Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Energy Procedia 4 (2011) 5350–5357

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-10

Sayindere cap rock integrity during possible CO_2 sequestration in Turkey

Chantsalmaa Dalkhaa[(a)] *, Ender Okandan[(a)]

[a]*Middle East Technical University*

Abstract

One way to reduce the amount of CO2 in the atmosphere for the mitigation of climate change is to capture the CO2 and inject it into geological formations. The most important public concern about carbon capture and storage (CCS) is whether stored CO2 will leak into groundwater sources and finally into the atmosphere. To prevent the leakage, the possible leakage paths and the mechanisms triggering the paths must be examined and identified. It is known that the leakage paths can be due to CO_2 - rock interaction and CO_2 – well interaction.

The objective of this research is to identify the geochemical reactions of the dissolved CO_2 in the synthetic formation water with the rock minerals of the Sayindere cap rock by laboratory experiments. It is also aimed to model and simulate the experiments using ToughReact software. Sayindere formation is a regionally extensive cap rock for many oil fields in southeastern Turkey.
The mineralogical investigation and fluid chemistry analysis of the experiments show that calcite was dissolved from the cap rock core as a result of CO2- water- rock interaction.

Using the reactive transport code TOUGHREACT, the modeling of the dynamic experiment is performed. Calcite, the main primary mineral in the Sayindere is dissolved first and then re-precipitated during the simulation process. The decreases of 0.01 % in the porosity and 0.03% in permeability of the packed core of the Sayindere cap rock are observed in the simulation. The simulation was continued for 25 years without CO_2 injection. However, the results of this simulation show that the porosity and permeability are increased by 0.001 % and 0.004 %, respectively due to the CO_2-water-rock mineral interaction. This shows that the Sayindere cap rock integrity must be monitored in the field if application is planned.

Keywords: CO_2 storage, cap rock integrity, CO_2- water- rock interaction, geochemical modeling and simulation
* Corresponding author. Tel.: +90 535 817 9919; fax: +90 312 210 4883.
E-mail address: dchantsa@gmail.com.

doi:10.1016/j.egypro.2011.02.517

1. Introduction

CO_2 is the main greenhouse gas emitted into the atmosphere, causing the global warming. The CO_2 sources responsible for its increased emission are thermal power generation, refineries, cement plants, petrochemical plants and growing large industrial complexes.

There are several means to reduce the amount of CO_2 emission into the atmosphere such as increasing the energy efficiency of energy production, reducing the carbon intensity by substituting lower carbon or carbon free energy sources and finally carbon dioxide capture and storage (CCS). CCS is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere. CO_2 can be stored into geological formation such as deep saline aquifers, depleted gas and oil reservoirs, oceans and unmined coal beds.
However, it is crucial to prove the long term reliability and safety of CO_2 geological storage. The injected and stored CO_2 may migrate into groundwater sources and contaminate them and may even reach the surface and leak back to the atmosphere. If it is the case, then it means the process is not working as a climate change mitigation method. Therefore, the assessment of CO_2 sequestration needs to be carried out on the basis of a better understanding of in situ physical and chemical processes induced by CO_2 injection and storage, of improved numerical modeling of CO_2 fate and a detailed knowledge of relevant site characterization. There are many risks associated with CO_2 storage. One of the risks is the dissolution of cap rock by acidic CO_2-rich fluids resulting from CO_2 injection. During underground CO2 storage, the containment of CO2 will be crucially dependent on the cap rock integrity above the CO2. Thus, it is necessary to evaluate how the CO2 might impact cap rocks, since this could control the ultimate longevity of CO2 storage.

It is known that the injected supercritical CO_2 moves upward with favorable vertical permeability and the buoyancy effects, from the injection point and accumulates under the overlying cap rock after a few years of injection. Once the CO_2 has reached the base of the cap rock it will dissolve into the cap rock formation water and then diffuse vertically upward into the cap rock. The cap rock formation water is acidized as the CO_2 dissolves in it. The acidification due the solubility of CO_2 into brine results in geochemical reactions with the rock minerals present in the cap rock.

Geochemical reactions between dissolved CO_2 and the minerals present in the cap rock lead to porosity and thus permeability changes. Porosity can be increased due the dissolution of initial cap rock minerals in the acidized formation water whereas it can be decreased as a result of the precipitation of secondary minerals (minerals which are not available at the beginning of the reaction). A porosity increase would be undesirable since this would make the injected CO_2 leak through the cap rock while this is good for the reservoir rock regarding the higher storage capacity. However, a porosity decrease is an advantage, which would further increase the sealing capacity of the cap rock.

