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A geochemical reaction-transport simulator for matrix acidizing analysis and design

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Abstract

A new two-dimensional geochemical simulator, CIRF.A, and its application to matrix acidizing analysis and design are presented. The simulator is based on the solution of the equations of fully coupled fluid flow, species transport and rock/fluid reactions and includes the effects of grain growth/dissolution and the alteration of porosity and permeability due to mineral reactions. Our program has a large built-in thermodynamic and kinetic database.

The simulator is tested by laboratory core acidizing results. It is demonstrated that simulation results are in good agreement with experimental observations. Both laboratory and simulation results indicate that an acidizing treatment may induce formation damage due to the precipitation of byproducts from the reactions of acids with rock minerals. A series of simulation runs have been carried out under different conditions to determine the strategy for minimizing the acid induced formation damage. High injection velocity and higher acid concentration are shown to reduce mineral precipitation and formation damage.

The simulator is also used to predict permeability and productivity improvements for typical acid treatments of undamaged and damaged wells in sandstone formations. Our simulator is shown to be capable of simulating all the sandstone acidizing procedures that include pre-flush, mud acid treatment, after-flush and back production.

In carbonate formations, matrix acidizing may lead to the development of dissolution fingers and the creation of wormholes. It is demonstrated that the simulator can also capture the fingering and wormholing phenomena. We believe this new geochemical simulator is an invaluable tool for matrix acidizing analysis and design.

Keywords: geochemistry; acidizing; formation damage; well simulation

1. Introduction

Matrix acidizing has long been used by petroleum engineers as a primary technique to remove near-wellbore formation damage and to improve well productivity. In matrix acidizing, appropriate acids are injected into the near-wellbore regions to dissolve some of the rock constituents so that rock permeability near wellbore and well productivity will be improved. A major aspect of matrix acidizing is that acids are injected at such a pressure so that fracturing the formation can be avoided, thus allowing the acids to penetrate the rock matrix near the wellbore. For sandstone matrix acidizing, the acids typically used are hydrofluoric and hydrochloric

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acids. In carbonate formations, hydrochloric acid is most commonly used for matrix acidizing.

Formation damage is a very common problem associated with almost every well operation from drilling to production. Formation damage is usually caused by a partial or complete plugging of the formation around the wellbore due to several mechanisms including particulate invasion, fines migration, clay swelling, emulsion block, and organic/inorganic scaling (Liu and Civan, 1995).

Although the purpose of matrix acidizing is to improve rock permeability, improper treatments may cause acid-induced formation damage. Such damage typically results from the precipitation of hydrated silica, fluosilicates, fluorite, and ferric hydroxide (Shaughnessy and Kunze, 1981; Crowe, 1986). These precipitates are byproducts from the reactions of acids with rock minerals. Therefore, appropriate matrix acidizing design is crucial to a successful field treatment.

Laboratory core tests have long been used as a common procedure for matrix acidizing analysis and design. These tests are usually carried out in short cores. As reported by Fambrough and Newhouse (1993), their long-core acidizing experiments show permeability improvement near core injection end and permeability reduction farther down the core. Mineral precipitation is shown to be the cause of the permeability reduction away from the core inlet. Extensive precipitation is not found for short-core acidizing. Laboratory studies are expensive and time consuming, and even a long-core acidizing test does not represent the actual field treatment. In field acidizing, the region closer to the wellbore is typically over-acidized while under-acidizing occurs away from the wellbore.

With advancements in computer technology and understanding of matrix acidizing complexities, geochemical modeling and computer simulation have provided another important alternative for effective matrix acidizing design. Geochemical modeling and computer simulation are especially helpful in understanding the damage caused by the precipitation of byproducts from the reactions of acids with formation minerals and providing guidelines for the prevention of such damage.

A number of geochemical models and simulators have been reported in the literature for matrix acidizing and other geochemical processes. Outstanding among these models and simulators are those developed by Fogler et al. (1976), Walsh et al. (1982), Bryant et al. (1986), Ortoleva et al. (1987a,b), W. Chen et al. (1990), Chang and Civan (1992), and Sevougian et al. (1995). A common feature of those geochemical models is the coupling between reaction and transport. But in most models, both the reaction chemistry and transport processes have been simplified. In this paper, our new geochemical simulator and its application to matrix acidizing analysis and design are presented.

Important applications of our simulator include the analysis of matrix acidizing (Y. Chen et al., 1994) and the assessment of deep well waste injection (Ortoleva et al., 1994; Liu et al., 1994, 1995). Although a detailed study of waste injection is beyond the scope of this paper, simulation studies (Liu et al., 1994; Ortoleva et al., 1994) show that waste fluids dissolve some minerals and precipitate others. Such reactions change rock permeability and the pattern of waste migration.

2. Model formulation

The model on which our simulator is based consists of a set of mass and momentum conservation equations. The mass conservation equations are supplemented with reaction rates and sink/source terms representing injection/production wells. Grain texture–porosity–permeability relations are also included to complete the model formulation.

