Salt can be precipitated around CO₂ 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 (Na₂SO₄ solution) were conducted in capillary high pressure optical cell (Fig. 1; Ch ou et al., 2005; Lu et al., 2008) at 60 °C and at CO₂ pressures of one atmosphere and 10 MPa. The change of the concentration of brine
(Na$_2$SO$_4$ 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$_2$SO$_4$ solution; Raman Spectroscopy

References

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| Table 1 PAR of Na$_2$SO$_4$ solution at 60 °C with several concentrations |
|-----------------------------|-----------------|-----------------|-----------------|
| Concentration               | 10%             | 15%             | 20%             | Saturation     |
| PAR                         | 0.022           | 0.051           | 0.070           | 0.091          |