2. Materials for the research

For this work, 6 core plugs were provided by Turkish National Oil Corporation (TPAO) from Sayındere formation which is a regionally extensive cap rock for many oil fields in southeastern Turkey, particularly; it is the cap rock the Caylarbasi field. The Caylarbasi field is selected site for a prefeasibility study on CO_2 storage project. The formation water analysis of Caylarbasi reservoir is available but not the Sayindere cap rock. Thus, the Sayindere formation water is assumed same as the Caylarbasi reservoir water and according to this water composition, the Sayindere cap rock water is synthetically prepared and used in the both static and dynamic experiments. Table 1 show the synthetic formation water analysis.

Table 1.The synthetic formation water composition

	ppm
Sodium	693.2
Calcium	41.92
Magnesium	47.36
Iron	1.190
Sulfate	15
Chloride	725
Bicarbonate	613
pH	7.453

3. Experimental investigation

Two different experiments are carried out: *static (batch)* and *dynamic (flow through)*.

3.1 Static experiment

The static experiment is performed at the temperature of 90 °C and the pressure of approximately 100 bar, representing the field condition. In the static experiment, the original cores from the Sayindere cap rock are kept within the CO_2-synthetic formation water under the given reservoir pressure and temperature. The experimental set-up is given in Figure 1. The static experiment is composed of two experiments: *30-day experiment and 100-day experiment*. After 30 and 100 days of the static experiments, SEM (Scanning Electron Microscopy) analyses of the cores are made to see any mineralogical changes on the core surfaces. Moreover, the fluid chemistry analyses of the mixtures in the core holders are made to investigate the possible geochemical reactions induced by CO_2 –formation water.

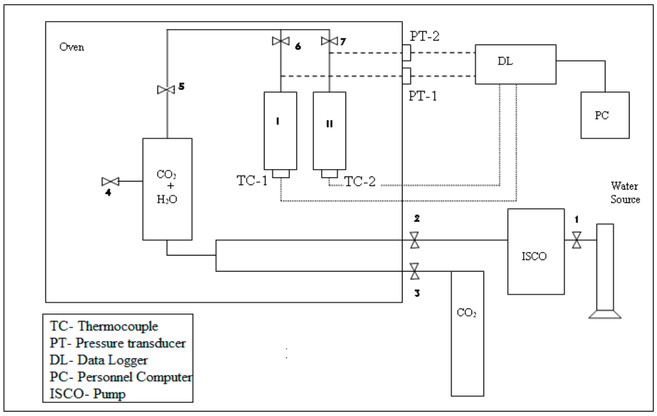

Figure 1. Scheme of the static experimental set-up

From the photos taken in SEM analysis of the 30 day experiment, it is seen that the near to surface are more loose than the inner part of the core, which shows the CO_2 diffusion into the core (Figure 2).

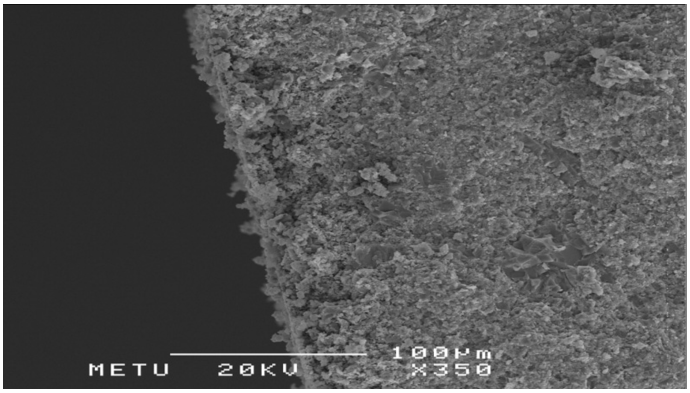

Figure 2. SEM photo of the core after 30- day static experiment

It is observed that there is a deposition layer, which is whiter colored in SEM photos of the 100 day experiment (Figure 3). Since there was no flow in the static experiment, there was no transport of the reactant and reaction products. Thus, the formation of deposition layer is explained as the dissolved particles, specifically the dissolved calcite from the core minerals were deposited back on the core surfaces. Moreover, it is observed in the mineral investigation by SEM analysis of 100-day experiment that there are wormholes on the core used in the experiment, possibly created due to the heterogeneous pattern of calcite dissolution induced by the CO_2-formation water (Figure 4)

