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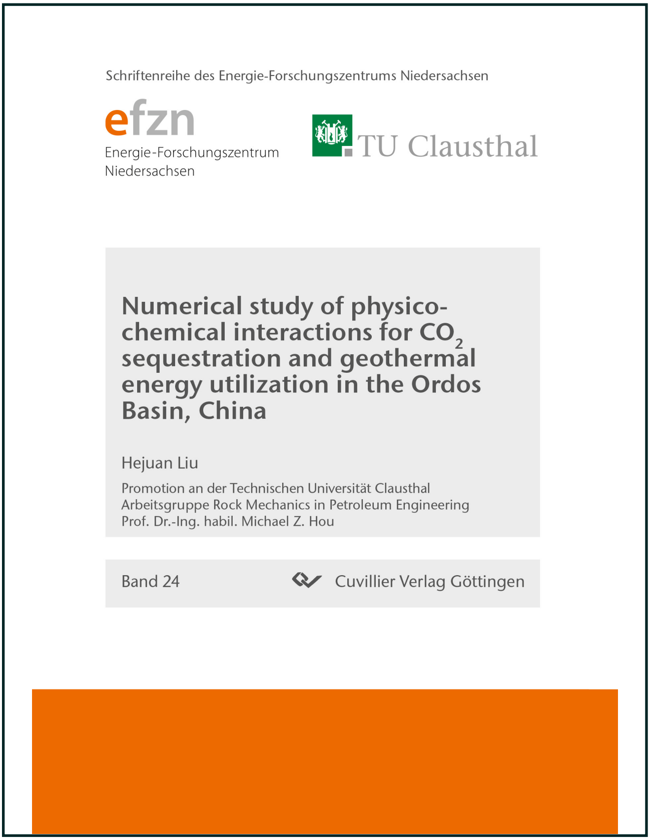

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Numerical study of physico-chemical interactions for CO_2 sequestration and geothermal energy utilization in the Ordos Basin, China

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1. Introduction

1.1 The carbon challenge

Carbon dioxide (CO_2) is a chemical compound composed of carbon and oxygen. A small amount of CO_2 in the atmosphere will play an important role in the Earth's environment which is regarded as an essential ingredient in the photosynthesis of plants and the life activities of animals (www.ipcc.ch). Plants can absorb CO_2 and release O_2 through photosynthesis. CO_2 can also be released through natural or human activities, for example, volcanic activity, combustion of fossil fuels (e.g. oil, natural gas and coal) and other organic compounds, the breathing processes of humans and other animals, etc.

Carbon dioxide (CO_2) has attracted worldwide attention since the last decade for being the main reason for global warming and the consequent potential threats to human beings (IPCC, 2007). Based on many investigations on climate change, it has been confirmed that the balance of the carbon cycle has been changing since the mid-20th century caused by the rapid development of industrialization (Court, 2011). The observed increase in global temperatures, which corresponds to the evolution of the CO_2 concentration in atmosphere (Fig. 1.1), makes the carbon dioxide (CO_2) emission problems become more obvious (IPCC, 2007).

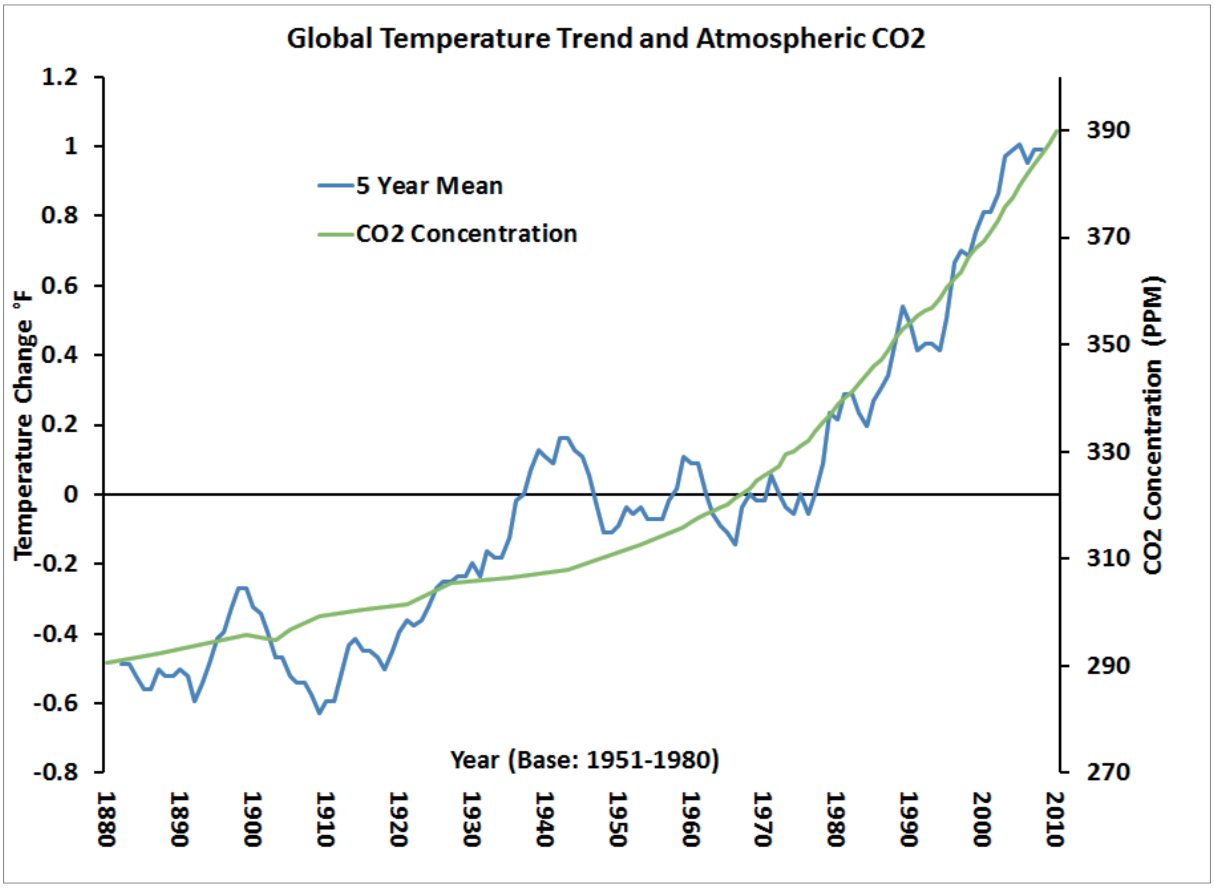


Fig. 1.1 Evolution of the concentration of atmospheric carbon dioxide with time over the past 130 years (from http://www.c2es.org/facts-figures/trends/co2-temp)

1.2 CCS introduction

1.2.1 CCS motivation

Aiming at the mitigation of global warming challenge, CO_2 emissions must be reduced through some strategies (Fig. 1.2), including the increase in energy efficiency, the use of renewable energy sources (i.e.

nuclear, wind, solar, geothermal, hydro power and marine energy) and clearner use of ordinary fossil fuels (De Visser et al., 2009). Based on the existing energy structure, coal still plays a dominant role in baseload electricity generation, satisfying 40% of the global electricity demand in 2010 (Court, 2011). In some countries, it may take a much higher percent. CO_2 emissions from large stationary sources, including power plants, cement factories, refineries etc., contributes almost 90% of the total amount of CO_2 in the atmosphere (IPCC, 2005). These point sources provide the possibility to reduce CO_2 emission by CO_2 Carbon Capture and Storage (**CCS**) technologies.

