Geochemistry

Developing the ability to model acid-rock interactions and mineral dissolution during the RMA stimulation test performed at the Soultz-sous-Forêts EGS site, France

Développement des capacités de modélisation des interactions acides-roche et des dissolutions de minéraux au cours des tests de stimulation acide de type RMA réalisés sur le site SGS de Soultz-sous-Forêts (France)

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France

ABSTRACT

The Soultz Enhanced Geothermal System (EGS) reservoir’s response to chemical stimulation is assessed by numerical simulation of coupled thermo-hydraulic-chemical processes. To assess chemical interactions between host rocks and a mixture of HCl and HF as well as its potential effects on the Soultz EGS reservoir, new modelling efforts using the FRACHEM code have been initiated. This article presents the model calibration and results. Simulations consider realistic conditions with available data sets from the EGS system at Soultz. Results indicate that the predicted amount of fracture sealing minerals dissolved by injection of a mixture of acids Regular Mud Acid (RMA) was consistent with the estimated amount from the test performed on GPK4 well at Soultz EGS site. Consequently reservoir porosity and permeability can be enhanced especially near the injection well by acidizing treatment.

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RÉSUMÉ

L’impact de la stimulation chimique sur le réservoir du Système Géothermale Stimulé (SGS) de Soultz est évalué par simulation numérique des processus couplés thermo-hydraulique-chimique. Les modélisations 2-D simplifiées du réservoir ont pour but d’interpréter et de prévoir les interactions acides-roche dans le granite fracturé du système géothermal stimulé de Soultz-sous-Forêts. Pour évaluer les interactions chimiques entre la roche hôte et un mélange de HCl et HF, ainsi que les effets potentiels du traitement chimique sur le réservoir SGS de Soultz, une nouvelle calibration du code FRACHEM a été intégrée. Les résultats de la simulation indiquent que la quantité prévue de minéraux...
1. Introduction

The Soultz-sous-Forêts Enhanced Geothermal System (EGS), established in the Rhine Graben, north of Strasbourg (France), has been investigated since 1986. Three wells (GPK3 as a central injection well and GPK2 and GPK4 as production wells) were drilled to 5000 m depth in the crystalline basement to build the EGS system. The shallow geology (0 to 1400 m depth) consists of sedimentary layers, overlaying the crystalline basement of Late Paleozoic granites containing hydrothermally altered and fractured zones related to graben normal faults (Genter, 1990; Traineau et al., 1991). It has been observed that deep fluid circulation is supported by the network of permeable fractures. Extensive research has been made to characterize the properties of the fractures. Geophysical borehole measurements including borehole image logs, coring and cuttings analysis showed that nearly-vertical fractures, which show a low permeability, are oriented in an almost north-south direction (Dezayes et al., 1995, 2005; Genter et al., 1995). Moreover, it appears that most of the fractures are sealed by hydrothermal deposits, mainly calcite, silica and clays, giving a random distribution to the overall permeability of the system.

The development of EGS depends on the creation of permeable and connected fractures. The Soultz wells have been stimulated hydraulically and chemically in order to develop the underground reservoir (Gérard et al., 2006). The first hydraulic stimulations of the three wells were carried out between 2000 and 2005, and resulted in an improvement of the productivity index of wells GPK2 and GPK4 by a factor of approximately 20 and of GPK3 by a factor of approximately 2 (Nami et al., 2007). Although the limited performance of hydraulic stimulation, with high costs and public concern about induced seismic events, provided an important set of reasons for undertaking chemical treatments as additional or even alternative method to hydraulic stimulation, the main argument for chemical stimulation was the evidence, based on drill cuttings and cores analysis as well as on geophysical logs, of fracture filling by carbonates and other soluble minerals.

Removal of secondary mineral filling natural or induced fractures from granitic formation in the near-wellbore vicinity can be accomplished by injecting strong acids (such as HCl and mixtures of HCl-HF). Acid treatments have been successfully applied in many cases to increase or to recover geothermal wells production rates to commercial levels (Entingh, 1999). In order to dissolve the hydrothermal deposits (like carbonates, clay, feldspars and micas) present in the main fracture and porosity zones of the Soultz granite to improve their permeability, Regular Mud Acid (RMA), a mixture of HCl and HF widely used in oil and gas wells, was injected in GPK4 well.

