Applied Geochemistry 53 (2015) 13-26

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

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

ARTICLE INFO

Article history: Available online 9 December 2014 Editorial handling by M. Kersten

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 power 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 H_4SiO_4 activity and CO_2 partial pressure or Ca^{2+} 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

* Corresponding author. Tel.: +33 (0)368 850 472.

E-mail addresses: vvngo@unistra.fr, vanvietngo@yahoo.com (V.V. Ngo).

http://dx.doi.org/10.1016/j.apgeochem.2014.12.003 0883-2927/© 2014 Elsevier Ltd. All rights reserved. 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 clav 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 Ferich silicates as the main corrosion products. Moreover, 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 mineralogical transformations of the aqueous and solid phases (e.g., Rivard et al., 2013a,b; Schlegel et al., 2008, 2010; Jodin-Caumon et al., 2010; Pignatelli et al., 2013; Wilson et al., 2006a).

In the literature, there are, however, limited modeling studies about the interactions between iron and clay materials (Bildstein et al., 2006; de Combarieu et al., 2007; Montes-H et al., 2005; Savage et al., 2010; Wilson et al., 2006b). Up to date, to our knowledge, there is even only one published modeling study undertaken by de Combarieu et al. (2007) about the interactions involving COx claystone and iron at the laboratory scale. Therefore, additional studies about this aspect would be useful since a thorough understanding of potential evolution and mechanism of the interactions between such materials via the modeling tools is crucial to underpin the Andra concept of radioactive waste confinement.

Kinetic modeling requires a dissolution equation for each primary mineral. The dissolution of primary minerals is one of the most important processes that control the evolution of the system when investigating the interactions of clay and water. The dissolution rate of a mineral depends on many factors. These include the temperature of the system, the surface area available for dissolution, the solution composition (in particular pH), and the deviation from reaction equilibrium. Several formulations with respect to the mineral dissolution and precipitation have been proposed in the literature (e.g., Arvidson and Luttge, 2010; Beig and Lüttge, 2006; Burch et al., 1993; Lasaga et al., 1994). The formulation developed by Lasaga et al. (1994) is widely applied and is expressed as follows:

$$r_d = k_d e^{-E_a/RT} S_i g(I) \prod_a \alpha_i^{ni} f(\Delta G) \tag{1}$$

where k_d is the dissolution rate constant, S_i is the reactive surface area of mineral *i*, E_a and ΔG are the apparent activation energy and the Gibbs free energy of the overall reaction, α_i and n_i are the activity of the *i*th species involved in the reaction mechanism and the reaction order with respect to this species, g(I) is a function of ionic strength, $f(\Delta G)$ is a function of the Gibbs free energy.

The formulation of the function $f(\Delta G)$ is generally based on the Transition State Theory (TST), which allows to express it by the linear relationship, $f(\Delta G) = (1 - \exp(\frac{\Delta G}{RT}))$. Depending on the types of

minerals and experimental conditions, the dissolution mechanism is more or less complex and may be very different. There is still a debate in the scientific community about the form of function $f(\Delta G)$ (e.g., Arvidson and Luttge, 2010; Daval et al., 2010; Hellmann and Tisserand, 2006; Schott et al., 2009, 2012). Some authors accept that there is a linear relationship between the mineral dissolution rate and ΔG while the others consider that it must be a non-linear dependence between them, especially at near equilibrium conditions.

The geochemical modeling tools being currently developed in our laboratory implement the rate law of mineral dissolution based on the TST. It is, thus, essential to assess their performance in reproducing dissolution–precipitation experiments. For this practical application with respect to the interactions of COx claystone and iron, we face some issues related to a large mineralogical variability of the clays used in the model 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 avoid any fluctuation. At the end of this experiment, different phases were analyzed. The second autoclave was used to perform the so-called "LG experiment", in which the solid and aqueous phases were sampled at different successive times to determine the evolution 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.



Fig. 1. Schematic view of the experiments that investigate the interactions between iron, COx claystone, and water at 90 $^\circ\text{C}.$

2.1.2. Summary of the experimental results

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 H_2 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 are based on the assumptions that corrosion of iron occurs at constant rate (1.41 mol m⁻² year⁻¹, equivalent to 10 μ m 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; Palandri and Kharaka, 2004):

$$R_{i}^{S} = S_{i} \left(1 - \frac{Q_{i}}{K_{i}} \right) \begin{bmatrix} k_{25}^{Acid} \exp\left[\frac{-E_{a}^{Acid}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \alpha_{Acid}^{n_{Acid}} \\ + k_{25}^{Neutral} \exp\left[\frac{-E_{a}^{Neutral}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \\ + k_{25}^{Base} \exp\left[\frac{-E_{a}^{Base}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_{Base}^{n_{Base}} \end{bmatrix}$$
(2)

where R_i^S (mol year⁻¹ kg_{H2O}⁻¹) is the dissolution rate controlled by surface reaction; S_i (m² kg_{H2O}⁻¹) is the surface area; for a given mineral i; Q_i is the activity product; K_i is the thermodynamic equilibrium constant at the given temperature; k_{25}^{Acid} , $k_{25}^{Neutral}$, k_{25}^{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; E_a^{Acid} , $E_a^{Neutral}$, E_a^{Base} (J mol⁻¹) are the activation energies with respect to the acid, neutral, and basic zones, respectively; n_{Acid} and n_{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.

