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A critical review of the valorization of industrial byproducts and designer biochar for restoring sulfur and organic matter interactions in degraded soils

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Abstract

Soil degradation expressed through salinization, organic carbon depletion, and contamination by persistent pollutants is intrinsically linked to the disruption of sulfur-organic matter interactions. This review critically evaluates engineered sulfur-based and organic amendments, focusing on industrial byproduct gypsum, elemental sulfur, designer biochar, and their composites, as tools for restoring these interactions. We synthesize mechanistic pathways governing sulfate retention, microbial sulfur cycling, and contaminant interference, and we assess field-scale performance using quantifiable engineering metrics. The central insight emerging from this synthesis is that no single amendment addresses all degradation pathways; rather, a fit-for-purpose selection guided by soil-specific constraints such as sodicity, pH, texture, and contaminant profile is essential. Key findings reveal that elemental sulfur oxidation achieves more than 80% sulfate yield within nine weeks under optimal conditions, while gypsum-biochar composites reduce bulk density by over 50% and enhance nutrient retention. However, significant contradictions persist sulfur oxidation rates vary markedly between soil textures, and the long-term stability of metal sulfide precipitates remains unconfirmed. We conclude that sustainable soil restoration requires an integrated framework that couples' material properties, microbial ecology, and site-specific engineering design. This review provides such a framework and identifies five research priorities including multi-year field trials, predictive kinetic modeling, and harmonized life cycle assessment to accelerate the translation of laboratory findings into field-scale implementation.

Keywords Soil degradation, Sulfur-organic interactions, Engineered soil amendments, Biochar composites, PFAS remediation, Flue gas desulfurization gypsum, Process intensification, Soil restoration

1 Introduction

Soil degradation manifested through salinization, sodicity, nutrient depletion, loss of soil organic carbon (SOC), and contamination by persistent pollutants such as per- and polyfluoroalkyl substances (PFAS) poses a growing threat to agricultural productivity and ecosystem resilience worldwide. In this review, the term "degraded soils" is defined operationally as soils that have experienced a significant decline in one or more of the following functional attributes: (i) chemical fertility (e.g., sulfur deficiency, elevated pH or salinity, cation imbalance); (ii) physical structure (e.g., compaction, reduced hydraulic conductivity, aggregate instability); (iii) biological activity (e.g., reduced microbial biomass, suppressed enzymatic function); and (iv) contaminant retention capacity (e.g., elevated mobile heavy metals or PFAS). Within this scope, we focus on degraded soils of agricultural relevance in arid and semi-arid regions, where salinization, sodicity, sulfur depletion, and organic carbon loss are particularly prevalent. Soils affected primarily by heavy metal contamination without concurrent sulfur-organic degradation, or by organic pollution without sulfur cycling disruption, are considered outside the scope of this review. Among the many biogeochemical cycles affected, the sulfur cycle is particularly vulnerable. In aerobic soils, sulfate (SO_4^{2-}) is the predominant inorganic sulfur species and the primary bioavailable form for plants and microorganisms. The retention and mobility of sulfate are governed by its interactions with mineral surfaces and organic matter, a set of phenomena collectively referred to as the sulfur-organic nexus. When soils degrade, disruption of this nexus leads to reduced sulfate availability, accelerated leaching of base cations (Ca^{2+}, Mg^{2+}), and diminished microbial activity, creating a negative feedback loop that progressively worsens soil quality [1, 2]. While the adsorption behavior of cationic species on mineral surfaces is well characterized, the mechanistic understanding of anion retention particularly sulfate remains comparatively underdeveloped, representing a significant knowledge gap with direct implications for the long-term fertility of managed ecosystems.

Sulfate retention in soil matrices is widely understood to occur via ligand exchange at variable-charge surfaces, wherein sulfate ions displace surface hydroxyl groups (M–OH or $M–OH_2^+$) on metal (hydr)oxide interfaces [2]. The primary lithogenic inputs of sulfur to terrestrial systems derive from the weathering of metal sulfides (e.g., pyrite, FeS_2) and evaporite minerals such as gypsum ($CaSO_4 \cdot 2\ H_2O$), which establish the baseline geochemical boundary conditions for subsequent biological processing [3]. In degraded soils, the disruption of native sulfur-organic matter interfaces introduces significant process inefficiencies. The loss of organic carbon binding sites and alterations in redox potential lead to diminished sulfate buffering capacity and suppressed microbial metabolic flux, effectively constituting a failure of in situ nutrient retention.

Soil organic carbon serves as the primary energy source for heterotrophic microbial communities that drive sulfur mineralization, immobilization, oxidation, and reduction. The biogeochemical cycling of sulfur is thus fundamentally a microbially catalyzed reaction network encompassing these transformations. Intensive agricultural management practices, characterized by unbalanced stoichiometric inputs of nitrogen and phosphorus relative to sulfur, exert selective pressure that depletes the labile sulfur pool, constraining catalytic turnover rates and limiting crop productivity. Extensive spatial surveys in agroecosystems such as those conducted across Indian agricultural regions indicate widespread prevalence of soils exhibiting acute to marginal sulfur deficiency,

underscoring the scale of this resource limitation [4]. In semi-arid tropical systems, accelerated mineralization of soil organic matter (SOM) driven by elevated temperatures and moisture fluctuations initiates a detrimental feedback loop: SOM depletion reduces the capacity for sulfur retention, leading to sulfur limitation, which in turn constrains microbial carbon use efficiency and further accelerates carbon loss [5].

The implementation of Integrated Nutrient Management (INM) the co-application of mineral fertilizers with recalcitrant organic amendments such as farmyard manure represents an effective strategy to augment SOC stocks. This organic carbon influx serves as a supplemental feedstock for microbial consortia, thereby elevating the specific activity of sulfur transformation pathways. Spectroscopic analyses via Fourier-transform infrared (FTIR) reveal that INM-derived SOC is enriched with stable functional moieties (e.g., sulfoxide S = O and complex polyphenols) that confer resistance to rapid microbial turnover [6]. Soil microbial biomass (SMB), comprising carbon (SMBC), nitrogen (SMBN), and sulfur (SMBS) pools, act as the biocatalytic inventory of the soil system both a source and sink of nutrients. The synergistic interaction between inorganic inputs and organic substrates under INM regimes significantly elevates SMB levels, thereby enhancing the rates of sulfur mineralization, immobilization, and redox transformations [6]. At the molecular scale, key enzymes urease, dehydrogenase, and aryl sulfatase govern the flux of sulfur through the system. Aryl sulfatase is the specific rate-limiting catalyst for cleaving ester–sulfate bonds to yield plant-available sulfate, while dehydrogenase reflects total oxidative metabolic throughput. Empirical data consistently demonstrate that INM regimes enhance these enzymatic activities, whereas exclusive nitrogen fertilization acts as an enzyme inhibitor, suppressing both catalytic function and SMB viability [7].

The introduction of persistent anthropogenic contaminants, notably per- and polyfluoroalkyl substances (PFAS), adds complexity to the sulfur-organic nexus. Certain PFAS compounds, including fluorotelomer sulfonates, can engage with the sulfur starvation regulon of soil microbes, with the *ssuD* gene mediating desulfonating under sulfate-limited conditions [8]. This metabolic link illustrates the broader principle that contaminant interference must be considered alongside nutrient dynamics in degraded soils. However, the primary focus of this review is on engineered materials for restoring sulfur-organic interactions; PFAS is addressed here as a contextual example of contaminant complexity rather than a central theme. Where relevant, the potential of specific amendments for PFAS sorption or degradation is noted in subsequent sections.

This review examines a range of engineered materials including industrial byproduct gypsum, elemental sulfur, designer biochar, and sulfonated polymers that have been specifically developed or repurposed to restore the sulfur-organic nexus. We analyze their chemical mechanisms, transformation pathways, and field-scale performance using quantifiable engineering metrics, and we evaluate synergistic composite systems, environmental trade-offs, and life cycle considerations. To systematically analyze and design interventions for these interacting phenomena, we conceptualize the degraded soil matrix as an integrated reactive system (Fig. 1), in which three principal operational zones intersect: (a) abiotic ligand exchange equilibria at mineral surfaces governing sulfate retention; (b) biologically catalyzed reactions wherein SOC amendments drive enzymatic flux and mineralization rates; and (c) contaminant interference pathways wherein PFAS compounds engage desulfonating genes and alter system stoichiometry.

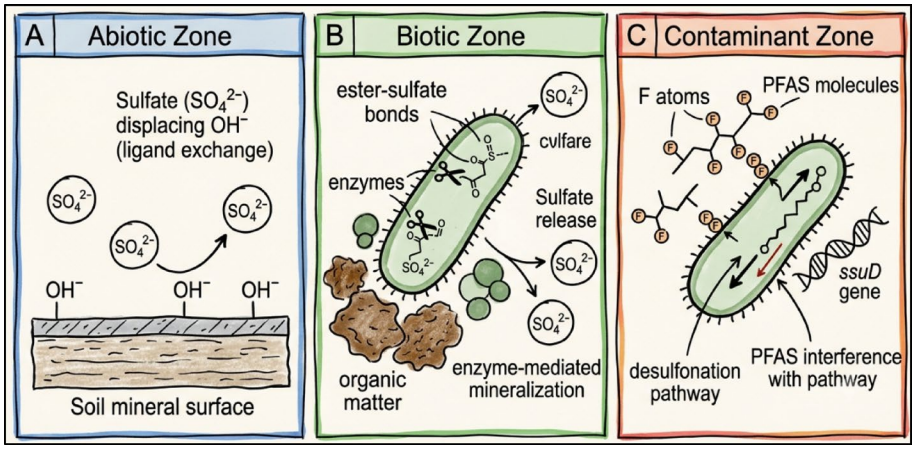

Fig. 1 Conceptual process flow diagram of the engineered soil-sulfur interface under degraded conditions. The diagram depicts (**A**) Ligand exchange sulfate retention on variable-charge surfaces, **B** Enzyme-mediated mineralization of ester-sulfates driven by SOC inputs, and **C** Interference pathways posed by PFAS contaminants via de-sulfonation (ssuD gene expression) and competitive binding at sorption sites

By adopting this process-oriented perspective, we aim to provide a critical synthesis of current knowledge and to identify practical pathways for sustainable soil restoration.

Despite the growing body of research on individual amendments and their mechanisms, several critical knowledge gaps remain unaddressed. First, current studies typically examine sulfur-based amendments (e.g., gypsum, elemental sulfur) and organic amendments (e.g., biochar, polymers) in isolation, without an integrated framework that links sulfur chemistry, organic matter transformation, microbial regulation, and engineering design principles. Second, the translation of laboratory-scale findings to field conditions is hampered by inconsistent reporting of performance metrics and a lack of standardized evaluation protocols. Third, the environmental trade-offs including trace element mobility, salinity buildup, and life cycle burdens are rarely considered alongside agronomic benefits, limiting the ability to make informed decisions about amendment selection. Fourth, the role of emerging contaminants such as PFAS in sulfur cycling has been explored only recently, and the implications for amendment design remain unclear.