FRACHEM, a thermo-hydraulic-chemical coupled code, was developed especially to forecast the evolution of the EGS project at Soultz-sous-Forêts. FRACHEM can simulate thermal, hydraulic and fluid-rock interactions within the fractures connecting the injection and the production wells, and determine the dissolution/precipitation reactions of carbonates, pyrite and silicated minerals in the Soultz granite (André et al., 2006; Bächler, 2003; Durst, 2002; Portier et al., 2007). The FRACHEM code has been improved to simulate the propagation of reacting fluids and to gain insight into the effectiveness of the acidizing treatment as a well stimulation technique. The RMA stimulation method has been applied by numerical modelling to the Soultz EGS system, to investigate its impact and effectiveness.

In this article, we first present the results of RMA injection performed at Soultz-sous-Forêts. Then we discuss the principle of minerals dissolution using RMA solution, and the calibration of a dissolution model using the FRACHEM code. Finally, we present simulation results of this stimulation method to assess chemical interactions between host rocks and a mixture of HCl and HF as well as its potential effects on the Soultz EGS reservoir. Simulation considers realistic conditions with available data sets from the EGS system at Soultz.

2. Field test: stimulation of GPK4 with Regular Mud Acid

Hydrofluoric acid (HF) is the only common acid that dissolves clay, feldspar and quartz fines. For years, mixtures of HCl and HF (RMA treatment) have been the standard acidizing treatment to dissolve these minerals that cause damage (Kalfayan, 2001). In sandstone acidizing treatments, a preflush of HCl varying between 7.5 to 15% is usually injected ahead of the HCl/HF mixture to dissolve the carbonate minerals and avoid precipitation of calcium fluoride (CaF$_2$). The minimum volume is determined by assuming that the HCl-carbonate reaction is very fast so that the HCl reaction front is sharp.

RMA was injected from the wellhead through the casing string in GPK4 well. The stimulation zones were therefore the whole openhole section of the well (500 to 650 m length). In May 2006, the RMA treatment was carried out in four steps with addition of a corrosion inhibitor when needed. Before the injection of RMA, 2000 m$^3$ of cold deoxygenated water were introduced in the well at 12 L/s, then at 22 L/s, and finally at 28 L/s. Later, to avoid CaF$_2$ precipitation that can lead to well damage, a preflush of 25 m$^3$ of a 15% solution of HCl in deoxygenated water (3.75 tons of HCl) was pumped ahead of the HCl-HF acid mixture for 15 minutes at 22 L/s. A main flush consisting of a total of 200 m$^3$ of 12/3 (wt%) RMA was then injected at a flow rate of 22 L/s for 2.5 hours. Finally, a postflush of 2000 m$^3$ of cold deoxygenated water, at a flow rate of 22 L/
s, then 28 L/s during 1 day, was injected after the RMA injection.

After the RMA stimulation, the wellhead pressure curve was smooth, indicating an efficient clean up of the hydrothermally fractured or porous zones in the first ten meters surrounding the open hole (GEIE, 2006) (Fig. 1). The step rate test performed later in May 2006, after the RMA-stimulation, shows that, after 3 days of injection, the wellhead pressure is about 65 bars, which is about 16 bars lower than before stimulation (step rate test performed on April 2006). Before the RMA treatment, the wellhead pressure curve raised with the flow increase showing a restricted storage capacity in the vicinity of the well. It can be estimated that the RMA-stimulation has therefore resulted in a maximum enhancement of the injectivity index of 35% (GEIE, 2006). However, no production test was performed after these operations to verify the productivity index.

3. Model set-up

The mineral dissolution and porosity enhancement near the injection well following short acid mixture injection has been reproduced by simulation using FRACHEM.

3.1. Geometrical and flow conditions

The present application of FRACHEM is the modelling of a 2-D simplified model with geometry close to the Soultz system. Injection and production wells are linked by fractured zones and surrounded by the impermeable granite matrix. The model is composed of 1250 fractured zones. Each fractured zone has an aperture of 0.1 m, a depth of 10 m, a porosity of 10%. This model allows an effective open thickness of about 125 m, while the mean openhole section of each well is about 600 m. Initially the temperature was set to the reservoir temperature of 200°C and the fractured zone contains the formation fluid.

