



Using the Common-Ion Effect Correctly in Hydrometallurgical Processing: Opportunities, Misinterpretations, and Process-Design Rules

Antonio Clareti Pereira, Ph.D.*

Department of Graduate Program in Materials Engineering Federal University of Ouro Preto (UFOP) Ouro Preto, MG, Brazil

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ABSTRACT

Original Research Article

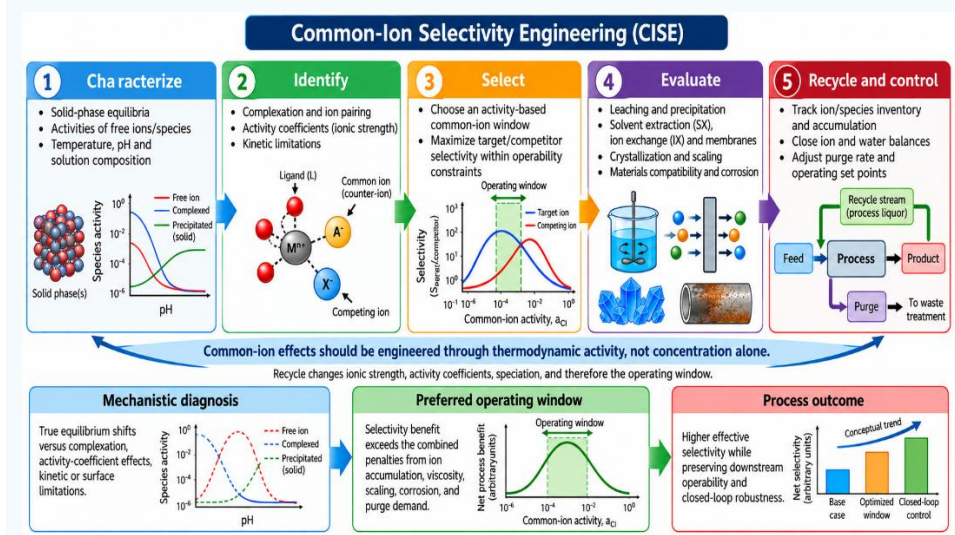
The common-ion effect is routinely invoked to explain changes in dissolution, precipitation, and crystallization, yet hydrometallurgical liquors rarely behave as the dilute, ideal solutions used to introduce the concept. This critical review reframes the common-ion effect as an activity-based process-design variable and asks when a measured process response can be attributed to true equilibrium displacement rather than to simultaneous changes in activity coefficients, complexation, ion pairing, hydrolysis, redox speciation, salting-out, supersaturation, nucleation, or surface kinetics. The evidence synthesis emphasizes recent chloride, sulfate, ammoniacal, carbonate, fluoride, hydroxide, and mixed-electrolyte systems and evaluates applications in selective leaching, staged impurity rejection, precipitation, crystallization, solvent extraction, ion exchange, membrane and electrochemical operations, and reagent recycling. Particular attention is given to concentrated and closed-loop circuits, in which a nominal common ion may accumulate through recycle rather than through deliberate dosing and in which metallurgical gains may be offset by corrosion, scaling, viscosity, osmotic pressure, impurity buildup, or purge demand. A four-stage Common-Ion Selectivity Engineering (CISE) framework is proposed—Characterize, Identify, Select, and Evaluate—with recycle and control treated as a feedback loop that updates the operating window. The central design target is therefore not the maximum common-ion concentration, but an activity-based window that maximizes net selectivity while preserving downstream operability. Practical design rules and minimum reporting requirements are proposed to strengthen mechanistic attribution, scale-up, and reproducibility in future hydrometallurgical studies.

Keywords: Common-Ion Effect, Hydrometallurgy, Selective Leaching, Solution Speciation, Selective Precipitation, Closed-Loop Hydrometallurgy.

Highlights

- The common-ion effect is treated as an activity-based process-design variable, not a concentration rule.
- True equilibrium displacement is separated from complexation, ionic-strength, salting-out, and kinetic effects.
- The four-stage CISE framework links activity-based selection to downstream evaluation and recycle-control feedback.
- Closed-loop operation requires an optimal common-ion window beyond which salt accumulation can erase metallurgical benefits.

Graphical Abstract



*Corresponding author: Antonio Clareti Pereira, Ph.D.

Department of Graduate Program in Materials Engineering Federal University of Ouro Preto (UFOP) Ouro Preto, MG, Brazil

Introduction

Why Revisit the Common-Ion Effect in Hydrometallurgy?

The common-ion effect is one of the most familiar consequences of chemical equilibrium, but familiarity can obscure its engineering complexity. Hydrometallurgical systems commonly contain multicomponent solids and concentrated electrolytes with high acid or base concentrations, multiple counter-ions, dissolved impurities, complexing ligands, and recycle-derived salts. Under these conditions, changing the concentration of an ion that participates in a dissolution or precipitation equilibrium can alter the process response, but the measured change cannot automatically be assigned to a textbook common-ion mechanism. Process design requires more than predicting the direction of an equilibrium shift; it requires predicting the magnitude, selectivity, reversibility, kinetics, and downstream consequences of that shift. Recent work on concentrated sulfate and mixed-electrolyte systems shows that ion association, hydration, interfacial chemistry, and electrolyte non-ideality can become first-order variables rather than secondary corrections (Al-Malki & Holt, 2026; Bialik & Abbas, 2025; Yang et al., 2026).

The industrial motivation is equally strong. Hydrometallurgical circuits increasingly process lower-grade ores, secondary resources, polymetallic feeds, and battery or electronic wastes while facing tighter constraints on reagent intensity, water use, residue generation, and product purity. Circular-hydrometallurgy principles therefore emphasize reagent recovery, water reuse, side-stream valorization, and minimization of irreversible reagent consumption (Binnemans & Jones, 2023). Closed-loop battery-recycling and waste-processing studies also show that recycle progressively changes electrolyte composition; solution chemistry therefore cannot be treated as a fixed background condition (Choi et al., 2025; Yang et al., 2024; Yetim et al., 2024). In practice, a common ion can be deliberately dosed, inherited from the feed, generated by neutralization, or accumulated through mother-liquor and wash-water recycle.

Figure 1 illustrates the central distinction used throughout this review. The classical common-ion prediction is only one contributor to the actual hydrometallurgical response; free-species activities, complexation, ionic strength, redox-pH coupling, interfacial state, and kinetics determine whether the classical effect is reinforced, attenuated, canceled, or reversed.

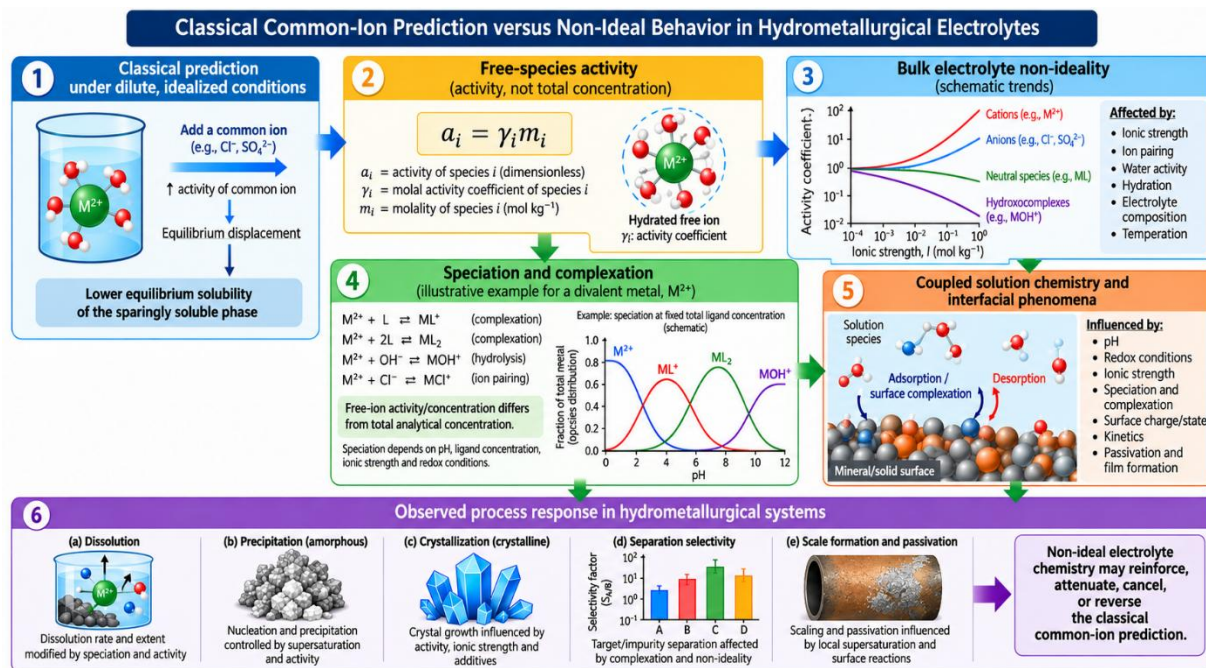


Figure 1: Classical prediction versus real common-ion behavior in hydrometallurgical electrolytes.

