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ADVANCES IN ACTINIDE AND TECHNETIUM KINETICS FOR APPLICATIONS IN PROCESS FLOWSHEET MODELING

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ABSTRACT

The kinetics of actinide and technetium redox reactions are important in many separations processes; for instance, in the reprocessing of irradiated nuclear fuel by the Purex process. In this process, the kinetics of reactions in both aqueous nitric acid and organic tributyl phosphate (TBP) solutions are important. Kinetic data are particularly necessary for the computer simulation of flowsheets and become increasingly important as the residence times in extraction contactors are reduced. Although a large body of literature exists, some potentially important process reactions have not been sufficiently studied for modeling purposes. Additionally, if new redox reagents are to be considered for process applications, their rates of reaction need to be determined. A program of work has been undertaken to:

- Compile known data for application in modeling of process flowsheets.
- Obtain kinetic data to fill in gaps in the literature.

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- Study the kinetics of new redox reagents using conventional and stopped-flow techniques.

This paper summarizes recent studies, including:

- U(IV) and Np(IV) oxidation by HNO_3 in TBP phases.
- Tc(VII) – hydroxylamine reactions in the absence and in the presence of U(IV).
- Np(VI) and Pu(IV) reduction by a variety of new organic reductants, including oximes, substituted hydroxylamines, and hydroxamic acids.
- Kinetics of U and Np mass transfer in a single-stage centrifugal contactor.

INTRODUCTION

Purex is a very well established process for the reprocessing of irradiated nuclear fuel, and a vast amount of research on all aspects of it has been undertaken [e.g. see (1) and references therein]. However, further development and a greater understanding of the process are still possible. This is particularly true of "Advanced Purex" processes, which use different reagents, fewer solvent extraction cycles, and intensified contactors such as centrifugal contactors (2). It is widely appreciated that chemical reaction and mass transfer kinetics are important within the process and become increasingly so as contactor residence times decrease. The kinetic data reported in the past [for example, see (3) and references therein] can be incorporated into a computer-based process simulation to design and model Purex flowsheets more accurately than simple simulations using only equilibrium solvent extraction data (4). There are, however, still many gaps in this kinetic "library", particularly when combinations of reagents are used. When new reagents are put forward for process applications, their kinetics need to be properly determined for accurate modeling.

This paper gives a brief overview of a research program designed to (i) increase this kinetic library to allow more accurate modeling of current reprocessing plants and (ii) to assess potential new redox-active reagents that are being considered for Advanced Purex processes.

RESULTS AND DISCUSSION

Extending the Kinetic Library

BNFL process models have been described elsewhere (2, 4) and it should be emphasized that kinetics are only one of the components necessary for reliable process simulation. Kinetic data needed for modeling are compiled in a Reaction Database, which is both easily understandable and ready for use in modeling.

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The kinetics of many process reactions have been investigated and, in some cases, re-investigated [e.g., see references 5-10 in (5)]. Compilations of the literature data have also been published [e.g., (3)]. For instance, to model the behaviour of Np only in one part of the cycle only (the U/Pu split), our Reaction Database contains the reaction kinetics published in the open literature for 21 relevant reactions. There are still some surprising gaps, however, particularly in TBP phases, in the presence of U(VI) and combinations of species including catalyzed cycles. We, therefore, have an ongoing program, in collaboration with the Bochvar Institute, Moscow, Russia, to measure reaction rates of process reactions previously undetermined or uncertainly characterized. Examples include:

- U(IV) and Np(IV) oxidation by HNO_3 and HNO_2 in TBP phases
- Np(V) and (VI) reduction by U(IV) in 30% TBP
- Pu-catalyzed oxidation of U(IV) in 30% TBP
- Tc-catalyzed U(IV) oxidation by HNO_2 and HNO_3 in 30% TBP
- Np(V) oxidation by HNO_2 and HNO_3 in 30% TBP
- Pu(IV) reduction by Np(IV) in 30% TBP
- Np(VI) reduction by U(IV) in HNO_3.

The results of some of these studies have been published elsewhere (5-7). The oxidation reactions of U(IV) and Np(IV) with nitric and nitrous acids in TBP phases are described and compared below as summary examples of this part of our research program.