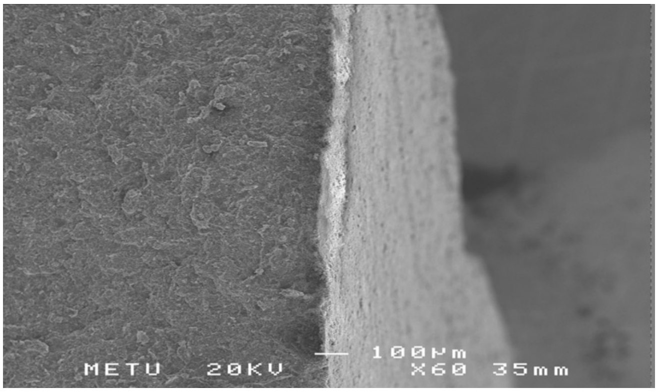

Figure 3. Deposition layer

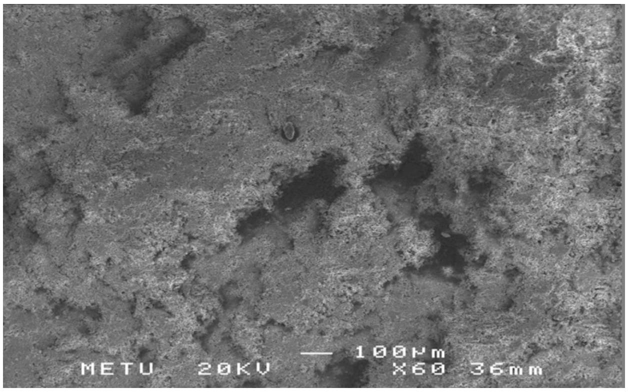

Figure 4. Wormholes

The fluid chemistry analyses of the 30- and 100- day static experiments show that the calcite is dissolved. The anions available in the water are measured by Ion Chromatography (IP) and the cations present in the water are measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Alkalinity is determined by titration technique.

3.2 Dynamic experiment

In dynamic experiment, the cores from Sayindere cap rock are grinded and packed into a core holder and CO_2 saturated- synthetically prepared water is injected through the packed core for 99 days. Since the cores were very impermeable, they were ground so that a flow could be maintained throughout the experiment. Moreover, grinding of solid cores increases the rate of reaction in three ways. The first effect is to increase the surface area of the grains which allows a larger interface for reaction; the second is that the creation of fresh surfaces often results in high energy sites being exposed; and the third effect is that grains which were previously armoured by other grains, now have surfaces which would be in direct contact with the water.

Before the dynamic experiment, the carbonate removal from the grinded powder of the cores with acid treatment and XRD analysis are performed. From these analyses, the core from the Sayindere cap rock is composed of 76% calcite, 22.7 % quartz and 1.3 % kaolinite. The experimental condition was at a temperature of 90 ˚C and an injection pressure of 75 bar. The outlet pressure is set at the pressure of 74 bar.

The dynamic experimental set-up is given in Figure 5. The fluid is discharging out of the core holder under 1 bar pressure difference. The discharged fluid is collected and water analyses are carried out from collected water samples at 3 different times (23, 75 and 99 days) throughout the experiment to see changes in the amount of the dissolved species in the synthetic formation water.

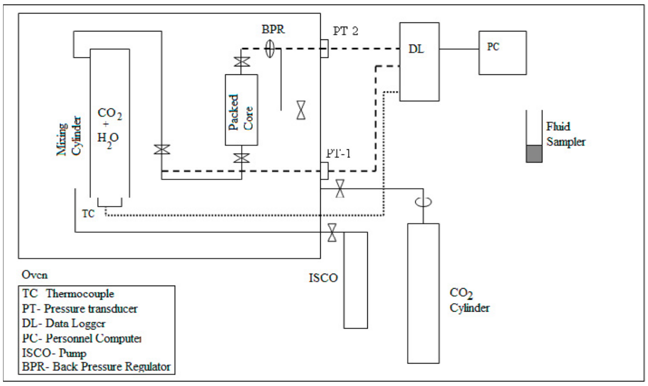

Figure 5. Scheme of the dynamic experimental set-up

Only water chemistry analyses of the dynamic experiment are made. Based on the water chemistry analysis, this is interpreted as calcite is dissolved. Table 2 shows the fluid analysis of the discharged water during the dynamic experiment

