A modeling tool for assessment of potential groundwater contamination in response to CO_2 leakage from geological disposal of CO_2

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Abstract

Geological disposal of CO_2 is potentially risky as this disrupts the balance of the aqueous chemistry and could cause water acidification, mineral dissolution and release of various heavy metals. Numerical simulation could be a viable approach to predict the long-term performance of the geological disposal of CO_2. A modeling tool has been developed by coupling FLAC3D^{DM} (mechanical damage model included) and TOUGHREACT codes in order to completely account for the coupled effects of thermal, hydraulic, geochemical and mechanical factors. The verification with reactive migration test demonstrates the suitability of this approach for the assessment of groundwater pollution resulted from carbon storage.

Keywords: Coupled modeling, carbon, geological disposal, assessment.

Résumé

Le stockage géologique du CO_2 peut potentiellement entraîner un déséquilibre des espèces chimiques. Ceci pourrait conduire à une acidification de l'eau, une dissolution de minéraux et la libération de divers métaux dans les eaux souterraines. La modélisation numérique pourrait être une approche adéquate pour prédire la performance à long terme du stockage géologique de CO_2 en ce qui concerne l'impact des fuites de CO_2 sur la qualité des eaux souterraines. Un outil de modélisation a été développé en couplant FLAC3D^{DM} (modèle d'endommagement mécanique inclus) et le code TOUGHREACT afin d'intégrer les effets couplés des facteurs thermiques, hydrauliques, géochimiques et mécaniques. Les validations avec des essais de transport réactif ont montré que l'outil proposé serait approprié pour évaluer la contamination des eaux souterraines résultant du stockage du carbone.

1. Introduction

Increases in global average temperature, melting of polar ice caps and more hurricanes are continuously recognized by more and more people as related to greenhouse gases, i.e. carbon dioxide (CO_2) and methane. One viable CO_2 mitigation measure is to obtain the CO_2 that is captured from CO_2 emission sources, like coal fired power plants, and then sequestered in geological formations. Industries have taken advantage of several types of geological formations for carbon sequestration, including: depleted oil and gas reservoirs, deep saline reservoirs, and unmineable coal seams [1-4]. In order to maintain long-term safety and stability, CO_2 is always injected under a supercritical state and deep enough into the underground with sufficient confining pressure. However, overpressure of the reservoir during CO_2 injection could

cause damage to the caprocks which would become fractured and thus vulnerable to CO_2 leakage. Fault zones and failed well plugs could also be conduits for CO_2 release.

In addition, CO_2-rock reactions will influence the hydrological, mechanical and geochemical behaviors of a reservoir system. As a weak acidic solution, CO_2 saturated liquid could cause chemical damage to minerals, increase permeability, and further mobilize toxicants by increasing the risk and possibility of contamination to aquifers near the ground surface. Experimental results have observed rapid dissolution of carbonate minerals and increased concentrations of heavy metals following CO_2 injection [5]. CO_2–brine–caprock interactions have been experimentally investigated in several studies, with focus placed respectively on shale caprock [6], sedimentary rocks [7], and sandstones [5] under a broad range of testing conditions (temperature and pressure, 50–200°C and 2–100 MPa). The co-injection of other more erosive gases are starting to generate interest in research and field applications [8]. Mineralogical alterations, reaction kinetics and thermodynamics are primary behaviors and parameters amongst others that have been intensively investigated. All these efforts are meant to reveal the intrinsic mechanisms that govern geochemical reactions, and also provide us with abundant data to validate theoretical modelings.

Numerical simulation could be a viable approach to predict the behaviors and long-term safety of the geological disposal of CO_2. Large scale of the field conditions needs the numerical computations to support various technical issues regarding the implementation of excavation, drilling and environmental issues regarding the assessment of long-term gas migration and relevant chemicals migration. This paper aims at developing a modeling tool by coupling FLAC3D^{DM} (mechanical damage model included) and TOUGHREACT codes in order to completely account for the coupled effects of thermal, hydraulic, geochemical and mechanical factors. Efforts have been made towards model setup, code integration, data interpolation and exchange, examining porosity-hydraulic-thermo-mechanical interrelationships, etc. A set of codes have been developed to achieve data processing and exchanges between FLAC3D (Ver 4.0) and TOUGHREACT (Ver 2.0). The simulator as well as the coupling scheme was verified by a complete series of experimental results.

