Controlled Decomposition and Selective Dissolution of Carnallite: Phase Equilibria, Reaction Mechanisms, and Potassium–Magnesium Separation—A Critical Review

Antonio Clareti Pereira, PhD

PhD in Chemical Engineering, Federal University of Minas Gerais (UFMG) Belo Horizonte, Minas Gerais, Brazil

DOI: https://doi.org/10.51584/IJRIAS.2026.11100007

Received: 14 October 2026; Accepted: 19 October 2026; Published: 29 October 2026

ABSTRACT

Carnallite ($KCl\cdot MgCl_2\cdot 6H_2O$) provides a potentially important potassium resource, but potassium recovery is constrained by strongly coupled phase equilibria, incongruent dissolution, secondary crystallization, and the circulation of concentrated magnesium chloride brines. This critical review examines the thermodynamic and mechanistic basis of controlled decomposition, cold and temperature-assisted treatment, compositional effects, kinetics, solids handling, and integration with flotation and crystallization. The evidence is organized to distinguish established measurements from process-level inference, with emphasis on the $KCl–MgCl_2–H_2O$ system and the influence of sodium, calcium, and other impurities. The analysis shows that equilibrium determines which selective transformation is feasible, whereas nucleation, mixing, interfacial transport, crystal morphology, and brine recycle determine whether the attainable selectivity is achieved operationally. We propose a material-balance framework to report potassium recovery and magnesium rejection consistently across solids, mother liquor, wash streams, and recycled brine. Research priorities include phase-model validation on representative feeds, time-resolved in situ observation, robust separation of fine KCl crystals, and quantified water–energy trade-offs. The resulting framework links chemical selectivity to industrially meaningful recovery and product quality without conflating equilibrium potential with demonstrated plant performance.

Keywords: Carnallite; Incongruent dissolution; Solid–liquid equilibrium; Potassium chloride; Magnesium chloride; Selective crystallization

Highlights:

• Phase boundaries define feasibility, but kinetics control attainable separation.

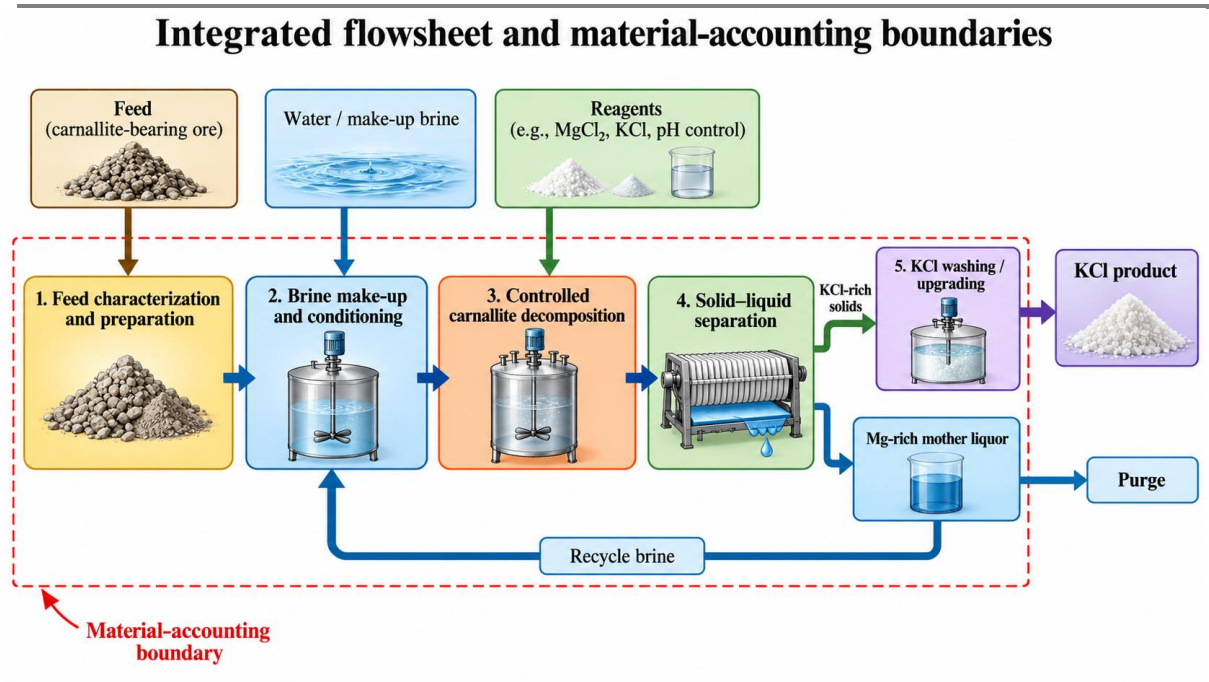
• Cold decomposition requires coordinated water dosing and brine composition.

• KCl crystal growth and washing determine downstream magnesium entrainment.

• A closed potassium–magnesium–water balance is essential for route comparison.

Graphical abstract

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026



Note. Original graphical abstract; conceptual material pathways and no measured recoveries are implied.

INTRODUCTION

Carnallite is a hydrated double chloride in which the desired potassium component coexists with magnesium chloride and bound water. Exploiting it requires more than dissolution: the process must drive potassium into a recoverable solid while preventing excessive transfer to the magnesium-rich mother liquor. Practical development therefore depends on an integrated understanding of mineralogy, solution activities, crystal formation, and brine circulation (Pannach et al., 2020; Szatmari et al., 2021; Tavares et al., 2018).

Unlike a simple selective-leaching problem, carnallite treatment typically proceeds through incongruent dissolution followed by crystallization. Controlled water addition can destabilize carnallite while leaving KCl as a stable or supersaturated solid phase; the resulting separation nevertheless depends on impurity salts, liquid composition, and washing losses (H. Cheng et al., 2020; Gan et al., 2024; Guo et al., 2024; Yu et al., 2023). This review uses Figure 1 to present the thermodynamic decision logic, Figure 2 to clarify phase partitioning, Figure 3 to show an integrated processing boundary, and Figure 4 to distinguish four kinds of selectivity. Tables 1–4 provide, respectively, an evidence map, operating-variable framework, kinetic and solids indicators, and the recommended quantitative reporting protocol.

The principal question is whether selective decomposition is governed primarily by phase equilibrium or by dissolution, nucleation, and mass-transfer kinetics. The answer is conditional: equilibrium defines accessible phase assemblages, while dynamic process conditions and solid–liquid separation determine product grade, actual potassium recovery, magnesium rejection, and reproducibility (C. Wang et al., 2024a, 2024b; Tavares et al., 2018; Zhang et al., 2026).

