Ruthenium Speciation in Model Nuclear Fuel Process Solutions.

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Abstract *– Ru speciation is being investigated systematically from models of high level waste solutions right through to the calcination process and the vitrified glass product. The characterisation of these species is complicated due to the fact that a wide range of ruthenium nitrosyl/nitrite/nitrate complexes can be present in nitric acid waste solutions. The general formula for these complexes is* $RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}^{+3-x-y-z}$*. A range of different techniques has been used for the characterisation of these species in solution, including electron absorption spectroscopy, vibrational spectroscopy, multi-nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy.*

INTRODUCTION

A wide range of fission products are formed in the nuclear reactions from the thermal fission of ^{235}U or ^{239}Pu. Most of these products are unstable, short-lived radioisotopes, although some can impinge on nuclear fuel reprocessing and waste management operations. The relatively long-lived, stable fission products ^{103}Ru (T = 39.8 days) and ^{106}Ru (T = 1 year) are two such isotopes [1].

During the dissolution of irradiated nuclear fuel in nitric acid in the Purex process, numerous neutral, anionic and cationic ruthenium nitrosyl nitrate/nitrite complexes are formed, which are in equilibrium with each other. These different complexes can be converted into one another by ligand exchange, depending on external conditions, such as the concentration of nitric acid, and temperature. Ruthenium(II) is the most common oxidation state in these solutions with the general formula $RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}^{+3-x-y-z}$. There is also the possible distribution of ruthenium species between the organic (30% tri-n-butylphosphate in organic diluent) and aqueous phases during solvent extraction which can affect the decontamination process [2]. Part of the ruthenium co-extracts with uranium and plutonium in the first cycle of the Purex process, enters the following purification cycle and is finally routed with the medium level aqueous waste.

Eventually most of the ruthenium is directed towards the highly active aqueous nitric acid liquors for eventual calcinations and vitrification. Care must be taken to prevent the release of volatile ruthenium (mainly in the form of ruthenium tetroxide) during these high temperature processes as both ^{103}Ru and ^{106}Ru are β-active radio nuclei [3].

Studies on the behaviour of the fission product ruthenium in the aqueous waste arising from the reprocessing of spent nuclear fuel are scarce and, of these few studies, most are based on ruthenium removal [3]. The research reported in this paper has been performed in order to obtain a better understanding of Ru speciation in simulated aqueous waste solution using a wide range of complimentary spectroscopic techniques, including vibrational spectroscopy, electronic absorption spectroscopy, multi-nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy.

EXPERIMENTAL

All chemicals used were obtained from standard supply. $RuNO(NO_3)_3(H_2O)_2$ and $Na_2[RuNO(NO_2)_4OH]$ were synthesised according to previously reported methods [4]. Infrared (ATR) and Raman spectra were recorded on a Bruker Elmar spectrometer. Variable temperature electronic absorption spectra were recorded in a specially adapted furnace using a computer controlled fiber optic Avantes Avaspec-2048-2 spectrometer with an Avalight-DH-S deuterium/halogen light source.

^{15}N NMR spectra were recorded on a Varian Aramis Inova 400 MHz spectrometer. EXAFS data were measured in the fluorescence mode on station BM20 of the ROBL beamline at ESRF Grenoble and on station 9.3 at the CLRC Daresbury Laboratory. The spectra were summed, calibrated and background subtracted using the Daresbury Laboratory programs EXCALIB and EXBACK. The spectra were simulated using the EXCURV98 program. Where necessary, the effects of multiple scattering were included in the analysis.

RESULTS AND DISCUSSION

The determination of the Ru speciation in a complex matrix is an exceptionally challenging task and requires a range of complimentary techniques. Infrared, Raman and UV/vis spectroscopy are all readily available. NMR is also available, but the ^{15}N enriched isotopes are expensive. Specialist facilities are required to undertake XAS measurements. The information that can be gained from each technique is listed in table 1.

TABLE 1. Properties of the characterisation techniques used.

Techn.	Information obtained	[Ru] conc. (mol L^{-1})
IR/ Raman	- ligands coordinated - coordination mode of $NO/NO_2^-/NO_3^-$	10^{-1} to 10^{-3} and solids
UV/vis	- ligands coordinated (NO_2^-/NO_3^-)	10^{-2} to 10^{-6}
Multi-nuclear NMR	- ligands coordinated - coordination mode	$> 10^{-1}$
XAS (Ru K edge)	- oxidation state - coordination number - bond distances	10^{-1} to 10^{-3}

Vibrational Spectroscopy

Solutions of $RuNO(NO_3)_3(H_2O)_2$ and $Na_2[RuNO(NO_2)_4OH]$ complexes were dissolved in various concentrations of $HNO_3/NaNO_2/NaNO_3$. The effect of the temperature on the speciation was investigated.