2.1. Mass conservation of solutes

The equation of conservation of mass for the concentration of aqueous species $\alpha$ is taken in the form:

$$\frac{\partial}{\partial t} \left( \phi s_w c_\alpha \right) = -\nabla \cdot \left( -\phi s_w D_\alpha \nabla c_\alpha + \bar{u}_w c_\alpha \right) + \sum_{j=1}^{N} N_j v_{\alpha j} W_j^f + \sum_{j=1}^{N} N_j v_{\alpha j} W_j^s + q_\alpha,$$

$$\alpha = 1, 2, \ldots, N$$ (1)

where $c_\alpha$ is the molar concentration of aqueous species $\alpha$; $\phi$ is porosity; $s_w$ is the saturation of the
water (aqueous solvent) phase; \( D_\alpha \) is the dispersion coefficient of species \( \alpha \); \( \bar{u}_w \) is the filtration or flow velocity of the aqueous phase; \( N_e \) is the number of aqueous reactions (equilibrium reactions); \( N_m \) is the number of mineral reactions (kinetic reactions); \( W_j^a \) and \( W_j^s \) are reaction rates of the \( j \)th aqueous and \( j \)th mineral reaction, respectively; \( q_\alpha \) stands for the source/sink term of species \( \alpha \) arising from injection/production well effects; and \( N \) is the number of aqueous species.

2.2. Reactions and rate laws

In this model, all reactions are grouped into two categories: aqueous and mineral reactions. An aqueous reaction only involves aqueous species while a mineral reaction involves both mineral and aqueous species. Acid dissociation is an aqueous reaction. Mineral dissolution and precipitation are mineral reactions.

An aqueous reaction can be written in the following form:

\[
\sum_{\alpha=1}^{N_e} v_{\alpha j}^a S_\alpha = 0 \tag{2}
\]

where \( v_{\alpha j}^a \) is the stoichiometric coefficient for aqueous species \( S_\alpha \) in aqueous reaction \( j \). The aqueous reactions are often fast relative to the mineral reactions. In the model, they are taken to be fast and hence are maintained at equilibrium. Because the aqueous reactions are fast it is necessary for computational reason to take a matrix transformation of Eq. (1) so as to eliminate the aqueous reaction rates.

In order to solve all aqueous species concentrations, the resulting equations must be supplemented with the following independent equilibrium relations:

\[
K_j^a = \prod_{\alpha=1}^{N_e} a_\alpha^{v_{\alpha j}^a}, \quad j = 1, 2, \ldots, N_e \tag{3}
\]

where \( K_j^a \) is the equilibrium constant of aqueous reaction \( j \) that depends on temperature and pressure; and \( a_\alpha \) is the activity of the aqueous species \( \alpha \). The extended Debye–Hückel corrections to the aqueous species activities are implemented in the simulator.

Consider mineral reaction \( j \) leading to the dissolution of mineral \( i \) of the form:

\[
M_i + \sum_{\alpha=1}^{N_m} v_{\alpha j}^i S_\alpha = 0 \tag{4}
\]

where \( v_{\alpha j}^i \) is the stoichiometric coefficient for aqueous species \( \alpha \) in mineral reaction \( j \) that affects mineral \( M_i \) (\( v_{\alpha j}^i < 0 \) for reactants, while for products \( v_{\alpha j}^i > 0 \)). With this we have:

\[
G_{i(j)} = k_j \left( \prod_{\alpha_{i,j}^i < 0} a_\alpha^{v_{\alpha j}^i} - \prod_{\alpha_{i,j}^i > 0} a_\alpha^{v_{\alpha j}^i}/K_j^s \right) \tag{5}
\]

where \( k_j \) and \( K_j^s \) are the dissolution rate and equilibrium constant, respectively, of mineral reaction \( j \). A positive value of \( G_{i(j)} \) stands for mineral dissolution while a negative value means mineral precipitation. The rate constant is taken to have the Arrhenius dependence on temperature:

\[
k_j = k_{o j} \exp\left(-E_{a j}/RT\right) \tag{6}
\]

where \( k_{o j} \) and \( E_{a j} \) are the high-temperature limit of rate constant and activation energy, respectively, for mineral reaction \( j \); \( T \) is absolute temperature; and \( R \) is the gas constant.

The reaction rate associated with the \( j \)th mineral reaction as it contributes to the conservation of mass in Eq. (1) for the solutes, \( W_j^s \), takes the form:

\[
W_j^s = n_i \rho_i 4\pi R_i^2 G_{i(j)} \tag{7}
\]

where \( n_i \) is the number of grains of mineral \( i \) per rock volume; \( \rho_i \) is the molar density of mineral \( i \) (number of moles of mineral \( i \) per grain volume). There can be several reactions for each mineral, Eq. (7) being one of them. Therefore, the grain dissolution rate for mineral \( i \) is given by:

\[
\frac{\partial R_i}{\partial t} = \sum_{j=1}^{N_m} G_{i(j)} \tag{8}
\]

The restriction of \( j \) on the sum is for only those reactions (of the \( N_m \) in total) affecting mineral \( i \), as indicated by the subscript \( i(j) \).

2.3. Texture–porosity–permeability relations

In the model, porosity is expressed in terms of the grain texture by:

\[
\phi + \sum_{i=1}^{N_m} n_i \bar{V}_i = 1 \tag{9}
\]

where \( N_m \) is the number of minerals; and \( \bar{V}_i \) is the volume of a grain of mineral \( i \). All the grains of a given mineral are assumed to be of the same size.
Under a further assumption that all mineral grains are spherical, the volume of a grain of mineral \( i \) with radius \( R_i \) is given by:

\[
V_i = \frac{4}{3} \pi R_i^3
\]  
(10)

As grains grow and dissolve, grain volumes and porosity vary.

