Preliminary Results of the Investigation of the Interaction of CO_2 and CH_4 Hydrate for the Determination of Feasibility of CO_2 storage in Black Sea Sediments

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PURPOSE OF THE WORK

Aim of this study is to determine the feasibility of CO_2 disposal below the methane hydrate stability zone in the Black Sea. Seismic studies conducted by Korsakov et al. (1989) suggests that the Black Sea is among the regions that have been cited in the literature as having conditions suitable for natural gas hydrate reserves. Also, Russian scientists confirmed by seismic studies that there are five regions in the Black Sea which are highly promising for hydrate formation. Furthermore, evidences of methane hydrate accumulation (Fig. 1) and volume of methane at STP (Standard temperature and pressure) (Fig. 2) makes the Black Sea technically and economically feasible site for the CO_2 sequestration, especially when the amount of CH_4 that might be produced from the hydrates is considered. As a result this study mainly focuses on the following topics;

- Interaction between the injected CO_2 and the methane hydrate.
- CO_2 and CH_4 hydrate formation within the sediments.
- Sealing efficiency of CH_4 hydrate.
- Possible CH_4 production while sequestrating CO_2.

INTRODUCTION

Recently, secure sequestration of anthropogenic carbon dioxide in geological formations has become one of the most important global scientific problems. Injection into deep sea sediments offers some unique and significant advantages such as, huge storage capacities and significant risk reduction for possible CO_2 leakage, when compared with the other potential geological storage options. Disposal of CO_2 into deep sea sediments is safer than disposal into land since the water pressure and dilution by oceanic water prevent direct emission of CO_2 into the air.

For the storage of huge amounts of CO_2, geological structure must contain an impermeable or low-permeable barrier. In general such a barrier may consist of clay or salt. In this study, sealing efficiency of methane hydrate and long term fate of the CO_2 disposal under the methane hydrate zone will be investigated.

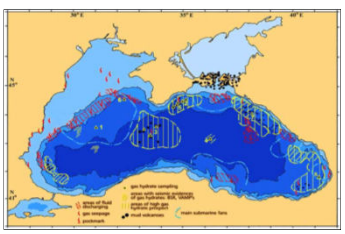

Figure 1. Evidences of methane hydrate from the Black Sea (L. Dimitrov and A. Vassilev)

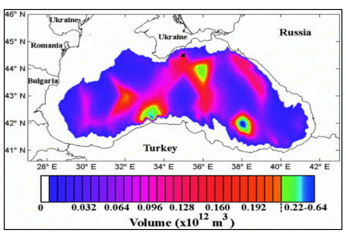

Figure 2. Volume of methane (STP) in hydrate at the Black Sea, (B.Klauda and I.Sandler,2003)

NATURAL GAS HYDRATES

Gas hydrates, also called gas clathrates, are solid, crystalline, ice like materials, which may form under suitable pressure and temperature values. In general, formation of gas hydrates requires low temperature and high pressure and most of the deep sea sediments satisfy these conditions. Gas hydrates consists of water cavities (host) that are composed of hydrogen-bonded water molecules and hydrophobic gas molecules (guests) that are encapsulated in water cavities. Methane, ethane, propane and carbon dioxide are the some common gas molecules which are trapped in water cavities to form clathrates.

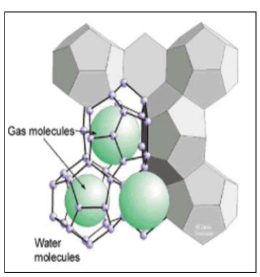

Figure 3. Structure of hydrate

THEORY

First of all, the deep storage of CO_2 requires injection into warm rocks that are at least 800 m deep. During deep storage of CO_2, there is always great possibility that some CO_2 may migrate upwards at some time. CO_2 leakage may occur through small faults/fractures, or poorly sealed boreholes. At this time, CO_2 hydrate stability zone become crucial phenomena. Because, if the CO_2 store laid below a deep enough and cold enough body of water, then leaked CO_2 may enter into CO_2 hydrate stability region. Therefore, formation of CO_2 hydrate may decrease the permeability of cap rock by partially or even completely plugging flow pathways (As in the case of methane hydrate plugs pipelines).

