



## CO<sub>2</sub> Reaction with Organic- and Carbonate-Rich Shales

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### Introduction

Among the possible sites studied for carbon storage, shale reservoirs are of major interest due to large storage capacity and low permeability. Almost 80% of gas in shale reservoirs is stored in adsorbed state. (Ambrose et al., 2010). CO<sub>2</sub> storage in shale reservoir occurs by several trapping mechanisms: structural and stratigraphic trapping, capillary trapping, solubility trapping and mineral trapping. Mineral and capillary trapping depend on rock-fluid reaction. This paper shows CO<sub>2</sub> reaction with specific minerals such as calcite and organic matter in shales.

Previous studies have shown correlation between mineralogy and CO<sub>2</sub>. In shales, CO<sub>2</sub> sorption increases with increasing organic matter content (Joewondo, 2018). Busch et al (2010) postulates that clay minerals swell upon CO<sub>2</sub> uptake. We show the reaction of CO<sub>2</sub> with calcite minerals and organic matter with different maturity states.

### Methodology

Subcritical adsorption is increasingly used in rock physics for pore characterization. In addition to characterization, we use this method to study the reaction of adsorptive (fluid such as N<sub>2</sub> and CO<sub>2</sub>) with the adsorbent (shales). Prior to conducting adsorption, the sample is crushed into powder and sieved with 40 meshes (Kuila, 2013). The crushed powder samples are outgassed under vacuum condition and 200°C to remove any moisture and other contaminants. The samples are then transferred to the analysis chamber where fluid is dosed with increasing pressure.

We also conducted solvent extraction to estimate CO<sub>2</sub> sorption capacity of organic rich shales after subsequent extraction with toluene and chloroform for 48 hours each. We also conducted N<sub>2</sub> sorption to estimate the specific surface area exposed after extraction of soluble organic matter. Any solvent with higher polarity than toluene and chloroform is shown to destruct pore morphology (Zargari et al., 2015). 3g of aliquots is separated for N<sub>2</sub> and CO<sub>2</sub> sorption. Remaining aliquots are placed in a cellulose in a Soxhlet extractor for toluene extraction. 2-3 grams of toluene extracted aliquots is separated for another run of N<sub>2</sub> and CO<sub>2</sub> sorption. Similarly, remaining aliquots are extracted with chloroform before a final run of N<sub>2</sub> and CO<sub>2</sub> sorption.

### Results

Figure 1 shows the isotherm and pore size distribution obtained from CO<sub>2</sub> sorption at the micropore region (<2nm) for a calcite-rich Niobrara shale and silt-rich Agardhfjellet caprock from Svalbard. Three repeated CO<sub>2</sub> sorption runs without intermediate degassing are performed. Each run shows an adsorption and desorption curve. The maximum CO<sub>2</sub> sorption capacity decreased with each run for the calcite-rich sample. The sample is again degassed before another adsorption analysis, but the adsorption capacity

did not return to the original value. This is not the case with silt-rich Agardhfjellet for which the maximum adsorption capacity remained the same for each run.

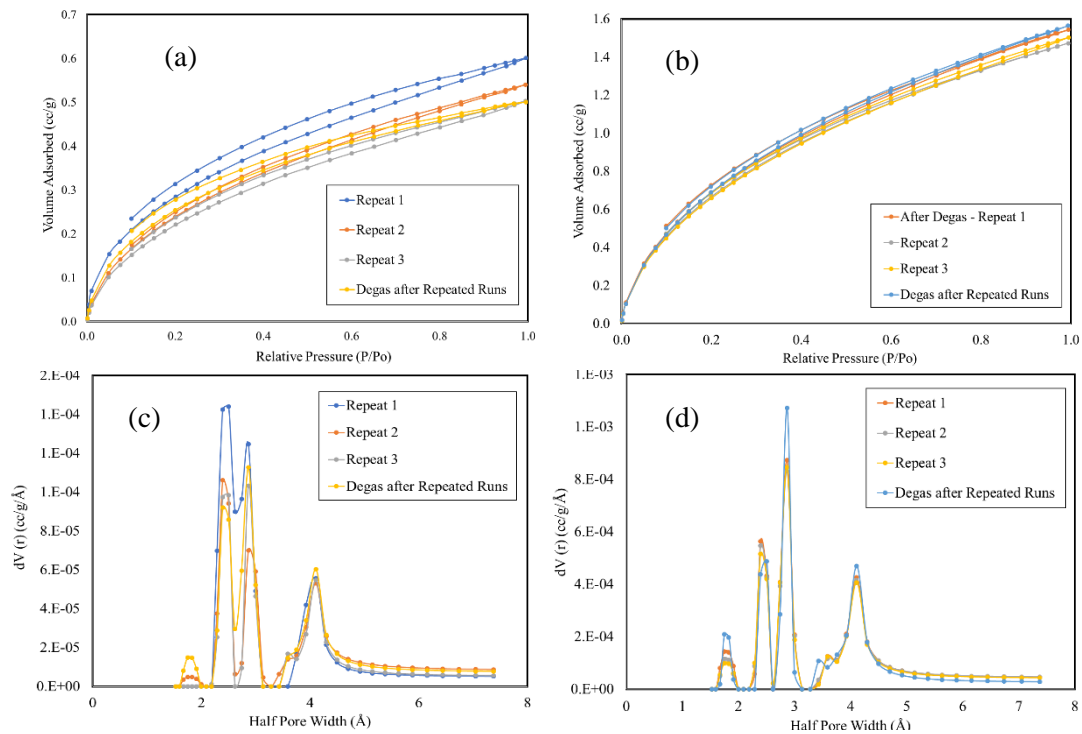


Figure 1: (a) Repeated Isotherm of CO<sub>2</sub> adsorption on carbonate-rich Niobrara shale and (b) silt-rich Agardhfjellet; (c) Pore size distribution at the micropore region of carbonate-rich Niobrara shale and (d) silt-rich Agardhfjellet.

## Discussion

Figure 1c indicates the loss of pore space near pore radius 3 Å. We estimate that previously run CO<sub>2</sub> is trapped in this pore space, blocking CO<sub>2</sub> in the repeated runs from entering. This is because the moisture contained by calcite minerals do not evaporate until a temperature of 500°C (Morimoto et al., 1980). Therefore, we did not lose the calcite moisture with an outgassing temperature of 200°C. This potentially causes CO<sub>2</sub> to be trapped in calcite's in-situ moisture. We will also distinguish the adsorption and absorption of CO<sub>2</sub> in the organic-rich samples with different maturity after subsequent solvent extraction.

## Conclusions

Abundance of specific mineral in shales governs the interaction with CO<sub>2</sub>. This provides insight into CO<sub>2</sub> transport and trapping in shale, information significant for CO<sub>2</sub> sequestration.

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