

Kinetics of Dissolution and Wormhole Formation in Carbonate Rocks Using Lactic Acid: A Laboratory Study

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ABSTRACT - Matrix acidizing in carbonate reservoirs typically relies on hydrochloric acid (HCl), which reacts rapidly, causes equipment corrosion, and limits penetration depth. Laboratory experiments confirmed that lactic acid exhibits measurable reactivity with carbonate rocks under reservoir-representative conditions, with apparent first-order rate constants of 0.0841 min⁻¹ (0.05 M), 0.0814 min⁻¹ (0.10 M), and 0.0788 min⁻¹ (0.15 M) at 60 °C and 500 RPM. Moderate R² values (48–49%) suggest partial mass-transfer control and limited acid concentration sensitivity in this range. Arrhenius analysis between 60–90 °C yielded an activation energy of 63.8 kJ/mol, consistent with organic acid–carbonate reaction behavior. Core flooding experiments at 80 °C and 100 psi confirmed that injection rate significantly influences wormhole formation efficiency. Permeability increased from 2.54 mD to 6.25 mD. PVbt analysis revealed an optimal condition at 0.3 mL/min (PVbt ≈ 0.73), supporting dominant wormhole formation, while lower rates (0.1 mL/min, PVbt ≈ 2.7) led to uniform dissolution and higher acid consumption. Intermediate and high rates (0.5 and 0.9 mL/min) generated ramified/branching channels. Overall, the study demonstrates that bio-derived lactic acid is a safer, less corrosive, and environmentally responsible alternative to conventional HCl acidizing, offering well-defined kinetic parameters and validated injection strategies that support efficient wormhole development.

Keywords: lactic acid, carbonate stimulation, dissolution kinetics, core flooding, wormhole formation.

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INTRODUCTION

The interaction between organic acids and carbonate rocks is a critical topic with implications ranging from geochemistry to industrial applications. Organic acids such as lactic acid, produced naturally through biological fermentation, have been widely studied for their ability to dissolve carbonate minerals, affecting soil chemistry, mineral weathering, and even the global carbon cycle (Stumm & Morgan 1996; Oelkers & Schott 1998). In these reactions, lactic acid interacts with carbonate minerals such as calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), leading to the release of carbon dioxide and the formation of calcium lactate (Fredd & Fogler 1998). Understanding the kinetics of these processes is essential for predicting environmental acidification and for developing more sustainable industrial and reservoir stimulation processes. For example, measurements of acid diffusivity in carbonate systems have provided insights for designing more effective acid treatments (Al-Khalidi et al. 2010).

In petroleum engineering, carbonate acidizing remains a widely used technique to enhance well productivity by dissolving formation damage and creating high-conductivity channels (Economides & Nolte 1998). National studies have also investigated carbonate reservoir stimulation techniques, including the development of organic-acid-based additives for scale removal and enhanced recovery (Kristanto et al. 2019). Traditionally, hydrochloric acid (HCl) has been used as the industry standard due to its high reactivity and effectiveness (Nasr-El-Din et al. 2001; Blauch et al. 2003). However, HCl-based treatments have drawbacks, including extremely fast reaction rates near the wellbore, shallow penetration, equipment corrosion, and safety hazards issues magnified at elevated reservoir temperatures (Gdanski 1993; Fredd & Fogler 1998). Various alternative stimulation methods have been proposed to mitigate these issues (Frenier & Ziauddin 2003; Frenier et al. 2001b). In particular, organic acids have a long history in carbonate reservoir stimulation, dating back to at least the 1960s (Harris 1961). Numerous studies have demonstrated their effectiveness in high-temperature applications (Chatelain et al. 1973; Crowe et al. 1988; Hall & Dill 1988; Blok & Milder 1985; Bourne & Reynolds 1991; Almond et al. 1995). As a response to these challenges, there is growing interest in using organic acids such as lactic acid as alternative stimulation fluids. Bio-acid solutions offer several advantages:

they are derived from renewable resources, are less corrosive, have slower and more controllable reaction rates, and are generally safer to handle (Burns 2002; Wu & Grant 2002). Comparable surfactant systems enhanced by the addition of anionic and non-ionic co-surfactants have been shown to improve solubility and performance under reservoir conditions (Alli et al. 2017). Regional research has also highlighted microbial enhanced recovery techniques that is a technology which can improve oil recovery by utilizing microbial activity. Through tube tests and microbial core flooding (MCF), a potential microbial culture was obtained. Microbial metabolism produces bioproducts including surfactants, polymers, acid compounds, and gas, which can lower oil-water interfacial tension, reduce viscosity, and increase rock permeability and porosity, thereby enhancing oil mobilization (Kussuryani 2016). Despite these promising attributes, the reaction kinetics of lactic acid with carbonate rocks under reservoir-like conditions are still not fully understood (Al-Otaibi et al. 2006; Al-Otaibi et al. 2008). Studying these rates is critical to optimizing injection strategies, achieving deeper penetration, and promoting effective wormhole formation (Fredd & Fogler 1998; Huang et al. 2003).

This study aims to investigate the kinetics of lactic acid dissolution in carbonate rock samples under controlled laboratory conditions. Using UV-Vis spectrometry to monitor calcium ion release, XRD to confirm mineral composition, and core flood experiments to observe wormhole formation and permeability enhancement, this work evaluates lactic acid's potential as an environmentally friendly alternative to conventional acid systems for carbonate reservoir stimulation. By gaining insights into reaction kinetics and optimal injection parameters, this research supports the development of safer, more effective, and more sustainable acidizing treatments.

