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Understanding Fluorine Behavior Across Copper Processing Routes: Mineralogy, Thermodynamics, Process Integration, and Environmental Control—A Critical Review

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Abstract

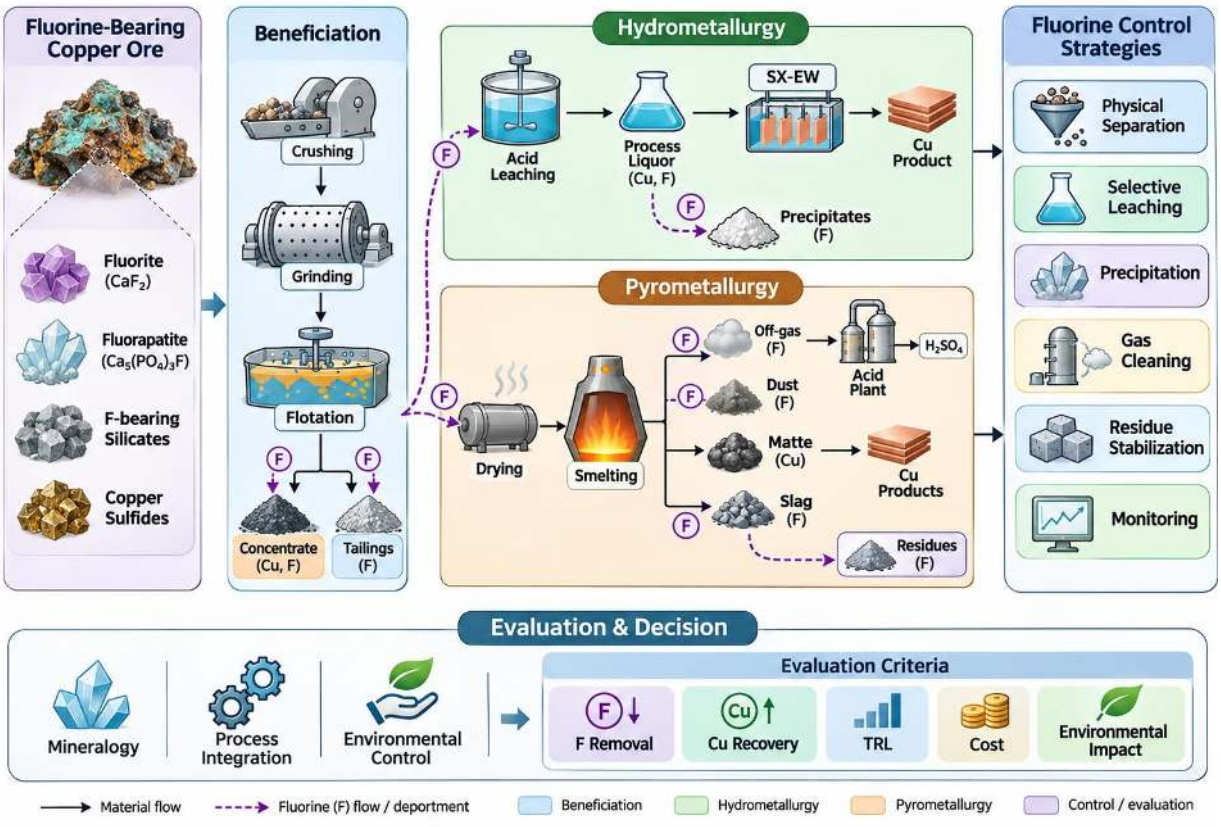
Fluorine is a process-dependent impurity in copper ores and concentrates because its mineralogical occurrence controls whether it can be rejected during beneficiation, mobilized into acidic process liquors, or redistributed between condensed and gaseous products during smelting. This critical review links fluorite, fluorapatite, fluorine-bearing silicates, and texturally associated phases to analytical quantification, comminution and flotation, aqueous speciation, hydrometallurgical and bioleaching responses, thermal transformations, and environmental management. A structured review of an reconciled 132-entry bibliography compares direct copper-system evidence with studies transferable from other mineral and wastewater systems. The analysis distinguishes total fluorine from soluble fluoride and phase-associated fluorine; thermodynamic feasibility from reaction kinetics; selective rejection from contaminant transfer; and laboratory feasibility from industrial implementation. An integrated selection framework centers on mineralogical deportment, copper recovery, fluoride mass balance closure, reagent consumption, corrosion exposure, residue stability, and process integration. The principal finding is that no universal defluorination technology is defensible across copper feeds: preconcentration is preferred for liberated fluorine-bearing gangue, targeted chemical conditioning may be useful for accessible fluoride phases, and robust gas, liquor, and residue management is required whenever fluorine enters downstream circuits. Evidence gaps include representative multi-stream fluorine mass balances, industrial smelter partition data, thermodynamic validation of concentrated electrolytes, and comparative techno-economic assessments.

Keywords: Fluorine-bearing copper ores; Fluorine deportment; Copper concentrate beneficiation; Fluoride removal; Metallurgical impurities; Environmental management

Highlights

- Mineralogical association determines the feasible location of fluorine control.
- Copper recovery and fluorine rejection must be assessed on consistent mass-balance boundaries.
- Evidence from fluorite flotation and wastewater treatment is not automatically transferable to copper circuits.
- A flowsheet-level decision framework links mineralogy, speciation, operational exposure, and environmental transfer.

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1. Introduction

Fluorine presents a different control problem depending on where it resides in a copper feed. Fluorite liberated from sulfide grains can, in principle, be rejected before smelting; fluorapatite attached to chalcopyrite may instead be carried into concentrate; and fluorine dissolved during leaching can circulate through equipment far removed from its mineral source. A bulk fluorine assay cannot distinguish these scenarios. Consequently, a useful flowsheet review must link mineral occurrence to deportment, process exposure, and fluorine's ultimate destination.

An earlier review, Fluorine in copper concentrates: Mineralogical occurrence, processing behavior, and environmental implications (Pereira, 2025), surveys occurrence, processing behavior, and environmental concerns at the concentrate level. The incremental contribution of the present article is a reconciled mine-to-environment fluorine-deportment and control-point selection framework. It jointly requires mineral-phase and liberation-by-size

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accounting, analytically distinguished fluorine species, paired copper-loss and fluorine-exclusion measurements, smelting and gas-cleaning partition boundaries, and downstream residue fate. Figure 1 provides the mineralogical starting point; Figures 2–4 illustrate the principal transfer pathways, and Tables 1–10 identify necessary reporting and decision criteria.

The practical question is not simply how to decrease the fluorine grade of a copper concentrate. It is where fluorine can be separated with the least copper loss, which secondary streams will receive it, and whether those streams can be treated reliably. Direct studies of copper systems are considered separately from findings transferred from fluorite flotation or fluoride-containing wastewater. Such transfer is informative for mechanisms, not proof of metallurgical performance.

