent extraction (SX) systems (24,38-41).

Phyllosilicates (biotite, muscovite): These minerals are highly resistant to aqueous leaching, displaying negligible fluoride release in both acidic and alkaline systems. However, they undergo thermal decomposition above 700°C , generating HF gas and posing environmental and corrosion risks to equipment in pyrometallurgical steps (23,36).

Implications: The distinct dissolution behaviors underscore the need for mineralogical characterization to predict fluorine department. In hydrometallurgy, monitoring fluoroapatite content is essential to control fluoride build-up in process solutions, while in pyrometallurgy, special attention must be given to phyllosilicates and fluorite due to HF emissions. These insights support targeted mitigation strategies, such as blending ores, optimizing roasting atmospheres, and incorporating advanced gas scrubbing technologies (26,38,59). Figure 4 illustrates the predominance of fluoride species as a function of pH. At pH below 2, hydrogen fluoride (HF) is the dominant species in solution. In the intermediate pH range (3–7), free fluoride ions (F^-) are prevalent. Above pH 7, the formation of stable complexes such as $(\text{AlF}_6)^{3-}$ and $(\text{FeF}_6)^{3-}$ becomes significant in the presence of trivalent metal cations.

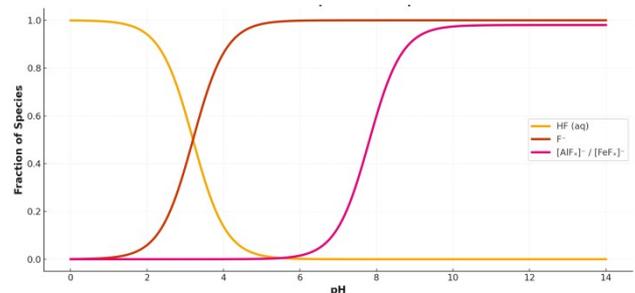


Figure 4. Fluoride speciation diagram as a function of pH. Source: Adapted from (36-38,67)

The diagram illustrates the pH-dependent equilibrium of fluoride species in hydrometallurgical systems:

Strongly acidic conditions ($\text{pH} < 2$):

- HF(aq) is the dominant species, indicating high volatility and potential for gaseous emissions during leaching, drying, or evaporation processes. This represents a significant environmental and occupational safety risk, especially in open systems or poorly ventilated operations (23,36).
- Moderate acidity to near-neutral pH ($\text{pH} 3\text{--}6$):
- Free fluoride ions (F^-) are predominant. In this range, fluoride remains dissolved, influencing solution chemistry, particularly in solvent extraction (SX) circuits where F^- may compete with target metal species, leading to reduced extraction efficiency and increased maintenance requirements due to scaling and corrosion (31,38).
- Alkaline conditions ($\text{pH} > 7$):

- Fluoride forms stable metal–fluoride complexes, especially with aluminum and iron ($(\text{AlF}_6)^{3-}$, $(\text{FeF}_6)^{3-}$). These complexes are difficult to precipitate or remove, complicating effluent treatment and recycling streams (26,38).

Implications: This behavior emphasizes the critical role of pH control in fluoride management. Maintaining leach solutions within controlled pH windows allows operators to minimize HF volatilization under acidic conditions while preventing the formation of persistent fluoride complexes under alkaline regimes. Accurate thermodynamic modeling using tools like PHREEQC (67) or HSC Chemistry (35) is essential for predicting speciation and guiding operational decisions in both hydrometallurgical and environmental management contexts. In summary, understanding fluoride speciation is fundamental for designing effective treatment systems, optimizing process performance, and mitigating environmental risks in copper processing circuits (31,26). Figure 5. presents a simplified flow diagram illustrating the major fluorine pathways across key units in copper hydrometallurgical processing. The diagram identifies three principal forms of fluorine: F^- in leach solutions, $\text{HF}(\text{g})$ in high-temperature gas streams, and solid CaF_2 in residues. Fluorine may enter the circuit through fluorine-bearing minerals such as fluoroapatite, fluorite, or phyllosilicates. During acid leaching, soluble fluoride (F^-) enters the pregnant leach solution (PLS). In thermal treatment stages (e.g., concentrate drying or roasting), fluorine may volatilize as HF gas, requiring gas treatment via scrubbers to mitigate emissions. Under certain conditions, fluoride can also reprecipitate as CaF_2 , becoming immobilized in the solid tailings stream (35).

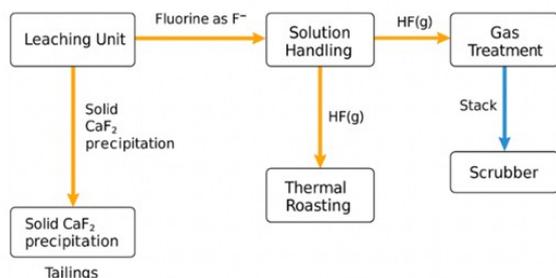


Figure 5. Simplified flow diagram of fluorine pathways in copper hydrometallurgical processing. Source for reactions and pathways: based on (1,4) (acid leaching), (23) (thermal volatilization), (38) (fluoride speciation), and (35) (thermodynamic modeling)

The flowchart illustrates the multiphase behavior of fluorine in copper processing, showing its transitions between solid, liquid, and gaseous forms throughout hydrometallurgical and pyrometallurgical circuits.

Leaching stage: Fluorine initially dissolves as F^- ions, primarily from fluoroapatite, while fluorite remains largely stable unless subjected to extreme acidity and temperature. By controlling pH and adding calcium ions, CaF_2 precipitation can be promoted, fixing fluoride in the solid phase and preventing its migration into process solutions. (31)

Solution handling: During intermediate storage and processing steps, dissolved fluoride may volatilize as HF gas, especially if solutions are heated or acidified. This represents a critical transfer point between liquid and gaseous phases (52–54).

Thermal roasting: In roasting or smelting operations, phyllosilicates and residual fluorite decompose, releasing HF at temperatures above 700–800 °C. This HF becomes a major contaminant in process off-gases, contributing to ductwork corrosion and environmental emissions (23).

Gas treatment: The diagram highlights the role of scrubbers and gas cleaning systems as essential mitigation steps. Without effective gas

treatment, HF emissions would exceed environmental limits and present safety hazards for workers (36).

Key implications: This integrated view demonstrates why single-stage mitigation measures, such as leach pH control alone, are insufficient. Effective fluorine management requires a systems approach involving (23,36,38):

- Scrubber installation for HF gas capture and neutralization.
- pH and calcium control to optimize CaF_2 precipitation and reduce fluoride solubilization in PLS.
- Leach residence time and temperature optimization to minimize unwanted dissolution of fluorine-bearing phases.

Understanding these dynamic pathways is essential to maintaining solvent extraction performance, preventing scaling and corrosion in downstream circuits, and ensuring compliance with environmental regulations (38).

Industrial specifications and fluorine limits in copper concentrates:

The commercial viability of copper concentrates is strongly dependent on their impurity profile, which directly influences smelter acceptance criteria and downstream environmental compliance. Among the most critical impurities, fluorine has attracted particular attention due to its corrosive behavior during smelting and its tendency to volatilize into hazardous compounds, such as hydrogen fluoride (HF) (23). When released, HF can cause severe damage to refractory linings, corrode gas-handling systems, and generate hazardous emissions that require advanced scrubbing systems (36). As a result, smelters and refineries worldwide impose strict contractual limits on fluorine content in purchased concentrates, both to protect equipment integrity and to comply with environmental regulations (59).