2.2.1.2. Diffusion-controlled reaction. The description of the mineral dissolution controlled by diffusion transport is based on Fick's law. It is expressed as follows:

$$R_i^D = -\frac{D_i S_i}{\varepsilon_i} \left(C_S^i - C_B^i \right) = -\frac{D_i S_i C_{eq}^i}{\varepsilon_i} \left(\frac{C_S^i}{C_{eq}^i} - \frac{C_B^i}{C_{eq}^i} \right) = -k_i^D S_i \left(\frac{C_S^i}{C_{eq}^i} - \frac{C_B^i}{C_{eq}^i} \right)$$
(3)

where R_i^D (mol year⁻¹ kg_{H2O}⁻¹) is the dissolution rate controlled by diffusion; D_i (m² year⁻¹) is the coefficient of diffusion in water, ε_i (m) is the thickness of the diffusional boundary layer, C_s^i and C_B^i (mol kg_{H2O}⁻¹) are the detached ion concentration at the mineral surface and in the bulk solution, respectively; C_{eq}^i (mol kg_{H2O}⁻¹) is the saturation concentration at equilibrium, $k_i^D = D_i C_{eq} / \varepsilon_i$ (mol m year⁻¹ kg_{H2O}⁻¹) 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):

$$\varepsilon_i = 5.74 (r_i)^{0.145} (\Delta \rho_i)^{-0.285} \tag{4}$$

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.

2.2.2. Initial conditions

2.2.2.1. 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

Table 1

Minerals	Structural formula	Mol of minerals (mol kg_{H2O}^{-1})	Molar volume (cm ³ mol ⁻¹)	LogK _{90 °C} (−)
Calcite	CaCO ₃	0.223	36.934	-9.24
Chamosite	Fe ₅ Al(AlSi ₃)O ₁₀ (OH) ₈	0.003	213.42	-3.47
Dolomite	$CaMg(CO_3)_2$	0.023	64.12	-19.07
Illite ^a	K _{0.834} Ca _{0.008} Mg _{0.25} Al _{2.35} Si _{3.4} O ₁₀ (OH) ₂	0.083	140.25	-38.16
Microcline	K(AlSi ₃)O ₈	0.010	108.69	-19.39
Smectite ^a	[Ca _{0.042} Na _{0.342} K _{0.024}][(Si _{3.738} Al _{0.262}]	0.021	134.92	-33.36
	[Al _{1.598} Fe _{0.208} Mg _{0.214}]O ₁₀ (OH) ₂			
Pyrite	Fe ^{II} S ₂	0.008	23.94	-57.34
Quartz(alpha)	SiO ₂	0.395	22.69	-3.07
Siderite	FeCO ₃	0.012	29.38	-11.43
Kaolinite	$Al_2Si_2O_5(OH)_4$	0.008	99.34	-34.19

Minoralogical composition of the COV of	laystone and iron and	thormodynamic	constant at 00 °C
Mineralogical composition of the COX C	laystone and fron and	unermouynamic	constant at 90 °C.

^a The structural formula of illite and smectite correspond to the formula after accounting for the quick initial exchange of Ca²⁺, K⁺, and Na⁺.

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 Ca²⁺, K⁺ and Na⁺ revealed that Ca²⁺ concentration is decreased by 1.4 mmol $kg_{\rm H2O}^{-1}$ and the sum of the concentration of K^+ and Na^+ is increased by 2.8 mmol kg⁻¹_{H2O} 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 Ca²⁺, K⁺ and Na⁺ is updated by using a simple balance approach where 1.4 mmol kg_{H2O}^{-1} of Ca^{2+} from the solution is added to illite and smectite and 1.4 mmol kg_{H20}^{-1} 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 the pH experiment. The initial Eh value is taken from the study conducted by De Combarieu et al. (2007) who also investigated the interactions of COx clay, iron, and water at 90 °C. Initial concentrations of other elements such as Fe, Mg, Si, S, Sr, Al are assumed to be very low in the initial solution and assumed to be equal to 10^{-9} mol kg⁻¹_{H20}.

Table 2

pH, Eh, CO ₂ pressure, and chemical composition of the aqueous s	olution at 90 °C after
accounting for the initial quick exchange of Ca ²⁺ , K ⁺ , and Na ⁺ .	

pH Eh Log[pCO ₂ (atm)]	7.01 430 1.85ª
Element	Concentration (mol kg_{H2O}^{-1})
Na	2.21E-2
К	1.40E-3
Ca	2.40E-3
Cl	2.83E-2
С	1.13E-3
S	1.0E-9
Mg	1.0E-9
Sr	1.0E-9
Fe	1.0E-9
Al	1.0E-9
Si	1.0E-9

^a The initial value of pCO₂ was determined by using the average value of total dissolved carbon and pH at the beginning of the experiment.

2.2.3. Input data

2.2.3.1. Thermodynamic data. The thermodynamic data at 90 °C are given in Tables 1 and 3 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 Ca²⁺ in the solution with Na⁺ and K⁺ of these minerals. For doing so, we assumed that 1.4 mmol kg_{H2O}^{-1} of K⁺ in illite and of Na⁺ in smectite are replaced by 1.4 mmol kg_{H20}^{-1} of Ca²⁺ 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, pCO₂ and iron/clay ratio (e.g. Bourdelle et al., 2014; Jodin-Caumon et al., 2012, 2010; Lantenois 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-phylloslicates (cronstedtite, berthierine, odinite, 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 beidelite-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., Rémazeilles and Refait, 2009; Saheb et al., 2010, 2012; Schlegel

Table 3

Thermodynamic constants at 90 °C of the potential secondary minerals tested in precipitation. These data were taken for the Thermoddem database and they are associated with the main species: H_4SiO_4 , CO_3^{2-} , $Al(OH)_{\bar{4}}$, Fe^{2+} , H^+ ... etc.

