Kinetic modeling of interactions between iron, clay and water:
Comparison with data from batch experiments

Viet V. Ngo a,⇑, Alain Clément a, Nicolas Michau b, Bertrand Fritz a

a Laboratoire d’Hydrologie et de Géochimie de Strasbourg, Université de Strasbourg/EOST, CNRS, 1 rue Blessig, F-67084 Strasbourg Cedex, France
b Andra, Parc de la Croix Blanche, 1/7 rue Jean Monnet, F-92298 Châtenay-Malabry Cedex, France

Abstract

It has been proposed that a carbon steel overpack is used as part of the engineered barrier system for the geological disposal of radioactive wastes developed by Andra. The direct contact of the iron with the geological environment creates potential physical and chemical changes in the near field environment of the repository. Therefore, a thorough understanding of the mineralogical/chemical evolution caused by the interactions of iron with clay is necessary to the assessment of the performance of the geological disposal. Geochemical models have been developed (using the code KINDIS) to simulate batch experiments on iron–claystone interactions. The experiments included iron powder and Callovo-Oxfordian (COx) claystone that were reacted at temperature of 90 °C for 90 days. The overall objective of this modeling work aims at an enhanced mechanistic understanding of clay–iron interactions observed in experimental studies and possible implications for engineered barrier performance.

The experimental observations were successfully reproduced by the model regarding geochemical evolution and mineralogical transformations. For example, the stability of pH around 7 and total dissolved carbon in the aqueous solution, which are controlled by saturation state of carbonates in the system, are predicted accurately. In addition, the model predicts that during the interactions between iron and clays greenalite, chukanovite, and saponite form as the main secondary minerals. Moreover, the destabilization of some important primary minerals in the claystone such as quartz, illite, and smectite are also indicated by the numerical simulations. The consistency of the predictions with the experimental observations can be shown in activity diagrams of these secondary minerals, which represent the relation of H4SiO4 activity and CO2 partial pressure or Ca2+ activity. Another important result is that both the model and experimental data indicated that magnetite is not formed in the experiments.

The analysis of three sensitivity cases made clear that the uncertainty in corrosion and dissolution rates for iron, quartz, and illite plays an important role on the predicted evolution of pH in the aqueous solution and the formation of secondary minerals. Through this modeling work, the controlling mechanism of the interactions of iron, clay, and water at the specific conditions is fairly well understood. However, the robustness of the geochemical code KINDIS should also be tested against other experiments with different experimental conditions.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The concept of deep geological repository developed by Andra generally consists of using the remarkable physical and chemical properties of the claystone (e.g., retention capability, low permeability, and homogeneity of the formation). The claystone has properties that are desirable for a host rock for radioactive waste disposal, in that it has low water flow, and radionuclide migration can only occur via very slow diffusion processes. The COx claystone from the Paris basin can satisfy all the above properties and hence these are investigated in various studies. Additionally, in Andra’s design, the confinement of high level radioactive waste requires a steel canister to avoid any release of the radioactive species for at least a few centuries. The direct contact between the steel canister and the geological barrier creates potential issues related to the iron corrosion that causes the mineralogical transformations in the near field environment. It is expected that during corrosion of the steel overpack, iron reacts with water, clay minerals, silicates and carbonates of the claystone to form corrosion products like: magnetite, dihydrogen, iron silicates and iron carbonates. Extension of this transformed zone and its chemical composition may influence the behavior and the transfer of radionuclides on the long term. Therefore, an understanding of the evolution of the
environment in the repository over long periods of time is essential for the performance assessment of the geological disposal.

Considerable attention has been paid to this system through the experimental investigations of the interactions between iron and clay host rock and/or bentonite using different approaches that try to represent different repository conditions. Such studies include the in situ field experiments (e.g., Gaudin et al., 2009, 2013) and the laboratory experiments (e.g., Guillaume et al., 2003, 2004; Jodin-Caumon et al., 2010, 2012; Lantenois et al., 2005; Martin et al., 2008; Mosser-Ruck et al., 2010; Perronnet et al., 2007; Rivard et al., 2013a,b; Schlegel et al., 2008, 2010; Wilson et al., 2006a; Lanson et al., 2012). Depending on the experimental conditions, mineralogical compositions, aqueous chemistry, and the physical chemical parameters such as pH, Eh, and temperature, the reaction pathways and evolution of the experimental systems are significantly different. A number of different alteration products have been observed, including Fe-rich clay minerals, zeolites and iron oxides. (Mosser-Ruck et al., 2010). Nevertheless, it is commonly found from these publications that the interactions between iron and clays can form magnetite and Fe-rich silicates as the main corrosion products. Moreover, some of the above experimental investigations have also reported the rich silicates as the main corrosion products. Additionally, some of the above experimental investigations have also reported the destabilization of quartz, illite, and smectite (e.g., de Combarieu et al., 2007; Mosser-Ruck et al., 2010; Perronnet et al., 2007). Recent technical developments, like electron diffraction tomography, X-ray absorption spectroscopy or scanning transmission X-ray microscopy, allow very fine characterization of the mineral phases, X-ray microscopy, allowing the detailed characterization of the mineral phases, and the difficulties in parameterization of kinetic data of a dozen of primary minerals. Therefore, the objective of the current study is not to attempt to reproduce exactly the experimental data, but aims at an enhanced mechanistic understanding of reaction pathways and controlling parameters for interactions of iron, COx claystone, and water in the given experimental conditions.

2. Materials and methods

2.1. Overview of the experiments

In the context of the geological disposal for high level radioactive waste, Andra has been supporting different studies about the interactions of iron, clays, and water. The experiments modeled in this work were carried out by the team of the GéoRessources laboratory (Bourdelle et al., 2014), University of Lorraine. The batch experiments were performed to investigate the mineralogical and chemical evolutions of the system in different conditions. They have been developing equipment in which pH can be measured in real time and in situ. Furthermore, the aqueous and solid phases were also sampled to analyze aqueous species and mineralogical fractions of the solid phase during the experiment. In this modeling work, two in situ batch experiments were selected, which had the highest resolution and quality of data. In this section, the overall description of the experiments and a summary of the results are given. Greater detail on the experiments is provided by Bourdelle et al. (2014).

2.1.1. Experimental description

The two experiments were carried out in parallel by means of two autoclaves with a volume of 250 cm³. One autoclave was used to measure the in situ pH evolution, called “pH experiment”, in which no fluid, gas, and solid phases were sampled during the experiment to allow for the determination of the solid phase and to analyze major ions and other species. Fig. 1 shows a schematic view of these experiments.

The temperature of both experiments was kept constant at 90 °C. It is assumed that the initial input of both experiments such as mineralogical composition of COx claystone, iron, and aqueous solution are the same. The experimental system contained iron and COx claystone in the form of powder with the following weight ratios: water/clay = 10 and iron/clay = 0.1. The water used in both experiments initially contained NaCl (20.7 mM L⁻¹) and CaCl₂ (3.8 mM L⁻¹). These experiments were carried out for a period of 90 days.