One of these fractured zones is modelled with the assumption that the fluid exchange with the surrounding low permeability matrix is insignificant. Due to the symmetrical shape of the model, only the upper part of the fractured zone is considered in the simulation. The area is discretised into 222 2D elements (Fig. 2).

Considering the main flush injection rate of 22 L/s, the fluid was initially re-injected in the modelled fractured zone at a rate of 1.76×10^{-2} L/s. During this simulation a constant overpressure of 70 bars was assumed at the injection well and an initial hydrostatic pressure of

| Table 1 |

| Thermo-hydraulic parameters for the main flush. |

<table>
<thead>
<tr>
<th>Reservoir properties</th>
<th>Fracture</th>
<th>Matrix</th>
<th>Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity [m²/Pa s]</td>
<td>7.4 × 10^{-8}</td>
<td>10^{-15}</td>
<td>–</td>
</tr>
<tr>
<td>Thermal conductivity [W/m K]</td>
<td>2.9</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>–</td>
<td>2650</td>
<td>1000</td>
</tr>
<tr>
<td>Heat capacity [J/kg K]</td>
<td>–</td>
<td>1000</td>
<td>4200</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>10</td>
<td>0</td>
<td>–</td>
</tr>
</tbody>
</table>

| Initial and boundary conditions |

| Injection overpressure [bar] | 70 |
| Reservoir pressure [bar] | 500 |
| Temperature (°C) | 200 |

| Injection conditions |

| Temperature (°C) | 65 |
| Initial rate (L/s) | 22 |
| Duration (hours) | 2.5 |
500 bars was assumed for about 5000 m depth. Dirichlet boundary conditions were applied to the upper, left and right side of the model. The values of thermo-hydraulic parameters considered in the simulation are listed in Table 1.

An injection temperature of 65 °C was used. Injection water chemistry was the same as in the field test, a 3 wt% HCl solution, and a density of 1075 kg/m³. The initial water chemistry is in equilibrium with the initial mineralogy at a reservoir temperature of 200 °C. A maximum test-period of 2 days was simulated, including injection of cold fresh water at 25 °C, a preflush of 15 wt% HCl solution during 0.25 h and a postflush period of one day after the 2.5 h injection of RMA.

### 3.2. Mineralogical and chemical settings

The mineralogical composition of Soultz granite is assumed to be the same for the three wells (GPK2, GPK3 and GPK4) (Table 2). In the following simulation, the fluids are assumed to circulate within the hydrothermally altered granite. Concerning the mineralogical composition of the fractured zone, only quartz (40.9%), K-feldspar (13.9%), calcite (3.3%), dolomite (0.8%) and illite (24.6%) are considered.

The geothermal fluid present in the formation is a NaCl brine with a pH of 4.9, a total dissolved solids of about 100 g/L and a temperature at the beginning of the simulation of 200 °C. The main characteristics of this fluid are given in Table 3.

### 3.3. Dissolution reactions driven by mud acid

The main readily HCl-soluble minerals are calcite, dolomite, and siderite, which additionally do not generate precipitates. The reactions are:

- **Calcite**
  \[
  2\text{HCl} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^- + \text{H}_2O
  \]

- **Dolomite**
  \[
  4\text{HCl} + \text{CaMg(CO}_3)_2 \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{Cl}^- + 2\text{H}_2O + 2\text{CO}_2(aq)
  \]

- **Siderite**
  \[
  2\text{HCl} + \text{FeCO}_3 \rightarrow \text{Fe}^{2+} + 2\text{Cl}^- + \text{H}_2
  \]

Siliceous minerals are dissolved by HF and its chemistry is much more complex than the HCl when reacting with carbonates (Walsh et al., 1982). Quartz, clay and feldspars are the main siliceous particles involved in damage of sandstones. The primary chemical reactions in sandstone acidizing are:

- **Quartz**
  \[
  \text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4(\text{silicon tetrafluoride}) + 2\text{H}_2O
  \]

- **Siliicic acid**
  \[
  \text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6(\text{fluorsilicic acid})
  \]

A convenient way to express reaction stoichiometry is with the dissolving power, introduced by Williams (1979). The dissolving power expresses the amount of mineral that can be consumed by a given amount of acid on a mass or volume basis, \(X_g\), the mass of mineral consumed by a given mass of acid, is defined as:

\[
X_g = \frac{v_{\text{mineral}}M_W}{v_{\text{acid}}M_{W,\text{acid}}}
\]