Minerals	Structural formula	Molar volume (cm ³ mol ⁻¹)	LogK _{90 °C} (−)
Magnetite	Fe ^{III} Fe ^{II} O ₄	44.52	3.59
Brucite	$Mg(OH)_2$	24.64	-11.30
Gibbsite	Al(OH) ₃	31.96	-13.14
Boehmite	AlO(OH)	19.54	-13.63
Halite	NaCl	27.02	1.59
Thenardite	Na ₂ SO ₄	53.34	-0.68
Anhydrite	CaSO ₄	45.94	-5.35
Gypsum	CaSO ₄ x2H ₂ O	74.31	-4.93
Amorphous silica	SiO ₂	29.00	-2.28
Albite(low)	NaAlSi ₃ O ₈	100.07	-17.55
Jarosite	$KFe_3^{II}(SO_4)_2(OH)_6$	153.90	20.32
Chrysotile	$Mg_3Si_2O_5(OH)_4$	108.50	25.78
Greenalite	Fe ^{II} Si ₂ O ₅ (OH) ₄	115.00	16.30
Illite-Fe ^{II}	$K_{0.85}Fe^{II}_{0.25}Al_{2.35}Si_{3.4}O_{10}(OH)_2$	140.53	-39.44
Vermiculite-Mg	Mg _{0.43} Mg _{3.00} Si _{3.14} Al _{0.86} O ₁₀ (OH) ₂	139.51	11.74
Vermiculite-Ca	Ca _{0.43} Mg _{3.00} Si _{3.14} Al _{0.86} O ₁₀ (OH) ₂	138.87	13.10
Nontronite-Ca	Ca _{0.17} Fe ^{II} _{1.67} Al _{0.67} Si _{3.66} O ₁₀ (OH) ₂	137.79	-1.21
Berthierine	(Fe ^{II} _{2.67} Al _{0.33})(Si _{1.34} Al _{0.66})O ₅ (OH) ₄	110.00	5.51
Beidellite-Ca	Ca _{0.17} Al _{2.34} Si _{3.66} O ₁₀ (OH) ₂	130.61	-42.27
Saponite-Fe ^{II} Ca	Ca _{0.17} Mg ₂ Fe ^{II} Al _{0.34} Si _{3.66} O ₁₀ (OH) ₂	139.96	12.60
Saponite-Fe ^{II} Mg	Mg _{0.17} Mg ₂ Fe ^{II} Al _{0.34} Si _{3.66} O ₁₀ (OH) ₂	140.21	12.67
Saponite-Fe ^{II} Na	Na _{0.34} Mg ₂ Fe ^{II} Al _{0.34} Si _{3.66} O ₁₀ (OH) ₂	140.82	12.41
Saponite	Ca _{0.17} Mg ₃ Al _{0.34} Si _{3.66} O ₁₀ (OH) ₂	138.84	13.94
Cronstedtite	Fe ^{II} ₃ SiAlO ₅ (OH) ₄	112.36	11.00
Chukanovite	$Fe_2^{II}(CO_3)(OH)_2$	55.94	-5.00^{a}

^a The thermodynamic constant of chukanovite at 90 °C was extrapolated from its value at 25 °C (Lee and Wilkin, 2010) and the variation with temperature of thermodynamic data of malachite.

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, $Cu_2(OH)_2CO_3$. 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 feed-back 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; Lüttge, 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; Lüttge 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, and iron at 25 °C and 90 °C.

	k_a	k _n	k_b	pHa	pH_{b}	n _a	n_b	E_a	En	E_b
Minerals		(mol m ⁻² year ⁻¹) 25 °C							$(kJ mol^{-1})$	
Calcite	1.58E+7 ^b	4.88E+1 ^b	4.88E+1 ^a	5.5 ^b	8.0 ^a	1.00 ^b	0 ^a	14.5 ^b	23.5 ^b	23.5 ^{a,b}
Chamosite	1.58E-2 ^c	9.97E-6 ^c	6.29E-10 ^c	6.0 ^c	9.5 [°]	0.53 ^c	-0.44 ^c	66.5 ^f	45 ^a	66.5 ^b
Dolomite	2.03E+4 ^b	9.31E-1 ^b	9.31E-1 ^a	8.7 ^b	11.0 ^a	0.50 ^b	0 ^a	36.1 ^b	52.2 ^b	52.2 ^a
Illite	6.29E-5 ^d	6.29E-8 ^d	3.15E-13 ^d	5.0 ^d	8.8 ^d	0.60 ^d	-0.60^{d}	46 ^{a,d,e}	14 ^{a,d,e}	67 ^{a,d,e}
Microcline	2.75E-3 ^b	1.23E-5 ^b	1.99E-14 ^b	4.7 ^b	10.7 ^b	0.50 ^b	-0.82^{b}	51.7 ^b	38 ^b	94.1 ^b
Smectite	3.30E-4 ^b	5.23E-6 ^b	9.52E-10 ^b	5.3 ^b	9.4 ^b	0.34 ^b	-0.40^{b}	23.6 ^b	35 ^b	58.9 ^b
Pyrite	9.52E-1 ^b	8.88E+2 ^b	8.88E+2 ^a	5.9 ^b	8.0 ^a	-0.50^{b}	0 ^a	56.9 ^b	56.9 ^b	56.9 ^{a,b}
Quartz(alpha)	$1.44E - 4^{a}$	$1.44E - 6^{b}$	1.62E-9 ^b	4.0 ^a	5.9 ^b	0.50 ^a	-0.50^{b}	99.2 ^{a,b}	90.1 ^b	108.4 ^b
Siderite	9.97E+1 ^e	9.97E-2 ^e	9.97E-2 ^e	6.0 ^a	8.0 ^a	0.50	0 ^a	61 ^g	48 ^g	48 ^g
Kaolinite	1.54E-4 ^b	$2.08E - 6^{b}$	2.81E-10 ^b	6.0 ^a	8.0 ^a	0.78 ^b	-0.47^{b}	65.9 ^b	22.2 ^b	17.9 ^b
		90 °C								
Calcite	4.50E+07	2.66E+02	2.66E+02	5.2ª	8.0 ^a	1.00 ^b	0 ^a			
Chamosite	1.92E+0	2.57E-04	7.66E-08	7.3 ^a	8.0	0.53 ^c	-0.44 ^c			
Dolomite	2.75E+05	4.04E+01	4.04E+01	7.7 ^a	11.0 ^a	0.50 ^b	0 ^a			
Illite	5.49E-04	1.29E-07	1.16E-11	6.0 ^a	6.7 ^d	0.60 ^d	-0.60^{d}			
Microcline	1.15E-01	1.91E-04	1.78E-11	5.6 ^a	8.6 ^a	0.50 ^b	-0.82^{b}			
Smectite	1.81E-03	6.55E-05	6.69E-08	4.2 ^a	7.5 ^ª	0.34 ^b	-0.40^{b}			
Pyrite	5.79E+01	5.40E+04	5.40E+04	5.9 ^a	8.0 ^a	-0.50^{b}	0 ^a			
Quartz(alpha)	1.95E-01	9.63E-04	4.05E-06	4.6 ^a	4.8+a	0.50 ^a	-0.50^{b}			
Siderite	8.16E+03	3.19E+00	3.19E+00	6.8 ^a	8.0 ^a	0.50	0 ^a			
Kaolinite	1.80E-02	1.03E-05	1.02E-09	4.2 ^a	8.5 ^a	0.78 ^b	-0.47^{b}			