Reduce CO_2 emission methods		
1. Efficient Energy use	**2. Renewable Energy Resources**	**3. Cleaner Use of Fossil Fuels**
-Consumer -Buildings -Industries -Transport	-Wind energy -Solar energy -Bio-energy -Geothermal -Hydro power -Marine energy	-Carbon Capture and Storage (CCS) -Hydrogen -Fuel Cells

Fig. 1.2 Three strategies for reducing the CO_2 emission (modified from De Visser et al., 2009)

Table 1.1 Number of large point sources of CO_2 worldwide, with emissions of more than 0.1 million tonnes (Mt) per year (sourced from IPCC, 2005)

Process	Number of sources	Emissions ($MtCO_2$/yr)
Fossil fuels		
Power	4942	10539
Cement production	1175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	Not available	50
Other sources	90	33
Biomass		
Bioehanol and bioenergy	303	91
Total	**7887**	**13466**

1.2.2 CO_2 capture and geological sequestration

CCS technology first emerged during the early 1990s and has since then become worldwide spread. Recently, a delivative of CCS, namely carbon capture utilization and storage (CCUS) has become more popular and created a stir among several states due to its ability to utilize underground resources and conditions to generate further economic benefits and therefore offset costs on CO_2 sequestration (Harrison and Falcone, 2014; Xie et al., 2014). CCUS technology may be divided into three classes, namely chemical, biological and geological utilization. Geological utilization may be further subdivided into several forms including the use of CO_2 to enhance the recovery of oil (EOR), natural gas (CO_2-EGR), coalbed methane (CO_2-ECBM), geothermal system (CO_2-EGS), shale gas (CO_2-ESG) and carbon mineralization utilization (CO_2-CMU) (Bachu et al., 2008; Xie et al., 2014).

In general, **CCS** technology proceeds in three steps from capture to storage (IPCC, 2005): (1) **C**apture of **C**O_2 from a point source (i.e. a power plant, gasification synfuels plant, a cement or natural gas factory, etc.); (2) Transport of CO_2 to a suitable field site by trucks or pipelines; and (3) Storage or Sequestration of CO_2 in a deep geological formation of sedimentary basins, such as deep aquifer formations, depleted oil and gas reservoirs, deep unmineable coal seams etc (Fig. 1.3).

The idea of CO_2 sequestration came from the presence of natural CO_2 reservoirs distributed in North America, Australia, China, and Europe, illustrating that CO_2 can be stored underground for millions of years or even longer (Benson, 2005). In addition, the fact that a large quantity of CO_2 can be kept intact in many oil and gas reservoirs over geologic time scales shows that oil and gas reservoirs can also be used as the repository sites for CO_2. Among all the potential sites for CO_2 repository, deep aquifer formations seem to be more promising due to its widespread distribution. The CO_2-EOR technology, which involves injection of CO_2 into depleted oil reservoirs to enhance production of oil, was started in 1972 in America (Mathiassen, 2003). Similarly, CO_2-EGR technology is another form of CCUS that has been proposed recently to enhance natural gas recovery by injecting CO_2 into depleted gas reservoirs.

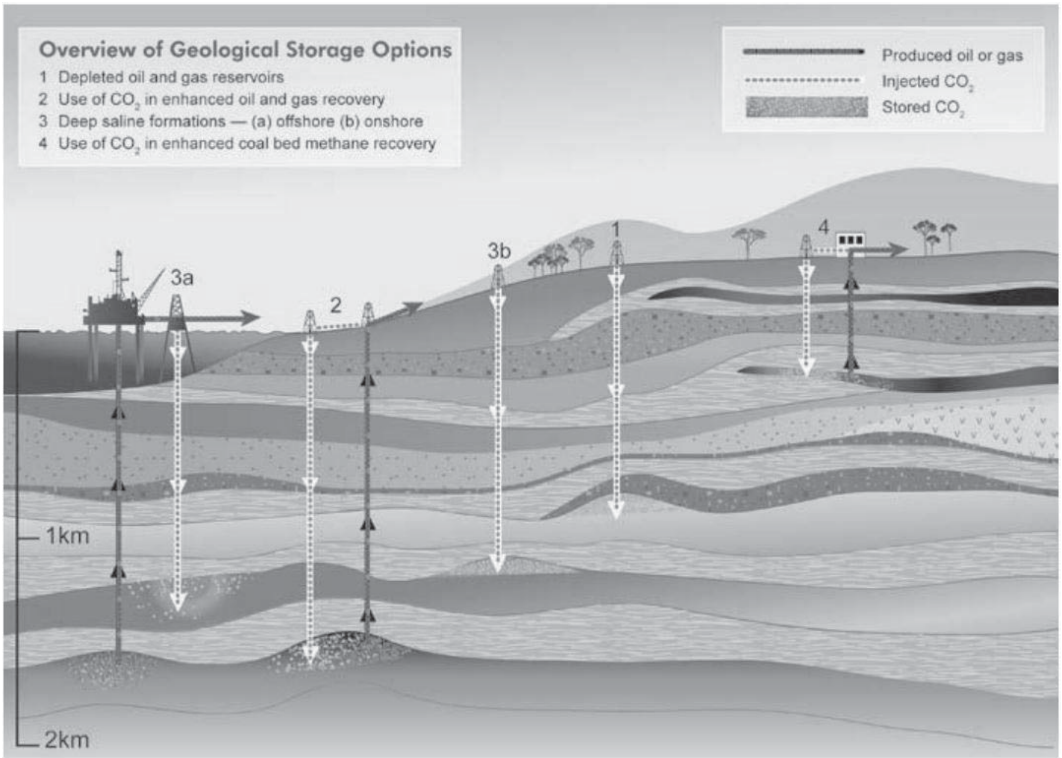


Fig. 1.3 Different CO_2 sequestration sites (IPCC, 2005)

Compared with hydrocarbon reservoirs, deep saline aquifers have the advantage that they are ubiquitous underground, and therefore possess the largest CO_2 sequestration capacity (Rutqvist, 2012). Moreover, it may be more economic if the CO_2 sequestration site in the deep saline formations can be launched close to a major CO_2 point source, saving the transport cost compared to other sites like depleted oil or gas reservoirs, coal beds, etc (Bennion and Bachu, 2005).

1.3 State-of-the-art and progress beyond

Based on ScienceDirect database, the number of the papers related to CO_2 sequestration has been analyzed. Fig. 1.4 shows the development trend of CCS technology during the last 20 years. The paper screening process has been carried out for three study categories: (1) total number of papers on studies about CO_2 storage, (2) papers on simulation studies related with CO_2 storage, and (3) papers on CO_2-rock-fluid interactions studies, see Fig. 1.4 A. In this dissertation, however, only study categories (2) and (3) have been considered, see Fig. 1.4 B. Furthermore, the two charts show that more attention has been paid on CCS sequestration particularly in the last 20 years.

