



## Barite Recrystallization to Witherite in the Presence of Carbonate, and the Impact on Radium Retention

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In deep geological repositories for nuclear waste, groundwater may saturate the (geo-) technical barriers, and waste container corrosion may be occurring. This may finally lead to radionuclides being released from the waste [1]. The sorption capacity of potential host rocks, such as crystalline rocks and clay rocks, and of potential secondary phases is an essential aspect in the Safety Case. Barite ( $\text{BaSO}_4$ ) can be present in crystalline rocks as a fracture filling material. In clay rocks, sulfate minerals ( $(\text{Ba},\text{Sr})\text{SO}_4$ ) are found as accessories. Barium (Ba) is present in the waste as a fission product and as sulfate containing groundwater contacts the waste, barite may form. Ra uptake by barite occurs when dissolved Ra reacts with barite, leading to Ra retention by  $(\text{Ba},\text{Ra})\text{SO}_4$  solid-solution formation [2]. Barite reaction with aqueous carbonate at high pH, e.g. due to cementitious material alteration inside a repository, may cause barite to convert into witherite ( $\text{BaCO}_3$ ) [3]. The presence of carbonate likely alters the chemical behaviour of barite surfaces, via surface mixing or by witherite layer formation through dissolution-precipitation [4]. Aim of this study is to investigate the effect of carbonate on Ra retention by barite.

The presented results highlight barite transformation into witherite in the absence and presence of Ra. Barite suspensions were contacted with carbonate solutions (1-100 mM, pH 7-11). X-ray diffraction (XRD) showed shifts of reflection peaks in batches with pH 9-11 and carbonate concentrations of 10-100 mM, indicating a witherite-barite solid-solution formation [3], though this is not energetically favorable according to Density Function Theory calculations. Reaction rates depend on the type of barite. Generally, reactions slow down after about 7 days, likely due to surface passivation. Cubes of natural barite were reacted with 100 mM carbonate solutions at pH 11. As a result, a porous witherite layer with  $(271 \pm 32)$   $\mu\text{m}$  formed, giving insight into recrystallization process progress and mechanism. Atomic Force Microscopy measurements were conducted for witherite growth. Barite was equilibrated at 35°C and contacted with a carbonate solution (0.01M, pH 10). Orientated particles with different shapes grew. More measurements will be conducted with different conditions to obtain a distinct growth. For Ra uptake, witherite batches (S/L 0.01, pH 8.7) were prepared for Ra to be spiked subsequently.

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