The dissolving power of any concentration of acid is the \(X_{5100}\) times the weight fraction of acid in the acid solution. For the commonly used preflush of 15 wt% HCl, \(X_{515} = 0.15(X_{5100})\). The stoichiometric coefficients \(v\) for common acidizing reactions are found from the reaction equations described above, while the molecular weights \(M_W\) of the acids and minerals considered in the simulation are listed in Table 4.
The volumetric dissolving power, $X_v$, similarly defined as the volume of mineral dissolved by a given volume of acid, is related to the dissolving power $X_g$ by density ($\rho$) ratio:

$$X_v = X_g \frac{\rho_{acidsolution}}{\rho_{mineral}} \quad (2)$$

The volumetric dissolving power of HCl with calcite and dolomite and for HF with quartz and albite are given in Table 5.

The volume of HCl preflush needed to consume the calcite to a short distance from the wellbore is the volume of calcite present divided by the volumetric dissolving power. The main acid stage requires the greatest emphasis because of the damage mechanisms, directly associated to precipitation of products from the HF reactions (Allen and Roberts, 1989; Kalfayan, 2001). Primary reactions describe the action of the unspent acid with the various minerals. The presence of calcium (Ca$^{2+}$) will cause CaF$_2$ to precipitate. Sodium (Na$^+$) and potassium (K$^+$) can create alkali-fluorosilicates and alkali-fluoroaluminates when formation minerals, or sodium or potassium brines, react with the hexafluorosilicic acid produced by this reaction. The fluosilicate and fluoroaluminate compounds are more likely to form during the initial phases of the dissolution, since a high concentration of HF relative to the clay enhances the reaction. Precipitation of these compounds will occur when the amount present increases above the solubility limit. Acid stimulation techniques have to account for both chemistry and treatment execution to accurately predict the effectiveness since the effect of these precipitates could bring into contact. The reaction rate for the HCl-CaCO$_3$ reaction is extremely high, so the overall rate of this reaction is usually controlled by the rate of acid transport to the surface. On the other hand, the surface reaction rates for many HF-mineral reactions are very slow compared with the acid transport rate, and the overall rate of acid consumption or mineral dissolution is reaction rate controlled (Fogler et al., 1976).

### 3.4. Acid mineral reaction kinetics

Reaction rates are affected for kinetics; among the factors that strongly influence the mineral reactions are acid concentration and temperature. Dissolution reaction rates are proportional to the HF concentration for most sandstone minerals. The dissolution of minerals is a thermally activated phenomenon; thus, the rates increase greatly as a function of temperature, and the penetration depths of live acid diminish accordingly. Reaction kinetics data have been found in the literature for the reactions of HCl with calcite and dolomite and for the reactions of HF with quartz, feldspars and clays. Efforts have been made to develop FRACHEM code to simulate the acidizing process.

Acid-mineral reactions are termed heterogeneous reactions because they are reactions between species occurring at the interface between different phases, the aqueous phase acid and the solid mineral. The kinetics of a reaction is a description of the rate at which the chemical reaction takes place, once the reacting species have been brought into contact.

The reaction rate for the HCl-CaCO$_3$ reaction is extremely high, so the overall rate of this reaction is usually controlled by the rate of acid transport to the surface. On the other hand, the surface reaction rates for many HF-mineral reactions are very slow compared with the acid transport rate, and the overall rate of acid consumption or mineral dissolution is reaction rate controlled (Fogler et al., 1976).

#### 3.4.1. Reactions of HCl with carbonates

HCl is a strong acid, meaning that when HCl is dissolved in water, the acid molecules almost completely dissociate to form hydrogen ions, H$^+$, and chloride ions, Cl$^-$. The reaction between HCl and carbonate minerals is actually a reaction of the H$^+$ with the mineral. The kinetics of the HCl-calcite and HCl-dolomite reactions have been measured (Lund et al., 1973,1975). The results were summarized as follows (Schechter, 1992):

$$r_{carbonate} = s k_c (C_{HCl})^a \quad (3)$$

$$k_c = k_{0c} \exp \left( - \frac{E_a}{RT} \right) \quad (4)$$

where $r$ is the reaction rate (mol/s), $C_{HCl}$ is HCl concentration (mol/kgH$_2$O), $k_c$ is the kinetic constant of the reaction (mol/m$^2$ s), $s$ is the surface area of the mineral (m$^2$/kgH$_2$O), $k_{0c}$ is the kinetic constant of the reaction at 25 °C (mol/m$^2$ s), $E_a$ is the activation energy (J/mol), $R$ is the universal gas constant (8.314 J/mol K) and $T$ is temperature (°K). The constants are given in Table 6.