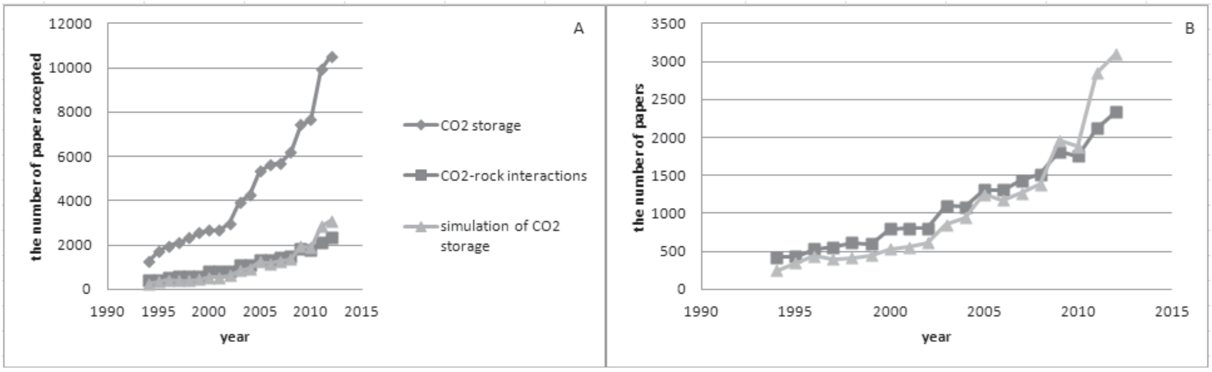


Fig. 1.4 Development of CCS technology in the last 20 years, (A) for all three study categories; (B) for only two study categories

CCS is a mature technology and can be applied immediately based, for example on the experiences already gained from almost 100 years of natural gas storage at numerous sites in North America and Europe (Perry, 2005). 30 years of CO_2-EOR in the USA and 15 years of acid gas (a mixture of CO_2 and H_2S) injection in western Canada (Bachu and Gunter, 2005b; Moritis, 2006), see Table 1.2. Carbon dioxide storage in depleted oil/gas reservoirs in conjunction with EOR and EGR are likely to be economically viable projects as the costs involved are likely to be offset by the production of the bypassed and residual oil and gas.

Governments, research centers, universities and several industries are working in conjuction to execute a large number of CCS projects for different purposes in various parts of the world. They cooperate with each other to ensure the successful running of the CCS projects. Usually, CO_2 sequestration projects are funded by different countries and companies, forming a close relationship with other countries and industries. From this point of view, CCS technology has already formed a big chain, connecting policy-makers, scientists, technologists and engineers together for a concrete solution.

Table 1.2 Examples of major CCS projects worldwide (adapted from IPCC, 2005)

Representa-tive project	**Country**	**Scale of project**	**Lead organizations**	**When Injection started**	**Injection rate**	**Total storage amount**	**Type of storage reservoir**	**Geological Storage formation**	**Age of storage formation**	**Lithology of storage formation**
Sleipner	Norway	Commerical	Statoil, IEA	1996	3000 t/day	20 Mt planned	Saline aquifer	Utsira formation	Tertiary	Sandstone
Fenn Big Valley	Canada	Pilot	Alberta Research Council	1998	50 t/day	200 t	CO_2-ECBM	Mannville Group	Cretaceous	Coal
Weyburn	Canada	Commerical	EnCana IEA	2000	3-5000 t/day	20 Mt planned	CO_2-EOR	Midale Formation	Mississippian	Carbonate
Minami-Nagoaka	Japan	Demonstration	Japanese Ministry of Economy, Trade and Industry	2002	Max 40 t/day	10,000 t planned	Saline aquifer	Haizume Formation	Pleistocene	sandstone
Recopol	Poland	Pilot	TNO-NITG	2003	1 t/day	10 t	ECBM	Silesian Basin	Carboniferous	Coal
Qinshui Basin	China	Pilot	Alberta Research Council	2003	30 t/day	150 t	ECBM	Shanxi Formation	Carboniferous-Permian	Coal
In Salah	Algeria	Commercial	Sonatrach, BP, Statoil	2004	3-4000 t/day	17 Mt planned	Depleted hydrocarbon reservoirs	Krechba Formation	Carboniferous	Sandstone
K12B	The Netherlands	Demonstration	Gaz de France	2004	100-10000 t/day (2006+)	about 8 Mt	EGR	Rotleigendes	Permian	Sandstone
Frio	USA	Pilot	Bureau of Economic Geology of the University of Texas	4-13 Oct. 2004	Approx. 177 t/day for 9 days	1600 t	Saline formation	Frio formation	tertiary	Brine-bearing sandstone-shale
Otway	Australia	Pilot	CO2CRC	late 2005	160 t/day for 2years	0.1 Mt	Saline formation and depleted gas field	Waarre Formation	Cretaceous	Sandstone
Ketzin	Germany	Demonstration	GFZ Potsdam	2006	100 t/day	60 kt	Saline formation	Stuttgart Formation	Triassic	Sandstone
CLEAN	Germany	Demonstration	GFZ Potsdam	2008-2011	274 t/day	0.1 Mt	Depleted gas reservoir	Rotliegend formation	Permian	Sandstone
Ordos Basin	China	Pilot	Shenhua	2010	100 t/day	Planned 0.1 Mt/year	Saline formation	Shanxi formation, Shihezi formation	Permian	Sandstone

1.3.1 Research scope of CO2 geological sequestration

Papers concerning the conceptual framework of Carbon Capture and Sequestration (**CCS**) were first presented in the early 1990s (e.g. Van der Meer, 1992, 1993; Winter and Bergman, 1993; Gunter et al., 1993; Holloway and Savage, 1993; Hendriks and Blok, 1993; Koide et al., 1993, 1995; Bachu et al., 1994; Bergman and Winter 1995; Holt et al., 1995; Weir et al., 1995). The injection sites are various, including deep saline formations, depleted gas or oil reservoirs, deep coal-beds and so on (Gunter et al., 1996; Byrer and Guthrie, 1997, 1998a, 1998b; Stevens et al., 1998a, 1998b; Somomon et al., 2007).

While rapid progress has been made in the development of CO_2 geologic sequestration since its inception (Benson, 2005), many countries take part in the exploration and engineering activities of suitable reservoirs. Lohuis (1993), for example, has worked on the feasibility of CCS in the Netherlands and Korbol and Kaddour (1995) introduced the practical situation of CCS in Norway. Furthermore, great progress has been made in the Alberta Basin of Canada (Bachu et al., 1994; Law and Bachu 1996; Gunter et al., 1996, 1997; Xu et al., 2003).

The worldwide implementation of CCS demands a comprehensive knowledge of the geological processes, safety and efficiency of the specific engineering project, impact on the environment, policy and law support. The main topics related with CO_2 sequestration have been concluded in detail by Benson (2005).

Geological Processes caused by CO_2 injection

Additional knowledge is needed in order to understand the physical and chemical geological processes that affect the long-term storage of CO_2 underground (Benson, 2005). These include its physical trapping beneath low-permeability cap rocks, immobile residual phase trapping, CO_2 plume movement in the reservoir or cap rock and geochemical solubility trapping in form of aqueous ions in solution or precipitation of solid carbonate minerals.