V.V. Ngo et al. / Applied Geochemistry 53 (2015) 13–26
The experimental data revealed that solid iron has totally disappeared by the end of the experiment but the precise moment corresponding to the end of corrosion could not be determined. The mean corrosion rate, which was estimated from the measured H₂ partial pressures in the system, varied in the range of 10–25 μm year⁻¹ (Bourdelle et al., 2014). In addition, iron-rich silicates, i.e., greenalite, were the main secondary minerals observed during the interactions between iron and clay material. Magnetite, a common product of the iron corrosion, was not observed in this system. It was also found that quartz, illite, and smectite were partly dissolved. Furthermore, calcite was at equilibrium over the course of the experiments.

### 2.2. Modeling approach

The interactions between iron, clay material, and water consist of various phenomena such as the corrosion of iron, dissolution and precipitation of minerals and ion exchange. In the current study, the numerical simulation is based on the assumptions that corrosion of iron occurs at constant rate (1.41 mol m⁻² year⁻¹), equivalent to 10 μm year⁻¹), secondary minerals precipitate at equilibrium, and the dissolution of primary minerals is kinetically controlled.

The mineral dissolution generally proceeds via two main processes: the diffusion transport of aqueous reactants and products to and from the surface of mineral and the reaction occurring at the surface (Schott et al., 2009). The dissolution rate is controlled by the slowest process. Depending on the types of minerals, the distance from the equilibrium and the temperature of the system, the mineral dissolution is controlled either by the surface reaction and/or diffusion transport. When the surface reaction rate constant is small compared to the diffusion-controlled rate constant, the dissolution of mineral occurs under the surface reaction (Jeschke and Dreybrodt, 2002; Lasaga, 1986; Murphy et al., 1989). Dissolution of minerals that are very soluble, e.g., calcite, tends to be controlled by diffusion. Systems being far from the equilibrium tend to be controlled by diffusion transport as well. In contrast, the systems close to the equilibrium are generally controlled by surface reaction (Lasaga, 1986). For the carbonate minerals, the dissolution mechanisms involving surface and diffusion controlled reactions have been reviewed in great detail by Morse and Arvidson (2002). In general, the activation energy of the surface reaction is higher than the one controlled by diffusion reaction (Murphy et al., 1989). Hence, this implies that when temperature increases, the surface-controlled reaction rate constant increases faster than the rate constant of the diffusion-controlled reaction. Therefore, the intrinsic rate of surface reaction tends to be higher than the intrinsic rate of diffusion-controlled reaction. This also means that the mineral dissolution proceeding via diffusion transport becomes more important at high temperature (Murphy et al., 1989). For this modeling work, both surface-controlled and diffusion-controlled reactions are included to describe the dissolution of primary minerals.

#### 2.2.1. Description of the KINDIS code

The simulations were carried out by means of the kinetic reaction code, called KINDIS (Madé et al., 1994). In this section, we present the main equations with respect to the dissolution of primary minerals controlled by the surface reaction and diffusion transport, respectively.

#### 2.2.1.1. Surface-controlled reaction

For the practical application of the dissolution law, the KINDIS code uses the following expression to describe the mineral dissolution controlled by surface reaction (Madé et al., 1994; Palandre and Kharaka, 2004):

\[
R_i^s = S_i \left( \frac{1}{K_i} \right) \left[ \exp \left( \frac{-E_{\text{acid}}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) - 1 \right] \left[ \exp \left( \frac{-E_{\text{neutral}}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) - 1 \right] \left[ \exp \left( \frac{-E_{\text{base}}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) - 1 \right]
\]

where \( R_i^s \) (mol year⁻¹ kg⁻¹) is the dissolution rate controlled by surface reaction; \( S_i \) (m² kg⁻¹) is the surface area; \( K_i \) is the thermodynamic equilibrium constant at the given temperature; \( E_{\text{acid}}, E_{\text{neutral}}, E_{\text{base}} \) (mol m⁻² year⁻¹) are the dissolution rate constants at 25 °C and pH = 0, which correspond to the acid, neutral, and basic pH zones, respectively; \( g_{\text{acid}}, g_{\text{neutral}}, g_{\text{base}} \) (J mol⁻¹) are the activation energies with respect to the acid, neutral, and basic zones, respectively; \( n_{\text{acid}} \) and \( n_{\text{base}} \) are reaction orders with respect to the pH of the solution; \( R \) (J K⁻¹ mol⁻¹) is the gas constant; \( T \) (K) is the temperature.

#### 2.2.2. Diffusion-controlled reaction

The description of the mineral dissolution controlled by diffusion transport is based on Fick’s law. It is expressed as follows:

\[
R_i^d = -\frac{D_i}{\varepsilon_i} \left( C_i - C_a \right) = -\frac{D_i C_i^C}{\varepsilon_i} \left( \frac{C_i}{C_{eq}^C} - \frac{C_a}{C_{eq}^C} \right) = -k_i^{eq} S_i \left( \frac{C_i}{C_{eq}^C} - \frac{C_a}{C_{eq}^C} \right)
\]

where \( R_i^d \) (mol year⁻¹ kg⁻¹) is the dissolution rate controlled by diffusion; \( D_i \) (m² year⁻¹) is the coefficient of diffusion in water, \( \varepsilon_i \) (m) is the thickness of the diffusion boundary layer, \( C_i \) and \( C_a \) (mol kg⁻¹) are the detached ion concentration at the mineral surface and in the bulk solution, respectively; \( C_{eq}^C \) (mol kg⁻¹) is the saturation concentration at equilibrium, \( k_i^{eq} \) is the rate constant of the diffusion-controlled reaction.

The thickness of the diffusion layer with respect to each mineral is estimated by the following empirical expression (Jeschke and Dreybrodt, 2002; Zhang and Nancollas, 1990):

\[
\varepsilon_i = 5.74 (r_i)^{0.145} (\Delta \rho_i)^{-0.285}
\]

where \( r_i \) (μm) is the radius of the mineral particle, \( \Delta \rho_i \) (g cm⁻³) is the density difference between the mineral and the aqueous solution.

#### 2.2.3. Initial conditions

#### 2.2.3.1. Composition of the experimental system

The mineral composition used in the model is given in Table 1. The system contains powders of iron and COX clay, and water with respect to the ratios of 10 and 0.1 for water/clay and iron/clay, respectively. There are
10 primary minerals and the main ones are calcite, quartz, and clays.

2.2.2.2 Initial aqueous solution. The composition of the initial aqueous solution is presented in Table 2 (Bourdelle et al., 2014). The analysis of evolution of Ca$^{2+}$, K$^+$ and Na$^+$ revealed that Ca$^{2+}$ concentration is decreased by 1.4 mmol kg$^{-1}$H$_2$O and the sum of the concentration of K$^+$ and Na$^+$ is increased by 2.8 mmol kg$^{-1}$H$_2$O during the first few hours. This clear change is believed to be associated with the quick cationic exchange after the starting of experiment. This process is not the focus of the current study and it is therefore not accounted for in the model. However, to increase the accuracy of the input data, the concentration of three cations Ca$^{2+}$, K$^+$ and Na$^+$ is updated by using a simple balance approach where 1.4 mmol kg$^{-1}$H$_2$O of Ca$^{2+}$ from the solution is added to illite and smectite and 1.4 mmol kg$^{-1}$H$_2$O of K$^+$ and Na$^+$ is transferred to the solution from illite and smectite. The composition presented in Table 2 is determined after accounting for the cationic exchange of Ca$^{2+}$ in the solution with K$^+$ and Na$^+$ of both illite and smectite.

