

## Ra-Ba precipitation in a large scale evaporitic system and in laboratory systems

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$^{226}\text{Ra}$  is a critical radionuclide with respect to the long-term safety of radioactive waste disposal. Moreover the fate of radium is of high relevance for the environmental safety of scales produced in geothermal energy facilities, oil and gas exploration, and evaporation ponds for the management of residual solutions of uranium and other metals mining, coal mining (settling ponds) and brackish water treatment plants,

During the last century the precipitation of  $(\text{Ra,Ba})\text{SO}_4$  solid solution was extensively studied in laboratory experiments at different temperature and salinities. The outcome of such small scale experiments often serves in theoretical safety assessments simulation, but was hardly tested over large scale field systems.

Precipitation of Ra was investigated in a large scale field system and found to be controlled by the formation of a  $(\text{Ra,Ba})\text{SO}_4$  solid solution. The results are comparable to laboratory based studies conducted with the same solution.

Laboratory studies on retention of  $^{226}\text{Ra}^{2+}$  by barite in aqueous solution was studied in (a) evaporation batch experiments at ionic strength  $I = 0.7 - 7.0 \text{ mol}\cdot(\text{kg H}_2\text{O})^{-1}$  and (b) batch experiments with  $^{226}\text{Ra}^{2+}$  doped barite suspensions at  $I = 0.1 \text{ mol}\cdot(\text{kg H}_2\text{O})^{-1}$ . In experiments of type (b), barite dissolution / (re)precipitation kinetics were determined by doping the suspensions with  $^{133}\text{Ba}^{2+}$  and measuring the  $^{133}\text{Ba}^{2+}$  uptake by barite.

In experiments of type (a) it was observed that  $^{226}\text{Ra}^{2+}$  co-precipitated with barite, despite the fact that the latter was a trace mineral compared to the precipitated gypsum. A relatively low *concentration*-based apparent partition coefficient,  $K'_{D,\text{barite}}$ , for the co-precipitation reaction was determined ( $1.04 \pm 0.01$ ; Rosenberg et al., submitted) compared to  $K'_{D,\text{barite}}$  for relatively diluted solutions ( $1.8 \pm 0.1$ ; Doerner and Hoskins, 1925). This low  $K'_{D,\text{barite}}$  is mainly the result of a kinetic effect but is also slightly affected by the ionic strength.

In experiments of type (b), isotopic equilibration of  $^{133}\text{Ba}^{2+}(\text{aq})$  with barite occurs within 50 – 100 days at  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}] = 1$ ; in sulfate rich suspensions (i.e.  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}] = 10^{-5}$ ),  $^{133}\text{Ba}^{2+}$  uptake is significantly slower. A steady state in the uptake of  $^{226}\text{Ra}^{2+}$  by barite is observed after 400 days. The  $^{226}\text{Ra}^{2+}(\text{aq})$  concentration is controlled by the solubility of a  $\text{Ra}_{0.00013}\text{Ba}_{0.99987}\text{SO}_4(\text{s})$  solid solution and several orders of magnitude below the  $\text{Ra}^{2+}$  solubility with respect to pure  $\text{RaSO}_4(\text{s})$ .