Table 2. Fluid Analysis of the Discharged Water during the dynamic experiment

	ppm (prior to the exp.)	ppm (after 23 days)	ppm (after 75 days)	ppm (after 99 days)
Sodium	519.0 ± 2.1	602.6±11.2	509.4±9.2	568±6.6
Calcium	37.5 ± 0.6	219.9±3.1	87.95±1.73	35.29±0.01
Magnesium	45.0 ± 0.3	52.97±0.33	44.99±0.33	52.63±0.96
Iron	0.05 ± 0.002	0.081± 0.001	0.146±0.004	0.676±0.004
Sulfate	14.0806	477.3	26.79	25
Chloride	746.8860	723.25	840.58	979
Bicarbonate	658	74	866	732
Normal carbonate	-	444	-	
Silicon		21.72± 0.19	17.58±0.16	5.55±0.03
pH (24 °C)	7.789	8.360	6.678	5.928

As shown in Table 2, at the end of 99 days, Ca^{+2} ion concentration is nearly same as that of the Ca^{+2} of injected water. This is interpreted as calcite is dissolved in earlier time, like 23 days, of the experiment and the calcite available for reaction in the core is decreased due to injected water sweeping the dissolved elements to production end. At the end of 99 days, it is anticipated that Ca^{+2} available for reaction is depleted and Ca^{+2} produced is equal to injected Ca^{+2} amount.

4. Modeling of the dynamic experiment

When assessing the impact of the long term CO_2 storage on geological formations, numerical modeling plays a crucial role geochemical reactions are very slow and laboratory work under the field conditions is limited in time and space.

The modeling and simulation study of the dynamic experiment is carried out by using the code TOUGHREACT. Simple 2-D radial model composed of 4 cells is used to simulate the CO_2 saturated fluid and Sayindere core minerals interaction in the dynamic experiment. In the simulation work, for the Sayindere cap rock formation water, the Caylarbasi reservoir formation water is modified in a way that the cap rock minerals and cap rock fluid chemistry are consistent. The results of the simulation work show that calcite is firstly dissolved and started to re-precipitated. Moreover, continuous dissolutions of quartz and kaolinite are observed. Formation of new, secondary minerals (hematite, magnesite and siderite) are observed but dissolved back in the simulation period. Dolomite, which is also considered to be a secondary mineral in the simulation, is continuously precipitated throughout the simulation time. Most importantly, the decreases in the porosity and permeability of the packed core minerals of the Sayindere cap rock are observed during the simulation. The porosity is decreased by 0.01% and, on the other hand, the permeability is decreased by 0.03%.

In addition to the simulation of the injection, the CO_2 saturated water injection into the packed core minerals of the Sayindere formation is stopped after 99 days of the injection and the simulation is continued for further 25 years to monitor the cap rock mineralogical and the water chemistry evolutions and particularly, the long term effect on the porosity and permeability of the packed Sayindere core. Different from the injection period, the porosity and permeability of the packed core are increased in long term after the injection process. The porosity and permeability are increased by 0.001% and 0.004%, respectively. From the point of view of the monitoring CO_2 storage after the injection and risk assessment associated with the CO_2 storage, the porosity and permeability increases as results of the geochemical reactions induced of CO_2 storage are not desirable since these increases can result in possible leakage paths for the CO_2 to escape into groundwater sources and finally into the atmosphere back.

5. Conclusion

The mineral investigation of the Sayindere cap rock is made. It is composed of the 76% calcite, 22.7% quartz and the remaining, 1.3% is kaolinite. From the photographs taken in SEM analysis of the 30 day experiment, it is interpreted that the near to surface appears looser than the inner part of the core, which may be due to CO_2 diffusion into the core. The fluid chemistry analyses of the both 30- and 100- day static experiments show that the calcite is dissolved in the water as a result of the CO_2- water-rock interaction. A deposition layer is observed in SEM photos of the 100 day experiment. The formation of deposition layer is explained as the dissolved particles, specifically the dissolved calcite from the core minerals were deposited back on the core surfaces. It is observed in the mineral investigation by SEM analysis of 100-day experiment that there are wormholes on the core used in the experiment, possibly created due to the heterogeneous pattern of calcite dissolution induced by the CO_2-formation water.