^a These values are assessed by the authors.

^b Palandri and Kharaka (2004).

^c Lowson et al. (2005).

^d Köhler et al. (2003).

^e Tang and Martin (2011).

^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. ε_i is estimated from Eq. (4). K_i^D is determined from the assumption $k_i^D = D_i C_{eq} / \varepsilon_i$. 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.

Minerals	D_i^{a} (m ² year ⁻¹)	ε _i (μm)	k_i^D (mol m year ⁻¹ kg ⁻¹ _{H2O})
Calcite	9.75E–3	4.93	1.14E–6
Dolomite	9.75E–3	6.72	1.23E–16
Pyrite	9.75E–3	5.40	8.25E–55
Siderite	9.75E–3	5.90	6.19E–9

^a Madé (1991).

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 μ m, and for all other minerals their radius are assumed to be 10 μ m. 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 1:* 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 μ m year⁻¹, see Section 2.1.2) to evaluate how the corrosion rate of Fe influences the mineralogical and chemical evolutions of the system.

 Table 6

 Radius and reactive surface area (S_i) of the primary minerals and iron.

Minerals	Mass fraction in the COx claystone (%)	Density (g cm ⁻³)	Radius (µm)	$S_i (m^2 kg_{H2O}^{-1})$
Calcite	22.31	2.71	10	2.47
Chamosite	2.03	3.34	1	1.82
Dolomite	4.28	2.87	10	0.45
Illite	33.65	2.77	1	36.44
Microcline	2.91	2.56	10	0.34
Smectite	7.77	2.79	1	8.35
Pyrite	0.96	5.02	10	0.06
Quartz(alpha)	23.76	2.65	10	2.69
Siderite	1.37	3.94	10	0.10
Kaolinite	2.00	2.63	1	2.28
Iron	-	7.87	-	0.8

- *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) CO₂ partial pressure in the system is not fixed but recalculated by the model at theoretical equilibrium, and (test 2) CO₂ partial pressure is fixed at its initial value (i.e. infinite CO₂ 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 with respect to two 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 $1.41 \text{ mol m}^{-2} \text{ year}^{-1}$ 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



Fig. 2. (a) Evolution of pH and Eh in the aqueous solution. (b) Evolution of total dissolved carbon in the experimental system.



Fig. 3. Corrosion amount of metallic Fe over time.

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).



Fig. 4. Dissolution amount of primary minerals in the reference case.

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

Table 7				
Dissolution	reaction	of the	primary	minerals.



Fig. 5. Simulated concentrations of the secondary minerals precipitated in the experimental system. Calcite is a primary mineral but precipitated as well.

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 odenitegreenalite. 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 CO_2 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.

Minerals	Structural formula	Dissolution
Calcite	CaCO ₃	$CaCO_3 = Ca^{2+} + CO_3^{2-}$
Pyrite	Fe ^{II} S ₂	$Fe^{II}S_2 + 8H_2O = Fe^{2+} + 2SO_4^{} + 16H^+ + 14e^{}$
Illite ^a	K _{0.834} Ca _{0.008} Mg _{0.25} Al _{2.35} Si _{3.4} O ₁₀	Illite + $0.6H_2O$ + $8.4H^+$ = 0.834 K^+ + 0.008Ca^{2+} + 0.25Mg^{2+} + 2.35Al^{3+} + $3.4\text{H}_4\text{SiO}_4$
	(OH) ₂	
Smectite ^a	[Ca _{0.042} Na _{0.342} K _{0.024}][(Si _{3.738} Al _{0.262}]	Smectite + 2.952H ₂ O + 7.44H ⁺ = 0.024 K ⁺ + 0.214Mg ²⁺ + 0.042Ca ²⁺ + 0.342Na ⁺ + 1.86Al ³⁺ + 3.738H ₄ SiO ₄ + 0.173Fe ³⁺
	[Al _{1.598} Fe _{0.208} Mg _{0.214}]O ₁₀ (OH) ₂	+ 0.035Fe ²⁺
Siderite	FeCO ₃	$FeCO_3 = Fe^{2+} + CO_3^{2-} + 0.392H^+$
Microcline	K(AlSi ₃)O ₈	$K(AISi_3)O_8 + 4H_2O + 4H^+ = K^+ + AI^{3+} + 3H_4SIO_4$
Quartz(alpha)	SiO ₂	$SiO_2 + 2H_2O = H_4SiO_4$
Dolomite	$CaMg(CO_3)_2$	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + CO_3^{2-}$
Chamosite	$Fe_5Al(AlSi_3)O_{10}(OH)_8$	Chamosite + $16H^+ = 2AI^{3+} + 5Fe^{2+} + 3H_4SiO_4 + 2H_2O$
Kaolinite	$Al_2Si_2O_5(OH)_4$	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$