After the injection of supercritical CO_2 gas injection into the aquifers, three trapping mechanisms (i.e. structural, solubility and mineral trapping) begin to work. Mineral trapping (a chemical process whereby CO_2 can react directly or indirectly with minerals and organic matter existed in the geologic formation leading to the deposition of secondary minerals and organic matter) is the most potential and safest way to withdraw CO_2 gas from the atmosphere (Xu et al., 2006), because it can immobilize CO_2 as solid minerals in the long-term.

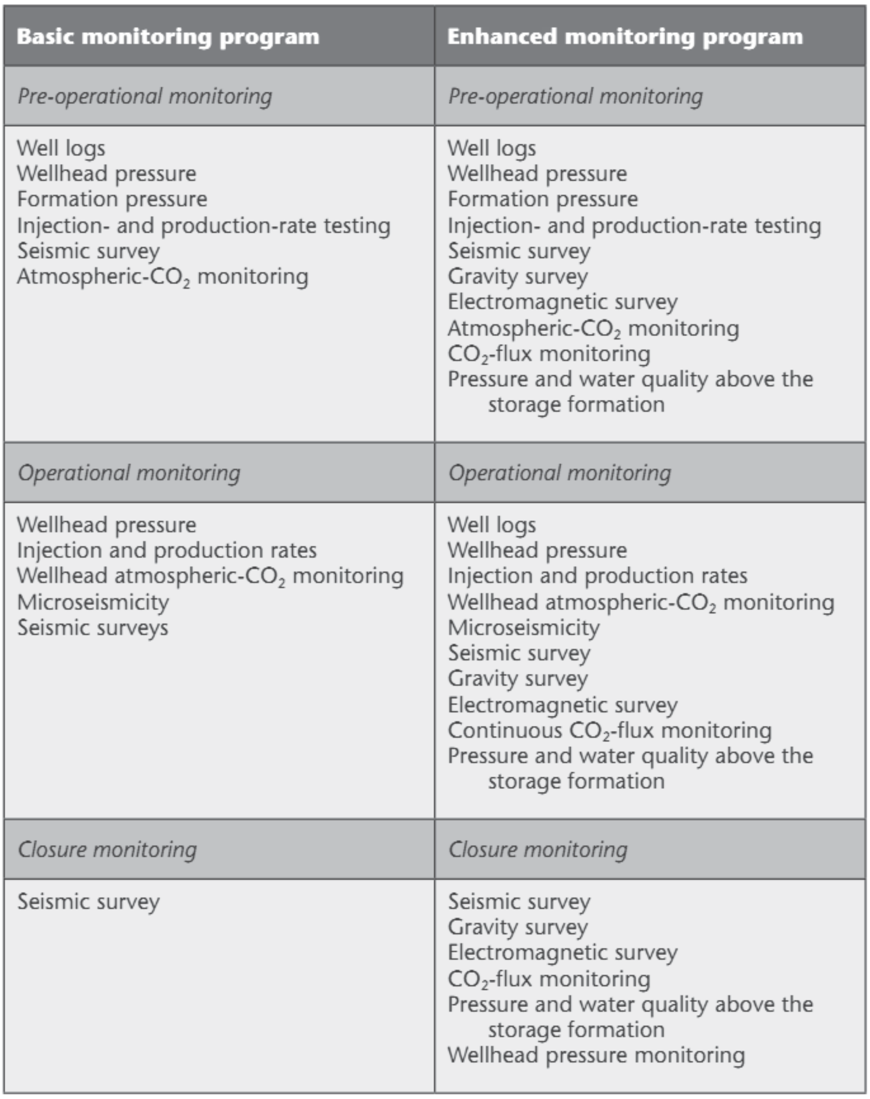
Storage efficiency

Geological sequestration of CO_2 can be economically efficiency by combination with its application for enhanced oil and gas production (Benson, 2005). Extra income from oil and gas recovery can offset the costs of CO_2 sequestration. Optimization can also be achieved through the efficient use of storage space underground. In brief, monitoring technologies can help to ensure storage efficiency in the following aspects: ① sweep efficiency monitoring; ② optimization EOR and enhanced coalbed-methane recovery.

Storage safety (Risk assessment and mitigation)

Engineering safety consideration is the highest priority when CO_2 storage project proceeds. Risk assessment and mitigation are essential during site selection processes. This allows the application of monitoring technology to provide us more detailed information about, for instance, the evolution of the reservoir, including pressure, composition of aqueous components changes, injection and production rates, geological structure and so on, from pre-operational to closure stage (Tables 1.3 and 1.4).

Table 1.3 Monitoring technology used in the lifespan of a detailed CO_2 sequestration project (adapted from Benson and Cole, 2008)



Basic monitoring program	Enhanced monitoring program
Pre-operational monitoring	*Pre-operational monitoring*
Well logs Wellhead pressure Formation pressure Injection- and production-rate testing Seismic survey Atmospheric-CO_2 monitoring	Well logs Wellhead pressure Formation pressure Injection- and production-rate testing Seismic survey Gravity survey Electromagnetic survey Atmospheric-CO_2 monitoring CO_2-flux monitoring Pressure and water quality above the storage formation
Operational monitoring	*Operational monitoring*
Wellhead pressure Injection and production rates Wellhead atmospheric-CO_2 monitoring Microseismicity Seismic surveys	Well logs Wellhead pressure Injection and production rates Wellhead atmospheric-CO_2 monitoring Microseismicity Seismic survey Gravity survey Electromagnetic survey Continuous CO_2-flux monitoring Pressure and water quality above the storage formation
Closure monitoring	*Closure monitoring*
Seismic survey	Seismic survey Gravity survey Electromagnetic survey CO_2-flux monitoring Pressure and water quality above the storage formation Wellhead pressure monitoring

Table 1.4 Monitoring methods and their purposes (adapted from Benson and Cook, 2005)

Surface devices	rates and compositions of injected and produced gases and liquids; atmospheric CO_2 concentration and flux monitoring; ecosystem monitoring;
Seismic methods	surface-to-borehole, single-well, and cross-borehole time-lapse seismic methods
Electrical methods	electrical resistance tomography and cross-well electromagnetic methods
Borehole Sensor methods	reservoir pressure and temperature measurements
Chemical tracers	quantify hydrodynamic, solubility, and mineral trapping rates and processes

Over the past few years, distinct progress has been made in risk assessment associated with CO_2 sequestration, especially with regard to the application of the features, events, and process (FEP) methodology (Benson, 2005). IPCC (2005) provides a detailed description of the potential environmental impacts caused by CO_2 leakage which can occur mainly through three ways: (1) abrupt leakage through injection well failure and abandoned wells; (2) gradual leakage through undetected faults and fractures; or (3) via diffusion leakage through bad qualified impermeable cap rock (Court, 2011).

Environmental friendly

Great progress has been made in understanding the severe consequences of CO_2 leakage on natural systems and human beings. Besides, some useful models have been applied to assess how CO_2 behaves after released into the near surface and the atmosphere (Benson and Cook, 2005; Morozova et al., 2011).