Note. Conceptual synthesis by the author, adapted from the activity/speciation perspectives discussed by Dickson et al. (2023), Manaure et al. (2021), dos Santos, Gaona, et al. (2024), dos Santos, Lassin, et al. (2024), and Bialik and Abbas (2025).

The aim is not to catalog every instance in which added salts change solubility. Instead, this review asks when, why, and how to deliberately engineer a common ion in a hydrometallurgical flowsheet. Five questions organize the analysis: (i) where can equilibrium suppression or enhancement create useful selectivity; (ii) how can a true common-ion contribution be separated from coupled physicochemical effects; (iii) which thermodynamic representation is defensible at industrial electrolyte concentrations; (iv) how does the intervention propagate into separation, crystallization, corrosion, recycle, and purge requirements; and (v) what evidence is needed before a laboratory observation can be treated as a scalable process-design rule?

To make the review architecture explicit, Figure 1 establishes the activity-based distinction between the classical prediction and real electrolyte behavior; Figure 2 diagnoses mechanisms that can mimic an apparent common-ion effect; Figure 3 locates common-ion intervention points across the hydrometallurgical flowsheet; Figure 4 defines the closed-loop operating-window concept; and Figure 5 formalizes the Common-Ion Selectivity Engineering (CISE) framework. Complementarily, Table 1 defines evidence classes; Table 2 separates the common-ion effect from confounding phenomena; Table 3 summarizes leaching applications; Table 4 compares precipitation families; Table 5 addresses crystallization and product recovery; Table 6 compares major electrolyte families; Table 7 balances recycle benefits and

penalties; and Table 8 specifies minimum reporting requirements for reproducible, scale-up-relevant studies.

Review Scope, Literature Strategy, and Evidence Classification

This article is a structured critical review rather than a statistical meta-analysis. The final evidence base prioritizes publications from 2020 through September 2026 because the objective is to assess current hydrometallurgical practice, concentrated-electrolyte modeling, and closed-loop process design. Foundational thermodynamic concepts are treated explicitly, but the synthesis does not claim exhaustive historical coverage. The evidence is organized by mechanism and unit operation rather than by commodity and spans aqueous thermodynamics, leaching, staged precipitation, sulfate and chloride solution chemistry, crystallization, solvent extraction, adsorption, electrodialysis, diffusion dialysis, nanofiltration, electrochemical recovery, corrosion, scaling, process recycling, techno-economics, and life-cycle assessment.

The working corpus was developed in September 2026 through targeted Google Scholar searches organized into Boolean families covering common-ion fundamentals, activity/speciation, leaching, precipitation, crystallization, separation technologies, recycle, corrosion/scaling, and techno-economic or life-cycle implications. Application-focused searches prioritized 2020–2026, with no more than 20 candidate references retained from any individual Boolean query before deduplication and relevance screening. Candidate records were checked against DOI and publisher metadata. We excluded preprints, duplicates, and papers not directly relevant to hydrometallurgical process design.

Equivalent Scopus TITLE-ABS-KEY and Web of Science TS syntax was prepared to make the Boolean logic transferable across databases; however, database-by-database hit counts and a formal PRISMA flow were not preserved for the working corpus. Accordingly, this article is presented as a structured critical review rather than as an exhaustive systematic review. The final cited corpus contains 92 publications, including three author publications used where they directly address coprecipitation, free acidity, or jarosite chemistry.

Mechanistic certainty is evaluated separately from process relevance. Direct evidence requires that the added ion participate in the controlling phase equilibrium and that the corresponding free-species activity be quantified or defensibly modeled. Inferred evidence is consistent with a

common-ion contribution but lacks a complete activity or speciation demonstration. Coupled evidence describes cases in which equilibrium displacement occurs together with complexation, acid-base reactions, ion pairing, or other specific-ion effects. Ionic-strength-dominated evidence is assigned when bulk electrolyte non-ideality provides the more defensible explanation. Kinetic or surface-coupled evidence describes rate, passivation, nucleation, or growth effects that occur before equilibrium is established. Empirical process responses remain valuable, but they are not relabeled mechanistically when the available data do not distinguish among these alternatives.

Table 1 defines the evidence classes used throughout the review and the minimum information required for a defensible diagnosis.

Table 1: Evidence classes for diagnosing common-ion behavior in hydrometallurgical systems.

Evidence class	Diagnostic basis	What should be reported	Representative evidence
Direct common-ion evidence	The added ion is part of the controlling dissolution/precipitation equilibrium, and its free-species activity changes in the expected direction.	Solid-phase identity; free-ion activity; temperature; equilibrium or approach-to-equilibrium.	Thermodynamic sulfate and phosphate systems (Belkhair et al., 2026; dos Santos, Gaona, et al., 2024; dos Santos, Lassin, et al., 2024)
Inferred common-ion contribution	The process trend is consistent with common-ion displacement, but free-species activity or complete speciation is not demonstrated.	Full solution composition; matched controls; sensitivity to added common ion; explicit statement of mechanistic uncertainty.	Process studies in which directionality is consistent with equilibrium displacement but attribution remains incomplete
Coupled common-ion/complexation	Equilibrium displacement occurs together with ligand complexation or ion pairing.	Full aqueous speciation; complex-formation constants; activity model.	Sulfate/chloride complexation (Jordan et al., 2022; Sun et al., 2026; Talreja-Muthreja & Steiger, 2026)
Ionic-strength dominated	Salt addition broadly changes activity coefficients, hydration, or ion association.	Ionic strength; model domain; water activity where relevant; matched ionic-strength control.	Concentrated electrolytes (Al-Malki & Holt, 2026; Bialik & Abbas, 2025; Manaure et al., 2021)
Kinetic/surface-coupled	Rate, nucleation, growth, or passivation changes before equilibrium is established.	Time-resolved dissolution/precipitation; surface characterization; equilibrium verification.	Olivine passivation and scale control (Alagia et al., 2025; Mondal et al., 2026)
Empirical process response	A useful process change is observed, but the mechanism is not uniquely resolved.	Complete solution composition; mass balance; repeatability; downstream consequences.	Industrial or flowsheet studies (Jin et al., 2023; Wang et al., 2026)

Note. Author synthesis based on the evidence-classification framework used in this review and the thermodynamic, kinetic, and industrial studies cited in the final column.

Evidence maturity is assessed on a separate axis from mechanistic certainty. A carefully controlled synthetic-solution experiment can provide strong mechanistic evidence but limited industrial representativeness, whereas plant-scale

crystallization or recycle data can demonstrate operability without resolving the dominant microscopic mechanism. Scale-up discussions therefore distinguish fundamental thermodynamics, synthetic solutions, real leachates, continuous laboratory operation, pilot demonstrations, and industrial implementation. This distinction avoids treating plant relevance and mechanistic proof as interchangeable forms of evidence.

Thermodynamic Basis of the Common-Ion Effect in Concentrated Hydrometallurgical Solutions

Classical Equilibrium and Conditional Solubility

For a sparingly soluble solid $M_aX_\beta(s)$ in equilibrium with dissolved species, the thermodynamic solubility product must be written in terms of activities rather than analytical concentrations. The rigorous common-ion effect is therefore an activity effect: increasing the activity of an ion shared with the solid lowers the equilibrium activity required of its counter-ion, provided that the controlling solid phase and reaction stoichiometry remain unchanged. In hydrometallurgy, however, the analytical concentration of a metal, sulfate, chloride, carbonate, hydroxide, phosphate, or oxalate can differ substantially from the activity of the species that enters the equilibrium expression. Conditional solubility consequently depends on the reactions that redistribute free species, including complexation, protonation, hydrolysis, and redox transformations. Reaction-equilibrium constants must therefore be coupled to speciation models appropriate to temperature and electrolyte composition (Dickson et al., 2023; Jordan et al., 2024).

$$(1) K_{sp} = a_M^a \cdot a_X^b$$

$$(2) a_i = \gamma_i \cdot m_i$$

$$(3) SI = \log_{10}(Q / K_{sp})$$

Here, a_i is species activity, γ_i is the activity coefficient, m_i is molality, Q is the ion-activity product, and SI is the saturation index. A positive SI indicates supersaturation with respect to the specified phase, but it does not by itself establish precipitation kinetics or product identity.