2. Development of the THMC Simulator

2.1 THMC Coupled Processes Considered

Thermo-hydro-chemical (THC) coupling that is related to CO_2 sequestration has been widely investigated [6, 7, 9-11]. Under geological conditions, CO_2 can either dissolve into the water phase or exist in a critical liquid state. Various physicochemical influences have to be taken into account for modeling. Chemical reactions and diffusive constants are influenced by temperature fluctuations. Since the temperature is comparatively stable in deep geological formations, the effect of thermal coupling is mainly related to the reaction rate of various geochemical species. Thermal gradients will further assert additional stress onto the porous media, thus altering the viscosity, density and saturation index of each phase. In the foreseeable future within thousands of years, geological fault zones could be screened out in the site-selection process, therefore avoiding the possibility of abrupt changes in ground temperature. Isothermal conditions are widely accepted in the THC coupled modeling of geological CO_2 storage.

Hydraulic flow enhances chemical dispersion (D_e). Changes in water saturation and capillary pore pressure together moderate the level of the effective stress and lead to mechanical strains

(ε) and porosity changes. One of the direct results of mechanical strains is the potential damage to the integrity of the rock mass. Damage takes the form of microcracks, either isolated or linked, and gives rise to permeability by 2-3 orders of magnitude [12-14].

The mechanical (M) effects on THC coupling are an open question for modelers. Within the poroelastic frameworks, injection of CO_2 into porous media will increase the pore pressure, result in shear strains and porosity variations, and change the heat conductivity and relative permeability for multiphase flow and also the effective diffusion coefficients for various chemical species. However, it is not sufficient to treat rocks as poroelastic material, especially when high stresses and large scale calculations are considered. Existing fault zones, discontinuity and fragility of rocks complicate the mechanical behaviors. The coupling of these effects into existing THC coupling schemes has been carried out in some recent studies, but more efforts are required.

Chemical effects on THM couplings include chemical erosion or precipitation, porosity variation, and also changes in water density (ρ), heat conductivity (λ), viscosity (η) and buoyancy. Chemical damage to caprocks affects their elastic modulus (E), Poisson's ratio (v) and effective stress (σ'). Chemical couplings prove to be significant in certain circumstances, e.g. contact of CO_2 solution with carbonate dominant rocks. Each chemical equation is based on thermodynamic principles, and thus closely coupled with the thermal effect. As CO_2 is sensitive to both temperature and pressure, as indicated by its phase diagram, these complex couplings have been considered in TOUGHREACT by incorporating a group of physical parameters, i.e. density, composition, saturation, activity, fugacity, etc.

All of these processes are explained in a diagram as shown in Fig.1. The key parameters are porosity and related permeability, which will be specifically discussed in the following parts.
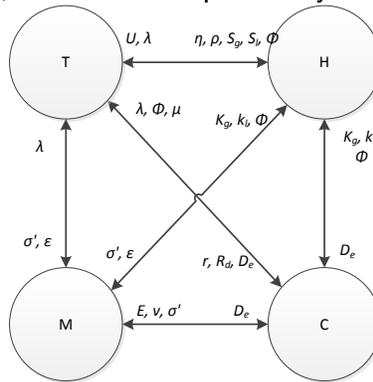

Figure 1. Conceptual diagram of THMC coupling and the affected parameters

2.2 Coupling scheme and simulator

Two well established numerical codes, FLAC3D (strong in Mechanics, M) and TOUGHREACT (THC code), have been coupled to develop a THMC simulator for the assessment of potential groundwater contamination in response to CO_2 leakage.

TOUGHREACT is designed to address the time dependent transport of non-isothermal multiphase/unsaturated flow and reactive transportation of chemical species in porous media. TOUGHREACT considers thermal, hydraulic and chemical couplings and permeability-porosity coupling the results from mineral dissolution and precipitation. A sequential iteration approach is used by running the solution of the flow equations first, and then by using the fluid velocities and phase saturations for chemical transport simulation. The chemical transport is solved on a component-by-component basis [15].

