The application of TOUGHREACT in the field of energy and environment

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Abstract. TOUGHREACT has been widely used as a chemical reaction simulation program for non-isothermal multiphase flow in pore and fracture media. By analyzing the comprehensive research results, the application status of TOUGHREACT in CO₂ geological storage, geothermal energy development, nuclear waste disposal, mineral recovery and silica fouling and environmental pollution remediation are summarized. Finally, the future development trend of TOUGHREACT is also analyzed. It can be used as a reference for the future application of TOUGHREACT in the field of energy and environment.

1. Introduction

At present, there are a large number of reaction migration software used for underground environment simulation, such as OpenGeoSys, TOUGHREACT, HYDROGEOCHEM, CRUNCHFLOW, PFLOTTRAN and MIN3P[1]. Many scholars have applied these software to solve problems in related fields, where TOUGHREACT can be applied to one-, two- or three-dimensional porous and fractured media with physical and chemical heterogeneity[2]. The code can accommodate any number of chemical species present in liquid, gas and solid phases. It is developed by introducing reactive chemistry into the multiphase fluid and heat flow simulator TOUGH2 V2.

The first version of the TOUGHREACT code was released to the public through the US Department of Energy’s Science and Technology Software Center (ESTSC) in August 2004. It has been used by about 300 laboratories and technology companies in 33 countries. Most scholars use it to study the migration of water and heat flow in groundwater, and have achieved fruitful results. Among them, foreign scholars apply TOUGHREACT in a wide range, including carbon dioxide geological storage, geothermal energy development, nuclear waste disposal, mineral recovery and silica fouling, and environmental pollution repair. Most Chinese scholars use TOUGHREACT to study carbon dioxide geological storage and geothermal energy development, but the research started relatively late in China.

At present, there are very few articles that systematically describe the current state of application of TOUGHREACT. Therefore, we mainly summarize the application of TOUGHREACT in five fields: carbon dioxide geological storage, geothermal energy development, nuclear waste disposal, mineral recovery and silica fouling, and environmental pollution repair.
2. Research on the application status of TOUGHREACT

TOUGHREACT has been widely used in the fields of carbon dioxide geological storage, geothermal energy development, nuclear waste disposal, mineral recovery and silica fouling, and environmental pollution remediation. In order to understand the application of TOUGHREACT, we have counted a total of 102 articles. The application of statistics in various fields is shown in Figure 1. It shows that geological storage of carbon dioxide accounts for 60.8%, geothermal energy development accounts for 16.7%, and nuclear waste disposal accounts for 6.8%. According to the statistical data, the researches are mainly focused on the geological storage of carbon dioxide, following by geothermal energy development.

![Figure 1. Percentage of the application areas of the TOUGHREACT.](image)

2.1. CO2 geological sequestration

TOUGHREACT’s ECO2N module is suitable for multiphase mixtures of water, CO2 and NaCl, mainly used for CO2 geological storage. TOUGHREACT/ECO2N contains the governing equations of heat transport, multiphase flow and solute transport (Table 1).

| Fundamental governing equation | $\frac{\partial M_k}{\partial t} = - \nabla F_k + q_k$ |
|--------------------------------|-------------------------------------------------|
| **Water**                     | Where $M_k$ is the mass per unit volume in the control unit; $F_k$ is the mass flux; $q_k$ is the source/sink. |
| $M_w = \varphi (S_l \rho X_{ul} + S_g \rho_g X_{ug})$ | $F_w = X_{ul} u_l + X_{ug} u_g$ |
| $q_w = q_{ul} + q_{ug}$ | $\varphi$ is porosity; $S$ is saturation; $\rho$ is density; $X$ is the mass fraction; $u$ is Darcys velocity; $q$ is the source/sink; $F$ stands for water, $l$ stands for liquid phase, $g$ stands for gas phase, $c$ stands for CO2, $r$ stands for chemical reaction. |
| **Gas** (CO2)                  | |
| $M_g = \varphi (S_l \rho X_{cl} + S_g \rho_g X_{cg})$ | $F_g = X_{cl} u_l + X_{cg} u_g$ |
| $q_g = q_{cl} + q_{cg}$ | |
| **Heat**                      | |
| $M_h = \varphi (S_l \rho u_l + S_g \rho_g u_g) + (1-\varphi) \rho u_s$ | $F_h = \sum_{\rho_{-1g}} h_{\rho_{-1g}} \rho_{-1g} \lambda \nabla T$ |
| $M_h$ is the total heat; $U$ is internal energy; $u_{\beta}$ is seepage velocity; $\lambda$ is thermal conductivity; $T$ is temperature. The subscript $h$ stands for heat; $s$ stands for solid phase. |