METHODOLOGY

Experimental material and methods

This study comprised laboratory experiments including fluid characterization, carbonate dissolution kinetics measurements, and core flooding under reservoir-like conditions.

Materials

Lactic acid with a nominal purity of 88% typically produced via fermentation was used as the primary reactive fluid. Carbonate rock samples

were prepared as powdered material for dissolution experiments and as cylindrical core plugs for core flooding tests. Standard calcium solutions were also prepared to generate calibration curves for spectrometric analysis.

Rheology tests

Prior to dissolution experiments, fundamental fluid properties of the lactic acid solution were measured to evaluate its injectivity under reservoir conditions: 1). pH was measured using a calibrated pH meter; 2). Density was determined with a density meter; 3). Viscosity was measured using a rotational viscometer at both room temperature and elevated temperatures up to approximately 80 °C, to simulate downhole conditions.

These measurements provided essential data on fluid behavior during the injection operation.

Kinetic dissolution experiments

The dissolution kinetics of carbonate minerals in lactic acid were evaluated using a jar-test flocculator setup. Powdered carbonate rock was added to the flocculator along with the lactic acid solution. Experimental variables included: 1). Mixing speeds of 500, 1000, and 1500 rpm; 2). Temperatures of 70 °C, 80 °C, and 90 °C; 3). Acid concentrations of 0.05 M, 0.1 M, and 0.15 M.

At predetermined time intervals, aliquots were sampled and analyzed for calcium ion concentration using a UV-Vis spectrometer by monitoring absorbance changes near 216-219 nm. Calibration curves from standard solutions were applied to convert absorbance data to molar concentrations. This procedure enabled the systematic assessment of temperature, mixing speed, and acid concentration effects on the carbonate dissolution rate.

Core flooding experiments

Core flooding experiments were conducted to simulate matrix acidizing under reservoir-like conditions and to evaluate wormhole formation effectiveness: 1). Cylindrical carbonate core plugs (1 inch diameter x 1.5 inches length) were cleaned, dried, and characterized for initial porosity and permeability; 2). Each core was mounted in a core holder capable of maintaining a temperature of 80 °C with confinement pressure near 100 psi; 3). Lactic acid solutions were injected at a controlled rate (0.3 cc/min) to evaluate the influence of injection rate on channel formation; 4). Pressure differential across the core was continuously recorded; 5). Pore volume to breakthrough (PVbt) was determined, providing

an indicator of acid efficiency in forming conductive channels; 6). Post-injection, cores were dried and re-measured for porosity and permeability changes; 7). Selected cores were examined via Scanning Electron Microscopy (SEM) to visualize dissolution patterns and wormhole development; 8). These tests provided practical insight into lactic acid performance for carbonate matrix stimulation.

Experimental design (DOE)

A factorial design of experiments (DOE) approach was employed to systematically evaluate the influence of key variables. For kinetic dissolution tests, three factors were varied at three levels each (temperature, mixing speed, acid concentration), yielding $3^3 = 27$ combinations, each tested in triplicate (81 total trials, ensuring repeatability). For core flooding tests, variations included acid type (comparing HCl and the bio-acid lactic acid) and injection rate, resulting in six experimental combinations. This systematic design facilitated the evaluation of individual factor effects and interactions, supporting the identification of optimal conditions for effective acidizing outcomes.

RESULT AND DISCUSSION

Experimental results

This section describes the experimental results in detail, along with analysis and discussion of their implications for carbonate matrix acidizing with bio-acid. The results cover lactic acid characterization, kinetic dissolution experiments, core flood tests, and supporting mineralogical and imaging analyses. These findings provide insight into not only the chemical reactivity of lactic acid with carbonate minerals but also its practical effectiveness in creating conductive channels under simulated reservoir conditions.

Rheology and acid characterization

Before testing its dissolution performance, the lactic acid solution was carefully characterized to ensure it was suitable for acidizing operations. The pH measurement consistently ranged between 3.0 and 4.0, confirming the solution's strong acidity but milder than traditional HCl, as shown in Figure 1 below. This moderate acidity is beneficial because it can slow down the reaction rate, potentially allowing for deeper penetration into the formation before significant face dissolution occurs.

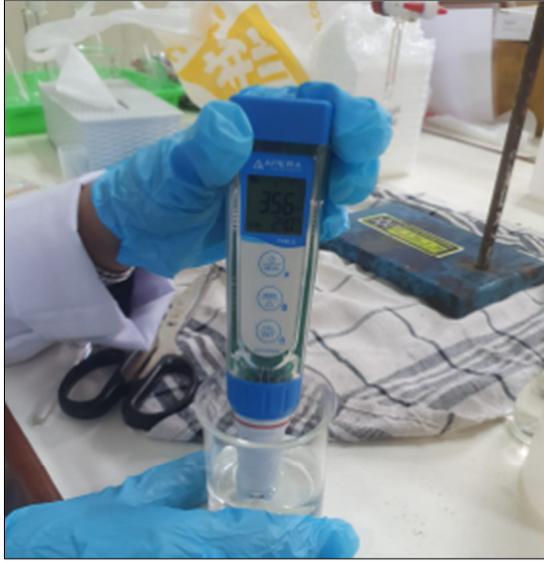


Figure 1. Lactic Acid pH

Density measurements yielded values around 1.23 g/cm^3 . This is comparable to many conventional acid systems, suggesting that there would be no major issues with fluid compatibility or injectivity in standard wellbore conditions.