The permeability of the porous medium is a function of texture. There are several empirical equations describing this dependence. The Fair–Hatch equation (Bear, 1972, p.134) is used in the modified form:

\[
k = \frac{\phi^3}{J(1-\phi)^2} \left[ \frac{1}{\sum_{i=1}^{n_o} \theta_i n_i V_i / R_i} \right]^2
\]  
(11)

where \( J \) is a packing factor (~5); and \( \theta_i \) is a geometric factor (~6 for spherical grains).

2.4. Mass conservation of fluids

A general mass conservation equation for the two-phase flow of water (\( w \)) and oil (\( o \)) is given by:

\[
\frac{\partial}{\partial t} (\phi s_i \rho_i) = \nabla \cdot (\rho_i \vec{u}_i) + Q_i, \quad l = w \text{ and } o
\]  
(12)

were \( \rho_i \) and \( Q_i \) account for the mass density and the source/sink term, respectively, of the fluid \( l \). This equation also applies to the single-phase flow \( (s_i = 1) \) and flow in free space \( (\phi = 1) \). By definition, the saturations add up to one:

\[
s_w + s_o = 1
\]  
(13)

2.5. Fluid motion

The Darcy law is typically used as the momentum equation to describe fluid motion through porous media. In two-phase flow, the Darcy law is of the form:

\[
\vec{u}_i = \frac{k k_{i,l}}{\mu_i} (\nabla p_i + \rho_i g \vec{z}), \quad l = w \text{ and } o
\]  
(14)

where \( k \) is rock permeability; \( k_{i,l} \) and \( \mu_i \) are the relative permeability and the viscosity, respectively, of the fluid \( l \); \( g \) is the gravitational acceleration; and \( \vec{z} \) is a unit upward pointing vector. The relationship between the pressures of water and oil phases is conventionally given in petroleum engineering by:

\[
p_o - p_w = p_c
\]  
(15)

where \( p_c \) is the capillary pressure in the porous medium.

Reactive infiltration coupling can lead to the development of dissolution fingers and the creation of flow channels or wormholes due to complete rock dissolution. These phenomena are observed in the case of the injection of acid into a carbonate mineral-bearing formation. In this case the Darcy equation cannot account for the transport of fluid in the completely dissolved matrix zone. An equation proposed by Brinkman (1946) allows one to describe the single-phase fluid motion in both porous media and free fluid domains:

\[
(\mu_i/k) \ddot{u}_i - \mu_i \nabla^2 u_i = -\nabla p_i, \quad l = w \text{ or } o
\]  
(16)

For fluid flow in a porous medium, the linear term in this equation is very large compared to the Laplacian term, and it reverts to the Darcy equation. For fluid flow in a channel, the linear term is negligible and it becomes the Stokes equation. Experiments (Arquis, 1994) show that the velocity field in the boundary layer between the porous medium and the channel can be adequately described by the Brinkman equation.

3. Simulator description

Our simulator has been developed for numerically solving the above coupled model equations. The partial differential equations associated with the model were discretized in a curvilinear grid system using the finite-difference method. Such discretization allows one to use adaptive gridding to accurately model reaction-front fingering and wormholing problems. The simulator includes a user interface that provides access to our equilibrium and kinetics database, which is essentially from Wolery (1983). The simulator allows for any combination of user-specified aqueous and mineral reactions.

Our simulator is designed for the study of a variety of water–rock interaction problems, such as reactive fluid infiltration, injection/production scenarios in petroleum reservoirs, and waste fluid dis-
posal by deep well injection. Features of the simulator include: (1) mineral and pore fluid interactions; (2) grain growth/dissolution kinetics; (3) porosity and permeability alteration due to mineral reactions; (4) multiphase flow in porous media; (5) fluid species transport; (6) energy conservation; (7) temperature, pressure and ionic strength corrections to equilibrium and kinetic rate constants; (8) adaptive gridding; and (9) implementation of representing a single or multiple injection/production wells.

4. Analysis of laboratory acidizing data

4.1. Experiment summary

Long-core laboratory acidizing studies were carried out by Bartko and Newhouse (1992) to optimize an acidizing treatment for well stimulation and remediation of near-wellbore damage in a sandstone reservoir. They determined that an optimal strength of mud acid for this sandstone is 6% HCl and 1.5% HF. In this section, one of their core tests will be simulated to illustrate the complexities of rock–fluid interactions in matrix acidizing, to calibrate our simulator, and to demonstrate its capability in matrix acidizing assessment.

The experiment involved acidizing an undamaged sandstone core sample. The core was 25.4 cm in length and 2.54 cm in diameter. The rock was composed of quartz (58% by volume), kaolinite (7% by volume), illite (6% by volume), and siderite (2.5% by volume). The test was conducted at the temperature of 82°C. First, flow through the core was established with NH₄Cl water and the rock permeability was determined. The initial porosity and permeability of the core sample were 26.5% and 0.365 D, respectively. After a pre-flush of 5 pore volumes (PV) of 7.5% HCl, mud acid (6% HCl and 1.5% HF mixture) was injected through the core at a rate of 11 ml/min for 10 PV (~ 31 min of injection).