FLAC3D is a robust finite-difference program for mechanics computation, capable of simulating the behavior of various geomaterials that undergo plastic flow under yield limit conditions [16]. Specific numerical algorithms e.g. the Lagrangian calculation scheme and the mixed-discretization zoning technique are used to ensure an accurate modeling of plastic flow. It is claimed to be able to handle any constitutive model with no adjustment to the solution algorithm, and is most effective when applied to nonlinear or large strain problems. FLAC3D also implements a flexible built-in programming language, providing a convenient interface for users to define new models. An elasto-plastic damage model was developed and then implemented into FLAC3D.

A FORTRAN subroutine code and FLAC3D FISH script were necessary to successfully combine both numerical codes. In this study, we have scripted a series of programs by using C++ and FISH languages to transfer primary variables, e.g. pore pressure, temperature and porosity between FLAC3D and TOUGHREACT. Figure 2 shows the schematic diagram of this coupling process. As variables are applied onto grids in FLAC3D instead of elements as in TOUGHREACT, data interpolation was exemplified when introducing these data from the simulation results of TOUGHREACT. On the other hand, the results from FLAC3D can be directly outputted in elemental centers, and as a result, no interpolation is necessary to import data into TOUGHREACT. Detailed illustrations on data interpolation and exchanges between FLAC-TOUGH have been reported [17]. Since TOUGHREACT shares the same numerical solvers with TOUGH and also accepts data input in the same format with those for TOUGH, the data manipulation process does not need much modification. All time-dependent variables are calculated by TOUGHREACT while FLAC3D only predicts the equilibration of mechanical stresses.
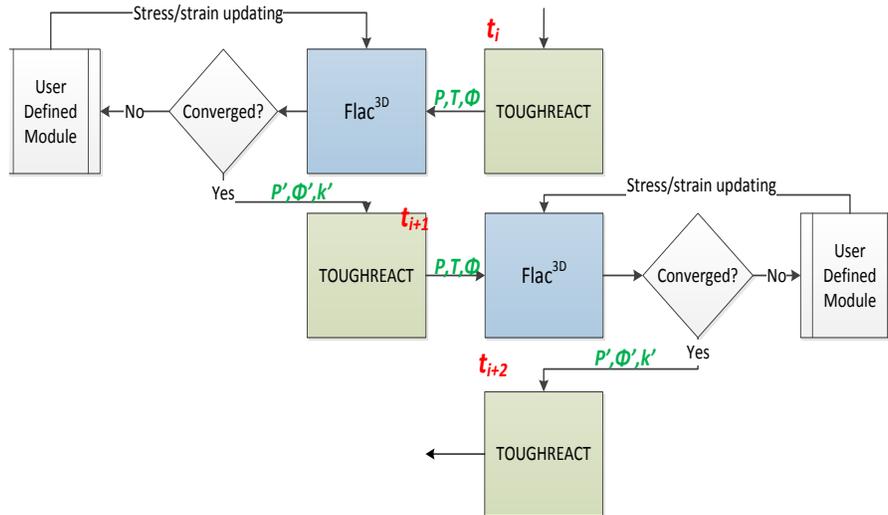

Figure 2. Schematic diagram of algorithmic and data exchange between FLAC3D and TOUGHREACT

3. Validation of the developed THMC Tool and Numerical Simulations

In this study, we first implement the TOUGHREACT-FLAC3D coupling scheme by numerical simulations of gas injection tests at the laboratory scale and compare those with experimental observations to validate the THMC coupling module of our simulator. A chemical kinetic database was developed and incorporated into TOUGHREACT, and has been validated by careful comparison with a series of experimental results [9]. However, more extensive work is still required to validate the kinetic database as well as the complex interaction amongst various

chemical species. Significant uncertainties in aluminosilicate mineral reactivities have been noted along with significant discrepancies between the experimental and modeled solubilities [6]. Therefore, further efforts are needed to update these kinetic data through validation of experimental studies. We conducted a detailed THMC coupled simulation of a CO_2 injection experiment with the focus placed on chemical analysis. Some examples of validation and simulation results are presented below.

