



Experimental determination of dawsonite stability and reactivity: Implications for geological CO₂ sequestration

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Identification and characterization of mineral assemblages that will influence mineral trapping and caprock integrity are essential to determine the economic, technical and environmental feasibility of sequestering large amounts of CO₂ in deep saline aquifers. When high pressure CO₂ is injected into deep aquifers, it acidifies the water, which in turn will react with the silicates in the host rock as well as in caprock, to the extent that the latter is permeable, to form new minerals. In this regard, numerous modeling studies (e.g., Johnson *et al.*, 2001, 2002; Zerai *et al.*, 2002) indicate that injection of CO₂ into these formations will stabilize various carbonate minerals (calcite, dolomite, magnesite and siderite), and an uncommon mineral, although very popular lately, the dawsonite [NaAlCO₃(OH)₂]. The formation of this mineral is enhanced by high Na⁺ concentrations in the brine, plume-induced CO₂ aqueous solubility, and acid-induced K-feldspar (orthoclase) dissolution, according to the following reaction:



In fact, there are natural analogs for this process in a variety of settings, for example, the presence of pervasive dawsonite cement in the Bowen-Gunnedah-Sydney Basin, Eastern Australia, which has been interpreted to reflect magmatic CO₂ seepage on a continental scale (Baker *et al.*, 1995). However, it is noteworthy that there are currently no data available to adequately assess either the equilibrium solubility of dawsonite or the rates of the relevant reactions controlling its precipitation. In most of reactive geochemical transport simulations, the rate constant for the dawsonite has been set to either K-feldspar (Xu *et al.* 2003 from Blum and Stillings 1995), siderite (Xu *et al.*, 2005) or estimated as intermediate to calcite and magnesite (e.g., Johnson *et al.* 2001,

2002, Gaus *et al.*, 2003 and Knauss *et al.*, 2005).

Before attempting to measure the rate of dissolution-precipitation of dawsonite, it was deemed necessary to study its stability and reactivity, the objective of this present study. As natural dawsonite samples are very hard to find in reasonable amount and with certainty that impurities are not present when extracting the dawsonite crystals from the matrix, we hydrothermally synthesized it following and optimizing two U.S. patents: Herold (1992) and van der Heem (1980). The syntheses were conducted in sealed pressure vessel (stirred) containing NaHCO_3 , Na_2CO_3 , gibbsite and de-ionized H_2O at 175°C . The solids obtained have then been used to study the stability of dawsonite as a function of temperature (50 to 200°C) and at 1.0 molal ionic strength NaCl .

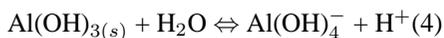
The results obtained show that the solution chemistry at temperature $\leq 100^\circ\text{C}$ is controlled by the equilibrium between dawsonite and bayerite ($\text{Al}(\text{OH})_3(\text{s})$), as confirmed by XRD and SEM performed on the recovered solid, and according to the reaction:



In order to be able to extract from these data the solubility product of the dawsonite, according to the reaction:



it was deemed necessary to measure the solubility of bayerite in the same experimental conditions, unknown up to now, from which we calculated the solubility quotients of this reaction:



By combining reactions (2) and (4) it was then possible to calculate the solubility quotient of the overall reaction (3). At 150 and 200°C , the dawsonite is not in equilibrium with bayerite anymore but with boehmite (AlOOH), also confirmed by XRD and SEM. As for lower temperature, combining reactions (2) and (5):



this time knowing very well the solubility product of reaction (5) (Palmer *et al.*, 2001), the solubility product of reaction (3) can then be calculated at 150 and 200°C .

The experimental values obtained in this study are in fairly good agreement with the values that were calculated only from other thermodynamic properties of dawsonite available in the literature from Ferrante *et al.* (1976). Our extrapolation to 25°C leads to a difference of 1.2 log units for the solubility product of reaction (3), which in turns gives a difference on the Gibbs free energy of dawsonite of $\sim 7\text{kJ/mol}$. From this work it is hard to believe that in saline aquifers mineral trapping will occur primarily in the

form of dawsonite. The kinetics of its formation remains also an open question.

References:

Baker J.C. et al. (1995): *J. Sedimentary Res.*, 65, 522-530

Blum A.E. and Stillings L.L. (1995): *Chemical Weathering Rates of Silicate ; Minerals: Rev. Min.*, 31, 291-351

Ferrante M.J. et al. (1976): *U.S. Bureau of Mines, Report Investigations 8129*

Gaus I. et al. (2003): *2nd Annual Conference on Carbon Sequestration, 2003, Alexandria, VA, USA, p. 1-13;*

Herold G. (1992): *US patent 5,078,983*

Johnson J.W. et al. (2001): *NETL Publications, 1st National Conference on Carbon Sequestration*

Johnson J.W. et al. (2002): *ACS Fuel Chemistry Division Symposia Preprints*, 47, 41-42;

Knauss et al. (2005): *Chemical Geology*, 217, 339-350.

Palmer D.A. et al. (2001): *Geochim. Cosmochim. Acta*, 65, 2081-2095;

Van der Heem (1980) Preparation of dawsonite. *U.S. Patent 4,221,771.*

Xu et al., (2003): *J. Geophys. Resear.* 108 (B2), 2071.

Xu et al., (2003): *Chemical Geology*, 217, 295-318.

Zerai B. et al. (2002): GSA, April 2002.