This review addresses these gaps by providing a critical synthesis of engineered sulfur-based and organic amendments from a chemical engineering perspective. Our specific objectives are to systematically evaluate the physicochemical mechanisms governing sulfate retention, sulfur oxidation, and contaminant interactions in degraded soils; to assess field-scale performance using quantifiable engineering metrics; to identify contradictions and uncertainties in the literature; and to propose a unified framework for amendment selection based on soil-specific constraints. The novelty of this review lies in its integration of material science, microbial ecology, and process engineering an approach that bridges the gap between descriptive agronomy and predictive design. By adopting this process-oriented perspective, we aim to provide actionable guidance for researchers, practitioners, and policymakers working toward sustainable soil restoration.

2 Engineered sulfur materials for feedstock characterization and process mechanisms

Sulfur (S) functions as an essential macronutrient governing both plant metabolic pathways and microbial community structure within the soil matrix. It exists in two principal operational pools: Organic S (OrgS), comprising proteinogenic amino acids such as cysteine and methionine, and Inorganic S, primarily as sulfate (SO_4^{2-}) and elemental sulfur (S^0). In undisturbed ecosystems, OrgS constitutes the dominant reservoir (> 95% of total soil S), representing a kinetically stable, slowly cycling pool that buffers long-term biological demand. The inorganic fraction, while quantitatively minor, governs the instantaneous bioavailability of sulfur. Notably, S^0 is not directly assimilable; its utility is contingent upon microbially mediated oxidative catalysis specifically, the activity of chemoautotrophic consortia (e.g., *Thiobacillus* spp.) which convert S^0 to SO_4^{2-} via a multi-step electron transfer process [9].

From a process engineering standpoint, the selection and application of exogenous sulfur amendments must be optimized based on reactivity profiles (oxidation kinetics), transport phenomena (leaching potential), and matrix compatibility (impurity effects on soil pH and electrical conductivity).

2.1 Industrial byproduct gypsum (BPG) as a circular economy feedstock with practical constraints

Industrial byproduct gypsum (BPG), predominantly calcium sulfate dihydrate ($CaSO_4.2H_2O$) or its anhydrous forms, represents a significant secondary resource stream generated across multiple industrial sectors. While stockpiling presents environmental liabilities related to land use and leachate management, the strategic valorization of BPG aligns with circular economy principles for soil amendment applications. Currently, process utilization is limited primarily to Flue Gas Desulfurization Gypsum (FGDG) and Phospho-gypsum (PG), with emerging streams such as Titanium-gypsum (TG) and Fluoro-gypsum (FG) remaining largely uncharacterized as viable feedstocks due to impurities and unfavorable hydration kinetics [10]. Table 1 provides a comparative analysis of these major BPG streams, highlighting critical process variables that dictate their suitability as engineered soil amendments.

Table 1 Comparative process analysis of industrial byproduct gypsum feedstocks

Type	Source industry	Primary composition	Radioactivity constraint	Estimated global flux	Current process utilization	Key engineering barriers
FGD Gypsum [11]	Coal Power (Wet Scrubbing)	$CaSO_4.2H_2O$ (≥ 95%)	< 1 Bq g^{-1}	~ 40 Mt yr^{-1}	Cement additive, Soil conditioner	Regional SO_2 emission dependence
Phospho-gypsum [12]	Phosphoric Acid Production	$CaSO_4.2H_2O + {}^{226}Ra$	10–100 Bq g^{-1}	100–280 Mt yr^{-1}	Restricted agriculture [13]	Regulatory limit (USEPA > 370 Bq kg^{-1})
Titanium-gypsum [14, 15]	TiO_2 Pigment Manuf.	$CaSO_4 \cdot xH_2O +$ TiO_2 residue	Not Applicable	Not Aggregated	Experimental	Acidic leachate (pH < 3)
Fluoro-gypsum [16]	HF Acid Production	Anhydrous $CaSO_4$	Not Applicable	Not Aggregated	Research Phase	Slow hydration kinetics, low mechanical strength

FGD: flue gas desulfurization; Bq: becquerel; USEPA: United States Environmental Protection Agency

The data in Table 1 reveals a clear trade-off between feedstock availability and regulatory constraints. Flue gas desulfurization (FGD) gypsum, with its low radioactivity (< 1 Bq g^{-1}) and high purity (≥ 95% $CaSO_4 \cdot 2\ H_2O$), is the most process-ready feedstock for soil application, but its availability is regionally constrained by coal-fired power plant emissions. In contrast, phospho-gypsum is generated in larger quantities (100–280 Mt yr^{-1}) but faces regulatory barriers due to ^{226}Ra content (10–100 Bq g^{-1}), with many jurisdictions imposing application bans despite column studies showing leachate concentrations below drinking water standards [13]. This divergence between regulatory perception and empirical leachability data represents a significant knowledge gap: are the risks of phospho-gypsum application overestimated, or do column studies fail to capture long-term radionuclide mobilization under field conditions? For engineering design, the practical implication is that FGD gypsum is the preferred feedstock where available, while phospho-gypsum may be viable only in regions with less stringent regulations or where blending with other materials dilutes radioactivity to acceptable levels. The lack of aggregated data for titanium-gypsum and fluoro-gypsum further complicates their assessment, highlighting the need for systematic characterization of these emerging feedstocks.

2.1.1 Types of industrial byproduct gypsum and their process implications

(i) **FGD gypsum**: This stream represents the benchmark for BPG valorization due to its high chemical purity and consistent particle size distribution. Its application in heavy clay matrices modifies pore architecture and enhances hydraulic conductivity via calcium-mediated flocculation, thereby improving mass transfer of oxygen and water [11].

(ii) **Phospho-gypsum (PG)**: The presence of Technologically Enhanced Naturally Occurring Radioactive Material (TENORM), specifically ^{226}Ra, imposes a significant process constraint. Even fractions classified as "low activity" (< 370 Bq kg^{-1}) face substantial public acceptance and regulatory hurdles, restricting large-scale deployment despite potential for aggregate stabilization [12, 13].

(iii) **Emerging streams (TG and FG)**: Titanium-gypsum and Fluoro-gypsum represent underutilized feedstocks requiring pre-treatment unit operations prior to soil incorporation. TG often necessitates neutralization of residual acidity, while FG may require the addition of activators to overcome the slow hydration kinetics characteristic of anhydrite [14–17].

2.2 The reactivity and transport kinetics for elemental sulfur (S0) and sulfate salts

Elemental sulfur (S^0) is a yellow, crystalline nonmetal that serves as a slow-release substrate for the in-situ generation of sulfuric acid. Unlike sulfate salts, which dissociate immediately upon dissolution, S^0 requires a two-stage biocatalytic conversion within the soil reactor. The overall process engineering objective is to synchronize the kinetics of S^0 oxidation with the mass transfer demand of the crop root zone while minimizing off-target proton accumulation.

2.2.1 Fate and transport pathways of sulfate

When sulfate (SO_4^{2-}) is introduced to the soil matrix as a soluble salt, its environmental partitioning follows three primary fates [18]. The first is adsorption or retention,

which involves reversible binding to soil colloids and organic matter surfaces via ligand exchange or electrostatic attraction. The second is biological assimilation or reduction, encompassing incorporation into microbial or plant biomass (immobilization) as well as conversion to insoluble metal sulfides such as FeS_2 under reducing conditions. The third is leaching, wherein sulfate is transported convectively through the soil profile with percolating water, representing a loss from the root zone. These pathways are not static; sulfate can be regenerated through the mineralization of organic sulfur, effectively creating an internal recycling stream within the system [18].

2.2.2 Surface-controlled oxidation dynamics of elemental sulfur

The conversion of elemental sulfur to plant-available sulfate is governed by biofilm kinetics on the sulfur particle surface. The rate-limiting step is often the transfer of oxygen to the chemoautotrophic bacterial community. Two key process parameters control this reaction rate [19]. The first is specific surface area: oxidation rate is directly proportional to the particle size distribution, with smaller diameters such as those in micronized sulfur increasing the reactive surface area-to-volume ratio and thereby accelerating microbial colonization and subsequent conversion. The second is nutrient stoichiometry: because the oxidation process is a growth-associated reaction, adequate availability of co-limiting nutrients specifically bioavailable nitrogen and phosphorus is required to sustain the metabolic flux of the Thiobacillus consortium.

In calcareous soil systems characterized by high buffering capacity due to the presence of $CaCO_3$, the net pH change induced by elemental sulfur oxidation is often attenuated. However, localized acidification at the microsite scale, specifically in the immediate vicinity of the sulfur particle, can significantly enhance the solubility of micronutrients such as iron and zinc. Experimental studies document that organic amendments can further modulate this process in several ways [20]: they decrease bulk soil pH by 0.16–0.24 units, increase the available sulfate inventory by 246–1455 mg kg^{-1}, and elevate electrical conductivity by 0.42–0.48 dS m^{-1}, indicating increased ionic strength. Notably, this can result in a paradoxical reduction in the culturable counts of chemoautotrophic sulfur-oxidizers, likely due to competitive exclusion by heterotrophic biomass utilizing the organic carbon source [20].

2.2.3 Dose-response relationships and operating windows

Establishing a robust dose-response curve is essential for process optimization, balancing the desired acidification and sulfate release with the risk of excessive salt accumulation or pH overshoot. Table 2 synthesizes kinetic data from controlled column leaching

Table 2 Parametric analysis of elemental sulfur (S^0) loading on calcareous soil physico-chemistry [21]

Parameter	0.5% S^0 (w/w)	1.5% S^0 (w/w)	3.0% S^0 (w/w)	Process notes
pH shift	Significant Decrease	Proportional Decrease	Proportional Decrease	Post 18-week incubation
SO_4^{2-} flux	Marked Elevation	Dose-Dependent Rise	Dose-Dependent Rise	Maximum yield in sandy loam
EC (salinity)	Substantial Increase	Linear Increase	Linear Increase	Correlated with SO_4^{2-} mobility
Leachate SO_4^{2-}	Detectable Export	Increased Export	Highest Export	Intermittent leaching events

studies [21], quantifying the impact of elemental sulfur loading rates (0.5–3.0% w/w) on the physicochemical dynamics of calcareous porous media.