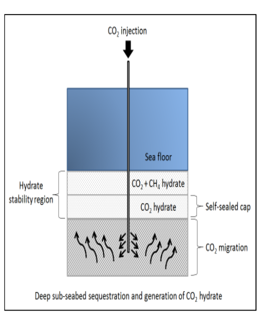

Figure 4. Schematic representation of the CO_2 disposal as hydrate

EXPERIMENTAL SETUP

The experimental setup that is shown in Fig. 5 was designed for the experiments and various different tests were performed to determine the feasibility of CO_2 sequestration in Black Sea sediments. These include the CH_4 hydrate formation in both bulk conditions and within sand particles, determination of the permeability of unconsolidated sand particles that includes 30% and 50% methane hydrate saturations and injection of CO_2 into the CH_4 hydrate for the observation of the interaction between CO_2 and CH_4 hydrate.

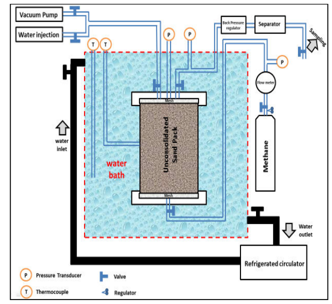

Figure 5. The Schematic Diagram of the Experimental Setup

EXPERIMENTAL RESULTS

Figure 6. Hydrate formation at the interface of water and free gas

Figure 7. Hydrate formation within the medium grained sediments

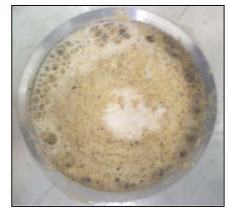

Figure 8. Hydrate dissociation within the medium grained sediments

During this study, CH_4 hydrate was formed in bulk conditions at the interface of water and free gas (Fig. 6), CH_4 hydrate was formed within the medium grained sediments (Fig. 7) and sediments that contain 50% of hydrate were left to dissociate (Fig. 8). Fig. 9 was taken from one of the hydrate formation experiments; the cell was packed with sand grains and 50% of the pore space was filled with water while remaining volume was filled with methane and the cell was placed into the water bath and cooling process was initiated. During hydrate formation, sharp pressure decline and small increase in temperature were observed. As the free methane enters into the hydrate cages amount of free methane diminishes that causes a decline in pressure and since hydrate formation is an exothermic reaction, an increase in temperature may be observed. After converting all water to hydrate, CO_2 injection can be performed. Because, in this way, one can be sure about that injected CO_2 only interacts with the CH_4 hydrate. Fig 10. was taken from one of the experiments, in which CO_2 was injected into methane hydrate abruptly. After the CO_2 injection cyclic behaviors were observed at the pressure gauges which suggest that CO_2 was entering into the cages while putting CH_4 out. Cyclic behaviors at the pressure transducers can be more easily seen from the Fig. 11. CO_2-CH_4 swap within the hydrate cages and the corresponding increase in pressure took approximately 6.5 hours and at the end of the process sample was taken from the cell in order to analyze the gas composition. Before the CO_2 injection there were 0.4799 gr mole of free CH_4 in the cell and then, 0.4883 gr mole of CO_2 was injected. Therefore, mole fraction of CO_2 was 0.504 and that of CH_4 was 0.496. At the end of the swap process Gas Chromatography analysis indicated that mole fractions of CH_4 and CO_2 were 92.310% and 7.690% respectively. According to the calculations, finally, 0.80518 gr mole of free CH_4 and 0.06708 gr mole of free CO_2 were present in the cell which suggest that 86.26% of the injected CO_2 was went into the hydrate phase. Furthermore, permeability tests were carried out. Results indicated that permeability of unconsolidated sand packs that includes hydrate saturation of %50 percent is about 4 md and flow is mostly occurs through the sideways and center of the system can be thought as impermeable.

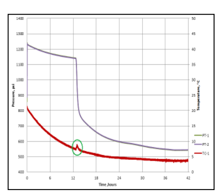

Figure 9. A typical Pressure and Temperature plot during hydrate formation

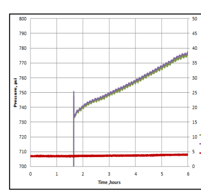

Figure 10. A plot that shows the CO_2 injection into CH_4 hydrate

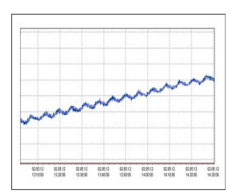

Figure 11. Cyclic behaviors at the pressure transducers

CONCLUSIONS

Following preliminary conclusions can be drawn from this study;

- If the hydrate saturation within sediments greater than %50, then the sediments may act as an impermeable layer.
- CO_2-CH_4 swap within the hydrate cages is technically feasible in laboratory scale.
- State of the CO_2-CH_4-H_2O system should be analyzed at various pressure and temperature values.