Smelter acceptance thresholds: Most copper smelters apply penalties or outright rejection for concentrates exceeding 0.2–0.3 wt% F, with the exact threshold depending on the smelting technology (e.g., flash smelting, bath smelting) and local emission control policies (59).

- Chinese and Japanese smelters, particularly those operating under oxygen-enriched conditions or located near urban zones, often enforce stricter limits, sometimes as low as 0.1 wt% F, to maintain compliance with stringent air quality regulations (75).
- Some modern smelters equipped with advanced gas cleaning systems may tolerate slightly higher F levels (up to 0.35 wt%) but apply steep financial penalties to compensate for the increased operating costs and environmental risks (46).

These specifications reflect not only technical limitations but also economic considerations, since excessive fluorine leads to higher consumption of neutralizing reagents (e.g., lime for CaF_2 precipitation) and increased maintenance of scrubber units and heat exchangers (38,59).

Critical perspective

Fluorine concentration control is no longer just a quality parameter but a strategic factor in global copper supply chains.

- For producers, meeting low F thresholds requires selective mining, ore blending, and sometimes pre-flotation or thermal pretreatment to remove high-fluorine gangue minerals before shipment (56,69,74).
- For smelters, tight F specifications are crucial to prevent process disruptions, emissions violations, and corrosion failures, which can lead to unplanned shutdowns and regulatory fines (59).

The growing prevalence of stricter F limits indicates a shift toward integrated management strategies that combine geometallurgical modeling at the mine level with real-time monitoring of concentrate quality at the shipping and reception stages (46,47).

Table 1. Fluorine-bearing phases in copper ores and their process implications Source: Elaborated by the authors

Mineral / Host	Occurrence in ores	Reactivity / Behavior	Process Implications
Fluorite (CaF₂)	Disseminated gangue; fracture fillings; sulfide inclusions	Stable under mild leaching; partial dissolution at pH < 1 and high T	May elevate fluoride in PLS; survives most flotation circuits
Fluoroapatite	Phosphate-rich zones; associated with Fe oxides, carbonates	Moderately soluble in acid; releases F ⁻ and PO ₄ ³⁻	Increases fluoride in solution; may interfere with SX and require phosphate control
Phyllosilicates (micas, amphiboles)	Sedimentary ores; African/Andean porphyries	Low solubility at ambient T; release HF at T > 600–800 °C	Source of HF in dryers/roasters; underreported in assays focused only on fluorite
Sulfides & Clay adsorption	Fine inclusions in sulfides; adsorption on smectite/kaolinite	Not liberated by standard flotation; often undetected in bulk assays	Contributes to fluorine in the final concentrate even when the head-grade is low

Table 2. Summary of fluorine behavior in copper processing Source: Elaborated by the authors

Process Condition	Main Fluorine Reaction / Behavior	Thermodynamic Conditions	Process Implications
Acid leaching (H ₂ SO ₄)	Partial dissolution of fluoroapatite; fluorite stable unless T > 80 °C and pH < 1	Strong acid (pH < 1); High T (> 80 °C); (H ₂ SO ₄) > 3 mol/L	Moderate F release; fluoroapatite contributes F ⁻ and PO ₄ ³⁻ to PLS; fluorite mostly inert
Silicate leaching (alkaline/mixed)	Slow release of F from phyllosilicates in carbonate or ammoniacal systems	T = 70–90 °C; long residence times	Low solubility but relevant in heap leaching and long-term leach circuits
Speciation in solution	F ⁻ ↔ HF equilibrium; complexation with Al ³⁺ , Fe ³⁺ , Mg ²⁺	pH < 2: HF(aq); pH 3–5: F ⁻ ; pH > 7: metal–F complexes	Direct impact on SX performance and effluent treatment (precipitation, ion exchange)
Thermal processing	HF release via decomposition of fluorite or phyllosilicates	T > 700–800 °C; oxidizing conditions	HF emissions cause refractory corrosion and air-quality issues, scrubbing essential
Thermodynamic modeling	Solubility prediction, HF volatilization, CaF ₂ reprecipitation	Software: HSC, PHREEQC, FactSage	Supports flowsheet design, impurity tracking, and environmental compliance

Table 3. Maximum allowable fluorine content in copper concentrates by smelter and country. Source: Elaborated by the authors based on global smelter specifications

Smelter / Country	Maximum Fluorine Content (wt%)	Remarks
Chuquicamata / Chile	0.25	Penalty applied above 0.20 wt% (48)
Kansanshi / Zambia	0.30	Accepted if gangue is easily separated during slag processing (49)
Jinchuan Group / China	0.20	Strict rejection policy due to urban location and environmental limits (45)
Aurubis / Germany	0.15	Applies environmental surcharge for F above 0.12 wt% (50)
PT Smelting / Indonesia	0.30	Requires declaration and control plan for F-bearing ores (51)
Horne Smelter / Canada	0.25	Equipped with internal HF abatement and monitoring system (52)

Table 4. Illustrative penalty structure for fluorine in copper concentrates. Adapted from Hoang et al. (2021), Chen et al. (2020), and Wang et al. (2023)

Fluorine grade in concentrate (wt%)	Penalty band	Penalty formula (USD/dmt)	Example surcharge (USD/dmt)*	Commercial status
F ≤ 0.20	No-penalty range	0	0 (e.g., F = 0.18 wt%)	Standard TC/RC, no penalty applied
0.201 – 0.250	Band 1 – moderate F	2 USD/dmt for each 0.01 wt% F above 0.20	F = 0.23 wt% → (0.03 / 0.01) × 2 = 6 USD/dmt	Concentrate accepted with minor penalty
0.251 – 0.300	Band 2 – high F	Penalty from Band 1 + 4 USD/dmt for each 0.01 wt% F above 0.25	F = 0.28 wt% → Band 1: (0.05 / 0.01) × 2 = 10; Band 2: (0.03 / 0.01) × 4 = 12; Total = 22 USD/dmt	Concentrate accepted, but subject to significant penalty
F > 0.300	Band 3 – very high F	Penalty from Bands 1–2 + 5 USD/dmt for each 0.01 wt% F above 0.30	F = 0.32 wt% → previous bands (F = 0.30): 30 USD/dmt; extra (0.02 / 0.01) × 5 = 10; Total = 40 USD/dmt	Concentrate may be rejected or traded only under special agreement

Table 5. Flotation-based techniques for selective fluorine rejection in copper concentrates—source: Elaborated by the authors

Strategy	Mechanism	Typical Result
Selective depressants	Adsorption on gangue surfaces to suppress flotation	↓ Floatability of fluorite/apatite
Tannins	Phenolic binding with fluorite	Upto 50% fluorine reduction
Starch/CMC	Hydrogen bonding with apatite/silicate surfaces	Improved selectivity
Collector modification	Molecular tailoring to favor chalcopyrite over F-bearing gangue	↑ Chalcopyrite recovery, ↓ gangue float
Regrinding (liberation control)	Liberation of locked F-bearing phases, improving separation in cleaner stages	↑ Fluorine rejection during cleaning stages

Table 3 summarizes the maximum allowable fluorine content in copper concentrates across selected international smelters. The data highlight significant variability in acceptance thresholds and mitigation policies, often driven by environmental regulations, process design, and local emission standards.

The fluorine tolerance among global copper smelters shows significant regional variation, directly reflecting environmental regulations, technology levels, and market dynamics.