2. Review Methodology and Literature Selection

The literature corpus originated from an earlier REV7 working inventory of 127 entries supplemented by three topic-specific studies. Reconciliation of the submitted bibliography identified an internal editorial note improperly listed among references; before revision, the document therefore contained 129 scholarly entries, not 130. This revision removes that note, replaces a conference dissemination record with the corresponding peer-reviewed Liu et al. (2023) article, and adds three copper-specific studies (Akerstrom et al., 2018; Cadorim et al., 2018; Ding & Qiu, 2021), yielding 132 references. Search themes B01–B11 addressed mineral carriers, chemical analysis, liberation, flotation, aqueous speciation, leaching/bioleaching, smelting, fluoride treatment, environmental management, and integrated process selection. Searches targeted 2020–2026, extending to older foundational evidence as warranted. These sources form a structured critical, not systematic, review.

The supplied inventory did not include dated, database-specific search exports, a duplicate-screening log, a full-text eligibility log, or a complete independently audited publisher-metadata file. The manuscript must therefore be described as a structured critical review; neither systematic coverage nor PRISMA compliance is claimed. Quantitative comparisons are withheld when the cited record does not establish feed composition, operating conditions, measurement basis, and relevant balance boundaries.

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AI-assisted drafting and graphic preparation supported the review. The author remains responsible for the accuracy of the scientific claims, bibliographic correspondence, and submitted manuscript.

Evidence was interpreted by directness. Copper ore, concentrate, or plant studies inform route-specific statements. Mineral-surface or aqueous-speciation work informs mechanisms, provided the solution and mineral conditions are comparable. Studies on potable-water defluoridation or other industries illustrate possible unit operations but do not establish effectiveness in acidic, sulfate-rich copper streams. This hierarchy prevents apparent citation accumulation from being mistaken for independent industrial validation.

Evidence was classified by its directness to copper operations: (i) copper-specific mineralogy, chemical analysis, beneficiation, leaching, smelting, or operating-plant evidence; (ii) mechanistic mineral-surface or speciation evidence; and (iii) contextual analogies from non-copper wastewater and chemical systems. Only group (i) supports direct copper-process performance conclusions. Industrial sampling studies that do not quantify fluorine are cited solely for methodological context. Cross-domain extrapolation is identified explicitly, without interpreting citation volume as process validation.

3. Geological Occurrence and Mineralogical Associations of Fluorine in Copper Ores

Fluorine may occur in discrete fluorite (CaF_2), fluorapatite [$Ca_5(PO_4)_3F$], fluorinated micas and amphiboles, and minor intergrowths or accessory phases. The geological setting influences the spatial distribution of these carriers, but deposit class alone does not define the removal strategy. Grain-size associations, liberation, mineral chemistry, and secondary alteration are the operationally decisive variables (Freitas et al., 2015).

Freitas et al. (2015) characterized copper ore by addressing fluorine- and chlorine-bearing mineral carriers, making their results more transferable to the present subject than generic fluorite flotation results. The methodology Mano et al. (2015) developed for lateritic copper clays provides a complementary basis for distinguishing clay-rich textural domains and fine-particle associations during sampling. The clay study, however, should not be read as an

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experimental measurement of fluorine deportment; that requires phase-specific fluorine assays and size-by-size mass balances.

A critical distinction is between accessible fluorite liberated from copper sulfides and F structurally incorporated within composite or silicate grains. The former may respond to classification and selective flotation; the latter may require finer grinding, chemical dissolution, or may be economically preferable to tolerate and manage downstream. These routes cannot be ranked from a bulk fluorine grade alone.

Select the removal mechanism after determining the actual association: a separate, liberatable fluoride grain may be physically rejected, whereas a solid solution or submicrometre inclusion may be inaccessible to a conventional cleaner circuit. Bulk X-ray diffraction alone cannot resolve low-abundance fluoride carriers or quantify their exposure at sulfide grain boundaries. A capital decision requires representative phase assays and liberation-by-size distributions.

Characterization should resolve F-bearing phase abundance, within-phase fluorine concentration, liberation distribution by size class, association with chalcopyrite/bornite and gangue, and variability between mining domains. A mineralogical deportment matrix is more informative than a single assay or presumed fluorite-only occurrence.

Mineralogical fluorine deportment for carrier k is defined as $D_{F,k}$ (%) = 100 × [m_k $C_{F,k}$ / (m_{feed} $C_{F,feed}$)], where m_k is the dry mass of the carrier, $C_{F,k}$ is its fluorine mass fraction, and m_{feed} $C_{F,feed}$ is total fluorine mass in the sampled feed. For size class j, $D_{F,k,j}$ (%) = 100 × [$m_{k,j}$ $C_{F,k,j}$ / (m_{feed} $C_{F,feed}$)]. The mineral–size matrix should cover fluorite, fluorapatite, fluorinated silicates, locked composites, and unassigned F, with the unassigned fraction retained as a measured reconciliation category rather than assumed fluorite.

Liberation degree must be measured by size class. Coarse liberated fluorite, liberated ultrafine fluorite, sulfide–fluorite binaries, gangue composites, and inclusions cannot be assigned equivalent physical-control accessibility. A size-by-size F inventory links ore texture to potential cleaner-circuit entrainment and copper-sulfide losses.

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Figure 1 illustrates the principal mineralogical carriers and textural associations of fluorine in copper ores. It distinguishes liberated particles from inclusions and intergrowths, a prerequisite for evaluating realistic physical or chemical separation pathways.