Several process engineering insights emerge from this dataset. First, threshold reactivity: even the lowest application rate (0.5% w/w) induced statistically significant ($p < 0.05$) acidification and sulfate release, indicating that the indigenous microbial oxidation capacity is highly efficient at sub-1% loading. Second, temporal dynamics: kinetic profiles reveal that more than 80% of the total sulfate yield is generated within the initial 9-week incubation period, a residence time that aligns favorably with the peak sulfur demand windows of many agronomic crops. Third, texture-dependent mass transfer: the data indicates that sulfate mobility was approximately 23% higher in sandy loam matrices compared to clay-rich counterparts, underscoring the need for texture-specific application protocols to mitigate leaching losses [21].

The dose-response data in Table 2 indicate that even low elemental sulfur loading (0.5% w/w) produces significant acidification and sulfate release, suggesting that the indigenous microbial oxidation capacity is highly efficient. However, the data also reveal a texture-dependent mass transfer effect: sulfate mobility was approximately 23% higher in sandy loam compared to clay-rich soils, underscoring that application rates must be adjusted for soil texture to avoid leaching losses. This finding is consistent with the broader literature, but contradictions remain: some studies attribute faster oxidation in calcareous soils to pH buffering preventing acid inhibition of *Thiobacillus* spp [19]., while others report slower oxidation due to calcium carbonate coatings on sulfur particles [20]. The methodological limitation here is that most dose-response studies are conducted in controlled column systems that do not capture field-scale heterogeneity in water flow, temperature fluctuations, or microbial community composition. For engineering design, the key implication is that a "one-size-fits-all" application rate is inappropriate; texture-specific protocols are needed. The unresolved knowledge gap concerns the temporal dynamics of oxidation: while more than 80% yield occurs within nine weeks, the long-term sustainability of this rate under repeated applications and varying environmental conditions remain unquantified.

The empirical data presented in Table 2 confirm that sulfur amendment performance is not governed by a singular parameter but rather by the interplay between reaction kinetics (oxidation rate) and transport phenomena (advective-dispersive flux). To guide the rational selection and process design of sulfur amendments for degraded soil systems, Fig. 2 provides a unified engineering analysis of these distinct reactivity regimes. The figure presents a comparative framework through two lenses: (i) a reaction coordinate diagram illustrating the relative energetic barriers and rate-limiting steps for the three principal sulfur feedstock classes soluble sulfate salts (instantaneous dissolution), elemental sulfur S^0 (biocatalytic oxidation-limited), and industrial byproduct gypsum (solubility product-limited); and (ii) idealized breakthrough curves modeling the advective transport of sulfate through porous media of contrasting texture. This integrated perspective enables the prediction of sulfate residence time and spatial distribution within the root zone, which are critical process metrics for mitigating leaching losses and synchronizing nutrient supply with plant demand.

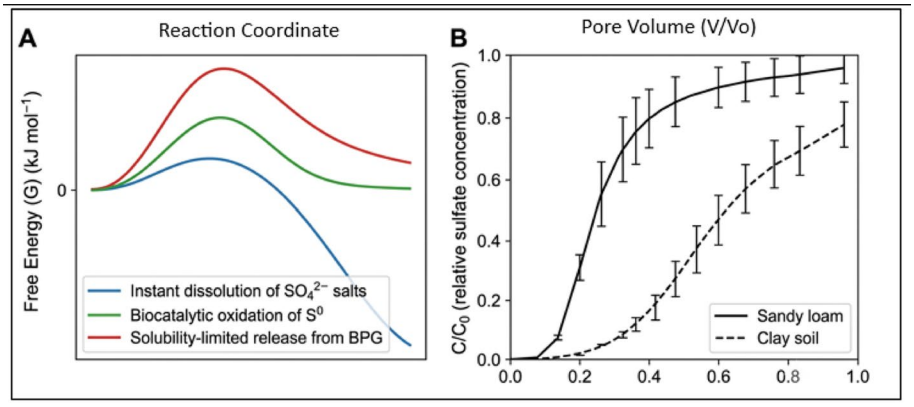

Fig. 2 Kinetic and transport characterization of sulfur sources. **A** Reaction coordinate diagram comparing the activation energy barriers for sulfate salt dissolution, biocatalytic S^0 oxidation, and gypsum solubility-limited release. **B** Sulfate breakthrough curves in sandy loam versus clay soil matrices amended with S^0. Curves are schematic representations derived from established thermodynamic principles, oxidation kinetics, and advective-dispersive transport theory rather than empirical experimental datasets

3 Engineered organic amendments for targeted sulfur-organic interactions

While sulfur-based amendments (Sect. 2) directly address nutrient deficiencies by supplying sulfate (gypsum, sulfate salts) or generating acidity through elemental sulfur oxidation, they do not address the underlying loss of soil's organic matter or the decline in microbial habitat quality that characterizes many degraded soils. Organic amendments particularly designer biochar and sulfonated polymers offer complementary benefits: they enhance soil structure, increase water and nutrient retention, provide surfaces for microbial colonization, and introduce functional groups that bind contaminants. The choice between sulfur-based and organic amendments depends on the dominant degradation pathway. In sodic or calcareous soils where sulfur deficiency and high pH are the primary constraints, sulfur-based amendments are the first-line intervention. In soils where organic carbon depletion, poor structure, or contaminant stress are the main limitations, organic amendments are preferred. However, the most effective restoration strategies often combine both classes, a synergy explored in Sect. 4 through gypsum-biochar and S^0-biochar composites. The following sections examine two advanced classes of engineered organic materials designer biochar and sulfonated polymers that function as multifunctional porous supports and reactive interfaces. These materials are strategically designed to modulate the coupled processes of nutrient retention, contaminant sequestration, and microbial habitat provision.

Biochar, a carbonaceous solid produced via the thermochemical conversion (pyrolysis) of biomass under oxygen-limited conditions, has been extensively investigated for environmental remediation and soil enhancement applications [22, 23]. However, pristine biochar (unmodified) frequently exhibits suboptimal performance characteristics, including limited specific surface area, a paucity of reactive surface functional groups, and variable sorption affinity for targeted analytes [24]. To overcome these intrinsic limitations, post-synthetic modification strategies have been developed to tailor the physicochemical properties of biochar for specific process objectives [25].

3.1 Designer biochar as a platform for tailored soil reactivity

The term "designer biochar" refers to a suite of engineered carbonaceous materials wherein the surface chemistry, pore architecture, and bulk composition are intentionally modified via physical, chemical, or biological unit operations. These interventions are designed to optimize performance metrics such as sorption capacity (q_{max}), cation exchange capacity (CEC), and catalytic activity for targeted applications including pollutant immobilization and soil structure amendment [26]. Modification strategies can be implemented pre-pyrolysis (feedstock impregnation), during pyrolysis (reactive atmosphere), or post-pyrolysis (surface activation) [27].

3.1.1 Physical modification for enhanced surface area and accessibility

Physical modification techniques are generally cost-effective and avoid the introduction of secondary chemical waste streams. These methods primarily enhance specific surface area and pore volume, thereby increasing the density of accessible sorption sites. Beyond heavy metals, physically modified biochar have shown promise for sorption of organic contaminants, including PFAS, though the mechanisms and capacity vary with feedstock, pyrolysis conditions, and pore structure [27]. Table 3 summarizes the principal physical modification techniques and their associated process outcomes.

The physical modification techniques summarized in Table 3 vary substantially in their mechanistic basis and process outcomes. Ball milling and steam activation are well-established and yield predictable increases in specific surface area, but microwave activation offers advantages in energy efficiency and pore structure control that warrant further investigation [27]. A notable contradiction in the literature concerns the comparative efficacy of steam versus CO_2 activation: while steam activation generally produces higher surface areas, CO_2 activation yields more uniform microporosity, with the optimal choice depending on the target application [27]. Methodological limitations include the lack of standardized protocols for assessing surface area enhancement, with studies using different measurement conditions (e.g., N_2 adsorption at 77 K versus CO_2 at 273 K) that complicate cross-study comparisons. For engineering design, the implication is that physical modification should be tailored to the target application: ball milling for heavy metal immobilization (where internal pore access is critical), microwave activation for organic contaminant sorption (where kinetics matter), and magnetic impregnation for recoverable sorbent applications. The knowledge gap concerns the durability of these modifications: do milled or activated biochar retain their enhanced properties after field exposure to wetting-drying and freeze-thaw cycles?

Table 3 Physical modification techniques for designer biochar production

Technique	Key process outcomes	Targeted applications
Ball Milling	Mechanical size reduction; ↑ SSA; enhanced exposure of internal pores	Heavy metal (Cd, Pb) immobilization in soil matrices [28, 29]
Microwave Activation	Generation of microporosity via dielectric heating; improved organic pollutant sorption kinetics	Aqueous phase contaminant removal [27]
Steam/Gas Activation	Partial gasification; ↑ SSA and oxygen-containing functional groups (OCFGs) relative to CO_2 activation	Soil amendment; preparation of catalytic supports [27]
Magnetic Impregnation	Incorporation of Fe_3O_4/γ-Fe_2O_3 nanoparticles; enables facile post-application separation via magnetic field	Wastewater treatment; recoverable sorbents [27]

SSA: specific surface area; OCFG: Oxygen-Containing Functional Groups

3.1.2 Chemical modification for enhanced reactivity

Chemical modification strategies are employed to introduce specific surface functional groups (e.g., carboxyl, hydroxyl, amine, sulfonic acid) that govern the material's acid-base character, cation exchange capacity (CEC), and coordination chemistry with metal ions [30, 31]. Three principal chemical modification strategies are commonly employed: acid/alkali treatment, H_2O_2 oxidation, and chitosan coating.

Acid/alkali treatment operates through two complementary mechanisms. Acid treatment (e.g., with HCl, HNO_3, or H_3PO_4) protonates surface functional groups and dissolves ash-forming mineral phases (e.g., carbonates, silicates) that block pores, thereby increasing the density of oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH), and lactone groups. These groups serve as binding sites for cationic contaminants through surface complexation and ion exchange. Alkali treatment (e.g., with KOH or NaOH) similarly removes inorganic components and can introduce potassium or sodium ions that enhance cation exchange capacity. The net effect is an increase in surface acidity and metal-binding capacity, though the specific outcome depends on the treatment concentration, temperature, and duration [30].

H_2O_2 oxidation is a milder and more selective method that introduces oxygen-containing functional groups without significantly altering the biochar's pore structure. The mechanism involves the generation of hydroxyl radicals (•OH) that attack the aromatic carbon framework, oxidizing surface carbon atoms to form carboxyl (-COOH), carbonyl (C = O), and phenolic (-OH) groups. These functional groups are particularly effective for binding heavy metals such as Pb^{2+} and Cd^{2+} through inner-sphere complexation. The advantage of H_2O_2 oxidation over acid treatment is that it preserves the biochar's microporous structure while selectively enhancing surface functionality; however, the oxidation efficiency is highly dependent on H_2O_2 concentration, treatment time, and the inherent reactivity of the biochar surface [31].