- Aurubis (Germany) enforces the strictest limit, at 0.15 wt%, driven by stringent EU environmental standards and urban location concerns (50,53).
- Kansanshi (Zambia) and PT Smelting (Indonesia) permit up to 0.30 wt%, leveraging operational flexibility and fluorine declaration protocols that allow proactive mitigation planning (49,51).
- Jinchuan Group (China) maintains a low threshold of 0.20 wt%, reflecting internal rejection policies and strict government oversight of industrial emissions (45).
- Home Smelter (Canada) accepts up to 0.25 wt%, supported by its integrated HF abatement system, which neutralizes gaseous emissions before release (52).

These differences demonstrate how fluorine content directly impacts the commercial value and marketability of copper concentrates, influencing penalty structures, contract negotiations, and ultimately, the global copper trade flow. For producers operating near or above penalty thresholds, strategic measures such as ore blending, selective mining, and pre-treatment steps are essential to maintain smelter compliance and avoid financial penalties (56). Table 4 summarizes a typical penalty structure for fluorine based on reported commercial practices, market data, and smelter disclosures cited in the literature. Although variations exist across regions and companies, most smelters apply incremental surcharges per 0.01 wt% F above a contractual threshold, usually set at 0.20 wt% F. The penalty rises sharply once fluorine reaches rejection levels (0.30–0.35 wt%), reflecting: (i) increased flux consumption in converting and slag cleaning, (ii) higher off-gas treatment costs due to HF and F-bearing particulates, and (iii) accelerated refractory wear in furnaces and waste-heat boilers, as documented by Hoang et al. (2021), Chen et al. (2020), and Wang et al. (2023).

A critical analysis of the penalty structure shows that fluorine affects smelting economics through multiple pathways—not only by reducing metallurgical performance but also by increasing indirect environmental and operational expenditures. For instance, concentrates with 0.25–0.30 wt% F may remain technically processable but become economically unattractive because penalties accumulate rapidly and can surpass the value of the contained copper. This phenomenon has already been reported in several case studies where high-F ores required blending, selective flotation, or pre-roasting to restore marketability. It is also important to note that penalty structures are dynamic and market-dependent. During periods of high treatment charges (TC/RC), smelters tend to enforce stricter fluorine restrictions and higher penalty rates, whereas during low TC/RC cycles, some smelters may temporarily relax thresholds to secure feedstock. This market sensitivity is highlighted in recent global copper concentrate trading reports (Li et al., 2022; Hoang et al., 2021), and suggests that fluorine-related surcharges cannot be interpreted in isolation but must be understood within broader economic cycles.

Regulatory influence and air emission standards: Environmental regulations, especially those targeting hydrogen fluoride (HF) emissions, are increasingly reshaping impurity management practices in the copper smelting industry. Regulatory frameworks in key jurisdictions — such as the European Union (EU), United States (EPA), and China — have established strict emission limits that indirectly dictate the acceptable fluorine content in copper concentrates (45,53,54).

For instance, the EU Industrial Emissions Directive mandates HF stack emission levels below 1 mg/Nm³, one of the most stringent global standards (45). Similarly, Chinese regulations impose limits of < 5 mg/Nm³, driving smelters to adopt enhanced scrubbing systems and concentrate control plans (45).

Critical analysis

These air quality standards function as both downstream environmental constraints and upstream process drivers:

- HF stack emission limits force smelters to implement advanced gas scrubbing, concentrate pre-treatment, or ore blending strategies to maintain compliance (52,53,59).
- Mine planning must consider deposits with known fluorine-bearing phases to avoid producing material that will face heavy penalties or rejection.(57)
- Concentrator flowsheets may be modified to include selective flotation, desliming, or ore sorting, minimizing F-rich gangue reporting to the concentrate stream (61,62,74).
- Marketability is directly affected, as traders increasingly avoid concentrates near penalty thresholds to mitigate financial and logistical risks (56).

Environmental policy is thus not merely a compliance issue but also a strategic factor shaping metallurgical planning and concentrate marketing on a global scale.

Blending and dilution practices

Ore blending remains a widely used strategy to manage fluorine content by diluting high-F concentrates with cleaner feedstock (42). This practice helps smelters maintain compliance without directly modifying upstream processes. However, several emerging challenges are reducing its effectiveness:

- Logistical constraints: blending requires multiple ore sources, which may be unavailable in single-deposit operations or geographically isolated mines (56).
- Batch-wise certification: many smelters now require lot-specific fluorine certification, reducing the ability to homogenize material through bulk blending (42,57).
- Hidden high-F zones: blending can mask localized F-rich material, leading to unexpected spikes in HF emissions, process upsets, and potential shipment rejections (56,59).
- As a result, the industry is shifting toward preventive upstream control, including:
- Selective mining of low-F ore zones (56).
- Early-stage deportment studies to understand fluorine distribution during flowsheet development (8,9).
- Ore sorting and pre-concentration to remove F-rich gangue before grinding (61,62).

These proactive strategies reduce downstream mitigation costs and increase compliance with increasingly strict smelter specifications.

Impact on economics and contracts

Exceeding industrial fluorine thresholds can severely impact the profitability of copper concentrate exports.

- Smelters typically apply progressive penalty schemes, with surcharges ranging from \$2–\$5 USD/dmt for every 0.01 wt% F above the contractual limit (commonly 0.20–0.25 wt%) (42,57).
- In severe cases, such penalties can erode profit margins by 10–20%, particularly for low-grade concentrates or during periods of metal price volatility (57).
- Logistical setbacks further compound these economic risks:
- Cargo rejection at port due to non-compliance with environmental regulations. (56,58)

- Demurrage fees caused by delays in unloading and additional testing (42).
- Potential loss of preferred-supplier status, damaging long-term relationships with key smelters and traders (42,64).

To mitigate these risks, producers may need to adopt costly pre-treatment strategies, such as thermal volatilization, selective leaching, or specialized flotation circuits, to bring fluorine levels below acceptance thresholds (37,67,69). Ultimately, the economic significance of fluorine control extends beyond compliance, becoming a determinant of commercial viability in an increasingly competitive and environmentally restrictive global copper market. (42,52,57,59)

Methods for fluorine removal from copper concentrates: The mitigation of fluorine in copper concentrates has become a strategic priority for mining companies and metallurgical operations, driven by tightening smelter specifications and increasingly stringent environmental regulations. Elevated fluorine levels negatively impact both pyrometallurgical performance—due to HF volatilization and refractory corrosion—and marketability, as concentrates exceeding contractual thresholds face heavy penalties or outright rejection (42,53,68). Several technological strategies have been investigated to reduce fluorine content to acceptable levels, ranging from mineralogical pre-selection to thermal and chemical treatments. This section summarizes the main technological pathways for fluorine removal, focusing on their mechanisms, removal efficiency, and industrial applicability (37,61,69).

Mineralogical pre-treatment and ore sorting

Pre-concentration of fluorine-bearing gangue minerals upstream of flotation circuits represents a preventive approach, targeting fluorine deportment before it enters the bulk concentrate. This strategy relies on differences in physical properties between fluorine-rich minerals (e.g., fluorite, fluoroapatite) and copper-bearing sulfides. (61,62,68)

- X-Ray Transmission (XRT) sorting has demonstrated high selectivity for fluorite-bearing particles due to their higher density and atomic number contrast, enabling early rejection of F-rich material with minimal loss of valuable sulfides (61,62).
- Desliming operations exploit the fine grain size and low settling velocity of fluorine-bearing phases, such as clays and alteration products, to remove them from the circuit before flotation, reducing downstream contamination (63,64,74).

However, the overall effectiveness of these techniques depends strongly on mineral association and textural liberation:

- When fluorine is finely disseminated within sulfide grains or locked within alteration halos, its physical separation becomes impractical, increasing reliance on downstream mitigation strategies (7,22).
- Additionally, implementing such methods may require substantial capital investment in advanced sensors, classifiers, and process control systems, which can pose challenges for existing plants not initially designed for fluorine control (53,59,69).