REVIEW METHODOLOGY AND EVIDENCE APPRAISAL

This critical narrative review synthesizes published studies from 2000–2026 on carnallite decomposition, concentrated-chloride equilibria, KCl crystallization, soluble-salt flotation, solids handling, and flowsheet integration. Literature was assessed for mechanistic relevance, feed and brine compositions, temperature domain, experimental basis, and transferability. Searches and source selection underlying the original bibliography were not logged sufficiently to reconstruct a systematic search; therefore, no complete platform history, formal language exclusion criterion, search yield, or PRISMA-style completeness claim is asserted. A targeted supplementary literature check was carried out on 15 October 2026 using publisher records and DOI-linked publications for reviewer-identified phase-equilibrium and crystallization–flotation evidence.

Representative search concepts included “carnallite decomposition”, “KCl MgCl2 water phase equilibrium”, “Pitzer chloride brine”, “KCl crystal nucleation”, and “carnallite flotation”. Citation links and reference lists were considered to identify mechanistically relevant supporting studies; this was not a comprehensive citation-chaining protocol. Original-language papers were retained where bibliographic information and the technical claim could be interpreted, rather than imposing an unverified language restriction. Primary measurements were distinguished from reviews, modeling studies, and conceptual extrapolations.

The synthesis does not constitute a systematic meta-analysis. No new experimental dataset or pooled extraction yield is reported. Cross-study quantitative comparisons are deliberately restrained because feed characterization, water/ore ratio, temperature histories, mixing intensity, residence times, and assay bases differ. The appraisal distinguishes measured phase equilibrium, laboratory kinetic observations, crystallization experiments, flowsheet simulations, and field-linked evidence (H. Cheng et al., 2020; Tavares et al., 2018; C. Wang et al., 2024b; Yu et al., 2023).

Table 1 summarizes the evidentiary roles of the main source groups. A central methodological constraint is that a valid phase diagram cannot, by itself, establish kinetic completion, filterability, or a plant-scale product specification.

Table 1. Evidence classes and their legitimate use in carnallite-process assessment

Evidence class	Representative literature	Strength and limitation
Carnallite decomposition	Cheng et al. (2020); Yu et al. (2023); Gan et al. (2024)	Direct transformation; feed and test windows differ
Chloride phase equilibria	Yu and Zeng (2010, 2011); C. Wang et al. (2024b); Wang et al. (2025)	Phase constraints; equilibrium not kinetic completion
KCl crystallization	Li et al. (2009); C. Wang et al. (2024a); Ren et al. (2025)	Nucleation and habit; system- and additive-specific
Flotation/upgrading	Laskowski (2013); Sun et al. (2022); Cheng et al. (2020)	Interfacial evidence; not direct decomposition yield
Integrated processes	Tavares et al. (2018); Ji et al. (2022)	Flowsheet potential; limited universal transferability

Note. Evidence classes are an author-developed interpretive framework for this narrative review, not a validated methodological quality scale or numerical ranking of study quality.

The evidence map shows why apparent agreement in potassium-product grade should not be mistaken for equivalence of mechanism or achieved recovery. Full circuit comparison requires matched feed bases and consistently reported phase distributions.

Chemical and mineralogical basis of carnallite decomposition

Hydration state and mineral associations

Carnallite has the formula $KCl \cdot MgCl_2 \cdot 6H_2O$. Structural water must be distinguished from free moisture on the ore surface and from adhering brine; these forms of water affect both the measured feed mass and the actual solvent inventory. Structural studies have also identified metastable carnallite modifications, demonstrating that mineral identification should not rely solely on bulk elemental chemistry (Pannach et al., 2020; Podder et al., 2014; Song et al., 2015).

Natural ores and solar salts can contain halite, sylvite, bischofite-related magnesium salts, and minor ions. Their proportions affect not only the theoretical potassium content but also the ionic strength, brine-saturation

trajectory, and contaminant burden of the recovered KCl. Petrographic and three-dimensional imaging studies illustrate the importance of impurity distribution, while Brazilian evaporite studies establish that natural feed associations must be characterized before transferring a flowsheet (Song et al., 2015; Szatmari et al., 2021; Tavares et al., 2018).

Stoichiometric limit and chemical interpretation

A useful idealized reaction is $KCl{\cdot}MgCl_2{\cdot}6H_2O(s)$ + excess aqueous phase → $KCl(s) + MgCl_2(aq) + 6H_2O(l)$. This relation expresses incongruent breakdown rather than a complete physicochemical mechanism: the chloride salts share a concentrated liquid medium, and some potassium remains dissolved even when solid KCl forms. Stoichiometry alone does not determine grade or recovery; these depend on saturation states, the liquid/solid ratio, and separation losses (H. Cheng et al., 2020; Yu & Zeng, 2011; Yu et al., 2012).

The mass fraction of KCl in pure carnallite is approximately 26.8% (74.55/277.85 on a molar-mass basis), on the conventional anhydrous KCl-equivalent basis. This is a stoichiometric ceiling for recovered KCl from a pure feed, not a predicted industrial yield. Before estimating a product balance, consider ore-grade dilution, residual dissolved potassium, fines loss, and entrained magnesium liquor.

Thermodynamic framework for selective dissolution

Multicomponent solid–liquid equilibria

The $KCl–MgCl_2–H_2O$ diagram is the primary reference for predicting phase stability, but industrial carnallite brines rarely remain ternary. Sodium, calcium, and other chlorides modify water activity and ion activities, shifting crystallization regions and potentially stabilizing additional solids. Modern experimentally determined equilibria extend the decision basis from ternary to quaternary and more complex systems (Cheng et al., 2018; C. Wang et al., 2024b; Wang et al., 2025; Yu et al., 2026; Zheng & Sang, 2024; Zhu & Sang, 2023).

A concentrated $KCl–MgCl_2–NaCl–CaCl_2$ brine cannot generally be evaluated with ideal-solution concentrations alone. Pitzer-type ion-interaction models, or other electrolyte activity models demonstrated to be valid at comparably high ionic strengths, can represent nonideal ion activities and water activity when their parameters are supported by data. Model selection must state the parameter set/database, temperature and composition ranges, relevant stable or metastable phase assemblages, and the experimental observations used to test the predictions. Validation should cover not merely one isotherm or feed but the K^+, Mg^{2+}, Na^+, Ca^{2+}, Cl^- and water-activity domain expected as brine is recycled and purged. Measured liquid concentrations, phase identities, saturation boundaries, and invariant regions should be compared directly; apparent agreement outside the parameter-validation domain must not be presented as verified process selectivity (Deng et al., 2009; C. Wang et al., 2024b; Wang et al., 2025; Yu et al., 2026). Stable and metastable equilibria should be distinguished because real residence times may restrict attainment of the stable assemblage.

Water activity and supersaturation

Water addition changes the solvent inventory and the activities of all dissolved ions simultaneously. A practical selectivity window occurs when carnallite destabilization and $MgCl_2$ transfer into liquor accompany the persistence, nucleation, or growth of KCl solids. The exact dosage depends on feed and recycle, not a universal water-to-ore ratio (H. Cheng et al., 2020; Guo et al., 2024; Yang et al., 2026).

Figure 1 translates this principle into a decision sequence linking characterized feed, thermodynamic state, KCl stability, and an attainable operating window. It is deliberately not a geometric phase diagram: rigorous phase boundaries would require tabulated equilibria at specified temperatures and ionic compositions.