U(IV) and Np(IV) Oxidation by HNO_3 and HNO_2 in TBP Phases

The oxidations of U(IV) and Np(IV) by HNO_3 have been studied in TBP solutions and both reactions have been shown to follow the overall stoichiometric equation:

$$\begin{aligned} &An(NO_3)_4.2TBP + HNO_3.TBP + H_2O + 2TBP \\ &\qquad = AnO_2(NO_3)_2.2TBP + HNO_2.TBP + 2HNO_3.TBP \end{aligned} \quad (1)$$

Both reactions involve an induction period in which the actinide is being oxidized by HNO_3 and HNO_2 is formed[1]. The initial reaction products are more rapid oxidants of the actinide ion than HNO_3 and so the reaction becomes auto-

[1] Both of these oxidation reactions are slow at ambient temperatures and thus were studied at elevated temperatures (generally 50-60°C). U(IV) oxidation was studied in 30% TBP solution, while Np(IV) was studied in 100% TBP due to the slow rate of oxidation. The oxidation of Np(IV) in 30% TBP is even slower and differs from that in 100% TBP. It can be described by first-order kinetics, but the autocatalytic mode reappears when the temperature is further increased to 80°C. This transition between autocatalysis and first-order kinetics can be qualitatively accounted for from the kinetics and the mechanism (7).

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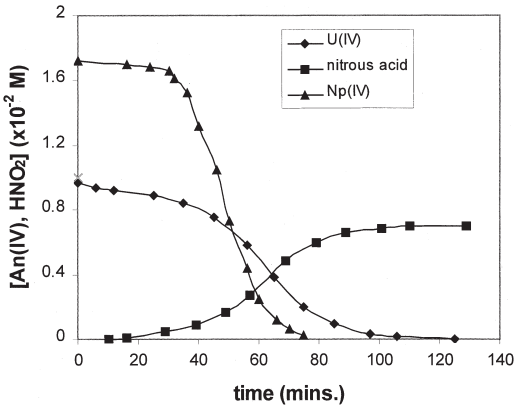

Figure 1. Autocatalytic oxidation of U(IV) (T = 55°C; [HNO3] = 0.05 M; $[H_2O]$ = 0.44 M) and Np(IV) (T = 60.2°C; $[HN0_3]$ = 0.2 M; $[H_2O]$ = 2.45 M) in 30% and 100% TBP phases, respectively. Also shown is the accumulation of HNO_2 during the autocatalytic cycle that corresponds to the oxidation of U(IV).

catalytic. Figure 1 illustrates the autocatalytic oxidations of U(IV) and Np(IV) and the corresponding growth of the autocatalyst, HNO_2, which is observed in the U(IV) experiment. Therefore, the overall rate equations for each reaction comprise a combination of non-catalytic and catalytic components. However, the TBP phase rate equations differ in their actual forms and (in the ionic form, ignoring TBP complexing) are described by (rate constants and activation energies are given in Table 1):

$$-\frac{d[U(IV)]}{dt} = k_1[U(IV)][HNO_3]^2 + k\frac{[U(IV)][HNO_2]}{[HNO_3]^2 + \beta_1'[HNO_3] + \beta_2'} \quad (2)$$

$$-\frac{d[Np(IV)]}{dt} = k_1''\frac{[Np(IV)]}{[H_2O]^{10}} + k_4\frac{[Np(IV)][Np(VI)][H_2O]^3}{[HNO_3]^4} \quad (3)$$

These differences are a consequence of their differing reaction mechanisms. The mechanism of U(IV) is likely to involve three steps:

$$U^{4+} + HNO_3 + H_2O \rightarrow UO_2^{2+} + HNO_2 + 2H^+ \quad (4)$$

$$U^{4+} + 2HNO_2 \rightarrow UO_2^{2+} + 2NO + 2H^+ \quad (5)$$

$$2NO + HNO_3 + H_2O = 3HNO_2 \quad (6)$$

Analysis of the data suggested that the autocatalytic reaction (5) is via the second hydrolysis product, $U(OH)_2(NO_3)_2$, and this leads to the hydrolysis con-

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Table 1. Rate Constants and Activation Energies for Rate Equations Described in the Text

