Experiments on Radium co-precipitation into sulfates and its implications for radium removal in wastewater

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In the process of hydraulic fracturing for oil and gas extraction, large volumes of wastewater returns to the surface. The wastewater is often saline, with Na, Ca, Ba, and Sr being the dominant cations, and is highly radioactive particularly rich in radium (Ra) (up to 7000 pCi/L). The wastewater with high Ra levels have been a threat to the environment and is, therefore, important to be treated properly prior to disposal. Due to the similar chemical properties of Ra, Ba, and Sr, the co-precipitation of these elements with SO_4^{2-} to form radio-barite/celestine has been taken as one method to remove Ra from water. Preliminary research by mixing wastewater with acidic mine drainage (rich in SO_4^{2-}) indicated influence of the Sr/Ba ratio on the Ra removal efficiency. In this study, we aimed to quantify the effects of Sr/Ba ratios, ranging from 0.1 to 100 under different background solution conditions, on Ra removal, and to investigate the mechanisms responsible for such an influence.

Co-precipitation experiments were conducted by titration of SO_4^{2-} ions into solutions of various Sr/Ba ratios and background compositions. At the end of each experiments, solids were separated from liquid to test for mineral phases, crystal morphologies, and elemental compositions. Total Ra co-precipitated in the solid was also measured. The liquid fractions were analyzed for Sr, Ba, and SO_4^{2-} concentrations.

The results show that the total Ra activity co-precipitated as solids decreased initially and then increased with increasing Sr/Ba ratio. At low Sr/Ba ratios, barite was likely the dominant precipitate, Sr and Ra competed for available sites in barite, and thus increasing Sr reduced the Ra uptake. At elevated Sr/Ba ratios, celestine formed. Celestine has a much higher partition coefficient, K_d, for Ra (K_d = $[RaSO_4/MSO_4]/[Ra^{2+}/M^{2+}]$, $K_{d,Ra\text{-}celestine}$ = 237) than barite ($K_{d,Ra\text{-}barite}$ = 1.54). As a result, high Sr concentrations led to significant celestine formation and the increased Ra removal. In addition, we noticed that high Ca^{2+} in background solution adversely influenced Ra removal. Our study has implications on effective treatment of radium in wastewater.