The measurement of total dissolved carbon in the aqueous solution showed a minor variation along the experiment. No measurement is available at the beginning of experiment. Therefore, the initial value is taken from its average measured concentration in clays. 

Table 2

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Structural formula</th>
<th>Mol of minerals (mol kg$^{-1}$H$_2$O)</th>
<th>Molar volume (cm$^3$ mol$^{-1}$)</th>
<th>Log$K_{sp}$ c (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>0.223</td>
<td>36.934</td>
<td>−9.24</td>
</tr>
<tr>
<td>Chamosite</td>
<td>Fe$_6$Al$_2$(Si$<em>4$O$</em>{10}$(OH)$_8$</td>
<td>0.003</td>
<td>213.42</td>
<td>−3.47</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO$_3$)$_2$</td>
<td>0.023</td>
<td>64.12</td>
<td>−19.07</td>
</tr>
<tr>
<td>Illite$^a$</td>
<td>K$<em>{0.83}$Ca$</em>{0.008}$Mg$<em>{0.25}$Al$</em>{2.35}$Si$_{3.4}$(OH)$_2$</td>
<td>0.083</td>
<td>140.25</td>
<td>−38.16</td>
</tr>
<tr>
<td>Microcline</td>
<td>KAlSi$_3$O$_8$</td>
<td>0.010</td>
<td>108.69</td>
<td>−19.39</td>
</tr>
<tr>
<td>Smectite$^a$</td>
<td>[Al$<em>{1.58}$Fe$</em>{0.28}$Mg$<em>{0.28}$Si$</em>{2.24}$]Si$<em>7$Al$<em>2$O$</em>{20}$(OH)$</em>$_2</td>
<td>0.021</td>
<td>134.92</td>
<td>−33.36</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>0.008</td>
<td>23.94</td>
<td>−57.34</td>
</tr>
<tr>
<td>Quartz(alpha)</td>
<td>SiO$_2$</td>
<td>0.395</td>
<td>22.69</td>
<td>−3.07</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>0.012</td>
<td>29.38</td>
<td>−11.43</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>0.008</td>
<td>99.34</td>
<td>−34.19</td>
</tr>
</tbody>
</table>

$^a$ The structural formula of illite and smectite correspond to the formula after accounting for the quick initial exchange of Ca$^{2+}$, K$^+$, and Na$^+$.

2.2.3.1 Thermodynamic data. The thermodynamic data at 90 °C are given in Tables 1 and 2 for the primary and secondary minerals, respectively. These data are taken from the Thermoddem database (Blanc et al., 2012), except for chukanovite, discussed below, and they are written in terms of the primary aqueous species in order that the basic soluble species are the same like in the database of the KINDIS code. The equilibrium constants of illite and smectite are adapted to account for the initial cationic exchange of Ca$^{2+}$ in the solution with Na$^+$ and K$^+$ of these minerals. For doing so, we assumed that 1.4 mmol kg$^{-1}$H$_2$O of K$^+$ in illite and of Na$^+$ in smectite are replaced by 1.4 mmol kg$^{-1}$H$_2$O of Ca$^{2+}$ from the solution. Based on the structural formula of illite and smectite before and after cationic exchange, and the thermodynamic constants of the cationic exchange couples K$^+$ – Ca$^{2+}$ and Na$^+$ – Ca$^{2+}$ taken from Fritz (1981), we can estimate the equilibrium constants of illite and smectite after accounting for the cationic exchange. The results obtained from this simple approach show that the values of equilibrium constant for illite and smectite are just changed a little, i.e. −38.16 and −33.36 compared to the initial values of −38.20 and −33.38 for illite and smectite, respectively.

The secondary minerals are chosen based on the literature review of the interaction between iron, clay, and water in anoxic conditions. The formation of secondary minerals is strongly dependent on the experimental conditions such as temperature, pH, pCO$_2$ and iron/clay ratio (e.g. Bourdelle et al., 2014; Jodin-Caumon et al., 2012, 2010; Lanterois et al., 2005; Mosser-Ruck et al., 2010, 2013; Perronnet et al., 2008; Pignatelli et al., 2013; Rivard et al., 2013a,b; Schlegel et al., 2008, 2010; Wilson et al., 2006a). Nevertheless, those previous experimental studies mostly reported the formation of Fe-rich minerals, including magnetite, siderite, Fe-saponite, Fe-phyllosilicates (crondstedite, berthierine, odlinite, and greenalite), etc. In addition, numerous modeling investigations on this topic using the thermodynamic and/or kinetic approaches also indicated the occurrence of these previous mineral precipitations (e.g. Bildstein et al., 2006; de Combarieu et al., 2007; Savage et al., 2010; Wersin and Birgersson, 2014; Wilson et al., 2006b). It is reported in a critical review on clay alteration due to hyperalkaline fluids by Savage et al. (2007) that the nature of secondary minerals and their uncertainty in thermodynamic data play an important role on the modeling results. This is also the case for iron–clay interactions. Therefore, in the present study, a large set of secondary minerals is considered to compare with precipitated phases observed either in the experimental or modeling studies. For example, the smectite group contains various Fe and Mg-end members such as beidellite-Ca, saponite-FeCa, saponite-FeMg and vermiculite-Mg (Table 3).

In recent years, chukanovite has been found in several studies that investigate the iron corrosion in clay media or soil (e.g., Remazeilles and Refait, 2009; Saheb et al., 2010, 2012; Schlegel...
et al., 2010, 2013). There is very limited thermodynamic data about chukanovite in the literature and none available at temperature above 25 °C. Therefore, the equilibrium constant at 90 °C for this mineral is extrapolated from the value at 25 °C, which is determined by Lee and Wilkin (2010), and the data for malachite, Cu₂(OH)₂CO₃.

Malachite was chosen because its structural formula is similar to chukanovite and its thermodynamic data at various temperatures is available in the Thermoddem database. It is assumed that the thermodynamic trend of chukanovite is similar to the one of malachite, which decreases around 1.5 units from 5.91 at 25 °C to 3.47 at 90 °C.

### 2.2.3.2. Kinetic data

Table 4 presents the kinetic data of the surface dissolution reaction for the primary minerals at 25 °C and 90 °C. The practical application of the mineral dissolution rate (Eq. (6)) requires to know various parameters for each primary mineral such as the reaction rate constant and reaction orders with respect to the pH of the solution. We used the data proposed by Palandri and Kharaka (2004), which are based on the kinetic data at 25 °C and an activation energy term, in order to extrapolate all necessary data at the chosen temperature. The diffusion length and rate constant of diffusion-controlled dissolution for several primary minerals are given in Table 5. The preliminary modeling tests indicated that the diffusion-controlled dissolution is the dominant process for calcite, dolomite, pyrite and siderite in the system. Dissolution of other minerals such as illite, smectite, microcline, kaolinite, chamosite and quartz is considered to be controlled by surface reaction only.