CO2 geologic sequestration is an emerging greenhouse gas sequestration technology in recent years. The sequestration forms of CO2 mainly include structural geological storage, dissolution storage,
mineral storage and residual gas storage. According to the storage form of CO₂ in the deep saline water and mineral reaction mechanism in TOUGHREACT, we draw the following diagram (Figure 2).

Figure 2. Diagram of CO₂ geological storage in deep saline water.

Figure 2 shows there are mainly four types of CO₂ sequestration in deep saline water layers:

1. Dissolve storage: When supercritical CO₂ is injected into the deep saline aquifer, CO₂ will be dissolved in groundwater and stored in the form of dissolved CO₂.

2. Mineral storage: Dissolved CO₂ combines with water to form carbonic acid. Unstable carbonic acid will further decompose to produce H⁺, which increases the acidity of the formation water. In addition, chlorite, calcite, and gypsum begin to dissolve, leading to the formation of carbon-fixing minerals such as ankerite, dawsonite, siderite and magnesite. Mineral storage is potentially attractive, because it can immobilize CO₂ for a long time, and prevent its release to the atmosphere.

3. Structural geological storage: Since the density of supercritical CO₂ is lower than that of water, it will migrate upward rapidly by buoyancy forces, but the upper low permeability caprock restricts the migration of CO₂. Structural geological storage includes anticline, closed block and pinchout.

4. Residual gas storage: Due to the interfacial tension between gas and liquid, part of CO₂ is trapped in the pores rock for a long time, forming residual gas storage.

There are many factors that affect CO₂ geologic sequestration, such as primary mineral composition[3-4], porosity and permeability[5], vertical to horizontal permeability ratio kᵥ/kₜ[6], temperature[7], initial salinity[8], residual gas saturation[9], etc. The main influencing factors are as follows:

1. Primary mineral composition: a higher volume fraction of chlorite in the initial mineral composition will significantly increase the storage amount of CO₂, while the volume fraction of oligoclase, k-feldspar, calcite and chlorite have less influence on the storage capacity of CO₂[3]. The research results of Yang et al. (2014) showed that when the content of chlorite were 1% and 9.112%, the CO₂ mineral storage were 5.9×10⁹ kg and 1.18×10¹⁰ kg[10]. When chlorite is absent from the
caprock, the CO₂ mineral capture is less than 0. However, when the volume fraction of oligoclase in the primary minerals is much higher than that of chlorite, the effect of oligoclase on CO₂ mineral storage is greater than that of chlorite[4].

(2) Reservoir heterogeneity: Most scholars assume that the reservoir is a homogeneous in the simulation, but the uneven distribution of pores in heterogeneous reservoirs leads to the uneven distribution of CO₂ plume. When the ratio of vertical permeability to horizontal permeability $k_v/k_h$ of the reservoir is lower, it will promote the dissolution and storage of CO₂. A large amount of CO₂ will accumulate in the middle and bottom of the reservoir, but in the upper part of the reservoir, the higher the value of $k_v/k_h$, the farther the vertical migration distance of CO₂[11-12].

(3) Temperature: On the one hand, temperature changes the solubility of CO₂ in saline water, and on the other hand, it affects the capture rate of CO₂ by affecting the reaction rate of primary minerals. When the temperature rises, the solubility of CO₂ and the amount of dissolved storage decreases, and more CO₂ migrates in the form of gas[5,8].

Due to the discontinuity of actual geological reservoir conditions, such as the faults, fractures or abandoned wells in the reservoir[13], CO₂ in the deep saline aquifer may leak into the shallow groundwater[14]. According to the reaction solute transport in TOUGHREACT and the change of water quality caused by CO₂ leakage, we draw the following diagram (Figure 3).