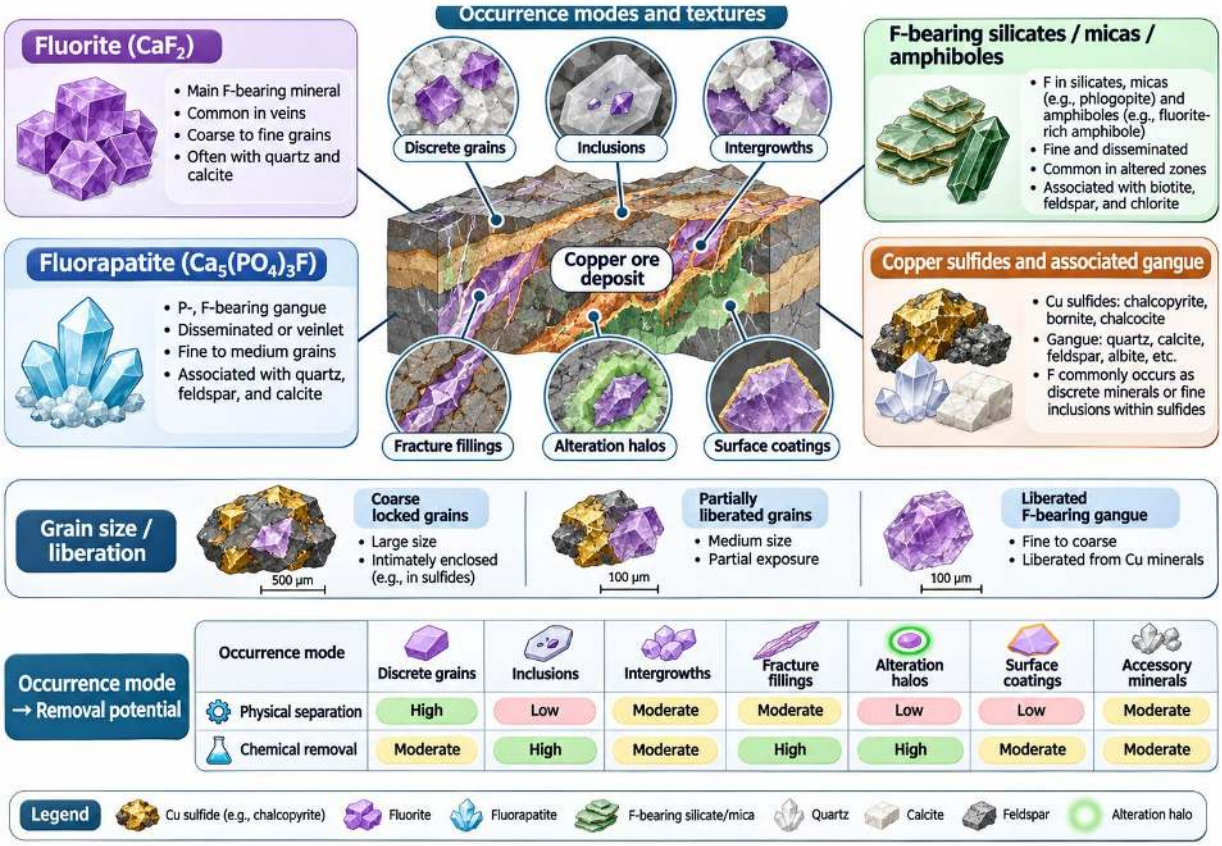


Figure 1. Mineralogical occurrence and associations of fluorine in copper ores.
Note. Conceptual, not to scale. The qualitative classes should be interpreted as candidate control accessibility, not validated treatment-efficiency rankings; mineral-specific testwork is essential. Conceptual diagram prepared with AI assistance (2026).

Table 1 relates fluorine-bearing phases to possible physical and chemical control points.

Table 1. Principal fluorine carriers and implications for copper processing

Carrier	Formula/mode	**Primary process implication**
Fluorite	CaF_2; discrete gangue	Potential liberation and selective rejection
Fluorapatite	$Ca_5(PO_4)_3F$; accessory phosphate	Association and dissolution must be tested
Fluorinated micas	F substitution in silicate structure	Often poor response to physical rejection

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Composite/inclusions	Mixed fine intergrowths	Comminution versus copper-loss trade-off

Note. Mineral classes and separability are screening hypotheses; direct quantitative mineralogy is required.

4. Analytical Characterization and Quantification of Fluorine

A defensible fluorine inventory requires complementary determination of total F, water- or acid-soluble fluoride, and phase-specific F. Ion chromatography and fluoride-selective electrodes provide dissolved fluoride information with matrix-dependent limitations. Bulk digestion, pyrohydrolysis, or other suitable decomposition is needed when quantitative total fluorine is required; check recovery against reference materials and spike tests.

X-ray diffraction identifies sufficiently abundant crystalline phases but does not independently quantify trace F. SEM–EDS screening and automated mineralogy resolve grain association and morphology, yet low concentrations, overlapping X-ray signals, and calibration uncertainty limit inference of fluorine mass. EPMA can quantify fluorine in appropriate grains when standards, detection limits, and beam effects are controlled; see the methodological discussion of automated sulfide mineralogy in Pereira (2026a).

For highly acidic sulfate liquors, fluoride quantification should be accompanied by an independently validated free-acidity determination. Two coauthored studies of the Gran and oxalate methods identify method scope, interference, and validation as central analytical questions (Pereira & Santos, 2025; Pereira et al., 2025). These studies address acidity determination rather than fluoride analysis; they matter here because poorly constrained acid strength makes comparisons of HF/F^- speciation and treatment performance difficult. Their findings cannot establish fluoride concentration or speciation without separate measurements.

Every unit-operation study should report sampling design, moisture correction, analytical digestion, units (mg/kg dry solid or mg/L liquor), uncertainty, fluorine-bearing standards, and closure across all solids, liquids, dust, and off-gas streams. A decrease in concentrate fluorine grade is not equivalent to removal from the overall plant boundary. Measure tailings, recycled water, precipitates, and bleeds to identify the receiving stream.

The minimum analytical reconciliation compares the mass of fluorine entering and leaving a specified boundary, with recoveries reported on dry-solid and solution bases. Where

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the residual exceeds analytical uncertainty, the appropriate conclusion is an unresolved balance, not presumed volatilization or unmeasured precipitation.

For direct copper-concentrate validation, Cadorim et al. (2018) evaluated high-resolution graphite furnace molecular absorption spectrometry with direct solid sampling and compared target molecules using actual copper concentrates and reference materials. Muhammad et al. (2020) studied steam-distillation-based digestion followed by ion chromatography for halogen determination in complex copper concentrates. These copper-specific methods should take precedence over techniques demonstrated only in drinking water when setting digestion recoveries, matrix-matched calibration, and analytical uncertainty.

The analytical hierarchy is therefore: direct copper-concentrate validation; suitable certified mineral reference materials and interlaboratory checks; and finally matrix-qualified aqueous fluoride methods. Total elemental F in solids, total dissolved fluorine in liquors, free-fluoride activity, neutral HF, and phase-associated F are distinct measurands. Fluoride-ion-selective electrodes alone must not be interpreted as a full-speciation determination in complex acidic liquors.

Table 2 compares complementary analytical methods and their limitations.

Table 2. Complementary fluorine analytical measurements

Method	Primary output	Principal limitation
Bulk decomposition + F analysis	Total elemental fluorine	Digestion completeness and calibration
Ion chromatography	Dissolved fluoride	Matrix effects, species conversion
Ion-selective electrode	Operational fluoride activity/concentration	Ionic strength and complexation
XRD/SEM–EDS/EPMA	Phase identity, texture, F in suitable grains	Low abundance and detection constraints

Note. Method selection depends on detection limits, sample dissolution completeness, and matrix effects.

5. Fluorine Behavior During Copper Ore Beneficiation

Grinding modifies fluorite liberation, exposes surface-active Ca sites, and produces fines susceptible to entrainment. F rejection therefore depends jointly on liberation and flotation hydrodynamics; excessive regrinding may increase slime carryover or copper loss even when it liberates additional fluorite.

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Automated sulfide mineralogy offers a basis for reconciling fluorine-bearing gangue liberation with copper recovery, but the liberation result is only actionable when paired with circuit testwork (Pereira, 2026a). Laboratory selectivity should not be extrapolated directly to plant conditions where residence-time distributions, fines entrainment, recycle water, and variable feed domains may alter performance (Pereira, 2026c).

In fluorite flotation, collector adsorption, calcium activity, depressant chemistry, and pulp conditions act together rather than as isolated variables. The review by Gao et al. (2021) and experimental separations of fluorite from calcite reported by Cui et al. (2020) and Huang et al. (2022) help explain possible selectivity mechanisms. However, their test feeds do not reproduce the electrochemical behavior, fine-grained associations, or reagent regime of a copper sulfide cleaner circuit. Translating them requires mineralogical measurements and paired copper–fluorine balances.

