

Effects of Temperature, Ionic Strength, and pH on Aqueous Plutonium(VI) Speciation in NaCl, MgCl₂, and Na₂CO₃

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Plutonium solubility and speciation in environmental systems are controlled by oxidation state, the presence and concentration of complexing or competing ions, and the geochemical boundary conditions of the system, which ultimately determine mobility and sorption behavior. This behavior is of particular interest to performance assessments for geologic repositories, where the release of plutonium is a critical performance measure. These assessments rely on the availability of experimental data across a wide range of variables to describe all pathways of potential release. Historically, experiments have been performed at 25 °C and relatively low ionic strength ($I \leq 0.1$ m); the high temperatures and ionic strengths expected in geologic repositories are not widely represented in the available data.

Conditions representative of geologic repositories, such as high temperature and ionic strength, will impact actinide solubility and speciation. Previous research shows that actinide hydrolysis and complexation increase with increasing temperature, leading to higher stability ranges of complexes with low or neutral charge.¹ Actinide complexation with chloride and carbonate is ionic strength dependent, with increasing complexation in higher ionic strength systems.^{2,3}

The lack of available data in thermodynamic databases and limitations of the models designed to predict the behavior of actinides in extreme environments highlights the need for reliable experimental data on the complexation of actinides in solutions at temperatures, ionic strengths, and pH values expected in a geologic repository. To address the complexity of expanding the range of temperature and ionic strength, UV-vis-NIR spectrophotometry was used to study the effect of temperature ($T = 25\text{--}95$ °C), ionic strength ($I = 0.1\text{--}10$ m), and pH ($pH = 5\text{--}12$) on Pu(VI) speciation. Salt solutions of NaCl, MgCl₂, and Na₂CO₃ were used for the ionic strength systems.

Pu(VI) complexation in chloride solutions is driven by increased ionic strength, pH, and temperature. In the NaCl and MgCl₂ systems, peaks indicative of the mono- (837 nm), di- (843 nm), and trichloro (849 nm) species were observed. Additional peaks were observed at 851, 857, and 861 nm, which may indicate the formation of the tetrachloro species, or products related to hydrolysis or carbonate complexation. Increased complexation with chloride was observed with increasing pH, ionic strength, and temperature in both systems. However, the impact of temperature on the Pu(VI) speciation in the MgCl₂ system was significantly less than in the NaCl system. The speciation of Pu(VI) in the presence of equimolar Na₂CO₃ was studied as a function of temperature to determine contributions from carbonate species in the chloride systems.

References:

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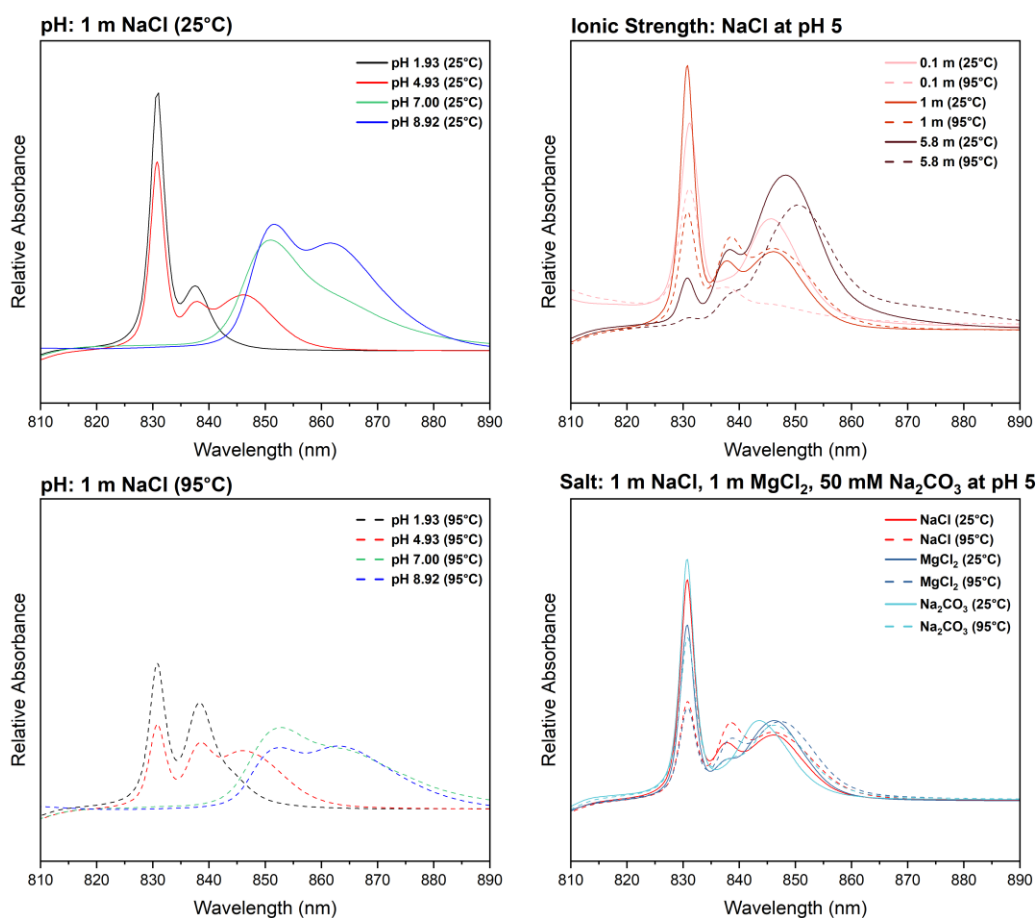


Figure 1: UV-vis-NIR data for Pu(VI) comparing speciation dependence on (Top, Left) pH in 1 m NaCl (25 °C), (Bottom, Left) pH in 1 m NaCl (95 °C), (Top, Right) ionic strength in NaCl at pH 5, and (Bottom, Right) salt content, including 1 m NaCl, 1 m MgCl₂, and 50 mM Na₂CO₃ at pH 5.