

Temperature and Ionic Strength Effects on Neptunium Speciation in Simplified Brine Systems

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Overview

Environmental Chemistry of Np

Neptunium primarily exists in the environment in the Np(IV) and Np(V) oxidation states, although there are some high-pH (pH >12) conditions where Np(VI) is also stabilized. Under oxic conditions in near-neutral pH, NpO_2^+ is the predominant species and is relatively mobile in the environment due to its high solubility and low tendency toward hydrolysis and complexation. Anaerobic microbial processes and iron(0, II) will reduce neptunium to the Np(IV) oxidation state, which has an analogous environmental chemistry to Pu(IV), e.g., very strong hydrolysis, very strong tendency towards polymer/colloid formation, and low solubility. For this reason, Np(IV) can be predominant under most anoxic conditions in brine or low ionic-strength groundwater.

Experimental Approach and Results

Absorption spectrometry was used to establish the speciation of neptunium. A Varian CARY 5000 spectrometer, equipped with a circulating water bath for temperature control (0 to 90°C) was used to obtain temperature-specific spectra. These spectra were obtained in gas-tight cuvettes by temperature-equilibrating the reference and sample cuvette prior to obtaining a baseline correction and then spiking in the neptunium (typically 5–40 μL) to obtain the spectrum as function of complexation, ionic strength and temperature. Pseudo-Voigt (Lorentzian/gaussian) fitting was done to model the absorption peaks and deconvolute the peaks and calculate λ_{max} and the half-height width of the spectra obtained.

Data from the following sets of experiments are reported: 1) the effect of ionic strength on the Np(V) aquo peak in simplified systems, 2) the effect of temperature on the Np(V) aquo peak, 3) Np(V)-borate complexation, and 4) the inorganic/organic complexation and hydrolysis of Np(IV). New band formation is almost always seen for both the Np(IV) and Np(V) systems investigated. Small, but significant, changes are noted with temperature and ionic strength that need to be accounted for to use the spectral changes to calculate formation constants. Pitzer data are obtained that can be used to model ionic strength effects.

These data collectively begin to address the speciation of neptunium as a function of temperature and ionic strength to understand its potential mobility in a salt-based thermal repository concept.

WIPP TRU Repository



Rationale for the Research

Neptunium, as NpO_2^+ or Np^{4+} , is a key actinide in performance assessment at long-times in a HLW repository. An understanding of the effects of temperature and ionic strength on its speciation is needed to address the possible long-term geologic disposal of HLW in a repository in salt that is analogous to the WIPP TRU site.

Summary of Observations

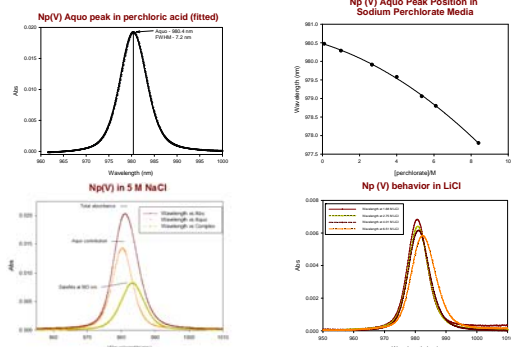
- New band formation for both Np(V) and Np(IV) make spectroscopy a good tool to investigate the effects of ionic strength and temperature on speciation.
- For Np(V), the effect of ionic strength is a blue shift in the peak location but little/no change in the peak shape. Increased temperature also caused a blue shift, but peak shape is also significantly impacted.
- A weak chloride complex and borate complexation lead to new band formation with Np(V).
- Np(IV) hydrolysis and complexation using spectroscopic methods leads to isobestic point formation that can be used for formation constant determination.