Figure 3. Changes caused by CO₂ leakage into shallow groundwater.

Figure 3 shows that the main changes in water quality caused by CO₂ leakage into shallow groundwater are as follows:

(1) CO₂ dissolved in water causes an increase in the acidity of groundwater, causing the dissolution of minerals such as calcite, dolomite, feldspar and chlorite. The Ca²⁺ and Mg²⁺ produced by the dissolution of these minerals will directly lead to an increase in the hardness of groundwater.

(2) The increase in acidity leads the metal mineral such as hematite, galenite and arsenic-containing minerals to dissolve, which further causes the concentration of Hg, As, Pb, Cd, Cr, Fe, Cu, Sb, Al, Mo, Mn, Cs, Rb, Ni and Se increasing in the shallow groundwater[15]. Wang et al.(2020) simulated the dissolution and transport of uranium in a deep CO₂ storage reservoir with two vertical leakage pathways, and found that the injected CO₂ could mobilize U from the UO₂ mineral in the reservoir rock[16]. In addition, an increase in the leakage rate leads to an increase in the partial pressure of CO₂, which consequently lower pH and higher maximum contaminant concentrations in the aquifer[11].
(3) The \( \text{CO}_2^2 \) produced by the carbonic acid and minerals will complex with metal and heavy metal ions in water to form a complex, thereby affecting the quality of shallow groundwater.

When \( \text{CO}_2 \) contains \( \text{SO}_2 \), \( \text{H}_2\text{S} \) and other acidic impurities, the impurities increase the acidity of the groundwater. The inclusion of \( \text{SO}_2 \) increased the porosity of the formation compared with pure \( \text{CO}_2 \)[17]. Jacquier et al. (2011) established a point source leakage model based on the Albian aquifer in the Paris Basin in France, and found that the pH decreased from 7.4 to 4.0-4.5 after the intrusion of \( \text{CO}_2 \) and impurities(\( \text{SO}_2^2 + \text{NO}_2 + \text{O}_2 \)), while the pH decreased to 5.0-5.5 after the intrusion of pure \( \text{CO}_2 \). The acidification of the water leads to the dissolution of minerals containing Fe and Mn, and a large number of elements such as Fe and Mn enter the groundwater and migrate accordingly[18]. When \( \text{CO}_2 - \text{H}_2\text{S} \) mixtures are co-injection into the shallow groundwater, the content of arsenic in the groundwater is higher than that of \( \text{CO}_2 \) leaks alone[19].

However, the widely used ECO2N module of TOUGHREACT can only handle pure carbon dioxide to predict the physical and chemical changes in deep saline aquifers[20]. This limits its feasibility to predict the microbial effects of carbon dioxide in deep saline aquifers and depleted oil reservoirs. For example, microbes convert crude oil and carbon dioxide to methane, which involves the continuous production and consumption of carbon dioxide, hydrogen and acetate. This will not only affect the dissolution of \( \text{CO}_2 \) and mineral capture, but also affect the generation of \( \text{CH}_4 \). Recently, Shabani et al. (2019) developed a new TOUGHREACT module called CO2Bio for predicting the long-term capture and fate of carbon dioxide in deep saline aquifers and depleted reservoirs under biological conditions. The model can predict the miscibility of \( \text{CO}_2 - \text{CH}_4 - \text{H}_2\text{S} - \text{H}_2 \) gas mixture and brine at deep geological formation conditions[21].

