Optimizing Radium Removal from Produced Water Utilizing the Sr/Ba Molar Ratio and Precipitate Seeding

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Oil and gas (O&G) produced waters are often highly saline solutions with elevated concentrations of naturally occurring radioactive material, such as radium (Ra), and other scalants, such as barium (Ba) and strontium (Sr). These alkaline earth metals pose issues for both industry recycling and reuse in agriculture, stream augmentation, and road maintenance. Co-precipitation of Ba and Ra by the addition of sodium sulfate (Na₂SO₄) is a common Ra removal technique in produced water treatment plants and typically forms ternary solids of the form (BaₓSr₁₋ₓ)SO₄ with trace amounts of incorporated Ra. Previous studies demonstrated the importance of the initial fluid’s Sr:Ba molar ratio with regards to specific Ra activity and sludge production, with increasing Sr:Ba molar ratio (in the range 1-10) leading to less precipitate production and higher precipitate-specific Ra activity (Bq/g). Existing models overestimate Ra, Ba, and Sr removal. This study was designed to provide laboratory-derived data necessary to fill the knowledge gap with regards to Ra, Ba, Sr, and SO₄ removal efficiency over a large range in the initial fluid’s Sr:Ba molar ratio under similar high ionic strength experimental conditions.

To generate modeling input parameters, a Na₂SO₄ solution was added to batch reactors of synthetic O&G produced waters with 12 Sr:Ba molar ratios ranging from 0:1 to 1:0. The supernatant was analyzed for major cations and anions. Precipitates were analyzed by powder X-ray diffraction, scanning electron microscopy (SEM), and electron microprobe analysis to characterize the crystallography, morphology, and microchemistry across the precipitate grains.

To investigate Ra removal optimization, we conducted seeding experiments. Seeding reactors with pre-formed precipitates enhances the precipitation of target minerals by lowering activation energies and thus increasing the reaction kinetics. Pre-formed (BaₓSr₁₋ₓ)SO₄ precipitates from initial batch reactors of known Sr:Ba molar ratios were then added to produced waters from the Niobrara and Utica Shales with matching Sr:Ba molar ratios. Removal efficiencies of Ba, Sr, Ra, and SO₄ from the O&G produced waters utilizing BaSO₄ or SrSO₄ were compared. Removal experiments provide critical perspective regarding Ra removal optimization and improve our ability to provide modeling benchmarks for these efforts.