Activities, Non-Ideality, and Model Selection

A simple concentration-based approximation becomes progressively less reliable as ionic strength increases. Davies or extended Debye–Hückel formulations can be useful in moderately dilute domains, whereas concentrated process liquors often require specific-ion-interaction approaches or Pitzer-type models. The issue is not mathematical sophistication for its own sake: a predicted common-ion benefit can be exaggerated, attenuated, or even reversed when activity coefficients and complex formation are treated

consistently. Pitzer and SIT treatments of sulfate systems containing rare-earth, alkali, alkaline-earth, and multivalent metal ions show that fitted interaction parameters and the selected dissociation scheme influence calculated free-ion activities and phase boundaries (Belkhair et al., 2026; dos Santos, Gaona, et al., 2024; dos Santos, Lassin, et al., 2024). Model-free and ion-interaction approaches likewise demonstrate that individual-ion activity estimates remain method-dependent in concentrated solutions (Manaure et al., 2021).

A practical consequence is that common-ion optimization should be expressed as an activity window whenever electrolyte concentration is high. Total sulfate, for example, may increase while free SO_4^{2-} activity changes nonlinearly because of HSO_4^- formation, metal-sulfate complexation, and ion pairing. The same logic applies to chloride in chloro-complexing systems and to carbonate in CO_2 -coupled liquors. Thermochemical modeling of $CuSO_4-H_2SO_4-H_2O$ and experimental work on divalent-metal sulfate hydration illustrate why total concentration is an incomplete state

Supersaturation, Phase Identity, and Kinetics

Precipitation adds another layer of ambiguity. A common ion can reduce equilibrium solubility and increase supersaturation, yet the measured solid yield also depends on induction time, nucleation pathway, crystal growth, agglomeration, metastable phases, and coprecipitation. Gypsum precipitation in saline media demonstrates the joint influence of thermodynamics, kinetics, morphology, and particle-size distribution (Reiss et al., 2021). Work on calcium phosphate precipitation similarly shows that open-system control requires explicit treatment of solution chemistry and phase selection rather than a single saturation index (Reynaud et al., 2021). The same distinction is fundamental for product crystallization, where the objective may be not only high yield but controlled hydrate, crystal size, morphology, impurity rejection, and filterability.

Figure 2 summarizes the principal mechanisms that can generate a superficially similar change in solubility, extraction, or precipitation. No single concentration trend is sufficient to identify the mechanism; phase identity, free-species activities, matched controls, and time dependence are required.

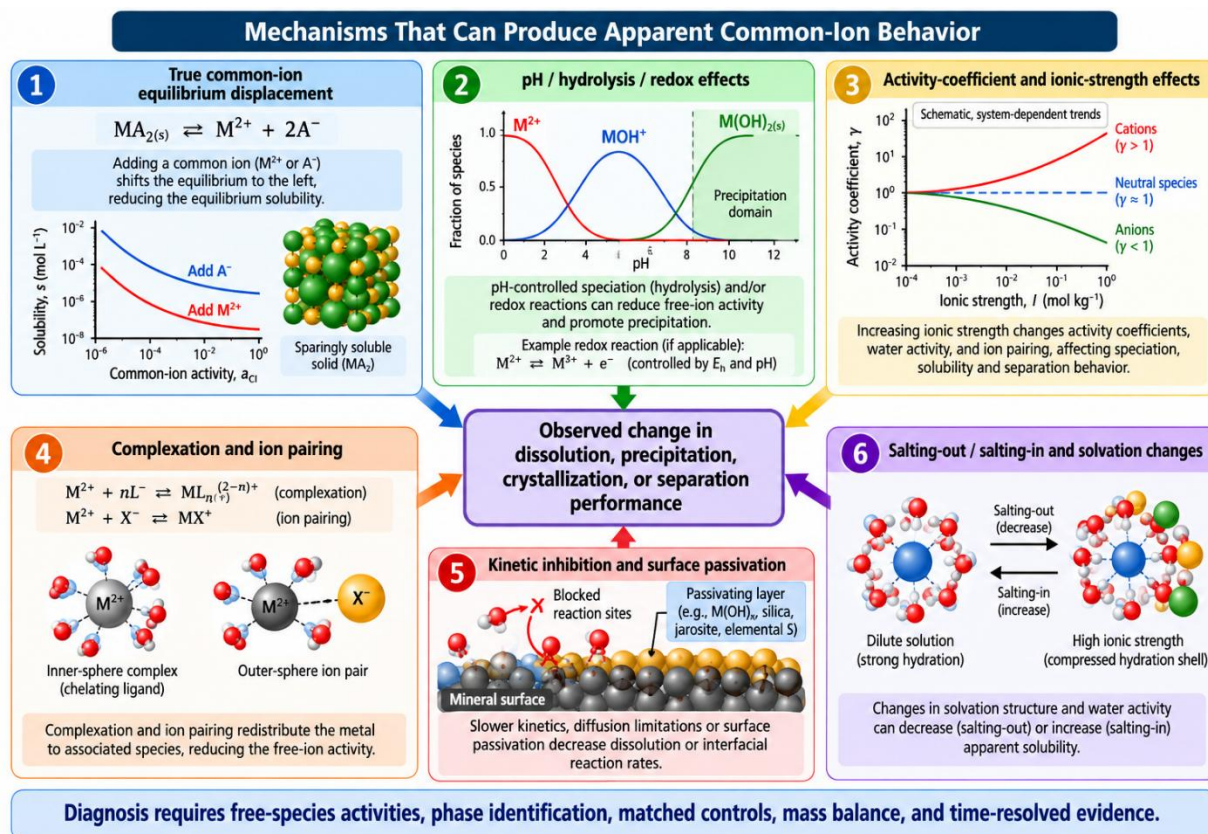


Figure 2: Mechanisms that can mimic an apparent common-ion effect.

Note. Conceptual synthesis by the author, adapted from concentrated-electrolyte, ion-pairing, speciation, precipitation, and surface-kinetic studies (Al-Malki & Holt, 2026; Alagia et al., 2025; Bialik & Abbas, 2025; Dickson et al., 2023; Reiss et al., 2021).

What Is—and Is Not—the Common-Ion Effect?

A rigorous diagnosis begins by asking whether the added species participates directly in the equilibrium controlling the phase of interest. If it does not, the term common-ion effect should not be used merely because a salt was added and solubility changed. Even when the added ion is genuinely common to the phase, a second question follows: did its free-

species activity change in the assumed direction? Complexation can consume the nominal common ion or its counter-ion, high ionic strength can change activity coefficients, ion pairing can reduce the free-species pool, and pH or redox changes can alter the relevant aqueous species and solids. These couplings are especially important in sulfate, chloride, ammoniacal, and mixed-anion media (Jordan et al., 2022; Lommelen et al., 2020; Saim, 2025; Sui et al., 2023; Yang et al., 2026).

Table 2 distinguishes phenomena commonly conflated with the common-ion effect. The table is intentionally diagnostic: several mechanisms can coexist, but they should be named separately because they imply different control variables and scale-up risks.

Table 2: Phenomena commonly misidentified as the common-ion effect.

Phenomenon	Dominant mechanism	Can mimic a common-ion response?	Diagnostic discriminator
True common-ion effect	Activity-driven equilibrium displacement involving an ion already present in the phase equilibrium.	Yes—this is the target mechanism.	Reaction stoichiometry + free-ion activity + phase confirmation.
Complexation	Ligand binding lowers free metal or ligand activity.	Yes.	Speciation calculation or spectroscopy; conditional constants.
Ionic-strength effect	Activity coefficients change as the electrolyte matrix changes.	Yes.	Compare at matched ionic strength or use a validated activity model.
Salting-out / hydration change	Solvation and water activity modify apparent solubility or extraction.	Yes.	Water activity, ion-specific trends, matched-common-ion controls.
Buffering / hydrolysis	pH controls metal hydrolysis and phase saturation.	Yes.	Report pH measurement conditions and hydrolysis speciation.
Redox shift	Oxidation state and ligand field change species and solids.	Indirectly.	Eh/redox couple, oxidation-state analysis.
Kinetic inhibition	Dissolution, nucleation, or growth rate changes without equilibrium shift.	Yes.	Time-resolved data and equilibrium verification.
Surface passivation	A reaction layer blocks reactive surface.	Yes.	Surface/mineralogical characterization (Alagia et al., 2025).
Ion pairing	Oppositely charged ions associate and alter free-species activities.	Yes.	Speciation/activity model (Bialik & Abbas, 2025).

Note. Author synthesis adapted from recent studies of aqueous speciation, concentrated electrolytes, interfacial dissolution, and precipitation. “Higher salt concentration” should not be used as a mechanistic synonym for “common-ion effect.”

This distinction also prevents a second error: assuming that a common-ion effect is necessarily beneficial. Lower solubility can be advantageous when it suppresses gangue dissolution or precipitates an impurity, but it can be detrimental when it reduces target-metal recovery, promotes scaling, or produces impurity-bearing crystals. The mechanism itself is neutral; process value depends on where the equilibrium shift occurs in the flowsheet and how it affects the complete mass balance.

