

Kinetics Regulation of Heterogeneous Reactions in Multicomponent Acid Systems for Well Stimulation in Tight Heterogeneous Reservoirs

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Abstract

This study investigates the kinetic and hydrodynamic behaviors of multicomponent acid systems during heterogeneous interactions with tight, non-uniform reservoir matrices (including carbonate, mixed, and sandstone formations with carbonate content ranging from 3% to 35%). A novel water-based multifunctional fluid was developed and experimentally validated. The formulation features an optimized 6:1 hydrochloric-to-hydrofluoric mass ratio, supplemented with acetic acid, a chelating agent (Trilon B), a mutual solvent (technical ethyl cellosolve), and a synergistic corrosion inhibitor mixture. Experimental results show that the developed system provides controlled reaction kinetics, reduces oil-acid interfacial tension to 0.12–0.35 mN/m, and completely suppresses secondary precipitation. Core-scale evaluations and numerical modeling reveal a controlled reduction in the dimensionless Damköhler number (Da) from 1.24 down to 0.15. This variation shifts the reactive dissolution from face-controlled erosion to an efficient kinetic wormholing regime, successfully generating a highly branched wormhole network. Furthermore, under high-temperature conditions ($T = 70^{\circ}\text{C}$), the corrosion rates of ASTM A36 and AISI 431 structural steels were significantly mitigated to 5.0–13.4 g/(m²·h), yielding an overall protection efficiency Z of up to 88.4%. These findings present new pathways for targeted matrix stimulation and dissolution channel engineering in deep, high-temperature reservoir environments.

Keywords

matrix acidizing; heterogeneous kinetics; interfacial tension; damköhler number; wormhole formation; tight reservoirs; well stimulation; Trilon B.



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Introduction

Effective well stimulation and drainage of tight, fractured-porous reservoirs represent some of the most critical challenges in modern subsurface hydrodynamics. Traditional matrix acidizing (MA) treatments within the near-wellbore region aim to generate highly conductive dissolution channels, commonly referred to as "wormholes". However, in deep formations with elevated temperatures and low ambient matrix permeability, conventional treatment fluids lose efficiency. This drawback stems from the rapid reaction kinetics of active hydronium (H_3O^+) ions with rock minerals. The overall efficiency of this stimulation process is fundamentally governed by the dimensionless Damköhler number Da (Fredd & Fogler, 1998; Furui et al., 2022; Panga et al., 2005), which defines the ratio of the chemical reaction rate to the rate of mass transport via diffusion to the mineral matrix, as well as the stochastic nature of the pore space geochemical rearrangement (Kalia & Balakotaiah, 2023; Bařaga et al., 2021).

The key physicochemical barrier in conventional acid systems stems from this diffusion-dominated regime. Under high-temperature thermal heating, instantaneous neutralization of H_3O^+ at the phase interface leads to excessive face dissolution and cavern formation at the wellbore wall. This localized over-acidizing induces sand production, matrix suffosion, and severe pore throat clogging by dispersed fine fragments and reaction products. Consequently, geomechanical degradation of the rock skeleton occurs, resulting in a premature decline in the well production rate.

To retard mass transfer rates and limit the diffusional transport of acid molecules to mineral surfaces, three primary approaches are traditionally deployed in global engineering practice (Chang et al., 2008; Economides et al., 2013): formulation of acid-in-oil emulsions, acid encapsulation, and the addition of synthetic polymers (e.g., polyacrylamides). Nonetheless, emulsion-based fluids possess high initial viscosities, which drastically amplify injection pressures and mechanical energy consumption. In contrast, conventional polymeric retarders are highly susceptible to thermal degradation above 80–85°C. Broken residual polymer chains frequently plug the narrow pore necks, impairing the relative permeability of hydrocarbons. Therefore, engineering thermally stable acid formulations that provide controlled kinetic retardation while preserving the native filtration and transport properties of tight formations remains an urgent technological necessity (Blaut et al., 2024; Mykhailiuk et al., 2024).

To mitigate these limitations, complex modified systems are essential to accurately regulate mass transfer rates and suppress the diffusional transport of acid molecules to mineral surfaces. Integrating specialized nanostructured polymer retardants temporarily passivates active sites on the rock surface, reducing the reaction rate by several orders of magnitude. This approach ensures controlled, sustained dissolution and facilitates the propagation of the active acid front deep into unrecovered zones of the reservoir matrix.

This study provides a kinetic and hydrodynamic substantiation for a newly developed multicomponent acid system (Ivanova et al., 2026). The formulation operates via the synergistic interaction of three distinct acid types, a chelating agent, and organic surfactants. This combination ensures uniform, deep stimulation across the entire net pay thickness while completely preventing the precipitation of gel-like iron and calcium scales.

