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Sulfuric Acid Regeneration from Magnesium Sulfate Streams: Process Chemistry, Recovery Technologies, and Industrial Challenges

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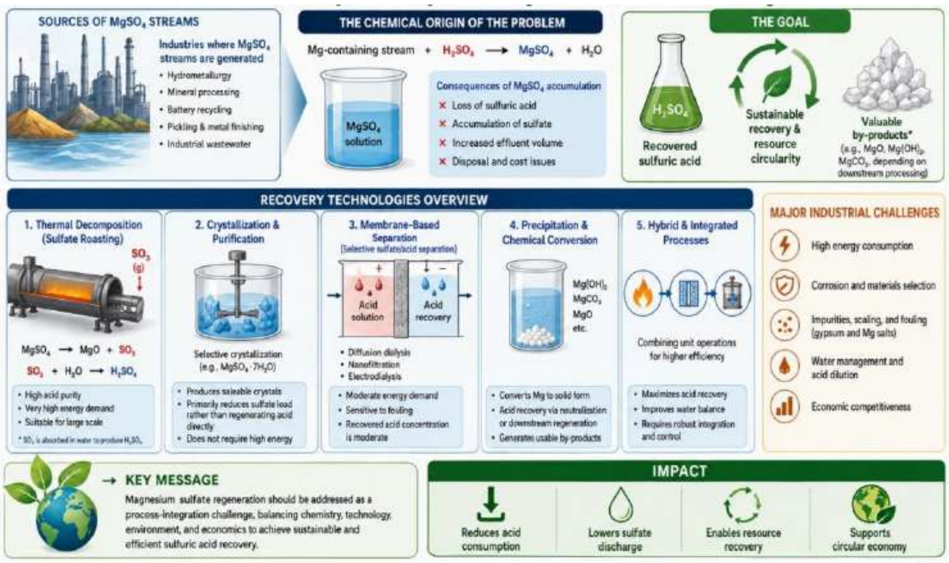
ABSTRACT: Sulfuric acid regeneration from magnesium sulfate streams is an increasingly relevant challenge in hydrometallurgy, mineral processing, battery recycling, pickling operations, and industrial wastewater treatment. Magnesium sulfate is often formed when sulfuric acid reacts with magnesium-bearing minerals, neutralizing agents, or process residues, resulting in acid loss, sulfate accumulation, increased effluent volumes, and challenging brine management. This critical review examines the process chemistry, recovery technologies, and industrial constraints associated with converting magnesium sulfate streams into reusable sulfuric acid or valuable by-products. The discussion covers thermal decomposition, crystallization, membrane-based acid recovery, electrodialysis, diffusion dialysis, solvent-assisted separation, precipitation routes, and hybrid process configurations. Particular attention is given to reaction equilibria, water balance, impurity behavior, energy demand, scaling risk, acid quality, and integration with upstream and downstream unit operations. Although several technologies are technically feasible, industrial application is limited by high energy consumption, low selectivity in multicomponent liquors, fouling, corrosion, and uncertain economics at large scale. The review highlights that magnesium sulfate regeneration should be evaluated as a process-integration problem rather than as an isolated acid-recovery step.

KEYWORDS: Sulfuric acid regeneration; Magnesium sulfate; Acid recovery; Hydrometallurgy; Sulfate waste management; Process integration

Highlights

- Magnesium sulfate streams represent both acid loss and sulfate-management challenges in industrial circuits.
- Thermal, membrane, crystallization, and hybrid routes differ strongly in energy demand and acid quality.
- Impurities, water balance, scaling, and corrosion often control industrial feasibility.
- Acid regeneration from $MgSO_4$ should be assessed through process integration and techno-economic criteria

Graphical abstract



1. INTRODUCTION

Sulfuric acid regeneration has become increasingly important in hydrometallurgy because large sulfur losses occur during acid consumption by alkaline or magnesium-bearing minerals (Wen et al., 2020; Agarwal & Pandey, 2023). In many industrial systems, sulfur is not primarily lost through volatilization but through the formation of stable dissolved sulfates that are difficult to reconvert into reusable acid. This issue has intensified as industries seek to reduce freshwater consumption, minimize liquid discharge, and improve sulfur circularity within processing plants (O'Sullivan & Williams, 2024; Yadav et al., 2026).

Among sulfate species, magnesium sulfate ($MgSO_4$) represents one of the most problematic. Magnesium is abundant in silicate minerals such as serpentine, olivine, and chlorite, which dissolve during sulfuric acid leaching and react with sulfate ions to form $MgSO_4$. Due to its high stability and elevated decomposition temperature, $MgSO_4$ frequently behaves as a terminal sulfur sink rather than a recoverable intermediate. Consequently, sulfur progressively accumulates in residues, brines, recirculating liquors, and wastewater streams.

This problem is crucial in nickel laterite processing, where the use of sulfuric acid depends on the dissolution of magnesium silicate and serpentine. Sulfation roasting, atmospheric, and pressure leaching produce large $MgSO_4$ inventories due to gangue dissolution and sulfate stabilization (Pereira, 2026; Zhao et al., 2024a). During sulfation roasting of limonitic laterites, the distribution of sulfur affects metal extraction and sulfate management (Zhao et al., 2024b). Sulfuric acid regeneration is linked to impurity buildup, water balance, sulfate transport, and residue handling.

The rapid expansion of lithium extraction and battery recycling has intensified interest in sulfate recovery. Sulfate roasting and sulfate-assisted leaching are increasingly used to recover lithium, nickel, cobalt, and manganese from ores and spent lithium-ion batteries (Tang et al., 2021; Di et al., 2020). Although ammonium sulfate roasting and sulfuric acid roasting may improve metal extraction, they also generate sulfate-rich liquors and secondary sulfate residues that require additional treatment. Similar challenges arise in titanium dioxide production and mineral-upgrading routes involving sulfate digestion or roasting. Ilmenite processing via ammonium sulfate roasting produces sulfate-containing streams with elevated magnesium and impurity levels (Abdelgalil et al., 2023). Sulfate-rich residues are also generated during the treatment of electric smelting dusts and titanium-bearing mineral concentrates (Karshyga et al., 2022; Ultarakova et al., 2022).

$MgSO_4$-rich streams are also relevant to acid mine drainage (AMD), industrial wastewater treatment, fertilizer production, and chemical manufacturing. In AMD systems, sulfate commonly coexists with elevated metal concentrations and high ionic strength, complicating water reuse and treatment operations (Wen et al., 2020). The fertilizer and phosphoric acid industries likewise generate sulfate-rich liquors during neutralization, impurity removal, and evaporation. Increasing environmental restrictions have therefore intensified pressure to reduce sulfate discharge and improve sulfur recovery strategies (Agarwal & Pandey, 2023).

Conventional sulfate management still relies primarily on neutralization and precipitation. Lime neutralization, gypsum formation, and alkaline stabilization remain operationally attractive because they provide rapid acidity control and remove dissolved metals. However, these methods largely destroy the chemical value of sulfuric acid by converting sulfate into low-value solids or dilute waste streams. In many operations, sulfur is simply transferred between liquid and solid waste forms rather than being regenerated into reusable acid, increasing sludge generation, water consumption, and long-term environmental burden (Yadav et al., 2026).

From a thermodynamic perspective, $MgSO_4$ is substantially more difficult to process than many transition-metal sulfates. Its high thermal stability, multiple hydration states, and slow decomposition kinetics require elevated temperatures and significant energy input for conversion into magnesium oxide and sulfur oxides. Consequently, technologies developed for regeneration of steel pickling acids or iron-rich sulfates cannot be directly transferred to $MgSO_4$-rich systems without major modification.

These limitations have spurred interest in alternative regeneration technologies, including membrane separation, electrodialysis, diffusion dialysis, selective crystallization, hybrid thermal systems, and integrated water–acid recovery. Electrochemical separation of sulfuric acid from magnesium sulfate solutions has recently attracted attention, particularly for laterite-processing applications (Ibrahim et al., 2024). Concepts such as circular hydrometallurgy and integrated sulfate management are also increasingly important as industries seek to reduce sulfur loss and improve resource efficiency (Binnemans & Jones, 2023a, 2023b). Nevertheless, many emerging technologies still face significant challenges related to energy demand, sulfate selectivity, scaling, impurity tolerance, corrosion, and industrial scalability.

This review critically analyzes sulfuric acid regeneration from magnesium sulfate streams, emphasizing process chemistry, thermodynamic limitations, recovery technologies, and industrial challenges. It examines $MgSO_4$ as a persistent sulfur sink in hydrometallurgical and chemical-processing systems and discusses how sulfate management is evolving from a wastewater-treatment issue into a broader challenge involving sulfur recycling, water recirculation, energy integration, and environmental sustainability.

2. METHODOLOGY

This review adopted a narrative-systematic critical approach that integrates thermodynamics, process chemistry, industrial operations, and recovery technologies related to sulfuric acid regeneration from magnesium sulfate streams. Instead of focusing only on bibliometric trends, the review emphasized mechanistic consistency, process integration, scalability, and industrial applicability of sulfate-management strategies.

The literature survey followed the PRISMA 2020 framework proposed by Matthew J. Page et al. (2021), adapted for engineering and hydrometallurgical systems involving sulfate generation, acid recovery, and magnesium-bearing streams. The PRISMA methodology was selected to ensure transparency throughout the identification, screening, eligibility assessment, and final inclusion of studies. Filtering criteria were applied to remove duplicates, exclude irrelevant publications, and prioritize studies that contain experimental, thermodynamic, operational, or process-design data related to $MgSO_4$ regeneration and sulfate management.

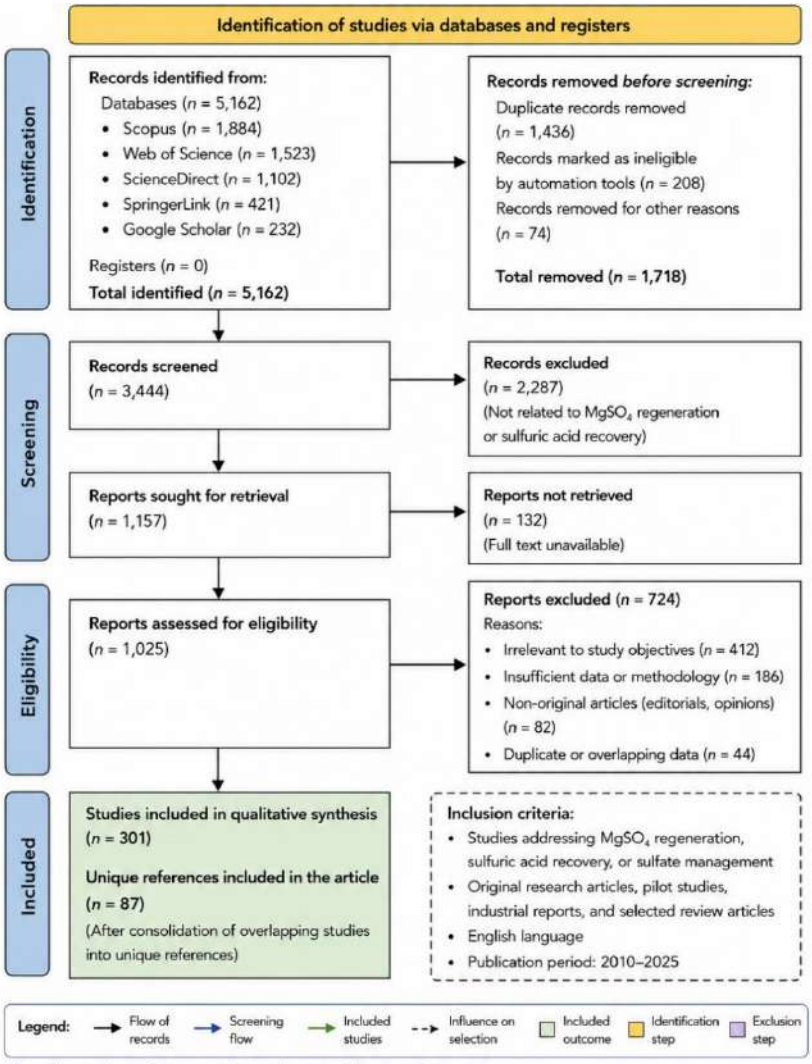
The search strategy covered sulfate chemistry, recovery technologies, and industrial sulfate-processing systems using terms such as “magnesium sulfate decomposition,” “sulfuric acid regeneration,” “sulfate recycling,” “$MgSO_4$ pyrohydrolysis,” “electrodialysis,” “diffusion dialysis,” “membrane sulfate recovery,” and “sulfate crystallization.” Additional sector-specific keywords related to nickel laterites, lithium extraction, sulfation roasting, titanium dioxide processing, acid mine drainage, wastewater treatment, and battery recycling were also included. The review focused mainly on publications from 2020–2026 to emphasize recent advances in membrane systems, electrochemical recovery, sulfate roasting, and circular hydrometallurgy.

The principal databases included Scopus, Web of Science, ScienceDirect, SpringerLink, ACS Publications, and Wiley Online Library because of their broad coverage of hydrometallurgy, chemical engineering, membrane science, thermodynamics, mineral processing, and sustainability. Conference proceedings, theses, review papers, and selected industrial reports were included when they provided mechanistic or pilot-scale information not sufficiently covered in peer-reviewed journals.

Engineering-oriented screening criteria were prioritized over purely environmental or analytical metrics, favoring studies on thermodynamic modeling, decomposition kinetics, membrane selectivity, impurity effects, energy consumption, process integration, industrial conditions, scalability, or environmental impact. Similar methods are used in sulfation roasting, sulfate processing, and metal recovery (Ju et al., 2023; Deng & Feng, 2026; Vivar et al., 2025).

Special attention was given to distributing references evenly across the manuscript to avoid citation clustering in isolated themes. References were assessed based on thematic consistency, journal reliability, experimental scope, and data interpretation coherence. Preprints and poorly documented sources were excluded when peer-reviewed options existed.

The study-selection workflow adopted in this review is summarized in Figure 1. It used a PRISMA-based screening strategy to identify studies related to $MgSO_4$ regeneration, sulfuric acid recovery, sulfate management, membrane separation, thermal decomposition, crystallization systems, and sulfate circularity in hydrometallurgical and industrial applications.



Note: The numbers refer to records at each stage of the screening process.

Figure 1. PRISMA 2020 flow diagram used for identification, screening, eligibility assessment, and inclusion of studies related to $MgSO_4$ regeneration and sulfuric acid recovery systems. Adapted from Adapted from Page et al. (2021).

Figure 1 summarizes database identification, screening, eligibility assessment, and inclusion of 87 references covering $MgSO_4$ thermodynamics, regeneration technologies, industrial integration, and sustainability.

3. SOURCES AND FORMATION OF MAGNESIUM SULFATE STREAMS

3.1. $MgSO_4$ Formation in Hydrometallurgy

Magnesium sulfate formation in hydrometallurgical systems occurs primarily by dissolving magnesium-bearing minerals under acidic conditions. During sulfation and leaching, magnesium becomes a major acid-consuming element because Mg-rich silicates react with sulfuric acid, generating large sulfate inventories. This behavior is particularly important in nickel laterite processing, where serpentine, olivine, and chlorite coexist with nickel- and cobalt-bearing phases (Hariyanto et al., 2023b; Ribeiro et al., 2021). Under acidic attack, magnesium dissolves and is stabilized as $MgSO_4$ in sulfate-rich liquors.

$MgSO_4$ formation depends on ore mineralogy, acid concentration, temperature, and roasting conditions. Serpentine-rich ores need more sulfuric acid because magnesium silicates dissolve extensively, lowering nickel and cobalt extraction (Hariyanto et al., 2023a). Similarly, olivine-rich systems show rapid proton attack on Mg–O bonds at higher temperatures. Ribeiro et al. (2022)

noted magnesium-rich laterites require significant acid during roasting–leaching, increasing sulfur use without better metal recovery.

Sulfation roasting further intensifies sulfate formation because sulfur reacts simultaneously with metal oxides and silicate phases. Zhao et al. (2024a) reported that nickel and cobalt extraction may stabilize sulfates both in solid phases and dissolved liquors, depending on roasting conditions and gangue composition. Excess sulfate associated with magnesium phases decreases sulfur efficiency. It enlarges the sulfate inventory, consistent with Yang et al. (2022), who identified strong interactions between magnesium extraction and sulfation reactions in serpentine-rich ores.

Acid attack mechanisms in magnesium silicates differ from transition-metal oxides, leading to lattice destruction, higher acid use, and sulfate stabilization. Hariyanto et al. (2024) showed MgO and SiO_2 contents affect extraction efficiency during sulfation roasting, as magnesium phases compete with metals for sulfate. $MgSO_4$ formation consumes sulfuric acid and alters solution chemistry and crystallization.

