Thermodynamic and Kinetic Controls on the Formation of Actinide(IV) Oxides in Aqueous Hydrothermal Systems and Groundwaters*

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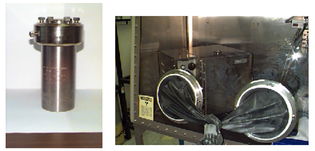


Experiments were conducted in Parr Reaction vessels in a safety vacuum oven inside a controlled atmosphere glove box.

The Issue

Anhydrous actinide(IV) oxides including NpO_2, PuO_2, and AmO_2 are highly stable thermodynamically according to extant data. These phases are basically known as ceramics, not aqueous precipitates.

Thermodynamic calculations suggest that NpO_2 and PuO_2 are the long-term solubility-controlling solids for Np and Pu respectively in reducing and oxidizing groundwaters, and that AmO_2 plays a similar role for Am in oxidizing groundwaters only. But spiked groundwaters precipitate other phases, such as Np_2O_5, Pu(IV) polymer, and $AmOHCO_3$.

Questions

Is actinide(IV) oxide precipitation limited by kinetics near room temperature, or is the thermodynamic data incorrect?

If kinetics is the factor:

Can actinide(IV) oxide solubility be counted on to limit migration from an underground repository over very long time periods (e.g., hundreds to thousands of years)?

Can actinide(IV) oxide precipitation be speeded up using temperature, pH, etc., for studying the kinetics and possibly also for use in separation chemistry and waste stream processing?

The Case of Neptunium

Np-237 has a very long half-life (2.14 x10^6 years) and has been shown experimentally to be highly soluble and relatively stable as aqueous Np(V) in solutions pertinent to a potential geologic repository for high-level waste.

Incorportation of published aqueous Np concentrations as limits in performance calculations has yielded dose values in excess of once proposed long-term, dose-based regulatory limits for such a repository.

Long-term solubility control by Np(IV) oxide would probably eliminate this issue.

Background

Under oxidizing conditions, Np(V) should predominate in near-neutral solution with the typical aqueous species being NpO_2^+, $NpO_2CO_3^-$, and $NpO_2(CO_3)_2^{3-}$.

Under reducing conditions, Np(IV) should predominate in near-neutral solution with the typical aqueous species being $Np(OH)_{4(aq)}$.

All known Np(V) solids (such as Np_2O_5) tend to be highly soluble. Anhydrous NpO_2 is extremely insoluble under reducing conditions and is considerably less soluble than any Np(V) solid under oxidizing conditions (if the thermodynamic data are correct).

Previous Work

Nitsche et al. measured the solublity of Np in J-13 Well Water from oversaturation by introducing an excess amount of Np(V). The pH values ranged from 6 to 8.5 and the temperatures ranged from 25 to 90 degrees C.

The observed solid phases were all Np(V) solids: $NaNpO_2CO_3.H_2O$ and Np_2O_5.

The measured aqueous Np concentrations ranged from ~10^{-3} to ~10^{-5} M.

Efurd et al. in a near-repeat of the Nitsche et al. experiments observed only Np_2O_5 as the solid phase, but also measured (slightly lower) aqueous Np concentrations that ranged from ~10^{-3} to ~10^{-5} M.

The Slow Kinetics Hypothesis

The hypothesis is that Np(IV) oxide is very slow to form in an aqueous solution of intially Np(V)(aq) [or Np(IV)(aq)] Even after more than a year of reaction time at 90 degrees C, previous experimental efforts starting with Np(V)(aq) have failed to observe the precipitation of NpO_2.

Our first approach is to use elevated temperature (~100-200 degrees C) to accelerate the kinetics of the reaction:

$$NpO_2^+ + 0.5\ H_2O = NpO_{2(s)} + H^+ + 0.25\ O_{2(g)}$$

Experiments

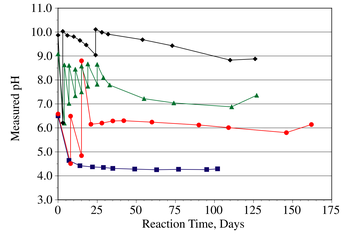
In each experiment, the initial Np concentration and pH were 10^{-4} M and 6.4, respectively. Thermodynamic calculations indicate that $NaNpO_2CO_3$ and Np_2O_5 should not form.

To three of the experiments, different amounts of NaOH was added to raise the solution pH, and periodically to try to restore it. In one (blue), the pH was allowed to drift.