Research Objective: To provide a physicochemical justification for the efficiency of regulating heterogeneous reaction kinetics and preventing formation damage during the matrix stimulation of tight, non-uniform reservoirs using the developed multicomponent composition.

Research Tasks:

- Evaluate the dissolution capacity and reaction rates of the formulation when interacting with diverse lithologies, specifically carbonate and sandstone matrices.
- Quantify the impact of the hydrophobizing agent on shifting the interfacial tension at the acid–crude oil boundary.
- Determine the corrosion degradation rates of structural and stainless steels exposed to the developed polyacid medium under elevated temperatures.

Materials and Methods

Experimental investigations of the physicochemical, kinetic, and electrochemical properties of the developed formulations were conducted at a research laboratory facility using precision analytical equipment.

The newly developed multicomponent modified acid system was the primary focus of this study [5]. The formulation consists of a hydrochloric acid (HCl, 18.0–60.0 wt.%) and hydrofluoric acid (HF, 3.0–10.0 wt.%) blend, strictly maintained at a 6:1 mass ratio, supplemented with acetic acid CH_3COOH , 1.0–6.0 wt.%. The functional additive package comprised: Trilon B (1.0–5.0 wt.%) acting as a chelating agent, technical ethyl cellosolve (1.0–2.0 wt.%) as a mutual solvent/hydrophobizing agent, and a corrosion inhibitor mixture (3.0–9.0 wt.%) composed of technical urotropine and sodium nitrite in a 1:2 ratio.

Heterogeneous dissolution kinetics and acid penetration capabilities were evaluated gravimetrically using plane-parallel cubic core plugs measuring 15×15×15. The experiments were performed on three distinct matrix

lithologies: Sample 1 (high-carbonate calcite, 90 wt.%), Sample 2 (dolomitized rock containing 73 wt.% dolomite and 15 wt.% insoluble residue), and Sample 3 (sandstone core with a carbonate content of 21 wt.%). The exposure tests were conducted inside sealed Teflon vessels at a simulated reservoir temperature of 70°C over discrete time intervals of 60, 120, and 240 minutes.

Laboratory replication of the hydrodynamic solution–rock interaction was carried out in specialized, hermetic, high-pressure autoclaves manufactured from corrosion-resistant Hastelloy C-276 alloy. The experiments were run under static conditions at fixed temperatures of 20°C and 70°C. To prevent localized fluid boiling and suppress carbon dioxide (CO₂) outgassing, we artificially maintained a constant hydrostatic overpressure of 2.0 MPa within the system.

The rock samples were retrieved from the reactive medium at strictly monitored time steps (60, 120, and 240 minutes), instantly quenched in a neutralizing buffer solution, rinsed thoroughly with distilled water, and dried to a constant weight. Final gravimetric measurements were performed on a precision analytical balance with an accuracy of ± 0.0001 g.

The specific heterogeneous dissolution rate of the carbonate material W , g/(m²·h), was calculated as follows (Bakalár et al., 2025):

$$W = \frac{m_1 - m_2}{S \cdot \Delta t} \quad (1)$$

where m_1 and m_2 are the core plug masses before and after interaction with the acid composition, respectively, in g; S is the total open reactive surface area of the sample, in m²; and Δt is the discrete exposure time interval, in h.

To evaluate the hydrodynamic efficiency of dissolution channel (wormhole) formation, the dimensionless Damköhler number Da , which characterizes the ratio of the surface chemical reaction rate to the diffusion-driven mass transport rate of the reactant to the mineral matrix, was determined using the following expression (Fredd & Fogler, 1998; Panga et al., 2005):

$$Da = \frac{k \cdot C_0^{n-1}}{D/d} \quad (2)$$

where k is the heterogeneous chemical reaction rate constant of rock dissolution derived from the gravimetric data W , g/(m²·h); C_0 is the initial concentration of active hydrogen ions in the acid system, mol/m³; n is the apparent chemical reaction order; D is the diffusion coefficient of hydronium ions within the polyacid solution considering the dynamic fluid viscosity, m²/s; d is the average hydrodynamic diameter of the reservoir pore channels, m.

Values of $Da \gg 1$ correspond to a diffusion-limited regime, characterized by instantaneous acid neutralization at the wellbore wall resulting in face dissolution and cavern creation (Kalia & Balakotaiah, 2024; Ziauddin & Bize, 2007). Conversely, reducing this parameter to the optimal range of $Da \approx 1 \dots 0.1$ signifies a transition to the kinetically controlled regime, ensuring deep propagation of the reactive front and extensive wormhole branching (Zhai et al., 2025).