4.2. Reaction mechanisms

Major constituents in a typical sandstone are quartz and clays. Compared to the high reactivity of HF acid with clays, HCl is practically considered not to react with clays. Nevertheless, HCl is needed to remove other minerals such as carbonates in the formation and to enhance the dissolving power of HF with clays by maintaining a low pH value in the acid (Muecke, 1982). An examination of the rock minerals and acids involved in the acidizing test by Bartko and Newhouse (1992) led us to what we consider the likely reaction mechanisms, as given in Table 1.

The reactions listed in Table 1 are determined by the problem. Our simulator allows users to model any combination of any number of aqueous and mineral reactions. If reactions do not exist in our database, users can also create new reactions and enter reaction data into the database.

The dissolution of iron-bearing minerals during an acidizing treatment is often an issue of concern (Shaughnessy and Kunze, 1981; Crowe, 1986). Iron commonly exists in two oxidation states: Fe(III) and Fe(II). As reported by Crowe (1986), Fe(III) in a spent acid will precipitate as gelatinous ferric hydroxide when the pH of the acid rises above 2 and Fe(II) will precipitate as ferrous hydroxide above a pH of ~7. In the case of Fe(II), the precipitated mineral is likely to be Fe(II)-carbonate instead of Fe(II)-hydroxide (Shaughnessy and Kunze, 1981).

The reaction involving siderite and H⁺ as given in Table 1 will automatically allow the secondary precipitation of Fe(II)-carbonate when the spent acid becomes supersaturated with respect to Fe(II)-hydroxide.

| Table 1 | Reaction mechanism for core acidizing |
| Minera reactions: |
| (1) quartz + 6HF → H₂SiF₆ + 2H₂O |
| (2) kaolinite + 18HF → 2H₂SiF₆ + 2AlF₃ + 9H₂O |
| (3) illite + 29HF → 0.6K⁺ + 0.25Mg²⁺ + 1.2AlF₃ + 1.1AlF₄⁻ + 3.5H₂SiF₆ + 12H₂O |
| (4) siderite + H⁺ → Fe²⁺ + HCO₃⁻ |
| (5) H₂SiF₆ + 4H₂O → Si(OH)₄(supercritical) + 6HF |

Aqueous reactions:

| (1) HF ⇌ H⁺ + F⁻ |
| (2) HCl ⇌ H⁺ + Cl⁻ |
| (3) AlF₃⁺ ⇌ Al³⁺ + 3F⁻ |
| (4) AlF₃⁻ ⇌ Al³⁺ + 3F⁻ |
| (5) AlF₄⁻ ⇌ Al³⁺ + 4F⁻ |
| (6) H₂SiF₆ ⇌ 2H⁺ + SiF₄⁻ |
| (7) CO₂(aq) + H₂O ⇌ H⁺ + HCO₃⁻ |
siderite. However, the secondary precipitation in our problem is unlikely to occur unless the acid is completely spent due to the presence of another mineral such as calcite according to the study in the literature (Shaughnessy and Kunze, 1981).

In our previous study (Ortoleva et al., 1994), an acidic waste fluid dissolved siderite and released Fe(II) into the fluid. Oxygen dissolved in the fluid converted a certain amount of Fe(II) to Fe(III), depending on the oxidation–reduction potential of the fluid. Once the pH risen, ferric gel precipitated, causing severe formation damage. In the current study, oxygen is not present in the acid used for the core acidizing test.

A summary of kinetic models for acidization reactions reported by Williams et al. (1979, p.20) suggests that aluminosilicate dissolution by HF is usually a first-order reaction. To ensure the first-order reaction in our simulations, the dissolution reactions of quartz, kaolinite, illite and montmorillonite by HF in Tables 1 and 2 are reorganized as follows. Each stoichiometric equation is divided by the stoichiometric coefficient of HF. As a result, all the stoichiometric coefficients of HF become one. Since the activity of a mineral is one, the kinetic rate laws implemented in our model as outlined in Eq. (5) thus yield first-order dissolution reactions of clays and quartz by HF.

4.3. Simulation of core test

Equilibrium constants for the reactions are from the program database (i.e. essentially those of EQ3/6; Wolery, 1983). Rate constant data for mineral reactions in the database are derived from experiments which were carried out under conditions not appropriate for matrix acidizing. Therefore by adjusting the mineral reaction rate constants, we attempted to match the experimental results. The concentration profiles of total aqueous silica and aluminum as a function of distance from the injection end of the core sample after injecting 9 PV of mud acid (~ 28 min of injection) were used for comparison with the predictions of our simulator.

Fig. 1 shows a comparison of experimental and simulated concentration profiles of total aqueous silica. It is found that the simulation results are in good agreement with the experimental results. It is interesting to note that the concentration of aqueous silica increases and reaches its maximum at ~ 12 cm from the injection end and then decreases. The decrease in silica concentration indicates the removal of silica from the fluid, i.e. the precipitation of hydrated silica in the rock.