Viscosity tests showed the lactic acid solution remained low-viscosity (2.4 cP) even at elevated temperatures (tested up to $80 \text{ }^\circ\text{C}$). This indicates that the acid would maintain good flowability when injected into the reservoir, with minimal risk of excessive frictional pressure losses in the tubing or formation, as shown in Figure 2 below.

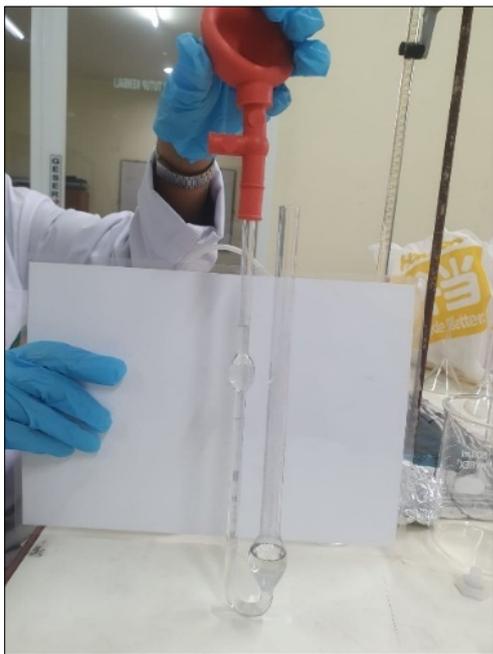


Figure 2. Lactic acid viscosity using ostwald viscosimeter

Mineralogical analysis of carbonate rocks (XRD)

Understanding the mineral composition of the target rock is essential for predicting and interpreting acid-rock reactions. X-ray Diffraction (XRD) analyses were performed on powdered samples of the carbonate cores to identify the dominant mineral phases.

As shown in Figure 3, the XRD diffractograms revealed strong, sharp peaks corresponding primarily to calcite (CaCO_3), with minor peaks indicating dolomite ($\text{CaMg}(\text{CO}_3)_2$) content. This is consistent with typical carbonate reservoir lithologies in many sedimentary basins.

The dominance of calcite implies that the main reaction mechanism with lactic acid is the proton-promoted dissolution of CaCO_3 , releasing calcium ions into solution. The minor dolomite content suggests additional magnesium release may occur, but at a slower rate due to dolomite's lower reactivity.

Kinetic dissolution experiments

The dissolution kinetics of lactic acid with carbonate powders were explored under controlled lab conditions to simulate acidizing reactions. Experiments were performed using a jar-test flocculator to maintain uniform mixing while varying three key parameters: 1). Temperature ($70, 80, 90 \text{ }^\circ\text{C}$); 2). Stirring speed (500, 1000, 1500 rpm); 3). Acid concentration (0.5, 1.0, 1.25 M).

Prior to the kinetic runs, a UV-Vis calibration curve specific to this system was developed to accurately relate absorbance readings to dissolved metal ion concentrations. Standard solutions of calcium (the primary cation from calcite dissolution) at 0.05 M, 0.10 M, and 0.15 M were measured at the characteristic absorbance peak (216–219 nm). The resulting linear fit had a high coefficient of determination ($R^2 \approx 0.99$), confirming the reliability and accuracy of using UV absorbance to quantify calcium in solution. Only three standard points were used because they correspond to the acid concentrations studied, providing calibration over the relevant concentration range. Despite the limited number of points, the relationship was essentially linear; any minor deviations (apparent slight non-linearity) did not significantly affect the fit. The high R^2 (0.99) for the calibration indicates excellent linear correlation, which is expected for an instrumental calibration and should not be confused with the more moderate R^2 values obtained later

