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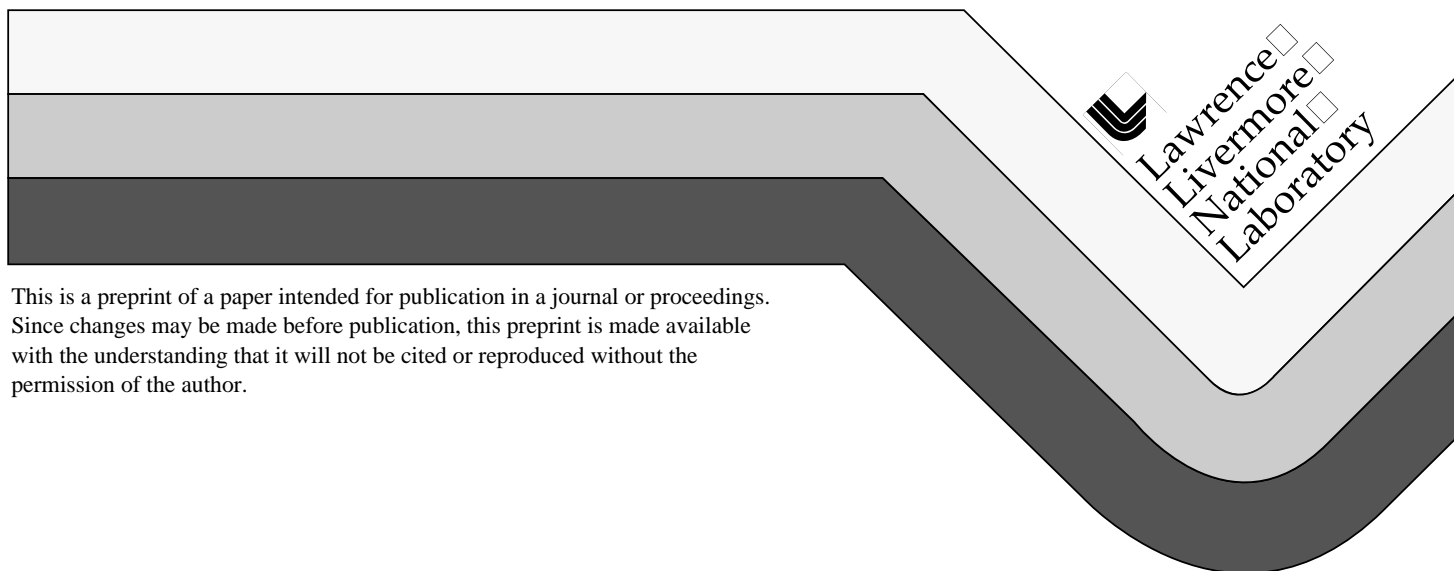
PREPRINT

The Hydrothermal Growth Kinetics of Np(IV) Oxide

T.J. Wolery
K.E. Roberts
C.E. Palmer

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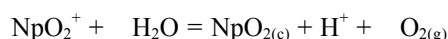
Thomas J. Wolery¹, Kevin E. Roberts², and Cynthia E. Palmer²

Lawrence Livermore National Laboratory, Livermore, CA 94550

¹Geologic and Environmental Technologies Division, L-219

²Isotope Sciences Division, L-231

Because of its long half-life, ²³⁷Np presents the possibilities of long-term radiological dose hazard in the geologic disposal of nuclear waste. In oxidizing groundwaters, dissolved Np is present as Np(V) mainly in the form of the NpO₂⁺ ion. In reducing groundwaters, it would be present as Np(IV), probably mainly as Np(OH)_{4(aq)}. EQ3/6 (Wolery, 1992) calculations based on existing thermodynamic data suggest that the stable solid phase under *both oxidizing and reducing conditions* in most groundwater systems is Np(IV) oxide, NpO_{2(c)}. Under oxidizing conditions, the reaction describing the relevant equilibrium is:



NpO_{2(c)} should be highly insoluble, corresponding to a dissolved Np concentration on the order of 1 x 10⁻¹³ molal in J-13 groundwater.

All previous knowledge leading to this estimate is of NpO_{2(c)} is indirect, based on thermodynamic cycles. The phase itself has heretofore not been observed as a precipitate from aqueous solution. Recent attempts (e.g., Nitsche et al., 1993; Efurud et al., 1996) to establish solubility controls on Np in oxidizing groundwaters (including J-13 groundwater) starting from high concentrations (i.e., supersaturation) have shown the formation of one or both of two Np(V) phases, NaNpO₂CO₃:3.5H₂O_(c) (with variable stoichiometry) and Np₂O_{5(c)}. These are both highly soluble, yielding Np concentrations on the order of 1 x 10⁻⁴ to 1 x 10⁻³ molal, in accord with existing thermodynamic data for these phases. No evidence was found of the formation of NpO_{2(c)}. Under reducing conditions, experiments (Rai et al., 1987 and references cited therein) have shown the formation of Np(IV) polymer, which may be viewed as a hydrated form of NpO₂. It is orders of magnitude less soluble than the Np(V) phases, but still orders of magnitude more soluble than NpO_{2(c)}. No undersaturation experiments with NpO_{2(c)} are known to have been performed. However, both NpO_{2(c)} and Np(IV) polymer are known to be difficult to dissolve.

We have hypothesized that NpO_{2(c)} is simply a phase that is slow to form at low temperature. In this regard, it would be analogous to such minerals as quartz, dolomite, and hematite. It is well known that it is difficult to impossible to demonstrate the formation of such minerals in low temperature experiments on feasible time scales. However, it is possible to demonstrate their formation and measure the kinetics of the process by conducting experiments at elevated temperatures, generally in the range of 150-300°C (e.g., Rimstidt and Barnes, 1980; Sibley et al., 1984). By developing kinetic models, it should be possible to estimate the appropriate time scales on which such solids might impose solubility constraints on natural groundwaters.

To test our hypothesis, we reacted solutions of 1 x 10⁻⁴ molal NpO₂⁺ (balanced with Cl⁻) at 200°C in closed Parr bombs (with air present). Some runs were conducted in teflon-lined reactors, others in titanium reactors with passivated surfaces. The pH was not buffered, and EQ3/6 calculations indicated that the initial solutions were supersaturated with respect to NpO_{2(c)} and undersaturated with respect to other possible Np solids. In the initial runs, the starting 25°C pH was 6-7. Periodically the reactors were cooled, opened, and the Np concentration and pH were measured. The Np concentration slowly dropped (Fig. 1), and the pH dropped to ~4.2. A very fine brown precipitate was observed. XRD analysis shows an eight-line match with NpO_{2(c)}, validating our hypothesis. Other experiments have been conducted with higher initial pH, and in which the original pH has been periodically restored by the addition of small amounts of base. These show a more rapid drop in dissolved Np (Fig. 1), indicating that the rate of precipitation is pH dependent. The precipitates are being characterized by XRD, EXAFS, and SEM. Additional experiments at 150, 250, and 300°C are currently planned to allow the development of a kinetic model that can be extrapolated to lower temperature. The use of a mixed flow reactor is also planned in future work.

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Figure 1. Neptunium molality as a function of time in 200°C experiments. Top curve (squares): initial (25°C) pH 6.5, no attempt to restore the original pH. Middle curve (circles): initial pH of 8, pH readjusted. Bottom curve (diamonds): initial pH of 10, pH readjusted.