Despite these limitations, selective removal at early stages offers several benefits:

- Reduces smelter penalties and risk of cargo rejection.
- Improves process predictability by stabilizing concentrate chemistry.
- Enhances environmental compliance through reduction of HF emissions during smelting (36,53,68).

For these reasons, mineralogical pre-treatment is emerging as a strategic tool in modern beneficiation flowsheets, especially in

regions where environmental standards and concentrate specifications are rapidly tightening. (53,68)

Selective leaching: Figure 6 presents a simplified flowchart of a selective leaching process designed to reduce fluorine content in copper concentrates before smelting. The process begins with a ground concentrate, which is fed into a leaching tank where it is treated with either sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH), depending on the mineralogical characteristics of the fluorine-bearing phases (37,74).

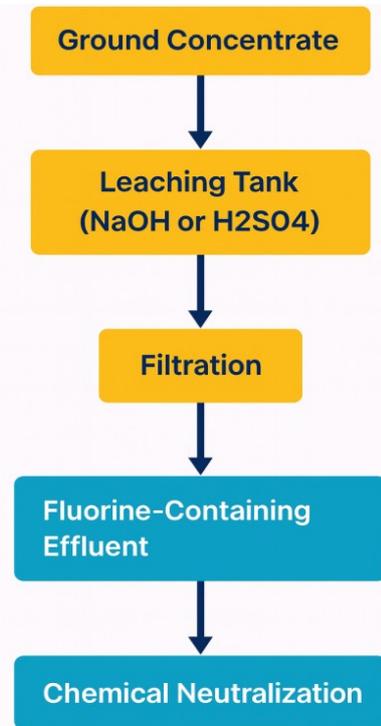


Figure 6. Selective leaching process Source: Elaborated by the authors

After leaching, the slurry undergoes filtration, producing two distinct streams

- Fluorine-rich effluent, which is routed to chemical neutralization units for treatment and safe disposal.
- Solid residue, which is dried and stored, ready for smelting operations.

This process achieves a dual objective: lowering fluorine levels to meet smelter specifications and ensuring environmental compliance by responsibly managing both liquid and solid outputs. Selective leaching is a targeted and effective strategy for reducing fluorine concentrations in copper concentrates, especially when the fluorine is present in soluble or weakly bonded gangue minerals, such as fluoroapatite or fine-grained micas (37,75). The selection of leaching reagent depends on the chemical nature of the host mineral:

- Sulfuric acid (H_2SO_4): More effective for fluoroapatite dissolution but may also release phosphate ions (PO_4^{3-}), requiring subsequent treatment to avoid interference with solvent extraction or effluent systems (37,38,75).
- Sodium hydroxide (NaOH): Preferred for silicate-hosted fluorine, offering higher selectivity, though it typically requires elevated temperatures and longer residence times, increasing operational energy demands (37,38,75).

However, the method presents economic and operational trade-offs

- Increased reagent consumption and energy costs, which can affect process economics.

- Generation of fluorine-rich effluents that demand neutralization and safe disposal, adding environmental management complexity (38,53).
- Risk of partial metal losses, such as copper and precious metals, if process parameters are not correctly optimized (37,53).
- Despite these challenges, selective leaching becomes critical when fluorine concentrations exceed acceptable smelter limits and upstream mitigation methods, such as blending or sorting, are insufficient. In high-value concentrates, where penalties or rejection could result in significant financial losses, the process can be economically justified, ensuring smelter compatibility and regulatory compliance (37,42,53,66).

Thermal volatilization

Figure 7 presents a simplified process flow for controlled calcination to reduce fluorine content in copper concentrates before smelting. The process begins with moist concentrate, which first undergoes pre-drying to minimize energy consumption and prevent vapor condensation inside the calcination unit. (64,66,68)

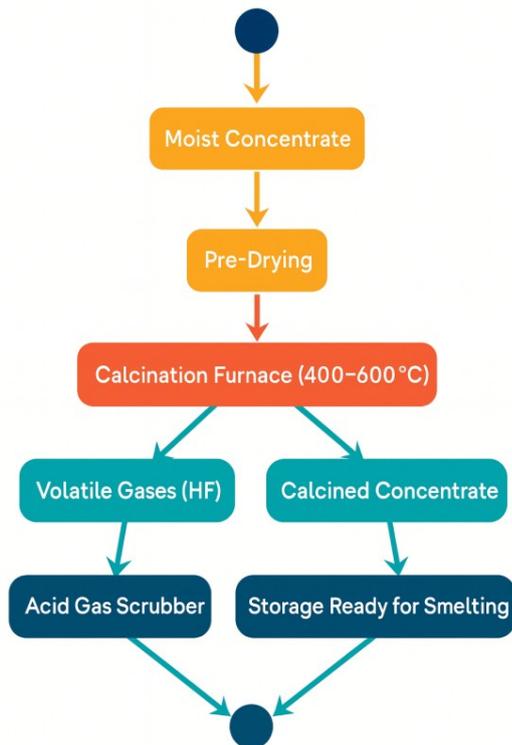


Figure 7. Controlled calcination for fluorine reduction. Source: Elaborated by the authors from (53,69,73)

The dried material is then processed in a calcination furnace operating at 400–600 °C, where fluorine-bearing phases—such as fluorite (CaF₂), fluorapatite, or F-substituted silicates—partially decompose, releasing hydrogen fluoride (HF) gas. (65,66,74)

This step produces two main streams:

- Volatile gases (HF) are directed to acid gas scrubbers for capture and neutralization, preventing environmental emissions. (36,53,65)
- Calcined concentrate, which is cooled and stored, is now compliant with fluorine thresholds required by smelters. (53,66,69)

Thermal treatment via controlled calcination has emerged as a technically robust pre-treatment method for fluorine removal in copper concentrates (22,65,69), particularly under the following conditions:

- When fluorine is present in volatile or semi-volatile forms, such as fluorite, fluorapatite, or mica-group minerals (7,22).

- When selective leaching is impractical, due to high reagent costs, challenges in water balance, or excessive residual moisture in the feed (37).

Operating temperature considerations

The optimal temperature range (400–600 °C) is selected to balance: (74)

- Sufficient thermal energy to promote HF volatilization and decomposition of fluorine-bearing phases. (67)
- Avoidance of copper sulfide oxidation or volatilization of valuable metals such as arsenic and precious metals (53,69).

Advantages

- Fast processing times, with typical residence periods of less than one hour.
- Scalability, as the process can be implemented in rotary kilns, multiple-hearth furnaces, or flash dryers, which are common in modern concentrators (53,69).
- Compatibility with existing infrastructure, particularly where gas scrubbing systems are already operational for SO₂ or HF capture (53,69).

Limitations

- High capital investment and energy requirements, especially at large scales. (69)
- Generation of corrosive HF gas, requiring the use of acid-resistant linings and components to prevent equipment degradation (36).
- Limited efficiency when fluorine is structurally bound in refractory silicate phases such as biotite or amphiboles, which require higher temperatures or longer residence times for partial decomposition (73).