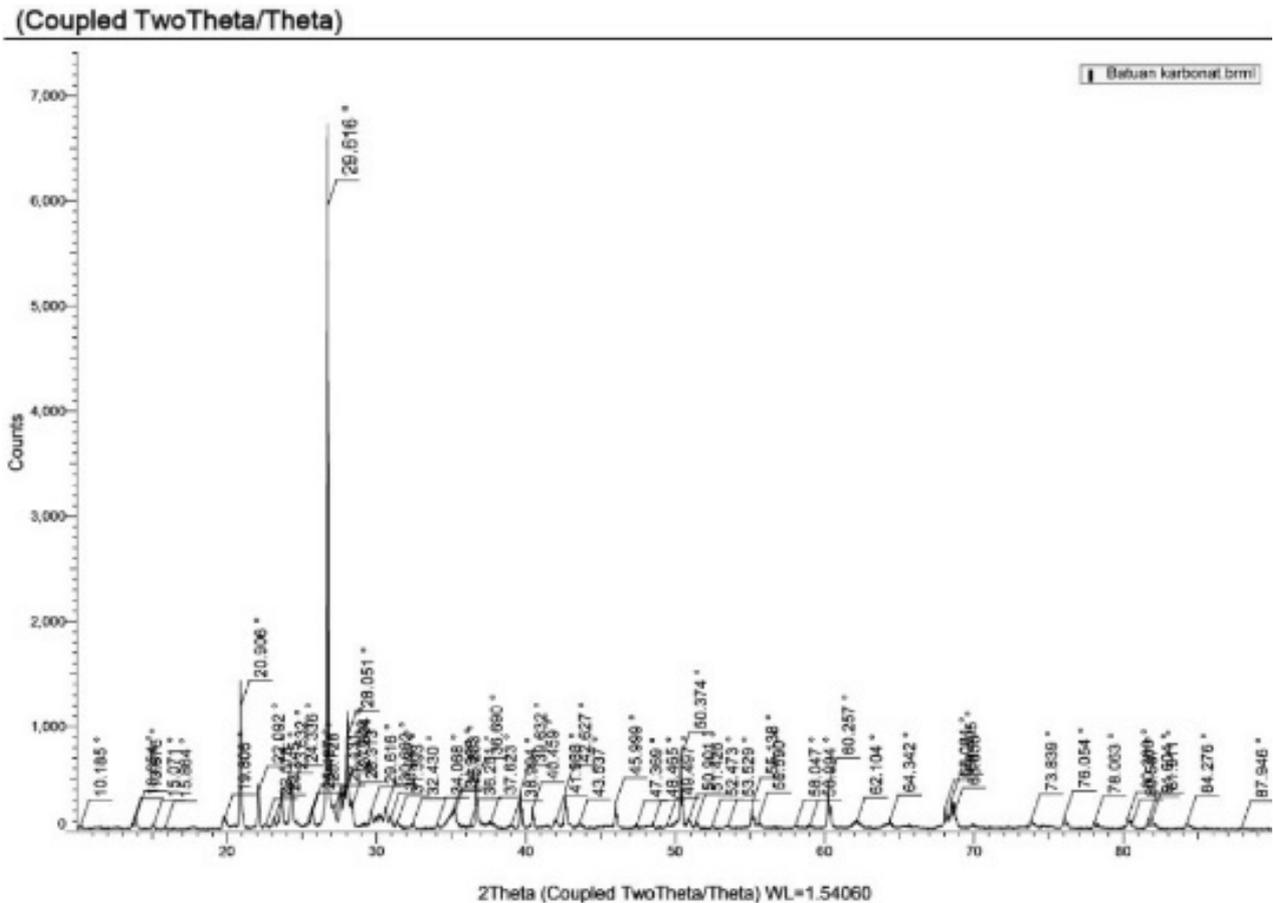


Figure 3. XRD pattern confirming dominant calcite composition with minor dolomite presence.

for reaction kinetics (which reflect experimental reaction dynamics rather than instrument response). Using the calibrated concentration-vs-time data, the extent of carbonate dissolution was quantified, and apparent reaction rate constants were determined for each condition. Assuming pseudo-first-order kinetics with respect to the amount of solid carbonate (valid when the acid is in excess), an exponential decay model was fitted to the calcium concentration curves. In practice, the natural logarithm of the remaining reactant concentration was plotted against time, and the slope of the linear portion provided the first-order rate constant k . This approach yielded an apparent k for each experimental run, allowing comparison of reaction rates across different temperatures, stirring speeds, and acid concentrations.

Figure 4 shows a clear trend: higher temperatures and faster stirring speeds significantly increased the dissolution rate. For example, experiments at 90 °C and 1500 RPM exhibited much steeper absorbance-versus-time curves (indicating faster calcium release) than those at 70 °C and 500 RPM. Similarly, higher

lactic acid concentrations accelerated dissolution, reflecting increased proton availability at the solid surface. These observations are consistent with expectations for acidizing reactions: elevated temperature enhances reaction kinetics (both by increasing intrinsic reaction rates and diffusivity of reactants), and greater agitation reduces the thickness of the diffusion boundary layer, thus mitigating mass-transfer limitations.

As shown in Figure 5a, linear regression of data at 70 °C, 80 °C, and 90 °C produced a slope of -7668.7 ($-E_a/R$), yielding an apparent activation energy E_a of 63.8 kJ/mol. The intercept ($\ln A = 23.93$) corresponds to the pre-exponential factor. A high coefficient of determination ($R^2 \approx 95.9\%$) confirms a strong fit to the Arrhenius model, supporting its use in describing the temperature dependence of the dissolution rate. These values align with prior studies on organic acid-carbonate systems reporting activation energies in the range of 40–80 kJ/mol (Fredd & Fogler 1998; Daccord et al. 1993b). This Arrhenius analysis provides a predictive basis for

evaluating lactic acid performance under different reservoir temperatures. It is noteworthy that the activation energy obtained here is similar to that of other organic acids reacting with carbonates, confirming that lactic acid follows the expected

temperature dependence for carbonate dissolution. Similar Arrhenius-type approaches have also been applied in Indonesian carbonate acidizing design to estimate dissolution rates and optimize treatment strategies (Nurwidyanto et al. 2021).