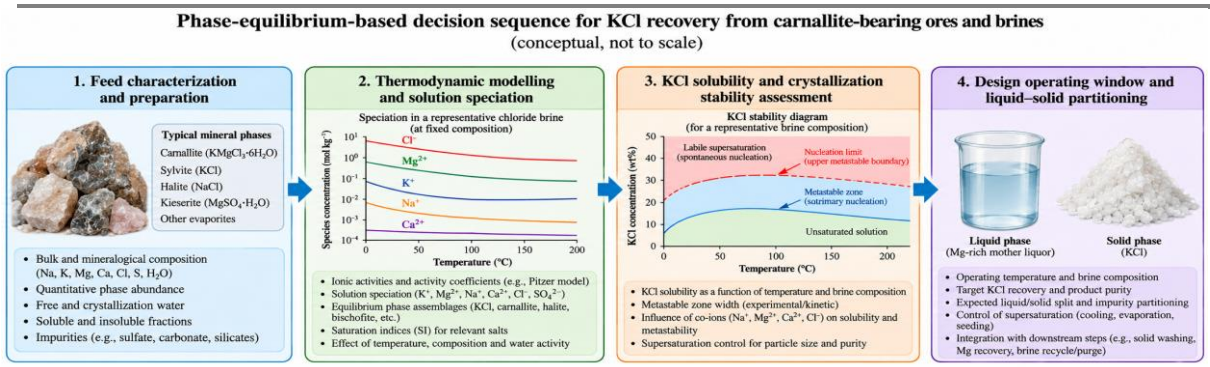


Figure 1. Conceptual decision sequence for brine-composition and temperature selection.

Note. Original conceptual illustration developed for this review; not adapted from a previously published figure, and no experimental data are plotted.

This decision sequence prevents overinterpretation of idealized KCl–$MgCl_2$–H_2O projections when calcium and sodium levels are variable. The appropriate validation criterion is experimental agreement of predicted liquid and solid compositions, not diagram resemblance alone.

Incongruent dissolution and phase transformation

Coupled dissolution and KCl formation

In controlled decomposition, carnallite dissolution releases K- and Mg-bearing species into a boundary layer; KCl may persist or crystallize later when the local and bulk liquid become supersaturated. The physical sequence can involve crystal-surface retreat, localized precipitation, secondary nucleation, and aggregation. Consequently, measured KCl grade may increase while the overall recovery decreases if fine particles are lost with liquor (H. Cheng et al., 2020; Yu et al., 2023; C. Wang et al., 2024a).

Figure 2 shows the desired material-direction logic: potassium predominantly to solids and magnesium predominantly to brine. It does not assume perfect separation, because potassium can dissolve and magnesium can remain with crystals through adhered liquor, inclusions, or incomplete decomposition.

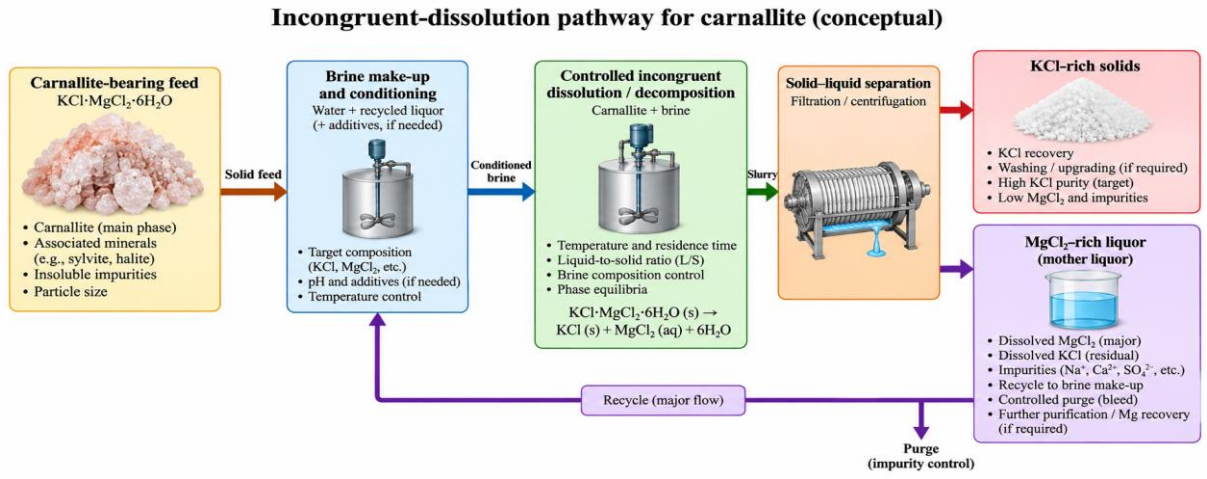


Figure 2. Conceptual incongruent decomposition and potassium–magnesium partitioning.

Note. Original conceptual illustration developed for this review; not adapted from a previously published figure, and no experimental data are plotted.

The simplified reaction path must be interpreted together with washing, brine carryover, and the possibility of re-precipitation during cooling or dilution. These mechanisms can reverse a product-grade improvement that appears favorable at the reactor discharge.

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

Interfacial and structural mechanisms

Different carnallite structural states can influence nucleation and transformation trajectories. Powder diffraction, scanning electron microscopy, and time-dependent liquid chemistry offer complementary evidence, whereas a single end-point assay cannot resolve intermediate transformations (Pannach et al., 2020; Podder et al., 2014; H. Cheng et al., 2020).

Cold decomposition: water dosage and operation

Cold decomposition uses aqueous contact without deliberate high-temperature dissolution as its central separation step. Practical variables include mixing temperature, water or recycled-brine addition, ore particle size, solids loading, residence time, and agitation. Recent experimental studies explicitly investigate cold-decomposition conditions and the impact of ore grade on KCl crystallization (Gan et al., 2024; Guo et al., 2024; Yang et al., 2026).

Excess water can improve carnallite breakdown while dissolving valuable KCl; insufficient water can leave unconverted carnallite and Mg-rich solids. The optimum should therefore be located by simultaneous measurement of potassium retained in solids, magnesium dissolved, final solution saturation, and the wash-water penalty, rather than by a single grade measurement (H. Cheng et al., 2020; Guo et al., 2024; Yu et al., 2023).

Table 2 distinguishes desired effects from failure modes of the main operating variables. The directions shown are qualitative hypotheses to test on each feed, not universal monotonic responses.

Table 2. Operating variables, competing effects, and control requirements

Variable	Desired function	Countervailing risk / validation
Water-to-feed ratio	Enable Mg-rich phase dissolution	KCl dissolution; track K in mother liquor
Temperature	Shift saturation and accelerate transfer	Additional KCl solubility; heat duty
$MgCl_2$ in brine	Adjust water activity and salt stability	Viscosity, entrainment, crystallization shifts
NaCl and $CaCl_2$	Represent real ionic background	Co-crystallization; invalid ternary model
Particle size/mixing	Improve contacting and conversion	Fines entrainment; crystal attrition
Residence time	Approach target transformation	Secondary nucleation/redissolution

Note. Qualitative design matrix synthesized from the cited equilibrium, decomposition, and crystallization literature; no numerical optima are asserted.