Rate equation	Description	Rate constant	Activation energy	Ref.
2	U(IV) oxidation by nitric acid in 30%	$k_1 \approx 0.3\ l^2 \cdot mol^{-2} \cdot min^{-1}$ (55°C)	103 ±15	5
2	TBP[a]	$k = 0.125 \pm 0.020$ $mol \cdot l^{-1} \cdot min^{-1}$ (55°C)	93 ±5	5
3	Np(IV) oxidation by nitric acid in 100%	$k_4 = (9.5 \pm 0.8) \times 10^{-4}$ min^{-1} (60.2°C)	$E_4 = 90 \pm 2$	6
3	TBP	$k_1'' = (0.70 \pm 0.43)$ $mol^{10} \cdot l^{-10} \cdot min^{-1}$ (60.2°C)	$E_4 = 63 \pm 6$	6
18	Tc(VII) reduction by NH_2OH in HCl	$k_1 = 7.6 \pm 0.7 \times 10^{-2}$ $l \cdot mol^{-1} \cdot min^{-1}$ (80°C)	$E_1 = 92 \pm 3$	9
18		$k_2 = 20 \pm 2\ l^2 \cdot mol^{-2} \cdot min^{-1}$ (80°C)	$E_2 = 85 \pm 2$	9
19	Oxidation of NH_2OH by HNO_3 in the presence of Tc (VII) and absence of HNO_2	$k_1 = (2.8 \pm 0.4) \times 10^{-4}$ min^{-1} (80°C)	$E_1 \approx 15 \pm 4$	10
19		$k_2 = 2.7 \pm 0.3$ $l^5 \cdot mol^{-5} \cdot min^{-1}$ (80°C)	$E_2 = 60 \pm 3$	10
20	Oxidation of NH_2OH by HNO_3 in the presence of Tc(VII)	$k = 120 \pm 10$ $l^{4.5} \cdot mol^{-4.5} \cdot min^{-1}$ (80°C)	E = 160-180	This paper
23	U(IV) oxidation in the presence of Tc(VII)	$k_1 = (1.16 \pm 0.08) \times 10^{-3}$ $l^{1.05} \cdot mol^{-1.05} \cdot min^{-1}$ (25°C)	$E_1 = 73 \pm 3$	This paper
23	and NH_2OH	$k_5 = 48.9 \pm 3.6\ l^{2.4}$ $mol^{-2.4} \cdot min^{-1}$ (25°C)	$E_5 = 86 \pm 2$	This paper
25	Np(VI) reduction by acetaldoxime	$k_2 = 254 \pm 10\ min^{-1}$ (26.0°C)	$E_2 = 62.6 \pm 2.6$	17
26	Pu(IV) reduction by acetaldoxime	$k_3 = 25.3 \pm 1.9$ $mol^{1.1} \cdot l^{-1.1} \cdot min^{-1}$ (19.5°C)	$E_3 = 87.7 \pm 9.8$	17
27	Np(VI) reduction by EHEH	$k = 334 \pm 12$ $l^{0.2} \cdot mol^{-0.2} \cdot min^{-1}$ (25.6°C)	$E = 42.3 \pm 2.7$	13
28	Pu(IV) reduction by EHEH	$k = 58700 \pm 10300$ $mol^{1.3} \cdot l^{-1.3} \cdot s^{-1}$ (11°C)	$E = 127.2 \pm 8.4$	13

[a] $[H_2O] = 0.44$ M.

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stants, β_1 and β_2, being included in the rate equation[2]. The mechanism of the non-catalytic reaction (4) is more difficult to understand, but there are indications that, like the aqueous phase reaction (3), it involves a rate-determining nitronium ion oxidation of $U(OH)_2(NO_3)_2$ and then presumably a rapid U(V)-NO_2 reaction (5):

$$U(OH)_2^{2+} + NO_2^+ \rightarrow UO_2^+ + NO_2 + 2H^+ \quad (7)$$

$$UO_2^+ + NO_2 + H^+ = UO_2^{2+} + HNO_2 \quad (8)$$

The differing stabilities of the pentavalent ions [U(V) << Np(V)] are reflected in the reaction mechanisms (above and below) and in the final products – an equilibrium mixture of Np(V) and Np(VI) is produced in the Np(IV) oxidation. The overall autocatalytic reaction route in the oxidation of Np(IV) is a combination of contributions due to the generation of two different autocatalysts, Np(V) and HNO_2. It can be shown from the kinetics that the major route is via Np(V) reproportionation (below) with HNO_2 oxidation being a minor route only:

$$2Np^{4+} + HNO_3 + 3H_2O = 2NpO_2^+ + HNO_2 + 6H^+ \quad (9)$$

$$NpO_2^+ + HNO_2 + H^+ = NpO_2^{2+} + NO + H_2O \quad (10)$$

$$Np^{4+} + NpO_2^{2+} + 2H_2O = 2NpO_2^+ + 4H^+ \quad (11)$$

$$2NO + HNO_3 + H_2O = 3HNO_2 \quad (12)$$

Like U(IV), it is thought that the direct oxidant of Np(IV) in the non-catalytic reaction is also nitronium nitrate, (NO_2NO_3) (6).

