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The applications of formo- and aceto-hydroxamic acids in nuclear fuel reprocessing

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Abstract

The Purex process has been successfully used to reprocess irradiated nuclear fuel for over 40 years. However, enhancements to the process are still possible; in particular the development of a single cycle flowsheet is a major objective of a future ‘Advanced Purex’ process. New salt-free reagents to separate Pu(IV) and Np(IV) from U(VI) suitable for use in a single cycle flowsheet have been developed. Formo- and aceto-hydroxamic acids (FHA; AHA) have been shown to preferentially complex tetravalent actinides and to strip them from 30% TBP/OK in to the aqueous nitric acid phase. Additionally these hydroxamic acids will reduce Np(VI) to inextractable Np(V) thus allowing the separation of Np from U. This reaction has fast kinetics which makes these reductants suitable for use in centrifugal contactors which have very short residence times. The use of FHA and AHA in reprocessing, particularly to control Np, has been demonstrated using laboratory scale experiments, single stage and multi-stage centrifugal contactor trials and computer simulation of the process. © 1998 Elsevier Science S.A.

Keywords: Neptunium; Hydroxamates; Complexation; Nuclear reprocessing; Spectrophotometry; Separation

1. Introduction

The development of a single cycle reprocessing flowsheet with the consequent reduction in plant size, complexity and waste volumes is a major objective of a future ‘Advanced Purex’ process. The efficient control of neptunium within the single cycle design has been identified as an important part of the process and a previous paper has discussed the requirements for methods of Np control within an Advanced Purex process in detail [1].

This paper will show that hydroxamic acids have useful physical and chemical properties that allow them to be effectively used in an Advanced Purex process to control both Np(IV) and Np(VI).

2. Experimental methods

Chemicals were either obtained from reputable suppliers (Aldrich, Fluka and Cookson Chemical companies) or prepared ‘in-house’ using standard methods. Following dissolution of solid NpO_2, Np is present almost exclusively at Np(VI) and, after quantification of the trace amounts of Np(V), this was used as the Np(VI) stock solution without further treatment. Np(IV) stock solutions were obtained by reducing the Np solution with Fe(II) and then separation of Fe and Np by solvent extraction in to 30% TBP/OK and backwashing in to 0.01 M HNO_3 if required.

A Perkin–Elmer λ19 spectrophotometer has been used as the standard method to follow the reduction and complexation of Np species in solution. The spectrophotometer is linked by fibre optics to either an external sample compartment or a dipping optrode for in-situ measurements. Total Np concentrations have been determined by low energy photon spectroscopy; uranium concentrations by X-ray fluorescence and acidities by titration with NaOH. Simple batch solvent extractions were used to determine Np and U distribution coefficients [2].

The hydrolysis of FHA was investigated by adding FHA solution to nitric acid in a constant temperature water bath and removing samples at specific time intervals. The FHA concentration of each sample was determined by a colorimetric method using the complex formed with

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Fe(III) which has a peak absorbance at 488.9 nm. The reaction with nitrous acid was followed spectrophotometrically using the HNO_2 peak at 372 nm.

3. Results and discussion

3.1. Properties of hydroxamic acids

Hydroxamic acids are organic ligands of general formula RCONHOH which can act as good chelating agents for metal ions by the formation of five-membered chelate rings. As O,O donor ligands they have a strong affinity for 'hard' metal ions such as Fe^{3+}, Al^{3+} and Pu^{4+} [3–5]. Simple hydroxamates such as acetohydroxamic acid ($R = CH_3$) and formohydroxamic acid ($R = H$) are hydrophilic ligands which are not extracted in to TBP to any appreciable degree. The extractability does however increase as the carbon chain length is increased so that valerohydroxamic acid is substantially extracted [6].

Since hydroxamic acids are composed of only C, H, N and O atoms they can be decomposed to gases so that their incorporation in to industrial processes will not lead to increases in waste volumes. The decomposition of FHA to gases in 6 M HNO_3 has been demonstrated using ^{13}C NMR [2]. Also FHA or the Np–FHA complex can be decomposed by the addition of HNO_2 but due to the rapidity of the reaction it could only be measured at low $[HNO_3]$ [7]. This is a useful property since the hydroxamic acid can be used to scavenge HNO_2 in the Purex process and an additional scavenger such as hydrazine may not be necessary.

In nitric acid (<3 M) hydroxamic acids hydrolyse to give hydroxylamine and the parent carboxylic acid. The kinetics of this hydrolysis reaction for FHA have been determined. No influence of U(VI) or nitrate ions on the reaction rate was observed. The rate of hydrolysis decreases as the carbon chain increases so FHA is the least stable hydroxamic acid in HNO_3. However, in an Advanced Purex plant using centrifugal contactors, this can be overcome by careful flowsheet controls and operation.

$$-\frac{\mathrm{d}[\mathrm{FHA}]}{\mathrm{d}t} = k[\mathrm{FHA}][\mathrm{H}^+]$$

where $k = 0.016 \pm 0.001\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}$ at 25°C; $E_{\mathrm{Act}} = 77.3 \pm 1.6\ \mathrm{kJ\ mol^{-1}}$.