Common-Ion Control of Mineral and Metal Leaching

Suppressing Undesirable Dissolution

A potentially valuable leaching application is selective equilibrium suppression: preserve the target dissolution pathway while reducing dissolution of gangue or a

problematic impurity. The strategy is most defensible when the unwanted solid dissolves through an equilibrium involving an ion that can be raised without creating a stronger competing complexation pathway. Sulfate-, chloride-, carbonate-, phosphate-, fluoride-, and hydroxide-bearing minerals are possible candidates, but each system must be evaluated using its complete aqueous chemistry. The downstream leverage can be substantial: every mole of Fe, Al, Ca, or Mg kept out of solution can reduce neutralization demand, precipitate volume, impurity loading to solvent extraction or ion exchange, and entrainment into the final product.

Actual leach systems show why simple predictions are risky. Chloride additions can suppress dissolution of some chloride-containing solids but can also enhance target or impurity dissolution through metal-chloro complexes. Chloride hydrometallurgy for secondary lead and polymetallic concentrates illustrates the importance of speciation and oxidation conditions (Nicol et al., 2025; Vivar et al., 2025). In sulfate systems, solution structure and sulfate association can affect dissolution and electrochemical behavior (Al-Malki & Holt, 2026). For olivine-type minerals, anion-dependent

formation of a passivating Fe-rich interfacial layer demonstrates that a reduced dissolution rate may arise from surface chemistry rather than from a thermodynamic common-ion shift (Alagia et al., 2025).

Acidic, Alkaline, and Ammoniacal Leaching

Acidic systems require separate consideration of free acidity and ligand identity. Free acidity is not equivalent to pH in concentrated metallurgical liquors, and neglecting this distinction can confound both equilibrium and kinetic interpretation (Pereira, 2026b). HCl systems are especially prone to coupled common-ion and chloro-complexation effects, whereas H₂SO₄ media add bisulfate formation, metal-sulfate association, and potential sulfate precipitation. In high-chloride lithium recovery, the chloride source can change extraction behavior not only through chloride inventory but also through interactions with iron and the extractant system (Bi et al., 2026). In alkaline processing, hydroxide and aluminate chemistry can shift dissolution and

aging pathways, as illustrated by NaOH-based recovery from lithium-containing aluminum electrolyte slag (Zhou et al., 2025).

Ammoniacal systems are similarly coupled. NH₃ acts as a ligand, NH₄⁺ participates in acid-base buffering, sulfate or chloride can act as counter-ions, and redox agents may be required. Reviews and recent studies of ammoniacal leaching of secondary resources show that metal-ammine complexation is often the dominant source of selective dissolution (Hubert et al., 2026; Saim, 2025; Wang et al., 2022). An NH₄⁺ concentration effect should therefore be described as common-ion control only when NH₄⁺ is part of the relevant equilibrium and the contribution of NH₃ complexation has been separated.

Table 3 maps representative leaching situations to the dominant opportunity and the principal mechanism that can defeat a naive common-ion interpretation.

Table 3: Common-ion opportunities and interpretive risks in hydrometallurgical leaching.

Leaching context	Potential common-ion strategy	Main competing mechanism / risk	Representative evidence
Chloride leaching	Use Cl ⁻ inventory to influence phase solubility or metal speciation while controlling target/impurity dissolution.	Strong chloro-complexation, redox coupling, corrosion.	Lithium, Cu/Au/U, Pb systems (Bi et al., 2026; Nicol et al., 2025; Vivar et al., 2025)
Sulfate leaching	Exploit sulfate-bearing equilibria to suppress or redirect dissolution.	HSO ₄ ⁻ , metal-sulfate complexes, ion pairing, sulfate precipitation.	Concentrated Li ₂ SO ₄ and FeSO ₄ systems (Al-Malki & Holt, 2026; Xing et al., 2021)
Ammoniacal leaching	Use NH ₄ ⁺ /counter-ion inventory while preserving selective ammine complexation.	NH ₃ ligand chemistry dominates many separations.	Secondary-resource studies (Farhan et al., 2026; Hubert et al., 2026; Wang et al., 2022)
Alkaline leaching	Use OH ⁻ or aluminate equilibrium control to retain unwanted phases.	Amphoterism, aging, gel/precipitate formation.	NaOH-based processing (Zhou et al., 2025)
Organic/complexing lixiviants	Use a common counter-ion only after accounting for ligand binding.	Complexation can overwhelm the classical effect.	Citrate REE recovery (Cunningham & Azimi, 2026)
Deep-eutectic / hybrid media	Treat common-ion language cautiously unless aqueous equilibrium is well defined.	Solvent-specific activity and complexation.	Closed-loop cathode recycling (Yetim et al., 2024)

Note. Author synthesis adapted from the leaching and solution-chemistry studies cited in the final column.

Selective Precipitation and Impurity Rejection

Selective precipitation is the unit operation in which a common-ion intervention most closely resembles the classical equilibrium problem because the intended outcome is often a controlled reduction in solubility. Even here, hydrometallurgical selectivity rarely follows solubility products alone. Hydrolysis, complexation, supersaturation, nucleation, coprecipitation, occlusion, and solid-solution formation can shift separation boundaries. Reviews of rare-earth-element (REE) precipitation and staged impurity removal emphasize the need to combine thermodynamic

windows with kinetic and environmental constraints (Chanouri et al., 2025; Hassas et al., 2023); jarosite chemistry similarly shows that sulfate, acidity, Fe speciation, and residue properties must be considered together (Pereira, 2026c).

Hydroxide and Sulfide Precipitation

Hydroxide precipitation introduces OH⁻ into equilibria for many metal hydroxides, but practical separation depends on pH-dependent hydrolysis and amphoterism as well as on the common-ion contribution. In battery-recycling liquors, Fe and Al removal can protect downstream Ni, Co, and Li recovery, yet coprecipitation must be measured rather than assumed negligible (Pereira, 2026a; Zou et al., 2024). MgO precipitation of Ni and Co from magnesium-rich sulfate liquors further shows how the neutralizing solid, sulfate

matrix, and competing cations affect apparent selectivity (K. Liu et al., 2021). Sulfide precipitation can provide stronger thermodynamic separation for selected metals, but sulfide dose, pH, metal competition, particle aggregation, and reagent form govern the achievable selectivity (Li et al., 2024; Zhang et al., 2023).

Carbonate, Phosphate, Oxalate, Sulfate, and Fluoride Routes

Carbonate and bicarbonate precipitation are widely used for battery and REE products, but CO_2 equilibria and complexation make carbonate activity sensitive to pH and gas-liquid conditions. Concentrated REE/magnesium sulfate solutions precipitated with NH_4HCO_3 demonstrate the need to evaluate magnesium rejection and reagent chemistry together (Wang et al., 2025). Lithium carbonate is particularly sensitive to mother-liquor composition, making conditional solubility, rather than pure-water solubility, the relevant design basis (Ge et al., 2025). Phosphate precipitation can form very low-solubility lithium or REE phases; lithium-phosphate recovery from brines and spent LiFePO_4 illustrates why phase engineering and reagent economy must be

considered together (D. Liu et al., 2021; Mahandra & Ghahreman, 2021).

Oxalate routes are highly effective for REE precipitation, but speciation, chloride concentration, kinetics, and crystal properties determine separation performance and solid-liquid handling. Sequential precipitation from ionic-clay lixivium and oxalate precipitation from acidic mine waters illustrate both the opportunity and the need for stagewise control (Anawati & Azimi, 2022; Crespo et al., 2026bb; Nawab et al., 2022). Sulfate double salts provide another common-ion-sensitive route; their performance depends on sulfate inventory, counter-cation identity, temperature, and downstream conversion (Guzhov et al., 2023; Han & Kim, 2021; Tolbert et al., 2025). Phosphate and fluoride routes likewise require explicit treatment of strong complexation and coprecipitation, as shown by REE/Th removal with Pb-phosphates and by strongly acidic fluoride-containing recycle streams (Lü et al., 2026; Sordyl et al., 2023).

Table 4 compares the main precipitation families from the perspective of common-ion engineering rather than merely reagent choice.

Table 4: Common-ion-assisted selective precipitation of metals and impurities.

