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Technical Note

Temperature influence on permeability of Sioux quartzite containing mixtures of water and carbon dioxide

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1. Introduction

CO_2 sequestration in aquifers and depleted hydrocarbon reservoirs is a promising option for reducing atmospheric CO_2. However, its implementation requires understanding how CO_2 propagates and how it is stored in the reservoir. CO_2 mixed with water exists in two forms, an immiscible phase (gas or liquid depending on the conditions of temperature and pressure) and a dissolved phase (a minor part of which reacts with H_2O to form carbonic acid, H_2CO_3). The motion of CO_2 in the reservoir is therefore a two-phase flow problem. Fluid/rock chemical reactions may also be important, but they are not considered here. When several immiscible fluids occupy the pore space, each phase may act as an obstacle to the motion of the others. Indeed, experimental evidence from oil production, vadose zone or CO_2 sequestration studies [1] demonstrates that permeability is affected by the presence of a second phase in the pore space. The motion and spatial distribution of pore fluids (like water and carbon dioxide) are controlled not only by pore geometry and fluid pressure, but also by the viscosity, solubility, surface tension and wetting characteristics of each fluid phase [2], properties that usually vary with temperature. In the case of carbon dioxide and water, the solubility of CO_2 is particularly sensitive to temperature. Thus, temperature variations may also affect the distribution and flow of the phases in the pore space.

In this work, we measured the effect of temperature variations on the permeability of a rock saturated with a mixture of carbon dioxide and water. We used the oscillating pore pressure method (OPPM) developed by Kranz et al. [3] and Fischer et al. [4], because it minimizes fluid flux and, therefore, is not expected to disturb the phase distribution in the pore space as much as a steadily flowing fluid would. Although the method was devised to measure permeability of rocks with a single fluid phase, we can assess the effect of the second phase by comparing the permeability measurements made using a single fluid to those with a two-phase mixture.

2. Materials and methods

2.1. Rock sample

Sioux quartzite is a proterozoic metamorphic rock about 99% quartz, found in a wide region of North America including the states of Minnesota, South Dakota and Iowa. We do not expect any extensive chemical interaction of this rock with water and/or carbon dioxide at the temperatures and conditions of our experiments. We used a single cylindrical plug, 22 mm in length and 10 mm in diameter, extracted from a large core. The sample had an initial porosity of about 1%. Its permeability was between 10^{-20} and 10^{-19} m^2 [5] (or equivalently between 0.01 and 0.1 microdarcy, where 1 microdarcy$=9.869233 \times 10^{-19}$ m^2). Since the initial permeability was too low for our purpose, the sample was heated to above 700 °C and then rapidly quenched in water at room temperature. This thermal shock created micro-cracks and consequently increased the rock permeability. Siddiqi [6] estimated the aperture width of thermally generated cracks in Sioux quartzite to be between 1×10^{-7} and 2×10^{-6} m.

2.2. Permeability measurements: oscillation pore pressure method (OPPM)

The OPPM technique was presented in detail in Kranz et al. [3] and Fischer et al. [4] and reanalyzed in Bernabe et al. [7]. The measurement involves a monochromatic sinusoidal pore pressure

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oscillation of small amplitude superposed on a much larger static pore pressure. The pressure oscillation is generated in the upstream reservoir (input) and the transmitted pressure signal is recorded in the downstream reservoir (output). The output signal consists of two terms, a short-term transient and a long-term harmonic signal. We removed the transient signal by discarding the first 3–5 cycles. Using Fourier analysis, the ratio of the input and output signals, A, is related to the dimensionless normalized permeability, η, by

$$\eta = \frac{2A}{\sqrt{1-A^2}}, \tag{1}$$

provided that the storage capacity of the sample is negligible compared to that of the downstream reservoir [7]. The simplicity of Eq. (1) makes it desirable to operate with a relatively large downstream reservoir, but it is then impossible to measure the storage capacity of the sample. The dimensionless permeability is related to the absolute permeability, k, by

$$k = \frac{\eta \pi L \mu \beta_D}{tS} \tag{2}$$

where μ is the fluid viscosity, t is the oscillation period, L is the sample length, S is the sample cross-section area, and β_D is the downstream reservoir storage (for more details see Bernabe et al. [7]).

2.3. Experimental procedures

For experiments with water only, the sample was jacketed with Teflon. Because Teflon is permeable to CO_2, an additional polyolefin jacket was added in all experiments involving CO_2. The sample was installed inside the pressure vessel, connected to the upstream and the downstream reservoirs and submitted to the desired background pore and confining pressure. The downstream reservoir was sufficiently large to ensure that Eq. (1) was valid.

