

Immobilization of borate and arsenate from geothermal waters by co-precipitation with hydroxyapatite

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In the south part of Kyushu, there is a gold mine activity where mine waters have been daily discharged at the rate of 12,000 m³. The water includes 24 mg/L borate and 450 µg/L arsenate and 3.3 mg/L fluoride in average, in addition to 107 mg/L silicate and 904 mg/L carbonate at pH 8.3, which is a very similar water chemistry to geothermal waters. Generally there is a variety of pollutants in anionic species of natural and anthropologically waste discharged waters. Up to now, co-precipitation with Al₂(SO₄)₃, ion-exchange, reverse osmosis membrane, graft resin etc have been tried to reduce the borate and arsenate concentrations, however, all of them have been unsuccessful. In the present work, co-precipitation of borate and arsenate with hydroxyapatite (HAp) successfully reduced their concentrations under the maximum concentration limits, by adding of Ca(OH)₂ as a Ca source in the targeted solutions. Arsenate and silicate were kinetically removed faster than borate. ¹¹B-NMR revealed that boron species were initially immobilized as tetragonal (⁴B), but a part of them was gradually transformed into trigonal (³B) at the equilibrium. Solid ²⁹Si-NMR revealed silicate was immobilized as ellestadite not amorphous silica. Coexisting 904 mg/L carbonate did not significantly disturb borate removal. By adjusting the initial pH, the molar ratio of Ca/P, and phosphate sources, enhancement of the removal rate of borate and minimization of the equilibrated borate concentration were efficiently achieved. Al³⁺ additives have not only further accelerated the removal rate of borate and lowered the equilibrium borate concentration, but also improved the chemical stability of borate in dissolution assay. TEM-EDX showed Al is evenly overlapped with Ca, P, O ions distributed in HAp particles, implying the mechanism is creation of precursors outside of Ca(OH)₂ particles. This results can be effectively extended to reduce different pollutant anionic species concentrations in aqueous systems, particularly radioactive nuclide waste waters in which a variety of anionic species with very long life-time are included, at the same time.