Alternative roasting systems involving ammonium sulfate have been investigated to improve extraction and reduce the demand for sulfuric acid. Duan et al. (2023) reported synergistic effects between sulfuric acid and ammonium sulfate during ferronickel slag roasting, improving metal extraction and sulfate distribution. Similar approaches have also been explored for the recovery of magnesium from ferronickel slags (Yang et al., 2021). However, these systems still generate $MgSO_4$-rich liquors requiring downstream treatment.

Accumulation of dissolved $MgSO_4$ progressively affects hydrometallurgical circuits by increasing ionic strength, altering evaporation and crystallization behavior, and complicating water recirculation. Tauakelov et al. (2025) emphasized that processing refractory oxidized nickel ores generates chemically complex sulfate streams, reinforcing the need for integrated sulfate-management strategies rather than neutralization alone.

3.2. Industrial Sources of $MgSO_4$

Nickel laterites are major sources of $MgSO_4$, but several other industries also generate sulfate-rich liquors that contain dissolved magnesium. In lithium extraction, sulfate roasting and acidic leaching of minerals such as lepidolite and spodumene dissolve magnesium-bearing gangue phases, producing $MgSO_4$-rich streams. Sulfate additives affect lithium salt formation and sulfate stability, creating operational challenges during roasting and downstream processing.

Battery recycling creates sulfate liquors with magnesium and impurities. Tang et al. (2021) described low-temperature ammonium sulfation roasting for recycling lithium nickel cobalt manganese oxides, while Di et al. (2020) studied sulfate roasting–water leaching for lithium recovery from spent batteries. Although these methods enhance metal extraction, they also produce sulfate-rich residues and secondary liquors needing sulfur management. As recycling expands, $MgSO_4$ production is expected to grow in secondary-resource hydrometallurgy.

Titanium dioxide production via sulfate routes also generates sulfate-rich waste acids and residues. Abdelgalil et al. (2023) investigated ilmenite processing through ammonium sulfate roasting–leaching and identified chemically complex sulfate streams generated during TiO_2 recovery. Related sulfate-bearing residues are also formed during processing of ilmenite smelting dusts and mineral concentrates (Karshyga et al., 2022; Ultarakova et al., 2022). These systems are additionally complicated by silica, suspended solids, and fluctuating acid composition. (Pereira, 2026)

$MgSO_4$-rich streams are also important in mining wastewater and industrial water treatment. Baena-Moreno et al. (2020) demonstrated that sulfate-rich acid mine drainage systems are chemically complex because magnesium remains dissolved due to high sulfate solubility. Foureaux (2021) further showed that membrane distillation and electrodialysis can partially recover water and metals from pressure-oxidation effluents, although sulfate progressively accumulates in residual streams.

Chemical and fertilizer industries also generate significant $MgSO_4$ inventories through neutralization, evaporation, and salt-separation operations. Magnesium accumulation in these sectors affects sulfate balance, scaling, and crystallization behavior, reinforcing the need for integrated sulfate management strategies that involve water recovery, sulfur reuse, and impurity control. Table 1 summarizes representative industrial $MgSO_4$-rich streams and their principal operational characteristics.

Table 1. Representative sources of $MgSO_4$-rich industrial streams and their main operational characteristics. Adapted from Hariyanto et al. (2023a), Zhao et al. (2024a), Abdelgalil et al. (2023), Tang et al. (2021), Baena-Moreno et al. (2020), and Foureaux (2021).

Industrial source	Typical sulfate concentration	Typical Mg concentration	pH range	Temperature range	Main impurities
Nickel laterite leaching	High	High	1–3	40–250 °C	Fe, Al, Si, Ni, Co
Sulfation roasting liquors	Moderate–high	Moderate–high	1–4	25–120 °C	Fe, Mn, Al
Lithium extraction systems	Moderate	Moderate	1–5	25–100 °C	Li, Na, K, Al
Battery recycling liquors	High	Low–moderate	<2	25–90 °C	Co, Ni, Mn, Li
Titanium dioxide waste acid	High	Moderate	<1	40–120 °C	Fe, Ti, Al
Acid mine drainage	Moderate	Low–moderate	2–5	Ambient	Fe, Ca, Mn
Fertilizer and phosphoric acid systems	Moderate–high	Moderate	1–4	30–90 °C	Ca, P, Na
Wastewater-treatment concentrates	Variable	Variable	2–7	Ambient–70 °C	Cl^-, Na, heavy metals

Table 1 shows $MgSO_4$-rich streams vary in composition, acidity, impurities, and temperature. These differences affect sulfate management choices, as technologies for concentrated liquors may not suit dilute wastewater.

Figure 2 summarizes the main industrial pathways producing $MgSO_4$ in sulfate-rich streams, including sources, formation mechanisms, operational factors, and key management challenges in hydrometallurgical and chemical systems.

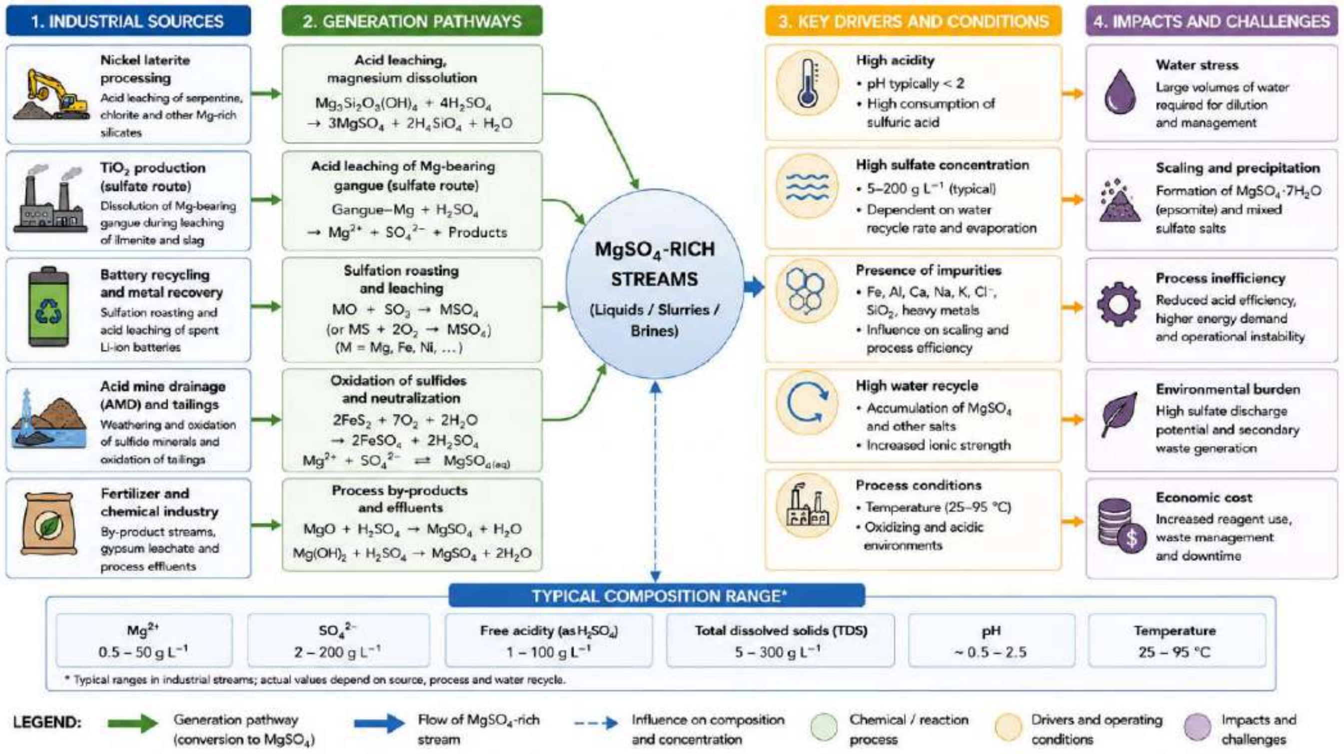


Figure 2. Generation pathways, operational drivers, and industrial sources of $MgSO_4$-rich streams in sulfate-based processing systems. Adapted from Hariyanto et al. (2023a), Zhao et al. (2024a), Tang et al. (2021), Abdelgalil et al. (2023), Baena-Moreno et al. (2020), and Yadav et al. (2026).

Figure 2 shows the formation of $MgSO_4$ from mineral dissolution, roasting, wastewater, and recycling, highlighting how sulfate accumulation drives scaling, inefficiency, and the need for integrated management.

4. THERMODYNAMICS AND CHEMISTRY OF $MgSO_4$ STABILITY

Magnesium sulfate thermodynamics strongly influence sulfuric acid regeneration because $MgSO_4$ exhibits high chemical and thermal stability, which affects decomposition, sulfur oxide formation, energy demand, and overall process viability. Understanding $MgSO_4$ stability is therefore essential for evaluating both conventional and emerging sulfate-recovery technologies.

Magnesium sulfate exists in several hydrated forms depending on temperature, humidity, and water activity. Epsomite ($MgSO_4 \cdot 7H_2O$) commonly forms during evaporation, whereas kieserite ($MgSO_4 \cdot H_2O$) becomes stable at lower water activity and higher temperatures. Intermediate hydrates also occur under industrial conditions. These hydration states influence crystal morphology, solubility, thermal behavior, and decomposition pathways. During thermal regeneration, dehydration generally occurs before sulfate decomposition, increasing total energy demand.

Zhong et al. (2025) demonstrated that $MgSO_4 \cdot 7H_2O$ undergoes stepwise dehydration before sulfate dissociation, forming intermediate hydrates and eventually anhydrous $MgSO_4$. Thermogravimetric analysis revealed distinct endothermic and mass-loss stages during water removal. Although dehydration itself does not regenerate sulfuric acid, it strongly affects subsequent decomposition because sulfate dissociation depends on crystal structure, particle morphology, and residual water content. Mello et al. (2020) similarly observed that alumina-supported palladium catalysts may accelerate decomposition kinetics but do not significantly reduce $MgSO_4$'s intrinsic thermal stability.

Thermal decomposition of $MgSO_4$ produces magnesium oxide together with sulfur dioxide (SO_2), sulfur trioxide (SO_3), or mixed sulfur oxides depending on reaction atmosphere and operating conditions. Oxidizing conditions favor SO_3 formation, whereas reducing atmospheres promote SO_2 generation. Decomposition behavior depends on temperature, oxygen partial pressure, gas residence time, and solid–gas interactions. Chikhalikar et al. (2022) emphasized that sulfate–oxide equilibria become highly complex at elevated temperatures.

Compared with sulfates of iron, copper, and zinc, $MgSO_4$ decomposes at substantially higher temperatures. These other sulfates decompose more readily, facilitating their use in conventional roasting and sulfuric acid regeneration processes. Deng and Feng (2026) noted that sulfate stability varies according to cation size, bonding characteristics, and oxide stability, which influence Gibbs free energy and decomposition behavior. Consequently, no universal decomposition hierarchy exists for all sulfate systems.

This thermodynamic distinction strongly affects industrial roasting operations. Iron and copper sulfates often decompose before $MgSO_4$, allowing sulfur to remain concentrated in magnesium-rich phases. Ju et al. (2023) highlighted this phenomenon in sulfation-roasting systems for metal extraction, while Castleman et al. (2024) observed that magnesium-bearing phases may retain sulfur even after decomposition of other sulfates during ammonium sulfate roasting.

$MgSO_4$ stability is closely related to the high thermodynamic stability of MgO, which maintains sulfate stability over wide temperature ranges. As a result, complete sulfate decomposition requires temperatures considerably higher than those needed for dehydration alone. This high thermal requirement is a major limitation for industrial acid regeneration, particularly in dilute sulfate streams or systems requiring extensive water evaporation before roasting.

Sulfur oxide formation during decomposition also involves complex equilibria. SO_3 is preferred for sulfuric acid regeneration through absorption, but maintaining stable SO_3 production requires strict temperature control because SO_3 may dissociate or react with water to form corrosive condensates. Khan et al. (2022) emphasized that efficient sulfur recovery often requires catalytic oxidation and carefully controlled operating conditions. Thermogravimetric analysis remains an essential tool for evaluating sulfate decomposition pathways, dehydration stages, catalytic effects, and reaction mechanisms in $MgSO_4$ regeneration systems (Castleman et al., 2024).

The stability of $MgSO_4$ differs significantly from that of many industrial sulfates in hydrometallurgical and sulfuric acid regeneration systems. Table 2 compares key thermal and chemical properties of major sulfates relevant to regeneration.

Table 2. Thermodynamic properties and decomposition behavior of representative industrial sulfates. Adapted from Zhong et al. (2025), Mello et al. (2020), Chikhalikar et al. (2022), and Castleman et al. (2024).

Sulfate	Main hydration states	Relative thermal stability	Approximate decomposition behavior	Main sulfur oxide products	Operational implication
$MgSO_4$	Epsomite, kieserite	Very high	Requires high-temperature decomposition	SO_2/SO_3	High energy penalty
Fe sulfate	Multiple hydrated phases	Moderate	Decomposes more readily	SO_2/SO_3	Easier sulfur recovery
Cu sulfate	Pentahydrate	Moderate	Lower decomposition temperature	SO_2	Compatible with roasting systems
Zn sulfate	Hydrated and anhydrous	Moderate–high	Intermediate stability	SO_2/SO_3	Industrial roasting applicability
Al sulfate	Hydrated phases	High	Complex decomposition behavior	SO_3 dominant	Corrosion and gas-control issues

Table 2 shows $MgSO_4$ hinders sulfuric acid recycling due to its high thermal stability, raising regeneration energy compared to typical sulfate systems.

Figure 3 summarizes the key thermodynamic and chemical factors affecting $MgSO_4$ stability in sulfate systems, including sulfate formation, aqueous equilibria, hydration, impurity interactions, and operational impacts of $MgSO_4$ buildup in hydrometallurgical and sulfate-rich environments.

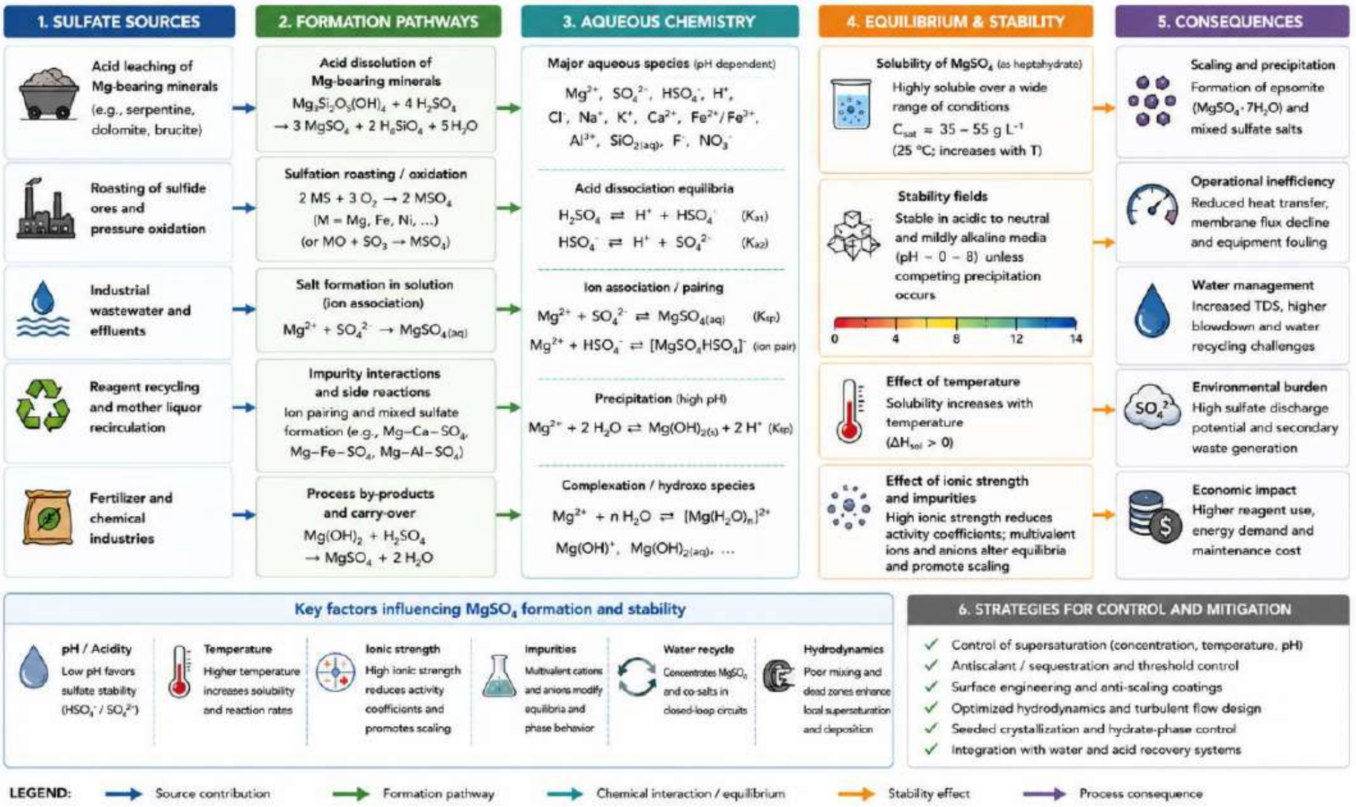


Figure 3. Thermodynamic stability, aqueous equilibria, and formation mechanisms of $MgSO_4$ in industrial sulfate-processing systems. Adapted from Zhong et al. (2025), Mello et al. (2020), Chikhalikar et al. (2022), Laasri et al. (2023), Zhao et al. (2024a), and Wang et al. (2024).