Chitosan coating introduces amine ($-NH_2$) and hydroxyl (-OH) groups through the deposition of a biopolymer layer on the biochar surface. Chitosan is a naturally derived polysaccharide rich in amine groups that become protonated under acidic conditions (pKa ~ 6.5), generating positively charged sites that are highly effective for the sorption of anionic contaminants such as arsenate (AsO_4^{3-}), phosphate (PO_4^{3-}), and chromate (CrO_4^{2-}). The coating mechanism involves electrostatic attraction between the positively charged chitosan and the negatively charged biochar surface, followed by hydrogen bonding and physical entrapment within biochar pores. While chitosan coating enhances selective anion sorption, its effectiveness diminishes under alkaline conditions where amine groups are deprotonated, and the long-term stability of the coating under field conditions remains a concern [31]. Table 4 outlines common chemical modification methods and their functional outcomes.

Table 4 Chemical modification methods and functional outcomes for biochar

Method	Key functional outcome
Acid/alkali treatment	Increases density of OCFGs; enhances mesoporous structure via dissolution of ash/mineral phases [30]
H_2O_2 oxidation	Boosts surface carboxyl group (-COOH) density for enhanced metal binding capacity [31]
Chitosan coating	Introduces amine ($-NH_2$) and hydroxyl (-OH) groups; improves selective adsorption of anionic species [31]

The chemical modification methods in Table 4 differ in their functional outcomes and selectivity. Acid/alkali treatment increases oxygen-containing functional groups broadly, while H_2O_2 oxidation specifically targets carboxyl group density, and chitosan coating introduces amine groups for selective anion sorption [30, 31]. A key contradiction in the literature concerns the optimal oxidation method: some studies report superior metal binding with H_2O_2 oxidation, while others find acid treatment more effective, likely due to differences in biochar feedstock, pyrolysis temperature, and the resulting surface chemistry [31]. Methodological limitations include the difficulty of quantifying functional group density with high precision; spectroscopic techniques such as FTIR, XPS, and Boehm titration yield different estimates, complicating direct comparisons across studies. For engineering design, the implication is that chemical modification should be matched to the target contaminant: carboxyl-rich surfaces for cationic metals, amine-rich surfaces for anionic species (e.g., arsenate, phosphate), and mixed functionality for complex contaminant mixtures. The unresolved knowledge gap concerns the stability of chemically modified surfaces under field conditions do grafted functional groups persist, or are they gradually oxidized, hydrolyzed, or leached over time?

3.1.3 Biological modification and bio-composite formation

Biological modification involves the immobilization of viable microbial consortia onto the biochar surface. In this context, biochar functions as a structured biofilm carrier. Its inherent porosity provides a protective habitat against environmental stressors (e.g., desiccation, predation, shear forces), while its nutrient content supplies essential co-factors for microbial metabolism. This synergistic approach enhances the bioavailability and degradation kinetics of organic pollutants within the rhizosphere [32].

The sequential application of physical, chemical, and biological unit operations transforms pristine biochar from a passive carbonaceous solid into a hierarchical, multifunctional reactive platform. Figure 3 provides a schematic representation of this design paradigm, illustrating the synergistic integration of modification strategies onto a single engineered particle. The figure delineates three operational tiers: (i) physical

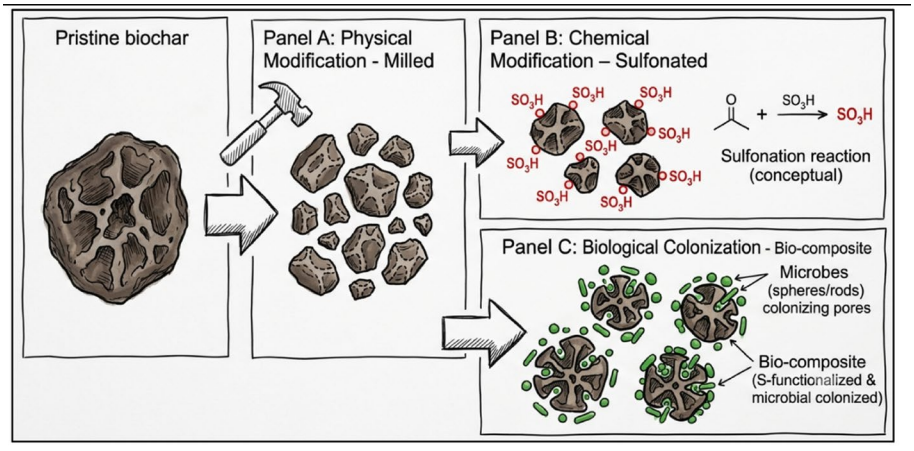

Fig. 3 Schematic representation of a designer biochar particle engineered for multifunctional soil amendment. The diagram illustrates the hierarchical structure resulting from **A** physical size reduction (ball milling) to expose internal pore volume, **B** chemical surface functionalization (sulfonation) to introduce strong acid sites (-SO_3H) for enhanced cation exchange, and **C** biological colonization wherein the porous architecture serves as a protective habitat for sulfur-oxidizing microbial consortia

comminution (e.g., ball milling), which reduces mass transfer limitations by increasing accessible surface area and exposing internal pore volume; (ii) chemical functionalization (e.g., sulfonation), which covalently anchors strong Bronsted acid sites (-SO_3H) to enhance cation exchange capacity and proton availability; and (iii) biological colonization, wherein the engineered pore architecture serves as a protective niche for microbial consortia capable of sulfur oxidation and pollutant degradation. This integrated materials-by-design approach exemplifies the principles of process intensification applied to soil amendment technology.

3.2 Sulfonated polymers as solid acid catalysts and ion-exchange resins

Sulfonated polymers represent a distinct class of engineered organic amendments characterized by the covalent incorporation of sulfonic acid groups (-SO_3H) onto a polymeric backbone. The presence of these strong Brønsted acid sites significantly enhances three key material properties [33]. First, acidity: the proton-donating capacity enables localized pH modulation. Second, hydrophilicity: improved wettability enhances water retention within the porous matrix. Third, cation exchange capacity: the sulfonate anion (SO_3^-) serves as a fixed anionic site, facilitating the reversible sorption and exchange of cationic species.

3.2.1 Applications in catalysis, sorption, and remediation

The integration of sulfonated polymers with biochar matrices producing sulfonated biochar yields multifunctional composite materials with dual capabilities: the high surface area and porous structure of biochar combined with the strong acidity and ion-exchange properties of the sulfonic acid moieties. These composites function through three principal mechanisms [34, 35]. In catalysis, sulfonated biochar composites act as effective heterogeneous solid acid catalysts; their Brønsted acidity facilitates industrially relevant reactions under mild conditions, including the transesterification of triglycerides for biodiesel synthesis and the hydrolysis of cellulosic biomass. Within the soil context, this catalytic activity could theoretically accelerate the hydrolysis of organic sulfur esters, although this remains an emerging area of investigation. In adsorption, the elevated cation exchange capacity conferred by sulfonation renders these materials highly effective for the sequestration of cationic contaminants, including heavy metals such as Pb^{2+} and Cd^{2+} as well as radionuclides, from both aqueous and soil pore water environments. The sorption mechanism is predominantly ion exchange at the sulfonate sites, a process characterized by favorable kinetics and high selectivity. In environmental remediation, beyond direct contaminant sorption, sulfonated polymers influence the speciation and bioavailability of soil pollutants. The localized acidification resulting from proton release can shift metal ion equilibria, potentially converting them to less mobile forms or, conversely, mobilizing them for subsequent capture by the polymeric sorbent. This dual-action mechanism simultaneous proton release and ion exchange offers a sophisticated tool for managing contaminant flux in degraded soils. Sulfonated polymers have also been investigated for PFAS sorption via ion exchange and hydrophobic interactions, though field-scale validation remains limited [35].

4 Synergistic hybrid composites for coupled sulfur-organic management

The individual material classes discussed in Sects. 2 and 3 industrial byproduct gypsum, elemental sulfur, designer biochar, and sulfonated polymers each offer distinct and valuable functionalities for soil remediation. However, the complex, multiphase nature of degraded soil environments often demands multifunctional intervention strategies that address nutrient availability, contaminant immobilization, and soil structure simultaneously. This section examines engineered hybrid composites, specifically gypsum-biochar and layered double hydroxide (LDH)-biochar systems, which are designed to exploit synergistic material interactions to achieve performance metrics unattainable by single-component amendments.

Biochar, as previously established, serves as a high surface area porous support with tunable surface chemistry [36]. When strategically combined with inorganic phases such as gypsum or LDHs, the resulting composite exhibits emergent properties that enhance both abiotic sorption processes and biological habitat provision.

4.1 Gypsum-biochar composites for enhanced nutrient management

Gypsum (calcium sulfate dihydrate, $CaSO_4{\cdot}2\ H_2O$) is a widely available, low-toxicity mineral with a long history of use as a soil conditioner and construction material [37]. However, its inherent density and limited capacity for organic contaminant sorption constrain its standalone utility in degraded soil remediation. The incorporation of biochar into a gypsum matrix yields a composite material with a significantly reduced carbon footprint and an expanded functional repertoire.

The synergistic benefits of gypsum-biochar composites arise from the complementary properties of the two phases. The biochar phase provides porosity, electrical conductivity (depending on pyrolysis conditions), and sorption sites for organic molecules and nutrients. The gypsum phase, in turn, serves as a calcium source for flocculation of clay particles, thereby improving soil structure and hydraulic conductivity and as a sulfate reservoir for sustained nutrient release. Table 5 summarizes the key engineering properties and process applications of gypsum-biochar composites.