Precipitation family	Common-ion lever	Selectivity opportunity	Key limitation	Representative evidence
Hydroxide	OH^- activity / pH	Staged Fe/Al and base-metal rejection.	Hydrolysis, amphoterism, coprecipitation.	Battery/recycle liquors (Pereira, 2026a; Zou et al., 2024)
Sulfide	$\text{S}^{2-}/\text{HS}^-$ activity	Very low solubility for selected heavy metals.	pH-dependent sulfide speciation, particle aggregation, H_2S risk.	Multimetal systems (Li et al., 2024; Zhang et al., 2023)
Carbonate	$\text{CO}_3^{2-}/\text{HCO}_3^-$	Li and REE product formation; Ca/Mg control.	CO_2 equilibrium, mother-liquor effects.	Li/REE systems (Ge et al., 2025; Wang et al., 2025)
Phosphate	PO_4^{3-} family	Low-solubility Li and REE phases.	pH-dependent phosphate speciation; competing Ca/Mg.	Li_3PO_4 and Ca-phosphate studies (Liu et al., 2021; Reynaud et al., 2021)
Oxalate	$\text{C}_2\text{O}_4^{2-}$ family	Selective REE recovery and purification.	Complexation, nucleation, morphology.	REE studies (Crespo et al., 2026; Nawab et al., 2022)
Sulfate/double sulfate	SO_4^{2-} inventory + counter-cation	Fractional REE precipitation/crystallization.	Ion pairing, hydrate/double-salt phase selection.	REE double-sulfate systems (Guzhov et al., 2023; Tolbert et al., 2025)
Fluoride	F^- activity	Strong selective precipitation in suitable systems.	Strong aqueous and complexation corrosion.	Acidic recycle treatment (Lü et al., 2026)

Note. Author synthesis adapted from recent staged precipitation, sulfate, oxalate, phosphate, carbonate, sulfide, and fluoride studies.

Crystallization and Product Recovery

Crystallization changes the design question from impurity removal to recovery of a saleable or recyclable solid. A common ion can lower equilibrium solubility and increase

supersaturation, but product quality introduces additional criteria: hydrate identity, crystal-size distribution, morphology, inclusions, impurity substitution, filterability, washing behavior, and drying. Phase diagrams are therefore indispensable. As emphasized in recent crystallization literature, a solute does not crystallize independently of the multicomponent phase relationships that determine which solid phase is stable (Martin, 2024).

Sulfate products provide a rich set of examples. Nickel sulfate crystallization and purification studies show that crystallizer conditions and post-crystallization treatment determine battery-grade quality (Choi & Azimi, 2023). Related work on $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ demonstrates that impurity incorporation can persist even when bulk solution chemistry appears favorable, so increasing sulfate or concentrating mother liquor does not guarantee higher-purity crystals (Choi et al., 2026a; Choi et al., 2026b). $\text{CoSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ phase diagrams and semi-batch evaporative crystallization of cobalt sulfate hydrates further illustrate the need to control acid concentration, temperature, hydration state, and supersaturation trajectory (Ma et al., 2024; Zhang et al., 2022).

Common-ion and salting effects can also be used deliberately in antisolvent or fractional crystallization. Solubility measurements for K_2SO_4 , Li_2SO_4 , and $(\text{NH}_4)_2\text{SO}_4$ in water-methanol mixtures show how solvent composition and Pitzer-type modeling can support design (Galvão et al., 2024). Antisolvent crystallization has been developed for hydrometallurgical product recovery and scaled toward rare-

earth recovery from NdFeB magnets (Pawar et al., 2026; Peters et al., 2022; Xu et al., 2026). Dimethyl ether combined with Na_2SO_4 provides another example of fractional lanthanide sulfate recovery in which a sulfate common ion and solvent-driven solubility reduction interact (Tolbert et al., 2025).

Other industrially relevant examples include freezing crystallization to remove Mg from zinc hydrometallurgy, phase-diagram-based separation of FeSO_4 and MnSO_4 , membrane crystallization of CuSO_4 from acidic mine water, and membrane crystallization of Li_2CO_3 in mixed chloride salts (Gómez et al., 2024; Jin et al., 2023; Shirazi et al., 2024; Wang et al., 2026). These studies reinforce the review's central rule: the useful variable is the full mother-liquor composition and its phase diagram, not the isolated concentration of the nominal common ion.

Table 5 summarizes product-recovery modes in which common-ion engineering can contribute to yield or selectivity, together with the principal product-quality constraint.

Table 5: Common-ion-relevant crystallization and product-recovery strategies.

Recovery mode	Common-ion role	Primary design objective	Representative evidence
Cooling crystallization	Shift hydrate/salt solubility as temperature changes.	Yield + phase identity + impurity rejection.	(Choi & Azimi, 2023; Ma et al., 2024)
Evaporative crystallization	Concentrate common ion and target solute.	Yield versus energy, scaling, hydrate control.	(Oskouei et al., 2026; Zhang et al., 2022)
Antisolvent crystallization	Reduce solvent power while exploiting salt/common-ion effects.	Selective crystallization and scalable particle formation.	(Farhan et al., 2026; Pawar et al., 2026; Peters et al., 2022)
Fractional sulfate crystallization	Use sulfate/counter-cation inventory to form low-solubility salts.	REE fractionation and product conversion.	(Guzhov et al., 2023; Tolbert et al., 2025)
Freezing/eutectic crystallization	Partition salts through temperature-dependent phase equilibria.	Impurity removal and water/salt recovery.	(Jin et al., 2023; Ma et al., 2024)
Membrane crystallization	Create supersaturation through controlled water removal.	Crystal recovery with lower thermal duty.	(Gómez et al., 2024; Shirazi et al., 2024)
Post-crystallization purification	Exploit differences in impurity incorporation/solubility.	Battery-grade product quality.	(Choi et al., 2026a; Choi et al., 2026b)

Note. Author synthesis adapted from the crystallization studies cited in the final column.

Common-Ion Effects Across Major Hydrometallurgical Electrolyte Families

A cross-electrolyte view is useful because the same nominal process operation can behave differently depending on the counter-ion and ligand environment. Chloride can be a common ion for chloride solids, a strong ligand for many metals, a salting agent, and a major corrosion driver. Sulfate

can participate in precipitates and double salts, form HSO_4^- and metal-sulfate complexes, and accumulate in recycle streams. Ammonium is coupled to NH_3 through acid-base equilibrium and can be intentionally recovered or unintentionally retained. Carbonate is coupled to CO_2 transfer and alkalinity, whereas fluoride can provide strong precipitation selectivity while also increasing complexation and corrosion risk. The recent corpus did not contain enough direct nitrate-specific common-ion evidence to justify a separate mechanistic category; nitrate-bearing systems are therefore not treated as a dedicated family in Table 6.

Table 6 compares these electrolyte families using the review's core question: where is a true common-ion lever

plausible, and what competing interaction is most likely to dominate if the system is interpreted too simply?

Table 6: Major common-ion opportunities and risks in hydrometallurgical electrolyte families.

Electrolyte family	Relevant common ion(s)	Main opportunity	Main interpretive/process risk	Representative evidence
Chloride	Cl^-	Solubility/speciation control; salting effects; acid recycle.	Metal-chloro complexes, corrosion, extraction changes.	(Lommelen et al., 2020; Myers et al., 2022; Nakhaie & Asselin, 2026; Nicol et al., 2025)
Sulfate	$\text{SO}_4^{2-} / \text{HSO}_4^-$	Precipitation, double salts, crystallization, recycle.	Ion pairing, bisulfate, high ionic strength, gypsum/scaling.	(Chen et al., 2025; Fuentes et al., 2023; Li et al., 2025; Reiss et al., 2021; Sun et al., 2026)
Ammoniacal	$\text{NH}_4^+ / \text{NH}_3$	pH/speciation control; ammonium recycle.	Metal-ammine complexes dominate selectivity.	(Hubert et al., 2026; Saim, 2025; Wang et al., 2022; Wu et al., 2024)
Carbonate	$\text{CO}_3^{2-} / \text{HCO}_3^-$	Selective precipitation of Li/REE and alkaline-earth control.	CO_2 equilibrium; pH-sensitive speciation; mother-liquor effects.	(Ge et al., 2025; Wang et al., 2025)
Phosphate	$\text{H}_3\text{PO}_4 / \text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-} / \text{PO}_4^{3-}$	Very low-solubility product formation.	Strong pH dependence and Ca/Mg competition.	(Liu et al., 2021; Reynaud et al., 2021; Sordyl et al., 2023)
Fluoride	F^-	Selective precipitation and impurity control.	Strong complexation, corrosion, difficult recycle.	(Lü et al., 2026)
Mixed-anion media	e.g., $\text{Cl}^- / \text{SO}_4^{2-}$	Tune conductivity, speciation, electrodeposition, and phase behavior.	Non-additive interfacial and activity effects.	(Nakhaie & Asselin, 2026; Yang et al., 2026)

Note. Author synthesis adapted from recent chloride, sulfate, ammoniacal, carbonate, phosphate, fluoride, and mixed-anion studies.

The sulfate family is particularly instructive because both thermodynamic and process studies are available. Rare-earth sulfate solubility depends on the identities and concentrations of other rare-earth ions and background salts (Chen et al., 2025; Sun et al., 2026). Tutton-salt solubilities in ammonium sulfate media further illustrate how double-salt formation can become the controlling phase behavior (Talreja-Muthreja & Steiger, 2026). Conversely, CaSO_4 behavior in rare-earth processing and electrolytic manganese residues shows that sulfate accumulation can create scaling or require deliberate dissolution/removal strategies (Li et al., 2025; Yao et al., 2026).