The interfacial tension (IFT) at the acid fluid–crude oil boundary was measured via the drop-volume stalagmometric method in strict accordance with API standards. The test hydrocarbon phase had a density of 878 kg/m³, a dynamic viscosity of 8.0 mPa·s, and a total resin and asphaltene content of 15.2 wt%.

The formulation's anti-corrosion performance with respect to downhole equipment was evaluated gravimetrically according to ASTM standards. The evaluations were performed using steel coupons (100×170×5 mm) of standard ASTM A36 carbon steel (Sample 1) and corrosion-resistant AISI 431 chromium-nickel stainless steel (Sample 2). The static exposure duration in sealed cells was 24 h, attributed to the formation of stable, chemisorbed passivating layers on the alloyed surfaces at elevated temperatures (Ahmad & Nasr-El-Din, 2026).

The metal corrosion rate K , g/(m²·h), was computed by the formula

$$K = \frac{M_1 - M_2}{S_{st} \cdot \tau} \quad (3)$$

where M_1 and M_2 are the masses of the steel coupon before and after exposure to the corrosive medium, respectively, in g; S_{st} is the total surface area of the steel specimen, in m²; τ is the total duration of the corrosion test, in h.

The relative corrosion inhibition efficiency Z , %, which reflects the degree of anodic process suppression on the metal surface due to the formation of an adsorptive nanostructured barrier, was calculated as follows (Ahmad & Nasr-El-Din, 2026):

$$Z = \frac{K_0 - K_{inh}}{K_0} \cdot 100\% \quad (4)$$

where K_0 is the corrosion rate of the ASTM A36 carbon steel in an unmodified baseline mud acid system (10% HCl + 5% HF), in $\text{g}/(\text{m}^2 \cdot \text{h})$, serving as the reference benchmark for the comparative efficiency evaluation, and K_{inh} is the corrosion rate of the steel exposed to the developed modified polyacid formulation, in $\text{g}/(\text{m}^2 \cdot \text{h})$.

To theoretically justify and visualize the spatial geometry of the dissolution channels (Fig. 2), we implemented a two-scale continuum model for fluid flow and geochemical interaction. This model describes reactant mass transport at the macroscale (Darcy core scale) while accounting for pore-structure evolution at the microscale.

The flow of the multicomponent acid composition within the anisotropic porous medium is governed by the continuity equation and Darcy's law (Economides et al., 2013; Hill et al., 2023):

$$\nabla \cdot \mathbf{u} = 0; \mathbf{u} = -\frac{K}{\mu} \nabla P \quad (5)$$

where $\mathbf{u}$ is the Darcy velocity vector, in m/s ; K is the absolute permeability tensor, in m^2 ; μ is the dynamic fluid viscosity, in $\text{Pa} \cdot \text{s}$; and P is the hydrodynamic pressure, in Pa .

The transport of active hydronium ions H_3O^+ due to convection, molecular diffusion, and heterogeneous dissolution kinetics is expressed by the convection-diffusion-reaction equation (Kalia & Balakotaiah, 2024; Panga et al., 2005):

$$\frac{\partial(\phi C)}{\partial t} + \nabla \cdot (\mathbf{u}C) = \nabla \cdot (\phi D_e \cdot \nabla C) - k_s a_v C^n \quad (6)$$

where ϕ is the current reservoir porosity; C is the acid concentration, in mol/m^3 ; D_e is the effective diffusion tensor, in m^2/s ; k_s is the surface reaction rate constant determined from gravimetric data in W ; a_v is the specific interfacial pore surface area, in m^{-1} ; and n is the chemical reaction order.

The local matrix porosity alteration rate driven by mineral dissolution is defined as (Panga et al., 2005; Szymczak et al., 2024):

$$\frac{\partial \phi}{\partial t} = \frac{k_s a_v C^n \beta}{\rho_s} \quad (7)$$

where β is the stoichiometric dissolution coefficient of the rock, in kg/mol , and ρ_s is the mineral matrix density, in kg/m^3 .

The coupling between porosity evolution ϕ and local permeability K was simulated using a modified Carman-Kozeny relationship [13]:

$$\frac{K}{K_0} = \left(\frac{\phi}{\phi_0} \right)^\gamma \left(\frac{a_{v0}}{a_v} \right)^2 \quad (8)$$

where K_0 , ϕ_0 , and a_{v0} are the initial unperturbed rock parameters, and γ is the pore structure empirical exponent (set to $\gamma = 3$ in this study).