^a 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 $\log[pO_2 (atm)] = -60$, (b) when fixing $\log[a(Mg^{2+})/a^2(H^*)] = 9$. 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:

Magnetite : $2Fe^{3+} + Fe^{2+} + 4H_2O = Fe_3O_4 + 8H^+$ (5)

Greenalite : $3Fe^{2+} + 2H_4SiO_4 + H_2O = Fe_3Si_2O_5(OH)_4 + 6H^+$ (6)

Chukanovite : $2Fe^{2+} + HCO_3^- + 2H_2O = Fe_2(CO_3)(OH)_2 + 3H^+$ (7)

Eqs. (6) and (7) indicate that the formation of greenalite is strongly related to the availability of Fe²⁺ and silicic acid while precipitation of chukanovite is closely related to the availability of Fe²⁺ as well, together with carbonate species in the system. The diagram in Fig. 6a reflects the fact that for a given concentration of Fe²⁺, a high H₄SiO₄ concentration favors the formation of greenalite while the intermediate CO₂ 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 H₄SiO₄ concentration and CO₂ 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 again when H₄SiO₄ concentration increases.

Fig. 6b shows the phase diagram for three other possible secondary minerals including saponite-Ca, clinochlore, and beidellite-Ca in the Ca–SiO₂ system. The precipitation of saponite-Ca is expressed as:

$$\begin{split} 0.34Al^{3+} + 0.17Ca^{2+} + 3Mg^{2+} + 3.66H_4SiO_4 \\ = Ca_{0.17}Mg_3Al_{0.34}Si_{3.66}O_{10}(OH)_2 + 7.36H^+ + 2.64H_2O \end{split} \tag{8}$$

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 Ca²⁺ 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. Regarding 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⁻¹_{H20} 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



Fig. 7. Comparison between simulated and measured concentrations of dissolved Fe and Si, K⁺, Ca²⁺.



Fig. 8. Evolution of the system with respect to three sensitivity tests. For the case 1: (a) corrosion amount of metallic Fe, (b) variation of pH, (c) formation amount of secondary minerals. For the case 2: (d) dissolution amount of quartz, (e) variation of pH, (f) formation amount of secondary minerals. For the case 3: (g) dissolution amount of illite, (h) variation of pH, (i) formation amount of secondary minerals.

were also included in Fig. 8. It is important to note that in all sensitivity tests, the CO_2 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 $20 \ \mu m \ year^{-1}$, the Fe corrosion phase is finished after about 28 days (red¹ 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.

 $^{^{1}\,}$ For interpretation of color in Fig. 8, the reader is referred to the web version of this article.

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 H₄SiO₄ 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 H₄SiO₄ 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



Fig. 9. Simulated saturation index, log(Q/K), of four main carbonates versus time in the reference case. The red points show the estimated saturation index of calcite based on the measurement of total carbon in the experimental system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 satisfactory 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 SiO₂ 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 H_2 , 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 COx 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 H_2 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 CO_2 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 numerical simulations indicate that during interactions between iron and COx clay, greenalite, chukanovite, and saponite-Ca precipitate as the main secondary minerals. Moreover, the destabilization of some important primary minerals such as quartz, illite, and smectite are also revealed by the model. Both primary minerals dissolution and newly-formed phases are 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, Chistophe Roszypal, in the GéoRessources 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

- Arvidson, R.S., Luttge, A., 2010. Mineral dissolution kinetics as a function of distance from equilibrium – new experimental results. Chem. Geol. 269 (1–2), 79–88.
- Bataillon, C., Bouchon, F., Chainais-Hillairet, C., Desgranges, C., Hoarau, E., Martin, F., Perrin, S., Tupin, M., Talandier, J., 2010. Corrosion modelling of iron based alloy in nuclear waste repository. Electrochim. Acta 55 (15), 4451–4467.
- Bataillon, C., Bouchon, F., Chainais-Hillairet, C., Fuhrmann, J., Hoarau, E., Touzani, R., 2012. Numerical methods for the simulation of a corrosion model with moving oxide layer. J. Comput. Phys. 231 (18), 6213–6231.
- Beig, M.S., Lüttge, A., 2006. Albite dissolution kinetics as a function of distance from equilibrium: implications for natural feldspar weathering. Geochim. Cosmochim. Acta 70 (6), 1402–1420.
- Bildstein, O., Trotignon, L., Perronnet, M., Jullien, M., 2006. Modelling iron-clay interactions in deep geological disposal conditions. Phys. Chem. Earth 31 (10– 14), 618–625.
- Blanc, P., Lassin, A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., Gaucher, E.C., 2012. Thermoddem: a geochemical database focused on low temperature water/rock interactions and waste materials. Appl. Geochem. 27 (10), 2107– 2116.
- Bourdelle, F., Truche, L., Pignatelli, I., Mosser-Ruck, R., Lorgeoux, C., Roszypal, C., Michau, N., 2014. Iron-clay interactions under hydrothermal conditions: impact of specific surface area of metallic iron on reaction pathway. Chem. Geol. 381, 194–205.
- Brandt, F., Bosbach, D., Krawczyk-Barsch, E., Arnold, T., Bernhard, G., 2003. Chlorite dissolution in the acid ph-range: a combined microscopic and macroscopic approach. Geochim. Cosmochim. Acta 67 (8), 1451–1461.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309–319.
- Burch, T.E., Nagy, K.L., Lasaga, A.C., 1993. Free energy dependence of albite dissolution kinetics at 80 °C and pH 8.8. Chem. Geol. 105 (1–3), 137–162.
- Daval, D., Hellmann, R., Corvisier, J., Tisserand, D., Martinez, I., Guyot, F., 2010. Dissolution kinetics of diopside as a function of solution saturation state: macroscopic measurements and implications for modeling of geological storage of CO₂. Geochim. Cosmochim. Acta 74 (9), 2615–2633.
- de Combarieu, G., Barboux, P., Minet, Y., 2007. Iron corrosion in Callovo-Oxfordian argilite: from experiments to thermodynamic/kinetic modelling. Phys. Chem. Earth 32 (1–7), 346–358.
- Fritz, B., 1981. Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques. Thèse d'état de l'Université Louis Pasteur, Institut de Géologie.
- Ganor, J., Mogollón, J.L., Lasaga, A.C., 1995. The effect of pH on kaolinite dissolution rates and on activation energy. Geochim. Cosmochim. Acta 59 (6), 1037–1052.
- Gaudin, A., Gaboreau, S., Tinseau, E., Bartier, D., Petit, S., Grauby, O., Foct, F., Beaufort, D., 2009. Mineralogical reactions in the Tournemire argillite after in-situ interaction with steels. Appl. Clay Sci. 43 (2), 196–207. http://dx.doi.org/ 10.1016/j.clay.2008.08.007.
- Gaudin, A., Bartier, D., Truche, L., Tinseau, E., Foct, F., Dyja, V., Maillet, A., Beaufort, D., 2013. First corrosion stages in Tournemire claystone/steel interaction: in situ experiment and modelling approach. Appl. Clay Sci. 83–84, 457–468.
- Gautier, J.M., Oelkers, E.H., Schott, J., 2001. Are quartz dissolution rates proportional to B.E.T. surface areas? Geochim. Cosmochim. Acta 65 (7), 1059–1070.
- Golubev, S.V., Bénézeth, P., Schott, J., Dandurand, J.L., Castillo, A., 2009. Siderite dissolution kinetics in acidic aqueous solutions from 25 to 100 °C and 0 to 50 atm pCO₂. Chem. Geol. 265 (1–2), 13–19.