The gypsum-biochar composites summarized in Table 5 offer multifunctionality that neither component provides alone. The reduction in bulk density from 1.08 to 0.46 g cm^{-3} with 50 wt% biochar loading is particularly significant for improving soil structure and water infiltration [37]. However, the trade-off is mechanical strength: flexural

Table 5 Engineering Properties and multifunctional applications of gypsum-biochar composites [36–39]

Property/functional benefit	Mechanistic description	Process notes/exemplary performance
Electromagnetic Interference (EMI) shielding	Exhibits attenuation of electromagnetic radiation, particularly in microwave frequencies	Attributed to the electrical conductivity of biochar, tunable via pyrolysis conditions [37]
Bulk density reduction	Density decreases from 1.08 ± 0.03 g cm^{-3} (pristine gypsum) to 0.46 ± 0.03 g cm^{-3} with 50 wt% biochar loading	Enables lightweight material applications; flexural modulus declines at > 20 wt% biochar [37]
Soil physical amendment	Improves soil aggregate stability, water infiltration rate, and water use efficiency (WUE)	Biochar component elevates pH, electrical conductivity (EC), moisture retention, and organic matter content [38]
Phosphorus capture and retention	Gypsum-incorporated biochar enhances the sorption capacity for dissolved inorganic phosphorus	Contributes to integrated nutrient management and mitigation of eutrophication [39]

modulus declines at greater than 20 wt% biochar, limiting applications where structural integrity is critical [37]. A key contradiction concerns the reported efficacy of phosphorus capture: while some studies report substantial enhancement [39], others find that gypsum can compete with phosphorus for sorption sites, reducing overall capture [38]. This discrepancy likely arises from differences in biochar pyrolysis temperature and gypsum-biochar mixing ratio, but systematic studies examining these variables are lacking. For engineering design, the implication is that composite composition must be optimized for the target property: low biochar loadings for structural applications, high loadings for nutrient retention and soil conditioning. The knowledge gap concerns long-term performance: do these composites maintain their enhanced properties after multiple years of field exposure, or does weathering degrade the synergistic interactions between the gypsum and biochar phases?

4.2 Layered double hydroxide-biochar composites for contaminant sequestration

Layered Double Hydroxides (LDHs) are a class of synthetic anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_{x}\,(\mathrm{OH})_2]^{\mathrm{x}+}\left[A^{n-}_{x/n}.\mathrm{mH_2O}\right]$. Their defining characteristic is a positively charged brucite-like layer balanced by exchanging interlayer anions. This structure confers a high anion exchange capacity (AEC), making LDHs particularly effective for the sequestration of anionic contaminants (e.g., arsenate, chromate, phosphate) and the controlled release of nutrient anions (e.g., nitrate, sulfate) [40]. When LDHs are synthesized in the presence of biochar, the resulting LDH-biochar composite integrates the high specific surface area and microporosity of biochar with the anion exchange functionality of the LDH phase. This hybrid architecture enables simultaneous cationic sorption (via biochar surface functional groups) and anionic sorption/intercalation (via LDH galleries). Furthermore, the composite can modulate soil pH and enhance microbial community structure. Table 6 outlines the key environmental functions and process performance metrics of LDH-biochar composites.

The layered double hydroxide (LDH)-biochar composites in Table 6 demonstrate high efficacy for heavy metal immobilization, with 2 wt% CaAl-LDH/biochar achieving 47.85% copper and 37.95% lead immobilization [40]. However, the mechanism is not simply anion exchange: the composites also modulate microbial communities, enriching phyla such as Actinobacteriota and Gemmatimonadota that enhance nitrogen fixation and stress tolerance [40]. This dual function direct contaminant sorption and indirect

Table 6 Environmental process functions of LDH–biochar composite materials [40, 41]

Application	Mechanistic description	Exemplary performance/conditions
Heavy metal remediation	Passivation and immobilization of Cu and Pb in contaminated soil matrices	2 wt% CaAl-LDH/BC composite: 47.85% Cu and 37.95% Pb immobilization efficiency [40]
Soil fertility enhancement	Increases Soil Organic Carbon (SOC), Available Potassium (AKC), Available Phosphorus (APC), soil pH, and Cation Exchange Capacity (CEC)	Promotes plant growth while reducing heavy metal Phytoavailability [40]
Microbial community modulation	Enrichment of beneficial bacterial phyla (e.g., *Actinobacteriota*)	Enhances biological nitrogen fixation and plant tolerance to heavy metal stress [40]
Wastewater nutrient recovery & valorization	Ca-modified biochar captures phosphorus; the spent "BC-Ca-P" material is subsequently repurposed for heavy metal sorption	Sustainable, circular economy approach for dephosphorization and remediation [41]

LDH: layered double hydroxide; BC: biochar; SOC: soil organic carbon; CEC: cation exchange capacity.

microbial modulation is a key advantage of LDH-biochar composites over simpler sorbents. A notable contradiction concerns the reported effects on soil fertility, while some studies report significant increases in available phosphorus and potassium [40], others find minimal effects, likely due to differences in LDH composition (CaAl vs. MgAl) and biochar feedstock. Methodological limitations include the difficulty of disentangling the contributions of LDH versus biochar to observed performance; without proper controls, attribution to specific mechanisms is speculative. For engineering design, the implication is that LDH-biochar composites are best suited for combined heavy metal remediation and soil fertility enhancement in moderately contaminated soils. The knowledge gap concerns the fate of immobilized metals: are they permanently sequestered, or can they be remobilized under changing pH or redox conditions, particularly in seasonally flooded or irrigated systems?

The data presented in Tables 5 and 6 underscore the potential of hybrid composite systems to address multiple soil degradation pathways concurrently. To elucidate the mechanistic basis for this observed synergy, Fig. 4 presents a conceptual schematic of a generalized gypsum-biochar-LDH composite particle. The figure illustrates the spatial distribution of functional domains within the engineered aggregate: the gypsum phase functions as a structural binder and a slow-release reservoir of calcium and sulfate; the biochar phase provides a high-surface-area porous network for the sorption of organic contaminants and serves as a carrier for microbial colonization; and the LDH phase offers selective anion exchange capacity for the sequestration of anionic pollutants (e.g., arsenate, chromate) and the controlled release of nutrient anions. This integrated architecture exemplifies the principles of multifunctional materials design applied to soil remediation process engineering.

5 Field performance and quantifiable metrics for amendment efficacy

The translation of material properties characterized in Sects. 2–4 to field-scale reclamation outcomes requires a rigorous framework of quantifiable engineering metrics. These metrics serve as key performance indicators (KPIs) that enable the objective comparison

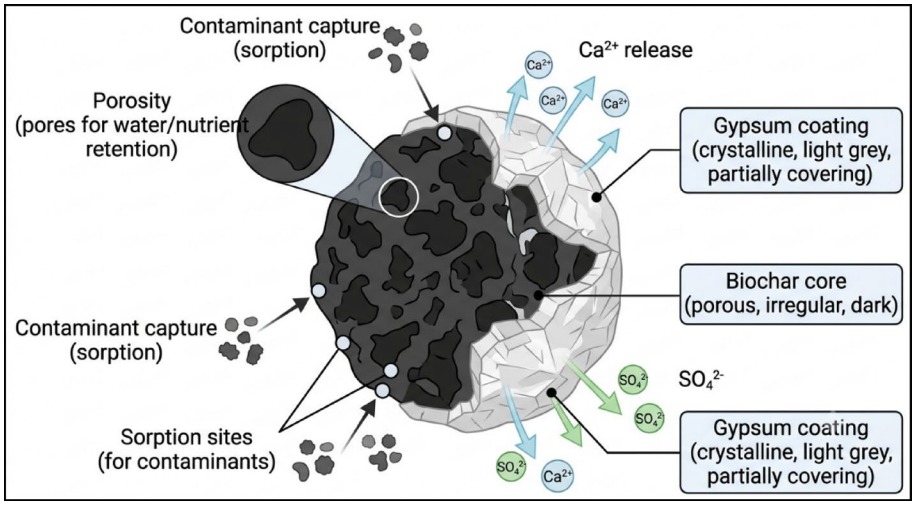

Fig. 4 Schematic representation of a multifunctional gypsum-biochar composite particle. The biochar core provides porosity and sorption sites, while the gypsum coating serves as a reservoir for sustained Ca^{2+} and SO_4^{2-} release. This dual-phase structure enables simultaneous soil structure improvement, nutrient supply, and contaminant sequestration

of amendment efficacy, the optimization of application rates, and the prediction of long-term system behavior. In the context of degraded soil remediation particularly saline-alkaline systems characterized by elevated pH, poor hydraulic conductivity, and nutrient imbalances the primary engineering objectives are: (i) pH modulation toward agronomic neutrality, (ii) sodicity mitigation (reduction of Exchangeable Sodium Percentage, ESP), (iii) enhancement of hydraulic transport properties, and (iv) augmentation of nutrient retention capacity [42].

This section presents a comparative process analysis of three distinct amendment classes: Flue Gas Desulfurization Gypsum (FGDG), Elemental Sulfur-Biochar (S^0-Biochar) Composites, and Sulfonated Polymers (e.g., polyacrylamide, PAM). The analysis is structured around a unified set of engineering metrics: soil pH, Electrical Conductivity (EC), bulk density and porosity, saturated hydraulic conductivity (K_{sat}), aggregate stability, and Cation Exchange Capacity (CEC).

5.1 Flue gas desulfurization gypsum (FGDG) for sodicity reclamation

FGDG ($CaSO_4 \cdot 2\ H_2O$) is deployed primarily as a source of soluble calcium (Ca^{2+}) to displace exchangeable sodium (Na^+) from soil colloid surfaces, a process described by the Gapon exchange equation. The subsequent leaching of soluble sodium sulfate (Na_2SO_4) reduces ESP and improves soil flocculation. Additionally, FGDG provides a source of plant-available sulfate (SO_4^{2-}) [42]. Table 7 summarizes the key engineering performance metrics for FGDG applications in degraded, particularly sodic, soil systems.

The flue gas desulfurization gypsum (FGDG) performance metrics in Table 7 confirm the well-established mechanism of sodium displacement: Ca^{2+} from gypsum replaces exchangeable Na^+, which is then leached from the soil profile [42]. However, the data reveal a counterintuitive observation: surface infiltration rate initially decreases due to aggregate dispersion before improving as subsurface hydraulic conductivity increases [42]. This suggests that FGDG application may require careful timing and irrigation management to avoid surface ponding and runoff during the initial application phase. A key contradiction concerns the magnitude of pH reduction: some studies report significant decreases [42], while others find minimal changes [43], likely due to differences in soil buffering capacity, initial pH, and the presence of carbonates that neutralize acidity. Methodological limitations include the short duration of most field trials (typically less than three years), which is insufficient to assess long-term sodium dynamics and the risk of re-sodification. For engineering design, the implication is that FGDG application rates should be based on exchangeable sodium percentage rather than fixed dose recommendations, and that post-application leaching is essential for effectiveness. The knowledge

Table 7 Engineering performance metrics for FGDG application in saline-alkaline soils [42–44]

Engineering metric	Mechanistic basis/process effect	Reference(s)
Soil pH reduction	Neutralization of alkalinity via Ca^{2+} driven conversion of soluble carbonates (Na_2CO_3, $NaHCO_3$) to neutral salts and precipitation of $CaCO_3$	[42]
Hydraulic conductivity (K_{sat})	Initially reduces infiltration rate at the surface due to aggregate dispersion, but improves subsurface K_{sat} via Na^+ leaching and enhanced macroporosity	[42]
Electrical conductivity (EC)	Transient increase in pore water EC due to dissolution and release of Ca^{2+} and SO_4^{2-}, which facilitates subsequent salt leaching below the root zone	[43]
Bulk density & porosity	Promotes aggregate formation and stability, leading to decreased bulk density and increased total porosity	[44]

gap concerns the effectiveness of FGDG in soils with high calcium carbonate content: do the Ca^{2+} ions simply precipitate as $CaCO_3$ rather than displacing Na^+, thereby limiting reclamation efficacy?

