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Mechanistic insights into the retention of Al(III) and its analogue Ga(III) on hematite surfaces

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Mechanistic insights into radionuclide transport are critical for assessing the long-term safety of deep geological repositories for radioactive waste. Crystalline rock formations, considered as potential host rocks in several countries, rely on mineral-water interactions to limit radionuclide migration. Sorption onto aluminosilicates, such as feldspars and mica, plays a key role in retention processes, but mineralogical variations affecting solubility and surface reactivity introduce complexities. In particular, dissolved Al^{3+} can re-adsorb onto mineral surfaces, potentially competing with radionuclides or altering sorption site availability.

This study investigates the influence of Al^{3+} on sorption processes using hematite (Fe_2O_3) as an aluminum-free model system. Batch sorption experiments (100 µM Al^{3+}, 0.1 M NaCl, S/L = 3 g/L) revealed that Al^{3+} sorption onto hematite occurs prior to $Al(OH)_3$ precipitation and is pH-dependent, with decreased retention above pH 10 due to the formation of the negatively charged $[Al(OH)_4]^-$ complex. Zeta potential measurements confirmed electrostatic interactions, suggesting the formation of inner-sphere surface complexes due to the sorption of Al^{3+} on a positively charged surface.

To further elucidate metal(loid) interactions, Ga^{3+} was employed as a spectroscopic proxy for Al^{3+}. It is also of critical importance in its own right, especially in the semiconductor industry, for renewable energy and future technologies. Sorption experiments (100 µM Ga^{3+}, 0.1 M NaCl, S/L = 3 g/L) demonstrated similar pH-dependent behavior, with a very low sorption edge at pH 2.5 and retention decreasing above pH 8 due to $[Ga(OH)_4]^-$ formation. X-ray absorption spectroscopy provided molecular-scale insights into binding mechanisms. Additionally, Eu^{3+} sorption was studied, as an analogue for trivalent actinides and lanthanides. Competitive sorption studies revealed that Al^{3+} did not significantly affect Eu^{3+} retention, except for a slight increase at low pH, suggesting limited competition under environmentally relevant conditions.

These findings contribute to a molecular-level understanding of metal(loid) sorption mechanisms, bridging the gap between microscopic and macroscopic observations. By integrating batch experiments with spectroscopic data, this study enhances predictive surface complexation models, supporting the development of more accurate radionuclide transport simulations. The results have broader implications for geochemical cycling, contaminant remediation, and resource recovery, aligning with efforts to improve environmental safety and sustainability.