- Guillaume, D., Neaman, A., Cathelineau, M., Mosser-Ruck, R., Peiffert, C., Abdelmoula, M., Dubessy, J., Villieras, F., Baronnet, A., Michau, N., 2003. Experimental synthesis of chlorite from smectite at 300 °C in the presence of metallic Fe. Clay Miner. 38 (3), 281–302.
- Guillaume, D., Neaman, A., Cathelineau, M., Mosser-Ruck, R., Peiffert, C., Abdelmoula, M., Dubessy, J., Villiéras, F., Michau, N., 2004. Experimental study of the transformation of smectite at 80 and 300 °C in the presence of Fe oxides. Clay Miner. 39 (1), 17–34.
- Helgeson, H.C., Murphy, W.M., Aagaard, P., 1984. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and the hydrolysis of feldspar. Geochim. Cosmochim. Acta 48 (12), 2405–2432.
- Hellmann, R., Tisserand, D., 2006. Dissolution kinetics as a function of the Gibbs free energy of reaction: an experimental study based on albite feldspar. Geochim. Cosmochim. Acta 70 (2), 364–383.
- Hodson, M.E., 2006. Does reactive surface area depend on grain size? Results from pH 3, 25 °C far-from-equilibrium flow-through dissolution experiments on anorthite and biotite. Geochim. Cosmochim. Acta 70 (7), 1655–1667.
- Holdren Jr, G.R., Speyer, P.M., 1985. Reaction rate-surface area relationships during the early stages of weathering-I. Initial observations. Geochimica et Cosmochimica Acta 49 (3), 675–681.
- Holdren Jr, G.R., Speyer, P.M., 1987. Reaction rate-surface area relationships during the early stages of weathering. II. Data on eight additional feldspars. Geochim. Cosmochim. Acta 51 (9), 2311–2318.
- Jeschke, A.A., Dreybrodt, W., 2002. Dissolution rates of minerals and their relation to surface morphology. Geochim. Cosmochim. Acta 66 (17), 3055–3062.
- Jodin-Caumon, M.C., Mosser-Ruck, R., Rousset, D., Randi, A., Cathelineau, M., Michau, N., 2010. Effect of a thermal gradient on iron-clay interactions. Clays Clay Miner. 58 (5), 667–681.
- Jodin-Caumon, M.C., Mosser-Ruck, R., Randi, A., Pierron, O., Cathelineau, M., Michau, N., 2012. Mineralogical evolution of a claystone after reaction with iron under thermal gradient. Clays Clay Miner. 60 (5), 443–455.
- Köhler, S.J., Dufaud, F., Oelkers, E.H., 2003. An experimental study of illite dissolution kinetics as a function of ph from 1.4 to 12.4 and temperature from 5 to 50 °C. Geochim. Cosmochim. Acta 67 (19), 3583–3594. http:// dx.doi.org/10.1016/s0016-7037(03)00163-7.
- Lanson, B., Lantenois, S., Van Aken, P.A., Bauer, A., Plançon, A., 2012. Experimental investigation of smectite interaction with metal iron at 80 °c: structural characterization of newly formed Fe-rich phyllosilicates. Am. Mineral. 97 (5– 6), 864–871.
- Lantenois, S., Lanson, B., Muller, F., Bauer, A., Jullien, M., Plançon, A., 2005. Experimental study of smectite interaction with metal Fe at low temperature: 1. Smectite destabilization. Clays Clay Miner. 53 (6), 597–612.
- Lasaga, A.C., 1986. Metamorphic reaction rate laws and development of isograds. Mineral. Mag. 50 (3), 359–373.
- Lasaga, A.C., Soler, J.M., Ganor, J., Burch, T.E., Nagy, K.L., 1994. Chemical weathering rate laws and global geochemical cycles. Geochim. Cosmochim. Acta 58 (10), 2361–2386.
- Lee, T.R., Wilkin, R.T., 2010. Iron hydroxy carbonate formation in zerovalent iron permeable reactive barriers: characterization and evaluation of phase stability. J. Contam. Hydrol. 116 (1–4), 47–57.
- Lowson, R.T., Comarmond, M.C.J., Rajaratnam, G., Brown, P.L., 2005. The kinetics of the dissolution of chlorite as a function of pH and at 25 °C. Geochim. Cosmochim. Acta 69 (7), 1687–1699. http://dx.doi.org/10.1016/ j.gca.2004.09.028.
- Lüttge, A., 2005. Etch pit coalescence, surface area, and overall mineral dissolution rates. Am. Mineral. 90 (11–12), 1776–1783.
- Lüttge, A., Bolton, E.W., Lasaga, A.C., 1999. An interferometric study of the dissolution kinetics of anorthite: the role of reactive surface area. Am. J. Sci. 299 (7–9), 652–678.
- Madé, B., 1991. Modélisation thermodynamique et cinétique des réactions géochimiques dans les intéractions eau-roche. Université Louis Pasteur.
- Madé, B., Clément, A., Fritz, B., 1994. Modeling mineral/solution interactions: the thermodynamic and kinetic code KINDISP. Comput. Geosci. 20 (9), 1347–1363.
- Martin, F.A., Bataillon, C., 2012. Modelling of the evolution of iron passivity: solving the moving boundaries problem. In: Materials Research Society Symposium Proceedings, April 9–13, San Francisco, CA, United States, pp. 275 –280. 10.1557/opl.2012.586.
- Martin, F.A., Bataillon, C., Schlegel, M.L., 2008. Corrosion of iron and low alloyed steel within a water saturated brick of clay under anaerobic deep geological disposal conditions: an integrated experiment. J. Nucl. Mater. 379 (1–3), 80–90.
- Marty, N.C.M., Fritz, B., Clément, A., Michau, N., 2010. Modelling the long term alteration of the engineered bentonite barrier in an underground radioactive waste repository. Appl. Clay Sci. 47 (1–2), 82–90.
- Metz, V., Raanan, H., Pieper, H., Bosbach, D., Ganor, J., 2005. Towards the establishment of a reliable proxy for the reactive surface area of smectite. Geochim. Cosmochim. Acta 69 (10), 2581–2591. http://dx.doi.org/10.1016/ j.gca.2004.11.009.
- Meunier, A., 2006. Why are clay minerals small? Clay Miner. 41 (2), 551-566.
- Montes-H, G., Marty, N., Fritz, B., Clement, A., Michau, N., 2005. Modelling of longterm diffusion-reaction in a bentonite barrier for radioactive waste confinement. Appl. Clay Sci. 30 (3–4), 181–198.
- Morse, J.W., Arvidson, R.S., 2002. The dissolution kinetics of major sedimentary carbonate minerals. Earth Sci. Rev. 58 (1–2), 51–84.
- Mosser-Ruck, R., Cathelineau, M., Guillaume, D., Charpentier, D., Rousset, D., Barres, O., Michau, N., 2010. Effects of temperature, pH, and iron/clay and liquid/clay