To capture the stochastic nature of wormhole branching (Fig. 2b), a spatial white noise with a normal (Gaussian) distribution ($\mu = \phi_{06 \text{ mean}}$) standard deviation $\sigma = 0.05$ was introduced into the initial porosity field ϕ_0 .

The system of partial differential equations was solved numerically on a two-dimensional (2D) grid within a rectangular domain $L \times W$ approximating the laboratory core sample. The numerical implementation was executed using a sequential iterative approach at each time step Δt :

- Step 1. Initialization: The initial distributions of porosity ϕ_0 (incorporating the stochastic noise) and permeability K_0 are defined.
- Step 2. Pressure Calculation: Based on the current permeability distribution, the elliptic pressure equation $\nabla \cdot \left(-\frac{K}{\mu} \nabla P \right) = 0$ is solved using the Finite Volume Method (FVM). An implicit approximation scheme was applied.
- Step 3. Velocity Calculation: The local field of Darcy velocity vectors $\mathbf{u}$ at the cell faces is computed according to Darcy's law.
- Step 4. Acid Transport Calculation: The convection-diffusion-reaction equation is solved to determine the acid concentration C . The convective terms were approximated using the Upwind Scheme, while the diffusive terms were discretized via the central-difference scheme. The time step size was selected in accordance with the Courant–Friedrichs–Lewy (CFL) condition.

• Step 5. Matrix Update: Based on the calculated concentrations C , the local porosity increment $\Delta\phi$ is determined, and the specific surface area a_v is updated. The permeability variation K for the subsequent time step is then recalculated using the modified Carman-Kozeny relationship.

The cycle (Steps 2–5) is repeated iteratively until the acid breaks through the outlet boundary of the computational domain or until the active acid composition is completely neutralized. The applied two-scale continuum model has been successfully verified by the authors previously for similar filtration conditions in anisotropic media (Ivanova et al., 2024).

Results and Discussion

The heterogeneous interaction between the developed modified acid formulation and the carbonate matrix is characterized by a pronounced alteration in the kinetic parameters of mass transfer. The formation of a macromolecular adsorptive barrier at the phase interface generates an additional diffusional resistance, effectively limiting the transport of active hydronium ions to the reactive surface of the mineral matrix. The heterogeneous interaction between the developed modified acid formulation and the carbonate matrix is characterized by a pronounced alteration in mass-transfer kinetic parameters. The formation of a macromolecular adsorptive barrier at the phase interface generates an additional diffusional resistance, effectively limiting the transport of active hydronium ions to the reactive surface of the mineral matrix (Cernecky et al., 2015). Several independent analytical studies support this synergistic effect of combining organic acids and chelating agents under low-permeability, high-temperature reservoir conditions. The coefficient of friction can also be monitored, as reported by Kelemenova et al. (2020).

Experimental evaluations of the heterogeneous kinetics reveal that the developed fluid provides controlled and sustained rock dissolution. The integration of acetic acid and the Trilon B chelating agent establishes a temporary diffusion barrier, successfully slowing down the mass transfer rate of active hydronium ions toward the mineral rock skeleton. The resulting dissolution parameters for the various reservoir lithologies are summarized in Table 1, while the corresponding reaction dynamics are illustrated in the heterogeneous kinetics plot (Fig. 1).

Table 1. Kinetic and hydrodynamic parameters of non-uniform reservoir matrix dissolution at $T = 70^\circ\text{C}$.

Contact time, min	Specific dissolution rate W_1 (Calcite), $[\text{g}/(\text{m}^2 \cdot \text{h})]$	Specific dissolution rate W_2 (Dolomite), $[\text{g}/(\text{m}^2 \cdot \text{h})]$	Specific dissolution rate W_3 (Terrigenous), $[\text{g}/(\text{m}^2 \cdot \text{h})]$	Damköhler number Da
60	1.3	1.9	6.5	1.24
120	2.3	3.5	8.3	0.58
240	4.2	4.9	10.6	0.15

Mathematical interpretation of the experimental data enabled the calculation of the dimensionless Damköhler number (Da) dynamics for the developed polyacid composition (Table 1). While the baseline unmodified system exhibits $Da \gg 10$, indicating severe diffusion limitation of mass transfer, the developed formulation reduces Da to the range of 1.24 to 0.15.