The variables are strongly coupled: changing water dosage modifies the same ion activities as changing recycled $MgCl_2$ concentration. One-factor experiments should thus be complemented with statistically designed studies and a thermodynamically constrained interpretation.

Temperature-controlled dissolution and brine chemistry

Temperature effects and hot processing

Temperature changes both salt equilibria and transport rates, but faster dissolution should not be conflated with greater selective potassium recovery. A hot-dissolution route may intentionally dissolve additional KCl followed by controlled cooling crystallization; this differs materially from cold decomposition that attempts to preserve or create solid KCl during leaching (Tavares et al., 2018; C. Wang et al., 2024b; Wang et al., 2025).

The decision between the routes requires matching equilibrium calculations to heating, cooling, evaporation, washing, and brine-recycle duties. A promising crystallization outcome from an integrated simulation provides useful proof of process potential, but it does not establish performance for every carnallite composition (Tavares et al., 2018; Ji et al., 2022).

Sodium, magnesium, and minor-ion effects

Magnesium chloride concentration affects solution activity and the fate of potassium, while sodium chloride may enter as halite or dissolved impurities. Calcium and strontium can further alter the solid–liquid envelope. Measurements of multicomponent chloride equilibria provide necessary constraints, yet extrapolation into untested compositional corners remains risky (Cheng et al., 2018; Wang et al., 2025; Yu et al., 2026; Zheng & Sang, 2024; Zhu & Sang, 2023).

The 2026 decomposition–flotation study emphasizes solution regulation as a determinant of KCl product grade, consistent with earlier studies of ore-grade dependence and decomposition monitoring. However, to claim superior selectivity, product grade must be reported alongside mass recovery and liquid-phase potassium losses (Zhang et al., 2026; Guo et al., 2024; H. Cheng et al., 2020).

Solid–liquid ratio, water consumption, and recycling

Water is simultaneously a reagent, solvent, carrier, and wash medium. An objective expressed only as minimizing fresh water is insufficient because concentrated recycles may increase brine viscosity and salt carryover, while strongly diluted liquors increase downstream evaporation demand. For a closed circuit, the relevant basis is net freshwater makeup, evaporation, moisture export, bleed, and wastewater discharge (Amadghous et al., 2025; Khakhar et al., 2026; Quilaqueo et al., 2024).

A transparent water balance should distinguish ore-associated moisture, hydrate water released during transformation, introduced process water, recycled mother liquor, wash liquor, and purge. These terms should be consistently measured at operating temperature, because precipitation during sampling can invalidate the apparent split between dissolved and solid KCl.

For an accounting boundary that encloses the process (including recycle), a generalized water inventory is: W(external liquid and moisture inputs) + W(feed crystal water) = W(product-associated water) + W(purge and other liquid exports) + W(evaporation and vapor exports) + ΔW(inventory). These quantities must be expressed consistently as water mass over the same time interval. Feed-associated free moisture and structural hydrate water should be recorded separately; hydrate release changes the liquid-phase inventory, but does not create water across the overall boundary. Internal recycle water cancels when the entire circuit is considered, whereas it must appear as both inlet and outlet for a single-unit boundary. Measurements should include feed moisture, product moisture, wash streams, vapor, purge, and changes in vessel and brine inventory.

The $MgCl_2$-rich mother liquor has potential value and processing cost, but do not assume by-product credit without a stated specification and a realistic market or internal-use route. Membrane-based crystallization and brine-recovery studies show potential process configurations, but not necessarily economic viability for every carnallite feed (Amadghous et al., 2025; Ji et al., 2022; Quilaqueo et al., 2024).

Kinetics, transport, and particle-size evolution

Competing rate processes

The observed decomposition rate can reflect surface reactions, concentration boundary layers, mixing, diffusion through adhering precipitates, and a time-dependent approach to KCl saturation. A single pseudo-first-order constant seldom establishes a unique governing mechanism without supporting particle-size, agitation, or temperature dependence. Monitoring Mg in solids and moisture provides a practical endpoint indicator, but the relation to phase identity should be calibrated (H. Cheng et al., 2020; Yu et al., 2023).

KCl crystal-size distributions evolve by primary and secondary nucleation, growth, breakage, and agglomeration. Population-balance approaches and measured metastable-zone widths offer more transferable quantities than unqualified elapsed decomposition time. Additives and flotation reagents may simultaneously affect crystal morphology and separation behavior (Li et al., 2009; C. Wang et al., 2024a; Wang et al., 2023; Ren et al., 2025).

Table 3 lists measurements required for mechanism identification and robust solids handling. The relevant operational performance parameter is not necessarily maximum conversion rate, but sufficient conversion together with a filterable and washable product.

Table 3. Kinetic, crystallization, and separation observables

For scale-up, mixing should be reported using power input and, where meaningful, power per unit slurry volume (P/V) rather than rotational speed alone; shear, slurry density, and geometric similarity must also be considered. A population-balance interpretation should connect local supersaturation and residence-time distribution to nucleation, growth, agglomeration, and attrition, and then to measured D10/D50/D90, fines losses, filtration response, and flotation performance. Specific cake resistance, wash displacement efficiency, filtrate clarity, and fine-particle carryover supplement filtration flux and cake moisture.

Measurement	Mechanistic interpretation	Reporting requirement
Time-resolved K and Mg in liquor	Partitioning and apparent approach to equilibrium	Full sampling times; temperature; liquid mass
Residual carnallite by XRD	Phase conversion and incomplete breakdown	Quantitative phase fractions and detection limits
Crystal-size distribution	Nucleation, growth, breakage, and entrainment	D10, D50, D90 and solids inventory
Agitation and particle size	External transport and surface-area sensitivity	Impeller power; feed PSD; residence time
Filtrate and wash analyses	Dissolved K losses and Mg entrainment	Separate mother liquor and wash streams
Filtration flux/cake moisture	Solids-handling feasibility	Area basis; pressure; final moisture

Note. XRD = X-ray diffraction; PSD = particle-size distribution. These are proposed reporting variables rather than a claim that all cited studies measured them.

Combining phase, solution, and particle-population observations is necessary to distinguish true incompletely decomposed carnallite from magnesium-rich liquor adhering to otherwise KCl-rich crystals.

Secondary crystallization and solid-phase evolution

KCl nucleation and growth can occur during decomposition, cooling, subsequent aging, or brine concentration. A process may therefore exhibit time-dependent potassium transfer back from liquid to solid after the nominal dissolution stage. Such secondary crystallization is potentially beneficial for recovery but may create fine crystals that are difficult to wash (Li et al., 2009; C. Wang et al., 2024a; Yu et al., 2023).