Evaluate the operational trade-off at matched concentrate grade, mass pull, and copper recovery: fluorine rejection alone can improve while copper-bearing fines are lost. Assess collector/depressant optimization, desliming, selective regrinding, and cleaner-circuit changes against metal losses and the destination of fluorine in tailings, not only the reduction of F in concentrate.

Any claimed improvement should be reported as paired measurements of Cu recovery, concentrate Cu grade, F rejection, mass pull, and water recovery. This is particularly important where desliming reduces both fluorine-bearing fines and fine copper sulfides.

At Cadia Operations, the direct industrial investigation by Akerstrom et al. (2018) identified free fluorite and slime entrainment as significant control factors in copper flotation; the study reported that approximately 65% of feed fluorine occurred as free fluorite and that much of this material was in very fine size fractions. Cleaner-circuit optimization, including Jameson-cell implementation, provides field-scale evidence that hydrodynamics and entrainment can govern fluorine reporting to concentrate. These site-specific observations are not generic recovery factors for other mineral deposits.

Fluorine exclusion from the selected concentrate should be evaluated on a Pareto plot against copper recovery at a matched system boundary. The design target is not maximum F

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exclusion alone, but the highest practicable F exclusion subject to a defined minimum copper recovery, concentrate quality, and acceptable water/reagent consumption. Mechanistic fluorite–calcite flotation tests cannot establish that frontier for a copper cleaner circuit.

Figure 2 shows the main routes of fluorine redistribution during comminution and flotation. In particular, it distinguishes entrainment of fluorine-bearing gangue from recovery of partially locked particles to the concentrate.

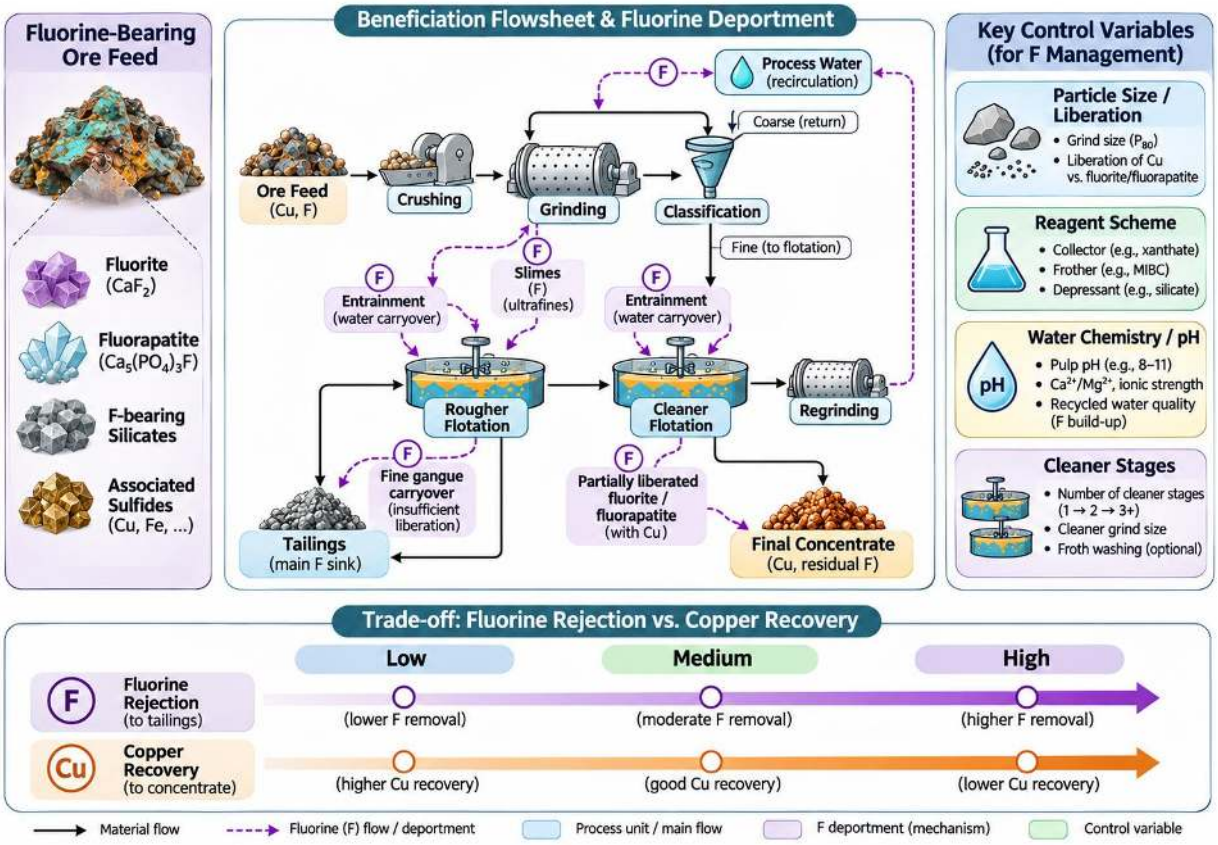


Figure 2. Fluorine deportment during copper ore beneficiation.
Note. Conceptual flowsheet; the qualitative trade-off implies no quantitative fluorine rejection or copper recovery values. Conceptual figure prepared with AI assistance (2026).

Table 3 differentiates liberation, entrainment, and flotation selectivity mechanisms.

Table 3. Beneficiation mechanisms and fluorine deportment

Unit operation	Opportunity	Critical trade-off
Classification/desliming	Remove F-rich fines selectively	Possible copper-rich slime losses

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Regrinding	Liberate discrete F phases	Overgrinding and entrainment
Selective flotation	Depress or reject F-bearing gangue	Sulfide flotation interference
Cleaner flotation	Reduce gangue carryover	Yield, water, reagents

Note. Fluorine transfer and copper loss must be measured on identical circuit boundaries.

6. Thermodynamic and Kinetic Behavior of Fluorine in Metallurgical Processing

The equilibrium $Ca^{2+} + 2F^- \rightleftharpoons CaF_2(s)$ illustrates why calcium availability can lower free fluoride activity. It does not by itself predict the residual concentration in a copper liquor: ionic strength, sulfate competition, complexation, solids residence time, and the chosen activity model alter the result. Magnesium, aluminum, iron, and dissolved silicon can change fluoride speciation or precipitation pathways; these interactions need measurement or a validated multi-component calculation.

The acid-base equilibrium $HF \rightleftharpoons H^+ + F^-$ makes total dissolved fluorine an incomplete descriptor of process exposure. Near highly acidic equipment, undissociated HF can become relevant even when free F^- appears low. Conversely, a higher-pH treatment stage may favor fluoride precipitation but also encourage hydroxide formation, entrainment, and sludge generation. Fluorapatite dissolution further couples fluorine release to phosphate and calcium chemistry, which must be separated analytically from fluorite behavior.