3.2. Complexation of actinides by hydroxamic acids

By inference from the published literature, it appears that trends in stability constants for actinide–hydroxamate complexes may increase in the order $\beta_{U(VI)} < \beta_{H+} < \beta_{U(IV)} < \beta_{Np(IV)} < \beta_{Pu(IV)}$ [3,8–11]. If benzohydroxamic acid is taken as an example then the ratio of $\beta_{Pu(IV)}$: $\beta_{U(VI)}$ equals 10^4 [10,11] and so in dilute acid solutions it should be possible to preferentially complex tetravalent actinides in the presence of U(VI).

To investigate the ability of hydroxamic acids to inhibit the extraction of Np(IV) in 30% TBP/OK, an intensive programme of simple distribution experiments coupled with spectrophotometric studies of Np(IV) complexation have been undertaken [2]. It has been shown that $D_{Np(IV)}$ values are decreased by increased formohydroxamic acid concentration and increased by increased nitric acid concentration. Thus at low HNO_3 concentration and high FHA concentration Np(IV) can be effectively stripped from 30% TBP/OK into the aqueous phase. At all stages of the distribution experiments the Np speciation was checked by vis/NIR spectrophotometry to ensure the absence of Np(V) and Np(VI) contamination and also the changing peak shapes of Np(IV) were used to follow the complexation of Np(IV) in both aqueous and solvent solutions (Fig. 1). Np(IV) exhibits characteristic absorption bands at 723 and 960 nm in 0.2 M HNO_3 and at 706 and 729 nm in 30% TBP/OK. The spectrum of Np(IV) does however vary with $[HNO_3]$ [12] and this is most probably explained by the presence of various nitrato species which dominate at different acidities (cf. Pu(IV) nitrates studied by Viers and co-workers [13,14]). On the addition of hydroxamic acid solution distinct peaks at 714, 732, 851 and 975 nm are observed. The change in the height of the absorption peak can be used to indicate when near complete complexation occurs (see Fig. 2) which for FHA and AHA was between 2–2.5 times excess of ligand. This suggests the formation of 1:1 and 2:1 complexes. Complex formation is inhibited at higher $[HNO_3]$.

The complexation of UO_2^{2+} by FHA and AHA occurs readily in near neutral solutions to give a red/orange solution and in some solutions a red precipitate is formed on standing for long periods (e.g. $[U] = 50\ \mathrm{g\ l^{-1}}$; $[\mathrm{ligand}] = 2$ M; $t = 24$ h). However, increased $[HNO_3]$ inhibits this reaction and in 1 M HNO_3 no precipitate is formed even after 3 weeks [2].

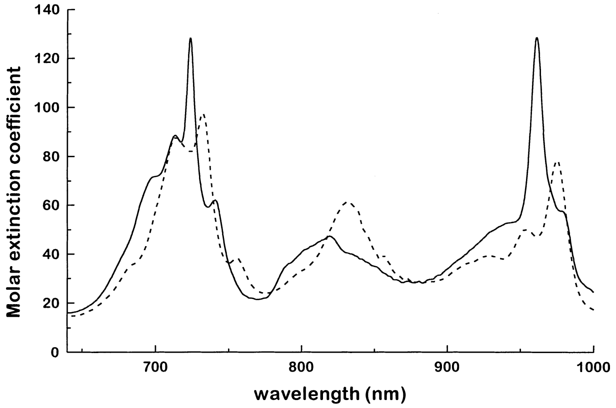

Fig. 1. Np(IV) absorption spectra in 0.2 M HNO_3 (solid line) and 0.2 M HNO_3 with excess FHA.

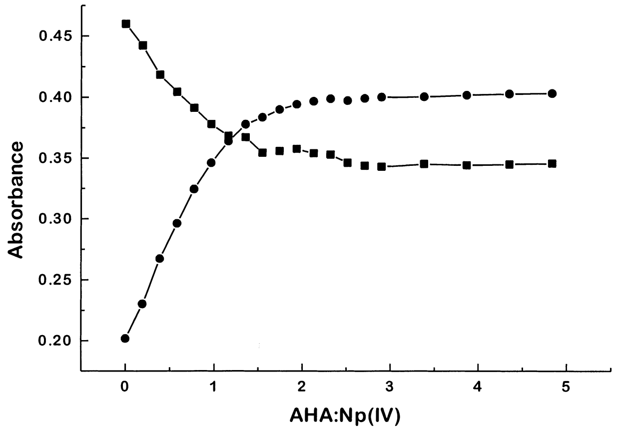

Fig. 2. Change in absorbance for Np(IV) peaks on complexation by FHA and AHA (■ = uncomplexed Np(IV) at 723 nm; ● = Np(IV)–AHA complex peak at 732 nm).