Water is known to have a significant effect on the rates of actinide reactions in TBP phases [(6) and references therein]. For Np(IV) oxidation, this is evident from the kinetic equation. For U(IV), preliminary results showed that the observed effect of [H_2O] on the rate of the autocatalytic reaction agreed with the predicted effect due to hydrolysis [as in equation (2)] and that the induction period was reduced with increased [H_2O], although the exact relationship was not discerned. The activation energies are listed in Table 1 and attention is drawn to the fact that the respective activation entropies for the non-catalyzed and catalyzed U(IV) reactions are close to zero (~-6 and 4 $J \cdot mol^{-1} \cdot K^{-1}$) whereas those for Np(IV) reactions are –101 and –75 $J \cdot mol^{-1} \cdot K^{-1}$ (5-6).

As [TBP] is diluted, changes in Np(IV) oxidation occur. It is likely that the contribution due to HNO_2 increases with dilution and that the k_1:k_4 ratio changes. Although much more study is needed, it may be that, in 30% TBP, the mechanism becomes more similar to that of U(IV) (7).

[2] $\beta_1' = \beta_1[H_2O] = 0.03$ M, and $\beta_2' = \beta_2[H_2O]^2 = 0.006$ M^2 at 55°C.

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Novel Process Reagents

Advanced Purex flowsheets, which use only one solvent extraction cycle and different redox-active reagents to alter routings of some species (2, 8), have been suggested, although further research is needed. Kinetic data are particularly important, both to assess potential and to enable flowsheet design. Examples of our studies in this area include:

- Tc(VII) – hydroxylamine reactions in the absence and in the presence of U(IV).
- Np(VI) and Pu(IV) reduction by a variety of new salt-free organic reductants, including oximes, substituted hydroxylamines and hydrazines, and hydroxamic acids.
- Reactions of these organic reagents with Tc(VII) and nitric and nitrous acids.
- Photocatalytic reduction.

The results of some of these studies have been published elsewhere (9-13). The interactions between Tc and NH_2OH and reduction of Np(VI) and Pu(IV) by some new organic reductants are described below as summary examples of this part of our research program.

Tc(VII) – Hydroxylamine Reactions in the Absence and in the Presence of U(IV).

Hydroxylamine has often been suggested for use in the U/Pu split as either a reductant for Pu(IV) (14) or an anti-nitrite (9), in which case it would be used in combination with U(IV). Hydrazine, which is the current anti-nitrite of choice in reprocessing plants, is known to undergo interfering catalytic reactions with fission product Tc(VII). When U(IV) is present, the same reaction cycles occur, except with the major difference that the induction period is removed due to the rapid reduction of Tc(VII) by U(IV) (15). Therefore, if hydroxylamine is to be used in the U/Pu split its interactions with Tc ions need to be understood, in both the absence and the presence of U(IV).

It should be noted that the oxidation of NH_2OH by HNO_3 and HNO_2 has been studied extensively and its behaviour is governed by two limiting reactions [references 4, 10, 12-23 in (9)]. The balance of the yields of N_2O and HNO_2 depends on the initial concentrations of NH_3OH^+ and HNO_3 and on the temperature[3].

[3] In acid, hydroxylamine and hydrazine are present as the protonated forms, NH_3OH^+ and $N_2H_5^+$, respectively.

