The Co-precipitation of Ra in a large scale evaporitic system

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High concentrations of radium pose environmental and health concerns in natural and industrial aqueous systems. Co-precipitation of Ra^{2+} with barite is an effective process in decreasing its concentration, and was extensively addressed in laboratory experiments. The outcome of such small scale experiments often serves in theoretical risk assessments simulation, but was hardly validated over large field systems.

The co-precipitation of Ra^{2+} with barite was studied in a large scale field system, comprising 6 sequential evaporation ponds, having a total volume of $3.25\cdot10^5$ m^3, in which a rejected brine of a desalination plant is evaporated. The non evaporated brine has an ionic strength of 0.7 m, ^{226}Ra concentration of 12 Bq kg^{-1}, and it is oversaturated with respect to gypsum, celestite and barite. Upon its evaporation the ionic strength increases up to 8.4 m, and a total amount of ~ $4\cdot10^6$ kg $year^{-1}$ of sulphate minerals precipitates.

Brine and salt samples were collected and analyzed for their chemical composition and radium isotopes. Precipitation rate of the different ions was calculated by assuming a steady state at each pond. The *apparent* partition coefficient of Ra in barite for pond *n* was calculated as: $K'_{d,\ n}=ln\{[Ra_n]/([Ra_{n-1}]\cdot EF)\}/ln\{[Ba_n]/([Ba_{n-1}]\cdot EF)\}$, where $[i]$ is the concentration of component i (mol kg^{-1}), and *EF* is the evaporation factor which corrects for concentration changes due to evaporation. Assuming that Mg is conservative, $EF= [Mg]_n/[Mg]_{n-1}$.

Preliminary results demonstrate that the increase in the amount of ^{226}Ra and Ba in the solid is concurrent and is not correlated with the increase of neither Ca or Sr. This indicates that barite precipitates as a separate phase and that Ra co-precipitates with barite. On the average, K'_d among all the ponds was calculated to be 1.1±0.1 in agreement with laboratory experiments carried out with the same brine (1.04±0.01). However, close examination reveals that K'_d increases by a factor of ~2 from 0.7±0.3 to 1.5±0.1 as barite precipitation rate decreases ~20 fold. This trend suggests that similarly to laboratory observations, kinetic effect lowers Ra co-precipitation.

Constrains given by the above field observations support experimental data, and thus strengthen the validity of the parameters needed for risk assessments.

Solubility of carbon dioxide in aqueous fluids at subcritical pressure: Testing the models

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Modelling of CO_2 storage in geological reservoirs indicates that solution trapping will become significant with time. However, there is little direct experimental data for CO_2 solubility in aqueous fluids at subcritical and near-critical pressures. We have therefore performed CO_2 solubility experiments in an intermediate pressure range, and made comparisons with model predictions.

Experiments are conducted at temperatures from RT to 70°C, with absolute pressures ranging from 4 bar to tens of bars. Our experimental setup allows pH-measurements to be conducted at pressure, for pressures ≤ 10 bar. The solution phase can be sampled at any pressure and the CO_2 solubility is determined to within 1% using alkalinity titrations.

Figure 1 shows coupled pH – solubility data at a total pressure of 4 bar. At this pressure the agreement between experiment and PHREEQC modelling is generally good, but anomalously high solubilities are predicted for calcite-bearing assemblages giving relatively high pH fluids. If confirmed at higher pressures, this discrepancy will have important implications for modelling CO_2 storage.

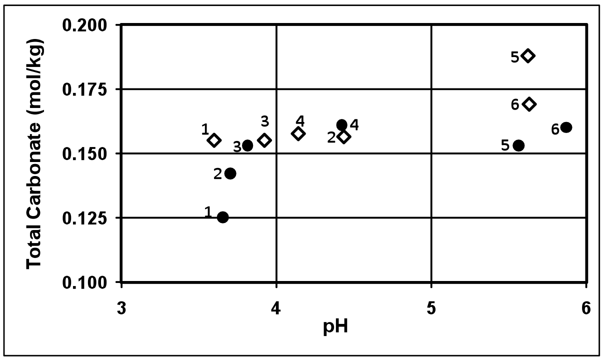

Figure 1: Solid symbols show experimental CO_2 solubility and pH, open symbols show results from PHREEQC calculations. Symbols numbered 1 are for pure H_2O - CO_2, while the others are for H_2O - CO_2 – mineral systems as follows: 2: K-feldspar 3: kaolinite 4: Na-montmorillonite 5: calcite 6: Na-montmorillonite + calcite.