Figure 3 shows that $MgSO_4$ stability depends on acidity, hydration, impurities, and temperature, while sulfate accumulation promotes scaling, fouling, instability, and non-ideal industrial behavior.

Magnesium sulfate's stability hinders sulfuric acid regeneration from $MgSO_4$-rich streams more than from conventional systems. Sulfate decomposition depends on temperature, hydration, oxide stability, sulfur oxide thermodynamics, and gas-phase reactions. These factors limit thermal regeneration and promote alternative sulfate-recovery methods.

5. CONVENTIONAL SULFATE MANAGEMENT AND NEUTRALIZATION

Simple, robust, and suitable for large-scale applications, but they rarely enable effective sulfur recovery. Instead, they convert dissolved sulfate into secondary solids, concentrated brines, or waste streams, destroying the chemical value of sulfuric acid and generating large sulfate inventories that require long-term management.

Lime neutralization remains the dominant sulfate-control strategy in mining and metallurgy. In acidic, sulfate-rich liquors, calcium hydroxide or oxide reacts with sulfuric acid to precipitate gypsum via the formation of calcium sulfate dihydrate. This process increases pH and partially removes sulfate from solution. However, sulfate removal efficiency depends strongly on ionic strength, temperature, magnesium concentration, and competing ions. In magnesium-rich systems, substantial sulfate frequently remains dissolved even after gypsum precipitation because $MgSO_4$ is considerably more soluble than calcium sulfate.

This behavior complicates sulfate management in laterite processing and other Mg-rich hydrometallurgical circuits. Shao et al. (2022) showed that magnesium accumulation influences sulfate balance, fluoride removal, and solution chemistry, while elevated $MgSO_4$ levels hinder water recirculation and evaporation. Consequently, sulfate progressively accumulates in recycled liquors and bleed streams.

Although gypsum precipitation is operationally attractive because gypsum solids are easier to filter and transport than hydroxide sludges, the process transfers sulfur from sulfuric acid into low-value solid residues. Conventional neutralization, therefore, prioritizes short-term acidity control over long-term sulfur circularity. Even when gypsum can be reused in agriculture or construction, industrial sulfate generation often exceeds its reuse capacity, leading to the accumulation of sulfate-bearing waste.

The stability of magnesium sulfate further complicates neutralization because $MgSO_4$ remains dissolved over wide pH ranges and precipitates poorly. Song et al. (2025) demonstrated that selective magnesium separation may be improved using citric acid and sodium sulfide, although these approaches increase reagent consumption and process complexity. Such studies reflect a growing interest in selective sulfate management strategies beyond conventional neutralization.

Reactive magnesia (MgO) systems represent an alternative approach. Pereira (2025) proposed a circular process in which $MgSO_4$ hydrates are thermally converted into reactive MgO for reuse in acid-neutralization systems. Pereira and Fonseca (2025) further investigated carbothermic reduction routes for producing reactive MgO from hydrated magnesium sulfate. These approaches suggest that $MgSO_4$ may potentially function both as a waste stream and as a precursor for secondary reagents. However, regeneration of MgO from $MgSO_4$ requires high temperatures and significant energy input because of magnesium sulfate’s high thermal stability.

Neutralization systems also generate substantial sludge and secondary residues that affect filtration, water recovery, residue handling, and long-term environmental liability. Calcium neutralization typically yields more predictable gypsum solids, whereas mixed-hydroxide systems often produce poorly settling, water-retentive sludges that complicate filtration and tailings management.

Environmental impacts extend beyond sludge generation. Sulfate-rich effluents may persist in mining environments because sulfate ions remain highly mobile in water systems. Agarwal and Pandey (2023) emphasized the increasing importance of acid recycling and sulfate recovery under stricter environmental regulations. Naukkarinen (2023) similarly noted that the management of sulfuric acid strongly influences water recirculation and environmental performance in industrial operations. As industries attempt to reduce freshwater consumption and increase recycling, conventional sulfate neutralization is increasingly at odds with long-term sustainability goals.

Some operations pursue partial valorization of sulfate through secondary by-products. Lei et al. (2021) investigated the production of calcium sulfate whiskers during manganese beneficiation, demonstrating that sulfate residues may be converted into value-added materials. Nevertheless, sulfur remains immobilized rather than re-entering active sulfuric acid cycles. Table 3 compares the principal neutralization routes according to sulfate stabilization behavior, sludge generation, and sulfur-regeneration potential.

Table 3. Comparison of conventional neutralization routes and sulfate-regeneration potential. Adapted from Pereira (2025), Pereira and Fonseca (2025), Shao et al. (2022), Myers and Nakagaki (2021), and Song et al. (2025).

Neutralization route	Main reagent	Sulfate stabilization mechanism	Sludge generation	Sulfur recovery potential	Main limitation
Lime neutralization	$CaO/Ca(OH)_2$	Gypsum precipitation	High	Very low	Large residue generation
Limestone neutralization	$CaCO_3$	Calcium sulfate formation	Moderate–high	Very low	Slow kinetics
MgO neutralization	Reactive MgO	Magnesium stabilization	Moderate	Low–moderate	Energy-intensive MgO regeneration
NaOH neutralization	NaOH	Sulfate remains dissolved	Low	Low	High reagent cost
Hybrid precipitation systems	Mixed reagents	Selective sulfate stabilization	Variable	Moderate	Operational complexity

Table 3 shows that conventional neutralization primarily controls acidity rather than sulfur recovery, with most systems stabilizing sulfate in solids or residual streams rather than regenerating reusable sulfuric acid.

Figure 4 summarizes key sulfur pathways in $MgSO_4$-rich liquors, including sulfate precipitation, sludge generation, persistence of dissolved sulfate, and the effects of sulfur immobilization during neutralization-based treatment.

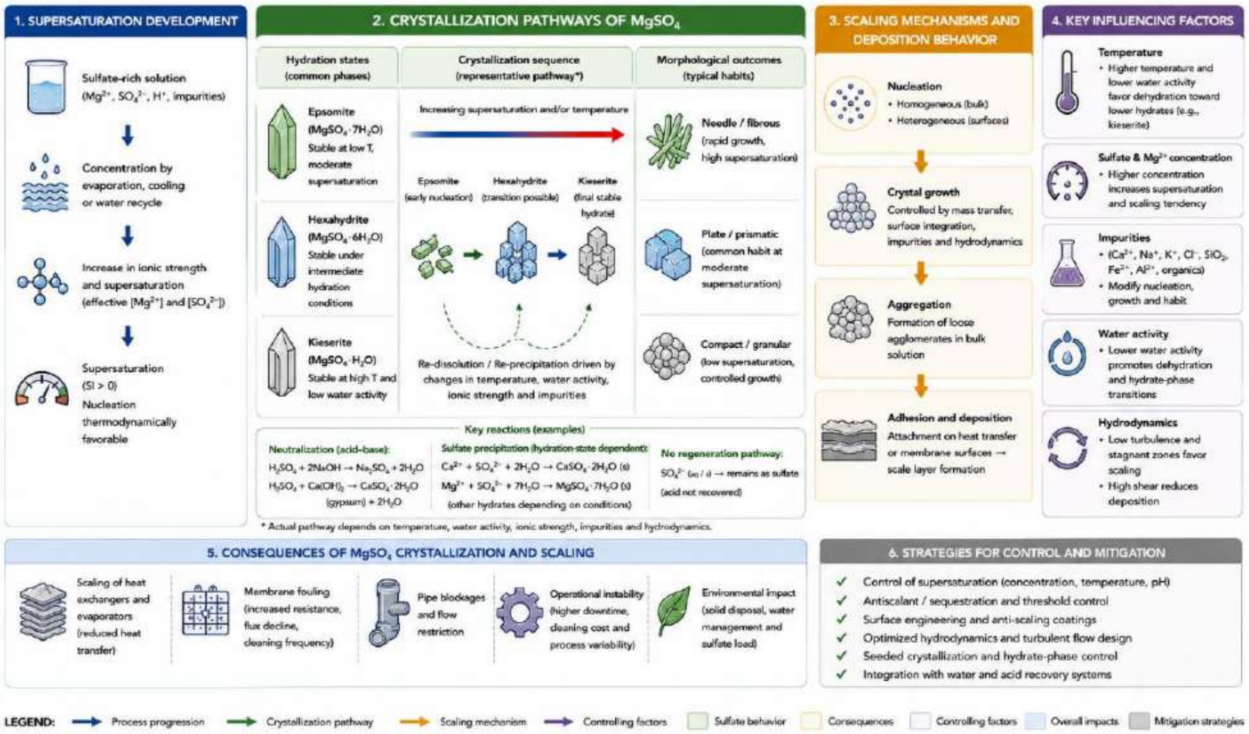


Figure 4. Sulfur pathways, sulfate stabilization behavior, and operational consequences during conventional neutralization of $MgSO_4$-rich industrial streams. Adapted from Pereira (2025), Pereira and Fonseca (2025), Shao et al. (2022), Myers and Nakagaki (2021), Lei et al. (2021), and Song et al. (2025).

Figure 4 shows that conventional neutralization stabilizes sulfur as gypsum and sulfate sludge, leading to scaling, fouling, maintenance issues, and limited sulfur recycling in industrial systems.

Conventional neutralization is vital for quick acid control in industries but often destroys sulfur instead of recovering it, leading to issues like dissolved $MgSO_4$, sludge, high water use, and residue management. The next section explains thermal regeneration of magnesium sulfate.

6. THERMAL REGENERATION OF $MgSO_4$

6.1. Direct Thermal Decomposition

Thermal regeneration recovers sulfur from magnesium sulfate by converting sulfate into sulfur oxide gases that can be reprocessed into sulfuric acid. During decomposition, $MgSO_4$ forms magnesium oxide together with SO_2- and SO_3-bearing gases, allowing partial sulfur recycling. However, industrial applications remain difficult because magnesium sulfate is one of the most thermally stable sulfates and requires substantial energy to decompose.

The process generally involves dehydration followed by sulfate dissociation. Hydrated magnesium sulfate phases, such as epsomite, first lose water to form anhydrous $MgSO_4$, which subsequently decomposes into MgO and sulfur oxides at elevated temperatures (Zhong et al., 2025). $MgSO_4$ decomposes at significantly higher temperatures than iron, copper, or zinc sulfates. Mello et al. (2020) showed that decomposition kinetics depend strongly on temperature, gas atmosphere, catalysts, and particle characteristics. Even with catalytic assistance, sulfate dissociation remains energy-intensive, limiting economic viability for dilute sulfate streams.

Roasting technologies are important for improving sulfate conversion and sulfur recovery. In sulfation roasting, sulfur-containing reagents react with minerals to form sulfates that may later be decomposed or leached. Ju et al. (2023) reviewed ammonium sulfate roasting systems and highlighted the influence of sulfate stability on metal selectivity and sulfur distribution. Although primarily developed for metal extraction, these systems also provide insight into $MgSO_4$ formation and decomposition behavior.

Nickel laterite processing frequently involves sulfation roasting to extract nickel and cobalt selectively. Zhao et al. (2024a) demonstrated that integrated sulfation–roasting–leaching systems improve metal recovery while simultaneously increasing sulfate formation. Zhao et al. (2024b) further observed that magnesium minerals stabilize sulfur during roasting, complicating sulfur recovery because $MgSO_4$ persists after many other sulfates have decomposed. Ribeiro et al. (2021) similarly reported that iron sulfates decompose at lower temperatures than $MgSO_4$, progressively enriching residues in magnesium sulfate as roasting temperature increases.

Pyrohydrolysis represents another thermally driven regeneration route in which sulfate-bearing solids react with high-temperature steam to produce gases and oxides. Zhou et al. (2021) showed that the evolution of sulfur oxides depends strongly on gas–solid equilibria and atmospheric conditions. However, pyrohydrolysis requires corrosion-resistant reactors and substantial energy input because of the aggressive sulfur-containing gases generated at high temperatures.

Spray roasting has also attracted interest because atomization improves heat transfer and gas–solid contact. Sulfate liquors are sprayed into high-temperature reactors where dehydration and decomposition occur almost simultaneously, reducing residence time and potentially improving thermal efficiency. Nevertheless, $MgSO_4$ stability still requires elevated operating temperatures, maintaining high energy demand as a major industrial limitation.

Several roasting systems developed for metal recovery provide additional insight into thermal sulfate regeneration. Abdelgalil et al. (2023), Chu et al. (2025), and Han et al. (2026) investigated ammonium sulfate roasting systems for extracting TiO_2, magnesium, aluminum, and iron from industrial residues. Similarly, Liu et al. (2021) and Ju et al. (2022) studied sulfate roasting routes for recovering rare earths and strategic metals from secondary resources. Deng and Feng (2026) emphasized that sulfate roasting involves competing decomposition pathways that are controlled by mineralogy, sulfate stability, and the roasting atmosphere. These studies collectively demonstrate that $MgSO_4$ decomposition cannot be treated as an isolated reaction because industrial sulfate regeneration involves multiple simultaneous sulfate transformations and gas-evolution mechanisms.

6.2. SO_2/SO_3 Recovery

Efficient thermal regeneration needs sulfate decomposition and effective recovery of sulfur oxide gases. Once SO_2 or SO_3 is produced, gas-cleaning and sulfur-conversion systems are vital to reduce sulfur losses and emissions. Industrial sulfur recovery typically includes particulate removal, catalytic oxidation, gas drying, and sulfuric acid absorption.

Catalytic oxidation is crucial when decomposition primarily produces SO_2, which must be converted to SO_3 for sulfuric acid production. Khan et al. (2022) reviewed catalyst development, emphasizing temperature control, oxygen availability, and catalyst stability. Catalyst deactivation, sulfur buildup, and gas impurities reduce efficiency, especially with metallurgical gases. Akola et al. (2024) showed that catalyst degradation remains a key limitation in high-temperature sulfur recovery.

Industrial sulfuric acid regeneration uses double-contact double-absorption (DCDA) systems to achieve high SO_2 conversion and low sulfur emissions. DCDA involves catalytic oxidation of SO_2 to SO_3, with intermediate absorption. Zöllner and Bollmann (2021) highlight that integrating gas cleaning, heat recovery, and sulfur conversion improves environmental and economic outcomes.

Despite technological advances, direct thermal regeneration of $MgSO_4$ remains costly for many industries due to high energy needs and corrosion challenges. It's more practical for concentrated streams or facilities with existing infrastructure.

Thermal regeneration technologies differ substantially in decomposition temperature, sulfur oxide generation behavior, and industrial applicability. Table 4 summarizes the principal thermal routes investigated for $MgSO_4$-containing systems.

Table 4. Comparison of thermal regeneration technologies for $MgSO_4$-rich streams.Adapted from Mello et al. (2020), Zhong et al. (2025), Ju et al. (2023), Han et al. (2026), and Khan et al. (2022).

Technology	Main principle	Typical temperature range	Sulfur oxide generation	Energy demand	Industrial applicability
Direct thermal decomposition	Sulfate roasting	Very high	SO_2/SO_3	Very high	Limited
Pyrohydrolysis	Steam-assisted decomposition	High	SO_2/SO_3	High	Moderate
Spray roasting	Atomized thermal decomposition	High	SO_2 dominant	High	Moderate
Sulfation roasting integration	Coupled roasting/leaching	Moderate–high	Mixed sulfur oxides	Moderate–high	High in metallurgy
Catalytic thermal decomposition	Catalyst-assisted sulfate conversion	Moderate–high	SO_3 favored	Moderate	Emerging

The data summarized in Table 4 indicate that thermal regeneration remains constrained primarily by energy demand and infrastructure requirements. Technologies that reduce the decomposition temperature may substantially improve the industrial viability of the future.

Figure 5 outlines the main technological pathways for thermal regeneration of $MgSO_4$-rich streams, including sulfate decomposition, sulfur oxide production, gas cleaning, catalytic conversion, and sulfuric acid recovery. It also highlights operational constraints of high-temperature sulfate decomposition and industrial sulfur recovery.