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$$NH_3OH^+ + HNO_2 \Leftrightarrow N_2O + 2H_2O + H^+ \quad (13)$$

$$NH_3OH^+ + 2HNO_3 \Leftrightarrow 3HNO_2 + H_2O + H^+ \quad (14)$$

The direct reaction between Tc(VII) and NH_2OH is very slow and could only be measured in HCl and at elevated temperature:

$$4TcO_4^- + 6NH_3OH^+ + 24HCl \Leftrightarrow 4TcCl_6^{2-} + 3N_2O + 19H_2O + 10H^+$$

It was found that Tc(VII) slowly oxidizes NH_2OH by an autocatalytic mechanism which involves a slow reduction to Tc(V) followed by a rapid reduction to Tc(IV) and then Tc(V) reproportionation. The data suggested that Tc(IV) ions in reaction (17) participate as $TcCl_5^-$ rather than $TcCl_6^{2-}$ ions:

$$2Tc(VII) + 2NH_3OH^+ \xrightarrow{k_1} 2Tc(V) + N_2O \quad (15)$$

$$4Tc(V) + 2NH_3OH^+ \rightarrow 4Tc(IV) + N_2O \quad (16)$$

$$Tc(VII) + 2Tc(IV) \xrightarrow{k_2} 3Tc(V) \quad (17)$$

The rate equation was found to be:

$$-\frac{d[Tc(VII)]}{dt} = k_1[Tc(VII)][NH_3OH^+] + k_2[Tc(VII)][Tc(IV)][H^+] \quad (18)$$

During the later stages of the reaction, Tc(IV) was also shown to form a complex with NH_2OH which retarded the oxidation reaction (9).

The Tc(VII)-catalyzed nitric acid oxidation of NH_2OH was then studied in the *absence* of nitrous acid (10). Again, this reaction was found to be autocatalytic, although since HNO_2 was not available in the solution (rapidly scavenged by the addition of sulfamic acid) the reaction mechanism was difficult to understand. However, for the purposes of modeling, the kinetics could be adequately described by the equation:

$$-d[NH_3OH^+]/dt = k_1[NH_3OH^+] + k_2[NH_3OH^+]([NH_3OH^+]_0 - [NH_3OH^+]')[Tc(VII)][HNO_3]^3 \quad (19)$$

The oxidation of NH_2OH by HNO_3, in the presence of Tc(VII) ions and with HNO_2 that was allowed to accumulate, unlike equation (19), was then studied. The observed reaction has an induction period that is dependent on the initial concentrations and temperature. There is then a catalyzed reaction in which HNO_2 is formed, and this product reacts rapidly with NH_2OH. Essentially, then, the rate of oxidation of NH_2OH by HNO_3, in the presence of Tc(VII), follows the same regularities as when Tc is absent [see (9) and references therein], with Tc ions having little observable effect (Table 2). Thus, the observed rate equation of the NH_2OH–HNO_3 reaction, catalyzed by HNO_2, is dependent only on $[NH_3OH^+]$, $[HNO_2]$, and $[HNO_3]$ – not on [Tc(VII)] ions:

$$-d[NH_3OH^+]/dt = k[NH_3OH^+][HNO_2][HNO_3]^{3.5} \quad (20)$$

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Table 2. Tc(VII) Ion-Catalyzed Oxidation of NH_3OH^+ by HNO_3 ($[NH_3OH^+] = 0.05$ M)

T (°C)	$[Tc(VII)]_o$ (M)	$[HNO_3]$ (M)	$[NaNO_3]$ (M)	τ (min)	$[HNO_2]_{max}$ (x 10^{-2} M)	k' ($l \cdot mol^{-1} \cdot min^{-1}$)
70	0	2.0	-	1.0	1.00	100
70	0.01	2.0	-	2	1.02	61
80	0	1.0	1.0	4	0.72	28
80	0	1.5	0.5	1,1	1.16	101
80	0	2.0	-	0.1	1.17	>300
80	0.005	1.0	1.0	14	0.75	24
80	0.01	1.0	1.0	33	0.93	27
80	0.01	1.5	0.5	1.5	1.18	114
80	0.01	2.0	-	0,4	1.07	>300

However, the presence of Tc does have one effect; that is, the induction period (τ) is increased as the Tc(VII) ion concentration is increased. The effects of Tc ions on τ at 80°C, $[HNO_3] = 1$ M, $[NH_3OH^+] = 0.05$ M, $\mu = 2$, are as follows:

[Tc(VII)] (M)	0	0.005	0.01	0.02
τ (min)	4	14	33	>120

At lower temperatures the induction period is long and NH_2OH is effectively stable. For instance, at 25 and 40°C, $[HNO_3] = 2$ M, $[NH_3OH^+] = 0.1$ M, $\mu = 2$, and $[Tc(VII)] = 0.01$ M; no HNO_2 was formed, and no change in $[NH_3OH^+]$ was observed for >8 hours.