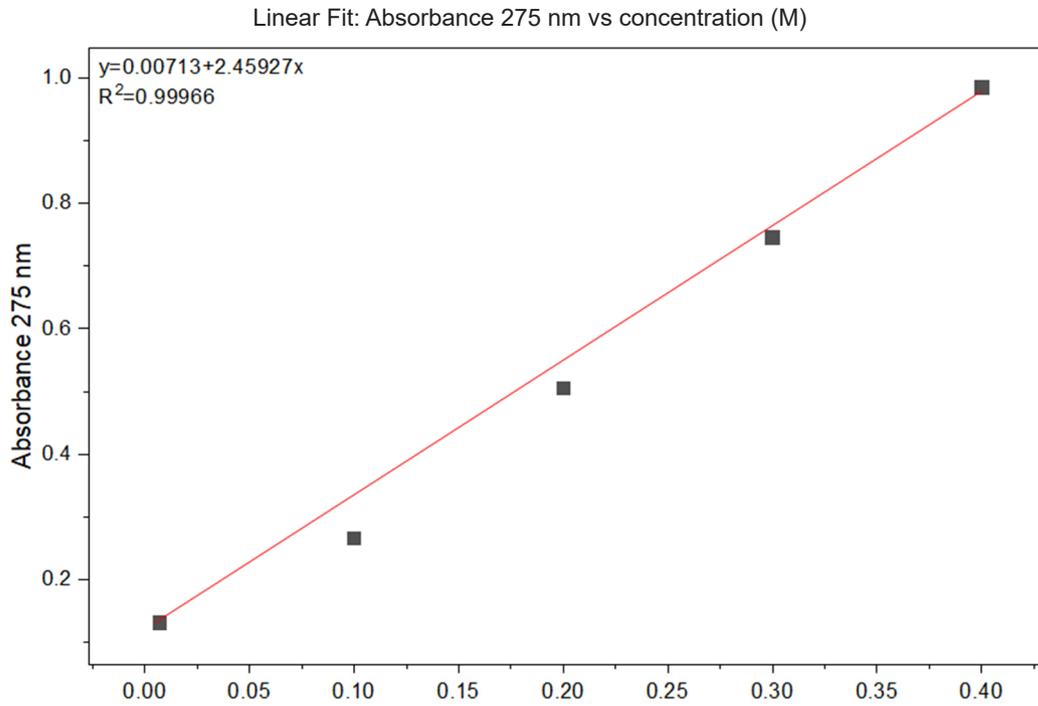


Figure 4. Calibration curve for Mg^{2+} in lactic acid solution (from dissolved carbonate).

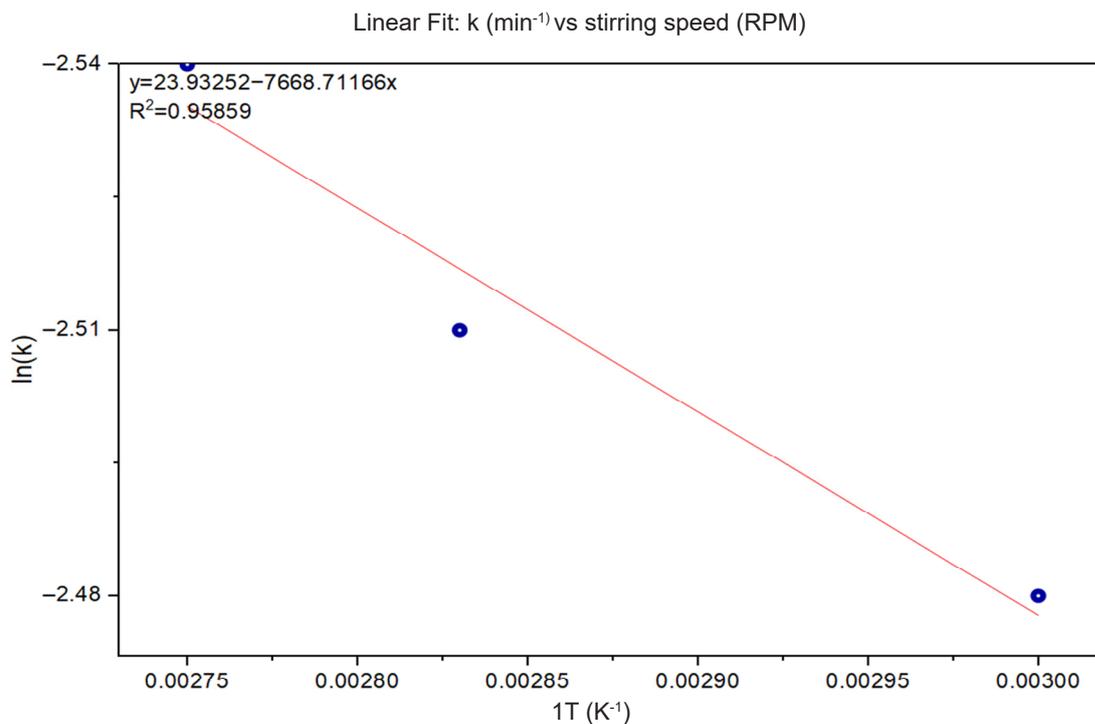


Figure 5a. Arrhenius plot of $\ln(k)$ versus $1/T$ (K^{-1}) for lactic acid-carbonate dissolution.