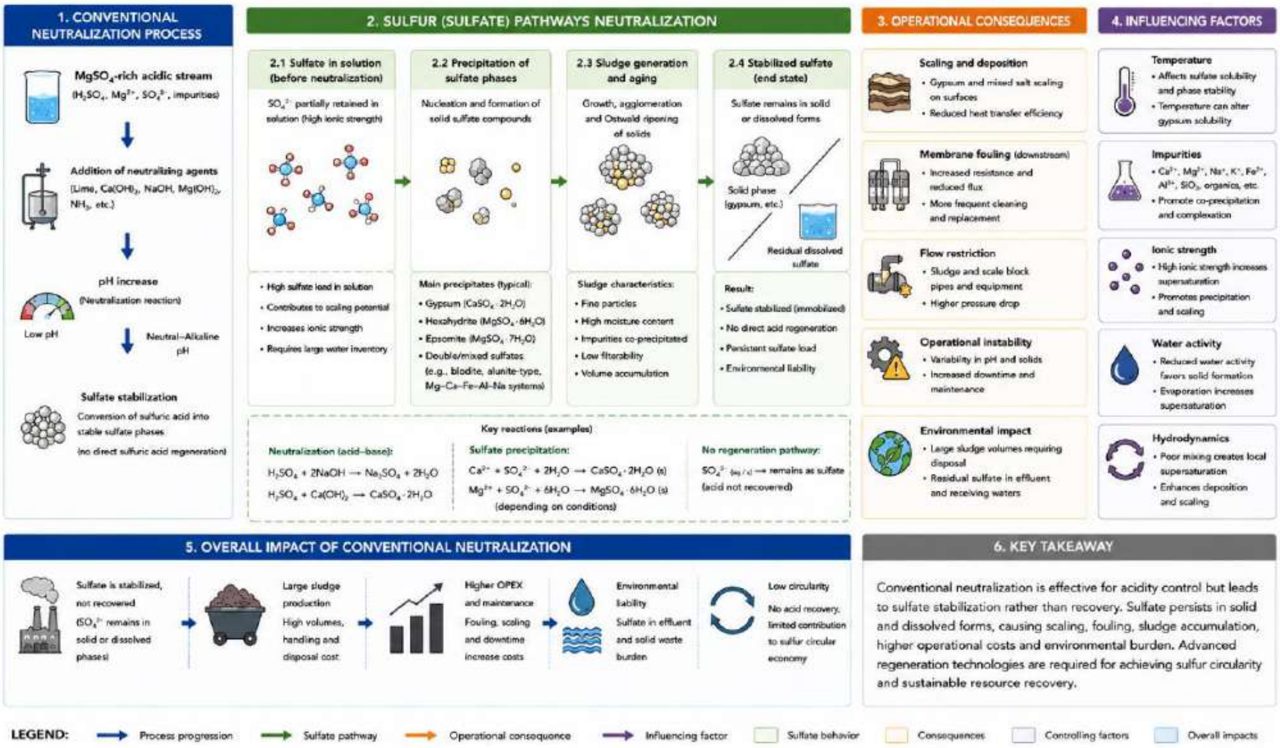


Figure 5. Integrated thermal regeneration flowsheet for $MgSO_4$-rich streams including roasting, sulfur oxide recovery, gas treatment, and sulfuric acid production pathways. Adapted from Mello et al. (2020), Zhong et al. (2025), Ju et al. (2023), Zhao et al. (2024a), Khan et al. (2022), Akola et al. (2024), and Zöllner and Bollmann (2021).

Figure 5 shows thermal $MgSO_4$ regeneration via decomposition, sulfur oxide recovery, and sulfuric acid production, highlighting energy demand, gas-treatment complexity, and infrastructure dependence.

7. MEMBRANE AND ELECTROCHEMICAL RECOVERY

Membrane and electrochemical technologies are increasingly studied for the regeneration of sulfuric acid from magnesium sulfate streams, as they enable selective acid recovery without complete sulfate decomposition. Unlike thermal methods, membrane systems separate protons, sulfate, or water via ionic transport at lower temperatures, reducing thermal energy needs. However, their practicality depends on membrane selectivity, ionic strength, impurities, osmotic behavior, and scaling, which are especially critical in $MgSO_4$-rich systems.

7.1. Diffusion Dialysis

Diffusion dialysis is a simple membrane method for recovering sulfuric acid from sulfate liquors. It uses concentration gradients across anion exchange membranes, allowing sulfate to diffuse while rejecting metal cations. Sulfuric acid can thus be recovered, leaving multivalent ions like Mg^{2+} in the feed. Cheng et al. (2021) showed that PVC/vinyl acetate-based membranes can effectively recover acid in labs.

Diffusion dialysis efficiency mainly depends on membrane selectivity between protons and cations. In $MgSO_4$ systems, sulfate's interaction with magnesium hampers proton mobility and alters transport. Zhang et al. (2020) noted that sulfuric acid recovery is sensitive to membrane structure, exchange capacity, and feed composition. High sulfate levels can boost osmotic effects and polarization, reducing proton transport efficiency.

A key limitation is the gap between laboratory solutions and real industrial liquors. Labs study simple sulfate systems with few impurities and stable pH, while industrial streams contain silica, iron, aluminum, fluoride, solids, and organics that affect membranes. Guo et al. (2025) noted non-ideal transport in mixed-salt nanofiltration, including negative rejection from ionic interactions. Similar effects likely occur in $MgSO_4$-rich diffusion dialysis, where multiple ionic interactions complicate sulfate transport and proton selectivity prediction.

7.2. Electrodialysis

Electrodialysis uses electric potential to move ions through membranes, separating acidic and salt compartments in sulfuric acid recovery. It offers better control than diffusion dialysis, but membrane stability, resistance, and energy use are challenges at high sulfate levels.

Ibrahim et al. (2024) studied electrochemical sulfuric acid recovery from magnesium sulfate in nickel processing. They found it feasible via selective ion migration, though Mg^{2+} transport, sulfate buildup, and scaling are challenges. Magnesium's strong hydration and low mobility help separate acid, but high $MgSO_4$ levels raise resistance and energy use.

Cathode scaling is a major challenge, as local pH rises near cathodes can cause magnesium hydroxide or sulfate deposits, reducing efficiency and increasing maintenance. Ibrahim et al. (2025a) showed CO_2-assisted pH control can reduce scaling and improve acid recovery in magnesium sulfate systems. This emphasizes the role of local chemical equilibria in electrochemical regeneration, not just membrane transport.

Electrodialytic acid recovery depends on current density, membrane spacing, flow regime, and electrode material. Sheth and Nath (2020) found that sulfuric acid concentration and recovery efficiency vary with operating conditions. Increasing sulfate concentration may boost conductivity but can also increase ionic competition and osmotic transport. Therefore, optimizing the process involves balancing recovery efficiency, membrane durability, sulfate rejection, and energy use.

7.3. Bipolar Membrane Electrodialysis

Bipolar membrane electrodialysis uses water dissociation at the membrane, producing H^+ and OH^- ions. It enables direct regeneration of sulfuric acid from sulfate salts and produces alkaline streams. Ivanov et al. (2026) studied electrochemical systems for magnesium leach liquors, showing potential for integrated sulfate processing.

Bipolar membrane systems convert $MgSO_4$ into sulfuric acid and magnesium precursors, but practical use faces challenges. Magnesium-rich solutions cause scaling near alkaline interfaces. Shabliy et al. (2023) showed electrochemical treatment involves complex ionic interactions, precipitation, and membrane stability. Effective operation requires careful hydrodynamic and chemical control to prevent performance loss.

Membrane durability is a key limitation. Bipolar systems operating under intense electric fields and high ionic fluxes may degrade more quickly and increase costs. Hence, stable long-term industrial operation is often harder to sustain than short-term lab acid recovery.

7.4. Membrane Distillation

Membrane distillation differs from ionic-separation technologies because it primarily targets water recovery rather than ionic transport. Using hydrophobic membranes and vapor-pressure gradients, it separates water vapor from sulfate-rich solutions and is commonly integrated with crystallization or electrochemical recovery systems.

Foureaux (2021) investigated membrane distillation combined with electrodialysis for recovering water and metals from pressure-oxidation effluents, demonstrating reduced freshwater consumption and concentration of sulfate-rich streams for downstream treatment. Murcia and Hidalgo (2021) also emphasized the importance of membrane distillation for high-salinity systems where reverse osmosis becomes inefficient.

Despite these advantages, membrane distillation remains highly sensitive to scaling and concentration polarization. In $MgSO_4$-rich liquors, sulfate concentration near membrane surfaces may exceed local solubility limits, promoting crystallization, pore wetting, and vapor-flux decline. Membrane selectivity and fouling also remain critical limitations. Schäfer and Fane (2021) noted that performance depends on coupled transport phenomena rather than membrane properties alone, while Sarkar et al. (2023) demonstrated that ionic interactions strongly affect selectivity behavior.

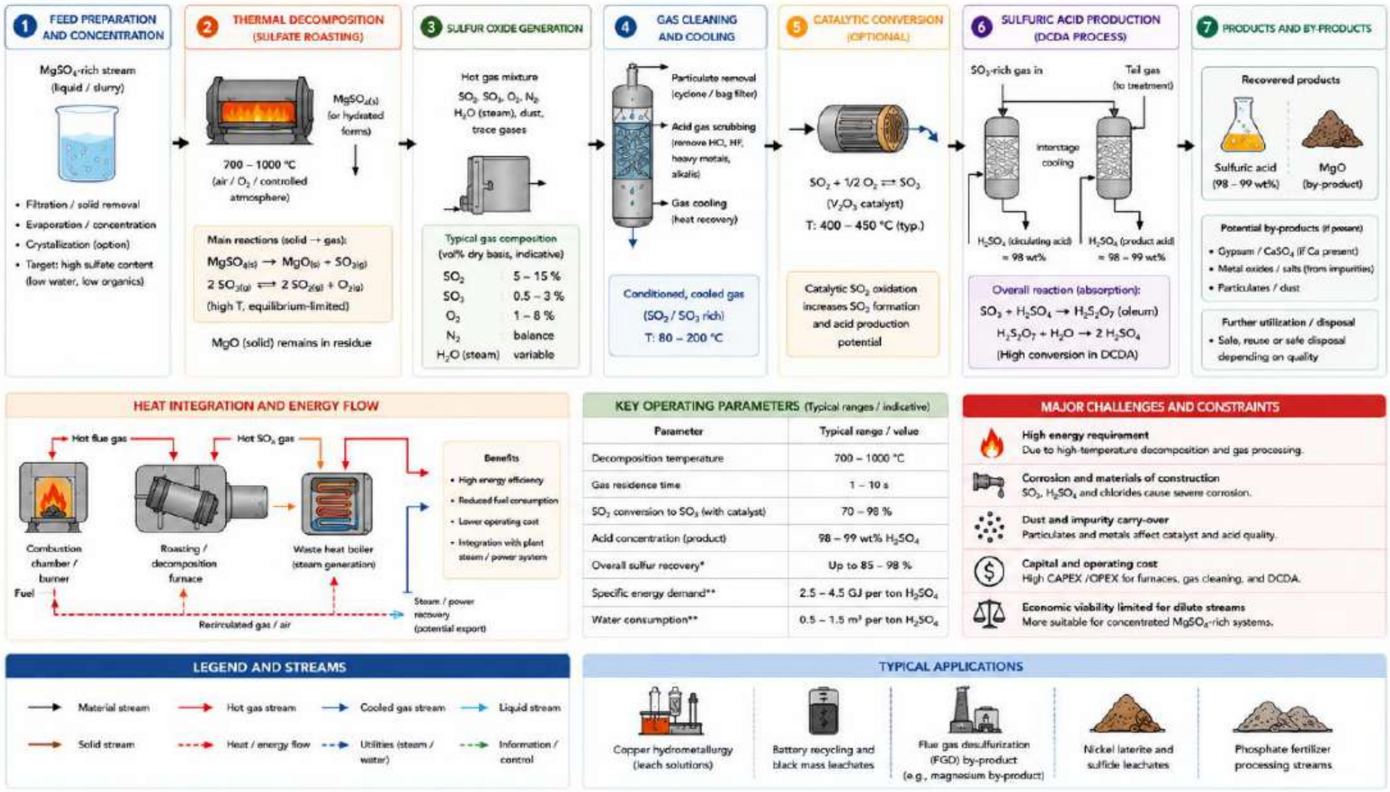
Industrial $MgSO_4$ liquors differ substantially from synthetic laboratory solutions because they contain suspended solids, silica, dissolved metals, and fluctuating sulfate concentrations. Gao et al. (2023) showed that mixed-salt systems exhibit complex rejection behavior, limiting direct extrapolation of laboratory membrane performance to industrial conditions. Table 5 compares the principal membrane-based recovery systems applied to $MgSO_4$-rich liquors.

Table 5. Comparison of membrane and electrochemical recovery technologies for $MgSO_4$ systems.Adapted from Cheng et al. (2021), Ibrahim et al. (2024), Ivanov et al. (2026), Foureaux (2021), and Schäfer and Fane (2021).

Technology	Main separation mechanism	Proton selectivity	Mg^{2+} rejection	Main limitation	Industrial maturity
Diffusion dialysis	Concentration-gradient transport	Moderate	Moderate	Limited selectivity	Pilot
Electrodialysis	Electric-field-driven migration	High	Moderate–high	Scaling	Pilot–industrial
Bipolar membrane electrodialysis	Water dissociation + ion separation	High	High	Membrane durability	Pilot
Membrane distillation	Vapor-pressure-driven separation	Indirect acid recovery	High	Scaling and wetting	Pilot
Hybrid membrane systems	Combined ionic/water separation	Variable	Variable	Operational complexity	Emerging

Table 5 shows that membrane technologies reduce thermal demand but depend on feed, scaling, and stability.

Figure 6 summarizes the main membrane and electrochemical pathways for sulfate recovery and sulfuric acid regeneration from $MgSO_4$-rich liquors. It covers diffusion dialysis, electrodialysis, bipolar membrane electrodialysis, membrane distillation, and hybrid membranes, along with their transport phenomena and operational constraints.



KEY OPERATING PARAMETERS (Typical ranges / indicative)

Parameter	Typical range / value
Decomposition temperature	700 – 1000 °C
Gas residence time	1 – 10 s
SO_2 conversion to SO_3 (with catalyst)	70 – 98 %
Acid concentration (product)	98 – 99 wt% H_2SO_4
Overall sulfur recovery*	Up to 85 – 98 %
Specific energy demand**	2.5 – 4.5 GJ per ton H_2SO_4
Water consumption**	0.5 – 1.5 m³ per ton H_2SO_4

Figure 6. Membrane and electrochemical recovery pathways for $MgSO_4$-rich streams including proton transport, sulfate separation, water recovery, and hybrid process integration. Adapted from Cheng et al. (2021), Zhang et al. (2020), Ibrahim et al. (2024), Ibrahim et al. (2025a), Ivanov et al. (2026), Foureaux (2021), Schäfer and Fane (2021), and Sarkar et al. (2023).

Figure 6 shows membrane and electrochemical systems recovering sulfuric acid and water from $MgSO_4$ streams, while scaling, fouling, impurities, and membrane durability limit industrial performance.

8. CRYSTALLIZATION, EVAPORATION, AND SALT RECOVERY

Crystallization and evaporation systems are vital in sulfate-rich industrial circuits, aiding water recovery, salt concentration, and sulfate control. In $MgSO_4$ streams, these technologies are crucial as magnesium sulfate remains dissolved after neutralization or precipitation. As sulfate builds up in recycled water, evaporation and crystallization often become necessary to maintain ionic balance, control dissolved solids, and stabilize water in closed-loop hydrometallurgical circuits. However, these systems require high thermal energy, face complex crystallization dynamics, and cause severe scaling, especially in concentrated multicomponent liquors.

Magnesium sulfate crystallization depends on temperature, water activity, evaporation rate, supersaturation, and impurities. Various hydrated phases, including epsomite, hexahydrite, and kieserite, may precipitate, impacting crystal shape, filtration, dehydration, and purity. In industry, crystallization is complicated by coexisting salts like sodium, calcium, and transition metals, making selective precipitation difficult and resulting in impurities and mixed phases.

Selective crystallization strategies exploit differences in sulfate solubility and precipitation kinetics among salts. Li et al. (2025) showed that solution chemistry influences sulfate partitioning, impurity incorporation, and crystal growth pathways. Wang et al. (2023) found that crystallization depends on thermodynamic equilibria, supersaturation gradients, evaporation, and nucleation kinetics. These effects are especially relevant in $MgSO_4$-rich systems because magnesium sulfate stays soluble longer than other phases like calcium, ferric, or aluminum sulfates. Consequently, $MgSO_4$ often remains in the final liquor, complicating sulfate removal and increasing ionic strength of recycled water.

Industrial crystallization systems often include evaporation units to concentrate dissolved salts before sulfate precipitation. Multi-effect evaporation, which reuses heat across stages, reduces steam use compared to single-stage systems, boosting thermal efficiency and lowering energy demand in large operations. However, $MgSO_4$-rich liquors are still energy-intensive, requiring removal of large water volumes to reach saturation. The high solubility of $MgSO_4$ is a key economic challenge for evaporation-based sulfate management.