1.3.2 THMC geo-processes

A series of physical and chemical processes take place in the deep geological system (Fig. 1.5). The reaction rate for some of the processes, are fast, while others, require hundreds to thousands of years to complete. Overall, four processes are mainly recognized in the deep geological system as a result of CO_2 injection and storage: (1) heat transport (T), (2) geo-hydrological transport (H), (3) geomechanics (M) and (4) geochemical process (C). These processes couple or interact with each other, impacting changes to the petrophysical properties of the rock (Wang and Wang, 2004). For example, the petrophysical reservoir parameters including porosity, permeability, fluid composition, mineral content and rock stiffness may be spatially heterogeneous, depending on temperature, pressure, effective stress, chemical potential etc. In particular, fractured rocks that are characterized by dual porosity and permeability, may be altered during the THMC processes through many coupled mechanisms, such as stress-driven asperity dissolution (MC), thermal-hydro-mechanical asperity compaction/dilation (THM), and mineral precipitation/dissolution (HC) (Taron et al., 2009).

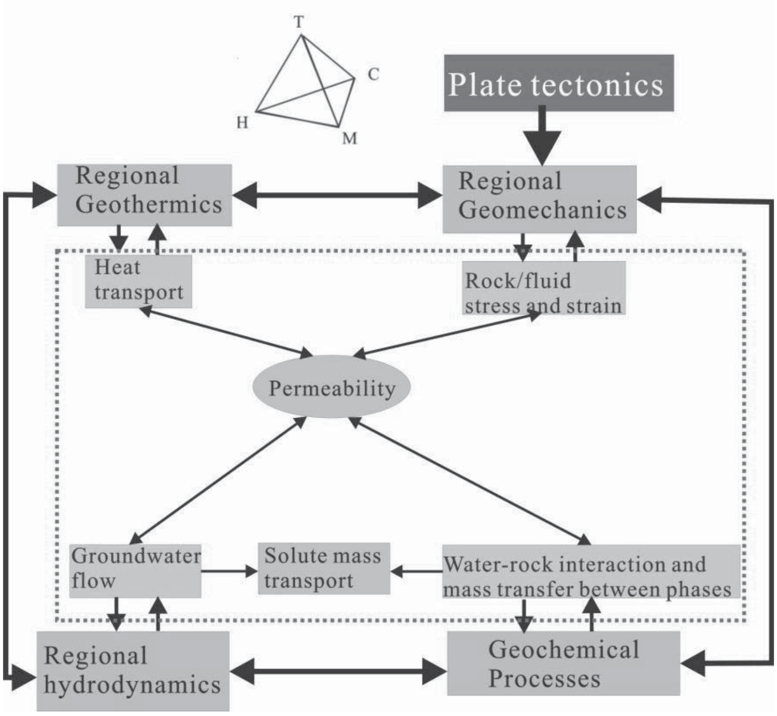


Fig. 1.5 Coupled thermo-hydro-chemo-mechanical effects in a large geosystem (after Stephansson et al., 2004)

Both experimental and simulation methods can be used in understanding the different scales of the T-H-M-C coupling processes (Schrefler and Gawin, 1996; Bower and Zyvoloski, 1997; Swenson et al., 2004; Taron et al., 2009). Within the context of numerical simulations, a diversity of complex T-H-M-C problems can be treated (e.g. coupling of different processes, consideration of heterogeneities under various geological conditions), although the development of efficiency and stability algorithms is always challenging (Goerke et al., 2011). Taron et al. (2009) proposed a method for fully THMC coupled study, using the simulators FLAC^{3D} and TOUGHREACT. However, it is still very little to know about the complex processes that are strongly dependent on a specific field with a range of uncertainties and scales (from micro-scale to macro-scale) of the geological model Furthermore, parameters of the physical structure of the reservoirs like permeability and strata geometries, description of multiphase fluid flow, behavior of the cap rock in response to CO_2-rich fluids etc., make it difficult to track the reality (Van der Meer et al., 2000; Huppert 2000; Rutqvist and Tsang, 2002; Johnson et al., 2001). Before the numerical model is used for prediction, the prescribed parameters must be adjusted to match the history of the real geological model. However, due to the limited availability of data, dubious parameters and the numerical dispersion problems make it hard to test the applicability of the assumptions inherent in simulation modeling (Bickle et al., 2007).

1.3.3 Geological model uncertainties

As regards to the site selection, suitable for CO_2 sequestration, it is essential to set up a 3-D geological model in terms of structure and heterogeneities (facies, mineral, petrophysical…) at different scales (basin, field, target formation). Structure information of the site can be understood using 2D or 3D seismic data. Different assumptions should be carefully used in light of the available data (Le et al., 2011). The heterogeneities at different scales cause the establishment of a geological model more difficult.

Petrophysical characteristics of a reservoir rock (Table 1.5) is mainly be composed of three main aspects: ① rock composition, including mineral composition and their relative contents, porosity, state of saturation state (unsaturated or saturated), properties of pore fluid (one phase/ multi-phase; one component or multi-component) and so on; ② rock structures, including grain size, grain shape, cementation, etc.; ③ thermodynamic environments, including temperature, pressure, stress fields etc (Wu and Yin, 2008).

Table 1.5 Petrophysical characteristics of a reservoir rock

Petrophysical properties	Parameters
Mechanical parameters	density, Young's modulus, bulk modulus, shear modulus, possion's ratio, compressive strength, tensile strength
Flow parameters	porosity, permeability, diffusion coefficient, dispersion
Electromagnetic parameters	magnetic conductivity, electric inductivity

To ensure the safety of a CCS project, more available data need to be added in the geological model. The geological uncertainties can be estimated using a statistical method, and the main risks associated with CO_2 storage should be assessed using key petrophysical characteristics of reservoir.

1.3.4 Dynamic simulation model

The injected CO_2 flows together with the other fluid components in the subsurface hydro-system which is a multiphase open system with changeable boundary conditions. Therefore, the flow and transport processes can occur at extremely different scales (see Fig. 1.6): including regional scale, geological structure scale, pore pace and molecular scale (Helmig, 1997).