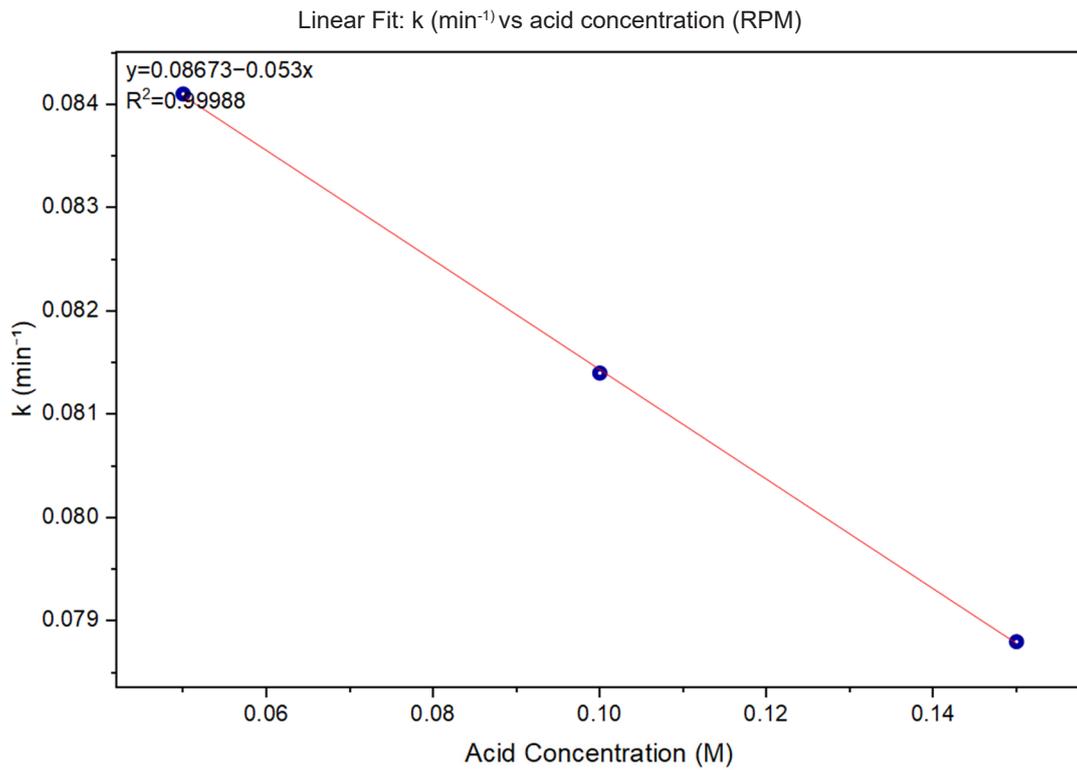


Figure 5b. Linear regression of apparent rate constant (k) versus stirring speed (RPM) with fitted line and statistical parameters.

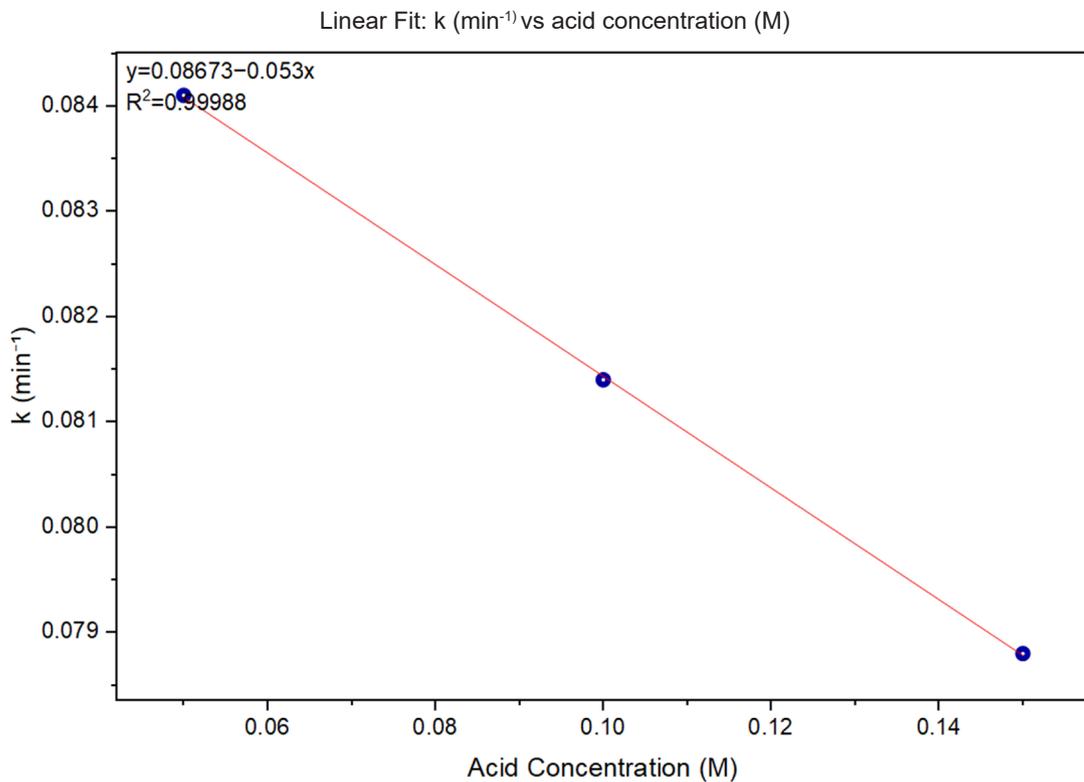


Figure 5c. Linear regression of apparent rate constant (k) versus acid concentration (M) with fitted line and statistical parameters.

Figure 5b shows the regression analysis for k as a function of stirring speed, which shows a slight negative slope at high agitation rates. Beyond ~1000 RPM, increasing agitation yields minimal further enhancement in the dissolution rate, suggesting that the system transitions toward a reaction-controlled regime once mass transfer is no longer the rate-limiting step. The excellent fit ($R^2 \approx 99.6\%$) reinforces this interpretation despite the limited data points, aligning with mass-transfer theory that predicts diminishing returns for turbulence at high Reynolds numbers (Daccord et al., 1993a). From a practical standpoint, this finding indicates that excessively high mixing or injection rates would waste energy without significantly speeding up the reaction once mass-transfer limits are overcome.