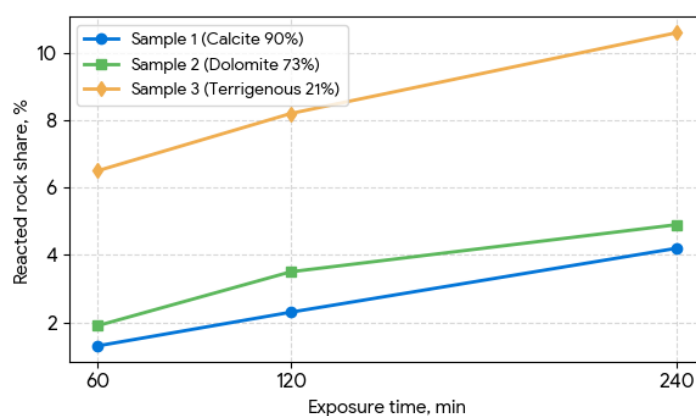


Fig. 1. Dissolution kinetics of various rock matrices exposed to the developed acid formulation at $T = 70^\circ\text{C}$.

The shift of the Damköhler number toward the optimal region of $Da \approx 1 \dots 0.1$ mathematically and physically proves a rebalancing between the mass transfer rate and the surface chemical reaction rate. Retaining the parameter within these boundaries suppresses localized washout of near-wellbore cavities and ensures the transition to the

efficient wormholing regime. The system propagates through the pore channels deep into the matrix before the active acids are completely neutralized, thereby forming an extensive fractal network of wormholes (see Fig. 1).

The low dissolution rate observed during the initial stage (up to 120 min) proves the successful regulation of the heterogeneous reaction kinetics. This retarded reaction within the sandstone and dolomitized matrices prevents instantaneous fluid depletion at the wellbore face, extending the reactive interaction time to 2.5–3.5 hours. Consequently, this ensures the formation of long, thin, and highly branched wormholes, thereby maximizing reservoir stimulation coverage.

An analysis of the kinetic test results (Table 1) indicates a stable decrease in the specific dissolution rate by a factor of 4.50–6.84 compared to the baseline mud acid system. This phenomenon shows a significant shift in heterogeneous dissolution from a diffusion-limited regime to a kinetically controlled regime.

However, rock-matrix dissolution does not directly translate into enhanced oil production. The hydrodynamic mechanism behind the increased fluid inflow is strictly governed by the geometric profile of the generated filtration channels (wormholes). The retarded reaction rate prevents instantaneous acid consumption at the wellbore face and promotes the formation of elongated, narrow, and branched wormholes instead of continuous face dissolution cavities. According to Darcy's law, the creation of such an advanced drainage network multiplies the effective wellbore radius, significantly reduces the skin factor, and enables physical oil inflow from remote, previously undrained reservoir zones, projecting a 2- to 3-fold increase in well production rates.

The mathematical modeling schematic clearly illustrates the generated filtration channels and a detailed spatial geometry comparison for both the baseline and modified systems (see Fig. 2).

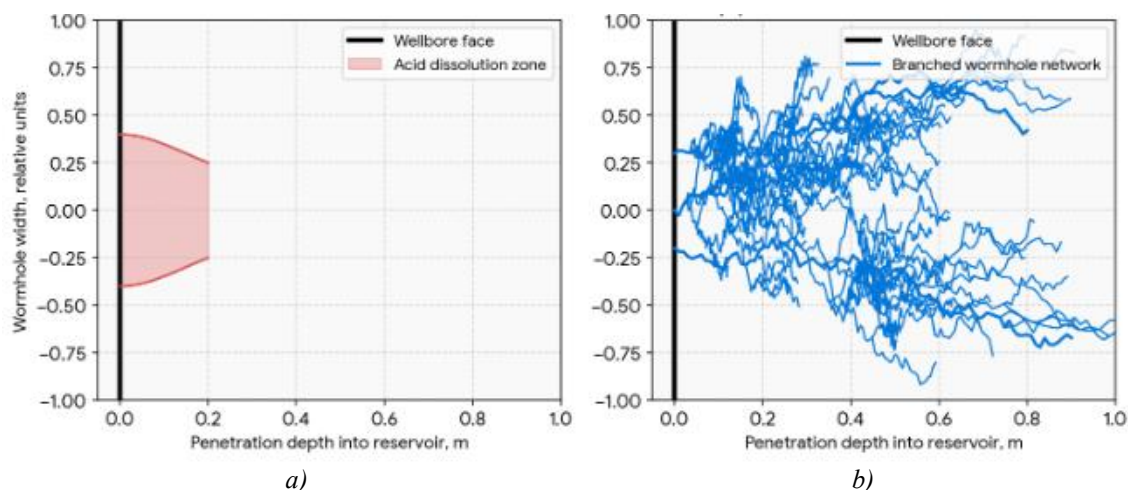


Fig. 2. Comparative numerical simulation of the dissolution channel (wormhole) spatial geometry under high-temperature conditions: a) baseline mud acid system (face dissolution and cavern creation); b) developed multicomponent acid formulation (controlled kinetics and branched wormhole network).