Zero liquid discharge (ZLD) systems extend evaporation–crystallization to maximize water recovery and eliminate effluent discharge. They are increasingly vital in mining, hydrometallurgy, and chemical manufacturing due to stricter regulations and water scarcity. Rodríguez (2020) highlighted the integration of membrane and evaporation systems for acid and water recovery, promoting closed-loop sulfate management. Foureaux (2021) studied membrane distillation and electrodialysis for pressure-oxidation effluents, where evaporation often serves as the final concentration step.

Water recovery is vital for evaporation–crystallization, especially in arid mining and hydrometallurgy with limited freshwater. Reusing process water can be more economical than sulfate recovery. Baena-Moreno et al. (2020) found that integrated systems reduce wastewater during acid mine drainage treatment. However, higher sulfate increases scaling, crystallization issues, and instability.

Scaling in $MgSO_4$ evaporation systems causes operational issues. Water removal leads to supersaturation, precipitating sulfate salts and mineral deposits that reduce heat transfer, increase resistance, and raise maintenance needs. Unlike gypsum systems, $MgSO_4$-rich liquors form complex, hard-to-remove scales composed of magnesium, silica, calcium, aluminum, iron, and transition metals, leading to more downtime and higher costs.

Gao et al. (2023) showed that mixed-salt systems exhibit highly non-ideal ionic interactions that affect precipitation and salt rejection. Sundarajan et al. (2021) highlighted the coupling of membrane transport, sulfate saturation, and crystallization in concentrated sulfate systems. Although these studies focus on membrane separation, similar thermodynamic interactions govern evaporation and crystallization in $MgSO_4$ liquors. As a result, simplified equilibrium calculations often fail to predict actual industrial crystallization behavior.

Crystallization selectivity decreases as impurity levels rise. Industrial sulfate-rich liquors contain various species, including sodium, potassium, chloride, silica, manganese, iron, and aluminum, which can affect nucleation and crystal shape or cause co-precipitation. Consequently, the recovered sulfate salt composition often differs from laboratory predictions. Bao et al. (2025) highlight the importance of predictive modeling and reactive transport approaches for understanding salt evolution in complex systems. Their findings underscore the need to combine thermodynamic models with process analysis for industrial sulfate crystallization.

Another key limitation is that crystallization and sulfuric acid regeneration are linked but not equivalent. Evaporation and crystallization reduce wastewater and recover process water, but they do not necessarily regenerate sulfuric acid. Sulfur often remains in solid sulfate salts rather than being converted back into reusable acid. Thus, crystallization primarily manages sulfate stability rather than true sulfur recycling. This distinction matters for long-term sulfur circularity in hydrometallurgical processes.

Energy demand limits the use of large-scale evaporation systems because of high operating costs for steam, crystallizers, and heat transfer, especially for dilute $MgSO_4$ streams that require extensive water removal. Although waste-heat recovery and vapor recompression can improve efficiency, evaporation remains energy-intensive compared with ionic-separation methods such as electrodialysis, diffusion dialysis, and nanofiltration.

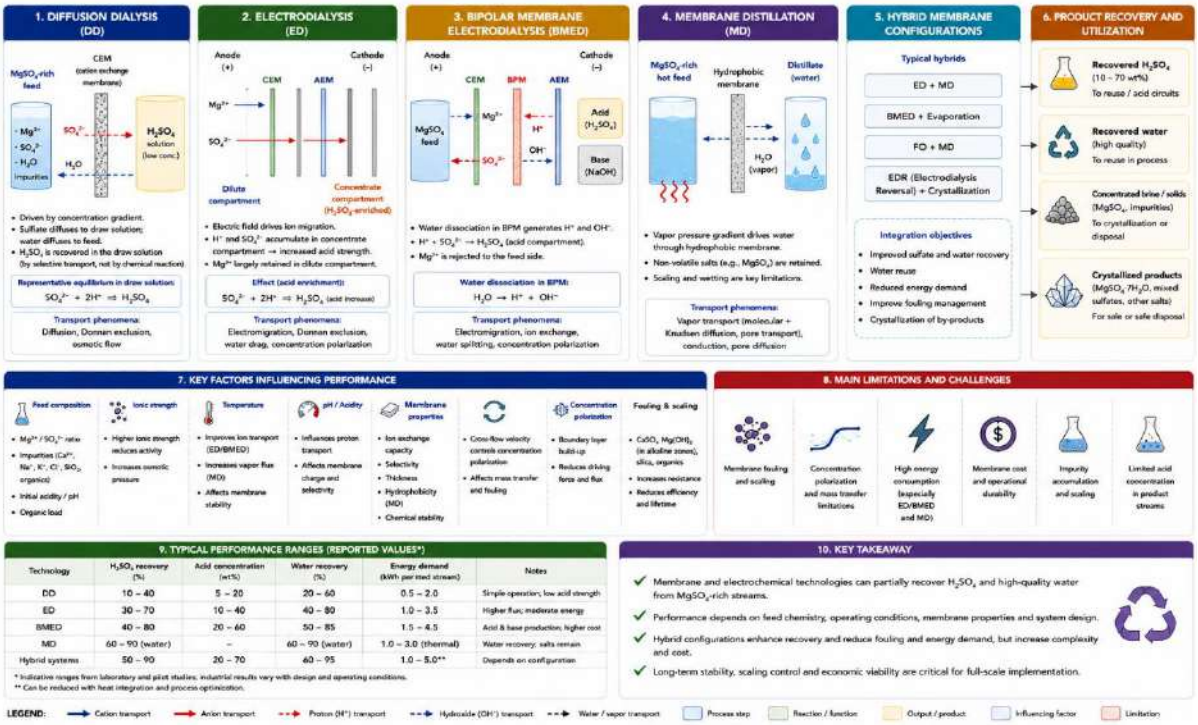
Evaporation and crystallization systems are frequently integrated into sulfate-management circuits to improve water recovery and control sulfate accumulation. Table 6 compares representative evaporation and crystallization strategies used in $MgSO_4$-containing systems.

Table 6. Comparison of evaporation and crystallization systems for $MgSO_4$-rich streams. Adapted from Li et al. (2025), Wang et al. (2023), Baena-Moreno et al. (2020), and Bao et al. (2025).

System	Main objective	Water recovery	Sulfate selectivity	Scaling tendency	Energy demand
Single-effect evaporation	Water removal	Moderate	Low	Moderate	High
Multi-effect evaporation	Energy-efficient concentration	High	Low	Moderate–high	Moderate
Forced-circulation crystallizer	Salt recovery	Moderate	Moderate	High	Moderate–high
ZLD system	Eliminate liquid discharge	Very high	Moderate	Very high	Very high
Hybrid evaporation–membrane system	Water and sulfate management	High	Moderate	Moderate–high	Moderate

Table 6 shows evaporation systems boost water recovery but tend to transfer sulfur into sulfate solids rather than regenerate reusable sulfuric acid.

Figure 7 summarizes the evaporation–crystallization pathways for $MgSO_4$-rich streams, covering sulfate concentration, water recovery, salt precipitation, and ZLD operation. It combines evaporation, crystallization, sulfate phases, and process strategies relevant to industrial sulfate management.



Technology	H_2SO_4 recovery (%)	Acid concentration (wt%)	Water recovery (%)	Energy demand (kWh per treated stream)	Notes
DD	10 – 40	5 – 20	20 – 60	0.5 – 2.0	Simple operation; low acid strength
ED	30 – 70	10 – 40	40 – 80	1.0 – 3.5	Higher flux; moderate energy
BMED	40 – 80	20 – 60	50 – 85	1.5 – 4.5	Acid & base production; higher cost
MD	60 – 90 (water)	–	60 – 90 (water)	1.0 – 3.0 (thermal)	Water recovery; salts remain
Hybrid systems	50 – 90	20 – 70	60 – 95	1.0 – 5.0**	Depends on configuration

* Indicative ranges from laboratory and pilot studies; industrial results vary with design and operating conditions.
** Can be reduced with heat integration and process optimization.

- ✓ Membrane and electrochemical technologies can partially recover H_2SO_4 and high-quality water from $MgSO_4$-rich streams.
- ✓ Performance depends on feed chemistry, operating conditions, membrane properties and system design.
- ✓ Hybrid configurations enhance recovery and reduce fouling and energy demand, but increase complexity and cost.
- ✓ Long-term stability, scaling control and economic viability are critical for full-scale implementation.

Figure 7. Integrated evaporation–crystallization pathways for $MgSO_4$-rich streams including water recovery, sulfate concentration, salt precipitation, and ZLD integration. Adapted from Li et al. (2025), Wang et al. (2023), Baena-Moreno et al. (2020), Foureaux (2021), Gao et al. (2023), Sundarajan et al. (2021), and Bao et al. (2025).

Figure 7 shows evaporation–crystallization concentrating sulfate streams for water recovery and salt stabilization, while increasing scaling, operational instability, and sulfur retention in solid phases.

9. HYBRID REGENERATION SYSTEMS

No current technology efficiently regenerates sulfuric acid from $MgSO_4$-rich streams. Thermal decomposition requires a high energy input, membranes suffer from fouling and ionic limitations, and crystallization stabilizes sulfur rather than regenerating a reusable acid. As a result, the industry is increasingly adopting hybrid systems that combine different technologies to improve sulfur recovery, water reuse, and overall process efficiency.

Hybrid systems commonly integrate membrane separation with evaporation or crystallization. Membranes are used first to recover water or partially separate acid, while crystallization controls sulfate accumulation and salt precipitation. Rodríguez (2020) reported that membrane preconcentration prior to evaporation reduces osmotic stress and membrane loading, especially in $MgSO_4$-rich liquors, where magnesium sulfate remains dissolved after proton separation. However, sulfate buildup can still promote supersaturation and scaling in downstream units, particularly at high ionic strength.

Integrated membrane–electrochemical systems are also receiving attention. Foureaux (2021) investigated the combination of membrane distillation and electrodialysis for sulfate-rich pressure-oxidation effluents. Membrane distillation concentrated sulfate streams, while electrodialysis recovered acid and improved water reuse. Compared with isolated operations, the integrated system reduced freshwater consumption and enhanced process integration. Nevertheless, impurity accumulation still generated scaling and operational instability, showing that hybrid systems are limited not only by individual technologies but also by interactions between process stages.

Electrodialysis coupled with electrochemical control can partially recover sulfuric acid from $MgSO_4$ solutions. Ibrahim et al. (2025b) demonstrated that integrated electrochemical control reduces cathode scaling and improves acid separation. In these systems, acid recovery depends on ionic migration, conductivity, precipitation behavior, and current efficiency rather than membrane selectivity alone. Consequently, hybrid-system performance is governed by interactions among transport phenomena, thermodynamics, and operating conditions.

Hybrid configurations also enable partial sulfur closure when complete acid regeneration is impractical. Many $MgSO_4$ streams are too dilute or chemically unstable for full recovery, so only part of the sulfur is regenerated as reusable acid while the remainder is stabilized, crystallized, or diverted to secondary uses. This approach differs from conventional neutralization by integrating sulfur recovery with water and reagent management.

Thermal systems can also benefit from hybrid integration. $MgSO_4$ decomposition units may be coupled with sulfuric acid plants so sulfur oxides generated during decomposition are processed using existing infrastructure. This reduces capital costs but requires stable sulfate feed composition and adequate gas purity, since fluctuations and impurities can reduce efficiency.

Water–acid–energy integration has become central to sulfate management. O'Sullivan and Williams (2024) emphasized that sulfate recovery must be evaluated together with water recirculation and energy consumption. In many $MgSO_4$-rich circuits, water removal is the main operational cost because sulfate concentrations often remain below the thresholds for efficient regeneration. Hybrid systems, therefore, integrate acid recovery, water reuse, and waste-heat utilization to improve overall economics even when sulfuric acid recovery remains moderate.

Heat integration is especially important in evaporation-intensive systems. Waste heat from roasting furnaces, sulfuric acid plants, and off-gases can supply energy for crystallization and concentration stages. Wang et al. (2024) showed that sulfate management increasingly depends on optimizing heat recovery, water recirculation, and reagent efficiency simultaneously rather than independently.

Emerging modular sulfate-management systems decentralize treatment stages according to local sulfate concentrations and infrastructure conditions. These systems may combine electrochemical recovery, membrane concentration, crystallization, and thermal treatment in flexible configurations suitable for remote mining operations and medium-scale facilities where dedicated regeneration plants are economically impractical. Despite their advantages, hybrid systems introduce operational complexity because interactions between unit operations can intensify scaling, alter impurity behavior, and reduce separation efficiency. Therefore, industrial sulfate management requires integrated evaluation of transport, thermodynamics, water balance, and impurity interactions rather than isolated optimization of individual technologies. Circular hydrometallurgy further reinforces this trend by promoting simultaneous recovery of reagents, water, and secondary materials to reduce environmental impact and operational costs.

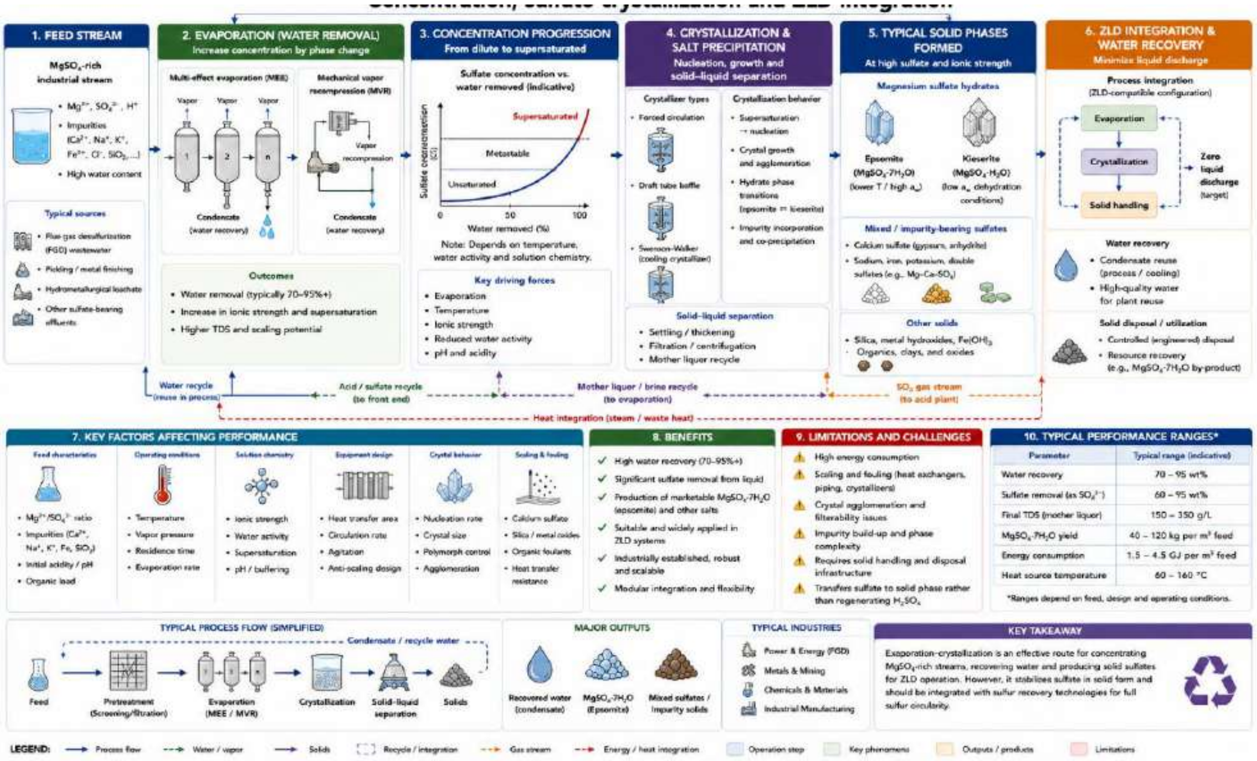
Hybrid regeneration systems attempt to integrate multiple technologies to balance sulfur recovery, water reuse, and operational flexibility. Table 7 summarizes representative hybrid regeneration strategies.

Table 7. Comparison of hybrid $MgSO_4$ regeneration strategies and process-integration characteristics. Adapted from Ibrahim et al. (2025b), Rodríguez (2020), Foureaux (2021), and Binnemans and Jones (2023b).

