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# Sustainable $CO_2$-basd acidizing: A comprehensive review of chemical additives for enhanced carbonate reservoir stimulation

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## Abstract

$CO_2$-based acidizing provides a corrosion-resistant alternative to potent mineral acids in carbonate reservoirs by producing carbonic acid in situ. This method synchronizes stimulation procedures with carbon-management objectives while minimizing the necessity for comprehensive corrosion-inhibitor systems. This review assesses six categories of chemical additives—amines, inorganic salts, inorganic bases, metal-oxide nanoparticles, biological macromolecules, and natural biopolymers—emphasizing their effects on $CO_2$ absorption, pH buffering, and wormhole morphology at reservoir-relevant temperatures and salinities. Experimental findings indicate that specific formulations can achieve $CO_2$ absorption levels reaching 2612 mg/L while maintaining pH levels between 4.5 and 5.2. Furthermore, computed CT imaging confirmed consistent wormhole development, indicating effective acid transfer and diminished corrosion risk. According to the reviewed literature, natural biopolymers and biological macromolecules provide the most advantageous equilibrium of reactivity and environmental compatibility; however, the heterogeneity of experimental data, diversity of reservoirs, and scalability are significant considerations. This review methodologically synthesizes peer-reviewed research and field reports published till October 2025, emphasizing mechanistic insights and identifying shortcomings in converting laboratory performance to field application. The proposed approach connects additive selection to carbonate reactivity, transport mechanisms, and operational limitations, thus informing the development of multifunctional fluids for sustainable stimulation and carbon-conscious reservoir management.

*Keywords: $CO_2$ acidizing; Carbonate reservoir stimulation; Chemical additives; In situ acid generation; Carbon sequestration; $CO_2$ uptake.*

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## 1- Introduction

Carbonate reservoirs account for approximately fifty percent of the global conventional oil reserves and are essential for natural gas production [1-3]. Operational activities can result in diminished matrix permeability, thereby hindering hydrocarbon extraction. Acidizing, the controlled dissolution of carbonate minerals, has become an essential method for improving reservoir permeability, typically utilizing hydrochloric acid (HCl) or combinations of HCl and hydrofluoric acid (HF) to form wormholes that link the wellbore to untouched areas of the reservoir [4]. Although effective, these potent acids provide considerable obstacles, including equipment corrosion, health risks, and environmental dangers [5].

A novel $CO_2$-based acidizing technique modifies this dynamic by dissolving $CO_2$ in formation brine under reservoir conditions, regulated by a particular carbonate system [6, 7]. This approach produces a regulated reaction process, as demonstrated in Eq. 1, creating wormhole networks that enhance acid efficiency during injection [8]. Research shows that $CO_2$-saturated brines sustain pH levels ranging from 3.5 to 5.0 [4, 9], exhibiting a gradual dissolving process that reduces early acid use. Furthermore, the corrosion rates of carbon steel are less when employing carbonic-acid brines in contrast to concentrated hydrochloric acid [10].

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{-2} \quad (1)$$

The combined advantage of $CO_2$-based acidizing encompasses both efficient reservoir stimulation and the facilitation of carbon management strategies [11]. Operators can inject $CO_2$ captured from power plants or air sources into geological formations, facilitating both resource exploitation and carbon sequestration. Such approaches provide enhanced oil recovery (EOR) by employing the identical $CO_2$ stream for hydrocarbon extraction while simultaneously guaranteeing permanent storage [12].

Recent improvements emphasize the integration of chemical additives to enhance $CO_2$ acidizing [13]. These additions augment $CO_2$ solubility, alter hydration rates, control pH levels, and enhance fluid flow properties. Categories of additives encompass amines, inorganic salts, inorganic bases, metal-oxide nanoparticles, biological macromolecules, and natural biopolymers, each offering distinct trade-offs concerning kinetics, environmental effect, and economic viability [9, 14].

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Amines, including monoethanolamine and diethanolamine, have traditionally functioned as primary agents for $CO_2$ collection, providing rapid reaction kinetics but encountering issues concerning cost and toxicity [15-17]. In contrast, biodegradable alternatives such as chitosan demonstrate potential owing to their same efficacy and diminished corrosion hazards [1]. Moreover, inorganic materials can regulate pH levels and preserve carbonate states, hence enhancing acid efficiency and carbon retention [18-20].

Metal oxide nanoparticles offer a promising approach for enhancing $CO_2$ acidizing, exhibiting significant reactivity attributed to their surface area and ability to trap carbon [21, 22]. Notwithstanding these advantages, their possible mobility within formations presents structural hazards, requiring rigorous validation processes before extensive implementation [23, 24].

Biological systems, specifically carbonic anhydrase, enhance the transformation of $CO_2$ into carbonic acid but encounter stability issues in outdoor circumstances [25-27]. Conversely, natural biopolymers such as alginate and cellulose provide multifunctional attributes that promote sustainability, with cellulose-based materials exceeding conventional alternatives in $CO_2$ binding capacity and biodegradability [28-31].

Despite this, translating laboratory achievements to field effectiveness is essential, since real-world obstacles involving reservoir complexity, flow dynamics, and material interactions necessitate comprehensive field trials and adaptive protocols [32-35]. Economic factors, such as carbon pricing mechanisms, may render $CO_2$ acidizing progressively more feasible in comparison to traditional approaches [36]. Lifecycle assessments advocate for environmentally sustainable, bio-based additives as optimal choices, particularly in regulated contexts [37].

## 2- Classification of chemical groups

$CO_2$-based acidizing performance hinges on additive chemistry that governs solubility, reaction kinetics, pH evolution, and transport behavior under downhole conditions. Six groups dominate the literature and field practice, each delivering distinct mechanisms for $CO_2$ capture, acid-front stabilization, and wormhole development. Selection depends on operational priorities, corrosion tolerance, biodegradability, cost, thermal stability, and reservoir characteristics such as temperature, salinity, mineralogy, and target permeability gain. This section presents the chemical basis, representative compounds, quantitative performance benchmarks, and field-deployment considerations for each family, drawing on batch-absorption experiments, core-flood tests, and pilot studies reported through October 2025.