3.1 Description of laboratory tests and modeling approach

Yu et al. [5] reported a detailed experimental study on CO_2 permeation through a sandstone sampled from the oil field. The sample was $2*17$ cm^2 (D*L) in size, and permeated with a CO_2 saturated brine solution under a confining pressure of 24 MPa and temperature of 100°C. The permeation velocity was maintained at 2.5 mL/min and sustained for 130 hours. Chemical species in the leachate and mineral compositions in the porous media were analyzed along with discussions on the mechanism of the permeability reduction.

Table 1. Kinetic rate constants for minerals analyzed in this study

Mineral	k_{25}(mols m^{-2} s^{-1})	E_a (kJ mol^{-1})	Surface area (g cm^{-1})	Volume fraction (%)		Note
				Initial	End	
Albite	1.00E-12	67.83	98	32.64	32.63	
Calcite	-	-		0.021	0.0	Equilibrium mineral
Celestine	1.26E-09	62.61	98	0.01	0.0	
Illite	1.00E-14	58.62	1516	2.76	2.76	
Kaolinite	1.00E-13	62.76	100	0.0	3.4E-8	
k-feldspar	1.00E-12	67.83	98	4.11	4.10	
Quartz	1.26E-14	87.50	98	57.21	57.21	
Smectite	1.69E-13	58.62	1516	0.0	2.75E-8	

We developed a numerical model from the TOUGHREAC-FLAC3D^{DM} coupled scheme with the same size, geochemical conditions, fluid flow conditions and boundary conditions as those as reported by Yu et al. [5]. The chemical concentrations in the outlet boundary were plotted with permeation time and further compared with the test data as shown in Fig.3. The solution pH greatly depends on the initial concentration of H$^+$ in the input file of TOUGHREACT. In order to achieve a better fit, several rounds of trial-and-error simulations were carried out by adjusting the setting of the relevant parameters. The specimen is reported to be sandstone with a permeability at 4.01E-15 m^2. Such a high level of permeability allows the effect of capillary pressure in our simulations to be neglected.

For reactive transport modeling, it is fundamental and also important to predict with the rate constants for mineral dissolutions or precipitations. TOUGHREACT accounts for kinetically-controlled reactions that occur between aqueous species [18]:

$$r = \pm kA \left| \Omega_n^\theta - 1 \right|^{\overline{\eta}} \tag{1}$$

where r is the reaction rate, A is the surface area of a specific mineral, Ω is the ionic activity product, θ and η are model constants. This equation can be used to calculate both dissolution and precipitation processes, which are dependent on the saturation index of each aqueous species or mineral component. The rate constant k is written as a function of temperature and activation energy:

$$k = k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$$

(2)

In the case that dissolution is governed by several other mechanisms, the rate constant becomes:

$$k = k_{25}^{nu} \exp\left[\frac{-E_a^{nu}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + \sum_i k_{25}^i \exp\left[\frac{-E_a^i}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \prod_j a_{ij}^{n_{ij}}$$

(3)

Table 1 shows the reaction kinetic data for the primary minerals considered in this study. A comparison with the reported data in similar studies shows a large discrepancy between these constants. The dissolution rate constant for dolomite was experimentally determined to be in the range of 1-4 E-8 mol/s, which is much higher than those used in other simulations [8, 10]. The predicted mineral composition after CO_2 injection shows minor changes from the original state, thus indicating the necessity to adjust these kinetic data in order for a better fit. Yu et al. [5] reported the calculated reaction rate for several minerals and generally in the range of 1E-6 cm^3/min. This is significantly higher compared to the average accepted values for these components.

Figure 3 shows a comparison of the test data with the simulated results for the evolution of various chemical species in the leachate. It can be seen that most of the primary chemical species fit with good agreement. It is noteworthy that the simulated Ca concentration and pH are on average, greater than the experimental results. This could be related to the assumption that calcite exists as an equilibrium mineral without consideration of reaction kinetics. The current version of TOUGHREACT only allows equilibrium calculation for calcite-CO_2 reactions in view of their comparatively high reaction rate (1000 times of that of albite) and the large time scale. In addition, the solution pH greatly relies on the hydration reactions of surface functional groups of a variety of minerals. Emberley et al. [19] found that paragonite, albite, and kaolinite may be influencing fluid pH and the rate at which carbonate minerals interact with the dissolved CO_2. The silicate hydrolysis process is the rate-limiting step while the equilibration may take up to 5000 years. For example, silicate mineral assemblage is a good buffer for solution pH and thus viewed as a net benefit to increase the potential of the geological storage of injected CO_2 [19, 20]. A good prediction of pH requires more detailed information about the surface properties, aqueous species, concentrations and equilibration constants. Regardless of these limitations, the current simulation provides an appropriate approximation of the chemical species, and generally reflects the chemical reactions.