Direct work on the carnallite crystallization–flotation interface indicates that regulating crystal size and surface morphology during decomposition can alter subsequent KCl flotation and bubble-adhesion behavior (Lei et al., 2024). This connection supports evaluating crystallization and upgrading as coupled steps rather than optimizing

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

particle size or collector response independently. The study provides targeted experimental evidence for the interface, not a universal prediction of plant recovery.

Crystal habit and surface chemistry matter because intercrystalline brine retention directly affects Mg contamination. Reports on surfactant adsorption, electrolyte-specific bubble attachment, and collector effects suggest that chemical conditioning can interact with both crystallization and flotation; however, a reagent beneficial for one separation stage can be detrimental to another (Li et al., 2016; Ren et al., 2025; Sun et al., 2023; Sun et al., 2022; Wang et al., 2023).

Seeded crystallization, controlled cooling, and residence-time distribution should be evaluated jointly. The most meaningful comparison is a full potassium balance at specified KCl purity and product particle-size range, rather than an isolated yield of crystals under favorable bench conditions (Ji et al., 2022; Tavares et al., 2018; C. Wang et al., 2024a).

Process integration: flotation, filtration, and washing

Flotation can recover or clean chloride salt particles, but the strongly saline medium modifies collector speciation, ion hydration, air–bubble attachment, and reagent adsorption. Carnallite flotation studies and broader soluble-salt surface-chemistry research show that reagent selection must be tied to the actual brine composition (Abu-Hamatteh & Al-Amr, 2008; Cao et al., 2011; C. Cheng et al., 2020; Huang et al., 2018; Laskowski, 2013; Sun et al., 2023; Sun et al., 2022).

The proposed integrated circuit is illustrated in Figure 3. Its critical feature is the accounting boundary around the decomposition reactor, solid–liquid separation, upgrading step, wash streams, and magnesium-rich liquor. Without such a boundary, comparisons between a decomposition–flotation route and a crystallization route may assign different potassium losses to different process stages.

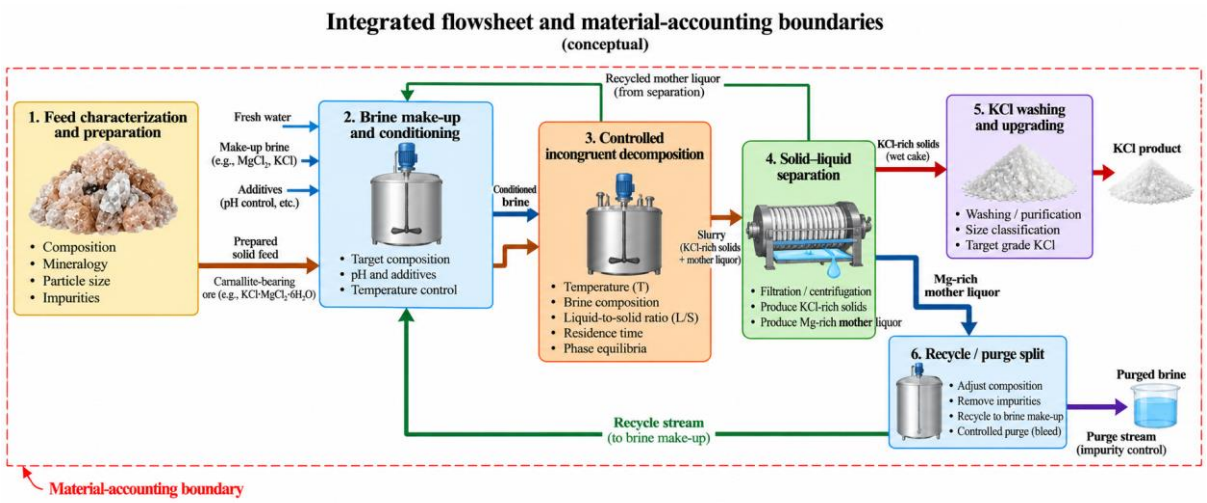


Figure 3. Conceptual integrated decomposition, separation, upgrading, and brine-management flowsheet.

Note. Original conceptual illustration developed for this review; not adapted from a previously published figure, and no experimental data are plotted.

To distinguish soluble-salt contamination from poor phase conversion, apportion Mg measured in a filter cake, where possible, among externally adhering mother liquor, occluded liquid, residual carnallite, and other Mg-bearing solids. Paired cake-moisture and filtrate-composition measurements, wash-liquor analyses, elemental assay, and quantitative XRD provide complementary constraints. Evaluate wash performance using Mg removal efficiency, $\eta(Mg,wash) = 100 \times$ Mg removed during wash / Mg entering the wash stage, and potassium wash loss, $L(K,wash) = 100 \times$ K lost to wash effluents / K entering the wash stage. Both indicators require a stated wash-stage boundary and inclusion of all relevant liquid and solid outputs.

Selectivity should be assessed for a clearly specified accounting boundary and time basis; steady-state conditions are preferred for continuous recycle circuits, while batch experiments require an explicit initial/final inventory. On an elemental mass basis, potassium recovery is R(K) (%) = 100 × M(K, saleable products) / ΣM(K, external inputs). All external K-bearing feed, reagents, and makeup salts must be included; internal recycle is excluded. Magnesium rejection is R(Mg) (%) = 100 × [1 − M(Mg, saleable KCl product) / ΣM(Mg, external inputs)] and must be reported alongside the Mg concentration or $MgCl_2$-equivalent contamination of dry saleable KCl, using a declared assay and conversion basis. For either element i = K or Mg, balance closure is C(i) (%) = 100 × [ΣM(i, external outputs) + ΔM(i, system inventory)] / ΣM(i, external inputs), where ΔM = final minus initial elemental inventory. Closure near 100% is expected within stated analytical uncertainty. Dry-basis KCl-equivalent calculated from elemental potassium must not be labeled phase-pure sylvite without phase evidence (quantitative XRD, other identified K-bearing solids, moisture, and major-element assay). Potassium lost to purge and wash, product purity, cake moisture, net freshwater use, and full-circuit energy should be disclosed separately.

Filtration and washing can dominate the actual separation after chemistry has established an apparently attractive solid phase. Washing reduces adhering magnesium brine but also redissolves KCl when the wash liquid is undersaturated. A countercurrent or KCl-conditioned wash may reduce losses, subject to experimental verification for each feed and product specification (Tavares et al., 2018; Weedon et al., 2007; Zhang et al., 2026).

Selectivity assessment, uncertainties, and research priorities

Metrics and process-window comparison

Selectivity must be assessed at a clearly specified steady-state accounting boundary. Potassium recovery (%) is 100 × [moles of K in saleable KCl product/moles of K entering in fresh feed]. Magnesium rejection (%) is 100 × [1 − (moles of Mg in saleable product/moles of Mg entering in fresh feed)], provided that no magnesium enters through other external inputs. If makeup salts or reagents import magnesium, all external inputs must be included. Internal recycle flows must not be counted again as fresh input. Product grade, dissolved potassium in purge and wash liquors, cake moisture, and specific freshwater and energy demands must be disclosed alongside these indicators.