### 2.1. Amines

Amines have historically prevailed in $CO_2$ capture owing to their rapid kinetics and substantial loading capacity. They markedly enhance $CO_2$ solubility through zwitterion and carbamate production (primary/secondary) or bicarbonate catalysis (tertiary), as demonstrated in Eq. 2 and Eq. 3 [38-41]. Commercial amines (MEA, DEA, and MDEA) encounter constraints in acidizing applications, such as elevated regeneration energy, thermal deterioration at temperatures over 120°C, and increased corrosion risks due to impurities like $H_2S$ and $SO_2$ [42].

$$RNH_2 + CO_2 \rightarrow RNHCOO^- + H^+ \quad (2)$$

$$CO_2 + H_2O + R_3N \rightarrow R_3NH^+ + HCO_3^- \quad (3)$$

Sterically hindered amines such as AMP and piperazine mixtures provide enhanced $CO_2$ loading, stability, and reduced regeneration requirements. AMP attains 0.8–1.0 mol $CO_2$/mol amine at 40–60°C (in contrast to 0.5 for MEA); however, viscosity and kinetic constraints necessitate optimization. Furthermore, 2–5 wt% piperazine enhances absorption in MDEA or carbonate solutions by 30–50% through carbamate catalysis, circumventing the elevated thermal requirements linked to MEA [43].

Chitosan salt provides a biodegradable amine carrier in which primary amine groups at the C-2 position of glucosamine enhance $CO_2$ binding. Al-Yasiri et al. (2025) documented a $CO_2$ absorption of 2612 mg/L at 1000 ppm and 50°C, with pH maintained between 4.5 and 5.2 to avert uncontrolled reactions. Core-flooding on 1.5×3-inch Indiana limestone validated effective acid transport, resulting in consistent, branched wormholes at 15–20 pore volumes as illustrate in Fig. 1. Corrosion experiments (72 h) indicated a 60% reduction in weight loss relative to 15 wt% HCl due to the less aggressive acidity and the protective film-forming properties of chitosan [1].

The field deployment of synthetic amines encounters financial and toxicological limitations that necessitate comprehensive waste management. In contrast, chitosan provides comparable absorption, biodegradability, and compatibility with standard equipment. Economic simulations indicate cost equivalence with HCl when factoring in corrosion savings and carbon credits. Current pilot studies (500–2000 ppm, 0.5–2.0 bbl/min, 50–200 bbl/stage) indicate permeability enhancements of 2–5 times and sustained production increases over a duration of 6–12 months [44].

### 2.2. Inorganic salts

Reaction with $CO_2$, $Na_2CO_3$, and $K_2CO_3$ produces bicarbonates as illustrated in Eq. 4, which buffer pH through proton consumption and increase soluble carbon species [45, 46]. Although it is less acidic than pure carbonic acid, effective dissolution is achieved by optimizing the injection rate, temperature, and $CO_2$ partial pressure. This buffering significantly reduces wormhole propagation in comparison to HCl, while strategically delaying face dissolution, thereby enhancing acid penetration and reducing wellbore corrosion [42].

$$CO_2 + Na_2CO_2 + H_2O \rightarrow 2NaHCO_3 \quad (4)$$

Laboratory data demonstrate $CO_2$ absorption ranging from 0.6 to 0.9 mol/mol carbonate at temperatures between 25 and 80°C and pressures of 500 to 1500 psi, with accelerated kinetics at higher temperatures offsetting the decrease in thermodynamic solubility [47]. Potassium carbonate is favored over sodium carbonate because of its greater solubility (111 g/100 mL compared to 21.5 g/100 mL at 20°C), which allows for higher concentrations and a decrease in the volume of carrier fluid required. Additionally, promoters such as borate and piperazine facilitate the conversion of bicarbonate, reducing absorption time by 20–40% and improving throughput [43].

Field applications favor reservoirs within the temperature range of 50–100°C, as this range provides stability and slower kinetics that are advantageous for near-wellbore stimulation. A pilot study in Saudi limestone involved the injection of 150 bbl of 5 wt% $K_2CO_3$ saturated with supercritical $CO_2$ at 1200 psi and 80°C, resulting in a 3.5-fold increase in permeability and sustained production of +180 bbl/day over eight months [44]. Post-treatment analysis confirmed far-field bicarbonate precipitation, validating simultaneous stimulation and in situ carbon sequestration eligible for carbon credits [43, 44].

Challenges include scaling risk when bicarbonate saturation is exceeded, potential for precipitation-induced formation damage if brine chemistry shifts during injection, and the need for precise $CO_2$ dosing to maintain the desired pH window. Real-time monitoring of pH, pressure, and $CO_2$ breakthrough at observation or offset wells helps operators adjust injection rate and additive concentration mid-job to preserve wormhole growth and prevent premature acid spending or pore blockage [42, 47].

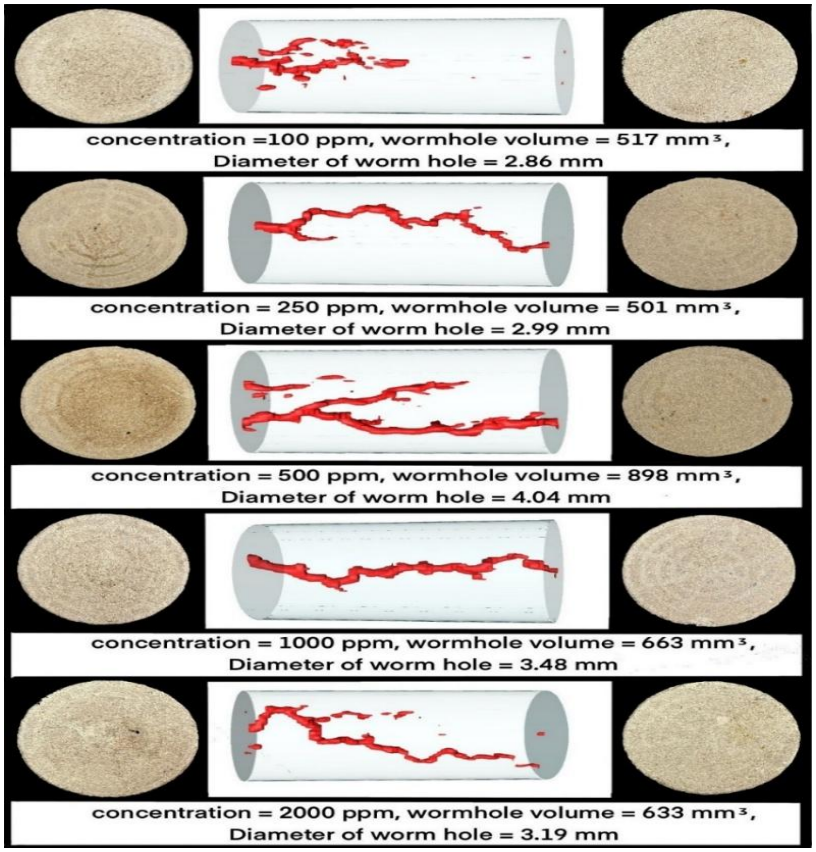


**Fig. 1.** CT visualization of wormhole morphology in amine-modified acidizing systems using chitosan salt [1]

2.3. Inorganic bases

Sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide (Ca $(OH)_2$) consume dissolved $CO_2$ rapidly via neutralization reactions that form carbonate or bicarbonate salts, as illustrated in Eq. 5, Eq. 6 [45].