Concluding remarks: Controlled calcination is a viable, scalable pre-treatment solution for copper concentrates with moderate to high fluorine levels, particularly in high-throughput operations or centralized processing hubs. Its successful implementation relies on precise temperature control, robust gas-handling systems, and integration with environmental compliance frameworks, ensuring both smelter acceptance and regulatory compliance. (53,69)

Flotation optimization: targeted reduction of fluorine-bearing gangue:

Selective flotation optimization is a cost-effective strategy for mitigating fluorine in copper concentrates, especially when fluorine-bearing minerals, such as fluorite (CaF₂) and fluorapatite (Ca₅(PO₄)₃F), are partially liberated and can be selectively rejected during flotation. (74). The focus is on reagent scheme adjustments and liberation enhancement to minimize fluorine entrainment without compromising copper recovery (72,74). Table 5 summarizes the main flotation-based strategies for fluorine reduction, highlighting the mechanisms and expected outcomes. These include selective depressants, collector modification, and regrinding to improve mineral liberation. Table 5. Flotation-based techniques for selective fluorine rejection in copper concentrates—source: Elaborated by the authors.

Mechanistic Insights

Selective depressants: Natural tannins demonstrate strong phenolic interactions with fluorite surfaces, significantly reducing floatability (70). Carboxymethylcellulose (CMC) and starch derivatives are highly effective for depressing fluorapatite and silicates, particularly under alkaline conditions, improving overall selectivity (71).

Collector modification: The use of dithiophosphates and thiol-functionalized collectors enhances chalcopyrite recovery while disfavoring F-bearing gangue, reducing fluorine entrainment in the concentrate (73).

Regrinding: By regrinding rougher concentrates, locked fluorine phases are liberated, facilitating their rejection in cleaner flotation stages. This step has proven especially valuable in ores with fine intergrowths between gangue and sulfides (72,74).

Performance and limitations: These methods have been shown to reduce fluorine content by 20–50% in final concentrates, depending on ore mineralogy, grinding fineness, and reagent optimization (70-72).

- Importantly, these reductions are often achieved without significant copper losses, making flotation optimization an attractive low-CAPEX alternative compared to thermal or chemical pre-treatments (72).
- However, successful implementation requires:
 - Comprehensive mineralogical characterization, using tools such as QEMSCAN or LA-ICP-MS to identify fluorine deportment. (22,38)
 - Bench-scale testing to fine-tune reagent dosages and flotation conditions. (38,71)
 - Careful monitoring of recycled water chemistry, as dissolved F⁻ can interact with flotation reagents and impact circuit performance (38,72).

When fluorine-bearing minerals are discrete and well-liberated, depressant-based flotation provides one of the most environmentally sustainable and economically viable solutions for meeting smelter specifications and complying with environmental regulations. (64)

Emerging technologies for fluorine removal: Recent research has focused on innovative techniques to address the challenges and limitations of conventional thermal and chemical processes for fluorine removal from copper concentrates. While most of these methods remain at laboratory or pilot scale, they hold promise for environmentally sustainable, selective, and cost-effective fluorine mitigation in the future (19,60,75,76).

Bioleaching of fluorine-bearing minerals: The use of fluorophilic microbial species, such as *Acidithiobacillus ferrooxidans* and *Leptospirillum* spp., under acidic conditions has demonstrated partial solubilization of fluorine from silicate and apatite minerals at moderate temperatures (30–50 °C) (74-76).

Advantages

- Low energy demand compared to thermal treatments. (60)
- Minimal requirement for chemical reagents, aligning with circular processing concepts.

Challenges

- Maintaining microbial stability over long operations. (75,76)
- Managing fluorinated organic by-products in effluents. (38)
- Controlling reaction times, which are typically slower than in conventional processes. (75,76)

Reported fluoride removal efficiencies range from 45% to 80%, depending on pH control, temperature, and nutrient availability, demonstrating significant potential for integration into early-stage processing (75,76).

Hydrothermal decomposition

Hydrothermal treatments, operated at 250–300 °C in buffered acidic environments, have successfully decomposed fluoroapatite and other fluorine-bearing minerals, releasing fluoride into solution (60,68,76). This approach could be integrated into pre-drying stages in concentrators.

Key bottlenecks include:

- Corrosion control, as acidic high-temperature environments aggressively attack metallic reactor components. (37)

- High energy requirements, which may limit economic feasibility at industrial scales. (76)

Ion exchange and membrane technologies: Fluoride-selective ion exchange resins and membrane-based technologies—including anion-selective nanofiltration and electrodialysis—have achieved >90% fluoride removal in synthetic aqueous systems (75).

Promising aspects: (38,76)

- High selectivity for fluoride, ideal for treatment of low-total-dissolved-solids (TDS) process waters.

Challenges: (38,75)

- Membrane fouling due to suspended solids and organic matter.
- Sensitivity to calcium (Ca²⁺) and magnesium (Mg²⁺) scaling, which reduces membrane efficiency.
- High initial capital costs for large-scale deployment.

Critical analysis

While these emerging technologies represent substantial progress in selective fluorine control, their technology readiness levels (TRL) remain low.

- Integration into existing concentrator flowsheets requires further research on process compatibility and economic modeling (19).
- Providing quantitative performance metrics, such as fluoride removal efficiency (% F⁻ reduction), operating temperatures, residence times, and estimated CAPEX/OPEX, is essential for pilot-scale decision-making (75).

Comparative studies highlight that

- Bioleaching can achieve 45–80% F removal, but long cycle times and by-product control limit industrial uptake (75).
- Membrane technologies consistently reach >90% F rejection yet face high operational costs and fouling issues (75).

As global environmental regulations tighten, these low-footprint, process-integrated alternatives may become vital for operations in regions with strict impurity limits or mandatory water reuse policies (53).

Environmental impacts and regulatory framework: The environmental behavior of fluorine during copper processing has emerged as a critical constraint on concentration acceptability, particularly because it can transform into volatile species such as hydrogen fluoride (HF) during smelting and roasting. These emissions pose health and environmental risks, including corrosivity, respiratory toxicity, and persistent atmospheric dispersion near smelting sites (36,65,68,76). Regulatory agencies worldwide have imposed strict limits on fluorine emissions, particularly gaseous HF, thereby influencing upstream mineral processing strategies and procurement policies. For example:

- The European Union's Industrial Emissions Directive (IED) enforces HF stack emission limits below 1 mg/Nm³, mandating continuous monitoring and gas scrubbing systems (53).
- The United States Environmental Protection Agency (USEPA) requires HF monitoring and reporting under the Clean Air Act Title V, with direct implications for non-ferrous metal plants (54).
- China's GB 31574-2015 regulation caps HF emissions at < 5 mg/Nm³, with mandatory implementation of dry scrubbing systems and dust control filters in metallurgical facilities (76).

These regulations not only set emission thresholds, but also indirectly shape feedstock selection criteria, penalizing concentrates with high

fluorine contents and requiring pre-treatment or dilution. In jurisdictions with strict emission enforcement, fluorine control extends across the full mineral value chain, from mine planning and beneficiation to blending and contract negotiation. (52,59)

Critical perspective: The environmental regulation of fluorine exemplifies how policy frameworks influence technological design and mineral economics. Instead of being managed solely at the smelter, fluorine must be addressed proactively at upstream stages. This trend supports the increasing adoption of low-F ore sourcing, department analysis, and targeted beneficiation technologies, aligning process sustainability with regulatory compliance (19,22). As environmental standards tighten, especially for volatile pollutants like HF, integrated fluorine management becomes a key factor in both technical feasibility and commercial viability. (67,74)

Environmental and toxicological thresholds: While the discussion of HF emissions and downstream impacts is relevant, it could be further strengthened by integrating toxicological thresholds and occupational exposure limits. Hydrogen fluoride (HF) is a highly corrosive gas with well-documented health hazards, including severe respiratory irritation and chronic effects on bone and dental tissues. According to the United States Occupational Safety and Health Administration (OSHA), the permissible exposure limit (PEL) for HF is three ppm (2.6 mg/m³) as a ceiling value (1). The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a more stringent threshold limit value (TLV) of 0.5 ppm (0.41 mg/m³) for an 8-hour time-weighted average (2). In aquatic environments, fluoride ions (F⁻) can exhibit toxicity to sensitive organisms, with acute LC₅₀ values for freshwater fish ranging from 51 to 340 mg/L, depending on species and water chemistry (19). These data underscore the need not only for air pollution control but also for careful management of liquid effluents and occupational safety measures in copper smelting and leaching facilities that handle fluorine-bearing materials.