Hybrid strategy	Main integration concept	Sulfur recovery behavior	Water integration	Main advantage	Main limitation
Membrane + crystallization	Acid recovery + sulfate concentration	Partial	High	Reduced membrane load	Scaling
Membrane + electrodialysis	Ionic separation integration	Moderate	Moderate–high	Improved selectivity	Conductivity losses
Thermal + sulfuric acid plant	Integrated sulfur oxide conversion	High	Low–moderate	Existing infrastructure use	High CAPEX
Evaporation + electrochemical recovery	Water removal + acid separation	Moderate	High	Flexible operation	Energy demand
Modular hybrid systems	Distributed recovery architecture	Variable	Variable	Operational flexibility	Complex control

Table 7 demonstrates that hybrid regeneration systems distribute sulfate management across interconnected unit operations instead of relying on a single recovery

Figure 8 depicts a sulfate-management framework with membrane separation, electrochemical recovery, thermal regeneration, evaporation–crystallization, and water recirculation for $MgSO_4$-rich streams. It shows how hybrid systems spread sulfate management across units, not a single technology.



Parameter	Typical range (indicative)
Water recovery	70 – 95 wt%
Sulfate removal (as SO_4^{2-})	60 – 95 wt%
Final TDS (mother liquor)	150 – 350 g/L
$MgSO_4·7H_2O$ yield	40 – 120 kg per m³ feed
Energy consumption	1.5 – 4.5 GJ per m³ feed
Heat source temperature	60 – 160 °C

*Ranges depend on feed, design and operating conditions.

Evaporation-crystallization is an effective route for concentrating $MgSO_4$-rich streams, recovering water and producing solid sulfates for ZLD operation. However, it stabilizes sulfate in solid form and should be integrated with sulfur recovery technologies for full sulfur circularity.

Figure 8. Integrated circular sulfate-management framework for $MgSO_4$-rich streams combining membrane separation, electrochemical recovery, crystallization, thermal regeneration, and water–energy integration. Adapted from Ibrahim et al. (2025b), Rodríguez (2020), Foureaux (2021), Binnemans and Jones (2023b), O'Sullivan and Williams (2024), and Wang et al. (2024).

Figure 8 shows a hybrid sulfate-management system integrating acid recovery, water reuse, crystallization, and energy recovery, while operational complexity and scaling remain major industrial challenges.

10. ENVIRONMENTAL AND SUSTAINABILITY CHALLENGES

Environmental management has become a major driver for sulfuric acid regeneration from magnesium sulfate ($MgSO_4$) streams. Historically, sulfate handling focused mainly on wastewater neutralization and residue disposal, but stricter environmental regulations, water scarcity, waste accumulation, and decarbonization targets have expanded the importance of sulfur management. Environmental performance in $MgSO_4$ systems depends not only on sulfur recovery efficiency, but also on water consumption, energy demand, residue generation, emissions, and long-term by-product stability.

Sulfate discharge remains a critical issue in mining, hydrometallurgy, and wastewater treatment because sulfate ions are highly soluble and persistent in aquatic systems. Wen et al. (2020) reported that sulfate-rich acid mine drainage can increase salinity and osmotic stress in aquatic ecosystems. Unlike many metals, sulfate is difficult to immobilize under neutral conditions, complicating long-term containment.

Secondary residue generation is another major limitation. Conventional neutralization transfers sulfur into gypsum or sulfate-containing solids instead of regenerating sulfuric acid, producing large residue volumes that require long-term disposal.

This issue is particularly severe for high-magnesium ores because $MgSO_4$ may remain partially dissolved after neutralization. Baena-Moreno et al. (2020) observed that integrated water and salt recovery systems can reduce sulfate discharge, although they frequently shift contaminants into concentrated brines or solid residues rather than eliminating them.

Membrane and evaporation systems also generate concentrated brines rich in sulfate, magnesium, chloride, and impurities. Technologies such as electrodialysis, reverse osmosis, and membrane distillation can recover water and partially recycle sulfur species, but brine disposal remains challenging because of high salinity, low biodegradability, and limited reuse potential.

Thermal regeneration presents different environmental trade-offs. Sulfate roasting and decomposition can regenerate sulfuric acid and reduce sulfate accumulation, but may release sulfur oxides (SO_2 and SO_3) if gas-cleaning systems are inadequate. Khan et al. (2022) emphasized the importance of catalytic conversion and gas treatment to minimize sulfur emissions. Although thermal systems reduce sulfate discharge, they generally require high energy input and may increase greenhouse-gas emissions.

Carbon footprint is therefore a critical factor in sulfate-management evaluation. High sulfur recovery efficiency does not necessarily correspond to low environmental impact. Naukkarinen (2023) demonstrated that sulfuric acid production and regeneration strongly affect environmental performance through energy use and emissions, while Myers and Nakagaki (2021) highlighted trade-offs among residue stabilization, energy demand, and sustainability.

Water recirculation further complicates sulfate management because closed-loop systems increase ionic strength and impurity accumulation. Bao et al. (2025) emphasized that predictive assessment of concentrated sulfate systems requires integrated understanding of reactive transport, salt evolution, and process chemistry. Circular hydrometallurgy concepts increasingly promote simultaneous recovery of reagents, water, and materials. Binnemans and Jones (2023b) argued that $MgSO_4$-rich streams should be viewed not only as environmental liabilities but also as potential sulfur reservoirs. However, Agarwal and Pandey (2023) stressed that sustainability assessment must integrate waste generation, energy demand, and operational feasibility in addition to sulfur recovery efficiency.

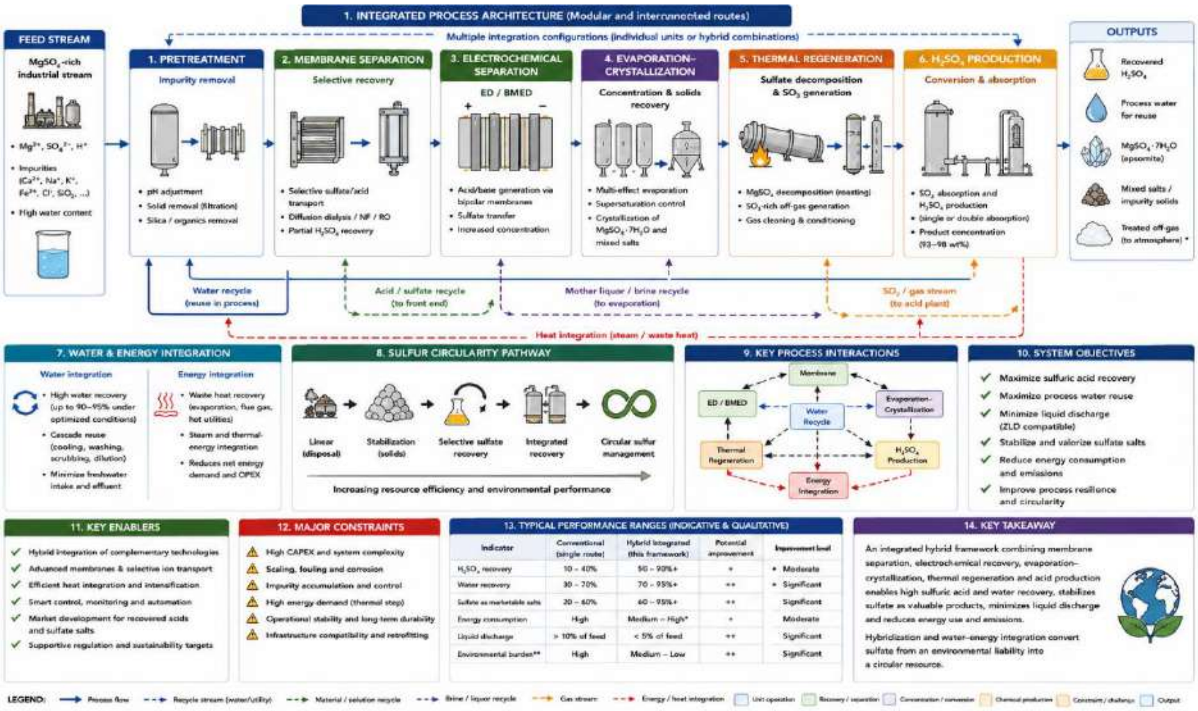
The environmental performance of $MgSO_4$-management technologies depends on interconnected trade-offs among water use, residue generation, energy demand, and sulfur emissions. Table 8 summarizes the principal environmental implications of sulfate-management routes.

Table 8. Environmental trade-offs associated with $MgSO_4$ management technologies. Adapted from Wen et al. (2020), Baena-Moreno et al. (2020), Khan et al. (2022), Naukkarinen (2023), and Vivar et al. (2025).

Technology	Sulfate discharge	Secondary waste generation	SOx emission potential	Water impact	Carbon footprint
Neutralization	Moderate	High	Low	High water use	Moderate
Thermal regeneration	Low	Moderate	High if uncontrolled	Moderate	High
Membrane systems	Low–moderate	Concentrated brines	Very low	Low–moderate	Low–moderate
Crystallization/ZLD	Very low	High salt generation	Very low	Very high recovery	High energy demand
Hybrid systems	Variable	Moderate	Moderate	High recovery potential	Variable

Table 8 shows that high sulfur recovery efficiency does not necessarily translate into lower environmental impact, as many regeneration systems simultaneously increase energy consumption or secondary residue generation.

Figure 9 outlines key environmental pathways in $MgSO_4$ management, including sulfate discharge, waste, emissions, disposal, and recovery in industrial systems. It shows how these relate to sulfate accumulation, sulfur recovery, residue stabilization, and water recirculation.



Indicator	Conventional (single route)	Hybrid integrated (this framework)	Potential improvement	Improvement level
H$_2$SO$_4$ recovery	10 – 40%	50 – 90%+	+	• Moderate
Water recovery	30 – 70%	70 – 95%+	++	• Significant
Sulfate as marketable salts	20 – 60%	60 – 95%+	++	Significant
Energy consumption	High	Medium – High*	+	Moderate
Liquid discharge	> 10% of feed	< 5% of feed	++	Significant
Environmental burden**	High	Medium – Low	++	Significant

An integrated hybrid framework combining membrane separation, electrochemical recovery, evaporation–crystallization, thermal regeneration and acid production enables high sulfuric acid and water recovery, stabilizes sulfate as valuable products, minimizes liquid discharge and reduces energy use and emissions.

Hybridization and water–energy integration convert sulfate from an environmental liability into a circular resource.

Figure 9. Environmental pathways associated with MgSO$_4$ management including sulfate discharge, sulfur recovery, residue stabilization, water recirculation, and atmospheric emissions.Adapted from Wen et al. (2020), Baena-Moreno et al. (2020), Bao et al. (2025), Khan et al. (2022), Naukkarinen (2023), Myers and Nakagaki (2021), and Binnemans and Jones (2023b).

Figure 9 illustrates environmental trade-offs in sulfate management across emissions, residues, water reuse, and energy demand, showing that high sulfur recovery does not guarantee a lower environmental impact.

The environmental performance of sulfate-management systems depends on trade-offs, not just sulfur recovery efficiency. In MgSO$_4$-rich circuits, reducing sulfate discharge can increase energy use, while maximizing water recirculation may worsen concentrate-management issues. This highlights the need for integrated assessment of water, energy, emissions, and residues in sulfuric acid regeneration.

11. THERMODYNAMIC, KINETIC, AND PREDICTIVE MODELING

Predictive modeling is vital for evaluating sulfuric acid regeneration from magnesium sulfate systems because experimental observation alone cannot fully describe the thermodynamic, kinetic, and transport phenomena influencing industrial operations. In MgSO$_4$-rich circuits, sulfate behavior hinges on hydration, gas–solid reactions, ionic interactions, heat transfer, and multicomponent transport. Thus, modeling helps predict decomposition, optimize recovery, estimate energy use, and assess operational constraints in industrial settings.

Thermodynamic equilibrium modeling underpins most sulfate-regeneration analyses, estimating sulfate stability, sulfur oxide production, phase changes, and decomposition points. In MgSO$_4$ systems, models identify temperature ranges favoring sulfate dissociation and predict SO$_2$ and SO$_3$ formation under various conditions. Nonetheless, equilibrium models alone often fall short of real-world accuracy due to kinetic and transport limitations in many systems.

Mello et al. (2020) showed magnesium sulfate decomposition depends on thermodynamics, catalyst behavior, particle shape, and gas atmosphere. Their thermogravimetric analyses revealed multiple intermediate stages, not just a single equilibrium-controlled transition. Zhong et al. (2025) also reported sequential dehydration and decomposition in hydrated MgSO$_4$, emphasizing hydration's strong effect on thermal response. These findings suggest equilibrium predictions alone cannot fully explain sulfate decomposition in industrial roasting.

Kinetic modeling is vital for predicting decomposition, residence times, and operational aspects in thermal regeneration systems, affecting furnace sizing, energy, sulfur oxide release, and heat transfer. Castleman et al. (2024) noted thermogravimetric methods with kinetic analysis enhance understanding of sulfate breakdown during roasting. Reaction-rate models help identify different regimes, crucial since $MgSO_4$ decomposition often occurs under uneven temperatures and transient conditions.

Computational fluid dynamics (CFD) is increasingly important for analyzing gas–solid interactions and thermal transport in roasting and decomposition systems. CFD models simulate temperature gradients, gas residence time, sulfur oxide distribution, and particle flow in reactors. In spray-roasting and pyrohydrolysis, these models are especially useful because sulfate decomposition depends on local heat transfer and gas mixing. However, CFD predictions are sensitive to assumptions about particle properties, reaction kinetics, and turbulence.

Transport modeling is crucial in membrane and electrochemical recovery, especially for acid separation in $MgSO_4$-rich liquors. Ibrahim et al. (2025c) found that ion transport in sulfuric acid recovery from magnesium sulfate can't be explained by ideal dilute-solution assumptions, as ionic interactions, conductivity changes, and pH gradients significantly influence electrochemical behavior.

Non-ideal solution chemistry hampers predictive accuracy in sulfate-management. Gao et al. (2023) showed mixed-salt systems often have coupled ionic interactions causing unexpected transport and rejection, especially in $MgSO_4$-rich industrial streams with high ionic strength. Under these conditions, activity coefficients, ion pairing, and supersaturation can diverge from ideal thermodynamics.

Reactive transport modeling integrates chemical and transport phenomena. Bao et al. (2025) highlight that sulfate-rich systems involve simultaneous reactions like dissolution, precipitation, evaporation, and ionic migration. These models predict sulfate buildup, salt pathways, and water recirculation, especially useful in closed-loop hydrometallurgical systems where sulfate levels change over time.

Artificial intelligence and machine-learning are emerging in sulfate-management studies, especially for membrane performance, crystallization, and process optimization. Sarkar et al. (2023) showed membrane transport involves complex, coupled variables that are hard to model mechanistically. ML may complement traditional methods by uncovering operational correlations in complex systems.

Despite advances, $MgSO_4$ regeneration modeling remains limited by lack of industrial validation. Many models are calibrated on simplified lab systems with controlled conditions, unlike industrial sulfate liquors. Industrial systems involve fluctuating compositions, transient conditions, solids, and variable heat, increasing predictive uncertainty during scale-up.

Another important limitation involves the integration of different modeling approaches. Thermodynamic calculations, kinetic decomposition models, CFD simulations, electrochemical transport models, and machine-learning tools are often developed independently rather than within unified frameworks. This fragmentation may reduce predictive consistency when evaluating integrated sulfate-management systems that simultaneously combine thermal, membrane, and crystallization technologies.

Predictive modeling has become increasingly important for understanding sulfate behavior in $MgSO_4$-rich industrial systems. Table 9 summarizes the principal modeling approaches applied to regeneration technologies.

Table 9. Predictive modeling approaches applied to $MgSO_4$ regeneration systems. Adapted from Mello et al. (2020), Castleman et al. (2024), Bao et al. (2025), and Sarkar et al. (2023).

Modeling approach	Main objective	Typical application	Main limitation
Thermodynamic equilibrium modeling	Predict sulfate stability	Decomposition prediction	Limited kinetic representation
Kinetic modeling	Predict reaction rates	Thermal decomposition	Requires experimental calibration
CFD	Simulate reactor transport	Roasting and pyrohydrolysis	Computational complexity
Reactive transport modeling	Coupled chemistry and transport	Sulfate accumulation	High parameter sensitivity
AI-assisted prediction	Multivariable optimization	Membrane/process control	Limited industrial datasets

The modeling approaches summarized in Table 9 demonstrate that industrial sulfate-management systems are governed by coupled non-ideal interactions rather than equilibrium chemistry alone.

Figure 10 shows the hierarchy of predictive frameworks for $MgSO_4$ regeneration and sulfate-management systems, combining thermodynamic equilibrium, kinetic analysis, CFD, reactive transport, electrochemical modeling, and AI approaches. It illustrates how methodologies progress from simple equilibrium calculations to integrated multiscale process-control frameworks for industrial sulfate systems.