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \quad (5)$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O \quad (6)$$

These reactions are highly exothermic and proceed within seconds at reservoir conditions, so hydroxide-based systems can cap acidity, improve conformance by diverting acid to lower-permeability zones, and immobilize $CO_2$ as solid carbonate for permanent sequestration [45, 48].

Calcium hydroxide enables safe storage through steady calcium carbonate mineralization. Laboratory analyses validate a 70–95% conversion rate within hours at temperatures ranging from 60 to 120°C and pressures between 500 and 2000 psi, with scanning electron

microscopy confirming the nucleation of rhombohedral calcite [48]. Field pilots administering 5–15 wt% $Ca(OH)_2$ slurries with supercritical $CO_2$ observed pressure stability and reduced porosity, corroborating in situ precipitation [49].

The primary operational difficulty is to avert near-wellbore precipitation that hinders injectivity. To resolve this, staged injection alternates $CO_2$-saturated acid (for wormholing) with hydroxide buffers (to seal high-permeability streaks), thus enhancing sweep efficiency and diversion. Optimization depends on reactive-transport simulations (e.g., PHREEQC integrated with TOUGH2) to calibrate slug dimensions and rates, balancing permeability augmentation with carbon mineralization [49, 50].

Sodium and potassium hydroxides offer faster dissolution kinetics and higher solubility than Ca $(OH)_2$, but the resulting carbonates and bicarbonates remain in solution rather than precipitating, so permanent sequestration requires secondary trapping mechanisms (solubility trapping, ionic trapping in formation brine) [45]. Field applications typically use NaOH or KOH at 0.5–2.0 wt% to moderate pH and improve acid penetration uniformity, reserving Ca $(OH)_2$ for dedicated carbon-storage operations where mineralization is the primary goal [48].

### 2.4. Metal-oxide nanoparticles

Metal oxides—CaO, MgO, $Fe_3O_4$, $TiO_2$, and ZnO—adsorb $CO_2$ and convert it to surface carbonates via chemisorption and mineral carbonation reactions [21+, 51]. High surface areas (50–300 $m^2/g$ for nanoparticles versus <1 $m^2/g$ for bulk oxides) and abundant basic sites (oxide anions and undercoordinated metal cations) enable rapid $CO_2$ uptake at moderate temperature (25–150 °C) without the thermal degradation or regeneration penalties of amine solvents, as illustrated in Fig. 2 [52].

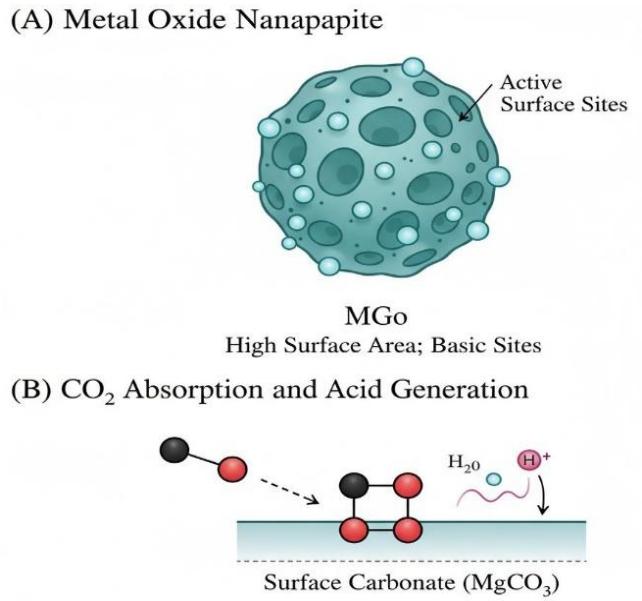


**Fig. 2.** Mechanism of $CO_2$ adsorption and in situ acid generation by metal oxides [21]

Eq. 7 demonstrates that CaO carbonation is thermodynamically advantageous for temperatures below 650°C and reservoir pressures ranging from 500 to 2000 psi. Water vapor accelerates the kinetics of nano-CaO (synthesized by sol-gel/flame methods) by promoting lattice diffusion [53, 54]. Core-flooding demonstrates a $CO_2$ absorption of 400–600 mg/g at temperatures ranging from 50 to 80°C. Moreover, the injection of 0.1–1.0 wt% nano-CaO suspensions resulted in permeability enhancements of 1.5–3.0× in Indiana limestone, due to buffering that inhibits face dissolution and facilitates wormhole branching [54, 55].

$$CaO + CO_2 \rightarrow CaCO_3 \quad (7)$$

Mixed Mg-Al oxides exhibit reactivity comparable to MgO while providing enhanced thermal stability and resistance to sintering [21]. They demonstrate $CO_2$ absorption of 300–500 mg/g, producing geologically stable magnesite essential for sequestration [55]. Moreover, the integration of MgO nanoparticles into chitosan or alginate matrices increases surface area and alters viscosity, thus increasing acid diversion and sweep efficiency in heterogeneous reservoirs [52, 56].

Magnetite ($Fe_3O_4$) and titanium dioxide ($TiO_2$) are chiefly examined for their roles in catalytic $CO_2$ reduction and pollutant elimination [57]. Although native absorption is limited (100–200 mg/g), surface functionalization improves capacity, and the magnetic characteristics ($Fe_3O_4$) provide electromagnetic conformity management in intricate or broken reservoirs [58].

Zinc oxide (ZnO) is particularly appropriate for high-temperature applications (100–150°C) where amines deteriorate. It interacts with $CO_2$ to produce smithsonite, with amine grafting enhancing absorption to 250–400 mg/g. Moreover, ZnO suspensions diminish steel corrosion by 40–50% by the creation of protective zinc-carbonate coatings [21].

Field deployment of metal oxides encounters issues with dispersion stability and aggregation in saline brines. To avert formation damage, stabilizers such as PVP, PAA, or biopolymers are necessary, but these incur additional costs [52]. Standard procedures include rigorous screening (filter, pore-size analysis), with formulations of 0.1–0.5 wt% resulting in enhanced absorption, pH regulation, and homogeneity of wormholes, while preserving injectivity [55, 59].