Table 4 establishes a minimum set of plant-relevant indicators and stream measurements. Figure 4 then separates equilibrium feasibility from conversion rate, actual physical separation, and plant-wide recovery; the framework resolves the central question without claiming that any one mechanism is universally dominant.

Table 4. Minimum standardized selectivity and circuit-accounting indicators

Indicator	Suggested mathematical basis	Interpretative caution
Potassium recovery (%)	100 × K in saleable products / ΣK in all external inputs	Account for all external K-bearing additives; exclude internal recycle
Magnesium rejection (%)	100 × [1 − Mg in saleable KCl / ΣMg external inputs]	Also report Mg assay or $MgCl_2$-equivalent on dry product
KCl product grade (%)	Quantitative KCl phase fraction on dry product basis	Report KCl equivalent separately; verify phase identity by XRD
K lost to purge (%)	100 × K in purge / ΣK external inputs	Track purge, wash and unrecovered outputs separately
Fresh-water demand	m^3 fresh water/t feed AND m^3 fresh water/t saleable KCl	Two separate functional units; account for moisture and vapor

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume XI Issue X October 2026

Energy intensity	kWh or MJ/t saleable KCl for stated full circuit	Include heating, cooling, evaporation, drying, pumping, mixing, filtration, flotation and circulation where material
K balance closure (%)	100 × (ΣK external outputs + ΔK inventory)/ΣK external inputs	Match accounting period; give reconciliation uncertainty
Mg balance closure (%)	100 × (ΣMg external outputs + ΔMg inventory)/ΣMg external inputs	Account for dissolved Mg and Mg-bearing solids
Mg removal by washing (%)	100 × Mg removed in wash / Mg entering washing	Define wash boundary and liquid/solid inputs
K loss in washing (%)	100 × K lost in wash / K entering washing	Measure wash discharge and fines

Note. Proposed reporting definitions synthesized for this review; all balance streams must be reconciled on a common time and dry-mass basis.

These indicators show whether improved KCl grade results from genuine magnesium removal, selective recrystallization, simple dilution, or an unmeasured increase in potassium discarded with liquor. Comparisons lacking complete stream assays should be considered provisional.

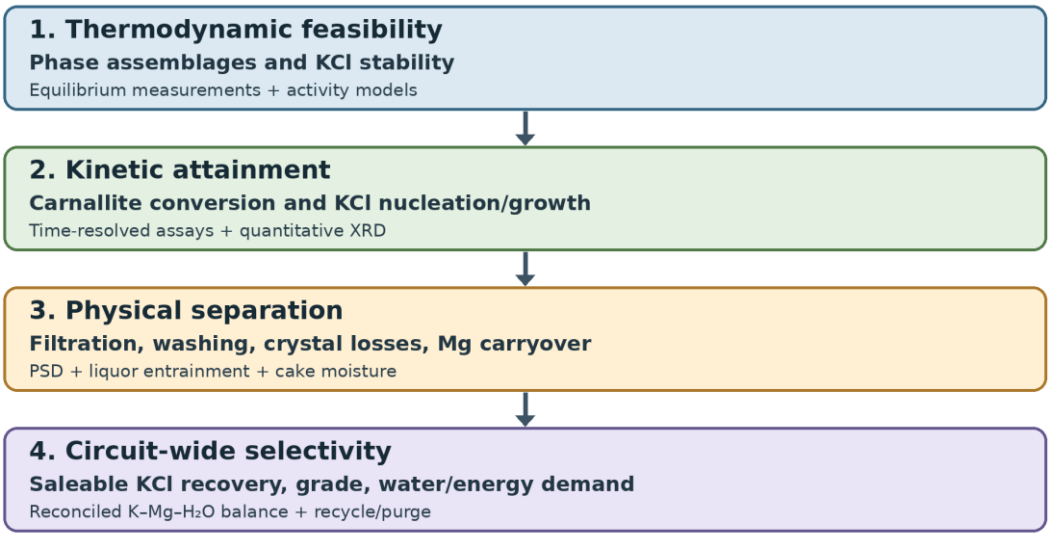


Figure 4. Hierarchy of equilibrium, kinetic, separation, and plant-wide selectivity.

Note. Original four-level conceptual hierarchy developed for this review. The arrows indicate sequential assessment criteria, not measured recovery or a universal rate-limiting sequence.

The hierarchy supports a conditional answer: equilibrium fixes what phase separation is thermodynamically possible; kinetics governs the time needed to approach it; separation behavior determines solid contamination and losses; and circuit recycles establish sustained performance.

Priority research and industrial validation

A discriminating validation program should couple independently checked electrolyte phase models with time-resolved K and Mg analyses, quantitative XRD, and measured crystal-size distributions at controlled temperature, liquid-to-solid ratio, and mixing power. Representative Na/Ca impurity matrices, repeated tests, and parameter-uncertainty analyses are essential. Equilibrium predictions should be compared against observed

solid assemblages and analyzed mother liquors, while kinetic inference should be supported by more than a single end-point sample (C. Wang et al., 2024b; Wang et al., 2025; Yu et al., 2026; Yu & Zeng, 2010, 2011).

For process development, a staged test program should first identify a thermodynamically permissible region, then optimize kinetic attainment and particle handling, and finally assess a steady-state recycle flowsheet. A technology readiness level should be invoked only after a specific process configuration, operational scale, and evidence of integrated demonstration are defined; a published bench-scale reaction alone does not justify a meaningful route-wide TRL assignment.

Economic and environmental conclusions remain site-dependent: ore grade, brine-disposal rules, water scarcity, heating and cooling integration, product-market specifications, and magnesium-brine outlets can reverse route rankings. Existing brine valorization literature supports investigating integrated product pathways, but quantitative comparison still requires a project-specific balance and cost basis (Amadghous et al., 2025; Khakhar et al., 2026; Mukhtar & Seitmagzimova, 2025; Quilaqueo et al., 2024; Tavares et al., 2018).

CONCLUSIONS

Controlled decomposition of carnallite is best understood as an integrated phase-transformation and separation problem rather than a single dissolution reaction. Solid–liquid equilibrium defines the possible distribution of potassium and magnesium, but it does not predict how rapidly that state will be reached or how much saleable KCl will be recovered. Feed mineralogy, brine composition, water dosage, crystal nucleation and growth, and the efficiency of washing and solid–liquid separation jointly determine attainable industrial selectivity.

The strongest route-comparison criterion is a reconciled potassium–magnesium–water balance supported by phase identification, solution analyses, and product specifications. Priority research should therefore integrate validated thermodynamic models, transient mechanistic measurements, representative impurity matrices, and steady-state recycle testing. Such a framework avoids confusing KCl grade with K recovery and provides a more defensible basis for scale-up and sustainability evaluation.

Declarations

Funding

This review received no specific external funding.

Conflict of interest

The author declares no conflict of interest.