As shown in Figure 5c, the linear regression displays a gentle negative slope, indicating a slight decrease in k as lactic acid concentration increases over the 0.05–0.15 M range. This trend, combined with moderate R^2 values (48–49%), suggests that the dissolution process in this regime is partially mass-transfer-limited and that active reaction sites on the mineral surface become saturated at higher acid concentrations. In other words, once a certain concentration threshold is reached, adding more acid yields diminishing increases in reaction rate. This behavior is consistent with a transition from surface-reaction-limited kinetics at low acid concentrations to diffusion-limited kinetics at higher concentrations, where the supply of protons is no longer the bottleneck. Such behavior has been observed in other acidizing studies (Gdanski, 1993; Daccord et al., 1993b). Importantly, this relatively flat dependence on acid concentration means that within practical field acid strengths, lactic acid’s effectiveness will not be overly sensitive to small concentration variations. UV-Vis calibration for Mg^{2+} (from minor dolomite

dissolution) was performed in a similar manner to ensure accurate quantification of magnesium release, confirming that the overall dissolution kinetics captured both calcite and dolomite contributions.

Core flood test results

The core flood tests confirmed a strong influence of injection rate on wormhole formation efficiency. Table 1 summarizes the initial and post-acid porosity and absolute permeability of each core, along with the breakthrough pore volume for each injection rate. At a low injection rate of 0.1 mL/min, the high PVbt value (~2.7 pore volumes) indicates inefficient acid usage, characterized by uniform face dissolution rather than focused channel formation.

This behavior is typical of a reaction-controlled regime at low flow rates, where limited convective transport fails to focus acid along preferential channels (Hoefner and Fogler, 1989; Fredd and Fogler, 1998). At 0.3 mL/min, the PVbt decreases to around 1.9, representing a more optimal regime for wormhole formation in which the balance between mass transfer and reaction kinetics favors development of a dominant conductive flow path while minimizing excess acid consumption. Increasing the rate to 0.5 mL/min results in a PVbt of only ~0.73, reflecting an extremely efficient breakthrough characterized by a single dominant wormhole. This condition appears to be near the optimum: higher flow rates reduce acid–rock contact time and can promote less efficient, ramified dissolution. At the highest tested rate of 0.9 mL/min (PVbt \approx 1.3), dominant wormhole features are again observed, likely due to a complex interplay between rapid acid delivery and limited reaction time. These results highlight the sensitivity of wormhole morphology to the injection flow regime and reinforce the importance of optimizing injection rates in carbonate acidizing (Bazin et al. 1995; Mahmoud et al. 2011; Munadi 2007).

Table 1. Core porosity and permeability before and after acid injection.

Tests	Injection Rate, q (mL/min)	Initial Porosity, Φ (%)	Initial k (mD)	PVbt (PV)	Final Porosity, Φ (%)	Final k (mD)	Permeability Increase (%)
1	0.1	8.75	2.54	2.7	9.15	5.14	102.40
2	0.3	9.25	3.12	1.9	9.45	6.15	97.10
3	0.5	10.15	3.14	0.73	11.5	7.13	127.10
4	0.9	9.8	3.21	1.3	10.2	6.25	94.70

SEM imaging of core samples

To visualize the results of acid–rock interaction and confirm wormhole development, selected post-injection cores were analyzed using Scanning Electron Microscopy (SEM). SEM images revealed clear evidence of dissolution channels cutting through the carbonate matrix. These wormhole-like channels and enlarged conduits observed under SEM confirm that significant pore structure alteration occurred, consistent with the macroscopic improvements in permeability. Figure 6 shows representative SEM micrographs highlighting the development of elongated dissolution channels (analogous to wormholes) in a core sample after acidizing.

Integrating these findings, lactic acid represents a viable alternative to hydrochloric acid (HCl) for stimulating carbonate reservoirs. Its acidity is sufficient to effectively dissolve carbonate minerals, but its milder nature compared to HCl helps reduce equipment corrosion risks and allows better control over the reaction near the wellbore. Rheological measurements indicate that lactic acid

maintains low viscosity and remains injectable even at elevated temperatures, making it operationally practical. Kinetic dissolution experiments confirm that the reaction rate can be controlled by adjusting temperature, mixing speed, and acid concentration, enabling tailored treatments for specific reservoir conditions. Core flood tests demonstrate that lactic acid can create effective wormhole channels at optimized injection rates, promoting deeper acid penetration with efficient use of fluid. SEM imaging further supports these results by showing clear evidence of channel formation and pore structure changes within the carbonate rock matrix. The slower and more predictable reaction of lactic acid offers operational advantages, helping engineers design acidizing treatments that minimize near-wellbore face dissolution and corrosion while maximizing stimulation effectiveness (Fathi et al. 2009). By carefully selecting parameters such as injection rate and temperature, lactic acid systems can be adapted to improve reservoir permeability in a more controlled and reliable manner.