### 2.5. Biological macromolecules

Carbonic anhydrase (CA), a zinc metalloenzyme, facilitates the hydration of $CO_2$ as illustrated in Eq. 8, achieving turnover rates of $10^6$ $s^{-1}$, far exceeding the uncatalyzed kinetics (k ~ 0.03 $s^{-1}$ at 25 °C) [60]. To improve stability and save expenses, CA is immobilized on substrates such as silica or alginate as shown in Fig. 3 [26, 61]. Silica beads enhance enzyme half-life by 3–5 times at 50 °C, whereas alginate matrices preserve approximately 70% activity after five reuse cycles,

demonstrating the feasibility of economical recurrent applications.

$$CO_2 + H_2O \xrightarrow{CA} H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (8)$$

Incorporating 0.01–0.1 wt% CA into amine or carbonate solutions enhances $CO_2$ absorption by 40–60% and decreases absorption duration by 30–50% [61, 62]. Mechanically, CA reduces the hydration activation energy from approximately 50 to 20 kJ/mol, enhancing the kinetics for a fast regenerative cycle [26]. In acidizing scenarios, its catalytic activity enables real-time pH control by altering enzyme dosage, injection rate, or fluid composition [63].

Traditional carbonic anhydrase encounters deployment constraints owing to denaturation at temperatures exceeding 60–80°C and susceptibility to elevated salinity (>100 g/L TDS) or shear stress [64]. To broaden the operating range, thermophilic variations (e.g., S. yellowstonense, functioning at 80–100°C) and modified isoforms (stabilized through disulfide bonds) are utilized [65, 26]. Field efficacy was established in the North Sea (55 °C), where 0.05 wt% CA-alginate beads attained a 2.8× increase in permeability, maintaining activity for 48 hours before declining to approximately 40% at 72 hours [31].

The economic feasibility depends on the efficiency of reuse. Industrial CA costs between 50 and 200 per kilogram, while immobilization incurs an additional premium of 2 to 5 times that amount [26]. Nonetheless, multi-well recovery can reduce lifespan costs compared to synthetic promoters [61]. Alternatively, in situ production by engineered microbial consortia is a burgeoning avenue, but now constrained by stringent GMO regulations and containment challenges [66, 67].

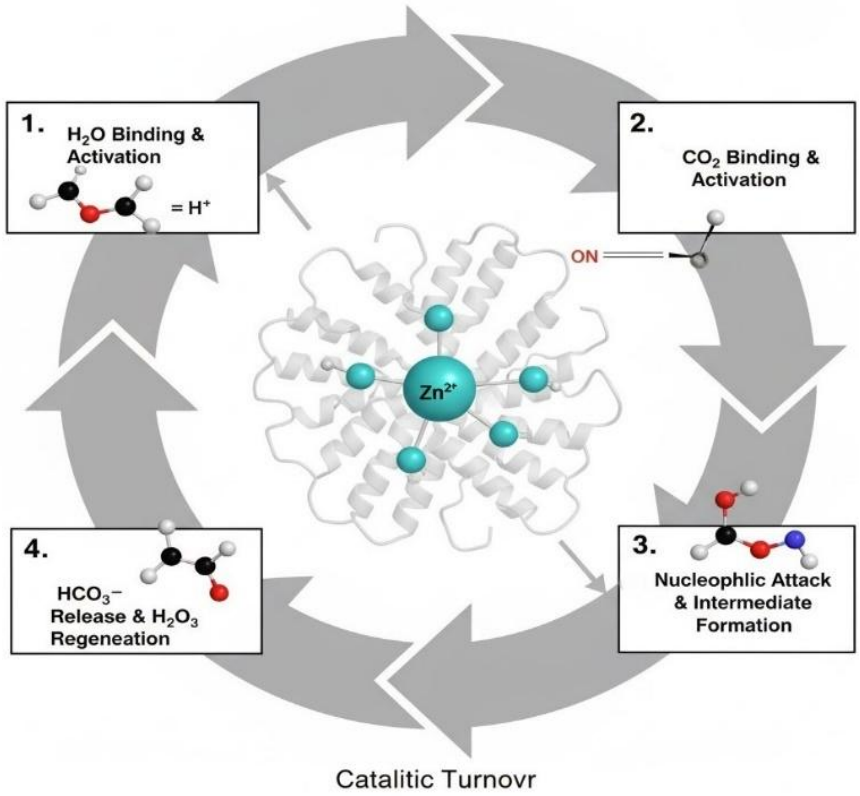


**Fig. 3.** Catalytic cycle of carbonic anhydrase for $CO_2$ hydration [60]

2.6. Natural biopolymers

Natural biopolymers, such as chitosan, alginate, and cellulose, provide a multifunctional platform characterized by the presence of amine, hydroxyl, and carboxyl groups. This additive integrates $CO_2$ capture, rheology modification for fluid-loss control and diversion, and formation protection, all within a single fully biodegradable material, thereby streamlining waste management for sustainable acidizing [68, 69].

Chitosan (β-(1→4)-linked d-glucosamine) carries primary amine groups on the C-2 position, providing reactive sites for $CO_2$ binding via carbamate or bicarbonate mechanisms. Chitosan acetate and chitosan lactate are water-soluble at pH <6.5 and form gels or viscous solutions that stabilize acid fronts and prevent premature breakthrough in high-permeability streaks, as demonstrated in Fig. 4 [70]. Al-Yasiri et al. measured 2612 mg/L $CO_2$ uptake at 1000 ppm chitosan salt and 50 °C, with pH buffered between 4.5 and 5.2—optimal for carbonate dissolution. Core floods in Indiana limestone showed uniform wormhole development to 15–20 pore volumes, CT imaging confirmed minimal face dissolution, and corrosion coupons exhibited 60% lower weight loss than HCl controls [63].