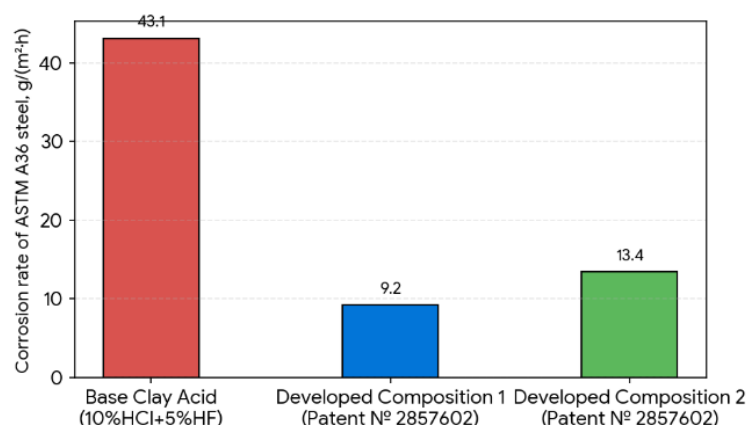
Simultaneously, integrating technical ethyl cellosolve sharply reduced the interfacial tension (IFT) at the crude oil boundary, drastically enhancing the system's sweeping and oil-displacing efficiency (Table 2; see Fig. 3 for comparative analysis).

The key difference between the newly developed formulations (Formulations 1 and 2) and the baseline mud acid is the optimized active acid concentrations and the incorporation of a multifunctional additive package designed to protect downhole assets and suppress secondary precipitation. The evaluated systems are specified as follows:

- Baseline System (Mud Acid): A conventional mud acid formulation containing 10.0 wt.% HCl and 5.0 wt.% HF.
- Developed Formulation 1 (Ivanova et al., 2026): An optimized polyacid composition comprising 60.0 wt.% of a 12% hydrochloric acid solution, 10.0 wt.% of a 10% hydrofluoric acid solution, supplemented with modifying additives: acetic acid (3.0 wt.%), technical ethyl cellosolve (1.0 wt.%), Trilon B (5.0 wt.%), and a corrosion-inhibiting mixture of urotropine and sodium nitrite (3.0 wt.%).
- Developed Formulation 2 (Ivanova et al., 2026): An alternative composition containing 42.0 wt.% of a 36% hydrochloric acid solution, 7.0 wt.% of a 40% hydrofluoric acid solution, acetic acid (1.0 wt.%), technical ethyl cellosolve (1.0 wt.%), Trilon B (4.0 wt.%), and the corrosion-inhibiting mixture (9.0 wt.%).

Table 2. Physicochemical and corrosion characteristics of the evaluated acid systems at $T = 70^{\circ}\text{C}$

Research parameter	Base system 10% HCl + 5% HF	Developed composition 1	Developed composition 2
Interfacial tension at the crude oil boundary, mN/m	2.0	0.35	0.12
Corrosion rate of ASTM A36 steel ($T=70^{\circ}\text{C}$), $\text{g}/(\text{m}^2\cdot\text{h})$	43.1	9.2	13.4
Corrosion rate of AISI 431 stainless steel, $\text{g}/(\text{m}^2\cdot\text{h})$	no data	5.0	12.5
Corrosion inhibition efficiency Z for ASTM A36 steel, %	-	78.6	68.9
Corrosion inhibition efficiency Z for AISI 431 steel, %	-	88.4	71.0
Secondary precipitation and emulsion sludge formation	CaF ₂ gel present	None	None

Fig. 3. Comparative analysis of the ASTM A36 carbon steel corrosion rate at $T = 70^{\circ}\text{C}$.

Particular attention was paid to evaluating the colloidal stability of the developed systems upon contact with mineralized formation fluids. Under reservoir conditions, matrix dissolution inevitably increases the concentration of free Ca^{2+} and Mg^{2+} cations, while iron compounds in the rock matrix trigger the accumulation of Fe^{3+} ions. For conventional acid systems, this phenomenon results in the precipitation of irreversible gelatinous by-products. Table 3 presents the laboratory compatibility test results of the developed polyacid compositions with model formation brines of various salinities.