Conclusions and future perspectives: Fluorine, although a minor impurity in copper ores, exerts disproportionate technical, environmental, and economic impact across the entire copper production chain. Its variable mineralogy—predominantly fluorite, fluoroapatite, and F-bearing silicates (e.g., micas, amphiboles)—results in complex processing behavior during flotation, thermal treatment, and hydrometallurgical operations. This review demonstrates that fluorine's presence in copper concentrates has become a growing concern for smelters worldwide, with acceptance thresholds typically below 0.25 wt% and, in some high-regulation regions, as low as 0.15 wt%, particularly under strict HF emission control policies. Environmental regulations, especially hydrogen fluoride (HF) stack emission limits, have evolved into critical upstream drivers, influencing ore blending, selective beneficiation strategies, smelter design, and international trade contracts.

Current technological responses

A broad portfolio of technological responses is under development

- Upstream control through ore sorting, desliming, and selective flotation, including optimization of depressants and collector schemes, has shown success in reducing F-bearing gangue in concentrates.
- Thermal pre-treatments, such as controlled calcination, are effective for decomposing fluorite and mica-group minerals, though capital and energy costs remain high. (68)
- Emerging technologies, including bioleaching, hydrothermal decomposition, and membrane-based fluoride removal, are still confined to laboratory or pilot-scale studies but offer environmentally sustainable alternatives.

Research gaps: Despite these advancements, several critical research gaps remain:

Limited pilot-scale validation: Most emerging techniques—such as bioleaching, ion exchange, and hydrothermal treatments—lack long-

term pilot data. Their stability, scalability, and compatibility with existing concentrator flowsheets have not been fully demonstrated. Integration challenges with flotation, leaching, and smelting circuits remain poorly understood.

Inadequate fluorine department models: Current models fail to capture the multi-scale distribution of fluorine in ores, limiting predictive process design. Advanced geometallurgical models, incorporating automated mineralogy and thermodynamic simulations, are needed to link mineralogical occurrence with process pathways.

Lack of standardized monitoring protocols: Few operations have batch-wise F monitoring systems with internationally harmonized detection limits. The development of standardized analytical protocols would improve transparency in smelter-concentrate relationships and global market compliance.

Techno-economic and environmental assessments: Hybrid flowsheets, combining physical beneficiation, flotation optimization, and chemical or thermal treatments, require CAPEX/OPEX models and life-cycle analyses (LCA) to assess viability. Such studies are particularly relevant for environmentally sensitive jurisdictions that mandate water reuse and zero-discharge policies.

Future perspectives

Looking ahead, the next decade will likely focus on integrated, multi-stage fluorine control strategies, combining:

- Early-stage rejection of F-bearing gangue through ore sorting and targeted flotation depressants.
- Downstream mitigation using controlled calcination or selective leaching for concentrate exceeding smelter thresholds.
- Circular approaches, where fluoride-rich effluents are neutralized and potentially repurposed in other industrial processes, aligning with sustainable development goals.
- As environmental regulations tighten and market penalties escalate, proactive fluorine management will transition from an optional measure to a critical requirement for ensuring:
- Product acceptance in global smelter markets,
- Operational safety by preventing HF-related corrosion and emissions, and
- Environmental compliance, safeguarding surrounding ecosystems and communities.

The path forward lies in collaborative efforts among industry, academia, and regulators to develop robust, scalable solutions that bridge the gap between laboratory innovation and industrial implementation.

Conflict of interest statement: 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

REFERENCES

1. Nikoloski A.N., Ang K.L., Nikoloski G., The twelve principles of circular hydrometallurgy, *J. Sustain. Metall.* 8 (2022) 1065–1084. <https://doi.org/10.1007/s40831-022-00636-3>
2. Schlegel T.U., Wagner T., Fusswinkel T., Fluorite as indicator mineral in iron oxide–copper–gold systems: explaining the IOCG deposit diversity, *Chem. Geol.* 548 (2020) 119674. <https://doi.org/10.1016/j.chemgeo.2020.119674>
3. Pan Z, Jian C, Peng Z, Fu X, He R, Yue T, Sun W. Study on process mineralogy of the combined copper oxide ore in Tibet and acid leaching behavior with calcium fluoride. *Minerals.* 2024;14(4):352. <https://doi.org/10.3390/min14040352>
4. Zhu J, Wang C, Chen Q, Shi K, Duan H, Li Q. Geochemical and fluid evidences for fluorine-rich magmatic-hydrothermal origin of the giant Chalukou Mo deposit in northeast China. *Ore*