Only water chemistry analyses of the dynamic experiment are made. Based on the water chemistry analysis, it is interpreted that calcite is dissolved, which is also observed in the static experiments.

The modeling and simulation study of the dynamic experiment is carried out by using the code TOUGHREACT. The results of the simulation work show that main mineral in the Sayindere cap rock, calcite is firstly dissolved and started to re-precipitated. Formation of new, secondary minerals (hematite, magnesite and siderite) are observed but dissolved back during the simulation period. Dolomite, which is also considered to be a secondary mineral in the simulation, is continuously precipitated throughout the simulation time. The decreases in the porosity (0.01%)and permeability (0.03%) of the packed core minerals of the Sayindere cap rock are observed during the simulation

The simulation is continued for further 25 years, without CO_2 saturated water injection to monitor the cap rock mineralogical and the water chemistry evolutions and particularly, the long term effect on the porosity and permeability of the packed Sayindere core. At the end of 25 years, the porosity and permeability increase of 0.001%

and 0.0039% respectively were simulated after stopping the injection process. This is a unwanted result in the monitoring and risk assessment of the CO_2 storage. The increases in porosity and permeability show that the Sayindere cap rock integrity must be monitored in the field if application is planned.

6. Acknowledgement

The authors would like to thank Turkish Petroleum Corporation for providing the cores from Sayindere formation and water analysis of the Caylarbasi field. Moreover, the Departments of Petroleum and Natural Gas Engineering, Geological Engineering and Metallurgical Engineering (METU), Petroleum Research Laboratory, METU, and the Plasma Laboratory of Central Laboratory of METU are appreciated for their analysis and support.
The one of the authors, Dalkhaa would also like to thank the Scientific and Technological Research Council of Turkey for awarding her the PhD Fellowship for Foreign Citizens.

7. References

Bachu, S., 2002. Sequestration of CO_2 in geological media in response to climate change: road map for site selection using the transform of the geological space into the CO_2 phase space, Energy Conversion and Management, 35, 269-279.

Bateman, K., Turner, G., Pearce, J.M., Noy, D.J., Birchall, D., Rochelle, C.A., 2005. Large-Scale Column Experiment: Study of CO2, Porewater, Rock Reactions and Model Test Case Oil & Gas Science and Technology – Rev. IFP, Vol. 60 No. 1, pp. 161-175

Calabrese, M., Masserano, F., 2006. Simulation of physical-chemical processes during CO_2 sequestration in Geological Structures, paper SPE 95820

Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., 2005. Reactive transport modelling of the impact of CO_2 injection on the clayey cap rock at Sleipner (North Sea). Chem. Geol. 217, 319–337

Gaus, I., Audigane, P., Andre,L., Lions, J., Jacquemet, N., Durst, P., Czernichowski-Lauriol, I., Azaroual, M., 2008, Geochemical and solute transport modelling for CO_2 storage, What to expect from it? International Journal of Greenhouse Gas Control 2, 60 5 – 62 5

Gherardi, F., Xu, T., Pruess, K., 2007. Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO_2 storage in a depleted gas reservoir. Chem. Geol. 244, 103-129
IPCC Special Report, 2005

Gunter,W.D.,Wiwchar, B., Perkins, E.H., 1997. Aquifer disposal of CO_2-rich greenhouse gases: extension of the time scale of experiment for CO_2-sequestering reactions by geochemical modelling. Mineral. Petrol. 59, 121– 140
TUBITAK KAMAG REPORT, "Evaluation of CO_2 Emission From Industrial Sectors in Turkey and Determination of Possible CO2 Storage Sites in Turkey and Modeling & Simulation of CO2 Sequestration in an Oil Field in Turkey"- funded by the Scientific & Technological Research Council of Turkey (2007- 2009)

Lagneau, V., Pipart, A., Catalette, H., 2005. Reactive Transport Modelling of CO_2 Sequestration in Deep Saline Aquifers. Oil & Gas Science and Technology 60, 231-247

Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone–shale system. Chem. Geol. 217, 295-318

Xu, T., Sonnenthal, E., Spucher, N., Pruess, K., 2008. TOUGHREACT User's guide:A Simulation Program for Nonisothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media, V1.2.1