Experimental investigation of the solubility of uranium under hydrothermal conditions

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Introduction

The understanding of the aqueous geochemistry of uranium is essential for the assessment of nuclear repository performance. It is also applicable to geological problems including the modelling of fluid-rock interaction in ore-forming systems and subduction zone dehydration processes. However, the solubility of uranium is still poorly defined, mainly due to its low concentration in solutions and its complex redox behaviour.

Uranium solubility has been shown to be influenced not only by redox conditions, but also by fluid composition, temperature and pressure, as well as degree of crystallinity and the presence of crystal defects or impurities. Previous studies determined the solubility of uranium under oxidising atmospheric conditions in contact with synthetic ground water to be 1.5×10^{-6} mol dm^{-3} (Johnson *et al.*, 1982). The solubility of schoepite ($UO_3 \cdot 2H_2O$) at 25°C in 0.5 mol dm^{-3} $NaClO_4$ ranges between 10^{-3}–10^{-4} mol dm^{-3} for the amorphous and 10^{-4}–$10^{-5.5}$ mol dm^{-3} for the crystalline form in the pH range 6–9 (Bruno and Sandino, 1989). This study indicated the presence of the polymeric species $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$ or $UO_2(OH)_3^-$ in solution. In more acidic solutions ($2 < pH < 5$), the general consensus is that $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$ and $(UO_2)_3(OH)_5^+$ are the main species (Grenthe *et al.*, 1992).

Results

The uraninite (UO_2) used as starting material for the experiments consisted of crystals grown from a melt. The crystals were pre-treated (crushed, sieved and washed), examined under SEM, and analysed with X-ray diffraction and X-ray photoelectron spectroscopy. These techniques confirmed the absence of impurities. The solid phase was re-examined after the run using the same techniques. Uranium (VI) oxy-hydroxides were found to have formed on the surface of the uraninite.

The experiments were performed in an extraction quench type hydrothermal apparatus (Walther and Orville, 1983) over a range of P-T conditions (Table 1). Uranium concentration in solution was determined by ICP-MS. The analytical precision of the method is in the order of ± 5%.

Discussion

In summary, the results of these experiments show that uraninite is least soluble under reducing conditions. Its solubility increases by more than

TABLE 1. Summary of results of the study on uraninite solubility (modified after Bailey, 1994)

Fluid	Uranium (mol dm^{-3})	Oxygen fugacity	pH*	Temperature (°C)	Pressure (bar)
Pure water	$10^{-9.5}$	low	5.6	270	750
Pure water	$10^{-7.0}$	high	5.6	350	500
Pure water	$10^{-6.7}$	high	5.6	410	750
0.02 M Cl^-	$10^{-8.1}$	high	2.5	290	500
0.02 M Cl^-	$10^{-7.0}$	high	2.5	350	1000

* High temperature pH was estimated using the EQ3/6 code of Wolery (1992).

one order of magnitude in oxidising hydrothermal environments. The presence of chloride results in a decrease of uranium concentration in solution at temperatures close to 300°C. However, uraninite solubility increases faster with temperature in a chloride solution rather than in pure water.

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