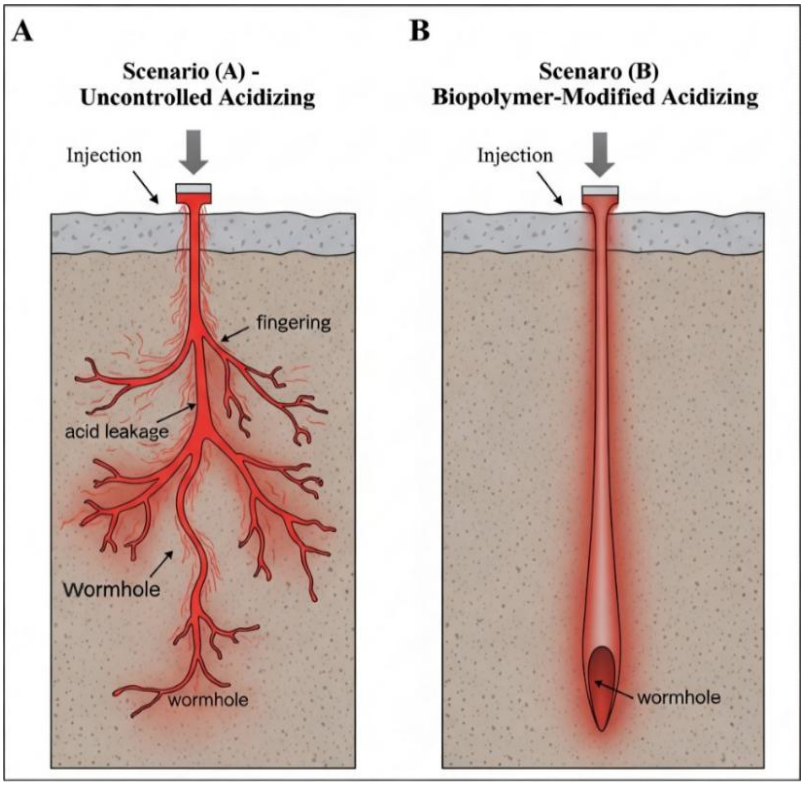


**Fig. 4.** Influence of biopolymer rheology on wormhole propagation [71]

Alginate, derived from brown seaweed, forms ionotropic gels with divalent cations ($Ca^{2+}$, $Mg^{2+}$) through the 'egg-box' mechanism [72]. At concentrations of 0.1–0.5 wt%, it provides viscosity control ranging from 10 to 100 cP for acid diversion, while the presence of carboxyl groups enhances $CO_2$ uptake to levels of 800–1200 mg/L at temperatures between 40 and 60°C. Additionally, crosslinked beads efficiently encapsulate enzymes or nanoparticles to enhance performance synergistically [31]. Biodegradation through alginases results in a half-life ranging from days to weeks, thereby mitigating long-term formation damage [73].

Cellulose derivatives, such as CMC and HEC, employ hydroxyl hydrogen-bonding to achieve moderate $CO_2$ solubility, ranging from 200 to 400 mg/L at a concentration of 0.5 wt%. Their main application lies in fluid-loss control. Specifically, 0.1–0.3 wt% CMC reduces leak-off, thereby enhancing wormhole penetration [74, 75]. Hydrothermal carbonization at temperatures ranging from 180 to 250°C produces hydrochars with a surface area of 100 to 400 $m^2/g$, demonstrating competitive uptake capacities between 1200 and 2400 mg/L. Sultana et al. (2024) demonstrated that these hydrochars outperform other biomass types in high-temperature reservoirs (>100 °C) [30, 76].

Carrageenan, obtained from red seaweed, exhibits thermoreversible gelation at concentrations of 0.1–1.0 wt%, imparting critical viscosity and fluid-loss management [77]. $CO_2$ absorption is modest (400–800 mg/L) through sulfate/hydroxyl binding, and its gel network distinctly safeguards enclosed additives (nanoparticles/enzymes) from degradation [78]. As a result, it is esteemed in composite formulations for compliance regulation in heterogeneous carbonates [77].

Nanocomposites that combine biopolymers with graphene oxide (GO) or carbon nanotubes (CNTs) improve surface area and reactivity. Chitosan-GO attains a $CO_2$ absorption of 1800–2600 mg/L (40–80 °C) through synergistic interactions between the π-π/carboxyl sites of GO and the amines of chitosan. Cigala et al. (2024) revealed that Chitosan-ZnO enhances thermal stability to 120°C, compared to 80°C for pure chitosan, with an absorption of 2400 mg/g. These composites effectively preserve injectivity, diminish corrosion by 50–70%, and enhance wormhole efficiency (PVBT) [79].

Chitosan, derived from abundant shrimp waste (~6–8 Mt/yr), is priced at $5–15/kg (technical grade), although alginate and cellulose are comparably affordable ($2–10/kg). Despite the elevated raw material costs of nanocomposites (GO: $50–200/kg; Metal-oxides: $10–100/kg), minimal loading needs (0.01–0.1 wt%) maintain their competitiveness relative to synthetic amines [73]. Biodegradability reduces disposal expenses and lifespan assessments indicate a 30–50% reduction in carbon footprint compared to traditional HCl [80].

Field techniques stipulate stringent criteria: particle size <1 μm, dispersion stability (zeta potential >±30 mV), filtration ratios <1.2, and rheological parameters (10–100 cP, yield point <5 lbf/100 $ft^2$). Quality control requires verification of $CO_2$ uptake under reservoir circumstances, representative core flooding, and corrosion testing for a duration of 72 to 168 hours. Compliance guarantees that biopolymer acidizing aligns operational benefits, permeability improvement, and corrosion reduction with carbon management objectives [81].

## 3- Mechanistic and functional overview

The effectiveness of chemical additions in $CO_2$-induced acidification is determined by two main factors: molecular structure and physicochemical interactions within the reservoir. These additions are designed to achieve essential functional goals, such as improving inherent $CO_2$ solubility, adjusting localized pH levels, altering fluid rheology, and expediting selected mineral dissolving rates.

Essentially, these mechanisms determine acid-rock interactions and the development of effective wormhole structures, directly influencing stimulation efficiency.

Table 1 presents a comparative functional analysis, evaluating reaction kinetics, pH buffering capacity, and $CO_2$ absorption thresholds. This classification highlights the operational efficacy of tailored additives, as well as their economic feasibility and environmental sustainability, which are increasingly vital indicators in contemporary subsurface engineering.

**Table 1.** Evaluating the functional performance of different additive groups in $CO_2$-based acidizing

| Additive Group | Reactivity with Carbonates | pH Control Capability | $CO_2$ Uptake (mg/L) | Representative Reference |
|---|---|---|---|---|
| Amines | Moderate | Strong buffering | ~1800–2200 | [13, 82] |
| Inorganic Salts | Low to moderate | Weak | ~900–1300 | [83] |
| Surfactants | Indirect (via foam stability) | Minimal | ~1500–2000 | [84] |
| Biopolymers | High | Moderate | >2600 | [30] |
| Nanomaterials | High (via catalytic effects) | Variable | ~2000–2400 | [85] |
| Hybrid Additives | Tunable | Strong | >2500 | [86] |

Amine-functionalized biopolymers demonstrate enhanced $CO_2$ absorption (>2600 mg/L) relative to traditional amines (~1800–2200 mg/L, Table 1). In addition to this quantitative benefit, their intrinsic biodegradability and reduced regeneration energy make them sustainable for extensive implementation. These characteristics render them ideal, environmentally friendly additions for $CO_2$ capture and carbonate reactivity regulation, emphasizing energy efficiency and ecological compatibility [1].

## 4- Environmental and economic considerations

Evaluating the environmental and economic feasibility of $CO_2$-based acidizing requires a thorough Life Cycle Assessment (LCA) based on ISO 14040/44 and ISO 14034 standards [87, 88]. This baseline measures emissions and costs along the full value chain—capture, compression, transport, and injection—recognizing unique profiles for sources such as fermentation, flue gas, or Direct Air Capture (DAC). These verifiable techno-economic comparisons, guided by the Global $CO_2$ Initiative, are vital. Fig. 5 demonstrates that the LCA boundaries span the entire stimulation workflow, matching usage with circular carbon strategies and global decarbonization objectives [89, 90].