With the ion exchange reaction accounted, the peak concentration of K in effluent was reflected by the simulation. A recent study by Apps et al. also observed increases in the concentration of dissolved trace metals, and explained that it is the result of Ca+2-driven ion exchange with clays (smectites) and sorption/desorption reactions that involve iron (Fe) hydroxides [21]. The peaks for Fe and magnesium (Mg) as shown in Fig.3 could not be reflected in this simulation, as these elements are probably leached out by low pH solution from relevant mineral components that are negligible in amount and thus not detected. The simulated curves for Fe and Mg consistently increase throughout the course of the experiment, thus indicating the continuous dissolution process of relevant minerals and agreeing well with the experimental observations [8]. Further fine-tuning of the initial mineral constituents could help to better fit the experimental results.
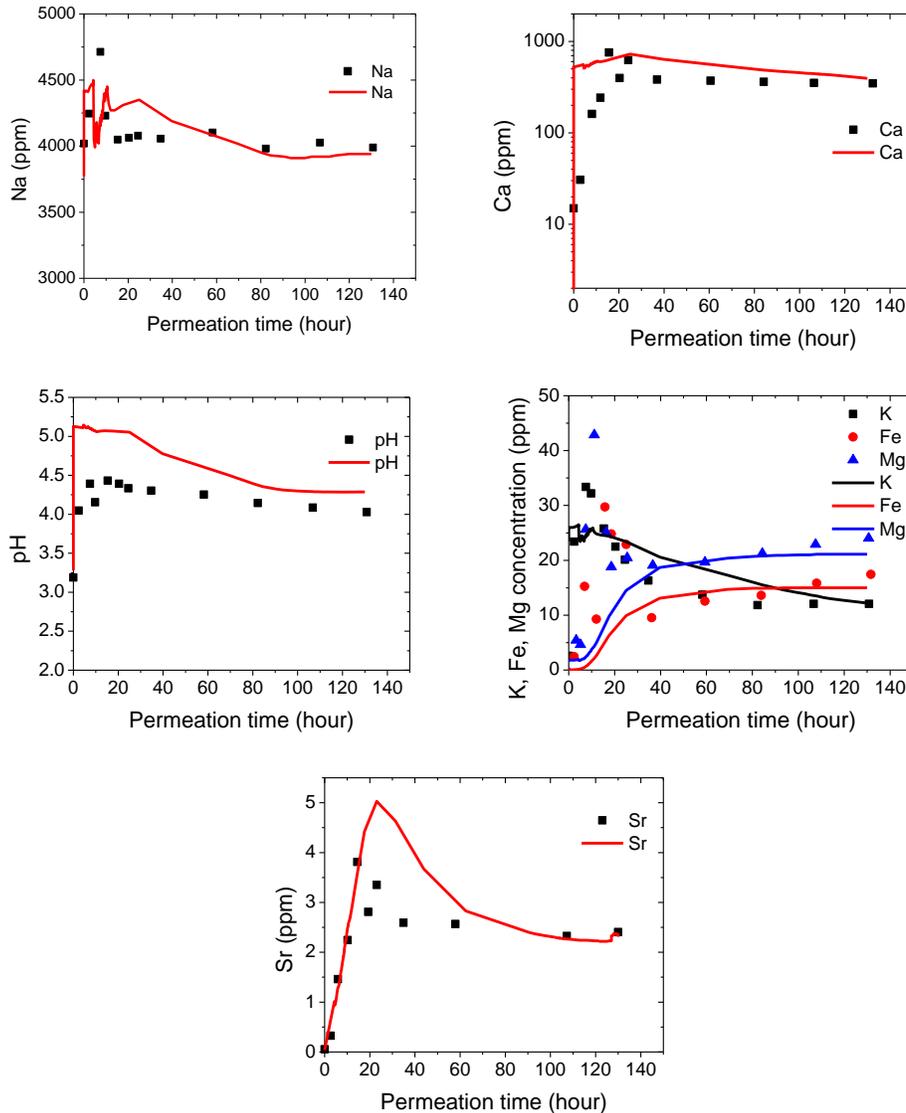
Figure 3. Variations in chemical concentration and solution pH of leachate with permeation time (scatter is test data and curve is simulated results; simulated curve considers effects of cation exchange)