Table 3. Compatibility test results of the developed compositions with model formation brines of various salinities ($T = 70^{\circ}\text{C}$)

№	Total Brine Salinity, [g/L]	Fe^{3+} Ion Concentration [ppm]	Developed Composition 1	Developed Composition 2	Base System (10% HCl + 5% HF)
1	12,3 (low)	1000	No precipitate	No precipitate	No precipitate
2	215,4 (medium)	3000	No precipitate	No precipitate	Opalescence, traces of CaF ₂ gel
3	332,5 (high)	5000	Stable solution	Stable solution	Heavy gelatinous Fe(OH) ₃ and CaF ₂ precipitate

The data analysis (Table 3) indicates that the base system loses its aggregate stability even at medium brine salinity. Conversely, integrating Trilon B chelant into the developed compositions ensures reliable binding of polyvalent metal cations into stable, water-soluble chelate complexes, thereby preventing secondary formation damage. An additional factor contributing to enhanced hydrocarbon inflow is the reduction in capillary pressure at the phase boundary due to the incorporation of a mutual solvent/surfactant. Figure 4 presents a comparative evaluation of the interfacial tension for the investigated systems. As shown in the chart, the developed composition 2 provides a record decrease in the parameter down to 0.12 mN/m (a 16.6-fold reduction compared to the base level), which crucially improves the oil relative permeability of the low-permeability reservoir.

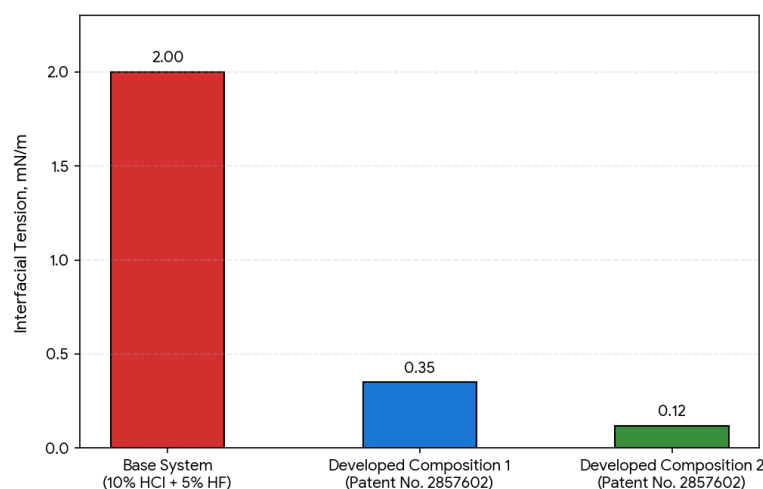


Fig. 4. Effect of acid system modification on the interfacial tension at the acid solution – oil boundary

The developed acid formulations reduce interfacial tension (IFT) to 0.12–0.35 mN/m, compared with the baseline conventional mud acid system (2.0 mN/m). This drastic reduction guarantees the complete recovery of reaction products from the pore space by the produced fluid. Furthermore, integrating Trilon B and acetic acid completely suppressed secondary precipitation of ferric iron (Fe^{3+}) up to 5,000 ppm and calcium ions, ensuring excellent fluid compatibility with formation waters across a wide salinity spectrum (2.3 to 32.5 g/L). Driven by donor-acceptor bond formation, the inhibitor package containing technical urotropine and sodium nitrite significantly reduced the metal degradation rate at 70°C compared with the baseline unmodified mud acid (Table 2). The developed polyacid fluids provide high corrosion inhibition efficiencies (Z) of 78.6% and 68.9% for ASTM A36 carbon steel, respectively, along with record-high protection efficiencies of up to 88.4% and 71.0% for AISI 431 chromium-nickel stainless steel.

Evaluating high-alloy AISI 431 stainless steel, widely used to manufacture highly loaded sucker rod strings in artificial lift well stocks, is of particular scientific and practical interest. Its corrosion rate within the newly developed media dropped to minimal values of 5.0 and 12.5 g/(m²·h). Meanwhile, the relative protection efficiency Z reached a record 88.4% compared to the reference carbon steel exposed to the unmodified acid. The alloying elements (chromium and nickel) embedded in the crystal lattice of the AISI 431 steel interact with the urotropine-sodium nitrite mixture to generate an ultra-robust passivating chemisorption complex on the metal surface. This protective layer ensures 100% preservation of the mechanical integrity of downhole assets and extends their operational lifespan (mean time between failures, MTBF), even under alternating cyclic loads and extreme thermodynamic conditions.

The experimentally established patterns governing the specific rock dissolution rate W and the dimensionless Damköhler number Da (Table 1), coupled with the corrosion degradation parameters of ASTM A36 structural steel and AISI 431 stainless steel (Table 2), robustly prove the high efficiency of regulating heterogeneous reaction kinetics via the developed multicomponent formulations.