2.2. Geothermal energy development

TOUGHREACT is used to describe the liquid, gas, and two-phase states of pure water, and can accurately describe the migration of water and heat in underground reservoirs. It is widely used in numerical simulation of geothermal development, especially enhanced geothermal systems (EGS). Enhanced geothermal system is an artificial system that forms reservoirs in high-temperature rock formation through techniques such as hydraulic fracturing, so as to extract economical amounts of heat from low-porosity and low-permeability geothermal resources. There searches mainly focus on the following two aspects:

(1) Water-rock interaction in EGS

After injecting \( \text{CO}_2 \) into the EGS system, the dissolved \( \text{CO}_2 \) will diffuse into the peripheral zone of the reservoir, and a series of water-rock interactions occur in the reservoir[22-23], causing the dissolution of primary minerals and precipitation of secondary carbonate[24]. The main dissolved minerals are calcite, k-feldspar and chlorite, and the secondary carbonates are dolomite, siderite and ankerite. A large amount of \( \text{CO}_2 \) is trapped through the precipitation of carbonate minerals[25]. Li et al. (2014) established a water-rock two-phase closed system and found that k-feldspar and biotite gradually transformed into Na-feldspar and quartz, Ca-feldspar gradually transformed into kaolinite, which increased the porosity and permeability of reservoir rocks[26].

(2) Heat extraction efficiency of EGS

There are many factors affecting the heat extraction rate of EGS, among which temperature is the most important factor, followed by salinity and pressure[27-28]. Reservoirs are usually selected according to the criteria of “high temperature, high permeability, high specific heat, low pressure, low salinity”; among them, high temperature and high permeability are the key factors to be considered[29-30]. Orogenic geothermal systems are also an ideal choice for geothermal power production[31].

At present, the thermal-hydrodynamic-chemical-mechanical (THCM) multi-physics coupling in porous media is a difficult point. However, in the engineering practice of enhanced geothermal system, on the one hand, the interaction between reservoir and wellbore is not considered uniformly; on the other hand, there is a need to further refine the THCM model of hydrothermal systems, including the improvement of thermodynamic databases and dynamics databases.
2.3. Nuclear waste disposal

TOUGHREACT can be used to simulate multiphase mixtures of water and air with typical applications to vadose zone and nuclear waste disposal problems. In the selection of nuclear waste repository sites, hydrogeological conditions are of paramount importance. During the process of migration, nuclides will constantly have physical and chemical interactions with groundwater and rocks, such as adsorption, dissolution, precipitation[32-34], nuclides will be affected by storage geological conditions and other factors in the process of migration. Through analysis and summarization of domestic and foreign scholars' research, it mainly focuses on the following two aspects:

(1) Site selection of nuclear waste repository

Nuclide in groundwater will be affected by factors such as temperature and storage conditions during the migration process[35]. The kaolinite generated by water-rock interaction can effectively adsorb the nuclide. With the increase of depth, the alkalinity and reducibility of groundwater are enhanced, and the solubility is reduced, which is conducive to the disposal of nuclear waste[36]. In addition, the heat released by radionuclides will increase the temperature of the disposal repository. The water-rock interaction will be more intense when the temperature is higher, which will affect the movement of radioactive components. Therefore, the temperature of the repository should be lower than the saturation temperature of the aquifer[37].

(2) Corrosion of steel cans in the radionuclide repository

After the underground nuclear waste repository is closed, the content of water in the repository is little, and the contact area with the steel tank is small, so the corrosion rate is low. After reaching the anaerobic condition, the relative humidity of the surface of the corrosion tank is higher than 90%. The corrosion rate is high and the anaerobic corrosion of the steel tank leads to the production of H2, which may affect the long-term safety of the reservoir[38]. However, under atmospheric conditions, when the relative humidity is less than 90%, the corrosion rate of iron is significantly reduced[39]. Currently, the corrosion under anaerobic conditions is mainly studied.

2.4. Mineral recovery and silica fouling

In TOUGHREACT's EOS1 module, we can simulate the hydrothermal problems of water or two types of water by setting up mineral alteration and silica scaling in hydrothermal systems under natural and production conditions. Mineral alteration and silica scaling can occur in hydrothermal system under natural and production conditions, which may cause reservoir damage. The main influencing factors are analyzed and summarized as follows:

(1) Temperature factor

Heat can enhance the dissolution of wall rock minerals, leading to an increase in the solubility of pyrite[40]. Amorphous silica will not precipitate at low temperature, but will precipitate at high temperature due to evaporation and concentration caused by boiling[34,41]. The precipitated silica will significantly reduce the porosity and permeability near cracks[42-43].