The process chemistry of hydrogen fluoride recovery from hexafluorosilicic acid illustrates the importance of silica equilibria, reactant quality, and downstream material compatibility when fluorine-bearing species are redistributed (Pereira, 2026b). This is a separate industrial chemical system: its process performance cannot be used to assign HF yields or partition fractions during copper smelting. Likewise, fluoride-assisted thermal potassium extraction from Verdete rock documents a distinct mineral–reagent reaction context (Pereira et al., 2019), not measured copper-concentrate fluorine volatilization.

Equilibrium calculations depend on which fluoride-bearing solids are permitted, which aqueous complexes are represented, and how non-ideal activity coefficients are evaluated. Equilibrium diagrams computed for dilute solutions should not be used as quantitative operating maps for concentrated acid or high-sulfate electrolytes. Reports should disclose the underlying database, temperature, ionic-strength range, solid phases admitted to precipitate,

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and sensitivity to uncertain constants. Kinetic restrictions and process mixing may prevent an apparently favorable phase from forming within plant residence times.

Thermodynamic interpretation should distinguish analytical total dissolved fluorine from the activities of F^- and HF and from complexes containing Al, Fe, Mg, Ca, and Si. For the HF dissociation reaction, $K_a = a_{H+} \times a_{F-} / a_{HF}$. In concentrated sulfate electrolytes, activities cannot reliably be replaced with analytical concentrations. Fluorosilicate and metal–fluoride associations must be considered when supported by solution composition and a compatible database.

Calcium-based fluoride precipitation competes with calcium sulfate association and gypsum/anhydrite formation in sulfate-rich liquors. Therefore, CaF_2 solubility-product calculations alone do not predict residual fluoride or reagent demand. Model specification must include temperature, accepted solid phases, ionic strength, validated activity-coefficient treatment, and sensitivity to uncertain association constants. Plant response additionally depends on nucleation, passivation, mixing, growth, and filterability; equilibrium prediction is not a kinetic performance guarantee.

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Figure 3 summarizes fluoride acid–base speciation and interactions with process-liquor constituents, highlighting how recirculation, precipitation, and complexation can modify process exposure and downstream treatment requirements.

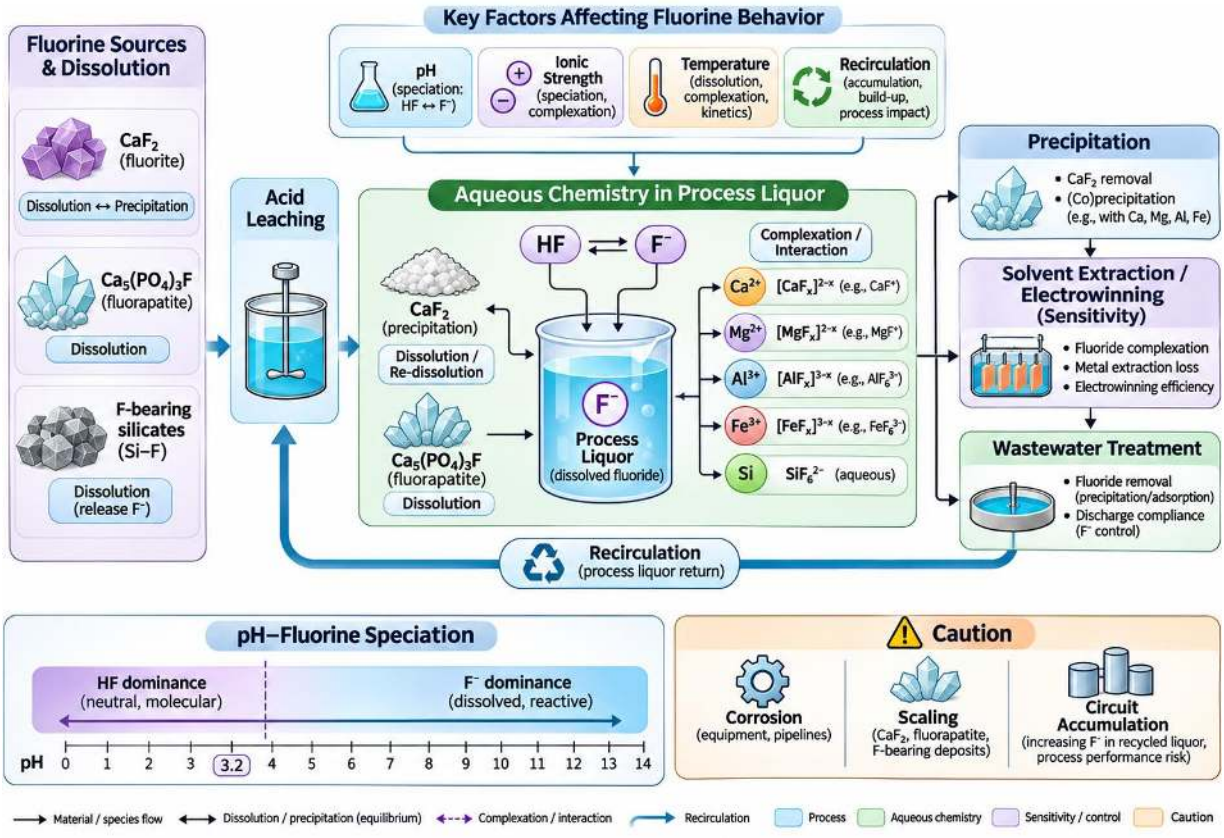


Figure 3. Fluorine speciation and behavior in aqueous processing systems.
Note. Schematic, not a numerical copper-electrolyte predominance diagram. The nominal HF/F⁻ transition near pH 3.2 represents illustrative dilute-water acid–base behavior only; activity corrections, temperature, and complexes shift the balance in process liquors. Conceptual diagram prepared with AI assistance (2026).

Table 4 sets out equilibria that require matrix-specific validation.

Table 4. Fluoride equilibria and interpretation

Equilibrium/process	Controlling variables	Interpretive limitation
$Ca^{2+} + 2F^- \rightleftharpoons CaF_2(s)$	Activities and precipitation kinetics	Calcium addition not universally sufficient
$HF \rightleftharpoons H^+ + F^-$	Acidity and ionic strength	Total F differs from free F^-
Fluorapatite dissolution	pH, calcium, phosphate	Surface kinetics and passivation

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Fluoride complexation	Al, Fe, Mg, Si; ionic strength	Database and validation uncertainty

Note. Equilibrium relationships are conditional on the thermodynamic model and operating matrix.

7. Fluorine in Copper Hydrometallurgical Processing

Acid leaching can mobilize fluorine from accessible fluorine-bearing phases, but dissolution behavior is mineral-specific and constrained by fluoride complexes, precipitation, and circulating-liquor chemistry. Selective oxidative sulfuric leaching of copper concentrates demonstrates the importance of distinguishing impurity removal from copper dissolution and acid consumption (Fu et al., 2020).