Coupling the Common-Ion Effect with Hydrometallurgical Separation Technologies

Solvent Extraction, Ion Exchange, and Adsorption

Common-ion engineering should not stop at the leach or precipitation reactor because electrolyte composition determines which species are presented to downstream separation units. In solvent extraction (SX), changes in chloride or sulfate can alter metal-complex charge,

extractable-species abundance, acidity, extractant loading, and phase disengagement. The cation effect of chloride salting agents on hydration and extraction by a basic extractant shows that bulk salt identity can influence extraction through ion-specific hydration rather than through a simple common-ion equilibrium (Lommelen et al., 2020). High-acid/high-chloride Ga/Fe separation likewise demonstrates that speciation and selective scrubbing must be designed together (Chen et al., 2026).

Ion exchange (IX) and adsorption are similarly sensitive to competing ions and complexing agents. Selective REE adsorption enhanced by aqueous complexing agents provides a direct example in which the ligand environment changes apparent selectivity (Sadler et al., 2026). A common ion can therefore lower capacity through competition, change the pool of resin-accessible species, or improve selectivity by suppressing a competing species. These responses can be operationally useful, but only the component attributable to the controlling phase equilibrium should be described as a common-ion effect.

Membranes and Electrochemical Operations

Membrane processes translate electrolyte composition into osmotic pressure, membrane partitioning, diffusion potentials, and scaling tendency. Diffusion dialysis has been applied to acid recovery from metallurgical waste streams and can reduce fresh-acid demand (López et al., 2021; Zhang et al., 2020). More recent work integrating acid recovery with

REE economics shows that the value of reagent recycling must be considered at flowsheet level (Crespo et al., 2026aa). Nanofiltration studies that couple reactive transport and speciation models demonstrate why membrane selectivity cannot be interpreted from total metal concentration alone (Porqueddu et al., 2025). Forward osmosis of hypersaline $\text{Na}_2\text{SO}_4/\text{NaCl}$ solutions further highlights the osmotic penalty of salt accumulation (Devaere & Papangelakis, 2026).

Electrochemical operations are affected through conductivity, metal-ion activity, complexation, interfacial structure, and competing deposition reactions. Thermodynamic analyses of

transition-metal electrodeposition in concentrated aqueous electrolytes and mixed-anion studies show that bulk speciation and interfacial dynamics are inseparable from deposition potential and selectivity (J. Liu et al., 2026; Yang et al., 2026). Electrodialysis metathesis for Ni/Co recovery illustrates how selective ionic transport can intentionally reshape the counter-ion environment rather than passively accept the leach-liquor composition (Isaksson et al., 2025).

Figure 3 maps these interactions across the flowsheet and shows that upstream reactions modify common-ion inventory, which can return through controlled recycle.

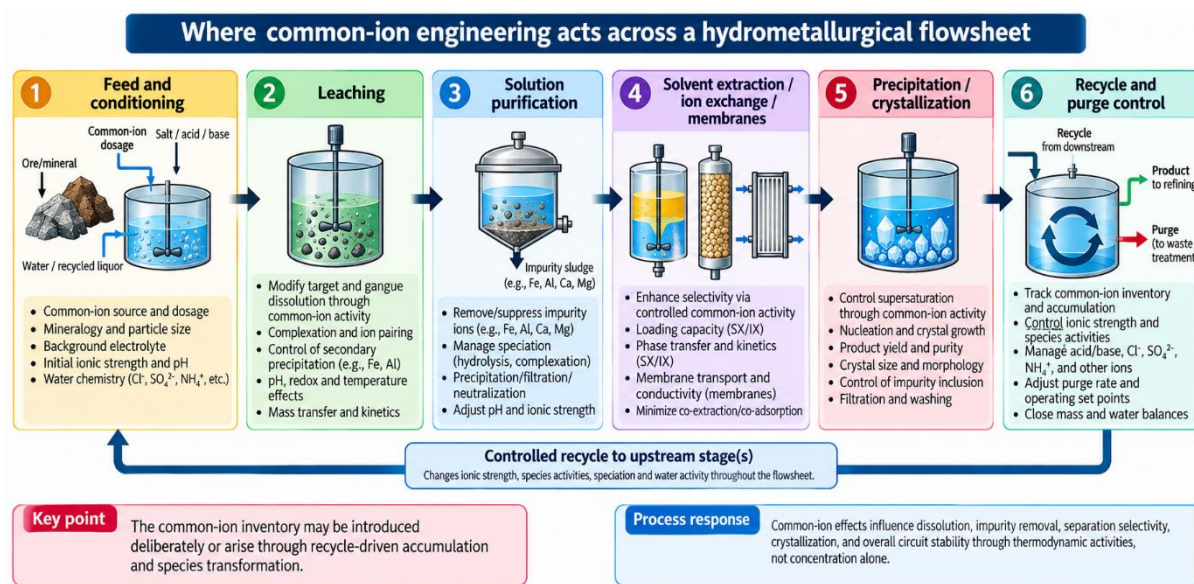


Figure 3: Application map for common-ion engineering across a hydrometallurgical flowsheet.

Note. Conceptual synthesis by the author, adapted from circular-hydrometallurgy, acid-recovery, membrane, crystallization, and recycle studies (Binnemans & Jones, 2023; Choi et al., 2025; Gómez et al., 2024; López et al., 2021; Porqueddu et al., 2025).

Common-Ion Engineering for Reagent Recycling and Closed-Loop Hydrometallurgy

Closed-loop operation changes the common ion from a discrete reagent addition into a circuit inventory variable. Acid, chloride, sulfate, ammonium, mother liquor, membrane retentate, crystallizer liquor, and wash water can repeatedly return ions to the front end. Recycle can reduce fresh-reagent demand and recover dissolved value, but species that are not consumed or purged accumulate until bleed streams, precipitation, entrainment, evaporation, or product removal control their steady-state concentrations. Circular-hydrometallurgy therefore requires a complete ion balance, not only a metal balance (Binnemans & Jones, 2023).

Several recent flowsheets illustrate different modes of recycle. Printed-circuit-board processing has combined semi-

continuous bioleaching with downstream precious-metal recovery (Adam et al., 2024), while lithium-ion battery studies increasingly incorporate wastewater reuse, closed-loop reagents, or value-retaining process configurations (Choi et al., 2025; Thompson et al., 2021; Yang et al., 2024; Yetim et al., 2024). Ammonium recovery from ion-adsorption rare-earth tailings shows that residual reagent can itself become a recoverable process stream (Wu et al., 2024). Chloride recovery from high-salinity rare-earth wastewater similarly couples reaction, extraction, crystallization, and CO_2 mineralization (Yao et al., 2023). Near-closed-loop treatment of strongly acidic wastewater demonstrates that fluoride and heavy-metal removal may be prerequisites for meaningful acid or water recycle (Lü et al., 2026).

The central design concept is beneficial accumulation versus detrimental accumulation. At low inventory, the common-ion effect may be too weak to change selectivity significantly. At intermediate inventory, equilibrium suppression or precipitation can improve selectivity and reduce fresh-reagent consumption. Beyond an optimum, however, viscosity, corrosion, scaling, ion pairing, complexation, osmotic pressure, impurity buildup, and downstream separation penalties can increase faster than the metallurgical benefit.

Corrosion and scaling studies in chloride-sulfate hydrometallurgical media show why materials-of-construction and operability constraints must be part of the optimum (Mondal et al., 2026; Nakhaie & Asselin, 2025, 2026).

Figure 4 presents this optimal-window concept schematically. The curves are not fitted to a universal process; each circuit must establish the preferred range experimentally using activity-based chemistry, downstream constraints, and multi-cycle recycle tests.