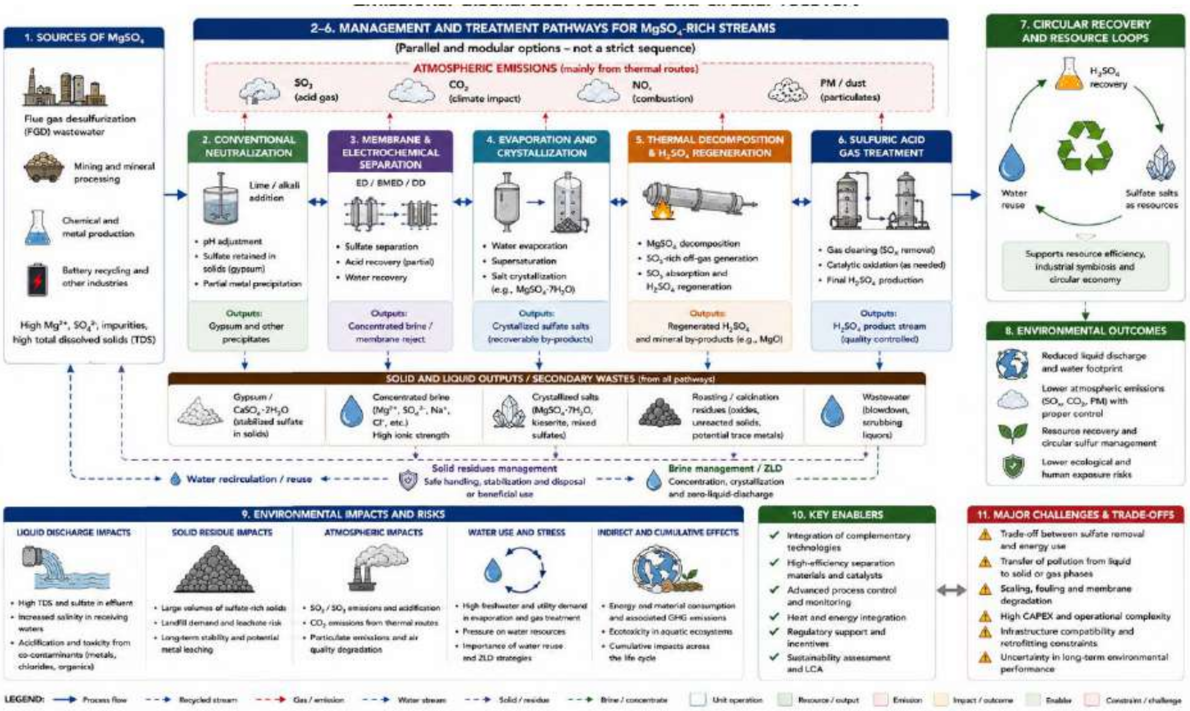


Figure 10. Hierarchy of predictive frameworks for $MgSO_4$ regeneration systems including thermodynamic, kinetic, transport, CFD, reactive transport, and AI-assisted modeling approaches. Adapted from Mello et al. (2020), Zhong et al. (2025), Castleman et al. (2024), Ibrahim et al. (2025c), Gao et al. (2023), Bao et al. (2025), Sarkar et al. (2023), and Schäfer and Fane (2021)

Figure 10 shows predictive $MgSO_4$ modeling that integrates thermodynamics, kinetics, transport, CFD, and AI, highlighting non-ideal industrial behavior and the growing need for integrated process prediction.

The growing complexity of sulfate-management systems demands predictive methods that integrate thermodynamics, kinetics, transport, and operational variability. In $MgSO_4$-rich systems, performance isn't solely dictated by equilibrium but results from non-ideal interactions among chemical stability, transport, energy, and dynamic conditions.

12. COMPARATIVE CRITICAL ANALYSIS

Comparative $MgSO_4$ regeneration shows performance depends more on energy use, impurity tolerance, robustness, and integration than sulfur recovery efficiency. Various systems like thermal, membrane, crystallization, and hybrid address specific limitations, but none excel in all conditions. Thus, technology choice depends on sulfate levels, water, infrastructure, and scale.

Thermal regeneration is a direct way to convert $MgSO_4$ into reusable sulfuric acid, as sulfur oxides can be reintegrated into traditional acid-production systems. The process needs very high temperatures due to magnesium sulfate's thermal stability. Mello et al. (2020) showed that $MgSO_4$ decomposition stays energy-intensive, even with catalysts. Consequently, thermal systems have high CAPEX from furnaces, refractory materials, gas-cleaning, and sulfuric acid absorption equipment. OPEX is also driven by fuel use and heat management.

Despite disadvantages, thermal systems have greater impurity tolerance than membrane tech, allowing use with sulfate liquors containing solids, silica, iron, and metals without severe selectivity loss. This robustness makes thermal regeneration attractive for sulfate streams in sulfuric acid plants. Zöllner and Bollmann (2021) noted that industrial acid-regeneration systems prioritize reliability and gas efficiency over maximum sulfur recovery.

Membrane and electrochemical technologies operate at lower temperatures, reducing thermal energy demand. Rodríguez (2020) discussed membrane systems recovering water and regenerating sulfuric acid from sulfate streams. Ibrahim et al. (2024) showed electrochemical sulfuric acid separation from $MgSO_4$ solutions is feasible in nickel laterite processing. These methods tend to emit less carbon than thermal decomposition.

Membrane systems often show lower tolerance to industrial impurities and changing solution chemistry. Factors like high ionic strength, suspended solids, and sulfate variations can affect membrane selectivity and transport, causing laboratory results with synthetic sulfate solutions to overestimate true industrial recovery. Thus, despite good energy profiles in controlled tests, membrane systems may have reduced robustness in actual industrial settings.

Centralized and distributed recovery strategies have trade-offs. Centralized systems benefit from economies of scale, integrated utilities, and shared sulfuric acid infrastructure, enabling stable long-term operation with high sulfate throughput. However, they require large capital and stable feed, making them less suitable for remote or moderate-scale operations.

Distributed or modular systems offer greater flexibility and can better handle variable sulfate inventories. Modular units can be placed closer to sulfate sources, reducing transport needs and enabling partial sulfur closure locally. However, they often have lower sulfur recovery and are more sensitive to feed changes. O’Sullivan and Williams (2024) highlighted that sulfate management now depends more on integrating with local water, energy, and scale than on recovery tech alone.

The comparison between regeneration and neutralization highlights a key difference in sulfate-management philosophy. Neutralization mainly controls acidity and stabilizes residues, while regeneration aims to retain sulfur in the industrial circuit. Agarwal and Pandey (2023) noted that neutralization often converts sulfur into low-value gypsum or sludge rather than recovering reusable acid. Neutralization systems are usually simpler and cheaper initially, but long-term operational costs for residue management, water use, and sulfate disposal can become significant.

Direct sulfate recycling converts sulfate to sulfuric acid via thermal or electrochemical methods, whereas indirect recycling integrates sulfate residues into other industrial uses, such as gypsum valorization or magnesia production. Indirect methods reduce waste but often don't fully restore sulfuric acid's functionality.

TRL varies across regeneration methods. Conventional neutralization and sulfuric acid plant integration operate at industrial scale, whereas thermal $MgSO_4$ decomposition is constrained by energy economics and infrastructure. Membrane and electrochemical systems are at intermediate TRL, with some pilot demonstrations but limited industrial use for $MgSO_4$-rich streams. Ju et al. (2023) noted scale-up challenges such as heat transfer, impurity buildup, and operational stability. Akola et al. (2024) also highlighted catalyst durability and sulfur oxide conversion as key operational limits.

Mends et al. (2025) showed that sulfate processing needs integrated evaluation of energy, infrastructure, and chemistry, not just technology optimization. Therefore, assessing $MgSO_4$ regeneration should go beyond sulfur recovery percentages. Factors like robustness, impurity tolerance, water use, and infrastructure often matter more than recovery efficiency.

Comparative assessment of sulfate-management technologies requires simultaneous evaluation of economics, robustness, energy demand, and impurity tolerance. Table 10 compares the principal $MgSO_4$ management routes.

Table 10. Comparative critical assessment of $MgSO_4$ management technologies. Adapted from Yadav et al. (2026), Ibrahim et al. (2024), O’Sullivan and Williams (2024), and Mends et al. (2025).

Technology	TRL	CAPEX	OPEX	Energy demand	Impurity tolerance	Operational robustness
Neutralization	High	Low	Moderate	Low	High	High
Thermal regeneration	Moderate	High	High	Very high	High	High
Membrane systems	Moderate	Moderate	Moderate	Moderate	Low–moderate	Moderate
Electrochemical recovery	Moderate	Moderate–high	Moderate	Moderate	Moderate	Moderate
Hybrid systems	Emerging–moderate	High	Moderate	Variable	Moderate–high	Moderate–high

Table 10 indicates that no single technology simultaneously maximizes sulfur recovery, impurity tolerance, operational stability, and economic performance.

Figure 11 compares key $MgSO_4$ management and sulfuric acid regeneration methods, covering thermal, membrane, electrochemical, crystallization, neutralization, and hybrid routes. It highlights trade-offs in TRL, CAPEX, OPEX, energy use, sulfur recovery, impurity tolerance, robustness, and scalability.

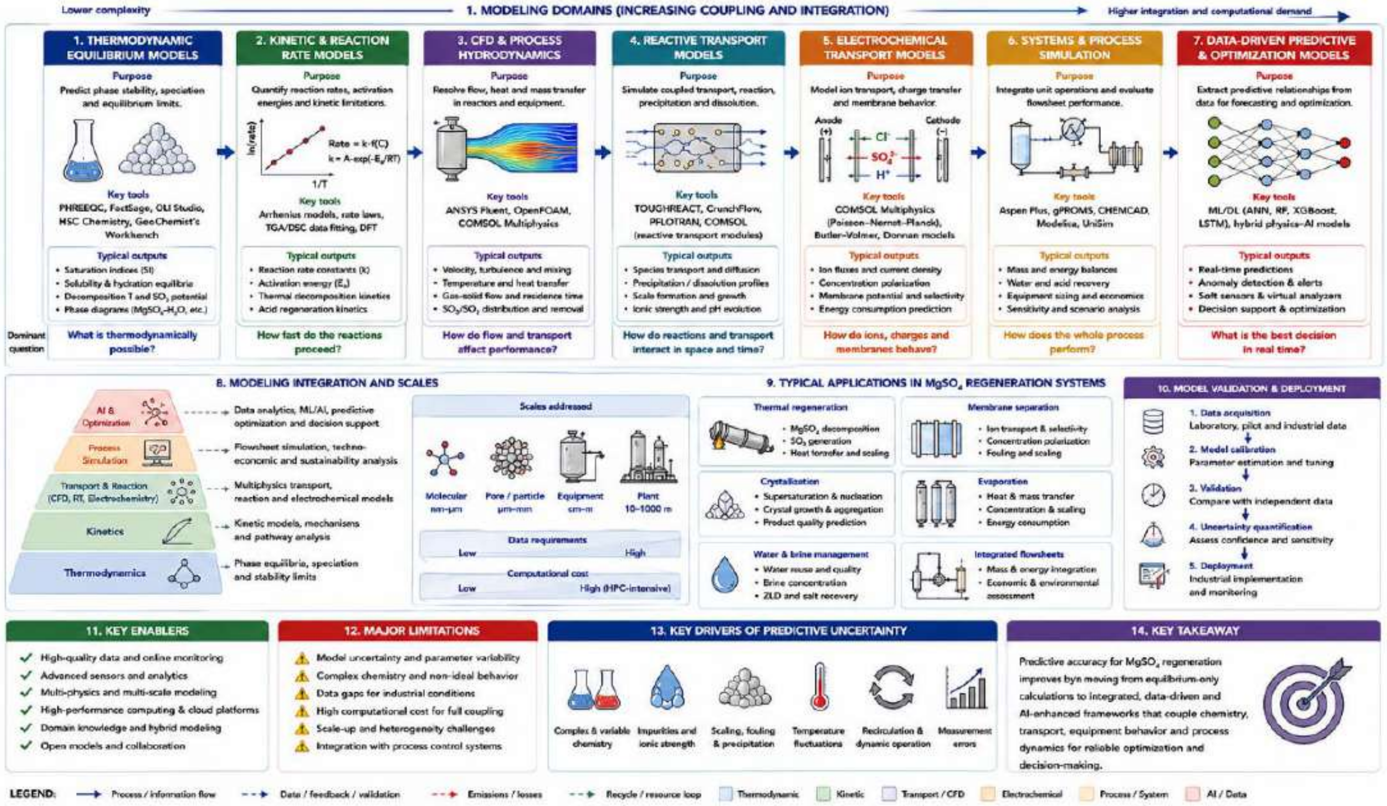


Figure 11. Comparative technological trade-offs among thermal, membrane, electrochemical, neutralization, crystallization, and hybrid $MgSO_4$ management systems.Adapted from Yadav et al. (2026), Agarwal and Pandey (2023), Zöllner and Bollmann (2021), Ibrahim et al. (2024), Mello et al. (2020), Rodríguez (2020), O'Sullivan and Williams (2024), Ju et al. (2023), Akola et al. (2024), and Mends et al. (2025).

Figure 11 shows no single $MgSO_4$-management technology optimizes recovery, cost, robustness, and sustainability, while hybrid systems provide the most balanced industrial pathway.

13. INDUSTRIAL CASE STUDIES

Industrial $MgSO_4$ management varies widely across sectors due to differences in sulfate load, process chemistry, infrastructure, and economic objectives. Sulfate control is generally integrated into broader hydrometallurgical, recycling, or wastewater-treatment systems, where sulfur management must balance water recirculation, residue stability, energy demand, and environmental compliance. Industrial maturity depends not only on technical feasibility but also on compatibility with existing infrastructure and operating costs.

Nickel laterite processing is one of the major industrial sources of $MgSO_4$ generation because magnesium-rich gangue minerals consume large amounts of sulfuric acid during leaching and sulfation roasting. Hariyanto et al. (2023b) reported that serpentine-rich laterites generate high sulfate concentrations through Mg-silicate dissolution, while Zhao et al. (2024a) demonstrated complex sulfur partitioning between dissolved sulfates and solid phases in sulfation-roasting-leaching systems. Large-scale laterite operations therefore face significant challenges related to sulfate accumulation and water recirculation.

Electrochemical sulfuric acid recovery has been investigated for $MgSO_4$-rich laterite liquors. Ibrahim et al. (2024) demonstrated partial acid recovery through electrodialysis, although scalability depends strongly on solution chemistry and membrane stability. Mu et al. (2024) further showed that magnesium-bearing phases influence sulfate behavior during roasting, reinforcing the importance of integrated sulfate-management strategies.

Titanium dioxide production via sulfate routes also generates $MgSO_4$-containing streams. Abdelgalil et al. (2023) studied ammonium sulfate roasting–leaching of ilmenite, producing sulfate-rich liquors containing magnesium and impurities. Similarly, Karshyga et al. (2022) and Ultarakova et al. (2022) described sulfate residues from mineral-processing and smelting operations. However, these sectors remain focused mainly on residue stabilization and acid recycling rather than complete sulfur recovery from $MgSO_4$.

Battery-recycling systems are emerging sources of sulfate-rich liquors. Tang et al. (2021) and Di et al. (2020) investigated sulfation roasting and sulfate leaching for lithium-ion battery recycling. These streams are chemically complex, containing lithium, nickel, cobalt, manganese, aluminum, and magnesium. Nikkhah (2025) highlighted that growing recycling infrastructure will increase demand for selective sulfate-management technologies capable of handling multicomponent acidic liquors. Nevertheless, sulfate-regeneration maturity in battery recycling remains lower than in traditional hydrometallurgy because of feed variability, impurity control, and decentralized infrastructure.

In acid mine drainage and industrial wastewater treatment, sulfate management focuses primarily on environmental discharge reduction rather than sulfur recovery. Baena-Moreno et al. (2020) and Foureaux (2021) showed that membrane-based systems can recover water and some dissolved species, although concentrate stabilization remains challenging. Unlike concentrated hydrometallurgical liquors, AMD systems typically involve dilute but very large sulfate volumes, making thermal sulfate regeneration less attractive and favoring hybrid water-recovery approaches.

Industrial evidence shows that $MgSO_4$ management strategies vary considerably across sectors, depending on sulfate load, impurity composition, and process scale. Table 11 summarizes representative industrial and pilot-scale case studies.

Table 11. Representative industrial and pilot-scale $MgSO_4$ management case studies. Adapted from Hariyanto et al. (2023a), Abdelgalil et al. (2023), Tang et al. (2021), Baena-Moreno et al. (2020), and Mends et al. (2025).

Sector	Main sulfate source	Sulfate load	Main operational challenge	Industrial maturity
Nickel laterites	Mg silicate dissolution	Very high	Acid consumption	High
TiO_2 sulfate route	Waste acid generation	High	Impurity accumulation	High
Battery recycling	Sulfation roasting liquors	Moderate	Variable feed chemistry	Moderate
Acid mine drainage	Sulfate-rich drainage	Moderate	Water treatment economics	Moderate
Fertilizer industry	Sulfate purification residues	Moderate–high	Water recirculation	High

The industrial evidence in Table 11 shows sulfate-management strategies are sector-dependent and must fit local constraints and infrastructure.