### 2.2.3.3. Reactive surface area of minerals

The reactive surface area of primary minerals is a sensitive parameter when the dissolution of mineral is controlled by the surface reaction (Ngo et al., 2014; Wilson et al., 2011). In general, the reactive surface area of mineral changes over the course of the dissolution/precipitation process as a feedback-effect of this process. The application of geochemical modeling tools requires estimates of the reactive surface area for all primary minerals. In the literature, modelers usually identify the reactive surface area with the BET, the edge site or the geometric surface area.

The BET surface area is measured by gas-adsorption technique (Brunauer et al., 1938). There is still a debate about the relationship between the BET surface area and the reactive surface area. Many authors accept that the BET surface area is proportional to the reactive surface area. However, other authors oppose this point of view and found that there is no direct proportionality between these types of area (e.g., Gautier et al., 2001; Hodson, 2006; Holdren and Speyer, 1985, 1987; Lütte, 2005; Tournassat et al., 2003; among others). The BET surface area may be some order of magnitude higher than the reactive surface area (e.g., Helgeson et al., 1984; White Art and Peterson Maria, 1990; Lütte et al., 1999).

Additionally, the atomic force microscopy (AFM) has been also used to determine the reactive surface area of minerals. This method allows to characterize edge sites, which react preferentially compared to the basal planes during dissolution of mineral (e.g. Ganor et al., 1995; Metz et al., 2005). It is found from the literature review that the AFM method is more appropriate than the BET to measure the reactive surface area of clay minerals, especially for the swelling clay minerals such as smectite and vermiculite (Sanders et al., 2010). However, the application of this method to normalize the dissolution rate to the edge site surface area remains difficult because the depletion over time and the difference in reactivity of the edge sites. The edge sites generally depend on the pH and the presence of charge within interlayered structure. Moreover, the AFM method has several limitations when studying mineral dissolution under large environmental pH conditions. The literature review shows that there are limited data for the edge site surface area; these are mainly measured for the clay minerals (e.g. Rozalén et al., 2008; Sanders et al., 2010; Sayed Hassan et al., 2006; Tournassat et al., 2003).

Gautier et al. (2001) have reported that the use of geometric area may be better to estimate the dissolution rate of quartz. Since there are still limited data of the BET and edge site surface area for all primary minerals involved in the model; in the current study the geometric approach was used to systematically estimate the
Table 4

Kinetic constants of dissolution reaction of the primary minerals of COx claystone, at iron at 25 °C and 90 °C.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>$k_a$ (mol m$^{-2}$ year$^{-1}$)</th>
<th>$k_b$ (mol m$^{-2}$ year$^{-1}$)</th>
<th>pH$_a$</th>
<th>pH$_b$</th>
<th>$n_a$</th>
<th>$n_b$</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$E_b$ (kJ mol$^{-1}$)</th>
<th>$E_c$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>1.58E+7</td>
<td>4.88E+1</td>
<td>5.5</td>
<td>8.0</td>
<td>1.00</td>
<td>0</td>
<td>14.5</td>
<td>23.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Chamosite</td>
<td>1.58E-2</td>
<td>9.97E-6</td>
<td>6.29E-10</td>
<td>6.0</td>
<td>9.5</td>
<td>0.53</td>
<td>0.44</td>
<td>66.5</td>
<td>45</td>
</tr>
<tr>
<td>Dolomite</td>
<td>2.03E+4</td>
<td>9.31E-1</td>
<td>9.31E-10</td>
<td>8.7</td>
<td>11.0</td>
<td>0.50</td>
<td>0.82</td>
<td>36.1</td>
<td>52.2</td>
</tr>
<tr>
<td>Illite</td>
<td>6.29E-5</td>
<td>6.29E-8</td>
<td>3.15E-13</td>
<td>5.0</td>
<td>8.8</td>
<td>0.60</td>
<td>0.60</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>Microcline</td>
<td>2.75E-3</td>
<td>1.23E-3</td>
<td>1.99E-14</td>
<td>4.7</td>
<td>10.7</td>
<td>0.50</td>
<td>0.82</td>
<td>51.7</td>
<td>38</td>
</tr>
<tr>
<td>Schemesite</td>
<td>3.00E-4</td>
<td>5.23E-6</td>
<td>9.52E-10</td>
<td>5.3</td>
<td>9.4</td>
<td>0.34</td>
<td>0.40</td>
<td>23.6</td>
<td>35</td>
</tr>
<tr>
<td>Pyrite</td>
<td>9.52E-1</td>
<td>8.88E+2</td>
<td>8.88E+2</td>
<td>5.9</td>
<td>8.0</td>
<td>0.50</td>
<td>0.50</td>
<td>56.9</td>
<td>56.9</td>
</tr>
<tr>
<td>Quartz(alpha)</td>
<td>1.44E-4</td>
<td>1.44E-6</td>
<td>1.62E-9</td>
<td>4.0</td>
<td>5.9</td>
<td>0.50</td>
<td>0.50</td>
<td>99.2</td>
<td>90.1</td>
</tr>
<tr>
<td>Siderite</td>
<td>9.97E-1</td>
<td>9.97E-2</td>
<td>9.97E-2</td>
<td>6.0</td>
<td>8.0</td>
<td>0.50</td>
<td>0.47</td>
<td>61.0</td>
<td>48</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.34E-4</td>
<td>2.08E-6</td>
<td>2.81E-10</td>
<td>6.0</td>
<td>8.0</td>
<td>0.78</td>
<td>0.47</td>
<td>65.9</td>
<td>22.2</td>
</tr>
</tbody>
</table>

a These values are assessed by the authors.
c Lowson et al. (2005).
d Köhler et al. (2003).
f Brandt et al. (2003).
g Golubev et al. (2009).

Table 5

Diffusion coefficient, diffusion length, and rate constant of diffusion-controlled dissolution of several primary minerals of the COx claystone at 90 °C. $k_i$ is estimated from Eq. (4). $k_i^2$ is determined from the assumption $k_i^2 = D_i C_{eq}/i$. Due to the lack of diffusion data for minerals in water, the diffusion coefficient, $D_i$, is assumed to be the same for all four investigated minerals.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>$D_i$ (m$^2$ year$^{-1}$)</th>
<th>$\iota$ (µm)</th>
<th>$k_i^2$ (mol m$^{-2}$ year$^{-1}$ kg CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>9.75E-3</td>
<td>4.93</td>
<td>1.14E-6</td>
</tr>
<tr>
<td>Dolomite</td>
<td>9.75E-3</td>
<td>6.72</td>
<td>1.23E-16</td>
</tr>
<tr>
<td>Pyrite</td>
<td>9.75E-3</td>
<td>5.40</td>
<td>8.25E-52</td>
</tr>
<tr>
<td>Siderite</td>
<td>9.75E-3</td>
<td>5.90</td>
<td>6.19E-9</td>
</tr>
</tbody>
</table>


reactive surface area of the primary minerals. For doing so, we assumed that the particles of all primary minerals are spheres and the size of each mineral is the same. In general, in the same conditions the clay minerals always form much smaller grain size than other types of minerals such as carbonates, sulfates and oxides (Meunier, 2006). Thus, in this study the radius of clay minerals is assumed to be equal to 1 µm, and for all other minerals their radius are assumed to be 10 µm. This assumption allows estimation of the reactive surface as well as the diffusion length with respect to each primary mineral (Eq. (4)). Table 6 presents the reactive surface area of all primary minerals.