The physicochemical mechanism underlying this regulation is rooted in the synergistic interaction between the polyacid base and the functional additives. The addition of acetic acid retards the dissociation of hydronium ions H_3O^+ , while the Trilon B chelating agent temporarily coordinates Ca^{2+} and Mg^{2+} cations at the phase interface. This mechanism triggers the formation of a stable, dynamic macromolecular barrier on the surface of the mineral matrix. Consequently, the heterogeneous interaction regime is artificially shifted from the diffusion-limited region to the kinetically controlled region, which is confirmed by the decline of the Damköhler number to the optimal value of $Da \approx 0.15$. Keeping the reactive process within this range prevents instantaneous neutralization of active acids at the wellbore face and ensures deep propagation of the reaction front into the tight matrix, generating a highly branched fractal network of wormholes.

Simultaneously, the integration of technical ethyl cellosolve causes a sharp drop in interfacial tension (IFT) at the acid fluid–crude oil boundary, reaching record-low values of 0.12–0.35 mN/m. From a hydrodynamic perspective, the Laplace equation shows that minimizing capillary pressure within pore throats drastically increases the phase relative permeability of the geologic medium to hydrocarbons and facilitates the complete cleanout of spent chemical agents along with well production. Thus, well stimulation is achieved not through chaotic matrix destruction, but via strictly targeted engineering of filtration channels in accordance with Darcy's law, while preserving the geomechanical stability of the reservoir matrix.

The high electrochemical stability of the passivating layers, formed on ASTM A36 carbon steel and AISI 431 chromium-nickel stainless steel by the urotropine-sodium nitrite inhibitor package, prevents anodic iron

dissolution and alloy hydrogen embrittlement. A protection efficiency Z of 78.6–88.4% guarantees accident-free matrix acidizing operations under severe alternating thermal and mechanical loads.

These results open new pathways for targeted engineering of dissolution channels in deep reservoir environments.

- First, this provides a mechanism for an artificial transition from uncontrolled face dissolution of the rock (which generates unproductive near-wellbore cavities) to fractal wormholing. By maintaining the Damköhler number within a strictly specified range of $Da \approx 0.15$, stimulation engineers gain a tool to control wormhole penetration length and branching intensity. This allows the fluid to penetrate deep into water-flooded or partially-sealed intervals, creating highly conductive channels without the risk of rock skeleton collapse.

- Second, reducing interfacial tension at the oil boundary to 0.12–0.35 mN/m enables a substantial reduction in capillary pressure within the microporous network, according to the Laplace equation. This reduces the barrier to back-filtration of hydrocarbons, allowing the reservoir fluid to recover spent reaction products unhindered and blocking the formation of stable water-in-oil emulsions.

- Third, the achieved synergistic inhibition efficiency Z of up to 88.4% enables large-volume, prolonged matrix acidizing operations (with fluid contact times extending up to 3.5 hours) in deep wells characterized by anomalously high hydrogen sulfide H_2S and salt concentrations. The high thermal stability of the passivating layer on ASTM A36 and AISI 431 metals eliminates hydrogen-induced cracking and embrittlement of sucker rod strings, guaranteeing the operational safety of downhole components during and after thermochemical treatment.

Conclusion

1. A novel method for regulating the heterogeneous reaction kinetics of multicomponent acid systems based on a 6:1 hydrochloric-to-hydrofluoric mass ratio blended with acetic acid was experimentally substantiated and physicochemically validated. This performance results from the formation of an adsorptive, macromolecular-chelating barrier at the solution–rock interface.

2. At 70°C, the formulation ensures a controlled decrease in the specific rock dissolution rate W and reduces the dimensionless Damköhler number to the optimal range of $Da = 1.24 \dots 0.15$. This behavior hydrodynamically demonstrates a rebalancing of mass-transfer processes and a successful transition to the kinetically controlled regime, enabling deep propagation of the reactive front and targeted engineering of highly branched wormhole networks to enhance fluid inflow.

3. The developed formulation exhibits excellent hydrophobizing capability, reducing the interfacial tension down to 0.12 mN/m and thereby completely preventing secondary aluminosilicate precipitation and sludge emulsion formation within tight, non-uniform matrices. Concurrently, the synergistic corrosion inhibitor limits the metal degradation rates to 9.2 g/(m²·h) for ASTM A36 carbon steel and 5.0 g/(m²·h) for AISI 431 stainless steel, providing a maximum protection efficiency Z of up to 88.4% and guaranteeing the mechanical integrity of downhole equipment.

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