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In Situ Raman Spectroscopic Study of the Evaporation and Salt Precipitation: Indicates to Carbon Dioxide Injection into Brine in Reservoir for Sequestration

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Salt can be precipitated around CO_2 injection well when dry carbon dioxide is injected in saline aquifers. The salt precipitation may produce a severe loss of well injectivity or even eventually results in a complete blockage of injection (Giorgis et al., 2007). Such precipitation is driven by the concentration of salt in the brine following water evaporation, since the solubility of water in carbon dioxide increases with increasing temperature and decreasing pressure (Spycher et al., 2003). The dry-out and salt precipitation have been investigated by some experimental and numerical studies (e.g. Laurindo et al., 1996, 1998; Giorgis et al., 2007; Pruess, 2009 a&b; Mullera et al., 2009), however, the behavior in the pore space has not been well revealed.

In this study, the experiments of evaporation of brine (Na_2SO_4 solution) were conducted in capillary high pressure optical cell (Fig. 1; Chou et al., 2005; Lu et al., 2008) at 60 °C and at CO_2 pressures of one atmosphere and 10 MPa. The change of the concentration of brine

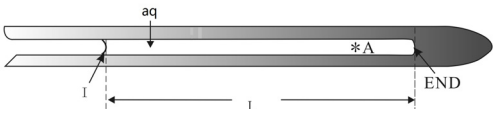

Fig. 1. A schematic diagram showing a section of Na_2SO_4 aqueous solution (aq) pressurized by carbon dioxide in the high-pressure optical cell, the gas/water interface (I), and sample spot at A (*) 1 mm away from the end of the tube (END) for the collection of Raman spectra during the evaporation. The initial length of the solution (L) is about 6 mm.

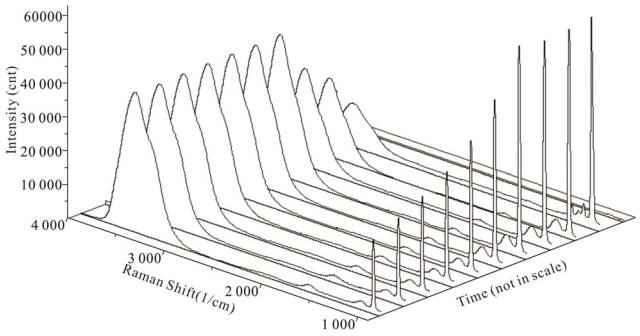

Fig. 2. Raman spectra of Na_2SO_4 aqueous solution collected at spot A during the evaporation at one 60 °C and at CO_2 pressures of one atmosphere. The intensity of the peak at 984 cm^{-1} increasing with time indicates the concentration increases with time. The occurrence of a peak near 994 cm^{-1} indicates the beginning of the precipitation of salt from the solution.

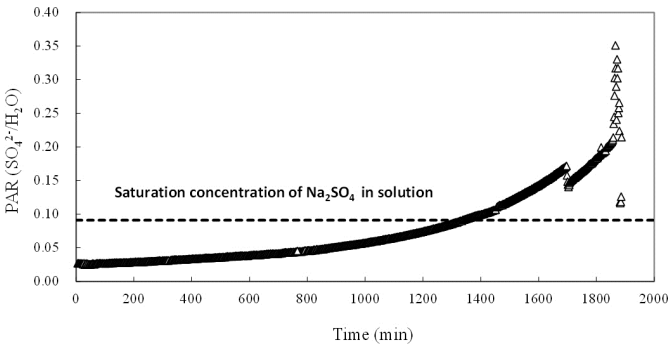

Fig. 3. Time dependence of sulfate concentration (PAR) monitored by Raman spectroscopy during the evaporation process, over-saturated concentration can be reached before the precipitation of the crystal of Na_2SO_4. The decease of concentration at about 1700 min, is related to the precipitation of crystals at about 2 mm away from the end of the tube, where the concentration is equal to the solubility, the salt ions should diffuse from spot A to the surface of the precipitating crystals, under the concentration gradient.

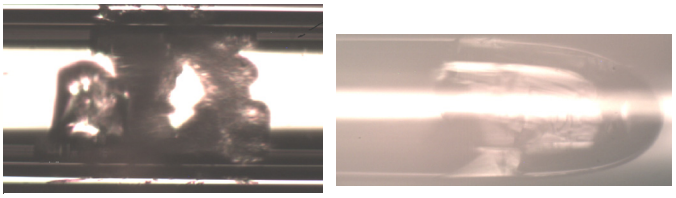

Fig. 4. Photos of two piles of Na_2SO_4 crystals precipitated in the high pressure cell. Spot A for Raman spectra collection is near in the middle of these two piles of crystals.
(a) ~2 mm away from the end of the tube; (b) Near the end of the tube

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Table 1 PAR of Na_2SO_4 solution at 60 ^oC with several concentrations

Concentration	10%	15%	20%	Saturation
PAR	0.022	0.051	0.070	0.091

(Na_2SO_4 solution) was monitored via in-situ Raman Spectroscopy (Figs. 2&3) after the Raman spectroscopic system was calibrated to detect the concentration of salt in the solution (Table 1). The concentration of the sulfate increases with time during the evaporation. Over-saturated concentration can be reached before the nucleation and precipitation of the salt crystals. And the position for the nucleation and precipitation of the salt can move with the moving the evaporation front (Fig. 4). It is also observed that the precipitation front can be recharged by the fast brine flowing along the wall of the capillary cell, due to the capillary pressure gradient driven by the evaporation. The precipitation process was found to be easier happened in the relative higher temperature and lower pressure. We demonstrated that in-situ Raman spectroscopic method can give lots of information of micro process in pore space during the injection of CO_2 into brine. 2D Raman imaging will be performed in the near future to get more information about the dry-out and salt precipitation processes.

Key words: carbon dioxide sequestration; salt precipitation; Na_2SO_4 solution; Raman Spectroscopy

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