Data availability

No new experimental datasets were generated. The literature references and conceptual figures support the analysis presented.

Author contributions

The author conducted the conceptualization, analytical synthesis, critical interpretation, and manuscript preparation.

REFERENCES

1. Abu-Hamatteh, Z. S. H., & Al-Amr, A. M. (2008). Carnallite froth flotation optimization and cell efficiency in the Arab Potash Company, Dead Sea, Jordan. Mineral Processing and Extractive Metallurgy Review, 29(3), 232–257. https://doi.org/10.1080/08827500801997894
2. Amadghous, Y., Ait-Khouia, Y., Aboulaich, A., Zagriri, A., Ouabid, M., Raji, O., Mansouri, S., Elghali, A., Taha, Y., & Benzaazoua, M. (2025). Resource recovery from potash brine effluent: Integrated

chemical precipitation and evaporative crystallization for zero liquid discharge and sustainable brine management. Chemosphere, 388, 144700. https://doi.org/10.1016/j.chemosphere.2025.144700

3. Cao, Q., Wang, X., Miller, J. D., Cheng, F., & Jiao, Y. (2011). Bubble attachment time and FTIR analysis of water structure in the flotation of sylvite, bischofite and carnallite. Minerals Engineering, 24(2), 108–114. https://doi.org/10.1016/j.mineng.2010.10.006
4. Cheng, C., Huang, Z., Zhang, R., Zhou, J., Liu, Z., Zhong, H., Wang, H., Kang, Z., He, G., Yu, X., Ren, Z., Qiu, T., Hu, Y., & Fu, W. (2020). Synthesis of an emerging morpholine-typed Gemini surfactant and its application in reverse flotation carnallite ore for production of potash fertilizer at low temperature. Journal of Cleaner Production, 261, 121121. https://doi.org/10.1016/j.jclepro.2020.121121
5. Cheng, H., Hai, Q., Song, J., Ma, X., & Li, C. (2020). The role of Mg value and moisture content of decomposed products during the decomposition process of carnallite in aqueous solution: A novel monitoring method. RSC Advances, 10(35), 20529–20535. https://doi.org/10.1039/D0RA03567J
6. Cheng, X., Zeng, Y., Wu, L., Ye, Y., & Yu, X. (2018). Metastable phase equilibrium in the quaternary system containing with potassium+magnesium+calcium+chloride in aqueous solution at 298.2 K. Journal of Chemical Engineering of Japan, 51(7), 544–550. https://doi.org/10.1252/jcej.17we324
7. Deng, T., Zhang, B., Li, D., & Guo, Y. (2009). Simulation studies on metastable phase equilibria in the aqueous ternary systems (NaCl–$MgCl_2$–H_2O) and (KCl–$MgCl_2$–H_2O) at 308.15 K. Frontiers of Chemical Engineering in China, 3(2), 172–175. https://doi.org/10.1007/s11705-009-0048-1
8. Gan, S., Ding, D., Sun, C., Jiang, S., & Guan, J. (2024). Study on cold decomposition crystallization process of underground primary high-sodium carnallite ore. Inorganic Chemicals Industry, 56(1), 67–72. https://doi.org/10.19964/j.issn.1006-4990.2023-0048
9. Guo, K., Fan, Y., Yang, J., Zhao, W., Jia, Y., & Wang, Y. (2024). Analysis of effect of carnallite raw ore grade on its cold decomposition and crystallization of potassium chloride. Inorganic Chemicals Industry, 56(8), 9–18. https://doi.org/10.19964/j.issn.1006-4990.2023-0516
10. Huang, Z., Cheng, C., Li, L., Guo, Z., He, G., Yu, X., Liu, R., Han, H., Deng, L., & Fu, W. (2018). Morpholine-based gemini surfactant: Synthesis and its application for reverse froth flotation of carnallite ore in potassium fertilizer production. Journal of Agricultural and Food Chemistry, 66(50), 13126–13132. https://doi.org/10.1021/acs.jafc.8b05560
11. Ji, G., Wang, W., Chen, H., Yang, S., Sun, J., Fu, W., Yang, B., & Huang, Z. (2022). Sustainable potassium chloride production from concentrated KCl brine via a membrane-promoted crystallization process. Desalination, 521, 115389. https://doi.org/10.1016/j.desal.2021.115389
12. Khakhar, R., Sahu, P., Paital, A. R., Vyas, B. G., Sanghavi, R. J., Shukla, J. J., Upadhyay, S. C., & Kumar, A. (2026). Harnessing mixed salt production from brine for value addition: A review of sustainable practices in the Indian context. Desalination and Water Treatment, 326, 101795. https://doi.org/10.1016/j.dwt.2026.101795
13. Laskowski, J. S. (2013). From amine molecules adsorption to amine precipitate transport by bubbles: A potash ore flotation mechanism. Minerals Engineering, 45, 170–179. https://doi.org/10.1016/j.mineng.2013.02.010
14. Lei, S., Yuan, Y., Zhu, H., Yi, H., Dong, G., Ma, S., Jia, F., & Song, S. (2024). Enhancement of KCl flotation through crystallization regulation during carnallite decomposition. Surfaces and Interfaces, 55, Article 105435. https://doi.org/10.1016/j.surfin.2024.105435
15. Li, E., Liang, H., Du, Z., Li, D., & Cheng, F. (2016). Adsorption process of octadecylamine hydrochloride on KCl crystal surface in various salt saturated solutions: Kinetics, isotherm model and thermodynamics properties. Journal of Molecular Liquids, 221, 949–953. https://doi.org/10.1016/j.molliq.2016.06.050
16. Li, X., Song, X., Liu, G., & Yu, J. (2009). Size-dependent nucleation and growth kinetics model for potassium chloride—Application in Qarhan salt lake. Journal of Crystal Growth, 311(11), 3167–3173. https://doi.org/10.1016/j.jcrysgro.2009.03.007
17. Mukhtar, A. A., & Seitmagzimova, G. (2025). An innovative environmentally friendly processing method of promising carnallite ores. Engineering, Technology & Applied Science Research, 15(4), 24321–24327. https://doi.org/10.48084/etasr.11159
18. Pannach, M., Paschke, I., Schmidt, H., Freyer, D., & Voigt, W. (2020). Crystallization of metastable monoclinic carnallite, KCl·MgCl2·6H2O: Missing structural link in the carnallite family. Acta

Crystallographica Section C: Structural Chemistry, 76(5), 507–512. https://doi.org/10.1107/S2053229620005197