5.2 Elemental sulfur-biochar composite for soil structure and pH management

The elemental sulfur-biochar composite represents a hybrid system wherein the biochar phase functions as a porous, high-surface-area soil conditioner, and the elemental sulfur phase serves as a slow-release substrate for microbial acidification. This dual functionality addresses both the physical constraints (poor structure, low water holding capacity) and chemical constraints (high pH) typical of degraded arid and semi-arid soils [45–48]. Table 8 outlines the quantifiable engineering metrics associated with elemental sulfur-biochar composite application.

Biochar pH effects: controlling factors and implications for composite design.

The pH effect of the biochar component is one of the most variable factors influencing composite performance. Depending on feedstock type, pyrolysis temperature, and production conditions, biochar can raise soil pH by more than 2 units, have a neutral effect, or in some cases, lower pH [47]. This variability has profound implications for composite design: in acidic soils, alkaline biochar can serve as liming agents, while in calcareous soils, neutral or slightly acidic biochars may be preferred to avoid exacerbating alkalinity.

The primary factor controlling biochar pH is pyrolysis temperature. At low pyrolysis temperatures (300–400 °C), biochar typically contain significant quantities of organic acids and phenolic compounds that can lower pH. As pyrolysis temperature increases to 500–700 °C, these organic acids are volatilized, and inorganic alkaline species particularly carbonates, oxides, and hydroxides of calcium, magnesium, potassium, and sodium become concentrated in the biochar matrix [47]. These alkaline species dissolve upon contact with soil water, releasing hydroxide ions (OH^-) that neutralize acidity. Consequently, high-temperature biochar (≥ 500 °C) are consistently more alkaline than their low-temperature counterparts, with pH values ranging from 8 to 11 depending on feedstock mineral content [47].

Feedstock type is the second major determinant of biochar pH. Biochar derived from herbaceous biomass (e.g., straw, grasses) and agricultural residues (e.g., corn stover, rice husks) generally have higher ash content and thus higher pH compared to those from woody biomass (e.g., pine, oak), which have lower mineral content [48]. For example, biochar produced from wheat straw at 600 °C typically has a pH of 9.5–10.5, whereas pine wood biochar produced under identical conditions has a pH of 7.5–8.5 [48]. This

Table 8 Engineering performance metrics for S^0-biochar composite application [45–48]

Engineering metric	Mechanistic basis/process effect	Reference(s)
Bulk density & porosity	Incorporation of low-density, high-porosity biochar reduces bulk density and increases total pore volume, thereby improving gas exchange and water retention	[45]
Water Holding Capacity (WHC)	Enhances plant-available water content, particularly in coarse-textured (sandy) soils with inherently low WHC	[46]
pH modulation	Biochar effect varies with feedstock and pyrolysis conditions (can be neutral to alkaline); S^0 oxidation generates H_2SO_4 in situ, providing controlled acidification to neutralize alkalinity	[47]
Cation Exchange Capacity (CEC)	Biochar surface functional groups increase the soil's intrinsic CEC, enhancing retention of nutrient cations (K^+, NH_4^+, Ca^{2+}, Mg^{2+}) and reducing leaching losses	[48]

difference arises from the higher concentrations of exchangeable cations (K^+, Ca^{2+}, Mg^{2+}) and carbonate phases in herbaceous feedstocks.

Interaction with elemental sulfur oxidation: The net pH change in S^0-biochar composites is the result of two opposing processes: the acidifying effect of S^0 oxidation (generating H_2SO_4) and the alkalinity of the biochar component. In calcareous soils, the buffering capacity of $CaCO_3$ further complicates the net effect. The optimal composite design therefore requires matching the biochar's pH characteristics to the target soil: alkaline biochar may be suitable for acidic soils where both S^0 acidification and biochar liming are beneficial, while neutral or slightly acidic biochar are preferred for calcareous soils where excessive acidification could mobilize trace metals or damage soil structure [47].

A critical caveat is that laboratory pH measurements (typically conducted in water or 0.01 M $CaCl_2$ at a 1:5 or 1:10 biochar-to-solution ratio) may not fully reflect field behavior. In soil systems, pH effects are modulated by soil buffering capacity, initial pH, organic matter content, and the presence of reactive minerals. For example, a biochar with a water pH of 10 may raise a sandy, poorly buffered soil pH by 1.5 units, while the same biochar applied to a calcareous, well-buffered soil may produce no measurable pH change [47]. This context dependency means that generic recommendations are unreliable; material-specific response surfaces calibrated to soil type are essential for predictive design, yet such surfaces are not currently available for most biochar-soil combinations. This represents a high-priority research area, as discussed in Sect. 7.3.

The elemental sulfur-biochar composite metrics in Table 8 combine the beneficial effects of biochar (reduced bulk density, increased water holding capacity, increased cation exchange capacity) with the acidifying and sulfate-releasing effects of sulfur oxidation [45–48]. This dual functionality makes sulfur-biochar composites particularly attractive for calcareous soils where both improved structure and pH modulation are desired. However, a major contradiction in the literature concerns the net pH effect: biochar can be neutral to alkaline depending on feedstock and pyrolysis temperature, while sulfur oxidation generates H_2SO_4 [47]. The net pH change is therefore unpredictable and requires material-specific response surfaces that are not yet available for most soil types. Methodological limitations include the lack of standardized protocols for sulfur-biochar mixing ratios and application methods; studies vary widely in how the composite is prepared (physical mixing vs. co-pyrolysis) and applied (surface broadcast vs. incorporation). For engineering design, the implication is that sulfur-biochar composites should be designed for specific soil types, with the biochar component chosen to complement the sulfur's acidifying effect (e.g., using alkaline biochar in acidic soils or neutral biochar in calcareous soils). The knowledge gap concerns the interaction between sulfur oxidation and biochar's recalcitrance: does the localized acidification accelerate biochar degradation, or does the biochar's porous structure protect the microbial community from acid stress while enhancing sulfur oxidation?

Biochar pH effects are highly feedstock- and pyrolysis-dependent, with some materials raising pH by > 2 units and others lowering it [47]. This variability confounds generic recommendations and underscores the need for material-specific response surfaces that are not yet available for most soil types.

5.3 Sulfonated polymers for water management and aggregate stability

Sulfonated polymers, particularly anionic polyacrylamide (PAM), function as high-molecular-weight flocculants and soil conditioners. Their primary mode of action is the bridging of soil particles via electrostatic interactions and hydrogen bonding, which stabilizes aggregate structure and modifies the rheological properties of the soil-water system. The sulfonate groups (SO_3^-) confer water solubility and anionic character, facilitating binding to positively charged edge sites on clay minerals [49–52]. While the primary function of sulfonated polymers is water management and aggregate stabilization, their ion-exchange capacity also offers potential for capturing cationic contaminants and, in some cases, PFAS, though this application requires further study [51, 52]. Table 9 details the engineering metrics pertinent to sulfonated polymer application.

The sulfonated polymer metrics in Table 9 demonstrate clear benefits for aggregate stability and infiltration management [49–51]. The polymer bridging mechanism is well understood, but the magnitude of aggregation depends on polymer molecular weight, charge density, and soil texture [49]. A key contradiction concerns the effectiveness across soil textures: some studies report significant aggregate stabilization in sandy soils [50], while others find negligible effects in clay-rich soils [51]. The mechanism underlying this texture-dependency is unresolved does the polymer preferentially adsorb to sand surfaces, or is it competitively excluded from clay surfaces by native organic matter? Methodological limitations include the short duration of most polymer studies (typically weeks to months); the long-term persistence of polymers in soil and their effects on microbial communities remain poorly characterized. For engineering design, the implication is that sulfonated polymers are best suited for erosion control and water management in coarse-textured soils, while their efficacy in fine-textured soils may be limited and requires site-specific testing. The knowledge gap concerns the fate of polymer degradation products: do they accumulate in soil, and are they toxic to soil biota or phytotoxic to crops?

5.4 Comparative analysis and selection criteria for amendments

The data presented in Tables 7, 8 and 9 reveal that flue gas desulfurization gypsum (FGDG), elemental sulfur-biochar composites, and sulfonated polymers operate via distinct and largely complementary mechanisms. Selection of the optimal amendment or amendment combination for a given degraded soil system requires a fit-for-purpose engineering assessment based on the dominant constraint limiting system performance. FGDG is the process-optimal choice for soils exhibiting high sodicity (exchangeable

Table 9 Engineering performance metrics for sulfonated polymer (e.g., PAM) application [49–52]

Engineering metric	Mechanistic basis/process effect	Reference(s)
Aggregate stability	Polymer bridging between soil particles increases the mean weight diameter (MWD) of water-stable aggregates, reducing surface sealing and crust formation	[49]
Infiltration rate & seepage control	Reduces vertical seepage losses by increasing the tortuosity of flow paths and stabilizing surface aggregates, thereby retaining water within the root zone	[50]
Soil mechanical strength	Improves shear strength and resistance to deformation (elastic modulus) under compressive stress, relevant for erosion control and slope stabilization	[51]
Organic matter dynamics	Influences the decomposition kinetics of incorporated plant residues and native soil organic matter (SOM) by altering microbial access and microsite water potential	[52]

sodium percentage > 15) and elevated pH, where the primary objective is the displacement and leaching of exchangeable sodium. Elemental sulfur-biochar composites are particularly suited for soils with poor physical structure characterized by high bulk density and low porosity and moderate alkalinity, where simultaneous improvements in water holding capacity, nutrient retention, and gradual pH adjustment are desired. Sulfonated polymers such as polyacrylamide offer superior performance in erosion control and water management scenarios, specifically where maintaining surface infiltration rates and stabilizing soil aggregates against raindrop impact or shear stress are critical process requirements.

The integrated application of these amendments leveraging their synergistic mechanisms represents a robust process intensification strategy for the holistic remediation of complex, multi-stressor degraded soil environments.

To facilitate the rational selection of engineered amendments for site-specific soil reclamation projects, Fig. 5 presents a comparative performance matrix evaluating FGDG, S^0-Biochar composite, and sulfonated polymer (PAM) across six critical engineering metrics with the cost/sustainability, Sodicity Mitigation (reduction in Exchangeable Sodium Percentage), Acidification Capacity (pH reduction potential), Hydraulic Conductivity Enhancement, Water Holding Capacity, and Aggregate Stability. The figure employs a normalized scoring approach (0-100 scale) derived from the mechanistic analysis presented in Tables 7, 8 and 9 and supporting literature, thereby providing a concise visual guide for amendment selection based on dominant soil degradation constraints.