Simulation cases without cation exchange/adsorption were also carried out and the results are shown in Fig. 4. The equilibrium concentration seems to agree well with the simulated curve. However, the fluctuation of the ionic species could not be precisely reflected, which might be ascribed to the conceptual rapid equilibration of the chemical reactions, as defined in the chemical database in TOUGHREACT.
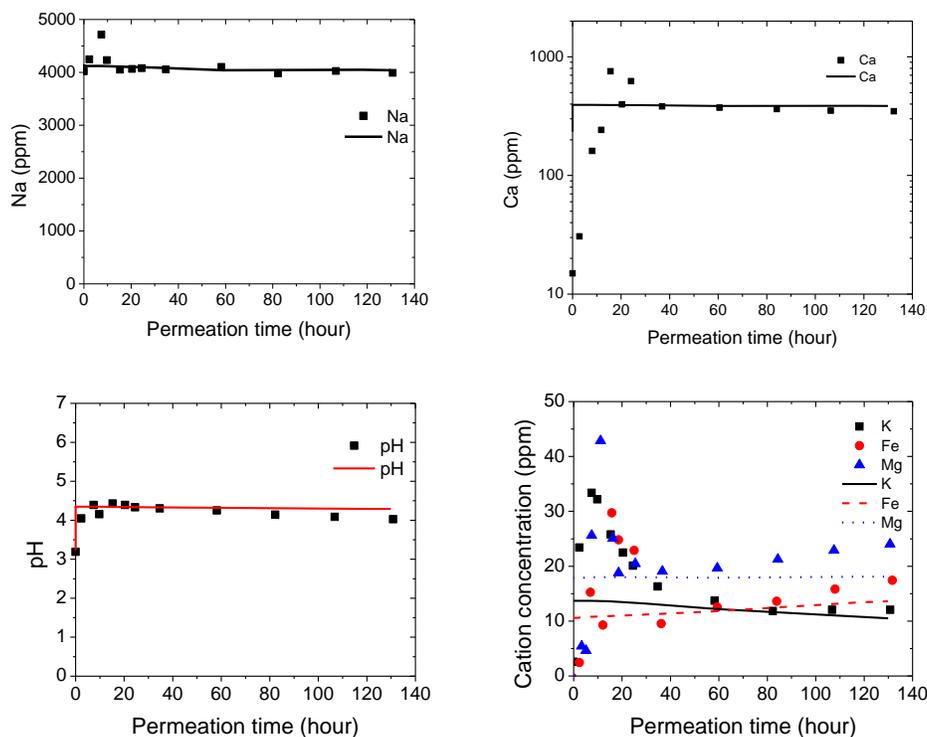
Figure 4. Variation in chemical concentration and solution pH of leachate with permeation time (simulation without consideration of cation exchange effect)

Figure 5 shows a comparison of the simulated mineral composition with the test data. Detailed information is shown in Table 3. We can observe a relatively good agreement between the experimental data and the predicted values. However, minor variations in the abundance of most of these minerals are observed in our simulation. This could be related to the reliability of the reaction kinetic parameters used in the thermodynamic database. Yu et al. reported the dissolution rate for several aluminosilicate minerals, and the values are in the range of 1E-6 cm^3/min, which are on average higher than those normally used in reactive transport simulations [5]. The temperature used in this experiment is 100^oC, which might greatly speed up the reaction rate. We attempted to adjust the parameter setting in our simulation for the reaction kinetics, but still failed to achieve the same level of mineral yield. With regards to the fact that few other experiments have shown such a high reaction rate, the authors would like to leave this issue to future investigations.