2.2.4. Modeling scenarios

In the geochemical modeling, the uncertainties identified are quite numerous. Among them, the parameterization of input data is generally considered as creating large uncertainty. The choice of the thermodynamic database used, the selection of the secondary mineral assemblage, the kinetic data associated with the dissolution and precipitation processes as well as the option to calculate the formation of secondary mineral influence the output predictions. In the context of geological disposal, relevant to the iron–clay interaction, the uncertainties regarding the previous possible causes are reported and discussed in several modeling studies (e.g. Savage et al., 2007, 2011; Wersin and Birgersson, 2014). In addition, the reactive surface area also plays a significant role on the modeling results (Ngo et al., 2014).

There is still a challenge in terms of determining the overall equation of dissolution for all primary minerals. Furthermore, the estimates of dissolution rate constant and reactive surface area of primary minerals can also cause difficulties in application of the geochemical modeling tools. Therefore, the primordial objective of this modeling work is not an attempt to reproduce exactly the measured aqueous species of the chosen experiments. It is rather to evaluate whether the KINDIS code can model general reaction pathways of the experiments in the given experimental conditions. Moreover, in the framework of this modeling attempt, the sensitivity of the system behavior to the corrosion rate of Fe and dissolution rate constant of quartz and illite will also be evaluated. The choice of the previous kinetic data to investigate was based on the preliminary modeling, which showed their significant impact on the modeling results. The uncertainties related to other kinetic data such as reactive surface area and precipitation rate were not the focus in the present modeling work.

The following model cases were developed:

- Reference case: this reference case used the input data presented in Tables 1–6. The modeling results are compared with the measured data to evaluate whether the model is able to predict the dominant mechanisms, the evolution and general reaction-paths of the system.
- Case I: in this case, the only difference came from the corrosion rate of metallic Fe in the system. It changes from 1.41 mol m$^{-2}$ year$^{-1}$ to 2.82 mol m$^{-2}$ year$^{-1}$ (equivalent to 20 µm year$^{-1}$, see Section 2.1.2) to evaluate how the corrosion rate of Fe influences the mineralogical and chemical evolutions of the system.
Case 2: in this case, the dissolution rate constant of quartz is decreased by one order of magnitude compared to its initial value in the reference case.

Case 3: the dissolution rate constant of illite is increased by one order of magnitude compared to its initial value in the reference case.

3. Results

3.1. Reference case

3.1.1. Evolution of pH and total carbon

Fig. 2a and b present the comparison of simulation and measurement of pH and total carbon in the aqueous solution over time. The initial value of Eh as well as its evolution during the experiment was not measured but the predicted Eh versus time is also included in Fig. 2a. It is found that the measured pH increased slightly until 25 days and then decreased a little. For this modeling work, two different tests were performed: (test 1) CO\textsubscript{2} partial pressure in the system is not fixed but recalculated by the model at theoretical equilibrium, and (test 2) CO\textsubscript{2} partial pressure is fixed at its initial value (i.e. infinite CO\textsubscript{2} reservoir). Globally, the measured pH values are between the two calculated lines corresponding to the sensitivity tests. The largest discrepancy between the calculated and measured pH locates at the end of the experiment but the difference is less than 0.5 units of pH.

In the current system, the measured pH stabilized around 7. The analysis of simulation results made clear that the evolution of pH in the experimental system is strongly related to the evolution of carbonate species. The buffering of pH in the current system is ascribed to the quick equilibrium with calcite, which is a dominant mineral in this case. This will be demonstrated in Section 4.1. Fig. 2b further confirms the dependence of pH with respect to total dissolved carbon in the aqueous solution. The measured values of total carbon decreased slightly at the beginning of the experiment and then increased. It is similar to the evolution of pH in terms of the general trend, the experimental data of total carbon also locate in the center of two predicted lines corresponding to tests. Overall, the modeling results of pH and total carbon in the aqueous solution compare well with the measured values.

3.1.2. Corrosion of iron in the system

The simulated corrosion of metallic Fe is presented in Fig. 3. When the corrosion rate of 1.41 mol m\textsuperscript{-2} year\textsuperscript{-1} is used in the model, solid Fe is totally corroded after 56 days. We should note again that the solid composition involving metallic Fe was analyzed only at 2, 4, and 90 days of the LG experiment, and hence no finer data about the quantity of solid Fe were available to determine the end of the iron corrosion stage in the experimental system. The experimental data only indicate that the metallic Fe had totally disappeared by the end of the experiment (experiment A in Bourdelle et al., 2014).
3.1.3. Dissolution of primary minerals

Fig. 4 presents the calculated dissolution of three main primary minerals that dissolved in the system. The dissolution reaction of the primary minerals is presented in Table 7. The dissolved amount of other minerals such as chamosite, dolomite, pyrite, siderite, and kaolinite is not significant. The analysis of mineral balance indicated that the dissolution quantities of quartz, illite, and smectite are respectively 30.1%, 0.3%, and 0.8% compared to their initial amounts. It can be seen from Fig. 4 that the dissolution of quartz ended after 56 days, which corresponds to the end of corrosion stage. This event is related to the precipitation of greenalite, which is the main secondary mineral of interactions between iron and clay (see next section).

3.1.4. Precipitation of secondary minerals in the system

The experimental results showed that there is a quick formation of Fe-rich phyllosilicates which then can convert to odenite-greenalite. In addition, it is also reported in Bourdelle et al. (2014) that saponite is precipitated as well, but the experimental method could not confirm whether this is Fe-rich saponite. Surprisingly, the magnetite is not precipitated in the experimental system. In the past, with the quite similar experimental conditions, Schlegel et al. (2010) reported the formation of chukanovite. The formation of chukanovite in their system is favored by the high CO₂ partial pressure.

The formation of secondary minerals is presented in Fig. 5. The model predicted that three main secondary minerals are greenalite, chukanovite and saponite-Ca. Calcite which is a dominant primary mineral also precipitated. Interestingly, the modeling results showed that there is no formation of magnetite in the system as observed in the experiments. This is a very good agreement between the model and the experiments.

It can be seen from Fig. 5 that there is an important change in behavior of the three newly-formed minerals after 56 days when the corrosion of solid Fe is finished. For example, there is no more precipitation of greenalite after 56 days and this mineral remains stable. Additionally, chukanovite is not formed after this moment and this mineral is then quickly redissolved. It means that the end of iron corrosion leads to the end of Fe²⁺ source in the solution and hence causes the end of the precipitation of greenalite and chukanovite. In contrast, saponite-Ca starts to appear after 56 days.