19. Podder, J., Gao, S., Evitts, R. W., Besant, R. W., & Matthews, D. (2014). Synthesis of carnallite crystal from KCl–MgCl2 solutions and its characterization. International Journal of Materials Research, 105(3), 308–313. https://doi.org/10.3139/146.111013
20. Quilaqueo, M., Seriche, G., González, C., Piaggio, G., Barros, L., Gallardo, F., Díaz-Quezada, S., Zamora, D., Barraza, B., Ruby-Figueroa, R., Santoro, S., Curcio, E., & Estay, H. (2024). Membrane distillation-crystallization applied to a multi-ion hypersaline lithium brine for water recovery and crystallization of potassium and magnesium salts. Desalination, 586, 117895. https://doi.org/10.1016/j.desal.2024.117895
21. Ren, Y., Song, L., Chen, M., Feng, H., Li, M., & Peng, J. (2025). Preparation of high-purity potassium chloride crystal particles in an octadecylamine hydrochloride–water system: The correlation between morphology and purity. Crystals, 15(11), 958. https://doi.org/10.3390/cryst15110958
22. Song, W.-J., Yang, S., Mbadinga, S. M., Sun, X.-Y., & Mu, B. (2015). Non-destructive characterization using MCT reveals the composition and distribution of impurities in solar carnallite. RSC Advances, 5, 16230–16233. https://doi.org/10.1039/C5RA00989H
23. Sun, K., Nguyen, C. V., Nguyen, N. N., Ma, X., & Nguyen, A. V. (2023). Crucial roles of ion-specific effects in the flotation of water-soluble KCl and NaCl crystals with fatty acid salts. Journal of Colloid and Interface Science, 636, 413–424. https://doi.org/10.1016/j.jcis.2023.01.038
24. Sun, K., Nguyen, C. V., Nguyen, N. N., & Nguyen, A. V. (2022). Flotation surface chemistry of water-soluble salt minerals: From experimental results to new perspectives. Advances in Colloid and Interface Science, 309, 102775. https://doi.org/10.1016/j.cis.2022.102775
25. Szatmari, P., de Lima, C. M., Fontaneta, G., de Melo Lima, N., Zambonato, E., Menezes, M. R., Bahniuk, J., Coelho, S. L., Figueiredo, M., & Florencio, C. P. (2021). Petrography, geochemistry and origin of South Atlantic evaporites: The Brazilian side. Marine and Petroleum Geology, 127, 104805. https://doi.org/10.1016/j.marpetgeo.2020.104805
26. Tavares, J. A., Moura, L. F., Bernardo, A., & Giulietti, M. (2018). Crystallization and separation of KCl from carnallite ore: Process development, simulation, and economic feasibility. Chemical Industry and Chemical Engineering Quarterly, 24(3), 239–249. https://doi.org/10.2298/CICEQ170119036T
27. Wang, C., Luo, M., Chen, H., Wang, R., Meng, H., & Song, X. (2024a). Metastable zone width and primary nucleation kinetics for crystallization of KCl from a KCl-MgCl2-H2O system. Industrial & Engineering Chemistry Research, 63(18), 8330–8340. https://doi.org/10.1021/acs.iecr.4c00450
28. Wang, C., Luo, M., Chen, H., Zhang, S., Zhong, D., & Song, X. (2024b). Measurement and model prediction of solid-liquid equilibrium in the ternary system KCl-MgCl2-H2O at 293.15, 298.15, 303.15, and 308.15 K. Fluid Phase Equilibria, 576, 113956. https://doi.org/10.1016/j.fluid.2023.113956
29. Wang, C., Zhang, L., Luo, M., & Song, X. (2025). Measurement and theoretical calculation of phase equilibrium in the quaternary system KCl-NaCl-MgCl2-H2O at 303.15 and 308.15 K. Journal of Chemical & Engineering Data, 70(1), 518–533. https://doi.org/10.1021/acs.jced.4c00329
30. Wang, G., Bian, X., Shang, Z., Dong, W., Zhang, Y., & Wu, S. (2023). Effects of different flotation agents on the nucleation and growth of potassium chloride. Molecules, 28(23), 7923. https://doi.org/10.3390/molecules28237923
31. Weedon, D., Grano, S., Akroyd, T., Goncalves, K., & Moura, R. (2007). Effects of high magnesium ion concentration on KCl flotation: Part II—Plant research. Minerals Engineering, 20(7), 716–721. https://doi.org/10.1016/j.mineng.2007.01.009
32. Yang, J., Zhang, Y., Gan, S., Feng, Y., Zhang, S., Pu, Q., Zhao, W., & Wang, Y. (2026). Study on thermodynamics of effect of impurities on carnallite cold-decomposition process and parameter models. Inorganic Chemicals Industry, 58(4), 27–34. https://doi.org/10.19964/j.issn.1006-4990.2025-0127
33. Yu, X., Fu, Z., Ma, Y., Li, C., Zhang, S., & Zhang, Z. (2023). Polyethylene glycol regulated carnallite decomposition-crystallization: Experimental and theoretical analysis. Minerals Engineering, 195, 108021. https://doi.org/10.1016/j.mineng.2023.108021
34. Yu, X., Pan, T., Jia, J., Liu, J., Chen, J., Li, Q., & Ma, Z. (2026). Solid–liquid equilibria (SLE) of aqueous quaternary system K^+, Mg^{2+}, Ca^{2+}//Cl^-–H_2O at 323.2 and 348.2 K. Journal of Chemical & Engineering Data, 71(3), 1473–1483. https://doi.org/10.1021/acs.jced.5c00844

35. Yu, X., & Zeng, Y. (2011). Metastable phase equilibria in the aqueous ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O at 298.15 K. Journal of Chemical & Engineering Data, 56(8), 3384–3391. https://doi.org/10.1021/je200360f
36. Yu, X., & Zeng, Y. (2010). Metastable phase equilibria in the aqueous ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O at 323.15 K. Journal of Chemical & Engineering Data, 55(12), 5771–5776. https://doi.org/10.1021/je100727g
37. Yu, X., Zeng, Y., Yin, Q., & Mu, P. (2012). Solubilities, densities, and refractive indices of the ternary systems KCl + RbCl + H_2O and KCl + $MgCl_2$ + H_2O at 348.15 K. Journal of Chemical & Engineering Data, 57(12), 3658–3663. https://doi.org/10.1021/je300868x
38. Zhang, S.-C., Yu, X.-S., Zhang, Y.-M., Wang, Y.-F., Ma, W.-B., Jiao, A.-J., Li, Z.-W., Su, T., & Fu, Z.-H. (2026). Enhancing KCl grade via decomposition solution regulation in cold decomposition-direct flotation of carnallite. Journal of Solid State Chemistry, 359, 125951. https://doi.org/10.1016/j.jssc.2026.125951
39. Zheng, W., & Sang, S.-H. (2024). Measurements and calculations of phase equilibria in the quaternary systems NaCl–MgCl2–SrCl2–H2O and KCl–MgCl2–SrCl2–H2O at 298.2 K. Journal of Chemical & Engineering Data, 69(3), 737–748. https://doi.org/10.1021/acs.jced.3c00446
40. Zhu, K.-Y., Gao, Y.-Y., & Sang, S.-H. (2023). Solid–liquid phase equilibria in the quinary system NaCl–KCl–MgCl2–SrCl2–H2O at 273 K. Journal of Chemical & Engineering Data, 68(1), 206–216. https://doi.org/10.1021/acs.jced.2c00407