3.3. *The reduction of Np(VI) by FHA and AHA*

It was observed during this research programme that in nitric acid FHA and AHA can reduce Np(VI) to Np(V) over a very short timescale. Pu(IV) is complexed and then slowly reduced and U(VI) is either not reduced or reduced at a negligible rate. The hydroxamic acid is oxidised probably to the parent carboxylic acid and nitrogen oxides [15].

Fig. 3 shows the fast reduction of Np(VI) by FHA which has been followed spectrophotometrically at 1223 nm using an in-situ VIS/NIR dipping optrode. The reaction is completed in <5 s and this has made the accurate determination of the reaction kinetics difficult although preliminary indications are that the kinetics are probably similar to the Np(VI) + NH_2OH reaction [16]. Experiments using stopped flow spectrophotometry are in progress to fully characterise the rate equation. The reduction of Np(V) to Np(IV) by FHA in HNO_3 essentially does not occur due to the hydrolysis of FHA.

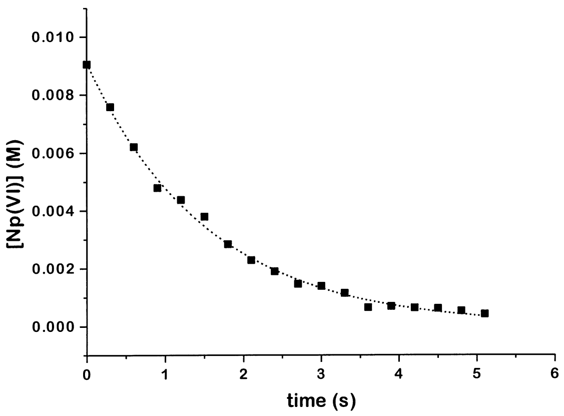

Fig. 3. Np(VI) reduction by FHA in 1.78 M HNO_3($[Np(VI)]_0 = 0.009$ M; $[FHA]_0 = 0.0099$ M; $T = 20.8$°C).

Table 2
The separation of U(VI) from Np(IV) by FHA ($[Np(IV)]_0 = 0.005$ M; $[U(VI)]_0 = 0.27$ M; $T = 23$°C).

Initial [FHA] (M)	D_{Np}	$D_{Np(IV-FHA)(calc.)}$	$D_{U(VI)}$	$D_{U(VI)(calc.)}$
0	0.12	0.074	2.99	2.62
0.1	0.0051	0.0077	2.96	2.66
0.5	0.010	0.0035	3.02	2.60
1.0	0.012	0.0031	2.81	2.78

3.4. *Np/U separation by FHA and AHA*

U/Np(VI) separation has been demonstrated by simple solvent extraction experiments in which a 30% TBP/OK solution of U(VI) and Np(VI) is contacted with an aqueous phase of HNO_3 and FHA. Distribution coefficients were calculated for both U(VI) and Np and compared to model results (based on BNFL algorithms derived from published literature such as [17] and in-house experiments – see Table 1). Similar experiments were performed with Np(IV) (see Table 2). It can be seen that in both cases there is a good agreement between model and experimental results. So these results do indicate that Np(VI) is fully reduced to Np(V) and stripped in to the aqueous phase and Np(IV) is stripped by the formation of an inextractable complex with FHA. In all the experiments U(VI) extraction is unaffected with $D_{U(VI)}$ remaining large and in agreement with the model prediction.

4. Conclusions

Hydroxamic acids offer significant advantages in the control of neptunium in Advanced Purex flowsheets. They

Table 1
The separation of U(VI) from Np(VI) by FHA ($[Np(VI)]_0$~0.006 M; $[FHA]_0 = 0.25$ M; $T = 22.8$°C; initial aqueous $[HNO_3] = 0.5$ M).

Equilibrium aqueous acidity (M)	Initial [U] (M)	D_{Np}	$D_{Np(V)(calc.)}$	$D_{U(VI)}$	$D_{U(VI)(calc.)}$
1.16	0.21	0.029	0.011	5.95	5.81
1.1	0.042	0.0045	0.016	8.26	8.21
2.66	0.22	0.018	0.013	16.56	14.65
0.86	0.24	0.0054	0.0080	3.88	3.99

can selectively reduce Np(VI) to Np(V) on fast timescales which are compatible with centrifugal contactors and they can preferentially complex tetravalent actinides (Np(IV) and Pu(IV)) in the presence of U(VI). They are salt-free reagents which can easily be decomposed to gases and they can scavenge nitrous acid so additional reagents such as hydrazine are unnecessary. Thus waste volumes can be minimised quite effectively. Flowsheet trials in centrifugal contactors have been carried out and Np/U separation has been demonstrated.

Further work is currently in progress to accurately determine the kinetics of Np(VI) reduction using stopped flow spectrophotometry. A large database of distribution data is being compiled for all the tetravalent actinides (U(IV, Np(IV) and Pu(IV)) to assist the simulation of hydroxamic acids in the Purex process. Further flowsheet trials are being performed to optimise the flowsheet and single stage centrifugal contactor experiments are also being used to follow the reaction chemistry in a controlled process environment.

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