The nitrosyl stretching frequency is typically found between 1900 and 1800 cm^{-1}. For ruthenium complexes only linear nitrosyl groups have been previously observed [5]. The coordinated nitrite ligand has two characteristic bands, one in the region 1500 to 1400 cm^{-1} ($\nu_{as}(NO_2)$) and one in the region 1350 to 1050 cm^{-1} ($\nu_s(NO_2)$). Nitrito (coordination through N) complexes also have a frequency at *c.a.* 620 cm^{-1} (ν (Ru-N)), which the nitro (coordination through O) complexes do not have. Nitrate complexes have three stretching frequencies in the IR in the regions 1500 – 1400 cm^{-1} ($\nu_{as}(NO_2)$), 1310 – 1250 cm^{-1} ($\nu_{as}(NO_2)$) and around 1000 cm^{-1}(ν (N=O)). The separation of the two highest frequency bands is generally larger for bidentate coordination compared to unidentate coordination [6].

The vibration stretches for coordinated nitrite and nitrate in solution are usually weak and are often obscured by bands for uncoordinated NO_3^- or NO_2^-. It is therefore more useful to study the coordination of nitrite and nitrate by examining the shift of the nitrosyl frequency. We observe that the nitrosyl stretching frequency for complexes containing nitrate ligands tend to come at higher energy (1925 cm^{-1}) than in complexes containing nitrite ligands (1890 cm^{-1}). Also, the asymmetric stretching frequency for the nitrate complex can be observed at higher energy than the stretching frequency for nitrite complexes.

When $Na_2[RuNO(NO_2)_4OH]$ was dissolved in NO_3^- solutions (either $NaNO_3$ or HNO_3), two nitrosyl stretching frequencies (around 1890 and 1910 cm^{-1}) were observed directly after dissolution, while only one frequency remained (at around 1905 cm^{-1}) after heating (9h, 80°C) (see figure 1). This indicates that at least some of the nitrite ligands are replaced by nitrate ligands.

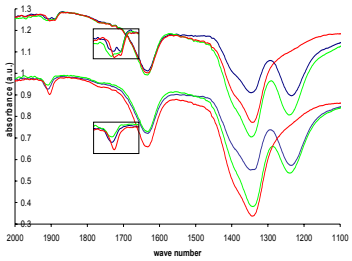

Figure 1. 0.25M $Na_2[RuNO(NO_2)_4OH]$ in 5M $NaNO_2$/2M $NaNO_3$ (blue), in 5M $NaNO_2$/5M $NaNO_3$ (green) and in 5M $NaNO_3$ (red). Spectra were measured directly after dissolution (top) and after 9h at 80°C (bottom).

For the nitrate complexes only one band could be observed, which shifted from around 1930 to around 1905 cm^{-1} upon the addition of $NaNO_2$. These frequencies shifted to around 1925 cm^{-1} upon heating (9h, 80°C). This indicates that the nitrate ligands are partially displaced by nitrite

ligands, although after heating the solutions possibly less nitrite ligands remain coordinated.

The addition of $NaNO_2$ to solutions of the nitrate complex in nitric acid (5M) did not show significant changes in the spectra, even after heating. This could be due to the fact that NO_2^- is not stable in nitric acid [7].

UV/vis Spectroscopy

The UV/vis spectra of ruthenium nitrate and nitrite complexes are expected to be dominated by broad metal-to-ligand-charge-transfer transition bands. Initial results indicate that it is possible to determine between the presence of coordinated nitrate and coordinated nitrite. Complexes with coordinated nitrite have one broad band in the visible region at ~ 420 nm, while complexes containing coordinated nitrate have a band at ~ 360 nm with an additional broad band at ~ 450 nm (see figure 2). It has been possible to monitor the displacement of nitrate ligands from $RuNO(NO_3)_3(H_2O)_2$ in 5M $NaNO_2$ and nitrite ligands from $Na_2[RuNO(NO_2)_4OH]$ in 5M HNO_3 at high temperature (80°C), using this technique.

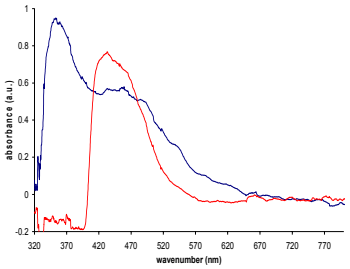

Figure 2. UV/vis spectra of 0.013M solutions of $RuNO(NO_3)_3(H_2O)_2$ in 7.5M HNO_3 (blue) and in 5M $NaNO_2$ (red).

Multi-nuclear NMR

^{15}N NMR has only been used to a limited extent to study transition metal nitrosyl complexes. However, ^{14}N and ^{15}N NMR are particularly suitable characterisation techniques to distinguish linear and bent nitrosyl ligands coordinated to transition metal complexes. The ^{15}N resonances for the different ligands are represented in table 2 [8].

Preliminary results show that the NO_3/NO_2 ligand exchange can be monitored using ^{15}N NMR.

TABLE 2. ^{15}N NMR resonances for nitrosyl, nitrate and nitrite.