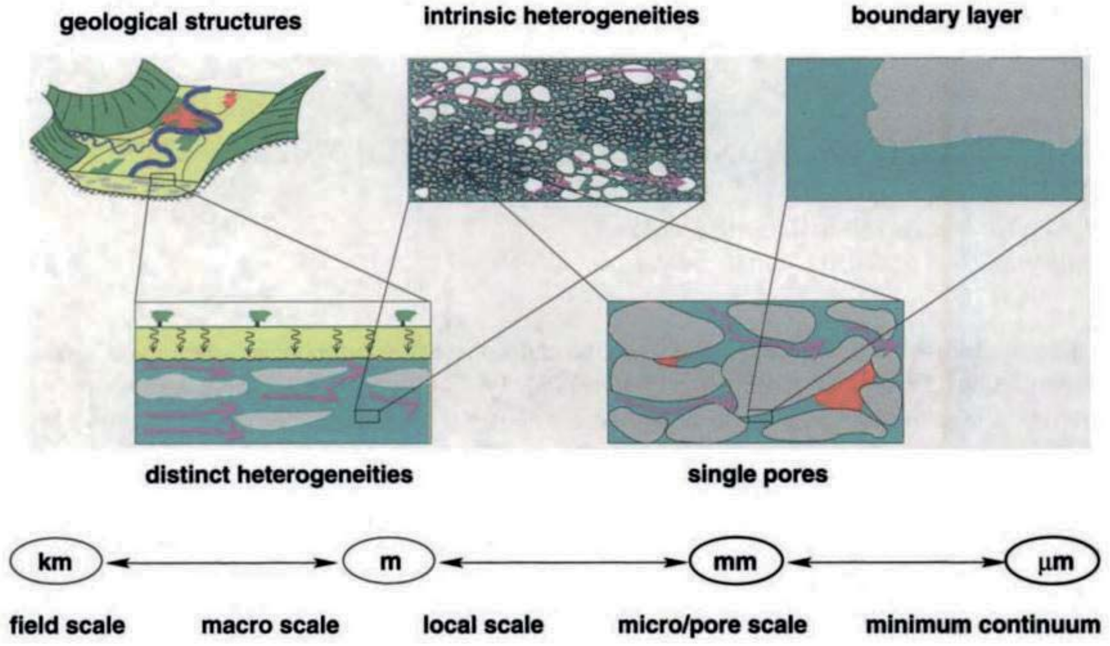


Fig. 1.6 Subsurface hydro-systems at different scales (Kobus and de Haar, 1995)

An optimal understanding of the complex physical, chemical and microbiological processes at different scales is fundamental to the efficient in-situ remediation techniques. Generation of the necessary model and of its corresponding prediction instruments is an interdisciplinary problem that combines several science research disciplines including many subjects from geology, geophysics, chemistry, hydrogeology, fluid mechanics, thermodynamics, mathematics and microbiology. The numerical models thus obtained, enable us to compare different hypotheses on the behavior of the complex system. Through numerical simulation, the following information about the geological processes can be obtained: (1) the CO_2 plume movement in porous media (as the CO_2 saturation changes); (2) the displacement of water, oil or gas by CO_2 in the pore space; (3) the pressure buildup during CO_2 injection; (4) the CO_2-water-rock interactions (the injected CO_2 can be immobilized in the form of dissolved aqueous phase-fraction of CO_2 dissolved in the water or mineral phase); (5) the variation of storage capacity and possibility of seismic events due to the changes in faults or failure stress field; (6) the potential risk of leakage through injection wells or abandoned wells.

Modeling of CO_2 sequestration processes involves the solutions of the component transport equations, the equations for thermodynamic equilibrium between the gas and aqueous phase, and the equations for geochemistry. The latter involves reactions between the aqueous species and mineral precipitation and dissolution. Modeling of reactive transport of components in the aqueous phase has also been a subject of the study in the field of hydro-geochemistry (Lasaga et al., 1993; Pruess et al., 2001). The main difficulties of the coupled modeling of transport and reactions are related to the size and nonlinearity of the resulting system of equations (Lichtner, 1985). There are mainly two approaches for solving the coupled system of equations: the **sequential solution method** and the **simultaneous solution method**. For the **sequential solution** approach, flow and chemical-equilibrium equations are solved separately and sequentially (Yeh et al., 1989, 1991; Mangold and Tsang, 1991; Sevougian et al., 1992; Reeves and Abriola, 1994; Steefel and MacQuarrie, 1996). Iteration methods are applied between the two systems until convergence is achieved. For the **simultaneous solution** approach (fully-coupled method), recognized as the most stable approach, all equations are solved simultaneously using Newton interation (Lichtner, 1992; Steefel and Lasaga, 1992, 1994).

The prediction model will be much precise when verifications are used. It is a step by step process from conceptual model to true 3D geological model, which can be described in detail in Fig. 1.7.

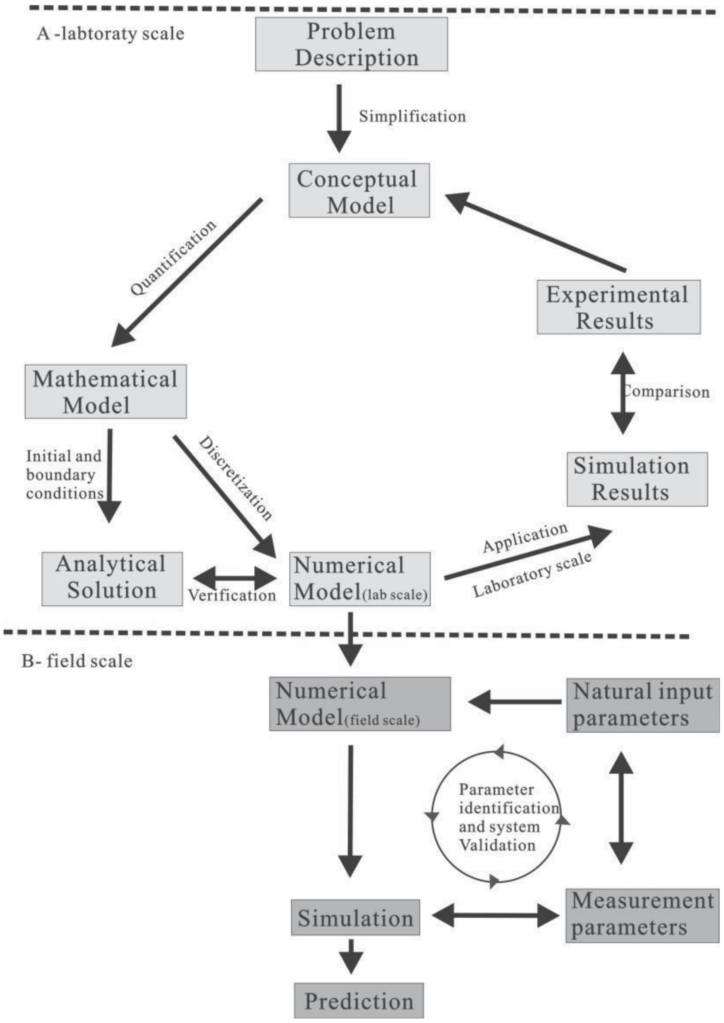


Fig. 1.7 Step by step processes from conceptual model to prediction (after Helmig, 1997)

Realistic 3D modeling of fluid flow in a sedimentary basin is almost impossible as the permeability distribution can not be predicted precisely due to the strong heterogeneity induced by the complicated sedimentary facies, diagenesis and tectonic development (Bjϕrlykke et al., 2004). Corresponding to the different scale of subsurface hydro-system, dynamic models for CO_2 sequestration can also be elaborated at different scales, for example, regional scale model, storage site model, near-well region model and pore-scale model (Table 1.6).