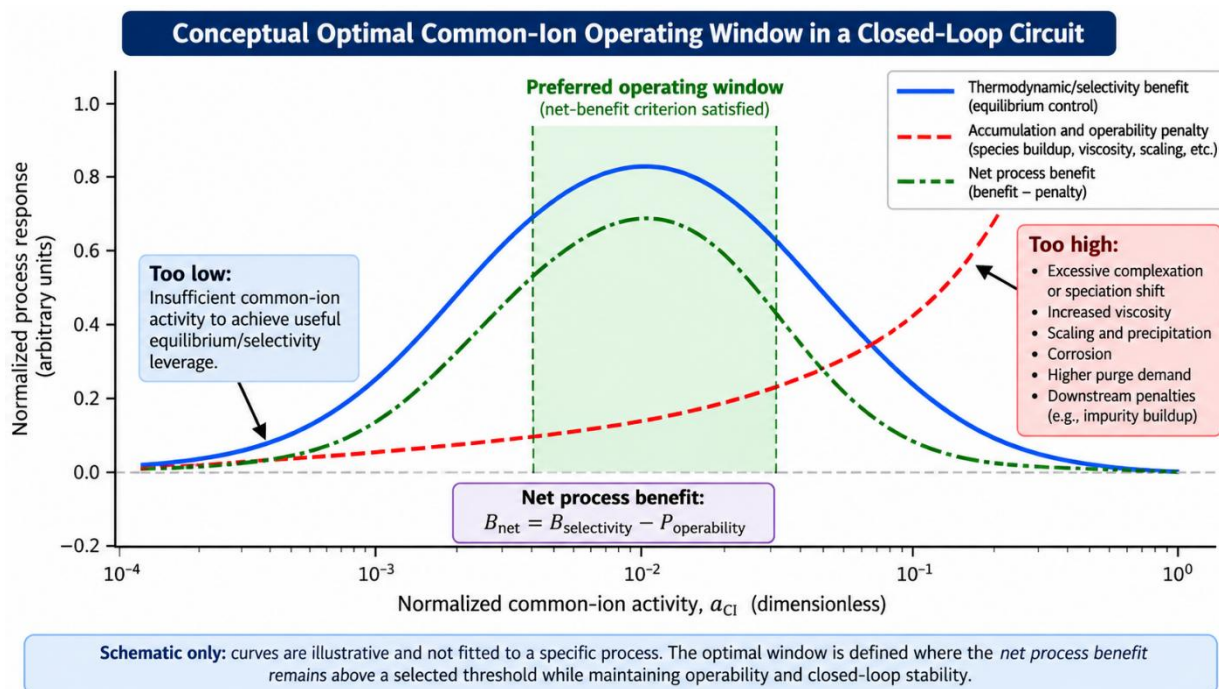


Figure 4: Conceptual optimal common-ion operating window in a closed-loop hydrometallurgical circuit.

Note. Conceptual synthesis by the author, adapted from circular-hydrometallurgy, hypersaline separation, corrosion, scaling, and recycle evidence (Binnemans & Jones, 2023; Choi et al., 2025; Devaere & Papangelakis, 2026; Mondal et

al., 2026; Nakhaie & Asselin, 2025, 2026). The curves are schematic and are not fitted to a specific process.

Table 7 summarizes the principal benefits and penalties that must be balanced simultaneously in recycle design.

Table 7: Benefits and penalties of common-ion accumulation in closed-loop circuits.

Circuit effect	Potential benefit	Potential penalty if accumulation is excessive	Representative evidence
Acid recycle	Lower fresh acid demand; reduced neutralization waste.	Impurity return, acid-strength constraints, membrane limits.	Diffusion dialysis (Crespo et al., 2026; López et al., 2021; Zhang et al., 2020)
Chloride recycle	Maintain chloride activity and enable selected chloride chemistry.	Corrosion, chloro-complexation, salinity.	Chloride recovery/corrosion (Myers et al., 2022; Nakhaie & Asselin, 2026; Yao et al., 2023)
Sulfate recycle	Promote sulfate precipitation/crystallization; reduce fresh sulfate.	Gypsum/scale, ion pairing, high ionic strength.	Sulfate studies (Li et al., 2025; Melo & Figueiredo, 2024; Reiss et al., 2021)
Ammonium recycle	Reduce reagent loss and residual N burden.	$\text{NH}_3/\text{NH}_4^+$ speciation drift and impurity accumulation.	REE tailings and ammoniacal systems (Wang et al., 2022; Wu et al., 2024)
Mother-liquor recycle	Recover residual metal and retain useful common ion.	Impurity buildup and crystal contamination.	Battery sulfate crystallization (Choi et al., 2026a; Choi et al., 2026b)
Water reuse / high salinity	Reduce freshwater demand and liquid discharge.	Osmotic pressure, viscosity, membrane duty.	Closed-loop and forward osmosis (Choi et al., 2025; Devaere & Papangelakis, 2026)
Purge	Stabilize impurity/common-ion inventory.	Loss of reagent, water, and dissolved value.	Circular-process analyses (Binnemans & Jones, 2023; Van Yken et al., 2023)

Note. Author synthesis adapted from the closed-loop, acid-recovery, crystallization, corrosion, salinity, and techno-economic studies cited in the final column.

A Common-Ion Process-Design Framework: CISE

The literature supports a process-design framework that is more rigorous than applying Le Châtelier's principle to analytical concentrations. The proposed Common-Ion Selectivity Engineering (CISE) framework contains four core

stages—Characterize, Identify, Select, and Evaluate. Recycle and control are treated as a feedback loop rather than as a fifth acronymic step, because circuit accumulation can force the selected operating window to be revised after downstream constraints are evaluated.

Figure 5 presents the four-stage CISE framework and the recycle-control feedback loop. The feedback is essential: an operating window selected from equilibrium and selectivity considerations must be revised if corrosion, membrane duty, crystallization, solvent extraction, or purge economics makes that window impractical.

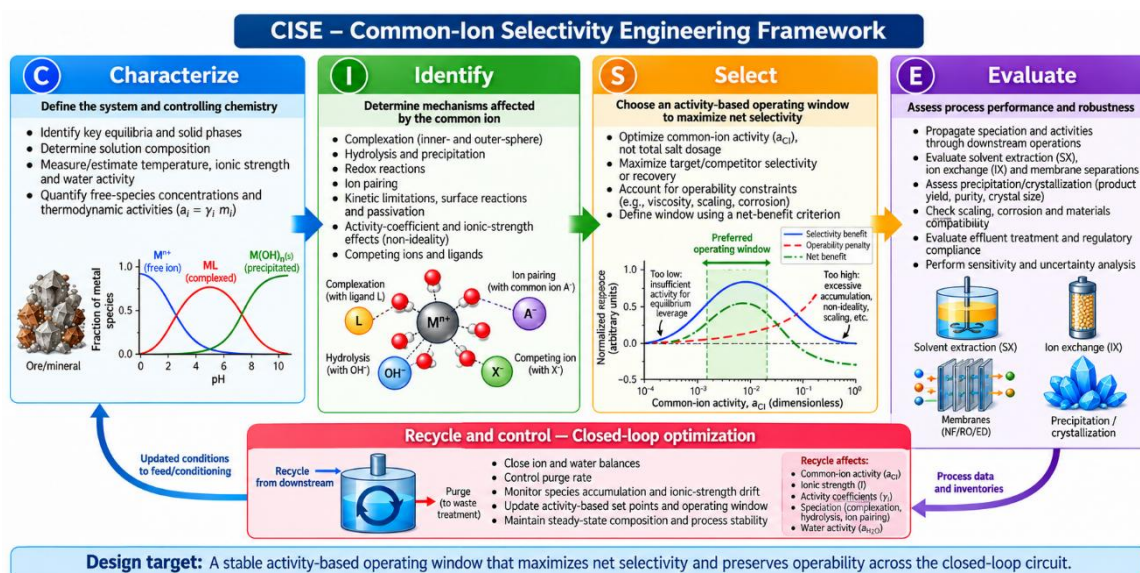


Figure 5: Common-Ion Selectivity Engineering (CISE) framework with recycle-control feedback for hydrometallurgical process design.

Note. The CISE framework is developed in this review; conceptual elements are adapted from activity/speciation, separation, crystallization, circularity, and corrosion literature (Binnemans & Jones, 2023; Choi & Azimi, 2023; Dickson et al., 2023; Nakhaie & Asselin, 2026; Porqueddu et al., 2025).

C — Characterize Equilibrium

Define the target solid or aqueous equilibrium, identify the actual solid phases, and write the controlling reaction in terms of species rather than total components. Determine which ion is genuinely common, which species enter the equilibrium constant, and whether the operating temperature or acid concentration requires temperature-dependent constants or conditional equilibria. Where sulfate, chloride, phosphate, or multivalent ions are concentrated, use an activity model with a documented validity range (Dickson et al., 2023; Manaure et al., 2021).

I — Identify Competing Interactions

Build the smallest speciation model that captures the first-order couplings: complexation, hydrolysis, acid-base speciation, redox, ion pairing, major competing precipitates, and surface or kinetic limitations. Experimental controls should then discriminate among mechanisms—for example,

matched ionic strength without the common ion, matched ligand concentration, or time-resolved tests that distinguish kinetic inhibition from equilibrium displacement. This step is particularly important in chloro-, sulfate-, and ammoniacal systems (Jordan et al., 2022; Lommelen et al., 2020; Saim,

S — Select the Common-Ion Operating Window

Rather than maximizing added salt, identify the activity range that optimizes a process-relevant selectivity metric. For leaching, this can be target extraction normalized by weighted impurity dissolution; for precipitation, target recovery at a defined impurity contamination; and for crystallization, product yield subject to purity and crystal-property constraints. The operating window should be expressed in terms of activities or a validated surrogate and should include temperature, pH or free acidity, residence time, and solid-to-liquid ratio.