Fig. 2 presents both experimental and simulated concentration profiles of total aqueous aluminum. Unlike the profile of aqueous silica, that for aqueous aluminum keeps increasing. Apparently, no aluminum precipitation occurs since it is not removed from the fluid. For aluminum, the experimental trend of monotonic increase was also predicted accurately in the simulation.
Fig. 3 shows changes in the volume fractions of kaolinite, illite, siderite and hydrated silica along the core predicted by the simulator after acidizing, i.e. after the injection of 10 PV of mud acid (~ 31 min of injection). Quartz is not included in this figure because no significant amount of quartz was dissolved during acidizing. As pointed out by Crowe (1986), the reaction rate of clays by HF is 100–200 times larger than that of quartz. The precipitation of hydrated silica is evident in Fig. 3 because there is no hydrated silica in the rock before acidizing. It is known that the precipitation of hydrated silica during acidizing can cause considerable formation damage (Shaughnessy and Kunze, 1981; Crowe, 1986). Mineral dissolution and precipitation lead to a change in the rock porosity. This is illustrated in Fig. 4.

The objective of matrix acidizing is to improve rock permeability. Fig. 5 illustrates the permeability profile after acidizing as a function of distance along the core. Compared to the initial rock permeability of 0.365 D, our simulator predicts that the permeability at the core inlet has increased to ~ 1.22 D and the permeability at the core outlet has reduced to ~ 0.31 D. The predicted overall (averaging across the core) permeability improvement is ~ 22%. This is close to the measured overall permeability improvement of 19%.

In this experiment, the precipitation of hydrated silica is identified to cause acid-induced formation damage. Here we present two such simulations: (1) increasing the concentrations of HF and HCl acids; and (2) increasing the acid injection rate. The results of the two new simulations are also compared with the original simulation results.

The reaction mechanism for hydrated silica precipitation given in Table 1 indicates that precipitation can be reduced by keeping a high HF concentration in the fluid. This can be achieved by increasing concentrations of both HF and HCl. The consequence of increasing HF concentration is evident. An increase in the HCl concentration will result in an increase in that of H+. In turn, higher concentration of H+ will keep more hydrofluoric acid in its complex form HF. A simulation run was then performed by increasing the concentrations of both HF and HCl by 50% (HCl increased from 6% to 9% and HF increased from 14% to 16%).

In this experiment, the precipitation of hydrated silica is identified to cause acid-induced formation damage further down the core as shown in Fig. 5. Simulation studies were carried out to minimize the acid-induced formation damage. Here we present two such simulations: (1) increasing the concentrations of HF and HCl acids; and (2) increasing the acid injection rate. The results of the two new simulations are also compared with the original simulation results.
increased from 1.5% to 2.25%). Simulation results shown in Fig. 6 indicate that a 50% increase in acid concentrations has reduced the amount of hydrated silica by ~ 100%. In field treatments, a significant increase in the acid concentrations may result in excessive rock dissolution in the region closer to the wellbore and cause formation collapse.

In the second example, the same amount of the same acids (10 PV of 6% HCl and 1.5% HF) was injected through the core at a flow rate of 22 ml/min that doubles the original flow rate. As illustrated in Fig. 6, this result is even more promising: the amount of hydrated silica precipitated after acidizing has reduced by 10 times! Such a good result will probably not be observed in field operations. The maximum injection rate and treatment pressure in field operations must be determined by the rock fracturing gradient so that fracturing the formation can be avoided. For the other, spent acid and reaction products in a core test quickly flow out of the core, thereby reducing the chances of mineral precipitation, although this is not the case in field treatments.

5. Prediction of stimulation potential

5.1. Undamaged well treatment

We have just calibrated our simulator using the data of a core test by Bartko and Newhouse (1992) in the previous section. Here we will use the same data to predict the stimulation potential of a typical acidizing treatment for a well in a reservoir having the same rock properties as the core. This well is thus an undamaged well since the rock used in the core test was not damaged before acidizing.

In this regard, we consider a well with a radius of 7.62 cm, a drainage radius of 200 m, and a formation thickness of 3 m. The formation depth is 3000 m. The reservoir temperature is 82°C which is the same as the temperature used in the core test. First, 4.73 m$^3$ of HCl acid (7.5% by weight) are injected from the well into the formation at a rate of $3.15 \times 10^{-3}$ m$^3$/s for 25 min. Following that, 9.46 m$^3$ of mud acid (6% HCl and 1.5% HF) are injected at the same rate for 50 min. Our simulator is then used to simulate this scenario.

Simulation results illustrated in Fig. 7 are the mineral alteration profiles for kaolinite, illite, siderite and hydrated silica as a function of the radial distance from the center of the well at the end of the simulated operation. Note that acids have dissolved large amounts of kaolinite, illite and siderite in the formation adjacent to the wellbore. As a byproduct of the reactions of HF with clays, hydrated silica precipitates in a region from a radius of 20 cm to a radius of 150 cm, reaching a maximum value at a radius of 40 cm. Although the mineral alteration zone is extended from the wellbore to a radius of ~ 200 cm, Fig. 8 illustrates that most change in porosity occurs in a region from the wellbore to a radius of 50 cm. As shown in Fig. 9, the permeabil-

![Fig. 7. Predicted mineral alteration profiles in the undamaged well acidizing treatment: volume fractions of kaolinite, illite, siderite and hydrated silica vs. radial distance after the treatment.](image-url)
Fig. 8. Predicted porosity alteration profile for the undamaged well after the acidizing treatment.