Future Plans:

- Investigate the effects of temperature on the carbonate, borate and chloride complexes of Np(V)
- Hydrolysis and complexation study with Np(IV) as a function of temperature

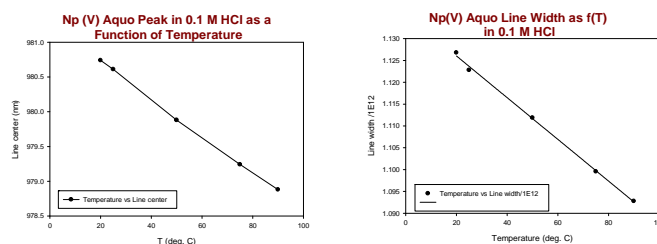
Effect of Ionic Strength on the Np(V) Spectrum

The Np(V) spectrum was obtained in perchloric, LiCl and NaCl media up to ionic strengths of ~8–10 M. In perchloric media, increased ionic strength did not change the band shape, but led to a blue shift in the peak position (~2.7 nm). In high ionic strength systems with chloride present (NaCl and LiCl) a red shift of up to 3 nm was observed when spectra were obtained and this was correlated with a change in the peak shape. This was interpreted, by peak deconvolution, as due to the formation of a weak Np(V)-Cl complex peak at 983 nm. Spectra below show the fitted peak in perchlorate media, the peak shift as a function of ionic strength (also perchlorate media), and the peak shifts due to chloride complexation in sodium and lithium chloride brines (bottom two spectra).



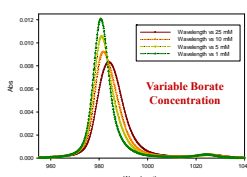
Effect of Temperature on the Np(V) Spectrum

The effect of temperature (20 – 90 °C) was established for Np(V) in 0.1 M HCl for the aquo species. The increase in temperature resulted in a steady blue shift in the absorption maximum (~2 nm) and a corresponding decrease in the line width. These changes, although small, are significant when deconvoluting the neptunium spectra at variable temperature given the very small spectral shifts observed in the complexes formed (e.g., chloride and borate). These data provide baseline spectra that are needed to evaluate the effects of temperature on complexation.



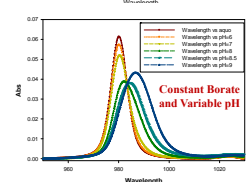
Complexation of Np(V) by Borate

In the presence of borate, Np(V) forms a 1:1 complex that leads to new band formation ($\lambda_{\text{max}} = 987 \text{ nm}$) as shown below. This forms an isobestic point and has a log(K) of ~2.11.

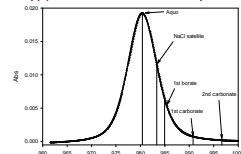


Formation Constant
Avg Log (K) apparent = 2.11 ±0.08

Borate concentration (M)	Np(V) with borate				Log K_{app}
	pH	Np borate peak*1000	Np aquo peak*1000	Np borate/Np aquo K_{app}	
1 mM	8.63	1.57	11.4	0.138	1.38
5 mM	8.99	3.80	7.61	0.487	1.988
10 mM	9.03	5.88	4.37	1.35	2.129
25 mM	9.07	7.55	2.03	3.72	2.173

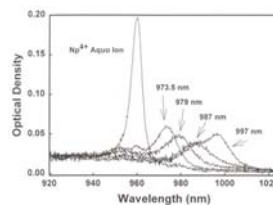


Np(V) Peak Positions for Various Complexants

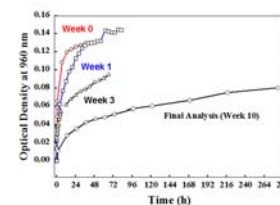


Hydrolysis and Complexation of Np(IV) and Associated Spectroscopy

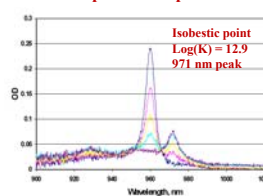
Np(IV) Hydrolysis



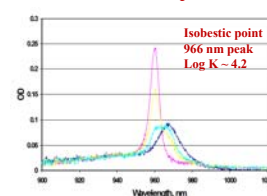
Aging Effect on Np(IV)



Phosphate Complexation



Succinate Complexation



Acknowledgements

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