Figure 12 summarizes $MgSO_4$ management pathways across hydrometallurgical, recycling, wastewater, and sulfation-roasting systems. It includes sulfate sources, sulfuric acid recovery, water recirculation, thermal and membrane technologies, and residue management.

TECHNOLOGY CATEGORY	1. THERMAL REGENERATION	2. MEMBRANE SEPARATION	3. ELECTROCHEMICAL RECOVERY	4. CRYSTALLIZATION & EVAPORATION	5. SULFATE STABILIZATION / NEUTRALIZATION (Non-regenerative)	6. HYBRID & INTEGRATED SYSTEMS
Typical feed $MgSO_4$-rich streams (high TDS, impurities, variable composition)	• Decomposition of $MgSO_4$ • SO_2/SO_3 generation • H_2SO_4 production (SO_3 absorption)	• Nanofiltration / RO • Sulfate concentration • Water recovery	• Electrodialysis / BPMED • Acid and base regeneration • Selective ion transport	• Evaporation & supersaturation • Crystal growth • Solid sulfate recovery	• Lime / alkali addition • Gypsum or ettringite formation • Stabilization of sulfate	• Membrane + electrochemical • Crystallization + thermal • Integrated heat & water mgmt.
Technology Readiness Level (TRL)	7 – 9 (Commercial)	5 - 7 (Demonstration)	4 - 6 (Pilot-Demo)	7 - 9 (Commercial)	9 (Mature)	5 - 7 (Emerging)
Sulfur (as H_2SO_4) Recovery Efficiency*	High (70–95%)	Low–Moderate (20–50%)	Moderate–High (50–80%)	Low (0–30%)‡	Very Low (<10%)§	High (60–90%)
Water Recovery Potential	Low–Moderate (20–50%)	High (50–90%)†	Moderate–High (60–85%)	High (70–95%)	Low–Moderate (10–40%)	High (70–95%)
Impurity Tolerance (Scaling/Fouling)	High	Low–Moderate (Sensitive to scaling)	Moderate (Affected by organics)	Moderate (Affected by co-precipitation)	High (Wide tolerance)	Moderate–High (Depends on integration)
Energy Demand (typical range)	Very High (0.8 – 2.5 GJ/t H_2SO_4) Process-dependent	Low–Moderate (0.1 – 0.4 kWh/m³)	Moderate (0.5 – 1.5 kWh/m³)	High (0.5 - 1.5 GJ/t evap. water)	Low (0.05 – 0.2 GJ/t)	Moderate–High (Integrated demand)
CAPEX	High	Moderate–High	High	Moderate	Low	High (Complex integration)
OPEX	High (Fuel & maintenance)	Moderate (Membrane replacement)	Moderate–High (Electricity & stack life)	Moderate (Energy & fouling)	Low–Moderate (Chemical cost)	Moderate–High (Depends on configuration)
Environmental Impact (direct emissions)	High (SO_2/SO_3, CO_2) Without gas treatment	Low (No direct emissions)	Low–Moderate (Indirect electricity)	Low–Moderate (Vapor/energy emissions)	Low–Moderate (Chemical use, sludge)	Moderate (Depends on mix)
Operational Robustness & Stability	High (Robust at high T)	Low–Moderate (Fouling & scaling)	Moderate (Feed variability)	Moderate–High (Scale & slurry mgmt.)	High (Simple & robust)	Moderate–High (Complex control)
Scalability & Industrial Maturity	High (Large scale proven)	Moderate (Module limits)	Low–Moderate (Pilot to early scale)	High (Proven at large scale)	Very High (Widespread)	Moderate (Depends on system)

RELATIVE STRENGTHS
- Proven thermal & stabilization at large scale
- High sulfur recovery potential (thermal, electrochemical, hybrid)
- High water recovery potential (membrane, electrochemical, hybrid)
- Low emissions possible with proper treatment & integration
- Flexibility through integration (hybrid systems)

MAJOR LIMITATIONS
- High energy & emissions (thermal routes)
- Low sulfur recovery for stabilization/neutralization (not a regeneration option)
- Scaling, fouling & membrane degradation
- High CAPEX for advanced & integrated systems
- Secondary waste (gypsum, sludge) in stabilization
- Operational complexity in hybrid systems

RATING SCALE (QUALITATIVE)
- Very High / Excellent
- High / Good
- Moderate / Medium
- Low / Poor
- Very Low / Very Poor

* Based on sulfur in feed converted to H_2SO_4 or recovered as equivalent acid. † Depends on feed TDS, pressure & membrane type. ‡ Typically sulfate crystallization, not acid regeneration. § Sulfur retained in stabilized sulfate (not recovered as acid).

11. KEY ENABLERS FOR BETTER PERFORMANCE
- ✓ Advanced anti-scaling & anti-fouling materials
- ✓ Catalysts & heat-efficient thermal processes
- ✓ Electrode & membrane durability (electrochemical)
- ✓ Process intensification & heat integration
- ✓ Digital monitoring, sensors & process control
- ✓ Policy support, carbon pricing & incentives

12. MAJOR CHALLENGES
- ⚠ High CAPEX & long payback
- ⚠ Scaling, fouling & impurity accumulation
- ⚠ High energy demand (thermal & evaporation)
- ⚠ Membrane lifetime & replacement cost
- ⚠ Hydrodynamic & operational complexity (hybrid systems)
- ⚠ Infrastructure compatibility & retrofitting

13. TECHNOLOGY DEVELOPMENT ROADMAP

Short term (0–3 years)	Mid term (3–7 years)	Long term (7–15 years)
• Pilot & demo validation • Anti-scaling solutions • Process optimization • Digital monitoring	• Scale-up & integration • Advanced membranes & electrodes • Durable materials • Heat & energy recovery	• Integrated hybrid systems • Advanced process control & digital optimization • Near-closed sulfur loop • High sulfur circularity

Goal: High sulfur recovery, low emissions, zero-liquid-discharge, and resource circularity

14. KEY TAKEAWAY

No single technology is universally superior for $MgSO_4$ management. Integrated systems that combine separation, recovery, stabilization and energy integration provide the most effective pathway to achieve high sulfur recovery, water reuse, economic viability, and environmental sustainability.

Figure 12. Industrial integration pathways for $MgSO_4$ management in hydrometallurgy, battery recycling, titanium dioxide processing, wastewater treatment, and sulfation-roasting systems. Adapted from Hariyanto et al. (2023a), Zhao et al. (2024a), Ibrahim et al. (2024), Abdelgalil et al. (2023), Tang et al. (2021), Di et al. (2020), Foureaux (2021), Baena-Moreno et al. (2020), Mends et al. (2025), and Smirnov et al. (2023).

Figure 12 shows that industrial $MgSO_4$ management relies on hybrid systems that balance sulfur recovery, water recirculation, impurities, infrastructure, and operational robustness.

14. RESEARCH GAPS AND FUTURE PERSPECTIVES

Future $MgSO_4$ regeneration depends on reducing energy use, improving selectivity, and enhancing process integration. Current methods face challenges due to magnesium sulfate's high thermal stability, sensitivity to impurities, and incomplete sulfur closure, creating a gap between lab results and industrial needs.

Research focuses on low-energy $MgSO_4$ decomposition because traditional thermal regeneration needs high temperatures and fuel. Yadav et al. (2026) cite energy demand as a key barrier to large-scale sulfur recovery. Alternative methods like catalytic activation, microwave heating, plasma treatment, and better gas–solid contact need more study. Taheri and Larachi (2025) highlight reactor intensification and heat integration to boost thermal efficiency.

Selective $MgSO_4$ recovery remains a major challenge. Current methods often recover sulfuric acid non-selectively or concentrate sulfate without effective magnesium control. Future systems need improved control over proton selectivity, sulfate partitioning, and magnesium rejection, especially in complex industrial liquors containing transition metals, chlorides, silica, and organics. A deeper understanding of ionic interactions will be crucial for effective separation.

Electrification and electrochemical recovery are increasingly important, operating at lower temperatures than thermal methods and benefiting from cleaner electricity. Ibrahim et al. (2025a) showed electrochemical sulfuric acid recovery from $MgSO_4$ can reduce scaling with specific conditions. Ivanov et al. (2026) proposed integrated electrochemical routes for sulfate management, combining acid recovery and magnesium valorization. However, membrane durability, conductivity loss, and efficiency improvements are needed for large-scale applications.

Artificial intelligence and digital process control could improve future sulfate-management systems. Bao et al. (2025) noted that sulfate-rich industrial circuits involve complex chemical and transport phenomena difficult to optimize empirically. AI prediction might enhance control of evaporation, membrane separation, electrochemical transport, and crystallization. Sarkar et al. (2023) found that multivariable membrane behavior often defies simplified mechanistic models. Future AI platforms might integrate thermodynamic, kinetic, and operational data to stabilize sulfate management under variable conditions.

A circular sulfate economy is increasingly relevant in hydrometallurgy and chemical processing. Binnemans and Jones (2023b) argued future systems should integrate reagent recovery, water recirculation, and waste reduction. $MgSO_4$ should be seen not only as waste but also as a secondary sulfur and magnesium resource. Pereira (2025) and Pereira and Fonseca (2025) suggested converting magnesium sulfate into reactive MgO, showing how sulfur and magnesium recovery can be part of broader circular schemes.

Modular recovery systems and ZLD are expected to grow, especially in remote mining and medium-sized hydrometallurgical facilities. Future systems may combine electrochemical recovery, membrane concentration, selective crystallization, and localized sulfate valorization instead of relying solely on centralized sulfuric acid plants. These setups can enhance flexibility, cut water discharge, and reduce transport needs. Success depends on better integration of energy management, sulfate chemistry, and process control.

Future development of $MgSO_4$ regeneration technologies will depend on reducing energy demand while improving sulfur selectivity, process integration, and operational flexibility. Table 12 summarizes the principal research priorities and technology-readiness gaps.

Table 12. Research priorities and technology-readiness gaps associated with $MgSO_4$ regeneration systems. Adapted from Yadav et al. (2026), Taheri and Larachi (2025), Ibrahim et al. (2025a), Bao et al. (2025), and Binnemans and Jones (2023b).

Research area	Main objective	Current limitation	Approximate TRL
Low-energy decomposition	Reduce thermal demand	High $MgSO_4$ stability	Low–moderate
Electrified regeneration	Replace fossil-fuel heating	Scaling and conductivity	Moderate
AI-assisted process control	Improve dynamic optimization	Limited industrial data	Low
Modular recovery systems	Flexible decentralized treatment	Integration complexity	Moderate
Circular sulfate economy	Integrated sulfur recovery	Incomplete sulfur closure	Low–moderate

Table 12 shows that future progress in $MgSO_4$ regeneration will rely on advances in electrification, predictive control, modular recovery, and circular sulfate management.

Figure 13 outlines a future roadmap for $MgSO_4$ regeneration and sulfate management, covering low-energy decomposition, electrified recovery, AI-driven process control, modular treatment, a circular sulfate economy, and ZLD strategies. It highlights key technological trends shaping sulfuric acid circularity in $MgSO_4$-rich industries.

11. KEY ENABLERS FOR BETTER PERFORMANCE

- ✓ Advanced anti-scaling and anti-fouling materials
- ✓ Catalysts and energy-efficient thermal processes
- ✓ Electrode and membrane durability (electrochemical)
- ✓ Process intensification and heat integration
- ✓ Digital monitoring, sensors, and advanced process control
- ✓ Policy support, carbon pricing, and economic incentives

12. MAJOR CHALLENGES

- ⚠ High CAPEX and long payback period
- ⚠ Scaling, fouling, and impurity accumulation
- ⚠ High energy demand (thermal routes)
- ⚠ Membrane lifetime and replacement cost
- ⚠ Hydrodynamic and operational complexity (hybrid systems)
- ⚠ Infrastructure compatibility and retrofitting

SHORT TERM (0–3 YEARS)

Demonstration & Proof-of-Concept

- Pilot and demo validation
- Anti-scaling and fouling strategies
- Process optimization and intensification
- Digital monitoring and benchmarking
- Improved SO_2 capture and absorption
- Life-cycle assessment and TEA
- Regulatory and economic evaluation

Key outcome: Validated technologies at pilot scale with improved performance and data

MID TERM (4–7 YEARS)

Scale-Up & Integration

- Pilot-to-industrial scale-up
- Advanced membranes and electrodes
- Corrosion-resistant materials
- Process integration and intensification
- Heat recovery and energy integration
- Digital process control and real-time optimization
- System reliability and operation under variable conditions

Key outcome: Economically viable systems with high reliability and improved resource efficiency

LONG TERM (8–15 YEARS)

Commercialization & Circularity

- Advanced hybrid and fully integrated recovery systems
- AI/ML-assisted process control and predictive optimization
- Near-zero waste and zero liquid discharge (ZLD) operation
- Near-closed sulfur cycle
- High sulfur recovery and recycling
- Resilient, flexible, and climate-resilient operations
- Global deployment and standardization

Key outcome: Circular, low-emission, and globally deployed solutions with maximum value

RELATIVE STRENGTHS

- Proven thermal & stabilization at large scale
- High sulfur recovery potential (thermal, electrochemical, hybrid)
- High water recovery potential (membrane, electrochemical, hybrid)
- Low emissions achievable with proper treatment & integration
- Flexibility through integration (hybrid systems)

MAJOR LIMITATIONS

- High energy & emissions (thermal routes)
- Sulfur retained in stabilized sulfate (neutralization; not a regenerative option)
- Scaling, fouling, and membrane degradation
- High CAPEX for advanced and integrated systems
- Secondary waste (gypsum, sludge) in stabilization
- Operational complexity in hybrid systems

GOAL: High sulfur recovery • Low emissions • Zero liquid discharge • Resource circularity

RATING SCALE (QUALITATIVE)

- ● Very High / Excellent
- ● High / Good
- ● Moderate / Medium
- ● Low / Poor
- ● Very Low / Very Poor

LEGEND (for main comparison matrix)

- → Process / material flow
- --→ Information / control
- --→ Recycle / resource loop

Note:
Ratings are qualitative and relative; actual performance depends on feed composition, concentration, impurities, temperature, scale, technology configuration, and operating conditions.
TEA: Techno-economic analysis; ZLD: Zero liquid discharge.

* Based on sulfur in feed converted to H_2SO_4 or recovered as equivalent acid.
† Depends on feed TDS, pressure, and membrane type.
‡ Typically sulfate crystallization; not acid regeneration.
§ Sulfur retained in stabilized sulfate (not recovered as acid).

Figure 13 shows the transition from conventional sulfate stabilization to integrated circular sulfate-management systems involving electrification, AI-assisted control, modular recovery, water reuse, and process integration

15. CONCLUSIONS

Magnesium sulfate hinders sulfuric acid recycling due to its stability, solubility, and persistence, especially in hydrometallurgical and recycling operations where sulfate accumulates. It has become a major process-integration challenge.

This review showed that conventional neutralization remains the dominant sulfate-management strategy due to its operational simplicity, rapid control of acidity, and industrial maturity. However, neutralization primarily converts sulfuric acid into gypsum-rich sludges, stable sulfate residues, or concentrated brines rather than regenerating reusable sulfur. Consequently, many industrial systems transfer sulfate between liquid and solid waste streams rather than achieving effective sulfur closure.

Thermal regeneration remains the most direct route for recovering sulfur from $MgSO_4$ because it converts sulfate into sulfur oxides that are compatible with sulfuric acid production. Nevertheless, the very high decomposition temperatures required impose major energy and operational penalties, particularly for dilute streams and for facilities lacking integrated sulfuric acid infrastructure or waste heat. Membrane and electrochemical technologies may reduce thermal demand, but industrial implementation remains constrained by sensitivity to impurities, scaling, fouling, and long-term operational stability.

The review also showed that industrial $MgSO_4$ systems rarely conform to simplified laboratory assumptions. Real process liquors contain multicomponent sulfate mixtures, suspended solids, fluctuating impurities, and evolving water balances that strongly affect regeneration performance. Therefore, sulfate management is governed more by coupled thermodynamic, transport, and operational interactions than by recovery efficiency alone. Predictive modeling, reactive transport analysis, and AI-assisted process control will likely become increasingly important for optimizing sulfate-management systems under industrial conditions.

No single technology fully achieves sulfur closure in $MgSO_4$-rich streams. Hybrid systems—combining membrane separation, electrochemical recovery, crystallization, evaporation, and thermal integration—are the most promising path for sulfur reuse. Their industrial success depends on robustness, process integration, impurity tolerance, and infrastructure, rather than just sulfur recovery.

Overall, $MgSO_4$ regeneration should be viewed as an integrated systems-engineering challenge that encompasses thermodynamics, energy management, process chemistry, water reuse, and sustainability.

DECLARATIONS

Availability of Data and Materials

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Competing Interests

The author declares no competing interests.

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Authors' Contributions

Antonio Clareti Pereira conceived the study, performed the literature review, analyzed the data, interpreted the results, and wrote the manuscript.

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