ratios on experimental conversion of dioctahedral smectite to berthierine, chlorite, vermiculite, or saponite. Clays Clay Miner. 58 (2), 280–291.

- Mosser-Ruck, R., Pignatelli, I., Bourdelle, F., Truche, L., Bartier, D., Cathelineau, M., 2013. Etude du système Verre-Fer-Argilite: Rôles du pH, du redox et de la pCO₂ sur la nature des phases minérales ferrifères néoformées au contact des colis et stabilité de ces phases lors d'un refroidissement entre 90 °C et 30 °C. vol. ANDRA report, RP OG2R.13.0001, pp. 147.
- Murphy, W.M., Oelkers, E.H., Lichtner, P.C., 1989. Surface reaction versus diffusion control of mineral dissolution and growth rates in geochemical processes. Chem. Geol. 78 (3–4), 357–380.
- Ngo, V.V., Delalande, M., Clément, A., Michau, N., Fritz, B., 2014. Coupled transportreaction modeling of the long-term interaction between iron, bentonite and Callovo-Oxfordian claystone in radioactive waste confinement systems. Appl. Clay Sci. 101, 430–443.
- Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of watermineral interaction kinetics for application to geochemical modeling. In: U.S. Department of the Interior U.S. Geological Survey 1849 C. Street, NW Washington, DC 20240.
- Perronnet, M., Villiéras, F., Jullien, M., Razafitianamaharavo, A., Raynal, J., Bonnin, D., 2007. Towards a link between the energetic heterogeneities of the edge faces of smectites and their stability in the context of metallic corrosion. Geochim. Cosmochim. Acta 71 (6), 1463–1479.
- Perronnet, M., Jullien, M., Villiéras, F., Raynal, J., Bonnin, D., Bruno, G., 2008. Evidence of a critical content in Fe(0) on FoCa₇ bentonite reactivity at 80 °C. Appl. Clay Sci. 38 (3–4), 187–202.
- Pignatelli, I., Mugnaioli, E., Hybler, J., Mosser-Ruck, R., Cathelineau, M., Michau, N., 2013. A multi-technique characterization of cronstedtite synthesized by ironclay interaction in a step-by-step cooling procedure. Clays Clay Miner. 61 (4), 277–289.
- Rémazeilles, C., Refait, P., 2009. Fe(II) hydroxycarbonate Fe₂(OH)₂CO₃ (chukanovite) as iron corrosion product: synthesis and study by Fourier Transform Infrared Spectroscopy. Polyhedron 28 (4), 749–756.
- Rivard, C., Montargès-Pelletier, E., Vantelon, D., Pelletier, M., Karunakaran, C., Michot, L.J., Villieras, F., Michau, N., 2013a. Combination of multi-scale and multi-edge X-ray spectroscopy for investigating the products obtained from the interaction between kaolinite and metallic iron in anoxic conditions at 90 °C. Phys. Chem. Miner. 40 (2), 115–132.
- Rivard, C., Pelletier, M., Michau, N., Razafitianamaharavo, A., Bihannic, I., Abdelmoula, M., Ghanbaja, J., Villiéras, F., 2013b. Berthierine-like mineral formation and stability during the interaction of kaolinite with metallic iron at 90 °c under anoxic and oxic conditions. Am. Mineral. 98 (1), 163–180.
- Rozalén, M.L., Huertas, F.J., Brady, P.V., Cama, J., García-Palma, S., Linares, J., 2008. Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25 °C. Geochim. Cosmochim. Acta 72 (17), 4224–4253.
- Saheb, M., Descostes, M., Neff, D., Matthiesen, H., Michelin, A., Dillmann, P., 2010. Iron corrosion in an anoxic soil: comparison between thermodynamic modelling and ferrous archaeological artefacts characterised along with the local in situ geochemical conditions. Appl. Geochem. 25 (12), 1937–1948.
- Saheb, M., Berger, P., Raimbault, L., Neff, D., Dillmann, P., 2012. Investigation of iron long-term corrosion mechanisms in anoxic media using deuterium tracing. J. Nucl. Mater. 423 (1–3), 61–66.
- Sanders, R.L., Washton, N.M., Mueller, K.T., 2010. Measurement of the reactive surface area of clay minerals using solid-state NMR studies of a probe molecule. J. Phys. Chem. C 114 (12), 5491–5498.