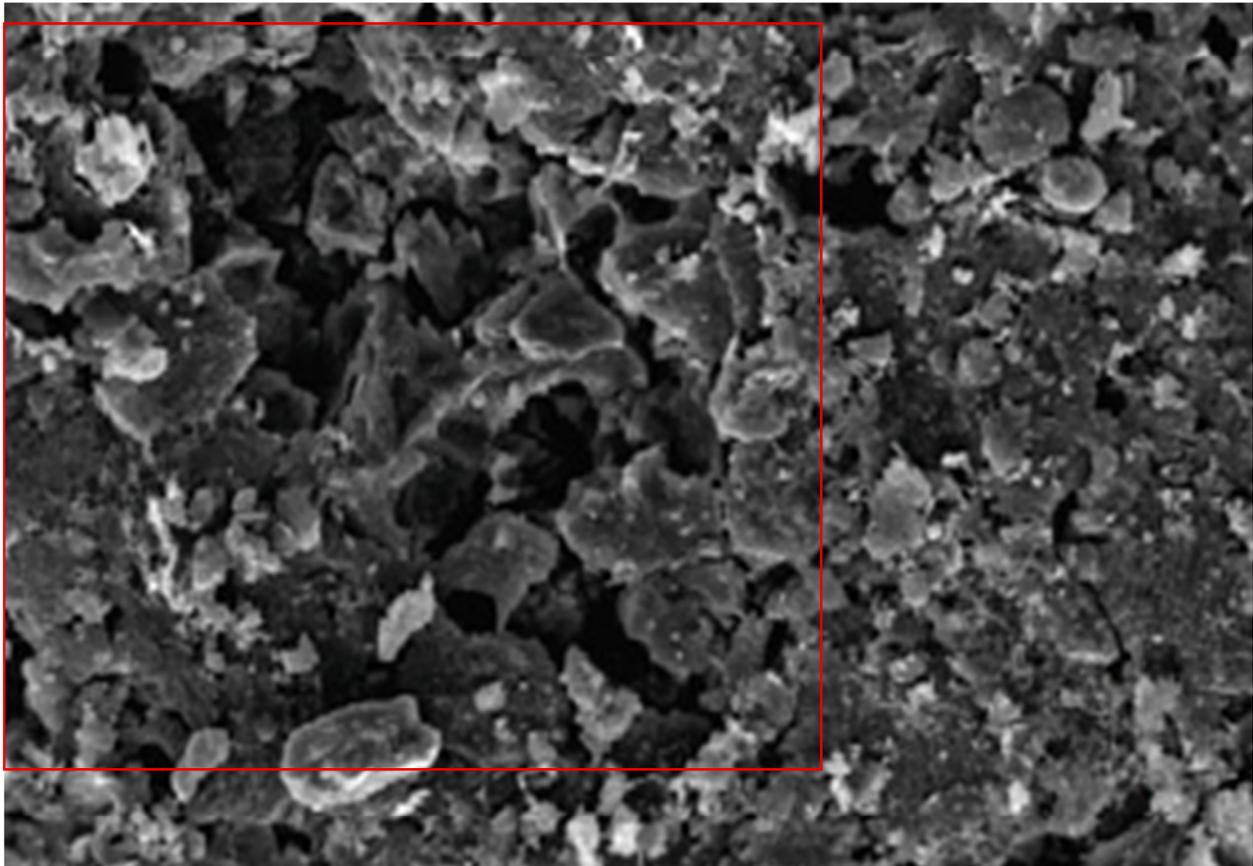


Figure 6. SEM micrographs showing wormhole-like channels in carbonate core post-acidizing.

CONCLUSION

This study demonstrates that bio-derived lactic acid is a viable, safer, and environmentally responsible alternative to conventional HCl for carbonate matrix acidizing, with measurable reactivity under reservoir-like conditions. Kinetic dissolution tests at 60 °C and 500 RPM yielded apparent first-order rate constants of 0.0788–0.0841 min⁻¹, with moderate R² values (48–49%) indicating partial mass-transfer control and minimal sensitivity to acid concentration in the range 0.05–0.15 M. An Arrhenius analysis over 70–90 °C gave an activation energy of 63.8 kJ/mol, confirming a temperature dependence consistent with organic acid–carbonate reaction systems (Fredd & Fogler 1998; Mahmoud et al. 2011). Core flooding experiments confirmed the critical role of injection rate in controlling wormhole formation efficiency. Absolute permeability increased from 2.54 mD to 6.25 mD after acidizing. PVbt analysis revealed a clear optimum around 0.3 mL/min (PVbt ≈ 0.73), supporting efficient wormhole formation, while a lower rate of 0.1 mL/min (PVbt ≈ 2.7) led to uniform dissolution and higher acid consumption. Higher rates (0.5 mL/min, yielding PVbt ≈ 0.73, and 0.9 mL/min, yielding PVbt ≈ 1.3) produced branching wormhole patterns (Hoefner & Fogler 1989). Overall, the results validate that a bio-acid such as lactic acid can be effectively used for carbonate reservoir stimulation, provided that treatment parameters are optimized. The well-defined kinetic parameters obtained in this work, along with the demonstrated wormholing efficiency at intermediate injection rates, give engineers a foundation for designing field treatments that maximize stimulation while minimizing risks. Bio-based lactic acid thus shows promise as an environmentally friendly matrix stimulation fluid with controllable reactivity and proven capacity to enhance permeability in carbonate formations.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
Lactic Acid	Bio-based organic acid used as a stimulation fluid	-
Carbonate Rock	Reservoir rock composed mainly of calcite and dolomite	-
pH	Measure of acidity of the solution	[-]
μ	Viscosity of lactic acid solution	cP
T	Temperature in dissolution experiments	°C
rpm	Stirring speed in flocculator experiments	revolutions/min
C	Acid concentration	M (mol/L)
Abs	UV-Vis absorbance value indicating dissolved species	[-]
[Ca ²⁺]	Calcium ion concentration in solution	ppm or mol/L
PVbt	Pore volume to breakthrough; volume of acid required for breakthrough	PV (pore volumes)
φ	Porosity of the rock sample	[%]
k	Absolute permeability of the rock	mD
SEM	Scanning Electron Microscope imaging for pore/channel analysis	-
XRD	X-ray Diffraction for mineralogical composition	-
Lactic Acid	Bio-based organic acid used as a stimulation fluid	-

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