Table 1.6 Different scales of dynamic modeling and their targets

Scale of modeling	Problems to solve
Regional-scale	Estimate migration pathways and constraint boundary conditions
Field storage site	Estimate overpressure and CO_2 plume behavior
Near-well region	Estimate chemical induced effects
Pore-scale	Estimate microscopic mineral and fluid changes

1.3.4.1 Multi-phase, multi-component reactive transport simulation (TH^2C)

Due to the geological heterogeneity of porous media and the multiple components involved, single phase reactive tranport process is complex. When two or multiple phases (water/oil or gas) are considered, the flow properties (EOS-equation of state) become even more complicated. For instance, when CO_2 is injected into deep saline formations, it is always at a supercritical state and flows together with the connate water. The mass balance equations in such a multiphase system are described by more complicated laws than in the case of single-phase condition (Bear, 1972; Lake, 1989; Pankow and Cherry, 1996).

In this dissertation, TOUGH2MP and TOUGHREACT codes have been used in the simulation of multiphase multicomponent fluid flow and derived multi-field coupled problems in the deep saline formation, e.g., CO_2 plume movement, pressure buildup, CO_2-water-rock interactions etc.

TOUGH2-MP is a product belonging to the family of TOUGH. TOUGH2MP is a numerical simulator for non-isothermal flow of multi-components, multi-phase fluids in one, two, and three-dimensional porous and fractured media (Pruess et al., 1999). The first TOUGH simulator, TOUGH2, was developed in 1991 (Pruess, 1991). Since then, more modules have been added. And TOUGH series products becomes more and more effective in handling scientific and engineering problems, including T2VOC, TMVOC, TOUGH2-MP, TOUGHREACT, TOUGH+, iTOUGH2. The TOUGHREACT simulator is a supplement to the TOUGH family and useful for geochemical reaction simulations. A wide range of complex subsurface thermo-physical-chemical heterogeneity processes are considered under various thermohydrological and geochemical conditions of pressure, temperature, water saturation, and ionic strength (Xu et al., 2003) inlcuding: (1) fluid flow in multiple phases under different pressure and gravity forces, (2) capillary pressure effects for the liquid phase, and (3) heat flow controlled by conduction, convection and diffusion mechanisms.

Many other computer code simulators have been developed to study the coupling effects of multi-scale, multi-phase, multi-physical, dynamic model in the geologically complex systems, for example, FEHM, COMSOL Multiphysics, SHEMAT, CMG- GEM and OGS etc (Table 1.7). The aim is to provide a flexible numerical framework for solving multifield problems in porous and fractured media for applications in geosciences and hydrology (Kolditz et al., 2012). Most of these simulators are able to solve partial differential equations that describe the complicated physical phenomenon, using either the finite element or finite difference theory.

Table 1.7 Simulators used in CO_2 sequestration

Simulator	**Full name**	**Research scope**	**Solution method**	**Developer**
FEHM	**F**inite **E**lement **H**eat and **M**ass	From single fluid/single phase to multi-fluid/multi-phase fluid flow	FEM (Finite Element Method)	Los Alamos National Laboratory (LANL)-1980s
TOUGH2	**T**ransport **O**f **U**nsaturated **G**roundwater and **H**eat	From single fluid/single phase to multi-fluid/multi-phase fluid flow (water, vapor, non-condensible gas and heat) in porous and fractured media	FDM (Finite Difference Method)	Lawrence Berkeley National Laboratory (LBNL) in the early 1980s
TOUGHREACT	Non-isothermal reactive geochemical transport model	Adding reactive geochemistry into the framework of TOUGH2	FDM (Finite Difference Method)	Lawrence Berkeley National Laboratory (LBNL) Version 1 at 1998
COMSOL Multiphysics	-	For various physical processes, especially coupled phenomena or multiphysics	FEM (Finite Element Method)	COMSOL GROUP, Sweden, 1986
SHEMAT	**S**imulator of **HE**at and **MA**ss **T**ransport	Simulating steady-state and transient processes in hydro-geothermal reservoirs in two and three dimensions, including fluid flow, heat convection and mass transport	FDM (Finite Difference Method)	RWTH Aachen, Germany,
CMG- GEM	**C**omputer **M**odeling **G**roup-**G**eneral **E**quation of state **M**odel	Thermodynamic properties, geochemical reactions and phase change during CO_2 sequestration in underground formation		Commercial software, CMG GROUP, 2008
ECLIPSE	**-**	Reservoir simulations: Black Oil module and Compositional module	FDM (Finite Difference Method)	Commercial software, Schlumberger Ltd.
O**pen**G**eo**S**ys**	-	Numerical simulations of individual or coupled thermo-hydro-mechanical-chemical (**THMC**)processes in porous and fractured media	FEM (Finite Element Method)	UFZ, Germany,

1.3.4.2 Rock mechanics simulation (THM)

FLAC3D is a three-dimensional explicit finite difference program used for the computation of geotechnical engineering mechanics (Itasca, 2009). It can simulate the behavior of three-dimensional structures comprised of soil, rock or other materials that can undergo plastic flow after yield state. Explicit formulation is used in the simulation, which can be overcome by both automatic inertia scaling and automatic damping.

FLAC3D offers several models to represent the mechanical response of the geological materials (Itasca, 2009). For example, the “null” model; the three elasticity models (isotropic, transversely isotropic and orthotropic elasticity); and the nine plasticity models (Drucker-Prager, Mohr-Coulomb, strain-hardening/softening, ubiquitous-joint, bilinear strain-hardening/softening ubiquitous-joint, double-yield, modified Camclay, Cysoil and Hoek-Brown).

1.4 Research objectives, contents and structure

When injected deep into saline formations, supercritical CO_2 will be able to both migrate and reside within the aquifer. However, the migration or leakage of the CO_2 plume into potable groundwater reservoirs can lead to pollution of the groundwater resources. In order to estimate the potential risk of CO_2 infiltration, and eventually plan an appropriate remedial program, the characteristic temporal/spatial changes of the CO_2 plume in the storage aquifer must be well known.

The purpose of CO_2 sequestration is to immobilize CO_2 into suitable underground reservoirs, on long-term basis. Therefore, its characteristic migration of CO_2 in the reservoir and cap rock, together with its corresponding response to changes in the reservoir temperature (T), hydraulic field (H), mechanical field (M) and chemical field(C) should be adequately investigated, to ensure the safety (avoidance the possible leakage of CO_2), capacity, and injectivity of CO_2 for sequestration at any specific site. In this thesis, the deep saline formations in Ordos Basin of China have been selected targets for demonstration of CO_2 sequestration.

This thesis finds basis on the reviews of the progress and probable problems associated with CO_2 sequestration, at the demonstration site located in the Ordos Basin. The project has selected for study the deep multilayered saline formations as CO_2 injection points using basic experiments, analytical methods and numerical simulations. In this dissertation, the following topics have been studied and discussed in detail (see Table 1.8): (1) the review on CO_2 flow and distribution characteristics, and CO_2 sequestration mechanisms; (2) a detailed summary of the geological characteristics of the Ordos Basin, particularly the target injection aquifer layers; (3) description of the two phase (CO_2 and H_2O) fluid flow processes in the multilayered reservoir-cap rock systems and analysis of uncertainties due to the heterogeneity of the geology in the Ordos Basin; (4) description of the coupled hydro-mechanical processes induced by CO_2 injection; (5) simulation of the water-rock interactions caused by CO_2 injection; (6) simulation of geothermal production associated with CO_2 sequestration. Consequently, site selection criteria have been discussed in detail, including their application to CO_2 sequestration and geothermal production in China.