At the end of the reaction, that is when all the NH_2OH has been oxidized, $[HNO_2]$ reaches a maximum value and then slowly decreases. This is due to the disproportionation of HNO_2:

$$3HNO_2 = 2NO + HNO_3 + H_2O \quad (21)$$

The presence of Tc does also apparently alter the rate equation for the disproportionation of HNO_2, which may be due to the incorporation of NO_2^- groups into a Tc(V)-hydroxylamine complex that is observed to form during the course of the reaction.

Therefore, it has been shown that, in the absence of U(IV), hydroxylamine does not undergo catalyzed reactions with Tc(VII) in the same manner as does hydrazine. Indeed, Tc(VII) actually has a stabilizing influence on NH_2OH oxidation.

When U(IV) is present, however, the situation becomes much more complex. Figure 2 illustrates the change in [U(IV)] with time. It can be seen that there is a very rapid initial oxidation of U(IV) followed by a slower zero order reaction and then an acceleration towards the end of the reaction. This is,

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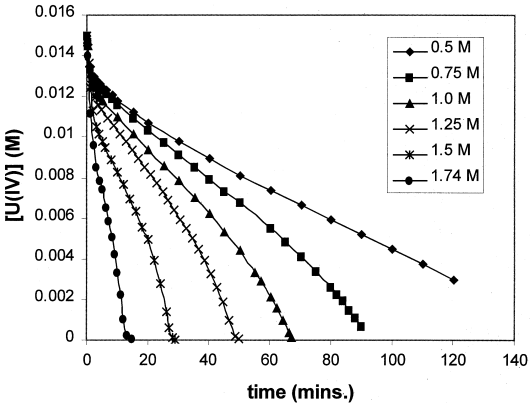

Figure 2. U(IV) oxidation in varying nitric acid solutions in the presence of hydroxylamine and Tc(VII) (T = 35°C; $[NH_3OH^+]$ = 0.1 M; [Tc(VII)] = 5 x 10^{-4} M).

therefore, very different from the situation where U(IV) is absent and where hydrazine–Tc(VII)–HNO_3–U(IV) reactions occur.

While the mechanism is still uncertain, there is evidence for a "critical zone" in which a transition occurs in the U(IV) oxidation rate. This may be due to the changing balance of reactions (13) and (14) and NH_2OH becoming a net generator of HNO_2 rather than a net scavenger. Figure 2 refers to the reactions outside the critical zone, and the rate-determining step in the zero-order reaction may be the re-oxidation of Tc(IV):

$$2TcO^{2+} + 3HNO_3 + 3H_2O \rightarrow 2TcO_4^- + 3HNO_2 + 6H^+ \quad (22)$$

If this is the case, then, excluding the initial fast reaction, the rate of U(IV) oxidation can be described by a combination of the rates of the slow Tc(IV)- and U(IV)-nitric acid oxidation reactions:

$$-d[U(IV)]/dt = k_1[U(IV)][HNO_3]^{1.05} + k_5[Tc(IV)]^{1.8}[HNO_3]^{1.6} \quad (23)$$

This equation describes the experimental data reasonably well although further investigations of the reaction mechanism are needed to properly understand this complex system.

Finally, the stabilization of U(IV) by blends of hydroxylamine and hydrazine has been investigated. In this case, as can be seen from Fig. 3, the oxidation of U(IV) is still accelerated as compared with hydrazine alone and the similarities with the U(IV)–Tc(VII)–HNO_3–NH_2OH system appear to be retained, although the presence of $[N_2H_5^+]$ has reduced the extent of the initial fast reaction.

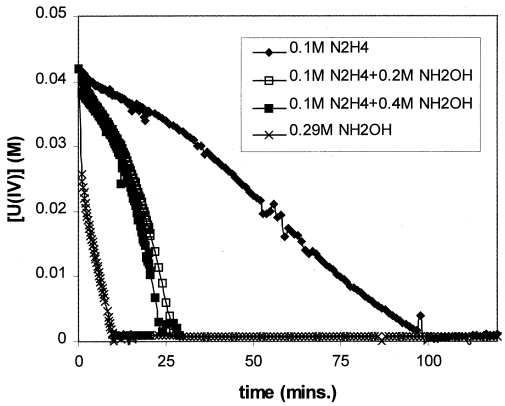

Figure 3. Effects of N_2H_4 and mixtures of N_2H_4 and NH_2OH on U(IV) oxidation in 1.2 HNO_3 in the presence of 0.0043 M Tc(VII) ions (T = 35°C).