Fig. 9. Predicted permeability alteration profile for the undamaged well after the acidizing treatment.

Fig. 10. Stimulation potential for the undamaged well: the ratio of the well productivity during acidizing to the original well productivity was plotted against the operation time.

Fig. 11-13. Porosity, permeability, and productivity alteration profiles for the damaged well.

5.2. Damaged well treatment

To demonstrate a successful field treatment, another scenario — matrix acidizing for a damaged well — will be simulated. In this case, we assume that a clean sandstone formation (mainly composed of quartz) was first damaged by the invasion of montmorillonite (a major constituent for some water-based drilling fluids). The clay invasion and resulting porosity and permeability alteration profiles in the formation near the wellbore are presented in Figs. 11–13, respectively. The maximum amount of montmorillonite invaded is 5% (by volume) that occurs at the wellbore. The invasion is extended to a radius of 25 cm. The porosity at the wellbore is decreased to 20% from its original value of 25%. The permeability at the wellbore is decreased to 0.005 D from its original value of 0.16 D.
Prior to acid treatment, the formation was assumed to be saturated with formation brine that contains 10% NaCl. Assuming the same well and reservoir size as for the undamaged well, a field treatment is then designed. Although fluid injection rate is determined by the rock fracturing gradient, here we assume that the injection rate is $1.58 \times 10^{-3}$ m$^3$/s.

First, 4.73 m$^3$ of pre-flush fluid (6% HCl) are injected for 50 min, followed by the injection of 9.46 m$^3$ of mud acid (6% HCl and 1.5% HF) for 100 min. After that, 4.73 m$^3$ of after-flush fluid (6% HCl) are injected for 50 min. In the end, all the injected fluids are produced back. The reaction mechanism involved in this case is given in Table 2.

During the period of mud acid treatment, invaded montmorillonite is dissolved as injection proceeds. The temporal evolution and the spatial distribution of montmorillonite in the formation is simulated as illustrated in Fig. 14. Consequently, porosity and permeability change with time and space. As indicated in Figs. 15 and 16, porosity and permeability in the formation have been fully recovered at the end of mud acid injection.

The simulated productivity ratio as a function of the operation time shown in Fig. 17 provides the productivity improvement in response to each treatment step. A few interesting phenomena are observed in this figure, as follows. Since the sandstone

**Table 2**

Reaction mechanism for damaged well acidizing

**Mineral reactions:**

1. quartz + 6HF → H$_2$SiF$_6$ + 2H$_2$O
2. Na-montmorillonite + 30HF → 0.33Na$^+$ + 0.33Mg$^{2+}$ + 0.68AlF$_3$ + 0.99AlF$_4^-$ + 4H$_2$SiF$_6$ + 12H$_2$O
3. H$_2$SiF$_6$ + 4H$_2$O → Si(OH)$_4$(ppt) + 6HF

**Aqueous reactions:**

1. HF ⇌ H$^+$ + F$^-$
2. HCl ⇌ H$^+$ + Cl$^-$
3. AlF$_3^-$ ⇌ Al$^{3+}$ + 2F$^-$
4. AlF$_4^-$ ⇌ Al$^{3+}$ + 3F$^-$
5. AlF$_5^-$ ⇌ Al$^{3+}$ + 4F$^-$
6. H$_2$SiF$_6$ ⇌ 2H$^+$ + SiF$_6^{2-}$
7. NaCl ⇌ Na$^+$ + Cl$^-$
formation does not contain any carbonate minerals, pre-flush with HCl does not improve the rock permeability nor the well productivity. Therefore, the productivity ratio during this period remains 0.3, which is the ratio of damaged well productivity to the normal well productivity (without damage). Upon the injection of mud acid, HF dissolves the invaded montmorillonite and formation damage is remediated. As a result, the productivity is rapidly improved. At the end of HF injection, the well productivity is brought to its normal value (i.e. a productivity ratio of one). However, the precipitation of hydrated silica during the periods of after-flush and back flow causes a slight productivity reduction. Fig. 18 illustrates the distribution profiles of the precipita-
tion of hydrated silica at the end of the mud acid treatment (150 min) and at the end of the operation (400 min). The productivity ratio at the end of the operation has been increased from 0.31 to 0.97, and hence this treatment has increased the productivity of the damaged well by a factor of ~ 3.

6. Prediction of dissolution fingers and wormholes

The stimulation efficiency of acidizing a carbonate-bearing formation is enhanced by generating dissolution fingers or wormholes. Theory (Chadam et al., 1986, 1988, 1990; Ortoleva et al., 1987a,b; W. Chen et al., 1990; Steefel and Lasaga, 1990) and experiments (Hoefner et al., 1987; Wang et al., 1993) show that high reaction rate, high flow rate and low dispersion coefficient favor fingering or wormholing. Here we present a number of examples to predict dissolution fingers and wormholes evolving from carbonate acidizing.

In the first example, dissolution fingers are predicted. We consider a calcite cemented sandstone that is 20 cm by 6 cm in size and initially consists of 80% quartz (by volume) and 15% calcite (by volume). Initial rock porosity and permeability are 5% and 0.14 D, respectively. At the beginning, we introduce a small, local non-uniformity with higher porosity (and also higher permeability) near the left-hand side of the system as shown by the porosity distribution in the top plot of Fig. 19.