Figures 6 and 7 show the contour mapping of various elemental concentrations at different durations of permeation. It can be seen that most of these contours are even and regular, which indicate that the simulation was carried out with good precision. The propagation of solute concentration from the bottom to the upper boundary with increased permeation time corresponds to the experimental conditions. The irregular contour of gas saturation at the end of the simulation (t=130 h) is likely caused by the larger incremental time step. However, the injection of a CO_2 saturated brine solution causes a minor increase in gas saturation which is mainly composed of CO_2 and generally less than 0.003. Due to the very small scale of the test sample that is considered in this study, i.e. L=17 cm, the long term fate and transportation

behaviors of these chemicals are not available for upscaled implementation in field conditions. However, the good agreement between the simulation and test data has clearly verified the applicability and potential of our simulator for the analysis of such problems in the future.
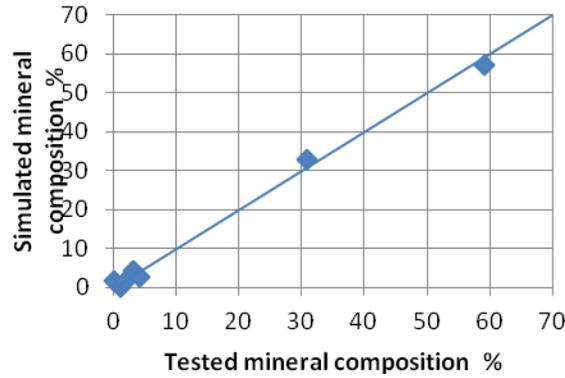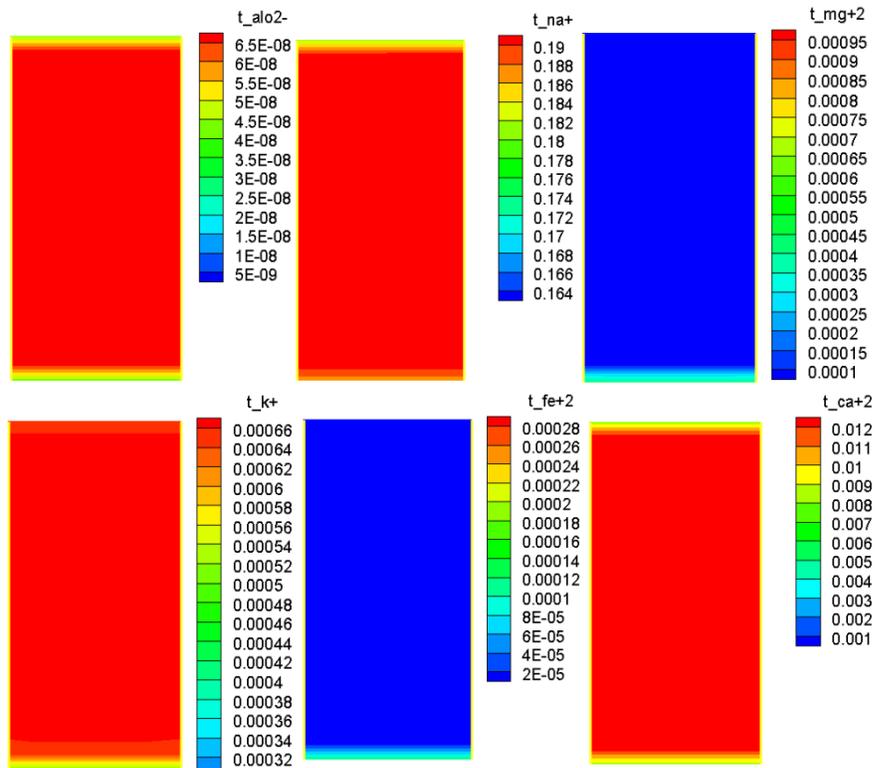

