CO₂ Sorption Capacity in Clay-rich Shales with Moisture Content

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Injected CO₂ in geological sites may contact the impermeable caprock/shales overlying the injection reservoirs. And in this case, shales may provide additional storage capacity due to CO₂ adsorption in the microstructures. Shales have heterogenous mineral compositions and nano-scale microstructures (pore width < 200 nm), which result in complex wetting properties and low permeability. In such nanoporous materials, a large percentage of gas in place is stored by adsorption to the high surface areas. Sorption capacity of CO₂ onto the surface of this porous media largely depends on the reservoir conditions and mineralogy, or better wettability. The complex mineralogy of shales, such as clay, quartz, carbonate and some organic matter, will control sorption properties in addition to environmental pressure and temperature effects.

The goal of this study is to determine effect of mineralogy and moisture on (i) CO₂ accessible surface area using subcritical adsorption and (ii) the adsorption capacity of Utica shales in reservoir condition using high pressure adsorption. Our measurements allow us to match the appropriate adsorbates with the adsorbent gas and to quantify the amount of subcritical and high pressure gas adsorption capacity.

Storage capacity due to adsorption at high pressure and temperature depends on specific surface area (SSA) accessible to the adsorbent. Specific surface area (SSA) of shales is normally measured using subcritical Nitrogen gas adsorption at 77 K. Subcritical adsorption is based on static volumetric method where the sample is completely outgassed before adsorption analysis takes place. Our studies show that Nitrogen probed SSA tends to significantly underestimate CO₂ probed SSA in shales. For instance, for a standard clay sample, Na-rich montmorillonite, the measured SSA using Nitrogen versus CO₂ are similar, however for an organic rich shale sample, CO₂ measured SSA is significantly larger than N₂ probed SSA. The measurement of CO₂ adsorption at 273 K should be used to characterize CO₂ accessible micropore surface area and to assess CO₂ storage capacity in caprocks. In this study, we present mineralogy control on CO₂ probed specific surface area. By adsorption of the adsorptive gas on the pores of shales, we determine the pore size distribution (PSD) of the shales, hence determining the availability of micropores (pore width < 2 nm) for storage due to adsorption.

Following subcritical adsorption experiment, we measure excess sorption isotherms in order to determine the high pressure CO₂ sorption capacity while monitoring an apparent reservoir temperature. There are possibilities for moisture evaporation and minerals decomposition at high temperature. The sorption of CO₂ onto the surface of porous shale depends on the moisture content and sorption as well.
Typically, both subcritical and high pressure adsorption experiments are conducted with dry samples after introducing them to ultra high vacuum for a minimum of 12 hours. However, irreducible water saturation is inevitable in reservoir conditions and may reduce CO$_2$ sorption capacity, therefore we introduce moisture content in these measurements. In order to determine the moisture content and possible minerals decomposition in the samples, we also conducted thermogravimetric analysis (TGA) at variable temperature. Both dry and water saturated samples are run to study the apparent effect of moisture content in the form of brine in the sample.

With moisture content and CO$_2$ both present in the porous sample, the sample may show traits of preferential wetting where one gas is more inclined to get adsorbed versus other. This preferential wetting is a result of the mineral composition on the surface of the rock. For this purpose, chemical composition on the pore surface is studied using the X-ray Photoelectron Spectroscopy (XPS) prior to and after the introduction of various adsorbent gases and vapor.