

Gypsum precipitation kinetics in Dead Sea brine - seawater mixtures

I.J. REZNIK^{1,2*}, G. ANTLER¹, J. GANOR¹
AND I. GAVRIELI²

¹Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, Beer-Sheva, Israel
(*correspondence: itayrez@bgu.ac.il)

²Geological Survey of Israel, Jerusalem, Israel

Experimental work and thermodynamic calculations show that mixing sulfate-rich seawater (SW) with calcium-rich Dead-Sea brine (DSB) results in supersaturation with respect to gypsum. In order to determine the relevant kinetic parameters for nucleation and crystal-growth, batch experiments were conducted with and without crystallization seeds, respectively, using various ratios of DSB-SW.

In the nucleation experiments, the induction time (the time elapsed before the detection of a new phase) varied dramatically from merely several days to more than 100 days. A U-shaped dependency curve of the induction time on Dead-Sea fraction (DSF) was observed, with a minimum at DSF of 85-88% (fastest nucleation kinetics). In the crystal growth experiments, the rate was found to be controlled by two concurrent mechanisms. The first, which dominates the overall rate under far-from-equilibrium conditions, shows a 15th order dependency with respect to $(DSG^{1/2}-1)$, where DSG is the degree of saturation with respect to gypsum. The second mechanism, which dominates the growth rate under close-to-equilibrium conditions, has a 2nd order dependency on $(DSG^{1/2}-1)$. Accordingly, the overall growth rate (mol s^{-1}) is described by the following equation:

$$\text{Rate}=[k_1(DSG^{1/2}-1)^2 + k_2(DSG^{1/2}-1)^{15}]m$$

where k_1 and k_2 are kinetic constants ($\text{mol s}^{-1} \text{g}^{-1}$) and m is the mass of crystallization seeds (g).

A U-shaped dependency curve of k_1 and k_2 on DSF was found, with a minimum (i.e. slowest growth rate) at DSF of 85%, exactly oppositely to nucleation rates. Previous studies suggested that adsorption of cations onto gypsum retards the precipitation kinetics. Since the concentrations of all cations change monotonically with DSF, this inhibitory mechanism cannot solely explain a U-shaped behavior. However, electrical conductivity measurements (EC) indicate that when DSB is slightly diluted by the addition of SW, EC increases, suggesting that the increase in the concentration of free ions, due to the break-down of ion pairs/complexes, is greater than the decrease in concentration due to dilution. Upon further dilution, the EC decreases, resulting in an overall U-shaped behavior of EC vs. DSF. Therefore, we suggest that k_1 and k_2 are controlled by an adsorption inhibitory mechanism which depends on the concentration of free ions.

Restoration of *in situ* leached uranium mines with iron nanoparticles

OLGA RIBA¹, THOMAS B. SCOTT², M. DICKINSON²
AND GEOFFREY C. ALLEN²

¹Amphos21, Passeig de Rubí, 29-31, 08197 Valldoreix, Spain
(*correspondence: olga.riba@amphos21.com)

²University of Bristol, Interface Analysis Centre, 121 St Michael's Hill, Bristol BS2 8BS, United Kingdom

In situ leaching (ISL) provides a method of extracting uranium from the subsurface without direct excavation or perturbation. Following ore removal at an ISL site, environmental responsibility lies with subsequent restoration of the groundwater system. The experiments outlined in the current study were driven by the possibility of injecting metallic iron nanoparticles into the ore zone with the purpose of (i) immobilising residual soluble uranium (VI) as insoluble uranium (IV) oxide and (ii) restoration of anoxic conditions within the subsurface. The study also explores the possibility of persistent inflow of oxygen into the ore zone or change in the redox conditions of the geological zone,

Solutions highly concentrated in uranium (1000 ppm) with an initial pH ranging from 3 to 7 were studied in presence of zero valent iron nanoparticles under mildly oxidic conditions (1.2 % O₂ and 0.0017 % CO₂) to simulate the oxidizing conditions of an exhausted uranium mine.

Characterisation of both solid and solution phases indicated that at 4 hours period of reaction the Eh stabilized at values ranging from -0.1 to -0.4 V. The addition of iron nanoparticles triggered the reductive precipitation of UO₂, which was demonstrated to be the main process responsible for the removal of uranium from solution at reaction times between 1 to 4 hours [1,2].

The reoxidation of uranite precipitated on the nanoparticle surface was studied at mildly acidic and at neutral-basic conditions to account for the possible disruption of the reducing conditions in the geological zone. Despite thermodynamic modelling calculations of the studied system using NEA-TDB [3] indicate UO₃·2H₂O as the only uranium solid phase for 4 < pH < 9, the experimental results indicated that a Fe-uranyl phase with becquerelite-like crystalline structure stabilized at neutral basic pH [4].

- [1] Chadwick (1973) *Chem. Phys. Lett.* **21** (2), 291-294.
[2] Scott *et al.* (2005) *Geochim. Cosmochim. Acta* **69** (24), 5639-5646. [3] Guillaumont *et al.* (2003) *Chemical Thermodynamics 5. NEA OECD, Elsevier*. [4] Burns *et al.* (1996) *The Canadian Mineralogist* **34**, 845-880.