First, the relevant data was collected from literature about the pilot CO_2 sequestration project launched in Ordos Basin. Geological models were then set up according to the input data. To understand the characteristic distribution and storage mechanisms of CO_2, characteristic movement of the CO_2 plume in the multi-layered reservoir (by the multi-layer injection technique) was studied. This was followed by studying the impact of some relevant factors (e.g. permeability, boundary conditions, injection rate, geological structure, irreducible gas saturation etc.). CO_2 migration and the induced physic-chemical processes during injection and post-injection periods were discussed, including coupled processes of H^2, H^2M, H^2C, etc. The utilization of CO_2 (for e.g. EOR, EGR, and EGS) has attracted much attention for further research, mainly due to the economical benefits involved in the processes. For instance, when CO_2 is injected into a geothermal reservoir, it will act to enhance the pressure driving force. Though a lot of research has been carried out on this topic, only a fundamental understanding of the processes related with CO_2 sequestration has been obtained so far. The fully coupled THMC processes still require more research studies, especially the constitutive relationships between the various physical fields established during and after the sequestration. Furthermore, realistic 3D modeling of fluid flow in a sedimentary basin is nearly impossible as permeability distribution can not be predicted precisely, due to the strong heterogeneity of the sedimentary basins, with respect to primary sedimentary facies, diagenesis and tectonic development (Bj*Φ*rlzkke et al., 2004). Though faced with many difficulties (e.g. the strongly varied heterogeneity of the geology, limited access to geological and operation data, etc.), simulation results of this thesis may provide some invaluable understanding of sequestration processes and some guidance for future commercial /industrial scale CCS operation.

Table 1.8 Research structure of this thesis

Literature Review • The relevant geological processes caused by CO_2 injection • CO_2 based geothermal production • Geological characteristics of the Ordos Basin		
Numerical simulation of CO_2 sequestration		
CO_2-H_2O two phase fluid flow (H^2)-by TOUGH2MP	**The interaction of fluid flow and mechanical changes (H^2M)-TOUGH2MP+FLAC^{3D}**	**CO_2-water-rock interactions (H^2C) -by TOUGHREACT**
Geometric model: simplified 3D multilayered reservoir-caprock system **Input data source:** Ordos Basin **Uncertainties, parameters and analysis:** Injection strategy; Boundary effect; Reservoir permeability; Geological structures; Multiphase effect (relative permeability and capillary pressure)	**Geometric model:** simplified multilayered reservoir-cap rock system **Input data source:** Ordos Basin **Uncertainties, parameters and analysis:** In situ stress fields; Reservoir permeability; Biot coefficient; **Results analysis:** Pore pressure; In situ stress changes; Fluid migration; Vertical displacement, etc.	**Geometric model:** batch, 1D and 2D studies **Input data source:** Ordos Basin **Uncertainties, parameters and analysis:** Water chemistry; Mineral composition **Results analysis:** Ion concentration changes; Mineral volume fraction Changes; Porosity and permeability; Propagation distance
Simulation of CO_2 sequestration associated with geothermal production		
Geometric model: simplified 3D multilayered reservoir-caprock system	**Parameters Data source:** some are from Ordos Basin, some are just assumed	**Well configuration:** one injection well+ two production wells + two reinjection wells
Site selection criteria for CO_2 sequestration and geothermal production		
Evaluation processes: Country-level; Sedimentary basin-level; Target area of interest-level; Site-level	**Different scales of the selection criteria:** Basin scale; Field scale; Target formation scale; Engineering operation scale	**Screening and ranking methods and its application in China**

2. CO_2 sequestration project in Ordos Basin

2.1 CCS project in Ordos Basin of China

In recent years many large projects related with coal transformation energy have been constructed in Ordos Basin, including many large coal chemical industry projects (coal to liquid, coal to methanol, coal to olefins, coal liquefaction (DCL), coal to gas). As much as 8.7 Mt/year CO_2 will be released if all the existing projects are in operation. If all the planned projects are completed, the emission amount will rise to about 54 Mt/year (Table 2.1, Ren et al., 2010). Therefore, CCS technology has the potential advantage to reduce CO_2 emission in Ordos Basin.

Table 2.1 Large coal chemical industrial projects constructed in the Ordos Basin (Ren et al., 2010)

Company	Project name	Scale	City
Shenhua GROUP	Direct coal liquefaction(DCL)	1.08 Mt/year	Ordos
Shenhua GROUP	Substitute natural gas(SNG)	2B m^3/year	Ordos
Shenhua GROUP	Coal to olefins (CTO)	0.6 Mt/year	Baotou
Datang GROUP	SNG	4B m^3/year	Ordos
Yidong GROUP	Coal to methanol(CTM)	1.20 Mt/year	Ordos
Xin’ao GROUP	CTM	0.6 Mt/year	Ordos
Jiutai ENERGY	CTM	1.00 Mt/year	Ordos
Yitai GROUP	Indirect coal liquefaction(ICL)	0.16 Mt/year	Ordos
Shenhua Ningxia Coal Industry Group (SNCIG)	CTO	0.52 Mt/year	Yinchuan
SNCIG	CTM	0.85 Mt/year	Yinchuan
Rong Yu Shi Ye company	CTMO	1.80 Mt/year	Yulin

The Ordos Basin has been a favorite for the generation of several petroleum systems (Fig. 2.1), including four large gas fields (i.e. Yulin, Wushenqi, Sulige and Jingbian) in the Upper Paleozoic and one large oil field (Mizhi), with an estimated reserve of more than hundreds of billon cubic meter (Yang et al., 2004). The CO_2 sequestration project launched in the Ordos Basin, under the leadership of SHENHUA GROUP, is the first full scale (from capture to injection) CCS project in saline formation in China. The purpose of CO_2 sequestration is to immobilize the CO_2 produced during the processes of coal liquefaction to oil, thus reduce the emission of CO_2 to the atmosphere. The CCS pilot project was started in 2010, with an estimated injection capacity of 0.1 Mt/year (Table 2.2). Till 2014.8, about 220,000 tons of CO_2 has already been injected into underground saline formations. The wellhead injection pressure is at 4.98 MPa, with a flow rate 17.23 m^3/h. Under this condition (injection pressure and ambient temperature), CO_2 is at liquid state at the surface. The CO_2 sequestration site belongs to Wulanmulun town (Fig. 2.1), about 17 km away from coal direct liquefaction factory of Shenhua GROUP. Three wells have been drilled for demonstration purpose, i.e. 1 injection and 2 monitoring wells located 31 m and 70 m away from the injection well.

Table 2.2 Timelines for the pilot scale CO_2 sequestration project launched in Ordos Basin (Liu et al., 2014a)

Start time	Task
2008.10	First-phase involved the preparation of a feasibility study of CO_2 capture and sequestraiton
2009.12	Feasibility study completed
2010.05	3D exploration seismics of demonstration area completed
2010.06	Installation of the CO_2 capture equipment started
2010.08	Drilling of injection well started
2010.12	Capture equipment switched on at the Shenhua CTL plant
2011.01	Injection test carried out
2011.05	Started injection successfully
Till 2014.8	Injection amount of CO_2 about 220,000 tones