Copper-specific diagnostic leaching supplies a useful experimental framework for separating process response from mineralogical accessibility (Pereira et al., 2016). Acidic pre-cleaning experiments on copper–gold ore also demonstrate the need to compare impurity removal against valuable-metal dissolution and reagent exposure (Pereira & Barbosa, 2017). Neither study is treated here as proof of fluoride rejection; analogous experiments must measure fluorine in feed, products, solutions, and residues. Sulfation and pH-controlled leaching of ferruginous oxidized copper ore further illustrate how iron management and acidity affect process selection without defining a fluoride-removal efficiency (Pereira, 2026d).

For biological operations, fluoride toxicity depends on the actual acidophilic community, exposure duration, pH, and aqueous speciation. A recent synthesis on acidophilic bioleaching microorganisms provides mechanistic warning but should not be applied as an industrial copper-heap threshold without process-specific tests (Fritze & Hedrich, 2026).

Fluoride entering extraction and electrowinning circuits raises questions about materials compatibility, impurity accumulation, electrolyte bleeding, and precipitation. Any study claiming tolerance must identify free versus total fluoride, temperature, acid strength, dissolved metals, organic phase exposure, and contact materials. Closed-circuit water recycling can increase impurity residence time; management requires a measured fluorine input–output inventory and a deliberate bleed or recovery mechanism.

As a measurement-control precaution, evaluate the Gran and oxalate acidity methods against the actual ionic background of copper sulfate solutions, rather than assuming they are interchangeable with pH (Pereira & Santos, 2025; Pereira et al., 2025). Any interference

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correction requires independent analytical validation; the acidity studies do not themselves establish HF/F^- activity coefficients.

A representative test matrix should vary free acidity, temperature, ionic strength, dissolved aluminum and iron, and fluoride concentration. Reporting only initial and final total fluoride cannot distinguish complexation, solids precipitation, bleed removal, or microbial inhibition.

Silva et al. (2021) reported markedly feed-dependent outcomes during selective sulfuric acid leaching of two copper concentrates: approximate fluorine extraction was 60% for the tested chalcocite/bornite concentrate but near 10% for the chalcopyrite concentrate under the respective experimental conditions, with different copper dissolution responses. These results demonstrate mineralogical sensitivity rather than transferable design efficiencies. Acid concentration, pretreatment, residence time, and reagent additions must be preserved when interpreting or reproducing the comparison.

In the same context, an aluminum-sulfate-related increase in fluorine extraction should not be described as simple fluorine removal by aluminum: dissolved aluminum–fluoride association may change free fluoride activity and dissolution driving force. Fluorine extraction into liquor also remains a transfer step until downstream fluoride capture and residues are included in the boundary.

Table 5 summarizes exposure pathways rather than proposing universal fluoride limits.

Table 5. Hydrometallurgical exposure pathways

Circuit	Potential issue	Required evidence
Leaching	F dissolution and reagent demand	Feed/liquor/solid F balances
Bioleaching	Microbial inhibition	Species, pH, time, adaptation
Solvent extraction	Impurity carryover and materials	Contact test under actual chemistry
Electrowinning	Electrolyte accumulation and corrosion	Speciation and long-term operating data

Note. Operational effects are possible exposure pathways, not universal concentration thresholds.

8. Fluorine Behavior During Copper Pyrometallurgy

Copper concentrate smelting creates several possible sinks for fluorine, but feed grade alone cannot assign a fixed partition fraction. Fluorine-containing minerals may break down or

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react with slag constituents, while volatile species and fine particles can enter the off-gas system. Slag basicity, calcium availability, oxygen potential, residence time, temperature, and gas cleaning influence the measured distribution. Fluorine in true gas-phase molecules must be distinguished from fluorine transported on entrained particulates.

An industrial assessment must sample fresh concentrate and fluxes, matte or metal, slag, collected dust, gas-cleaning liquor, sulfuric acid, and final emissions, and reconcile all streams on a defined dry and wet basis. Recycled dust is an internal stream: counting it repeatedly as fresh input will exaggerate fluorine throughput. Report sampling positions, temperature, collection efficiency, analytical recovery, and reconciliation residuals before comparing furnaces. Apparent partition differences may otherwise arise from incompatible measurement boundaries.

The engineering consequences likewise depend on exposure rather than on total feed fluorine alone. Deposits and corrosion occur locally, under particular combinations of moisture, temperature, acidity, and materials of construction. Assess acid-plant risk using actual gas-cleaning performance and fluorine reaching sensitive equipment, not by inferring HF transfer from concentrate analysis. Coupling the smelter, dust recycle, wet cleaning, and acid plant is essential for selecting a practical control point.

Ding and Qiu (2021) described fluorine-related acid-making challenges at an operating copper smelter and engineering measures spanning concentrate management, gas scrubbing, sodium-silicate use, and downstream monitoring. Their operational account provides relevant industrial context, but does not establish a universally applicable gas-phase partition coefficient. Fluorine captured in scrubber solutions must be reconciled with fluorine reaching the acid plant and with final treated residues.

Industrial gas sampling should discriminate F in entrained particulate matter from actual gaseous fluorine species where technically feasible. Corrosion and fouling interpretation requires measured gas temperature, moisture/dew point, acidity, exposed construction materials, contact time, and gas-cleaner efficiency. Finnholm et al. (2026) supports industrial minor-element sampling and reconciliation methods, but it is not used here to claim measured fluorine-specific smelter partitions.

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Figure 4 presents the potential distribution of fluorine among slag, dust, off-gas, and gas-cleaning residues in copper pyrometallurgy. The schematic emphasizes that dust recycling and gas treatment influence fluorine's ultimate destination rather than eliminating it.