(2) pH factor

Low pH value enhances the dissolution of sphalerite, but too low pH value will lead to the precipitation of sphalerite. The simulation shows that the most effective pH value is 4, which has certain guiding significance for the recovery of silica, manganese, silver, lead and lithium in the future[44].

At present, most simulation studies do not consider conditions such as gas species and ion exchange. In addition, the coarse grid model and uniform medium assumption conditions may not be able to estimate the degree of silica fouling in some zones.

2.5. Environmental pollution repair

In recent years, more and more attention has been paid to the impact of nitrogen fertilizer. Nitrogen fertilizer in agriculture has a direct impact on water (NO3-) and air pollution (N2O, NO and NH3)[45]. The N cycle model (TOUGHREACT-N) can test soil pH, NO, N2O, NH3 emissions after fertilization.
and irrigation and before emergence of plants[46-47]. With the increase of fertilizer application, the content of nitrifying bacteria is greatly increased, and the increase of application water leads to the decrease of nitrifying bacteria, but the amount of denitrifying bacteria is increased[46]. In coarse-textured soil, fertilizers containing NO$_3^-$ emits less N$_2$ than fertilizers containing NH$_4^+$, but releases more NO, while in fine-grained soil, N$_2$O is released more[48]. When soil alkalinity is high, NH$_3$ volatilization will be caused. Urea can produce the maximum nitrogen emission at a high fertilization rate[47].

In the future, TOUGHREACT can be applied to plant growth, carbon cycling, climate and agricultural production irrigation practices.

2.6. Others
In addition to the above five application areas, TOUGHREACT is also applied in the following six aspects:

1) Simulation of precipitation/dissolution of minerals in fractured caprock of magmatic hydrothermal systems[49].
2) Relationship between calcite precipitation and evaluation of infiltration fluxes in unsaturated fractured rock[50].
3) Multiphase reaction transport of stable isotope fractionation in pore water and steam in the unsaturated zone[51].
4) Geothermal convection and brine reflux of carbonate platform under hydrothermal drive[52].
5) The influence of the dope backflow mode of dolomitization on reservoir physical properties[53].
6) Supergene copper enrichment of a typical copper atom in fractured rocks[54].

3. Future trends
In the process of numerical simulation using TOUGHREACT, the following aspects can be considered in the future:

1) Most scholars only set up the one-dimensional and two-dimensional models in the process of numerical simulation. Affected by the method on mesh generation and reservoir heterogeneity, the established numerical model may be different from the actual formation. In future studies, in order to establish numerical models close to the actual situation, three-dimensional models can be combined with one-dimensional and two-dimensional models for analysis, which will be the trend of numerical simulation in the future.

2) Some scholars have combined the TOUGHREACT and FLAC$^{3D}$ to simulate the thermal-hydrodynamic-mechanical (THM) coupling process in porous media, which has certain guiding significance for the future development of the program code. In the future, it is necessary to consider the modelling of high salinity brines and reservoir modelling, coupling with geomechanics.

3) The current TOUGHREACT model only considers the most simplified transportation and dissolution reaction processes, excluding the dynamic evolution of complex solutions and leakage pathways such as fracture propagation. In the future, other factors of geochemical retention rate should be considered in order to develop refined models coupling more processes.

4) The overall parallelization of TOUGHREACT has not been fully realized, and it is necessary to parallelize the solute transport part of the coupling process. In the future integration, the coordination and synchronization of multiple processes will become the focus of a parallel integration task.

4. Conclusion
TOUGHREACT has been successfully applied in solving various energy and environmental issues. Its development has promoted the research on coupling simulation of complex physical and chemical reaction process in underground environment. The code has been widely used in CO$_2$ geological storage, geothermal energy development, nuclear waste disposal, mineral recovery and silica fouling, environmental pollution remediation fields, among which CO$_2$ geological storage is the most widely used. The main factors influencing CO$_2$ storage are primary mineral composition, reservoir
heterogeneity and temperature. CO₂ dissolved in shallow groundwater causes an increase in the acidity and the dissolution of minerals. The future trends of TOUGHREACT development may focus on the combination analysis of three-dimensional with two-dimensional models, development of refined models coupling multiple processes and connection of TOUGHREACT with other software to apply to more fields.

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