Table 7

Dissolution of the primary minerals.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Structural formula</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>CaCO₃ = Ca²⁺ + CO₃⁻</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>FeS₂ + 8H₂O = Fe²⁺ + 2SO₄⁻ + 16H⁺ + 14e⁻</td>
</tr>
<tr>
<td>Illite</td>
<td>K₀.₈₃₄Ca₀.₀⁰₈Mg₀.₂₅Al₂.₃₅Si₃.₄O₁₀(OH)₂</td>
<td>Illite + 0.6H₂O + 8.4H⁺ = 0.₈₃₄K⁺ + 0.₀⁰₈Ca²⁺ + 0.₂₅Mg²⁺ + 2.₃₅Al³⁺ + 3.₄₄SiO₄⁻</td>
</tr>
<tr>
<td>Smectite</td>
<td>[Ca₀.₃₄₂Na₀.₃₄₂K₀.₀₂₄][Si₇.₃₅₈Al₀.₂₆₂]</td>
<td>Smectite + 2.₉₅₂H₂O + 7.₄₄H⁺ = 0.₀₂₄K⁺ + 0.₂₁₄Mg²⁺ + 0.₄₂₄Ca³⁺ + 0.₃₄₂Na⁺ + 1.₈₆Al⁺³ + 3.₇₃₇H₂SiO₄ + 0.₁₇₃Fe²⁺</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>FeCO₃ = Fe²⁺ + CO₃⁻ + 0.₃₉₂H⁺</td>
</tr>
<tr>
<td>Microcline</td>
<td>K(AlSi₃)O₈</td>
<td>K(AlSi₃)O₈ + 4H₂O = 4H⁺ + K⁺ + Al⁺³ + 3H₂SiO₄</td>
</tr>
<tr>
<td>Quartz(alpha)</td>
<td>SiO₂</td>
<td>SiO₂ + 2H₂O = H₂SiO₄</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>CaMg(CO₃)₂ = Ca²⁺ + Mg²⁺ + CO₃⁻</td>
</tr>
<tr>
<td>Chamosite</td>
<td>Fe₅Al(AlSi₃)O₁₀( OH)₆</td>
<td>Chamosite + 16H⁺ = 2Al³⁺ + 5Fe²⁺ + 3H₂SiO₄ + 2H₂O</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₃</td>
<td>Al₂Si₂O₅(OH)₃ + 6H⁺ = 2Al³⁺ + 2H₂SiO₄ + H₂O</td>
</tr>
</tbody>
</table>

* The dissolution of illite and smectite corresponds to the formula after accounting for the initial quick exchange of Ca²⁺, K⁺, and Na⁺.
Fig. 6. Phase diagrams of quartz and different minerals that potentially precipitated at 90 °C in the experimental system: (a) when fixing log[pO2 (atm)] = -60, (b) when fixing log[\(\text{Mg}^{2+}/\text{Mg}^{2+}(\text{H}^+)] = 9. The red points are determined from the measured concentrations of Si, C_total, Ca^{2+}, and H^+. The green line is the equilibrium saturation of quartz at 90 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6 represents the activity diagrams of some potential minerals susceptible to precipitate in the system. In this figure, the red points are determined from the experimental data while the blue point lines are the output predictions of the model at different times. The first left point in these blue point lines corresponds to the first increment of the numerical calculations and hence it associates with the very low calculated concentrations of H_4SiO_4 in the system.

Fig. 6a presents the phase diagram of magnetite, greenalite, chukanovite, and siderite, which are considered as the main corrosion products, as a function of the pCO_2 and the activity of silica. Note that this diagram is established with the assumption that pO_2 in the system is constant. The formation of magnetite, greenalite, and chukanovite are written as follows:

\[
\text{Magnetite : } 2\text{Fe}^{3+} + \text{Fe}^{2+} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}^+ \\
\text{Greenalite : } 3\text{Fe}^{2+} + 2\text{H}_2\text{SiO}_4 + \text{H}_2\text{O} = \text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \\
\text{Chukanovite : } 2\text{Fe}^{2+} + \text{HCO}_3^- + 2\text{H}_2\text{O} = \text{Fe}_2(\text{CO}_3)(\text{OH})_2 + 3\text{H}^+ 
\]

Eqs. (6) and (7) indicate that the formation of greenalite is strongly related to the availability of Fe^{2+} and silicic acid while precipitation of chukanovite is closely related to the availability of Fe^{2+} as well, together with carbonate species in the system. The diagram in Fig. 6a reflects the fact that for a given concentration of Fe^{2+}, a high H_4SiO_4 concentration favors the formation of greenalite while the intermediate CO_2 partial pressures stabilize chukanovite, as is the case in the experimental study. This diagram shows that the system moves towards the stability domain of quartz, and that at the given experimental conditions in terms of silica and carbonate concentration the system almost reaches the greenalite-quartz boundary. This reaction pathway is supported by the experimental observations. As seen in Fig. 5a that, in these experiments, the evolution of H_4SiO_4 concentration and CO_2 partial pressure, which is presented by the red points in Fig. 6a, falls in the stability zone of greenalite, near the one of chukanovite, but far from the zone of magnetite. Furthermore, Fig. 6a also explains why chukanovite is initially formed in the simulation and then has tendency to dissolve when H_4SiO_4 concentration increases.

Fig. 6b shows the phase diagram for three other possible secondary minerals including saponite-Ca, clinochlore, and beidellite-Ca in the Ca-SiO_2 system. The precipitation of saponite-Ca is expressed as:

\[
0.34\text{Al}^{3+} + 0.17\text{Ca}^{2+} + 3\text{Mg}^{2+} + 3.66\text{H}_2\text{SiO}_4 = \text{Ca}_{17}\text{Mg}_3\text{Al}_{26}\text{Si}_{60}\text{O}_{110}(\text{OH})_2 + 7.36\text{H}^+ + 2.64\text{H}_2\text{O} 
\]

It is found from Fig. 6b that the evolution of H_4SiO_4 activity and Ca^{2+} activity in the experiments, which are presented by the red points, fall in the stability zone of saponite-Ca, and at the equilibrium with quartz. This evolution provides a qualitative evidence for the potential precipitation of saponite-Ca in the experiment. Both Figs. 6a and b indicate the close match of the predicted and experimental evolution of H_4SiO_4 at almost constant CO_2 pressure and Ca^{2+} activity. These activity diagrams suggest that greenalite and saponite-Ca are expected to be the main secondary minerals and that magnetite and chukanovite are probably not stable in the system and may not form. The agreement between the model and experimental observation for the mineralogical transformation will be discussed in detail in Section 4.2.

3.1.5. Evolution of some aqueous species

The evolution of some important elements for clay phases such as Fe, Si, K^+, and Ca^{2+} is presented in Fig. 7. It can be seen that the measured values at the end of the pH experiment, i.e. red points in Fig. 7, are quite different from the corresponding ones of the LG experiment. In addition, the measured values at the end of the LG experiment also systematically departed from the earlier measured ones in this experiment. This systematic departure is attributed to the disturbing and/or contamination of the sample at the end of the LG experiment. However, the total concentration of ions in the aqueous solution, the experimental data indicate that their concentration remains around 4 ppb and the model predicted reasonably this low concentration. With respect to the Si concentration in the system, the simulated values also match quite well the measurements (around 400 ppb). In these experiments, the main source of Si in the aqueous solution mainly comes from the dissolution of quartz (illite and smectite are secondary sources). The dramatic increase of the calculated Si concentration after 56 days relates to the end of formation of greenalite in the system. The Si concentration reaches about 0.85 mmol kg_\text{sol} that is equivalent to the equilibrium value of quartz at 90 °C. Overall, there is a reasonable agreement between the calculations and experimental measurements. However, the model did not particularly well predict the trends in the Fe, Si concentrations. This discrepancy partly reflects that there is uncertainty in input data and that the modeling approach used in this work could not predict all the mechanisms occurring in the experiments.