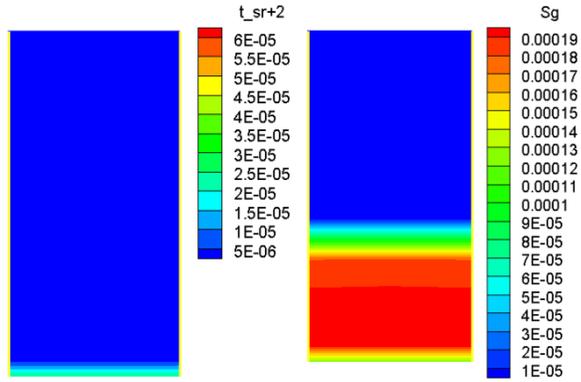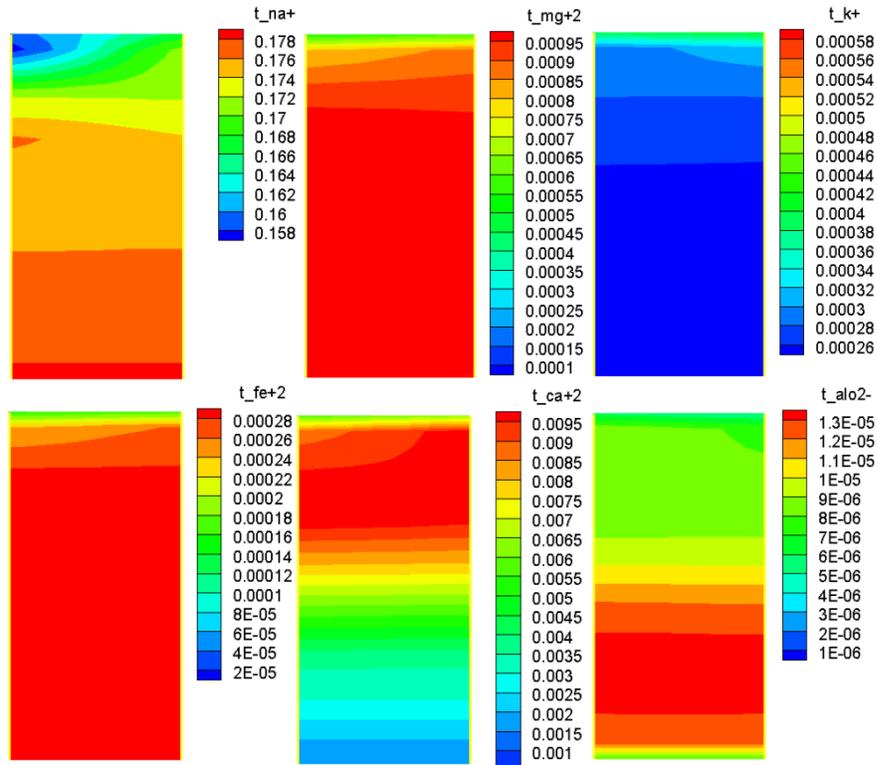Figure 5. Comparison of simulated weight ratio of mineral components with test data

Figure 6. Contour distributions of the total molar concentrations of various elements and gas saturation (S_g) at t=10.0 h
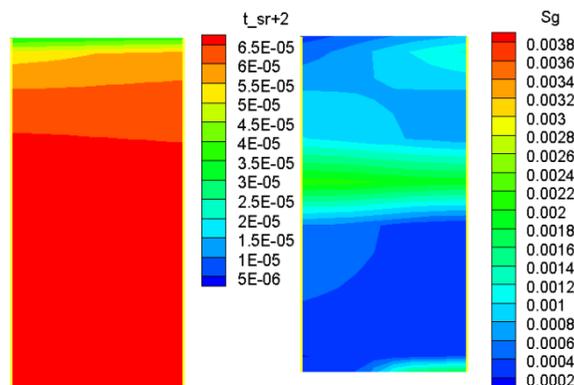
Figure 7. Contour distributions of the total molar concentrations of various elements and gas saturation (S_g) at t=130.0 h

4. Conclusions

A THMC coupling simulator is developed by coupling FLAC3D and TOUGHREACT with a group of codes for data exchange and interpolation. The simulator is successfully validated by a permeation test of reactive CO_2 migration and interaction with rock samples. The numerical simulation has systematically analyzed the effect of CO_2 injection on the evolution of chemical species concentration in pore fluid. The geochemical reactions that occur between CO_2-H_2O and minerals were numerically predicted by choosing carefully the thermodynamic parameters for these reactions. Existence of ion exchange between Na/Ca and K/Fe/Mg that are naturally contained in fine particle of clay minerals is confirmed by simulations. Rapid reduction in solution pH and quick dissolution of alkaline minerals, i.e. calcite, are clearly observed in the simulation results. Good agreement with the experimental data provides successful validation of the capability of our simulator. Future work will involve applications in large scale field conditions.

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