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Pu(VI) Hydroxamate Complex Formation at Circumneutral pH

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Plutonium represents a major environmental and public health concern due to its long half-life ($t_{1/2} \sim 24000$ yrs.), toxicity and ability to migrate (kilometers) in the environment. Understanding the fate of radionuclides in the environment requires knowledge of the fundamental biogeochemical processes that control actinide speciation, precipitation and transport. One such example is the ability of microorganisms to react with Pu through surface adsorption, redox or the secretion of chelating agents. Siderophores are produced by microorganisms and plants to chelate insoluble Fe(III), making it available for cellular uptake. Siderophores with hydroxamate functional groups also form strong pH dependent complexes with Pu(IV), influencing Pu transport in the environment. The degradation of siderophores leads to the release of simple mono- and di-hydroxamates with somewhat lower metal affinities. Interestingly, these types of simple hydroxamates (acetohydroxamic acid, AHA) have been used in nuclear fuel processing due to their ability to selectively reduce Np(VI) and Pu(VI) in the presence of nitric acid (1-4M). These studies suggest that Pu(VI) reduction to Pu(IV) occurs by a rapid electron exchange with AHA followed by slow continued reduction by AHA acid hydrolysis products (hydroxyl amine). By analogy, it has been suspected that hydroxamate moieties may reduce Pu(VI) to Pu(IV) under environmentally relevant solution conditions at circumneutral pH as well. However, the reactions of Pu(VI) with AHA at environmentally relevant pH (6-8) have not been reported in the literature. We measured the reactions of Pu(VI) with varying concentrations of AHA at circumneutral pH using UV-Vis-NIR spectroscopy to track the reduction of Pu(VI) (absorption band at 831nm) and GC-MS to measure the breakdown of AHA to hydroxylamine. Our results show that Pu(VI) forms a stable complex with AHA at pH 6-8, which results in the loss of the Pu(VI) peak at 831nm. The concentrations of AHA remained constant and no production of hydroxylamine occurred, suggesting that the loss of the Pu(VI) absorption peak occurred due to ligand formation rather than reduction to Pu(IV). Subsequent acidification (0.5M HNO₃) caused dissociation of the of the Pu(VI)-AHA ligand complex and the reappearance of the free Pu(VI) peak at 831nm. These results suggest that Pu(VI) will form a stable complex with AHA, at environmental pH, that does not result in the reduction of Pu(VI) to Pu(IV).