New Organic Reductants for Np(VI) and Pu(IV)

To enable the specific routing of Np and Pu to various process streams in Advanced Purex flowsheets (2, 8) we have been investigating various classes of organic salt free reagents [e.g., see (11-13, 16, 17)].

Hydroxamic acids have previously been suggested as hydrophilic *complexants* for tetravalent actinides [Np(IV) and Pu(IV)] to enable their separation from $UO_2(NO_3)_2.2TBP$ (16, 18). Hydroxamic acids are also *reducing agents,* which, as the determination of onset potentials has shown[4] (20), are probably thermodynamically capable of reducing Np(VI) and Pu(IV). The reduction of Np(VI) by formo-hydroxamic and aceto-hydroxamic acids (FHA and AHA) is particularly fast, probably proceeding according to the reaction:

$$4NpO_2^{2+} + 2HCONHOH + H_2O \rightarrow 4NpO_2^{+} + N_2O + 2HCOOH + 4H^{+} \quad (24)$$

The kinetics, as determined by stopped-flow spectrophotometry, have been shown to be first order with respect to [FHA] and [Np(VI)] with a rate constant $k'' = 1019$ $M^{-1}s^{-1}$ at 22°C and $[HNO_3] = 2M$[5]. The reduction of Pu(IV) ions is, however, much more complex (20) since, (i) hydroxamic acids hydrolyze in acid; (ii) the hy-

[4] The conversion of onset potentials to standard redox potentials using the methodology of (19) is ongoing.

[5] In excess HNO_3. The order with respect to $[H^+]$ and $[NO_3^-]$ has not yet been verified.

drolysis products are hydroxylamine, which itself reduces Pu(IV), and the corresponding carboxylic acid, which we have observed enhances the rate of the Pu(IV)-hydroxylamine reaction; (iii) the hydroxamate ligand complexes Pu(IV), thus altering the reduction potentials and probably stabilizing Pu(IV) against reduction; and (iv) evidence exists that the hydroxamate bound to the metal ion hydrolyzes at a slower rate than does free hydroxamate. Due to the very complex nature of this system, the kinetics have not yet been determined.

We have also studied other organic reagents capable of converting both Np(VI) and Pu(IV) to their inextractable forms, Np(V) and Pu(III), including acetaldoxime and a disubstituted derivative of hydroxylamine, ethyl(hydroxyethyl) hydroxylamine (EHEH) (12, 13). Both are very effective reductants for Np(VI) and Pu(IV). The kinetic equations for the reduction of Np(VI) and Pu(IV) by acetaldoxime are:

$$-\frac{d[Np(VI)]}{dt} = k_2 \frac{[Np(VI)][CH_3CHNOH]}{[HNO_3]} \tag{25}$$

$$-\frac{d[Pu(IV)]}{dt} = k_3 \frac{[Pu(IV)]^2[CH_3CHNOH]^{1.1}}{[Pu(III)][HNO_3]^{2.2}} \tag{26}$$

Note that, like mono-substituted hydroxylamines, the rate of Pu(IV) reduction is inhibited by the product Pu(III) ions. The reductions of Np(VI) and Pu(IV) ions by EHEH are described by:

$$-\frac{d[Np(VI)]}{dt} = k \frac{[Np(VI)][HOC_2H_4(C_2H_5)NHOH^+]}{[H^+]^{0.8}} \tag{27}$$

$$-\frac{d[Pu(IV)]}{dt} = k \frac{[Pu(IV)]^2[HOC_2H_4(C_2H_5)NHOH^+]^{1.4}}{[HNO_3]^{3.7}} \tag{28}$$

The major advantage of EHEH is that it is a very fast reducing agent for Pu(IV). For instance, the calculated time for 99% Pu(IV) reduction with 0.1 M EHEH at 25°C and $[HNO_3] = 1.0$ M is 0.342 s, which is ~16 times faster than with the very similar diethylhydroxylamine. It is suggested that the incorporation of the OH group into EHEH makes it such an effective reductant due to the consequent large increase in the activation entropy (i.e., $\Delta S^*_{EHEH} = 270$ cf. $\Delta S^*_{diethylhydroxylamine} = 54$ J·mol^{-1}·K^{-1}). The reaction mechanisms have been described in similar terms to mono-substituted hydroxylamines, for acetaldoxime, and other di-substituted hydroxylamines for EHEH. Acetaldoxime is thought to interact with the hydrolyzed forms of Np(VI), i.e., NpO_2OH^+, and Pu(IV), i.e., $PuOH^{3+}$. Simple solvent extraction experiments have confirmed that both of them are effective in the reductive stripping of Np(VI) and Pu(IV) in the presence of U(VI) in two-phase systems.