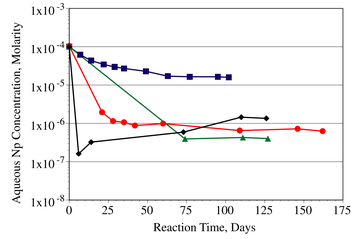
All vessels were placed into an oven preheated to 200 degrees C and allowed to react until steady-state aqueous Np concentrations were observed.

The solids were then collected by centrifugation and analyzed by XRD, XAS, and SEM.

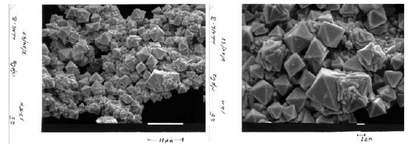
Measured pH Values Over Time



Aqueous Np Concentrations Over Time

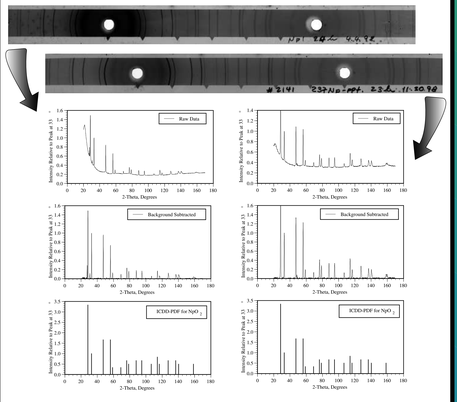


Scanning Electron Microscopy



The octahedra ranged in size from a few tens of microns to nearly 100 microns, and indicate the formation of high-purity NpO_2 crystals.

X-ray Powder Diffraction Analysis



X-ray Absorption Spectroscopy

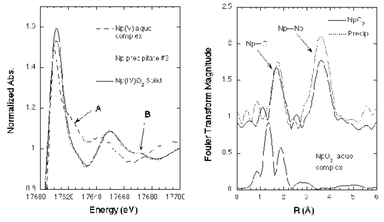


Figure 1. Np L3 Extended X-ray Absorption Fine Structure (EXAFS) Fourier Transforms for a reference neptunyl [NpO2+] penta-aquo complex, NpO2 solid, and the Np compound precipitated from our experimental study. Fourier peaks are shifted to lower R due to the EXAFS phase shifts. The strong correspondence in the Np-O and Np-Np peak positions and amplitudes for NpO2 and the precipitate indicates that the Np precipitate has a local structure similar to that in NpO2.

Figure 2. Np L3 X-ray Absorption Near-Edge Structure (XANES) for a reference neptunyl [NpO2+] penta-aquo complex, NpO2 solid, and the Np compound precipitated from our experimental study. Feature "A" is noted for the NpO2+ speices and originates due to multiple scattering within the linear neptunyl group. The XANES of the precipitate lacks any pronounced feature "A" and closely matches the XANES of NpO2 (see feature "B"). This "fingerprinting" along with spectral modeling indicate that the precipitate is composed primarily (>85%) of an amorphous or crystalline Np(IV) oxide.

Conclusions

Each elevated temperature solubility experiment showed a significant decrease in aqueous Np.

The solid phases from each experiment were identified by XRD as crystalline Np(IV) oxide.

XAS measurements confirmed that the solid phases were at least 85% Np(IV) oxide.

SEM micrographs showed that the NpO_2 was in the form of octahedra, which is indicative of high-purity crystals.

Final solution compositions are consistent with expectations based on existing thermodynamic data. The notion of high thermodynamic stability of NpO_2 is basically correct.

Conclusions (continued)

A tentative model rate law for NpO_2 growth suggests that at sufficient supersaturation, the rate is proportional to the thermodynamic activity of NpO_2^+, inversely proportional to the activity of H^+, and inversely proportional to the 1/4 power of the oxygen fugacity. This is currently based more on theoretical notions than real data, though the expected dependence of rate on pH is supported by the data shown above.

It seems highly likely that the precipitation of PuO_2 and AmO_2 from aqueous solution is also kinetically limited. This has implications for both long-term actinide migration in groundwaters and also possible use of temperature-accelerated reactions in chemical separation and waste stream processing. Much work remains to be done on the hydrothermal chemistry of the actinides in general.

Future Work

We will be continuing work to quantify the precipitation kinetics of NpO_2. We will be using previously used apparatus plus a mixed-flow reactor.

We plan to conduct one or two simple experiments with Pu similar to our first Np experiments. We will probably do one or two with Am as well, although this is less certain.

References

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