- Savage, D., Walker, C., Arthur, R., Rochelle, C., Oda, C., Takase, H., 2007. Alteration of bentonite by hyperalkaline fluids: a review of the role of secondary minerals. Phys. Chem. Earth 32 (1–7), 287–297.
- Savage, D., Watson, C., Benbow, S., Wilson, J., 2010. Modelling iron-bentonite interactions. Appl. Clay Sci. 47 (1–2), 91–98.
- Savage, D., Arthur, R., Watson, C., Wilson, J., Strömberg, B., 2011. Testing geochemical models of bentonite pore water evolution against laboratory experimental data. Phys. Chem. Earth 36 (17–18), 1817–1829.
- Sayed Hassan, M., Villieras, F., Gaboriaud, F., Razafitianamaharavo, A., 2006. AFM and low-pressure argon adsorption analysis of geometrical properties of phyllosilicates. J. Colloid Interface Sci. 296 (2), 614–623.
- Schlegel, M.L., Bataillon, C., Benhamida, K., Blanc, C., Menut, D., Lacour, J.L., 2008. Metal corrosion and argillite transformation at the water-saturated, hightemperature iron-clay interface. A microscopic-scale study. Appl. Geochem. 23 (9), 2619–2633.
- Schlegel, M.L., Bataillon, C., Blanc, C., Prêt, D., Eddy, F., 2010. Anodic activation of iron corrosion in clay media under water-saturated conditions at 90 °C: characterization of the corrosion interface. Environ. Sci. Technol. 44(4), 1503–1508.
- Schlegel, M.L., Bataillon, C., Blanc, C., Foy, E., Brucker, F., 2013. From the ex-situ steel-clay to the in situ steel-porewater interfaces: comparing the results of ArCorr and MCO experiments. In: 4ième Réunion plénière du Groupement de Laboratoires Verre/Fer/Argile, GL-VFA Andra. 17–18 Juine, 2013, Paris, France (personal communication).
- Schott, J., Pokrovsky, O.S., Oelkers, E.H., 2009. The link between mineral dissolution/ precipitation kinetics and solution chemistry. Rev. Mineral. Geochem. 70, 207– 258.
- Schott, J., Oelkers, E.H., Bénézeth, P., Goddéris, Y., François, L., 2012. Can accurate kinetic laws be created to describe chemical weathering? Comptes Rendus – Geoscience 344 (11–12), 568–585.
- Tang, Y., Martin, S.T., 2011. Siderite dissolution in the presence of chromate. Geochim. Cosmochim. Acta 75 (17), 4951–4962. http://dx.doi.org/10.1016/ j.gca.2011.06.024.
- Tournassat, C., Neaman, A., Villéras, F., Bosbach, D., Charlet, L., 2003. Nanomorphology of montmorillonite particles: estimation of the clay edge sorption site density by low-pressure gas adsorption and AFM observations. Am. Mineral. 88 (11–12 Part 2), 1989–1995.
- Wersin, P., Birgersson, M., 2014. Reactive transport modelling of iron-bentonite interaction within the KBS-3H disposal concept: the Olkiluoto site as a case study. Geol. Soc. Lond. Spec. Publ. 400. http://dx.doi.org/10.1144/sp400.24.
- White Art, F., Peterson Maria, L., 1990. Role of reactive-surface-area characterization in geochemical kinetic models. Chemical Modeling of Aqueous Systems II, ACS Symposium Series, vol. 416. American Chemical Society, pp. 461–475.
- Wilson, J., Cressey, G., Cressey, B., Cuadros, J., Ragnarsdottir, K.V., Savage, D., Shibata, M., 2006a. The effect of iron on montmorillonite stability. (II) Experimental investigation. Geochim. Cosmochim. Acta 70 (2), 323–336.
- Wilson, J., Savage, D., Cuadros, J., Shibata, M., Ragnarsdottir, K.V., 2006b. The effect of iron on montmorillonite stability. (1) Background and thermodynamic considerations. Geochim. Cosmochim. Acta 70 (2), 306–322.
- Wilson, J., Savage, D., Bond, A., Watson, S., Pusch, R., Bennett, D., 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. In: vol. Quintessa Report for NDA RWMD, Report number: QRS-1378ZG-1. Oxfordshire, United Kingdom.
- Zhang, J.W., Nancollas, G.H., 1990. Mechanisms of growth and dissolution of sparingly soluble salts. Rev. Mineral. Geochem. 23 (1), 365–396.