6 Environmental and economic trade-offs

The deployment of engineered sulfur amendments for soil remediation is not without attendant environmental and economic considerations. A comprehensive process systems analysis requires the evaluation of potential secondary impacts, including the

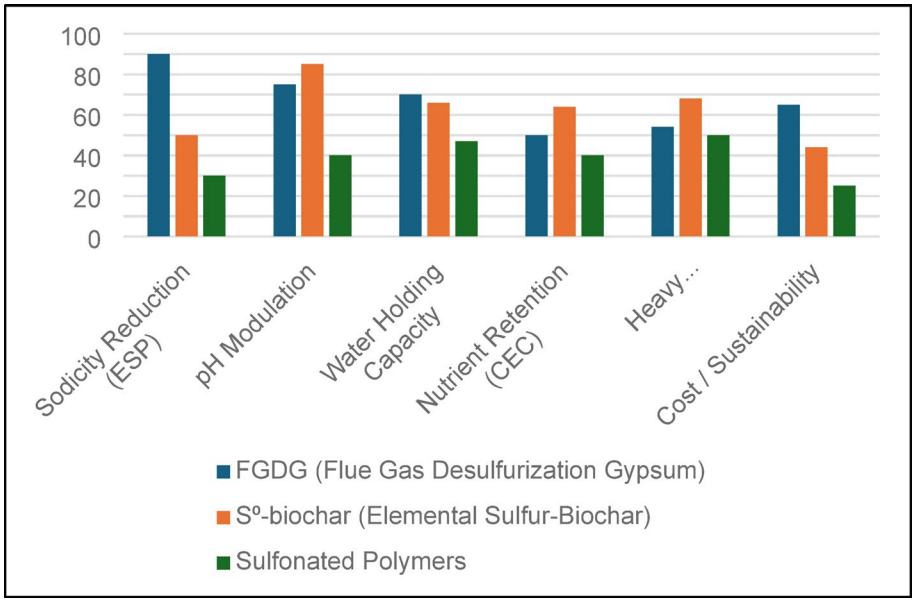

Fig. 5 Comparative performance assessment of engineered sulfur-based amendments. Metrics are normalized to the maximum observed value for each parameter. FGDG shows superior performance in sodicity reclamation, S^0-biochar excels in pH modulation and nutrient retention, while sulfonated polymers are most effective for water management and erosion control. (Data synthesis from Tables 7, 8 and 9)

mobilization or immobilization of trace elements, alterations in pore water chemistry (specifically Total Dissolved Solids, TDS), and the cumulative resource and emission burdens associated with material production and application. This section applies a life cycle thinking framework to assess the net sustainability of the engineered solutions discussed previously.

6.1 Trace element mobility-speciation control and remediation

Trace elements (e.g., As, Cd, Cr, Cu, Hg, Pb, Zn) exist as natural constituents of soil and geological materials; however, their anthropogenic enrichment and geochemical mobilization can elevate concentrations to levels that pose ecotoxicological and human health risks. The mobility and bioavailability of these elements are not governed by total concentration alone but rather by their speciation of the specific chemical form in which they exist. This speciation is a dynamic function of master geochemical variables including pH, redox potential (Eh), dissolved organic carbon (DOC), and competitive ion effects [53].

6.1.1 The source and sink dynamics of flue gas desulfurization gypsum (FGDG)

FGDG, as a byproduct of coal combustion, contains a characteristic suite of trace elements derived from the parent coal feedstock. Of particular concern is the presence of mercury (Hg) and other chalcophile elements, which may be mobilized if the gypsum matrix undergoes dissolution or weathering [54]. Conversely, FGDG can also function as a sorbent or stabilizing agent for certain anionic species (e.g., arsenate) via surface precipitation or incorporation into the calcium sulfate lattice.

From a process engineering perspective, the management of FGDG-derived trace elements relies on Stabilization/Solidification (S/S) unit operations. These techniques employ cementitious binders (e.g., Portland cement) or pozzolanic materials (e.g., fly ash) to encapsulate the FGDG matrix. This encapsulation serves a dual purpose: (i) it reduces the effective diffusivity of contaminants by creating a low-permeability barrier, and (ii) it provides a high-pH chemical environment that favors the precipitation of metal hydroxides and carbonates, thereby minimizing leachability as measured by standard protocols (e.g., Toxicity Characteristic Leaching Procedure, TCLP) [55].

6.1.2 Elemental sulfur-biochar composites for sulfidogenesis-driven immobilization

The elemental sulfur-biochar composite represents an engineered system for the in-situ immobilization of cationic heavy metals. The mechanistic pathway involves two sequential process steps [56, 57]. First, microbial sulfate reduction: the elemental sulfur component undergoes microbially mediated oxidation to sulfate. Under the locally reduced microenvironments created within biochar pores, this sulfate can be further reduced by sulfate-reducing bacteria to dissolved sulfide (S^{2-}, HS^-). Second, metal sulfide precipitation: the generated sulfide reacts rapidly with labile cationic heavy metals such as Pb^{2+}, Cd^{2+}, and Cu^{2+} to form highly insoluble metal sulfide precipitates including PbS, CdS, and CuS. The solubility product constants for these metal sulfides are exceptionally low, rendering the metals effectively sequestered against leaching or plant uptake.

The process efficiency of this immobilization pathway is contingent upon key operational parameters, including the biochar feedstock and pyrolysis temperature (which govern surface area and redox activity), the particle size of the S^0 (which controls

oxidation kinetics), and the prevailing soil geochemistry (e.g., availability of electron donors for SRB activity) [58].

6.1.3 Sulfonated polymers for ex situ and in situ ion exchange capture

Sulfonated polymers, functionalized with strong Bronsted acid groups (-SO_3H), operate as high-capacity cation exchange resins. In their dissociated form (-SO_3^-), they exhibit a strong electrostatic affinity for cationic heavy metal species (e.g., Cu^{2+}, Zn^{2+}, Cd^{2+}). The sorption process is governed by ion exchange equilibria and is particularly effective for the polishing of wastewater streams or the creation of reactive permeable barriers in soil systems [59]. The selectivity of the polymer can be tuned by controlling the degree of sulfonation and the cross-linking density of the polymer matrix.

6.1.4 The role of sulfur-organic interactions in trace element speciation

The native soil organic matter (SOM) pool and the introduced organic carbon from biochar amendments play a pivotal role in modulating trace element fate. SOM contains a diverse array of complex ligands, including thiol (-SH), carboxyl (-COOH), and phenolic (-OH) functional groups. These ligands can form stable organo-metallic complexes with trace elements, which may either mobilize the elements (by forming soluble complexes that resist sorption) or immobilize them (by forming insoluble macromolecular aggregates). Understanding the net effect of these sulfur-organic interactions on contaminant transport is critical for predicting long-term remediation outcomes [60].

6.2 Total dissolved solids dynamics and pore water chemistry

Total Dissolved Solids (TDS) is a bulk parameter quantifying the mass concentration of all dissolved inorganic and organic constituents in aqueous solution. Elevated TDS in soil pore water or receiving water bodies is a primary indicator of salinization and can arise from multiple sources, including:

- **Agricultural return flows**: Leaching of soluble fertilizers and soil amendments.
- **Industrial discharges**: Brines and process effluents.
- **Amendment application**: The dissolution of gypsum (FGDG) directly contributes calcium (Ca^{2+}) and sulfate (SO_4^{2-}) to the pore water, resulting in a transient increase in TDS and electrical conductivity (EC) [61].

While this transient TDS spike is often necessary to facilitate the leaching of deleterious sodium salts in sodic soil reclamation (as discussed in Sect. 5.1), it represents a trade-off process. Unmanaged, elevated TDS in leachate can impact the quality of downstream groundwater or surface water resources, imposing osmotic stress on aquatic biota and limiting the suitability of water for downstream irrigation or potable use. Therefore, effective remediation design must incorporate a salt mass balance to ensure that the net export of sodium exceeds the temporary TDS load imposed by the amendment itself [61].

6.3 Life cycle assessment framework for environmental burden

Life Cycle Assessment (LCA) is a standardized analytical methodology (ISO 14040 and 14044) employed to quantify the cumulative environmental impacts associated with all

stages of a product's life cycle from raw material extraction and processing ("cradle") through manufacturing, distribution, use, and end of life management ("grave") [62].

In the context of engineered soil amendments, life cycle assessment provides a rigorous, quantitative framework for comparative process evaluation. Key applications include three principal areas [62]. First, hotspot identification: this involves pinpointing the life cycle stages such as pyrolysis energy demand for biochar or transportation of bulk FGDG that dominate the overall environmental footprint. Second, beneficial reuse assessment: this compares the environmental burdens of landfilling an industrial byproduct such as FGDG against those associated with its processing and beneficial application as a soil amendment, a step that is essential for validating circular economic claims. Third, avoided burden accounting: this quantifies the environmental credits associated with the displacement of virgin materials or the reduction in fertilizer requirements due to enhanced nutrient retention.

An effective LCA for the systems described in this review must carefully define the system boundary (e.g., should it include changes in crop yield and associated carbon sequestration?) and select appropriate functional units (e.g., impact per hectare of land reclaimed, or per ton of contaminant immobilized). The application of Life Cycle Assessment to engineered soil amendments requires a transparent and well-defined system boundary. Figure 6 presents a comparative process flow diagram illustrating the cradle to field system boundaries for two representative amendment pathways: (i) the beneficial reuse of Flue Gas Desulfurization Gypsum (FGDG) and (ii) the production and application of a S^0-Biochar composite. The diagram explicitly delineates the included unit processes raw material acquisition, transport, processing, and field application as well as the key mass and energy flows that must be inventoried. This boundary definition is essential for ensuring that comparative LCA studies are conducted on an equivalent functional unit basis, thereby avoiding the erroneous attribution of environmental burdens or benefits.