#### 3.4.2. Reaction of hydrofluoric acid with sandstone minerals

HF reacts with virtually all of the many mineral constituents of sandstone. Reaction kinetics have been reported for the reactions of HF with quartz (Bergman, 1963; Hill et al., 1981), feldspars (Fogler et al., 1975), and clays (Kline and Fogler, 1981). These kinetic expressions

---

### Table 4

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>36.5</td>
<td>15%wt HCl solution: 1.07</td>
</tr>
<tr>
<td>HF</td>
<td>20</td>
<td>3%wt HF-12%wt HCl solution: 1.075</td>
</tr>
<tr>
<td>Calcite</td>
<td>100.1</td>
<td>2.71</td>
</tr>
<tr>
<td>Dolomite</td>
<td>184.4</td>
<td>2.84</td>
</tr>
<tr>
<td>Siderite</td>
<td>115.8</td>
<td>3.94</td>
</tr>
<tr>
<td>Quartz</td>
<td>60.1</td>
<td>2.65</td>
</tr>
<tr>
<td>Albite</td>
<td>262.3</td>
<td>2.61</td>
</tr>
<tr>
<td>K-feldspars</td>
<td>278.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Ilelite</td>
<td>389.3</td>
<td>2.75</td>
</tr>
<tr>
<td>Am.Silica</td>
<td>60.1</td>
<td>2.07</td>
</tr>
</tbody>
</table>

---

### Table 5

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Acid concentration 12%wt HCl–3%wt HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.067</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.058</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.010</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>0.011</td>
</tr>
</tbody>
</table>
can all be represented by:

\[ r_{\text{mineral}} = sk_c \left(1 + K(C_{\text{HCl}})^\alpha \right) \cdot (C_{\text{HF}})^\beta \]  \hspace{1cm} (5)

where \( r \) is the reaction rate (mol/s), \( k_c \) is the kinetic constant of the reaction (mol/m².s), \( s \) is the surface area of the mineral (m²/kgH₂O), \( C_{\text{HCl}} \) is HCl concentration (mol/kgH₂O), \( C_{\text{HF}} \) is HF concentration (mol/kgH₂O), \( K \), \( \alpha \) and \( \beta \) are dimensionless parameters and the constants are given in Table 6.

These expressions show that the dependence on HF concentration is approximately first order (\( \alpha = 1 \)). For the feldspar reactions, the reaction rates increase with increasing HCl concentration, even though HCl is not consumed in the reaction. Thus, HCl catalyzes the HF-feldspar reactions. Also, the reaction rates between clay mineral and HF are very similar in magnitude, except for the illite reaction, which is about two orders of magnitude slower than the others.

Per unit mass of rock, the specific surface area of each mineral is its specific surface area times the mass fraction of the mineral present in the sandstone. The fraction of HF expended in a particular reaction is the overall reaction rate for that mineral divided by the sum of the reaction rates. The reaction rates of HF with clays and feldspars are approximately two orders of magnitude higher than that between HF and quartz. Because the clay and feldspars reaction rates are relatively high and they generally comprise a small portion of the total rock mass, they will be consumed first in sandstones acidizing. The quartz reaction becomes important in regions where most of the clay and feldspar have already been dissolved.

4. Simulation results

To test the above findings, the numerical model was applied to hydraulic data measured during the RMA stimulation test. Since, in the numerical model, the pressure at the injection and the production point was fixed, pressure cannot be used for comparison. Instead, the resulting flow rate evolution in the fractured zone is illustrated in Fig. 3. The flow rate evolution as a percentage of the initial value in the first ten meters of the fractured zone increases by 35%.

Overall enhancement of porosity and permeability obtained from the simulation is presented in Fig. 4. The permeability increases in the vicinity of the injection well.
The porosity increases to about 0.17 from an initial value of 0.1 close to the injection well. The enhancement of porosity and permeability extends to a distance of about 40 m from injection well. Increases in porosity and permeability are mainly caused by dissolution of calcite, K-Feldspar, albite and illite (Fig. 5).