In the case of K^+ and Ca^{2+}, the predicted concentrations agree well with the measured ones. In this modeling work, the assignment of the initial cationic exchange of Ca^{2+} in the solution with K^+ and Na^+ for illite and smectite, as it obviously occurred in experiments, contributed to this good agreement.

3.2. Sensitivity cases

The sensitivity results with respect to three parameters are shown in Fig. 8. For each sensitivity case, three main types of output involving the corroded amount of metallic Fe, the amount of dissolved minerals, the evolution of pH in the aqueous solution, and the formation of secondary minerals are selected. Furthermore, to have a comparable view with the reference case, its corresponding results.
were also included in Fig. 8. It is important to note that in all sensitivity tests, the CO₂ partial pressure is not imposed in the system during the simulation.

3.2.1. Case 1: increased corrosion rate

When the corrosion rate is equal to 20 µm/year, the Fe corrosion phase is finished after about 28 days (red line in Fig. 8a). The higher corrosion rate of Fe leads to a higher increase of pH (red line, Fig. 8b). When the corrosion is completed, pH in the system decreased and reached the same level as in the reference case. It can be seen from Fig. 8c that in this case magnetite has also precipitated. Three other secondary minerals involving greenalite, chukanovite, and saponite-Ca are formed as in the reference case. Regarding the two newly-formed minerals, greenalite and chukanovite, their behavior is similar to the reference case, i.e. after the end of the iron corrosion, greenalite does not precipitate anymore, and chukanovite is quickly redissolved.
3.2.2. Case 2: decreased $k_d$ of quartz by one order of magnitude

The relative dissolution amount of quartz, the evolution of pH in the aqueous solution, and the formation of secondary minerals are presented in Fig. 8d, e, and f, respectively. At the end of the simulation, the dissolution amount of quartz is 9% compared to 30% in the reference case. The simulated pH in this case is slightly higher compared to the reference case and it remains constant at about 7.5. The four secondary minerals precipitated in the system are magnetite, greenalite, chukanovite, and saponite-Ca. Magnetite is even more dominant than greenalite during the corrosion phase. Chukanovite remains stable until the end of the simulation. The quantitative estimation of the dissolved iron being taken by the secondary minerals showed that magnetite accounted for 65% of the dissolved iron, compared to 30% for greenalite and 5% for chukanovite. Fig. 8f further shows that the behavior of secondary minerals is closely related to the dissolution of quartz in the system, which releases $H_4SiO_4$ in the aqueous solution. In this case the corrosion rate is the same like the reference case but the lower dissolution rate of quartz decreases the availability of silica and then limits the formation of greenalite. As a consequence, this favors the formation of magnetite and chukanovite.

3.2.3. Case 3: increased $k_d$ of illite by one order of magnitude

For this case, the corresponding results with respect to the dissolution quantity of illite, the evolution of pH, the precipitation of secondary minerals are shown in Fig. 8g, h, and i, respectively. The results show that when the dissolution rate constant of illite increases one order of magnitude, the relative dissolved quantity increases significantly from 0.5% in the reference case to 15.1% in the case 3, and the pH in the solution increases accordingly. Here, the evolution of pH shows a clear difference compared to the reference case, especially in the second part of the simulation where the dissolution of illite becomes significant (Fig. 8h). For example, the predicted pH reaches about 8.5 (instead of 7.5 in the reference case) and then decreases slightly after the end of iron corrosion. Three secondary minerals involving greenalite, chukanovite, and saponite-Ca are formed in the system. Greenalite shows a similar behavior compared to the reference case: its formation ends at the end of iron corrosion. Moreover, saponite-Ca precipitated after the redissolution of chukanovite, but this phase transition moment occurred earlier compared to the reference case. This can be explained by the fact that the increase in dissolution rate of illite increases the $H_4SiO_4$ concentration in the aqueous solution, which favors the formation of saponite-Ca as revealed in Fig. 6b. Note that in this case, the dissolution amount of quartz remained 28.5% compared to 30.0% in the reference case.

4. Discussion

4.1. Evolution of pH and total carbon in the aqueous solution

It can be seen that pH in the aqueous solution stabilized around 7.0 in the reference case. When the corrosion rate increases, pH increases only about 0.3 units (case 1 in the sensitivity). The sensitivity case 3 indicates that the pH in the system can reach a value of about 8.5 when the dissolution constant of illite increases by one order of magnitude. The saturation index of calcite, dolomite, chukanovite, and siderite in reference case is presented in Fig. 9. It is particularly interesting to observe that the experimental concentrations are found to be very close to the equilibrium with calcite along the experiment. Siderite is always under saturated and thereby can not cause any perturbation to the other carbonates. In these specific experiments, the stability of measured pH was probably controlled by carbonates in the system. This result was not obvious before being able to experimentally measure in situ pH.

In the reference case, the calculated value of the $CO_2$ partial pressure remained close to its initial value. It can be concluded that calcite has remained close to equilibrium, without providing carbonate to the solution, limiting the formation of chukanovite.

4.2. Mineralogical transformations due to the interactions between iron and COx clay

As seen earlier, the model could satisfactorily reproduce the mineralogical transformations observed in the experiments by using the equilibrium assumption for mineral precipitation, especially for the formation of greenalite. Precipitation of this typical Fe-rich silicate is favored by the excess of Fe$^{2+}$ released from the corrosion process and the high SiO$_2$ concentration, which mainly comes from the quartz dissolution in this case. The very rapid formation of greenalite probably results from the equilibrium assumption used for the secondary minerals.

In the reference case, the model predicted that there is no formation of magnetite, which is in good agreement with the experimental observations. On the opposite, many studies in the literature have reported the formation of magnetite and Fe-rich silicates as the main products of the corrosion process; these include the experimental investigations (e.g., de Combarieu et al., 2007; Mosser-Ruck et al., 2010; Rivard et al., 2013a,b; Schlegel et al., 2008, 2010; Lanson et al., 2012) and modeling works (e.g., Bildstein et al., 2006; de Combarieu et al., 2007; Wilson et al., 2006b). It is commonly found from these previous studies that pH in the system was significantly increased and might reach around 10–11 because of the iron corrosion. It is important to note that these studies were performed in the reducing conditions which correspond to anoxic corrosion stage of the nuclear waste repository.