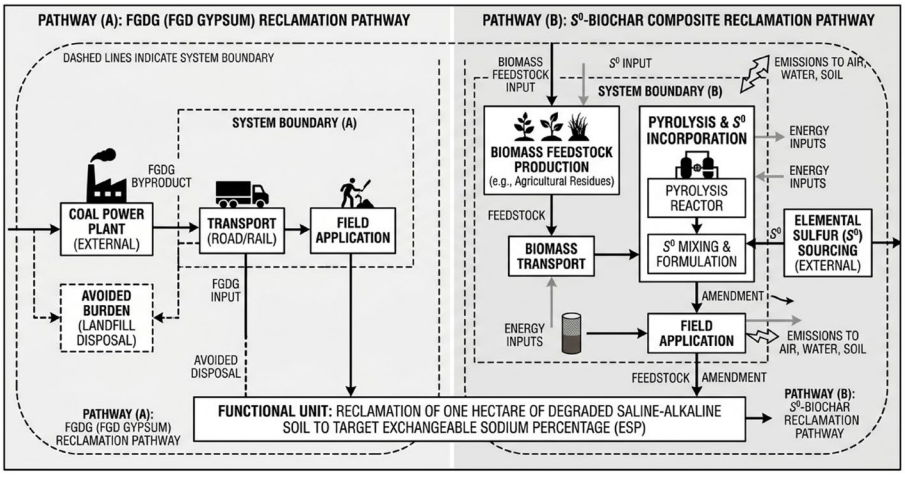

Fig. 6 Comparative system boundary diagram for Life Cycle Assessment (LCA) of two engineered soil amendment pathways. **A** FGDG pathway, illustrating the avoided burden of landfill disposal and the transport and application of the byproduct. **B** S^0-Biochar composite pathway, encompassing biomass feedstock production, pyrolysis, elemental sulfur sourcing, and field application. Dashed lines indicate the system boundary; flows crossing the boundary represent inputs (energy, materials) and outputs (emissions, co-products) to be quantified in the Life Cycle Inventory (LCI) phase. The functional unit is defined as the reclamation of one hectare of degraded saline-alkaline soil to a target Exchangeable Sodium Percentage (ESP)

7 Current state of knowledge and open questions

7.1 Established knowledge

Research over the past two decades has converged on several foundational findings regarding engineered sulfur-organic interactions in degraded soils. Regarding sulfate retention mechanisms, ligand exchange on variable-charge mineral surfaces (≡M–OH, ≡M–OH_2^+) is the dominant sulfate sorption mechanism in non-calcareous soils, while in calcareous systems, precipitation as gypsum and co-adsorption with calcium play larger roles than previously assumed [2]. In terms of SOC-sulfur coupling, soil organic carbon depletion consistently correlates with reduced sulfur mineralization capacity, creating a feedback loop that accelerates both carbon loss and sulfur deficiency [5]. With respect to microbial enzymatic activity, aryl sulfatase activity is a sensitive and reliable biomarker for sulfur limitation, and integrated nutrient management that includes organic amendments reliably upregulates both aryl sulfatase and dehydrogenase activities [6, 7]. Concerning amendment efficacy for sodicity, flue gas desulfurization gypsum effectively reduces exchangeable sodium percentage and improves hydraulic conductivity in sodic soils when applied at rates that replace exchangeable Na^+ with Ca^{2+} [42, 43]. For elemental sulfur oxidation kinetics, oxidation to sulfate is primarily limited by particle surface area and microbial accessibility, with sub-1% w/w applications capable of achieving significant acidification within nine weeks under favorable conditions [19, 21]. In heavy metal sulfidogenesis, combined elemental sulfur-biochar amendments can immobilize Pb^{2+} and Cd^{2+} through microbially mediated sulfate reduction to sulfide, forming highly insoluble metal sulfide precipitates [56, 57]. Finally, regarding PFAS-sulfur linkages, certain PFAS compounds notably fluorotelomer sulfonates such as 6:2 FtS can be desulfonated by soil bacteria expressing the ssuD gene under sulfate-limited conditions, linking PFAS fate to the sulfur cycle [8].

7.2 Critical knowledge gaps and open questions

Despite these advances, significant uncertainties remain that constrain the rational deployment of engineered sulfur-organic amendments at scale. Table 10 summarizes the major knowledge gaps and their practical implications.

7.2.1 Fundamental mechanistic uncertainties

Several fundamental mechanistic uncertainties remain unresolved. First, long-term contaminant aging effects: laboratory studies demonstrating metal sulfide immobilization typically span weeks to months, but whether precipitated PbS and CdS remain stable over decadal timescales under fluctuating redox conditions is unknown. Evidence from natural sulfidic environments suggests that re-oxidation can remobilize metals, yet engineered soil systems lack long-term monitoring data. Second, amendment-microbiome feedback: while biochar and elemental sulfur stimulate specific microbial guilds such as Thiobacillus spp. and sulfate-reducing bacteria, the broader consequences for soil food webs, fungal-to-bacterial ratios, and ecosystem-level functions remain poorly resolved. Third, PFAS desulfonation stoichiometry and end-products: the ssuD pathway cleaves the C–S bond in fluorotelomer sulfonates, but the carbon-chain defluorination products formed under environmentally relevant conditions are incompletely characterized. The potential accumulation of shorter-chain PFAS which may possess their own toxicities remains an open concern.

Table 10 Critical Knowledge Gaps in Engineered Sulfur-Organic Soil Remediation

Domain	What is known	What is unknown	Implications for practice
Contaminant stability	Metal sulfides form rapidly under sulfate-reducing conditions	Long-term (decadal) stability under fluctuating redox	Unknown remobilization risk limits regulatory acceptance
PFAS transformation	6:2 FtS desulfonation via ssuD gene confirmed	Full defluorination extent; accumulation of toxic intermediates	Potential for incomplete detoxification
S^0 oxidation kinetics	Rate depends on particle size and microbial activity	Quantitatively predictive model for field conditions lacking	Application rates remain empirical
Amendment-microbiome interactions	Biochar stimulates sulfur-oxidizers and reducers	Long-term community shifts; effects on non-target functions	Unintended ecosystem consequences possible
Phospho-gypsum safety	Leachate is often below regulatory limits	Public perception and regulatory acceptance remain barriers	Beneficial reuse constrained despite favorable data
LCA system boundaries	Single-product studies exist	No harmonized multi-amendment comparison with consistent boundaries	True sustainability rankings unavailable
Field validation	Promising plot-scale results reported	Multi-year, multi-location trials largely absent	Scalability and reliability uncertain

7.2.2 Contradictions in existing literature

Several findings in the current literature are in direct tension, and resolving these contradictions is essential for predictive design. Regarding elemental sulfur oxidation rates in calcareous versus non-calcareous soils, some studies report faster oxidation in calcareous soils due to pH buffering preventing acid inhibition of Thiobacillus spp [19]., while others find slower oxidation attributed to calcium carbonate coating of sulfur particles [20]. The net effect likely depends on particle size distribution and soil texture, but a unified quantitative model is lacking. Concerning biochar pH effects, biochar produced from different feedstocks at different pyrolysis temperatures can raise or lower soil pH by more than two units [47]. This variability undermines generic application recommendations and necessitates feedstock-specific response surfaces that are not yet available for most soil types. With respect to phosphor-gypsum radioactivity risk perception versus measured leachability, while phosphor-gypsum is classified as technologically enhanced naturally occurring radioactive material due to its ^{226}Ra content, column studies frequently report leachate concentrations below drinking water standards when applied at agronomic rates [13]. The divergence between regulatory thresholds and empirical data limits beneficial reuse. Finally, regarding sulfonated polymer effectiveness across soil textures, some studies show significant aggregate stabilization by polyacrylamide in sandy soils [50], while others report negligible effects in clay-rich soils [51]. The mechanisms underlying this texture-dependency remain unresolved.

7.2.3 Methodological and scale-up challenges

Several methodological and scale-up challenges persist. First, laboratory-to-field translation: most engineered amendment studies are conducted in laboratory batch or small column systems that do not capture field-scale heterogeneity in water flow paths, plant root interactions, or seasonal redox cycling. Second, lack of standardized testing protocols: there is no consensus method for assessing the remediation efficiency of sulfur-based amendments. Metrics such as exchangeable sodium percentage reduction, hydraulic conductivity, and cation exchange capacity are reported inconsistently across

studies, complicating meta-analysis and comparative assessment. Third, life cycle assessment boundaries: LCA studies for FGDG valorization rarely include the full avoided burden of landfill disposal or the downstream benefits of increased crop carbon sequestration. The sensitivity of net environmental impact to system boundary choices has not been systematically quantified.

7.3 Research priorities for the next decade

To address these gaps and enable rational deployment of engineered sulfur-organic amendments, the following research priorities are identified. First, establish multi-year field observatories that monitor contaminant stability, soil carbon dynamics, and microbial community succession under representative pedoclimatic conditions. Second, develop predictive kinetic models for elemental sulfur oxidation that integrate particle size, soil pH buffering capacity, and microbial population dynamics. Third, conduct comprehensive PFAS transformation product analysis under varying sulfur availability to define the full degradation pathway and identify potential toxic intermediates. Fourth, standardize reporting of amendment performance using a core set of engineering metrics including exchangeable sodium percentage, saturated hydraulic conductivity, cation exchange capacity, aggregate stability, and total dissolved solids flux to enable robust cross-study comparisons. Fifth, perform harmonized life cycle assessment studies with consistent system boundaries that account for avoided burdens and long-term carbon soil sequestration.

7.4 Concluding remarks

The engineered sulfur-organic nexus is no longer a black box. Significant mechanistic understanding has been achieved, and a portfolio of amendment technologies flue gas desulfurization gypsum (FGDG), elemental sulfur-biochar composites, sulfonated polymers, and layered double hydroxide hybrids has transitioned from laboratory curiosity to field-deployed tools. Among these, FGDG emerges as the most mature and process-ready technology for sodicity reclamation, with well-established mechanisms and extensive field validation. Elemental sulfur-biochar composites offer the greatest multifunctionality, simultaneously addressing pH modulation, nutrient supply, and soil structure improvement, though their performance is highly soil-specific. Sulfonated polymers are uniquely suited for erosion control and water management in coarse-textured soils, while LDH-biochar composites show promise for combined heavy metal remediation and fertility enhancement, though field-scale data remain limited.

However, the field now faces a critical juncture: the knowledge base is sufficient to demonstrate promise, but insufficient to guarantee long-term efficacy and environmental safety. The open questions and contradictions identified in this review particularly concerning the long-term stability of immobilized contaminants, the inconsistent oxidation rates of elemental sulfur across soil types, and the lack of standardized field protocols define the frontier. Addressing them through interdisciplinary, systems-level research will determine whether engineered sulfur-organic interactions become a mainstream pillar of sustainable soil management or remain a niche technology with unrealized potential.

We conclude that a fit-for-purpose, soil-specific approach guided by quantifiable engineering metrics and informed by harmonized life cycle assessment is essential for

sustainable deployment of these amendments. The five research priorities outlined in Sect. 7.3 provide a roadmap for accelerating the transition from laboratory proof-of-concept to field-scale implementation, ultimately contributing to the restoration of degraded soils and the circular economy valorization of industrial byproducts.

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A.A. wrote the main manuscript text and prepared figures.

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