Operationally, $CO_2$ stimulation fluids surpass traditional mineral acids by providing inherent environmental advantages. The in-situ production of carbonic acid substantially reduces wellbore corrosion, thereby decreasing the necessity for high-dose inhibitors [91, 92]. This reduction directly mitigates $CO_2$ compression and handling expenses. Moreover, the removal of volatile mineral acids reduces harmful byproducts and VOCs, hence improving site safety and facilitating compliance in environmentally sensitive areas [93].

Economically, while infrastructure necessitates increased capital expenditure, ISO 14034-compliant evaluations demonstrate that long-term operational savings in consumables, maintenance, and compliance counterbalance these fixed costs. Comparative techno-economic assessments demonstrate that when lifespan externalities are incorporated, $CO_2$ acidizing attains cost parity or even superiority compared to HCl [94, 95]. Moreover, the combination of CCS and EOR workflows enhances financial sustainability by creating dual revenue streams from carbon credits and increased efficiency.

$CO_2$-based acidizing solutions create a beneficial and enhancing equilibrium between environmental responsibility and economic feasibility. Their proven capacity to mitigate operating risks, prolong equipment longevity, and conform to CCS–EOR standards establishes them as a persuasive alternative to traditional acid systems. The continuous enhancement of asset lifespan models and repetitive cost framework analyses will expedite implementation across various reservoir conditions, guaranteeing the practical realization of both environmental and economic advantages.

## 5- Challenges and limitations

Engineering and safety challenges related to $CO_2$ acidizing necessitate stringent risk management, especially due to the intricacies of managing supercritical fluids ($scCO_2$) [96]. Unlike ordinary activities, the high density and odorless characteristics of $CO_2$ create particular occupational hazards; accumulation in confined or low-lying places can displace oxygen, resulting in significant asphyxiation risks [97]. Thus, specialized infrastructure is essential to support volatile phase transitions. Adherence to industry standards (e.g., DNV, PHMSA) necessitates rigorous pipeline integrity management, sophisticated leak detection, and emergency procedures to guarantee safe containment and transportation [98, 99].

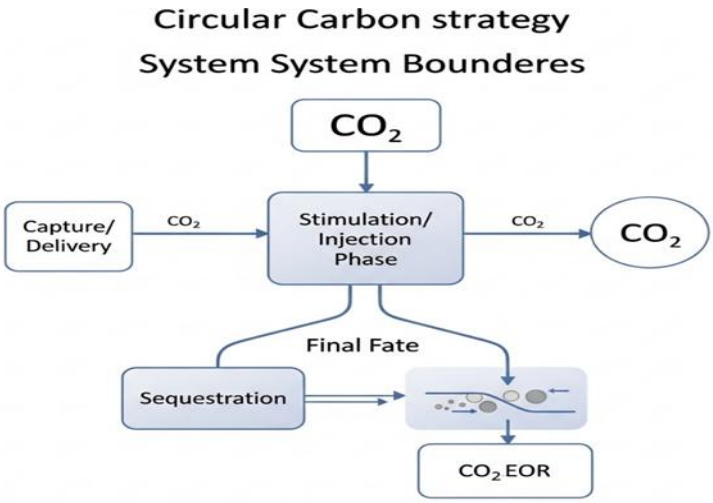


**Fig. 5.** Life cycle assessment boundaries for $CO_2$-based acidizing [89]

5.1. Downhole equipment compatibility and material science

Ensuring material compatibility constitutes a substantial technological challenge [100]. Despite in-situ carbonic acid ($H_2CO_3$) being less corrosive than mineral acids, it compromises wellbore integrity, particularly affecting tubing, packers, and the cement sheath, under high-pressure/high-temperature (HPHT) conditions [101]. Dissolved $CO_2$ mechanistically increases stress corrosion cracking and localized pitting in ordinary carbon steel [102]. Thus, mitigation necessitates the utilization of expensive Corrosion-Resistant Alloys (CRAs) or specific protective coatings. Moreover, the solubility and reactivity of $CO_2$ are significantly influenced by reservoir salinity and geothermal gradients [103]. These variables directly affect acid generation rates, thereby injecting uncertainty into stimulation results [104].

5.2. Field implementation and regulatory barriers

Scaling up $CO_2$-based stimulation from controlled laboratory settings to field applications presents significant challenges [105]. Laboratory conditions that are idealized frequently do not accurately reflect subsurface heterogeneity, intricate reaction kinetics, or dynamic gradients within reservoirs [106]. Successful deployment requires strong numerical modeling to enhance transport mechanisms and forecast mineral dissolution. Fig. 6 demonstrates that this modeling is essential for predicting physical impairments, specifically pore throat plugging resulting from nanoparticle aggregation. The secure supply, storage, and transport of $CO_2$ pose considerable techno-economic challenges, especially for isolated offshore assets [107, 108]. Operational reliability fundamentally depends on adaptable system designs, real-time diagnostic monitoring, and seamless integration with legacy infrastructure [14, 109].

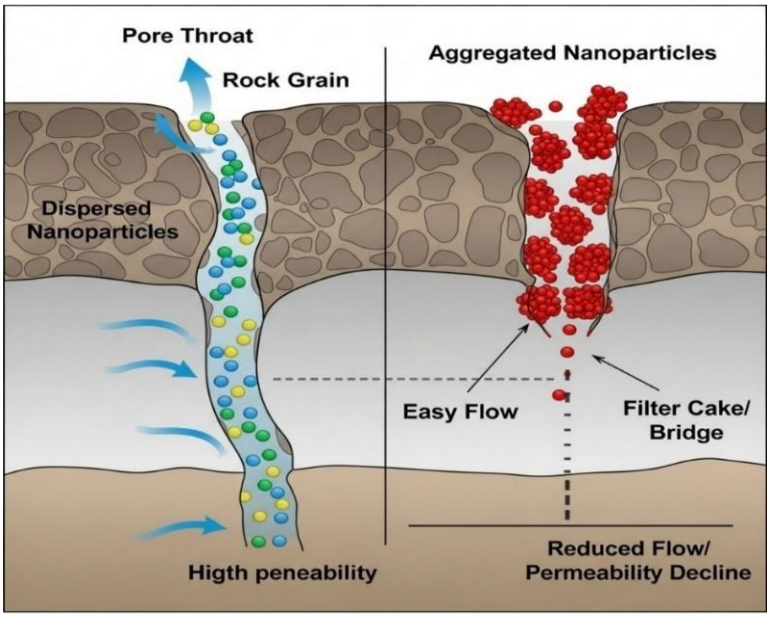


**Fig. 6.** Pore throat blockage mechanisms in nanofluid stimulation [108]

Regulatory frameworks introduce a unique level of complexity [110]. Although jurisdictions implement environmental regulations for CCS and CO2-EOR [111], the licensing framework for acidizing is complex. Despite the implementation of stricter industrial emission limits [112], systemic administrative delays continue to occur, frequently due to the unique kinetics and formation-specific challenges associated with the technology. Thus, global scalability requires comprehensive long-term risk assessment of subsurface $CO_2$ injection, focusing on regional social acceptance and strict environmental protection standards [111].