HCl acid of 0.1 mol/l is then injected into the rock from the left at a differential pressure of $10^5$ Pa across the system. The acid tends to focus into the local non-uniformity with higher porosity and higher permeability. The more the acid comes in, the more calcite dissolves and the higher the local permeability increases. In turn, the flow of even more acid in the region leads to even further local dissolution. As a result, a dissolution finger evolves.

After 20 min of acid injection, two fingers grow out the original one as indicated by the porosity profile in Fig. 19. From that time on, the two fingers compete each other to have more acid flow through. At the end (50 min of injection), the top finger becomes the dominant one as shown in Fig. 19. The porosity distribution in Fig. 19 also indicates that calcite is completely removed in the dissolution fingers.

In the following, simulation studies will be presented for predicting wormholes. Here we consider a limestone that is 20 cm by 6 cm in size. Initial rock porosity and permeability were 10% and 0.04 D, respectively. An initial heterogeneity with a porosity of 100% was introduced at the inlet side (left) of the domain, as indicated by the top plot in Fig. 20.

HCl acid of 4.0 mol/l was injected at a constant pressure difference of $10^5$ Pa across the system. Fig. 20 shows the development of a wormhole starting from the initial heterogeneity at different injection times. At the beginning, the reaction front adjacent to the heterogeneity advances more slowly than that within the heterogeneity. When the width of the dissolved zone is large enough, almost all the fluid is focused into the wormhole. At this time the reaction front adjacent to the wormhole almost stops progressing, while the wormhole grows faster with time. The wormhole advancement rate increases as the system evolves.

Since the pressure is almost constant in the free fluid region, the variation in the pressure occurs in the porous medium only. As the wormhole grows,
the pressure gradient and fluid velocity in the porous medium increase with time. This phenomenon results from the feedback between reaction and transport. Streamlines are parallel to the reaction front everywhere except at the tip of the wormhole. The flow at the tip is normal to the reaction front, explaining why the front is broader there.

The influence of three parameters on the development of wormholes is investigated as follows. The three parameters of interest are injection rate, injection HCl concentration and the dispersion coefficient. Table 3 is the summary of the results of six simulations. Case 1 corresponds to Fig. 20. The results given are in terms of the wormhole width and growth rate. These simulations were performed in a domain with the same size and the same initial porosity and permeability as for the simulation shown in Fig. 20.

6.1. The effect of injection rate

Experiments (Wang et al., 1993) show that at low injection rates the acid is spent near the core inlet surface because planar (non-focused) reaction front advances slowly. At high injection rates, more complex wormholes form, while at intermediate rates a single wormhole penetrates the rock. In each of the six cases in our study, we obtain a single straight wormhole. Hung et al. (1989) observed a linear dependence of wormhole length on injection rate.

Since the length of our simulation domain was smaller than the wormhole size for steady-state condition, in every case the wormhole reached the end of the domain before the steady-state condition was obtained. Cases 1, 2 and 3 show that the growth rate increases with injection rate, as expected. More precisely, we observe that with an increase of the injection rate by a factor of 10 between Cases 1 and 2 and Cases 2 and 3, the increase in growth rate is not linear but is 11.4 and 22 times, respectively. When an increase in velocity does not have an increase in the dispersion coefficient (in Cases 1, 2 and 3), the increase of velocity leads to a decrease in the wormhole width.

6.2. The effect of fluid dispersion

As the dispersion coefficient increases, the width of reaction front also increases. We have modeled the dispersion coefficient to be proportional to the fluid velocity and the grain size. From Cases 2 and 5 we observe that the effect of increasing dispersion on the wormhole width balances the effect of increasing velocity. From Cases 3 and 5 we observe that lower dispersion favors a narrower wormhole; this has a strong effect on the growth rate of the wormhole. In the narrower wormhole the fluid is more focused to the tip, increasing the wormhole growth rate.

---

The simulations were performed with the same initial conditions as in Fig. 20.

### Table 3

<table>
<thead>
<tr>
<th>Case</th>
<th>$U_m$ (cm/s)</th>
<th>$C_m$ (mol/l)</th>
<th>$D$ (cm$^2$/s)</th>
<th>W (cm)</th>
<th>GR (cm/s)</th>
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<td>1</td>
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<td>4.0</td>
<td>$5 \times 10^{-5}$</td>
<td>1.5</td>
<td>$1.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
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<td>4.0</td>
<td>$5 \times 10^{-5}$</td>
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<td>$1.60 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>2.4</td>
<td>4.0</td>
<td>$5 \times 10^{-5}$</td>
<td>1.1</td>
<td>0.325</td>
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<tr>
<td>4</td>
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<td>$6.17 \times 10^{-2}$</td>
</tr>
<tr>
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<td>4.0</td>
<td>$1 \times 10^{-4}$</td>
<td>1.2</td>
<td>0.257</td>
</tr>
<tr>
<td>6</td>
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<td>1.0</td>
<td>$5 \times 10^{-5}$</td>
<td>1.2</td>
<td>$3.83 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The simulations were performed with the same initial conditions as in Fig. 20.