However, the absence of the magnetite precipitation can be found in some recent studies that have been carried out in the oxic conditions (Gaudin et al., 2009, 2013). These in situ investigations of the interactions between iron and clay in the initial corrosion stage reported the formation of goethite and siderite, rather than the formation of magnetite. The presence of oxygen together with the high CO$_2$ partial pressure are responsible for these preferentially newly formed minerals. According to the pH-Eh diagram obtained from the thermodynamic modeling by Gaudin et al. (2013), the high pH (>7.5) and the oxidizing conditions could favor the formation of magnetite. The similar conclusion was also demonstrated in the pH-Eh diagram by Bourdelle et al. (2014) for the
absence of magnetite formation in their experiment, which was shown as evidence by the degassing of H₂, the anoxic conditions and the very low negative Eh value. In the experiments modeled in this present paper, pH is buffered at around the neutral value by the excess of CO₂ and the precipitation of Fe-rich phyllosilicates (Bourdelle et al., 2014). In addition, it is found that Fe²⁺ concentrations are maintained at low levels and Eh at the low negative value. The released Fe²⁺ is believed to be immediately incorporated into the newly-formed Fe-rich phyllosilicates (e.g., greenalite). Therefore, these could explain why magnetite is not precipitated in the current study.

Chukanovite is also initially formed in the simulations but this mineral is redissolved later because of the driving force of the greenalite precipitation. Experimentally, the behavior of chukanovite closely relates to the carbonate species in the aqueous solution and to a close interface of iron/COx claystone (Schlegel et al., 2010, 2012). Hypotheses can be made that either strong iron gradient in solution is needed or iron surface may play a role in the precipitation, or both. In the current modeling work, the predicted early and quick precipitation of chukanovite reflects broadly the equilibrium assumption for this mineral precipitation.

From these observations and the behavior of carbonates, it can be proposed that the equilibrium of calcite in the system gives limited pathways to iron–claystone transformations: when enough silica is available (reference case and sensitivity case 3) greenalite forms. When the corrosion rate is high enough or when less silica is provided to the solution, a mixture of greenalite with magnetite precipitates (sensitivity cases 1 and 2). Chukanovite precipitation is not a driving force strong enough to destabilize calcite.

Note again that up to date there is only thermodynamic data available for chukanovite at 25 °C. Therefore, the equilibrium constant at 90 °C for this mineral was extrapolated from its data at 25 °C and the trend with temperature of the thermodynamic data of malachite. As a consequence, there is surely uncertainty in the thermodynamic data used in the model for chukanovite.

4.3. Influence of input kinetic data

It can be seen from the three sensitivity cases that the corrosion rate and dissolution rates of quartz and illite may play a significant role on the evolution of pH and the formation of secondary minerals. The lesson to learn from this modeling work is that a careful attention should be paid to the input kinetic data of the dominant and important minerals such as quartz and illite and the corrosion rate used in the model because they can control the outcome of the model compared to experimental observations.

4.4. Limitations of the work and future study

As seen earlier, the mean corrosion rate used in the model is deduced from experimental evolution of the H₂ partial pressures. We assume that this rate is constant during the corrosion process. It is surely not the case as iron is brought to the system as powder which dissolves faster at the beginning and because no passivation is taken into account. Even if in the context of geological disposal the modelers generally assume that the corrosion rate of iron is constant (e.g., Marty et al., 2010; Montes-H et al., 2005; de Combarieu et al., 2007), a better model for iron corrosion is needed to produce more reliable iron flux in the geochemical system.

Recently, a sophisticated model for corrosion, called Calipso, allowing a better description of iron corrosion at various conditions has been developed (Bataillon et al., 2010, 2012; Martin and Bataillon, 2012). The coupling of this model with the KINDIS code is in progress. It is expected to give a better description of the evolution of the corrosion processes. In this modeling work, the KINDIS code has demonstrated its performance in modeling the interactions of iron, COx clay, and water at the given conditions.

5. Conclusions

Two in situ batch experiments investigating the interactions between iron, COx claystone, and water are modeled by the KINDIS code. These experiments consist of iron and COx claystone powder with water at weight ratios of 10 and 0.1 for water/clay and iron/clay, respectively. Both experiments were carried out at a constant temperature of 90 °C for 90 days. Modeling of these two experiments is based on the assumptions that the corrosion rate is constant over time, the precipitation of possible secondary minerals occurs at equilibrium and the dissolution of primary minerals is kinetic. The dissolution process of mineral is treated by the surface-controlled and diffusion-controlled reactions.

The evolution of pH in the aqueous solution stabilizing at a value around 7 is believed to relate to the carbonates behavior. The measured pH and total carbon settles between the two predicted lines corresponding to two simulations in which the CO₂ pressure is fixed or freely varied. Overall, there is a good agreement between the simulated and measured pH and total carbon concentration in solution. Furthermore, the modeling results indicate that calcite reaches quickly equilibrium state as observed in the experiments. The calculated concentrations of some aqueous species such as Fe, Si, K+, and Ca²⁺ were well in agreement with the experimental observations. In addition, magnetite is not formed in the reference case, in agreement with the experimental data, although this mineral is commonly reported as the main product of the corrosion process. To be formed and stable, magnetite needs an excess in iron, either from a high corrosion rate or a low activity of silica and/or carbonate in solution, and an alkaline medium. The agreement between the model and experimental observations is supported by activity diagrams, which present the evolution of H₄SiO₄ activity and CO₂ pressure or Ca²⁺ activity.

The calculated concentrations of some aqueous species such as Fe, Si, K+, and Ca²⁺ compare reasonably well with the measurement although a quantitative assessment of these parameters was not the emphasis of this modeling work.

The analysis of three sensitivity cases made clear that the uncertainty in input kinetic data of iron, quartz, and illite plays an important role on the evolution of pH in the aqueous solution and formation of secondary minerals. These modeling results suggest that more experimental and modeling efforts in determining the kinetic data of such important minerals are necessary to investigate the interactions of metallic Fe with COx claystone. As introduced in Section 2.2.4 that the uncertainty related to the precipitation rate of secondary minerals and the evolution of mineral surface reactive are still major issues for the investigation of water/clay interaction. Therefore, a great attention should also be paid for these challenging aspects.

The current study has several limitations related to the input data of the corrosion rate and kinetic data. But the model could satisfactorily reproduce the observations by using the equilibrium approach for mineral precipitation, especially for the formation of the typical Fe–rich silicates such as greenalite and the absence of magnetite. The accuracy in predicting the corrosion products is important in the context of geological disposal because this is associated with the repository safety assessment. The comparison
of these modeling results with the experimental data has proven to be helpful in understanding the processes at the interface between clay and iron, the controlling mechanism and parameters of the processes. To further confirm the robustness of the modeling, a better coupling between geochemistry, corrosion, and transport phenomena has to be tested and assessed. Our understanding of clay–iron interactions could be improved by ongoing laboratory experiments and geochemical modeling of these experiments, with upscaling to repository scale systems.

Acknowledgements

We are grateful to the experimental team, Régine Mosser-Ruck, Michel Cathelineau, Frank Bourdelle, Laurent Truche, Isabella Pignatelli, Catherine Lorgeoux, Christophe Roszypal, in the GéoResources laboratory, Université de Lorraine, for providing the experimental data. We would also like to thank the Agence nationale pour la gestion des déchets radioactifs (Andra) for the financial support of this work. We warmly thank Dr. James Wilson and the anonymous reviewer and associate editor for their very helpful and constructive comments.

References

Clément, A., Fritz, B., 2006. Theoretical and experimental evaluation of the role of iron in the 

...