Ligand	δ (ppm)
Nitric acid	-22
Uncoord. nitrate ($NaNO_3$)	0
Uncoord. nitrite	235
Coordinated NO_2^- (through N)	75 to 100
Bridging NO_2^-	110
Linear NO^+	-40 to -20
Bent NO^-	600 to 700
Coordinated NO_3^-	0 to -20

A solution of $Na_2[Ru^{15}NO(^{15}NO_2)_4(OH)]$ in 7.5M $H^{15}NO_3$ was measured over time while heating (80°C) and the growth of a resonance attributed to a coordinated nitrate ligand at -19.26 ppm can be observed (see figure 3). Interestingly, the nitrosyl resonance does not appear to shift upon the exchange of nitrite for nitrate.

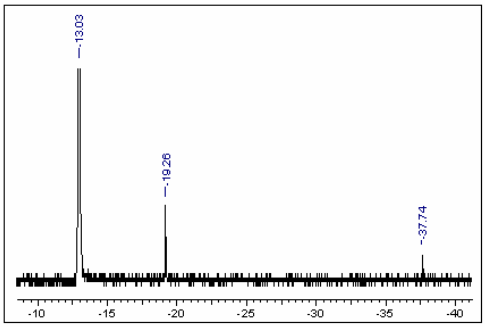

Figure 3. ^{15}N NMR spectrum of $Na_2[Ru^{15}NO(^{15}NO_2)_4(OH)]$ in 7.5M $H^{15}NO_3$ measured after heating to 80°C.

X-ray Absorption Spectroscopy (XAS)

XAS is a highly versatile and element specific technique that allows the study of the oxidation state (XANES) and coordination environment (EXAFS) (Extended X-ray Absorption Fine Structure). XAS experiments were carried out at the Ru K-edge (22 keV). EXAFS spectra have been recorded on a solution of 0.25M $Na_2[RuNO(NO_2)_4OH]$ in nitric acid and $RuNO(NO_3)_3(H_2O)_2$ in 5M $NaNO_2$. The solutions were measured immediately after dissolution and were then heated to 80°C and measured at various time intervals (10, 40 and 105 minutes) to determine the change in speciation. The spectra were compared to those of the nitrate complex in nitric acid and the nitrite complex in sodium nitrite.

It is difficult to distinguish between nitrogen and oxygen atoms, because O and N have similar backscattering properties. The Ru – nitrate and

Ru – nitrite (coordinated through O or N) bond lengths are similar, however the Ru – NO (nitrosyl) bond is significantly shorter. It is also possible to distinguish between nitro and nitrito coordinated ligands because of the different ratios of filling the first and second shell. However, it is not possible to distinguish between species when a number of complexes coexist since only average bond lengths can be observed. It is thus difficult to determine nitrite or nitrate is coordinated in the solutions. However, it is possible to see subtle changes in the spectra over time and the spectra can be compared to those of the reference solutions (see figures 4 and 5), and it is possible to see the speciation change from the nitrate complex into the nitrite complex with heating and *visa versa*. Finally, it is possible to fit Ru – Ru interactions in some of the spectra, indicating dimerisation. However, these results need confirmation.

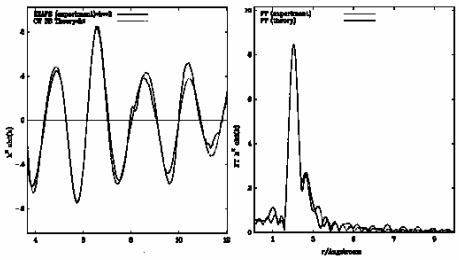

Figure 4. EXAFS (Ru K-edge) and associated Fourier transform of 0.25M $RuNO(NO_3)_3(H_2O)_2$ in 7.5M HNO_3. Solid lines represent experimental data, dashed lines the fit.

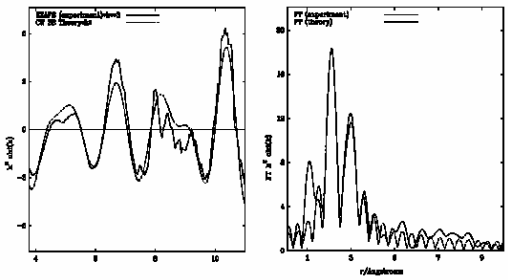

Figure 5. EXAFS (Ru K-edge) and associated Fourier transform of 0.25M $Na_2[RuNO(NO_2)_4(OH)]$ in 5M $NaNO_2$. Solid lines represent experimental data, dashed lines the fit.

CONCLUSIONS

Determining the ruthenium speciation and NO_3^- /NO_2^- ligand exchange in model nuclear waste solution is a difficult task, because of the complexity of the system. The possibility of the formation of dimeric or even polymeric species (especially at higher Ru concentrations) gives an even greater level of complexity. The need for a variety of spectroscopic techniques is required to be able to characterise the speciation in solution. Even though the concentration of ruthenium in nuclear waste is lower than required for many of these spectroscopic techniques, a good indication can be obtained of the behaviour of ruthenium species in nitric acid solutions.

It is possible to distinguish between nitrate and nitrite coordination to the $\{RuNO\}^{3+}$ core through the use of a multiple spectroscopic technique approach. In addition, the higher solution temperature leads to the formation of more thermodynamically favourable products. Future work will focus on the attempt to determine the solution structures of the major complexes that exist in solution.

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