E — Evaluate Downstream Consequences

Propagate the selected composition through the downstream flowsheet. Evaluate how the changed electrolyte affects extractable species, ion-exchange competition, membrane osmotic pressure, electrodeposition potential, scaling risk, crystallizer phase behavior, corrosion, and effluent treatment.

This step converts a local equilibrium improvement into a system-level process decision (Chen et al., 2026; Devaere & Papangelakis, 2026; J. Liu et al., 2026; Nakhaie & Asselin, 2025).

Recycle and Control as a Feedback Loop

Close the common-ion balance over multiple cycles. Identify sources, sinks, product losses, entrainment, wash-water return, bleed streams, precipitation losses, and volatilization where relevant. Define a control variable that can be measured online or with sufficiently rapid laboratory turnaround, and update the selected operating window when recycle changes speciation or downstream constraints. The design is complete only when a stable inventory can be maintained without progressive impurity accumulation. This feedback connects CISE directly to circular-hydrometallurgy principles (Binnemans & Jones, 2023).

Techno-Economic and Environmental Implications

A common-ion strategy is economically meaningful only if the benefit survives outside the equilibrium calculation. Potential advantages include reduced fresh acid/base or precipitant consumption, lower impurity dissolution, smaller neutralization circuits, reduced sludge production, increased product purity, higher reagent recovery, and lower water demand. Potential penalties include the cost of salt addition, corrosion-resistant materials, scaling control, evaporation or membrane duty, crystallizer complexity, purge treatment, and

metal losses in bleed streams. These competing effects make the optimum inherently flowsheet-specific.

Techno-economic assessments of hydrometallurgical recycling show the importance of preserving value across the full process chain rather than maximizing a single extraction step (Thompson et al., 2021; Van Yken et al., 2023). Life-cycle studies likewise demonstrate that reagent production, water treatment, energy demand, and waste management can change the environmental performance of alternative routes (M. Liu et al., 2026; Maritz et al., 2025). A common-ion strategy that reduces impurity dissolution but requires energy-intensive purge concentration or high-alloy equipment may therefore fail to deliver a net process benefit.

Industrial crystallization and acid-recovery studies provide useful scale-up anchors. REE antisolvent crystallization has been evaluated at scale together with life-cycle impacts (Pawar et al., 2026), whereas diffusion dialysis has been linked explicitly to extraction economics (Crespo et al., 2026aa). Industrial-scale battery-recycling LCA and zinc-hydrometallurgy freezing crystallization show that energy, water, and operability effects can become visible only at larger scale (Jin et al., 2023; M. Liu et al., 2026). Common-ion studies intended for process design should therefore report not only recovery and selectivity but also reagent intensity, recycle ratio, purge fraction, energy-relevant concentration changes, and consequences for materials of construction.

Table 8 provides a minimum reporting set intended to make future common-ion studies comparable and scale-up-relevant.

Table 8: Recommended experimental variables and reporting requirements for common-ion hydrometallurgy studies.

Variable	Minimum reporting requirement	Why it matters
Total common-ion concentration	mol L ⁻¹ or mol kg ⁻¹ , with analytical basis.	Defines inventory but not necessarily free-ion activity.
Free common-ion activity	Measured where possible or calculated with stated model.	Required for a thermodynamic common-ion diagnosis.
Ionic strength / water activity	Report model and basis; include high-salinity domain.	Separates common-ion and bulk-electrolyte effects.
pH and/or free acidity	Measurement method, temperature, calibration, acid matrix.	Prevents conflating pH with acid inventory (Pereira, 2026b).
Temperature	°C, with equilibrium constants corrected if needed.	Controls speciation, solubility, kinetics, hydrate stability.
Full solution composition	Major metals, counter-ions, ligands, redox agents.	Enables reproducible speciation and downstream assessment.
Solid phase identity	XRD/mineralogy and, where relevant, surface characterization.	Confirms the equilibrium actually being discussed.
Extraction/precipitation/crystallization metrics	Target recovery plus impurity dissolution/incorporation and mass balance.	Prevents single-response optimization.
Kinetic information	Time profile or equilibrium verification.	Separates thermodynamic and kinetic effects.
Recycle cycles and purge	Number of cycles; recycle ratio; purge % of circuit flow.	Tests accumulation and steady-state feasibility.
Corrosion/scaling observations	Materials, temperature, salt composition, deposit identity.	Captures hidden operating cost (Mondal et al., 2026; Nakhaie & Asselin, 2025).
TEA/LCA boundary	Functional unit, system boundary, key assumptions.	Allows net benefit to be evaluated (Liu et al., 2026; Maritz et al., 2025).

Note. Original reporting framework developed in this review and informed by recent thermodynamic, corrosion, scaling, techno-economic, and life-cycle studies.

Research Gaps, Practical Design Rules, and Conclusions

Research Gaps

The evidence base reveals a recurring gap between sophisticated solution chemistry and practical hydrometallurgical experimentation. First, many studies report total concentration without calculating free-ion activity even when the electrolyte is concentrated. Second, validation of thermodynamic predictions is often limited to synthetic solutions, whereas real leachates contain multicomponent impurities and recycle-derived ions. Third, studies rarely separate ionic-strength controls from true common-ion controls using matched-composition experiments. Fourth, long-duration, multi-cycle recycle experiments remain scarce, leaving the transition from beneficial salt retention to detrimental accumulation poorly quantified.

Further gaps concern integration. Corrosion, scaling, membrane osmotic pressure, solvent-extraction performance, product-crystal contamination, and purge treatment are commonly evaluated in separate literatures even though all respond to electrolyte composition. The same is true for water balance, free acidity, and reagent regeneration. Bridging these domains will require coupled thermodynamic-process models calibrated with real liquors and validated under continuous operation. Emerging membrane, electrochemical, and solvent-driven crystallization studies provide suitable building blocks, but the common-ion inventory must be included explicitly as a state variable (Devaere & Papangelakis, 2026; Isaksson et al., 2025; Porqueddu et al., 2025; Xu et al., 2026).

A final research need is to express selectivity benefits in forms that are useful to process engineers. A selectivity enhancement factor should be defined against a reference electrolyte at matched temperature, residence time, and, where possible, ionic strength. For closed-loop circuits, a complementary net common-ion benefit index could combine gains in target recovery, impurity rejection, and reagent savings with penalties for purge, energy, scaling, corrosion, and downstream separation. Such indices should remain transparent bookkeeping tools rather than be presented as universal thermodynamic constants.

Practical Design Rules

The critical synthesis supports ten practical rules for hydrometallurgical common-ion engineering:

- Never diagnose a common-ion effect from analytical concentration changes alone.

- Use activity-based equilibrium whenever the electrolyte is concentrated or strongly associating.
- Include the major aqueous complexes, hydrolysis reactions, and redox states that control free species.
- Confirm the relevant solid phase experimentally rather than assuming the intended precipitate or mineral controls equilibrium.
- Evaluate target and impurity equilibria simultaneously; selectivity, not solubility alone, is the process objective.
- Determine an operating window rather than maximizing common-ion concentration.
- Test real leach liquors after mechanism screening in synthetic solutions.
- Carry the selected electrolyte composition through SX, IX, membranes, electrochemistry, crystallization, corrosion, and effluent treatment.
- Perform multi-cycle recycle experiments and close the ion balance, including purge requirements.
- Confirm that the metallurgical gain survives techno-economic and environmental assessment.

Conclusions

The common-ion effect should be used in hydrometallurgy as an activity-based process-design principle, not as a shorthand explanation for every salt-induced change in dissolution or precipitation. A defensible diagnosis requires identification of the controlling equilibrium, confirmation of the relevant phase, separation of free-species activities from analytical concentrations, and explicit testing of competing effects such as complexation, ionic strength, redox chemistry, salting-out, nucleation, and surface kinetics. The most useful applications are those in which a controlled common-ion inventory suppresses unwanted dissolution, sharpens staged precipitation, supports selective crystallization, or reduces fresh-reagent demand without transferring the penalty to downstream separations, corrosion, scaling, or purge treatment. In closed-loop circuits, the design variable is the steady-state common-ion inventory, and the appropriate target is an operating window rather than a maximum concentration. The four-stage CISE framework, coupled to a recycle-control feedback loop, provides a practical route from equilibrium chemistry to flowsheet implementation and a basis for more reproducible, mechanistically defensible, and industrially relevant research.

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Author contributions: Antonio Clareti Pereira: Conceptualization, methodology, investigation, formal analysis, writing—original draft, writing—review and editing, and visualization.

Data availability: No new experimental dataset was generated for this review; the evidence base consists of the published literature cited in the manuscript.

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