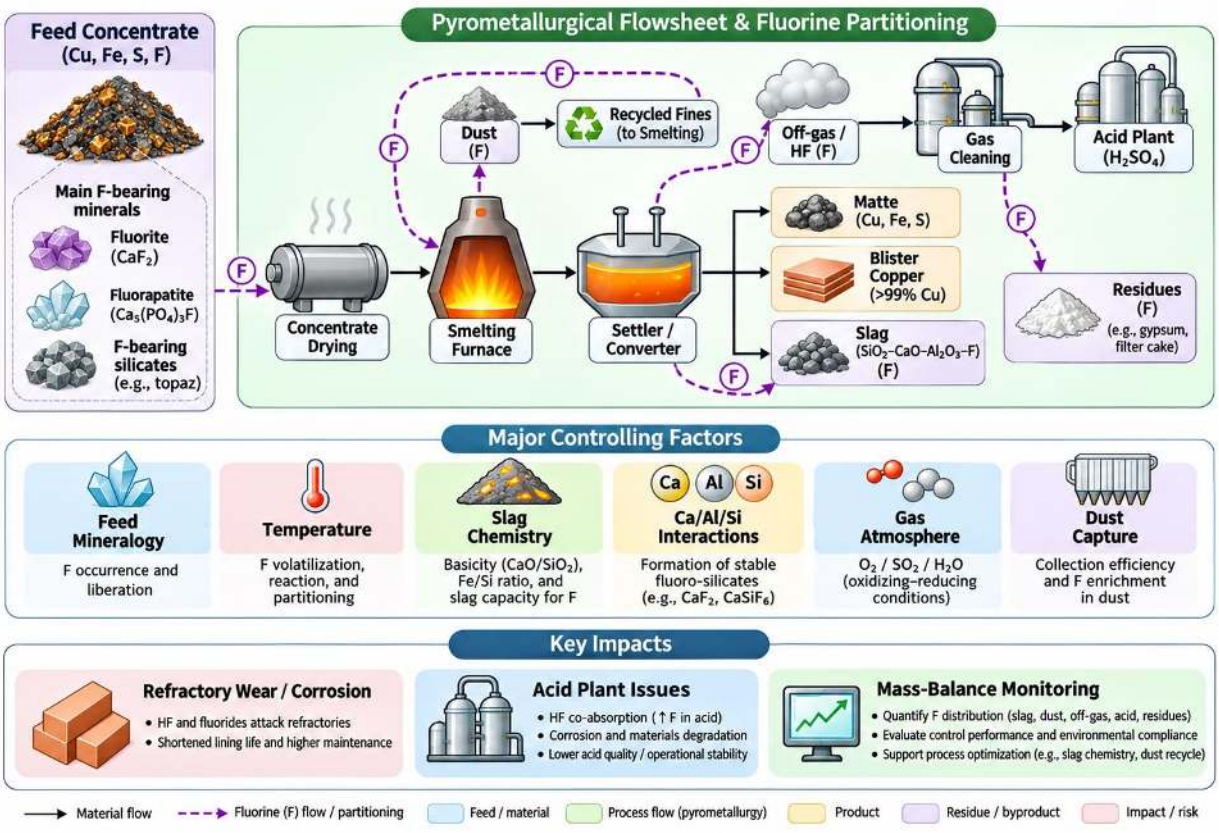


Figure 4. Fluorine partitioning during copper pyrometallurgy.
Note. Conceptual representation of possible fluorine pathways; actual partition fractions and chemical species are technology- and feed-dependent. Conceptual figure prepared with AI assistance (2026).

Figure 4 should be interpreted as a list of candidate transfer pathways, not as a quantitative split. In a plant audit, every apparent sink must be assigned a sampling location and a mass-flow estimate before the furnace and acid-plant balances can be reconciled.

Table 6 specifies the streams necessary for a complete smelter balance.

Table 6. Copper-smelter fluorine balance boundaries

Input/output	**Relevant stream**	**Monitoring requirement**
Input	Concentrate, flux, recycled dust	Dry-basis flow and total F

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Product	Matte/blister metal	Elemental F and associated phases
Solid reject	Slag, captured dust	Sampling, mass, leachability
Gaseous / liquid	Off-gas, scrubber liquor, acid plant	Particulate versus gas-phase split

Note. Reconcile outputs and recycled dust within a consistent smelter boundary.

9. Fluorine Removal and Control Technologies

Physical rejection is attractive where a liberated fluorine carrier differs sufficiently from copper sulfides in flotation response. The advantage can disappear when fluorite is locked with valuable sulfides or when fine particles enter the froth by entrainment. Selective leaching shifts the challenge to mineral accessibility, copper dissolution, wash efficiency, and treatment of fluorine-rich liquor. Neither operation should be favored on a single concentrate-grade measurement.

For dissolved fluoride, precipitation and induced crystallization target recoverable solid phases, whereas adsorption, ion exchange, membranes, and electrocoagulation separate or concentrate fluoride by different mechanisms. Reports on CaF_2 recovery (Cao et al., 2024), crystallization (Gao et al., 2025), and broader defluoridation methods (Ahmad et al., 2022) establish a technology landscape, not copper-plant performance. Acid concentration, competing metals, sulfate, suspended solids, and regeneration residues can substantially change feasibility.

Hybrid treatment is justified only when mineralogical mapping identifies a separable F carrier and bench or pilot tests show F rejection with acceptable copper recovery and reagent demand. Subsequent polishing and residue management are part of the same decision, not optional downstream add-ons. Comparative trials should use identical boundaries and include reagent manufacture, water management, energy use, solid–liquid separation, waste stabilization, and long-term operating variability.

For calcium-fluoride precipitation, report calcium dose and speciation, competing sulfate consumption/gypsum formation, total fluoride captured, residual dissolved F, solids settling and filtration, CaF_2 purity, hazardous co-contaminants, and precipitate leachability. A precipitated CaF_2-rich solid is a marketable circular product only if product specifications, impurities, and viable offtake have been demonstrated.

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For adsorption, report fluorine loading $q = m_{F,adsorbed} / m_{adsorbent}$ together with competing-ion effects, regeneration, cycle stability, and spent-media disposal. For electrocoagulation, quantify electrical energy, sacrificial electrode usage, sludge output, Cu co-removal, sulfate effects, and continuous-operation hydraulic behavior. Dilute potable-water evidence remains contextual, not validation for acidic copper solutions.

Table 7 compares treatment principles and the major barriers to copper-circuit application.

Table 7. Comparative fluorine-control technologies

Route	Appropriate feed/stream	Principal constraint
Physical rejection	Liberated F-bearing gangue	Copper recovery loss
Selective chemical leach	Chemically accessible F phases	Fluoride-rich liquor treatment
Thermal conditioning	Thermally responsive mineral phases	Energy, gas treatment
CaF_2 precipitation	Soluble fluoride	Sludge management, complex chemistry
Adsorption/membranes	Suitable clarified wastewaters	Fouling and competing ions

Note. Scale, liquor composition, solid–liquid separation, and secondary residue requirements govern transferability.

Table 8 defines the common accounting boundary for comparing fluorine rejection with copper recovery.

Table 8. Performance-reporting equations and minimum reporting boundary

Indicator	Equation/definition	Reporting requirement
F exclusion from selected product, $R_{F,product}$ (%)	$R_{F,product} = 100 \times [1 - (m_F,product / m_F,feed)]$	Defined product boundary; F is redirected, not destroyed. Report paired Cu recovery.
Copper recovery, R_{Cu} (%)	$R_{Cu} = 100 \times (m_Cu,product / m_Cu,feed)$	Use the same system boundary as for fluorine rejection; report copper masses consistently.
Fluorine balance closure (%)	$Closure_F = 100 \times (\Sigma m_F,out / \Sigma m_F,in)$	Account for all outgoing solids, liquors, dusts, off-gases, and residues; distinguish internal recycle from external feed.
Assessment basis	m_i,k = dry mass or volume × measured concentration of species i in stream k	Specify measurement basis, uncertainties, sampling points, and stream flow rates.
Fluorine balance residual, ε_F (%)	$\varepsilon_F = 100 \times [(\Sigma m_F,out - \Sigma m_F,in) / \Sigma m_F,in]$	Exclude internal recycle from external inputs/outputs; unresolved residuals are not presumed volatilization.

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Note. m denotes the mass of the indicated element in the specified stream. Product refers to the explicitly defined concentrate or metal output. Fluorine removal from a selected product is not equivalent to destruction of fluorine; all transferred fluorine must be accounted for.