Since we wished to isolate the effect of temperature on flow of CO_2/H_2O mixtures, we performed all the measurements in identical conditions of pore pressure (10 MPa) and confining pressure (25 MPa), thus avoiding any loading history effects. We cycled the temperature from room temperature to as high as 110 °C and back to room temperature again. In this way, we verified that the changes in permeability were reversible, and that fluid–rock interactions were negligible.

We performed two sets of experiments: one set with a single aqueous fluid phase and a second with two fluid phases. In the first set, the sample was saturated with distilled water. We also attempted to run experiments with pure CO_2, but due to the high compressibility and low viscosity of CO_2 we were not able to conduct the experiments under the same pore pressure conditions as when using pure water as the pore fluid. In the second set, the fully saturated sample and pore pressure system initially contained a total of 17.59 cm^3 of distilled water at a pressure of 10 MPa. We then injected 2.85 g of CO_2 (or 3.66 cm^3 at the operating fluid pressure) into the upstream reservoir. After injection, the pore pressure system was closed, preventing any subsequent exchange of fluids with the exterior. The H_2O/CO_2 mixture was then left to equilibrate for about 12 h. A computer-controlled syringe pump was used to maintain the fluid pressure in the pore pressure system during the ensuing temperature cycles and, after closure of a by-pass valve, to generate the upstream pressure oscillations for the permeability measurements. Different injection procedures were tested in two preliminary sets of experiments using argon and CO_2 but the amount of gas injected was not accurately known.

The amplitude of the pore pressure oscillation was 0.6 MPa in all experiments; periods between 10 s and 1200 s were used. Since Eq. (2) requires an accurate value of the downstream reservoir storage, β_D, we determined β_D separately at each temperature and for each fluid, by measuring the change in pore pressure produced by a precisely known change in downstream volume (generated using a calibrated volumometer).

We estimated the relative uncertainty of dimensionless permeability, $\delta\eta/\eta$, by perturbing Eq. (1), which yields

$$\frac{\delta\eta}{\eta} = \frac{2\delta A}{A(1-A^2)}. \tag{3}$$

The uncertainty of the amplitude ratio, δA, is on the order of 0.02 (see Fig. 2a and c), based on the transducer characteristics published by the manufacturer. From Eqs. (2) and (3), we find that the uncertainty of permeability increases when A goes to zero and when A approaches unity. Thus, there is a window of relatively low uncertainty between these two extremes (see Fig. 2b and d). In the measurement window, the main cause of measurement errors in permeability is the influence of temperature on fluid viscosity. Here we used an upper bound of the variations in viscosity corresponding to temperature fluctuations of plus or minus 5 °C.

2.4. Characterization of the mixtures of water and CO_2

After a known volume of carbon dioxide gas was injected into upstream reservoir, the pore fluid system was closed and allowed to equilibrate for about 12 h. The initial masses of the two chemical components were determined using measurements of the total volume of the system and the equations of state of the fluids. After injection, part of the injected CO_2 dissolved into H_2O, forming a carbonated-water phase, while the rest remained as a separate immiscible fluid (hereafter called free CO_2) (Fig. 1). All the experiments were conducted under chemically closed conditions, so the masses of H_2O and CO_2 in the system were constant as temperature was varied. Assuming that the pressures of the immiscible phases are equal to the total fluid pressure and that surface tension effects are negligible, we can estimate the total volume of free CO_2, V_{CO_2}, at each temperature, from the known values of the densities of each phase and their solubilities [11].

However, if one phase is dispersed in the other as a set of very fine bubbles, then interfacial surface tension will result in decrease of the relative volume of that phase. The magnitude of this effect depends on bubble size, or more specifically, the radius of curvature of the bubbles and the specific energy of the interface. Thus, the volume calculated for negligible interfacial tension is an upper bound for V_{CO_2} and a lower bound for V_{H_2O}. It is possible that the immiscible phases were uniformly distributed throughout

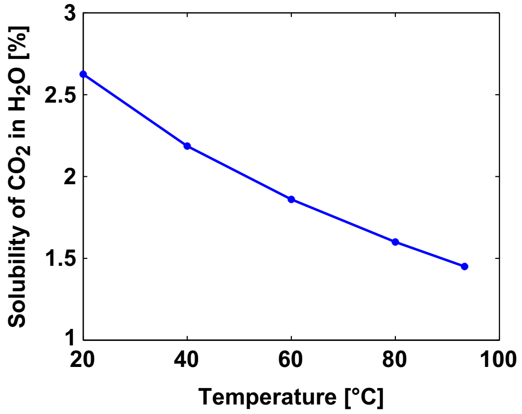

Fig. 1. The solubility of carbon dioxide in water as a function of temperature [11].