### 5.3. Additional limitations and research gaps

Beyond the operational and regulatory challenges already discussed, several technical gaps remain that warrant explicit attention. The stability of additives under reservoir shear remains poorly characterized, and polymers, enzymes, and nanoparticle suspensions may deteriorate or lose efficacy under high-rate pumping conditions [113, 114]. Systematic study of thermal and chemical breakdown processes is essential, especially for biopolymers and protein catalysts subjected to elevated temperatures and high salinity [115, 116]. The transport of particulates and nanoparticles poses hazards of pore-throat obstruction and fines migration, potentially undermining permeability improvements if dispersion stability is not preserved [117, 118]. Regulatory considerations encompass not just $CO_2$ management but also the approval processes for innovative additives, including modified enzymes or nanomaterials, necessitating the demonstration of environmental safety and long-term implications [119, 120]. Mitigating these limitations via focused laboratory investigations, core-flood experiments, and field pilots will be crucial to confirming the sustainability and scalability of $CO_2$-based acidizing systems.

Table 2 summarizes the six additive families studied to date, highlighting experimental scales, conditions, data types, and key outcomes.

**Table 2.** Structured synthesis of additive families investigated for $CO_2$-based acidizing, including experimental scales, conditions, data types, and key outcomes

| Additive family | Experimental scale | Conditions (T, salinity, conc.) | Data type (CT, uptake, etc.) | Key outcomes / limitations |
|---|---|---|---|---|
| Amines | Batch absorption | 25–60 °C, varied salinity | $CO_2$ uptake only | High absorption capacity, but no core-scale wormhole data |
| Inorganic Salts | Batch absorption | Ambient–50 °C, brine solutions | $CO_2$ uptake | Moderate uptake, buffering effect, limited scalability |
| Inorganic Bases | Batch absorption | Ambient–50 °C, brine solutions | $CO_2$ uptake | Strong pH buffering, but limited stability under reservoir shear |
| Metal-Oxide Nanoparticles | Batch absorption / core | High T, heterogeneous fluids | Uptake, stability tests | Good uptake, risk of aggregation, fines migration concerns |
| Biological Macromolecules | Batch absorption | Salinity-sensitive, moderate T | Uptake, activity assays | High catalytic efficiency, but degradation under salinity/temperature |
| Natural Biopolymers | Core-flood + CT imaging | 50 °C, 1000 ppm, brine medium | $CO_2$ uptake, CT, corrosion | Uniform wormholes, reduced corrosion, promising scalability |

This synthesis illustrates both the diversity of approaches and the heterogeneity of outcomes, reinforcing the need for systematic evaluation and standardized reporting frameworks.

## 6- Future directions

The current development of advanced acidizing methods is significantly influenced by the increasing demands for subsurface accuracy, environmental sustainability, and operational flexibility in complicated reservoir lithologies. The market is witnessing an increasing demand for these attributes.

### 6.1. Hybrid acid systems and advanced formulation chemistry

A promising frontier exists in the development of hybrid systems that integrate supercritical carbon dioxide ($scCO_2$) with sophisticated chelating agents to create synergistic effects. These tailored formulations offer crucial performance advantages: meticulously regulated reactivity, substantial corrosion mitigation, and broad physicochemical compatibility across diverse lithologies. In carbonate and sandstone reservoirs, chelant-enhanced systems effectively sequester dissolved metal ions, thereby preventing secondary mineral scaling. Nonetheless, High-Temperature, High-Pressure (HTHP) conditions present stability concerns. Therefore, forthcoming research should emphasize the development of biodegradable chelants that can endure severe downhole environments.

### 6.2. Integrated $CO_2$ utilization and intelligent design

Combining $CO_2$ stimulation with existing Carbon Capture and Storage (CCS) and Enhanced Oil Recovery (EOR) frameworks creates a transformational dual-benefit

model. This collaboration optimizes hydrocarbon output while simultaneously aiding in global climate mitigation efforts. The injected $CO_2$ functions on two timescales: it acts as a temporary stimulation fluid for immediate production enhancements and as a medium for long-term geological sequestration. Current research aims to ensure the technical feasibility and environmental sustainability of this technique by concentrating on sophisticated conformance control and reservoir-specific gel systems intended to enhance sweep efficiency and inhibit undesired migration.

Simultaneously, the swift rise of Artificial Intelligence (AI) is transforming the formulation and implementation of acidizing protocols. Machine Learning (ML) methods are essential for delineating permeability heterogeneity, refining intricate acid formulations, and adjusting injection parameters using high-resolution reservoir data. These data-driven solutions reduce operational uncertainty by facilitating swift, adaptive modifications informed by real-time downhole feedback. With the progression of computer sophistication, 'intelligent acidizing' is poised to emerge, allowing autonomous systems to adjust dynamically to changing subsurface conditions. As depicted in Fig. 7, these intelligent procedures integrate effortlessly into the overarching operational frameworks of CCUS and EOR.