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Fig. 20. Wormhole evolution in a limestone formation with the initial porosity of 10%. The system is 20 cm by 6 cm in size and has no-flow top and bottom boundaries. HCl acid of 4.0 mol/l was injected at a differential pressure of 10$^5$ Pa across the system.
6.3. The effect of acid concentration

A comparison of Cases 1 with 6 and 4 with 5 shows that there is a linear dependence of the wormhole growth rate on the concentration of acid in the inlet fluid. In Cases 4 and 5, acid concentration seems to have little influence on the width of the wormhole.

It is noteworthy that our simulations are two-dimensional and real wormholes exist in three dimensions. The flow self-focusing for the creation of wormholes is intense in three dimensions. This may explain some differences between simulations and observations.

7. Effects of multi-phase flow on acidizing

Acid treatments are often conducted to improve the productivity of oil or gas wells. In these cases, multi-phase flow of aqueous fluids with oil or gas is then encountered. In multi-phase flow, other parameters such as fluid saturations, capillary pressure and relative permeabilities come into play. In the literature, most acidizing studies focused on the single-phase flow of aqueous acidic fluids.

To determine the effects of multi-phase flow on acidizing results, we carried out simulation studies for the core test, undamaged well and damaged well treatments in two-phase flow conditions. We assumed that prior to acid injection all the rocks involved in the three cases were saturated with oil in the presence of connate water. Our simulation results indicated that multi-phase flow had little influence on mineral dissolution and porosity and permeability alteration if the amount of injected acid was the same and oil was completely displaced. This is because saturation front advances much faster than mineral reaction fronts. If the treatment pressure was kept constant, the amount of acid that could be injected for a given time was less in the two-phase flow due to the effects of relative permeabilities. In this situation, the permeability enhancement was correspondingly less.

Rock wettability is a major factor when ascertaining the location and distribution of fluids in a formation. In an oil-wet formation, oil contacts most of the rock surfaces. When acid displaces oil, thin oil films still exist on the pore surfaces. If the oil films do not break during acidizing, the chances for the acid to contact the pore surfaces and react with rock minerals are then greatly reduced. Further theoretical and modeling studies are undertaken to understand the complexities of acid treatments in multi-phase flow (Liu and Ortoleva, 1996).

Another interesting phenomenon — viscous fingering — may develop when a less viscous acid solution displaces a more viscous petroleum fluid (Ortoleva et al., 1994; Liu et al., 1995). It is found that the coupling between the viscous fingering and reaction-front fingering leads to very complex fingering patterns (Ortoleva et al., 1994; Liu and Ortoleva, 1996). This would be very difficult to predict without a multi-phase, reaction-transport simulator.

8. Conclusions

A general, coupled reaction–transport model and simulator has been presented in this paper. This study has demonstrated the potential applications of this geochemical simulator to matrix acidizing analysis and design.

Simulation results are in good agreement with experimental results of a laboratory core acidizing test. The simulator can predict damage potential caused by mineral precipitation as byproducts of the reactions of acids with formation minerals. Our results show that during sandstone acidizing hydrated silica may precipitate at a few centimeters away from the core inlet, depending on the injection velocity and acid strength. This phenomenon may not be observed by flow-through experiments in short-core samples.

In field simulation studies, permeability and productivity improvements are predicted using the simulator for typical acid treatments in undamaged and damaged sandstone formations. Simulation results indicate that the efficiency for acidizing an undamaged well is limited. It has been demonstrated that the simulator is capable of simulating all the sandstone matrix acidizing procedures that include preflush, mud acid injection, after-flush, and production of the spent acids from the well.

During the matrix acidizing of carbonate-bearing formations, a high reaction rate of hydrochloric acid
with carbonate rocks and flow self-focusing promote the creation and growth of dissolution fingers and wormholes. Simulation results have demonstrated that the simulator can also predict the fingering and wormholing phenomena. In summary, the complexities of matrix acidizing, acid-induced formation damage, and the creation of dissolution fingers and wormholes make the simulator an invaluable tool for matrix acidizing analysis and design.

9. Notation

- $s_t$: saturation of fluid $l$ (dimensionless)
- $S_a$: aqueous species $\alpha$ (dimensionless)
- $t$: time [s], s
- $T$: temperature [K]
- $\vec{u}_t$: filtration or flow velocity of fluid $l$ [L/t], m/s
- $V_t$: grain volume of mineral $i$ [L$^3$], m$^3$
- $W_{j}$: reaction rate of aqueous reaction $j$ [1 L$^{-3}$ t$^{-1}$], mol/m$^3$/s
- $W_{j}^s$: dissolution rate of mineral reaction $j$ [1 L$^{-3}$ t$^{-1}$], mol/m$^3$/s
- $\vec{z}$: unit upwardly pointing vector

Greek symbols:

- $\phi$: porosity (dimensionless)
- $\mu_t$: viscosity of fluid $l$ [M L$^{-1}$ t$^{-1}$], Pa s
- $\nu_{aoj}$: stoichiometric coefficient of species $\alpha$ in mineral reaction $j$
- $\nu_{aoj}^f$: stoichiometric coefficient of species $\alpha$ in aqueous reaction $j$
- $\theta_i$: geometric factor for mineral $i$ (dimensionless)
- $\rho_i$: molar density of mineral $i$ [1/L$^3$], mol/m$^3$
- $\rho_l$: mass density of fluid $l$ [M/L$^3$], kg/m$^3$

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References