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Mass Transfer Rates

As well as chemical reaction rates, the rate of mass transfer of species becomes increasingly important as the residence time in solvent extraction contactors decreases. Therefore, we are also studying the rates of mass transfer in centrifugal contactors.

Considerable research has been done in the past relative to mass transfer and, particularly, in reference to solvent extraction systems in the Purex process, mainly focusing on U(VI) and HNO_3 extraction (21-23). Some development work has been conducted with centrifugal contactors, although few relevant data are available in the open literature (24, 25). Previous α-active centrifugal contactor rig trials have indicated that our understanding of actinide mass transfer between nitric acid and 30% TBP/OK is incomplete, particularly with respect to Np(IV) stripping in a Np rejection stage of an advanced reprocessing plant (16). In general, the controlling mechanism of extraction/back extraction is still a topic for debate and could be controlled by either a chemical or a mass transfer step, or a combination of both. The high mass transfer area generated in centrifugal contactors also increases the degree of difficulty in modeling extraction data in these systems.

Initial single stage mass transfer studies using a 1-cm single stage centrifugal contactor have focused on U(VI) and Np(IV) extraction. In a series of U(VI) experiments, the major effect on extraction was the increase in flow rate of the feed solutions, which led to a decrease in residence time and hence a decrease in mass transfer. From our U(VI) extraction data, it is noticeable that the rate of mass transfer (mass transfer efficiency) was increased with increased U(VI), HNO_3 and free TBP concentrations at the interface, although we have not yet fully quantified these effects. The most noticeable effect was free TBP. Such results provide good evidence that mass transfer efficiency is, at least in part, controlled by chemical kinetics not just by physical rates of mass transfer (26, 27). As of yet, the effect of rotor speed has not been fully investigated and is complicated by the competing effects of changing mixing volume and mass transfer surface area as the rotor speed is varied. These data have been incorporated into process models and, with the exception of variable rotor speed results, they are in good agreement with ongoing model development.

Recent Np(IV) trials in the absence and in the presence of U(VI) have indicated that the rate of mass transfer for Np(IV) is far slower than that for U(VI) at different flow rates (Fig. 4). This difference in mass transfer rates for different metal ions has previously been observed in centrifugal contactor systems (28). Further Np(IV) extract and strip single-stage mass transfer experiments are under way in the presence of hydroxamic acids to evaluate the effect of Np(IV) mass transfer on Np rejection flowsheets (4, 16, 29).

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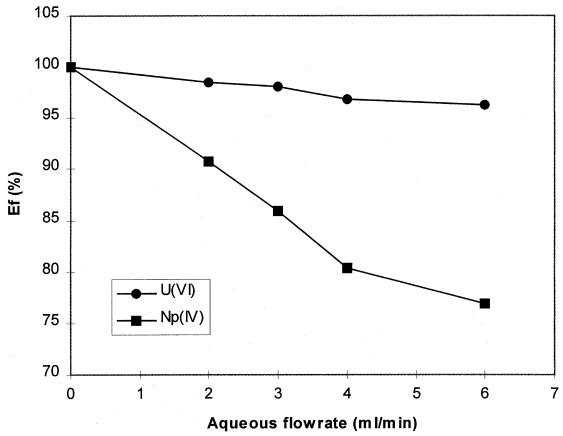

Figure 4. Single-stage 1-cm centrifugal contactor trials at variable flow rates (2:1 30% TBP/OK: 1.8 M HNO_3). Initial U(VI) and Np(IV) concentrations in the aqueous phase were 20.1 g/l and 0.3 g/l, respectively. Ef is the fractional approach to equilibrium and is calculated from aqueous actinide ion concentrations before and after extraction and is related to the equilibrium value. The equilibrium experiment was undertaken separately and is included at flow rate = 0 ml/min.

CONCLUSIONS

Chemical reaction and mass transfer kinetics are important components of Purex process simulations. A co-ordinated research program is being undertaken to provide base data necessary for the computer modeling of current and future Purex flowsheets.

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