The Table 8 definitions are boundary-specific accounting indicators, not literature-derived performance results. $R_{F,product}$ measures the fraction of feed fluorine excluded from one selected product, not overall destruction or permanent immobilization of fluorine. Copper recovery, F exclusion, closure, and residual must use identical system boundaries and stated uncertainty; internal recycle is excluded from external input and output sums. An unresolved nonzero closure residual should prompt further measurement rather than assignment to off-gas loss.

10. Environmental Management, Residues, and Circular Economy

Fluorine control shifts environmental responsibility across tailings, leach residues, smelter dust, wastewater treatment sludges, and possible recovered fluoride products. Reduced F concentration in a commercial concentrate is advantageous only if transferred fluoride can be handled with durable containment, water protection, and transparent monitoring.

Environmental mobility depends on pH, calcium availability, complexation, weathering, and residue physical stability. Laboratory leach tests should not be equated with long-term field behavior; they require a defined liquid-to-solid ratio, exposure time, particle size, and solution chemistry. The literature on wastewater precipitation and adsorption can inform treatment options, but variability in copper-site effluent demands pilot validation (El Diwani et al., 2022; Du & Li, 2024).

Circular opportunities include recovering usable CaF_2 or other fluorine-bearing products when purity, market demand, and contamination control justify the extra separation. A life-cycle comparison should include reagent production, energy, water reuse, secondary wastes, emissions, transport, and downstream durability rather than assuming that recovery is inherently superior to controlled stabilization.

Wastewater data from neutral or dilute systems should be screened for relevance to copper circuit liquors before selecting a reagent or sorbent. Regeneration demand, sludge

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stability, and the fate of co-removed metals can dominate environmental performance even when laboratory fluoride removal is high.

Tailings, precipitates, and spent sorbents require both total-fluorine and leachable-fluorine assays, with specified extraction pH, liquid/solid ratio, contact duration, mineralogy, and aging or weathering regime. Short-term leach compliance does not establish long-term stability; fluoride captured from one process stream must be assigned to its receiving residue or discharge stream.

Table 9 lists the environmental measurements needed to assess fluorine transfer.

Table 9. Environmental inventory and treatment checks

Stream	Potential release mechanism	Required evaluation
Tailings	Weathering and porewater migration	F leach tests and long-term drainage
Smelter dust	Handling and leaching	Dust mass and aqueous release
Wastewater	Direct discharge or accumulation	Speciation, flow, treatment performance
Treatment sludge	Secondary transfer of fluoride	Stability and disposal suitability

Note. Waste immobilization and water protection require site-specific long-term testing.

11. Industrial Integration, Techno-Economic Assessment, and Research Gaps

Control-point selection should follow a measured fluorine inventory across mine domains and plant operations. Early rejection may reduce smelter exposure but increase tailings loading; downstream aqueous treatment may protect equipment while creating a concentrated solid requiring disposal. The governing criterion is risk- and cost-adjusted system performance, subject to copper recovery and product specifications. A decision tree must therefore allow a "no additional treatment" option where the impurity is reliably contained, and specifications are met.

Techno-economic comparisons require a common throughput, feed grade, copper-recovery basis, availability assumption, and waste-treatment boundary. Cost ranges cannot be interpreted without equipment duty, consumption rates, scale, and local constraints. Laboratory proof of fluoride uptake is not evidence of industrial readiness: continuous operation, hydraulic behavior, solids handling, corrosion, maintenance, and upset recovery must be demonstrated

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separately. Technology readiness level assignments should identify the specific demonstrated system and scale.

The MINESCALE framework stresses that process-scale transfer depends on preserving controlling mechanisms across laboratory, pilot, and operating scales (Pereira, 2026c). For fluorine control, the relevant demonstration is not simply an improved grade in a batch test, but closure of the fluorine inventory across continuous operation, along with copper recovery, circuit water, and residue management. This is a methodological scale-up criterion, not independent evidence of a commercial copper defluorination plant.

Four evidence gaps dominate: paired mineralogy and F balances during copper flotation; activity-model validation in concentrated sulfate liquors; measured fluorine deportment around smelter dust and gas-cleaning circuits; and comparative plant-scale costs that include transferred fluorine. Recommended experiments should sample all output streams, report uncertainty, compare matched feed domains, and measure copper loss alongside fluorine rejection. These requirements would move the literature from plausible mechanisms toward testable flowsheet decisions.

The economic functional unit should be explicit: annualized treatment cost per tonne of dry concentrate meeting the applicable F specification, C_treated = C_annual / t_dry,compliant concentrate. If copper recovery changes, also report C_Cu = C_annual / t_Cu recovered. Include acid, calcium and other reagents, electricity, heat, water, Cu loss, gas treatment, corrosion allowances, residue stabilization, maintenance, and permitting costs. Commercial penalties cannot be generalized without contract, region, date, and product-specification evidence.

Life-cycle comparisons require declared upstream reagent and electricity burdens and downstream waste-disposal and product-credit assumptions. Technology-readiness claims should separate laboratory proof, representative pilot operation, continuous demonstration, and site-specific industrial deployment. No F-control option can be assigned a universal readiness or cost rank without its stream composition, operating envelope, and plant boundary.

Table 10 summarizes the decision variables needed to judge industrial implementation.

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Table 10. Decision criteria for industrial fluorine control

Criterion	Indicator	Decision consequence
Mineralogy	F phase, liberation by size	Physical vs chemical control point
Metallurgy	Cu recovery, F rejection	Selectivity and value loss
Operations	Water recycle, acid, wear	Compatibility and control cost
Environment	All-stream F mass balance	Transfer vs genuine removal
Scale	Pilot duration, reproducibility	TRL and uncertainty
Economics	CAPEX/OPEX on same basis	Whole-flowsheet preference

Note. Readiness and cost are not assigned without evidence from a stated operating scale.

12. Conclusions

Mineralogy is the first-order determinant of fluorine control in copper processing: liberated fluorite is not operationally equivalent to fluorapatite intergrown with sulfides or structurally bound fluorine in silicates. The analytical program must combine total F, dissolved fluoride, and phase association before selecting a removal route.

Beneficiation, leaching and thermal processing each offer potential control points, but the preferred position depends on copper recovery and the overall destination of fluorine. A route cannot be deemed environmentally superior merely because it lowers F in the concentrate; it must demonstrate manageable outputs across all solids, liquors and gases.

The present evidence base remains uneven. Controlled laboratory studies are comparatively abundant for fluorite flotation and wastewater defluoridation, while quantitative, plant-specific copper smelting, complex hydrometallurgical circuit, and integrated cost data are less complete. Future investigations should prioritize mineralogical variability, closed mass balances, validated speciation and kinetic models, and transparent pilot-to-plant performance before advancing universal process recommendations.

Fluorine control is fundamentally a whole-flowsheet deportment problem: lower fluorine grade in a concentrate or liquor can mean transfer to tailings, bleed, sludge, scrubber solution, or another monitored stream rather than elimination. A defensible control decision therefore reports mineral liberation, F speciation, product-specific F exclusion, paired copper recovery, closure and environmental fate within the same clearly defined boundary.

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Data Availability

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The author performed conceptualization, critical analysis, literature synthesis, visualization, and manuscript preparation.

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