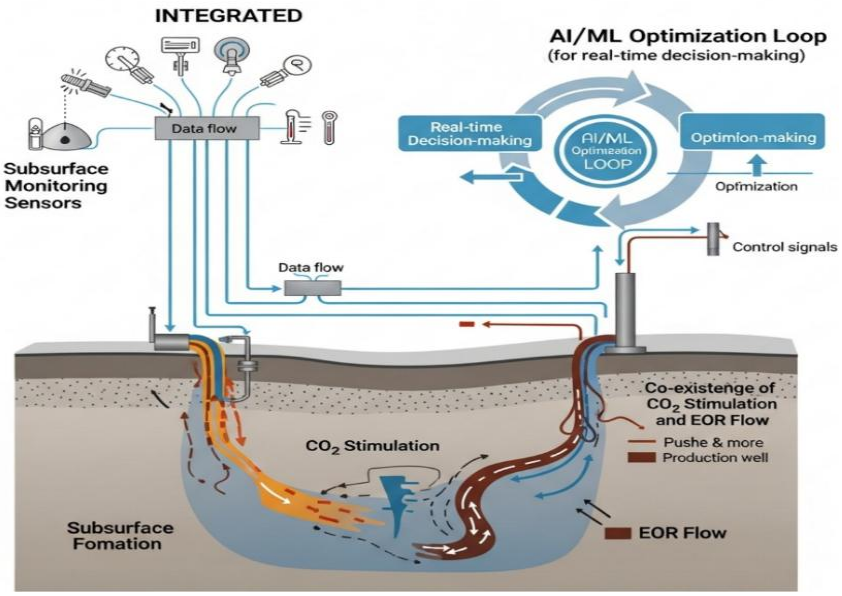


**Fig. 7.** Integrated AI-EOR-stimulation subsurface framework

6.3. Advanced materials for in situ carbonic acid generation.

A pivotal research avenue involves harnessing specialized materials engineered to enhance $CO_2$ adsorption and facilitate controlled in-situ carbonic acid ($H_2CO_3$) generation. Highly porous adsorbents, specifically tailored zeolites, activated carbon composites, chitosan salt derivatives, and Metal-Organic Frameworks (MOFs), exhibit significant potential for maximizing $CO_2$ loading capacity under reservoir conditions. Additionally, the integration of reactive mineral phases, leveraging Enhanced Weathering (EW) principles, can kinetically accelerate the geochemical conversion of $CO_2$ into stable bicarbonates. This material-driven approach not only optimizes immediate stimulation efficiency but also secures long-term sequestration, aligning operational acidizing objectives with rigorous environmental sustainability mandates.

## 7- Conclusion

There has been a recent paradigm shift toward acidizing procedures that are based on carbon dioxide ($CO_2$), which constitutes a substantial and consequential evolution in the methodologies that are employed for reservoir stimulation. As a result of this transformation, the dual aims of simultaneously decreasing the impact on the environment and simultaneously boosting the operational efficiency of the organization are directly dependent on one another.

This exhaustive review has made it abundantly evident that the selection of chemicals through thorough consideration is of the utmost relevance when it comes to enhancing $CO_2$ absorption and subsequent in situ acidification processes. This is the case because the choice of chemicals is of the utmost importance. When compared to the six distinct chemical groups that were investigated, it was discovered that the Natural Biopolymers and Biological Macromolecules possessed the greatest significant potential for prolonged reservoir stimulation. One of the most adaptive and leading examples of this potential is chitosan salt, which emerged as a potential. It is the high intrinsic reactivity, predictable biodegradability, and structural flexibility that they possess that contribute to their applicability. These are the qualities that contribute to their use. On the other hand, the general usability of conventional amine-based solvents is restricted by persistent restrictions, the most notable of which are their high corrosivity profile and the

large energy requirements associated with solvent regeneration. In spite of the fact that it has been demonstrated that these solvents provide functional benefits, their application in more general contexts is restricted.

By strategically integrating inorganic salts, bases, and specialized nanomaterials, there is the possibility for the development of sophisticated hybrid stimulation solutions. This could be accomplished. On the other hand, in order to guarantee the dependability of the implementation of these technologies, it is essential to conduct exhaustive testing that is tailored to the reservoir. This testing needs to establish beyond a reasonable doubt that the technologies are effective over the long term and that they are compatible with the materials used in downhole environments.

In the end, the future expansion of the next-generation acidification technology calls for a concentrated research effort that focuses on additive synergy, detailed reservoir-specific compatibility studies, and a thorough examination of the long-term environmental imprint. Equally important, artificial intelligence and machine learning models should be integrated to predict heterogeneity effects across complex reservoir architectures. By coupling ML-driven simulations with hybrid $scCO_2$–chelants, additive synergies can be validated at the field scale, ensuring both reliability and scalability. Chemical additives that are sensitive to carbon dioxide ($CO_2$) serve as a powerful enabler for subsurface engineering within the context of a carbon-aware energy framework, which is undergoing rapid evolution. This makes it possible for chemical processes to properly align with bigger aims regarding carbon management and utilization.

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# التحفيز الحمضي المستدام باستخدام ثاني أكسيد الكربون: مراجعة شاملة للمضافات الكيميائية لتحسين تحفيز المكامن الكربوناتية

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## الخلاصة

يُعد التحميض القائم على ثاني أكسيد الكربون ($CO_2$) بديلاً مقاوماً للتآكل مقارنة بالأحماض المعدنية القوية في المكامن الكربوناتية، وذلك من خلال توليد حمض الكربونيك داخل المكمن. تعمل هذه الطريقة على مواءمة إجراءات التحفيز مع أهداف إدارة الكربون، مع تقليل الحاجة إلى أنظمة شاملة لمثبطات التآكل.

تستعرض هذه المراجعة ست فئات من الإضافات الكيميائية: الأمينات، الأملاح غير العضوية، القواعد غير العضوية، جسيمات أكسيد المعادن النانوية، الجزيئات الحيوية الكبيرة، والبوليمرات الحيوية الطبيعية، مع التركيز على تأثيراتها في امتصاص ثاني أكسيد الكربون، ضبط الأس الهيدروجيني (pH)، وتشكيل القنوات (wormholes) عند درجات حرارة وملوحات مماثلة لظروف المكامن.

أفاد الياسري وآخرون (٢٠٢٥) [١] بأن امتصاص ثاني أكسيد الكربون بلغ ٢٦١٢ ملغم/لتر عند تركيز ١٠٠٠ جزء في المليون ودرجة حرارة ٥٠°م، مع الحفاظ على مستويات pH بين ٤.٥ و٥.٢؛ كما أكدت صور الأشعة المقطعية المحوسبة (CT) تطوراً متسقاً للقنوات، مما يشير إلى انتقال فعال للحمض وانخفاض خطر التآكل.

وبحسب الأدبيات المستعرضة، توفر البوليمرات الحيوية الطبيعية والجزيئات الحيوية الكبيرة أفضل توازن بين النشاط الكيميائي والملاءمة البيئية؛ إلا أن تباين البيانات التجريبية، وتنوع المكامن، وقابلية التوسع تبقى اعتبارات جوهرية.

تقوم هذه المراجعة بدمج منهجي للأبحاث المحكمة والتقارير الحقلية المنشورة حتى أكتوبر ٢٠٢٥، مع التركيز على الرؤى الميكانيكية وتحديد أوجه القصور في تحويل الأداء المخبري إلى تطبيقات ميدانية. ويربط النهج المقترح اختيار الإضافات بتفاعلية الكربونات، وآليات النقل، والقيود التشغيلية، مما يساهم في تطوير سوائل متعددة الوظائف للتحفيز المستدام وإدارة المكامن بوعي كربوني.

**الكلمات الدالة:** التحفيز الحمضي باستخدام ثاني أكسيد الكربون، تحفيز المكامن الكربوناتية، المضافات الكيميائية، توليد الحمض داخل المكمن، احتجاز الكربون، امتصاص ثاني أكسيد الكربون.