First, a 15%wt HCl solution was injected to dissolve calcite in the first metres of the fractured zone. Because dissolution rate of dolomite is two orders of magnitude smaller than calcite, dolomite is not attacked by the acid preflush. Then, when injecting the RMA treatment, the calcite dissolution zone extends up to 50 metres from the injection well, whereas dolomite is dissolved near the well (Fig. 5).

Because the clay and feldspars reaction rates are relatively high and they comprise a small portion of the total rock mass, they are consumed first in RMA acidizing. The first 40 metres around the injection well are affected by acid mixture (Fig. 5). K-feldspar, illite and albite dissolution occurs close to the injection point (Fig. 5). The quartz reaction becomes important in regions where most of illite and feldspars have already been dissolved. However, amounts of quartz dissolution are very small because of lower reaction rate.

During RMA injection in-situ, the change of the measured wellhead pressure slope points to geochemical processes in the reservoir (Fig. 1). The permeability enhancement calculated by numerical model (Fig. 4), mainly due to the dissolution of calcite and feldspars (Fig. 5), confirms this assumption. As the reservoir permeability and porosity are controlled by the occurrence of mineral precipitation and dissolution, the mineral dissolution implies an improvement of the reservoir properties, namely the hydraulic impedance of the injection well.

5. Conclusions

Recently, sandstone-acidizing treatments have been successfully performed in geothermal granitic reservoirs such as at Soultz and encouraging results were obtained on GPK4 well. Some numerical simulations using FRACHEM code were performed to better understand the behaviour of acid mixtures within the reservoir. Considering the geometrical model used for the simulations and the different assumptions about the fluid and rock compositions, some estimation has been proposed. The injection of a RMA solution results in dissolution of calcite, clays and feldspar minerals. Consequently reservoir porosity and permeability can be enhanced in a region extending several meters around the injection well. Nevertheless, the high reactivity and a weak flow prevent the penetration of acid in the far field between the wells. This high reactivity also involves the risk of creating wormholes, able to increase the porosity but not always the permeability of the fractured reservoir (Kalfayan, 2001; Schechter, 1992).

Many factors affect mineral dissolution and associated enhancement in formation porosity and permeability, including mineral abundance and distribution in the formation, reaction kinetics, and injection rate. More detailed investigations will be conducted in the future. Moreover, this technique is still considered risky because of secondary and tertiary reactions between the spent acid and the rock. Precipitates resulting from these reactions can deposit in the pores and fractures of the rock and eventually negate the positive impact of the primary reaction. Being able to assess the extent of the secondary and tertiary reactions under reservoir conditions is therefore critical for the acid treatment success. Since the secondary reaction kinetics is included, an improved prediction will be achieved. Secondary reactions result from the action of the hexafluorosilicic acid with remaining acid and the rock. The driving force for this reaction is the greater affinity of fluorine for aluminum than for silicon. Silica gel precipitation is well documented (Gdanski, 1997; Walsh et al., 1982). This precipitation occurs when the initial HF is nearly consumed. An exchange reaction occurs on the surface of the clays and fines to generate fluoaluminates and silica gel. The silica is deposited on the surface of the mineral particles, and the fluoaluminates remain in solution. This precipitate is more likely to occur when fast-reacting aluminosilicates, such as clays, are present. The damaging effect of silica gel precipitates is still a point of debate; however, it does appear that they are more damaging at higher than lower temperatures. Tertiary reactions are the reactions of the aluminum fluorides and aluminosilicates. The reaction is insignificant at temperatures below 90 °C. At higher temperatures, the reaction can be considerable depending on the stability of the formation clays with HCl. Careful selection of mixtures, additives, acids formulations, and treatment volumes must be accounted to minimize these secondary adverse effects.

Finally, this study demonstrated that acid mixtures injection can play a significant role in the development of porosity around injection wells. It was shown by numerical modelling that mixtures of acids have the possibility to
react with carbonates and silicates, dissolving them and opening new pores within the reservoir. Looking for commercial production rates of the wells, other chemical stimulation techniques should be considered such as fracture acidizing. This type of acid job should reach the fracture network of the far field and connect the injection and production wells.

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