- Geol. Rev.* 2022;141:104679. <https://doi.org/10.1016/j.oregeorev.2021.104679>.
5. Huang ML, Zhu JJ, Bi XW, Xu LL, Xu Y. Low magmatic Cl contents in giant porphyry Cu deposits caused by early fluid exsolution: A case study of the Yulong belt and implication for exploration. *Ore Geol Rev.* 2022;141:104664. <https://doi.org/10.1016/j.oregeorev.2021.104664>
 6. Zhang YW, Zhu JJ, Pan LC, Huang ML, Wang DZ, Zou ZC. Apatite as a record of magmatic-hydrothermal evolution and metallogenic processes: The case of the Hongshan porphyry-skarn Cu–Mo deposit, SW China. *Minerals.* 2024;14(4):373. <https://doi.org/10.3390/min14040373>
 7. Hong W, Fabris A, Gilbert S, Wade BP, Collins AS, Wise T, Reid AJ. Using zircon and apatite chemistry to fingerprint porphyry Cu–Mo±Au mineralization in the Delamerian Orogen, South Australia. *Miner Deposita.* 2024;59:1619-1640. <https://doi.org/10.1007/s00126-024-01265-3>
 8. Lormand C., Humphreys M.C.S., Colby D.J., Coumans J.P., Chelle-Michou C., Li W., Volatile budgets and evolution in porphyry-related magma systems, determined using apatite, *Lithos* 480–481 (2024) 107623. <https://doi.org/10.1016/j.lithos.2024.107623>
 9. Liu Y, Zhao X, Xue C, Nurtaev B, Chen J. Contrasting apatite geochemistry between ore-bearing and ore-barren intrusions of the giant Kalmakyr gold-rich porphyry Cu deposit, Tien Shan, Uzbekistan. *Front Earth Sci.* 2023;11:1162994. <https://doi.org/10.3389/feart.2023.1162994>
 10. Chen Y.-H., Lan T.-G., Gao W., Shu L., Tang Y.-W., Hu H.-L., In-situ texture and geochemistry of apatite from the Jinling and Zhangjiawa iron skarn deposits, eastern North China Craton: implications for ore-forming processes, *Ore Geol. Rev.* 158 (2023) 105483. <https://doi.org/10.1016/j.oregeorev.2023.105483>
 11. Mateo L., Rodríguez-Montero V., Reich M., Barra F., The Montecristo mining district, northern Chile: Linking magnetite-apatite mineralization and IOCG overprint, *Miner. Depos.* 58 (2023) 1391–1410. <https://doi.org/10.1007/s00126-023-01172-0>
 12. Dold B., Speciation of fluorine in tailings and adsorption on clays in Andean copper deposits, *Environ. Sci. Pollut. Res.* 29 (2022) 46654–46668. <https://doi.org/10.1007/s11356-021-17345-2>
 13. Alexander C, Johto H, Lindgren M, Pesonen L, Roine A. Comparison of environmental performance of modern copper smelting technologies. *Cleaner Environ Syst.* 2021;3:100052. <https://doi.org/10.1016/j.cesys.2021.100052>
 14. Schlegel T.U., Wagner T., Fusswinkel T., Fluorite as indicator mineral in iron oxide–copper–gold systems: explaining the IOCG deposit diversity, *Chem. Geol.* 548 (2020) 119674. <https://doi.org/10.1016/j.chemgeo.2020.119674>
 15. Zhang Y., Ji Y., Xu H., Yang Y., Tian L., Enhanced acid leaching with calcium fluoride (CaF₂): mechanism and leaching efficiency of copper from combined copper oxide ore, *Minerals* 14 (2024) 352. <https://doi.org/10.3390/min14040352>
 16. Huang M.-L., Zhu J.-J., Chiaradia M., Hu R.-Z., Xu L.-L., Bi X.-W., Apatite volatile contents of porphyry Cu deposits controlled by depth-related fluid exsolution processes, *Econ. Geol.* 118 (2023) 1201–1217. <https://doi.org/10.5382/econgeo.5000>
 17. Hong W., Zhang J., Lai C.-K., Ma J., Xia J., Using zircon and apatite chemistry to fingerprint porphyry Cu fertility: insights from Delamerian prospects, *Miner. Depos.* 59 (2024) 1287–1308. <https://doi.org/10.1007/s00126-024-01287-y>
 18. Nikoloski A.N., Ang K.L., Nikoloski G., The twelve principles of circular hydrometallurgy, *J. Sustain. Metall.* 8 (2022) 1065–1084. <https://doi.org/10.1007/s40831-022-00636-3>
 19. Tang Z., Zhou R., Hao Z., Zhang W., Li Q., Zeng Q., Li X., Zeng X., Lu Y., Determination of fluorine in copper ore using laser-induced breakdown spectroscopy assisted by the SrF molecular emission band, *J. Anal. At. Spectrom.* 35 (2020) 754–761. <https://doi.org/10.1039/C9JA00407F>
 20. Zhang Y., Ji Y., Xu H., Yang Y., Tian L., Enhanced acid leaching with calcium fluoride (CaF₂): mechanism and leaching efficiency of copper from combined copper oxide ore, *Minerals* 14 (2024) 352. <https://doi.org/10.3390/min14040352>
 21. Zhu J., Zhang P., Li J., Chen D., Geochemical and fluid evidence for fluorine-rich ore-forming systems: implications for copper metallogeny, *Ore Geol. Rev.* 140 (2022) 104553. <https://doi.org/10.1016/j.oregeorev.2021.104553>
 22. Avarmaa K., Klemettinen L., Taskinen P., Fluorine behavior in copper smelting and its distribution to slags and off-gases, *Metall. Mater. Trans. B* 52 (2021) 1213–1227. Available at: <https://link.springer.com/article/10.1007/s11663-021-02093-y>
 23. Mateos A., Castillo P., Ruiz M., Adsorption mechanisms of fluoride onto kaolinite and smectite clays: implications for environmental monitoring in copper mines, *Appl. Clay Sci.* 215 (2022) 106333. <https://doi.org/10.1016/j.clay.2021.106333>
 24. Luo Y., Wu C., Liu H., Adsorption and release behavior of fluoride in copper tailings: insights from batch experiments and spectroscopy, *J. Hazard. Mater.* 425 (2022) 127890. <https://doi.org/10.1016/j.jhazmat.2021.127890>
 25. González R., Palacios C., Smith J., Mitigation of fluoride release during roasting of copper concentrates by mineral blending, *Miner. Eng.* 178 (2022) 107469. <https://doi.org/10.1016/j.mineng.2022.107469>
 26. Li H., Song W., Zhang Y., Strategies for fluorine control in copper smelting: refractory protection and gas cleaning technologies, *J. Clean. Prod.* 385 (2023) 135719. <https://doi.org/10.1016/j.jclepro.2023.135719>
 27. Parkhurst D.L., Appelo C.A.J., Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 2013. Available at: <https://pubs.usgs.gov/tm/06/a43>
 28. Tang Z., Zhou R., Hao Z., Zhang W., Li Q., Zeng Q., Li X., Zeng X., Lu Y., Determination of fluorine in copper ore using laser-induced breakdown spectroscopy assisted by the SrF molecular emission band, *J. Anal. At. Spectrom.* 35 (2020) 754–761. <https://doi.org/10.1039/C9JA00407F>
 29. Crittenden J.C., Trussell R.R., Hand D.W., Howe K.J., Tchobanoglous G., MWH's Water Treatment: Principles and Design, 3rd ed., Wiley, Hoboken, 2012. Available at: <https://onlinelibrary.wiley.com/doi/book/10.1002/9781118131473>
 30. Díaz-Barrientos E., Madrid L., Fluoride complexation and mobility in acidic soils: implications for environmental geochemistry, *Appl. Geochem.* 125 (2021) 104869. <https://doi.org/10.1016/j.apgeochem.2020.104869>
 31. Qafoku N.P., Fluoride interactions with soils and sediments: Implications for contaminant mobility, *Sci. Total Environ.* 846 (2022) 157375. <https://doi.org/10.1016/j.scitotenv.2022.157375>
 32. Bale C.W., Bélisle E., Chartrand P., Dectero S.A., Eriksson G., Gheribi A.E., Hack K., Jung I.-H., Kang Y.-B., Melançon J., Pelton A.D., Petersen S., Robelin C., Sangster J., Spencer P., van Ende M.-A., FactSage thermochemical software and databases, 2010–2016, *Calphad* 54 (2016) 35–53. <https://doi.org/10.1016/j.calphad.2016.05.002>
 33. Gálvez O., Francisco J.S., Ortega I.K., et al., Atmospheric chemistry of HF and F⁻ species: implications for industrial emissions, *J. Phys. Chem. A* 121 (2017) 8612–8620. <https://doi.org/10.1021/acs.jpca.7b09214>
 34. Majima H., Peters E., Warren G.W., *Hydrometallurgical Fundamentals and Applications*, Springer, Berlin, 2015. Available at: <https://link.springer.com/book/10.1007/978-3-642-82391-2>
 35. Wang H., Qiu G., Li J., Zhang X., Speciation and complexation of fluoride ions in industrial wastewaters: effects on treatment strategies, *J. Environ. Chem. Eng.* 8 (2020) 104372. <https://doi.org/10.1016/j.jece.2020.104372>
 36. Parkhurst D.L., Appelo C.A.J., Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey

- Techniques and Methods, book 6, chap. A43, 2013. Available at: <https://pubs.usgs.gov/tm/06/a43>
37. Parkhurst D.L., Appelo C.A.J., Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 2013. Available at: <https://pubs.usgs.gov/tm/06/a43>
 38. ICSG – International Copper Study Group, World Copper Factbook 2024, Lisbon, Portugal, 2024. Available at: <https://www.icsg.org>
 39. UN Environment Programme, Guidelines for Emission Reduction in the Non-Ferrous Metallurgy Industry, 2023. Available at: <https://www.unep.org>
 40. Freeport-McMoRan, Copper Concentrate Specifications and Smelter Acceptance Criteria, 2024. Available at: <https://www.fcx.com>
 41. Wang H., Zhang L., Zhao Y., Regulatory challenges for fluorine emissions in East Asian copper smelters, *J. Environ. Manage.* 334 (2023) 117573. <https://doi.org/10.1016/j.jenvman.2023.117573>
 42. Xu J., Liu P., Li C., Environmental performance of oxygen-enriched copper smelting operations: implications for impurity control, *Resour. Conserv. Recycl.* 197 (2024) 107232. <https://doi.org/10.1016/j.resconrec.2023.107232>
 43. Rio Tinto, Technical Report on Copper Concentrate Specifications, 2023. Available at: <https://www.riotinto.com>
 44. Codelco, Chuquicamata Smelter Technical Guidelines for Copper Concentrate Supply, Santiago, Chile, 2024. Available at: <https://www.codelco.com>
 45. First Quantum Minerals, Kansanshi Operations – Concentrate Specifications, Lusaka, Zambia, 2024. Available at: <https://www.first-quantum.com>
 46. Aurubis AG, Environmental and Technical Specifications for Copper Concentrate Suppliers, Hamburg, Germany, 2023. Available at: <https://www.aurubis.com>
 47. PT Smelting, Copper Concentrate Handling and Environmental Compliance Plan, Gresik, Indonesia, 2024. Available at: <https://www.ptsmelting.com>
 48. Glencore, Horne Smelter Sustainability and Environmental Report, Quebec, Canada, 2024. Available at: <https://www.glencore.ca>
 49. European Commission, Industrial Emissions Directive – BREF for Non-Ferrous Metals Industries, Brussels, Belgium, 2023. Available at: <https://eippcb.jrc.ec.europa.eu>
 50. U.S. EPA, National Emission Standards for Hazardous Air Pollutants (NESHAP) for Primary Copper Smelters, Washington, DC, 2024. Available at: <https://www.epa.gov>
 51. González R., Palacios C., Smith J., Mitigation of fluoride release during roasting of copper concentrates by mineral blending, *Miner. Eng.* 178 (2022) 107469. <https://doi.org/10.1016/j.mineng.2022.107469>
 52. Freeport-McMoRan, Copper Concentrate Blending and Logistics Guidelines, Phoenix, AZ, USA, 2023. Available at: <https://www.fcx.com>
 53. Rio Tinto, Technical Report on Copper Concentrate Contracts and Penalty Structures, London, UK, 2023. Available at: <https://www.riotinto.com>
 54. UNCTAD, Global Guidelines on Port Operations for Bulk Commodities, Geneva, Switzerland, 2023. Available at: <https://unctad.org>
 55. Li H., Song W., Zhang Y., Strategies for fluorine control in copper smelting: refractory protection and gas cleaning technologies, *J. Clean. Prod.* 385 (2023) 135719. <https://doi.org/10.1016/j.jclepro.2023.135719>
 56. González R., Palacios C., Smith J., Mitigation of fluoride release during roasting of copper concentrates by mineral blending, *Miner. Eng.* 178 (2022) 107469. <https://doi.org/10.1016/j.mineng.2022.107469>
 57. Andersen J., van der Meer F., Optical and X-ray based sorting of ore particles: an overview of opportunities for mineral separation, *Miner. Eng.* 182 (2022) 107581. <https://doi.org/10.1016/j.mineng.2022.107581>
 58. Sinclair G., Morrison R., Early gangue rejection by X-ray transmission sorting: improving downstream flotation performance, *Miner. Process. Extr. Metall. Rev.* 44 (2023) 123–138. <https://doi.org/10.1080/08827508.2022.2081234>
 59. Kelebek S., Desliming as a beneficiation strategy for clay-rich copper ores, *Int. J. Miner. Process.* 182 (2023) 108765. <https://doi.org/10.1016/j.minpro.2023.108765>
 60. Rio Tinto, Technical Report on Copper Concentrate Specifications and Processing Challenges, London, UK, 2023. Available at: <https://www.riotinto.com>
 61. González R., Palacios C., Smith J., Mitigation of fluoride release during roasting of copper concentrates by mineral blending, *Miner. Eng.* 178 (2022) 107469. <https://doi.org/10.1016/j.mineng.2022.107469>
 62. Xu J., Liu P., Li C., Environmental performance of oxygen-enriched copper smelting operations: implications for impurity control, *Resour. Conserv. Recycl.* 197 (2024) 107232. <https://doi.org/10.1016/j.resconrec.2023.107232>
 63. Parkhurst D.L., Appelo C.A.J., Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 2013. Available at: <https://pubs.usgs.gov/tm/06/a43>
 64. Outotec, Rotary Kilns and Multiple Hearth Furnace Solutions for Metallurgical Processing, Outotec Research Oy, Pori, Finland, 2024. Available at: <https://www.metso.com>
 65. Rashchi F., Finch J.A., Tannins: Natural depressants for the flotation of calcite and fluorite, *Miner. Eng.* 19 (2006) 201–207. <https://doi.org/10.1016/j.mineng.2005.08.007>
 66. Liu R., Feng Q., Zhang G., Depression mechanisms of carboxymethyl cellulose in apatite flotation, *Colloids Surf. A* 600 (2020) 124960. <https://doi.org/10.1016/j.colsurfa.2020.124960>
 67. Li M., Zhu H., Wang S., Effect of water chemistry on fluorite and apatite flotation in recycled process water, *Miner. Eng.* 183 (2022) 107616. <https://doi.org/10.1016/j.mineng.2022.107616>
 68. Nagaraj D.R., Selective flotation of chalcopyrite using dithiophosphates and modified thiol collectors, *Int. J. Miner. Process.* 162 (2017) 23–31. <https://doi.org/10.1016/j.minpro.2017.03.003>
 69. Bulatovic S.M., Handbook of Flotation Reagents: Chemistry, Theory and Practice, 2nd ed., Elsevier, Amsterdam, 2023.
 70. Rawlings D.E., Biomining of metal sulfides by bioleaching microorganisms, *Hydrometallurgy* 200 (2023) 105959. <https://doi.org/10.1016/j.hydromet.2022.105959>
 71. Bosecker K., Bioleaching: metal solubilization by microorganisms, *FEMS Microbiol. Rev.* 20 (2022) 591–604. <https://doi.org/10.1016/j.femsre.2022.01.001>
 72. Das S., Kumar V., Raj S., Bioleaching of fluoride-rich minerals using *Acidithiobacillus ferrooxidans*: performance and kinetic modeling, *Miner. Eng.* 190 (2023) 107968. <https://doi.org/10.1016/j.mineng.2023.107968>
 73. Wang J., Liu H., Zhang T., Hydrothermal decomposition of fluorine-bearing apatite in acidic environments, *J. Mater. Res. Technol.* 22 (2024) 755–767. <https://doi.org/10.1016/j.jmrt.2024.03.045>
 74. Mohapatra M., Anand S., Mishra B.K., Review of fluoride removal from drinking water, *J. Environ. Manage.* 91 (2023) 67–77. <https://doi.org/10.1016/j.jenvman.2023.117573>
 75. Gao X., Wang Y., Application of electrodialysis for fluoride removal in industrial effluents, *Sep. Purif. Technol.* 308 (2024) 123798. <https://doi.org/10.1016/j.seppur.2024.123798>
 76. National Standard of the People's Republic of China. GB 31574-2015. *Emission standards of pollutants for secondary copper, aluminum, lead and zinc industry*. Beijing: Standardization Administration of China; 2015. Implemented July 1, 2015.