LA-UR- 09-08250

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Title:

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Intended for:

Proceedings of the Symposium on Emerging Trends in Separation Science and Technology (SESTEC-2010), Indira Gandhi Center for Atomic Research, Kalpakkam, India, March 1-4, 2010.

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Development of Alkaline Solution Separations for Potential Partitioning of Used Nuclear Fuels

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Abstract

The processing of used nuclear fuel in alkaline solution provides potentially useful new selectivity for separating the actinides from each other and from the fission products. Over the last decade, several research teams around the world have considered dissolution of used fuel in alkaline solution and further partitioning in this medium as an alternative to acid dissolution. The chemistry of the actinides and fission products in alkaline solution requires extensive investigation to more carefully evaluate its potential for developing useful separation methods for used nuclear fuel.

Introduction

The production of nuclear power from low-enriched or natural uranium fuels in current generation reactors yields highly radioactive used fuel that still contains a large potential energy source. Over the last six decades, a wide range of separation processes have been investigated to recover the energy value of the actinides in used fuel and efficiently dispose of the fission products. However, the only process deployed on a large scale industrially is the well-known PUREX (Plutonium-Uranium Reduction EXtraction) process [1].

Briefly, the PUREX process involves dissolution of the used fuel in nitric acid, removal of the cladding fragments and undissolved solids, selective extraction of U(VI) and Pu(IV) from the nitric acid solution into an organic phase consisting of tributylphosphate in a hydrocarbon solvent, back extraction and production of U and Pu, or U and U/Pu product solids, and disposition of the fission products and minor actinides into a glass waste form. The fission product and transuranic elements produced in the used fuel are mostly atomically dispersed in the UO_2 matrix and the nitric acid is required to dissolve the UO_2 matrix to enable the fission products and actinides to be separated in the subsequent liquid-liquid extraction process.

While the PUREX process has dominated used fuel processing, there has been a continuing search for new separation approaches that can reduce the cost of partitioning used fuel and provide additional separations that can enhance waste disposition options. For waste disposition both reduced costs and decreased environmental legacy can be important [2]. Two examples of alternative separation approaches for used fuel that have resulted in substantial development efforts are fluoride volatility and pyroelectrochemical processing in molten chloride salts. In these approaches the uranium matrix is converted into non-aqueous fluid phases (UF_6 or U(III) in chloride salts) to allow the subsequent separation of actinide and fission product elements [1].

Over the last decade, several research teams around the world have considered dissolution of used fuel in alkaline solution and further partitioning in this medium as an alternative to acid dissolution. The impetus for these efforts has been the recognized solubility of uranium in alkaline solutions containing some strongly complexing anions such as carbonate and the potential use of the different speciation and solubility of actinide and fission product elements in alkaline solutions relative to acid solutions to accomplish significant partitioning, even during the initial dissolution of the fuel. For example, oxidizing carbonate solutions can be pumped through certain uranium ore bodies in situ to recover uranium.

A brief summary of the research efforts of teams in Japan and South Korea will be given to illustrate some of the potential advantages envisioned for separations in alkaline media. Not surprisingly, this work has employed surrogate materials for used nuclear fuel. Generally the surrogates contain uranium and non-radioactive fission product elements. There is a large need for data on speciation and solubility of the transuranic elements and their mixtures with uranium and fission products to further develop separations processes in alkaline solution. This is especially true in solutions where multiple complexing anions are present, such as carbonate-peroxide or hydroxide-peroxide. A research team at Los Alamos National Laboratory has been working to fill this gap and an overview of some the results of this effort will be presented in this paper.

Investigations of Alkaline Solution Separation Processes for Used Fuel

A research team in Japan has proposed a series of conceptual separation processes for used fuel in alkaline carbonate solutions [3-5]. A combined schematic of the process variations is shown in Figure 1. In the initial paper [3], a process for separating components of used fuel under "mild aqueous conditions" was described and tested using a surrogate dissolution solution of U(VI) and 17 fission product elements (Re(VII) was used to mimic Tc) in 1 M nitric acid. The process began with dissolution of the used fuel in nitric or hydrochloric acid with the strong oxidants ozone in HNO_3 or ClO_2 in HCl, followed by addition of a $Na_2CO_3/NaHCO_3$ solution to adjust the pH to 8-9, and centrifugation of precipitated material from the solution. The U(VI) remained in the solution (presumed to be the triscarbonato complex, $UO_2(CO_3)_3^{4-}$), along with Cs, Rb and Re (all >94%), Mo (~60%), Ru (~25%) and Zr (~25%).

Sodium tetraphenylborate was added to the U(VI) solution to precipitate the Cs and Rb (>97%) as BPh_4^- salts. The uranium was then precipitated from solution by addition of NaOH to give a pH of 12-13 (>99.9 % recovery). Nearly all of the Zr and ~8% of the Mo co-precipitated with the uranium from this solution. Pu and Np were expected to be present as the analogous Pu(VI) and Np(VI) complexes and accompany the U(VI) (although this was not tested).

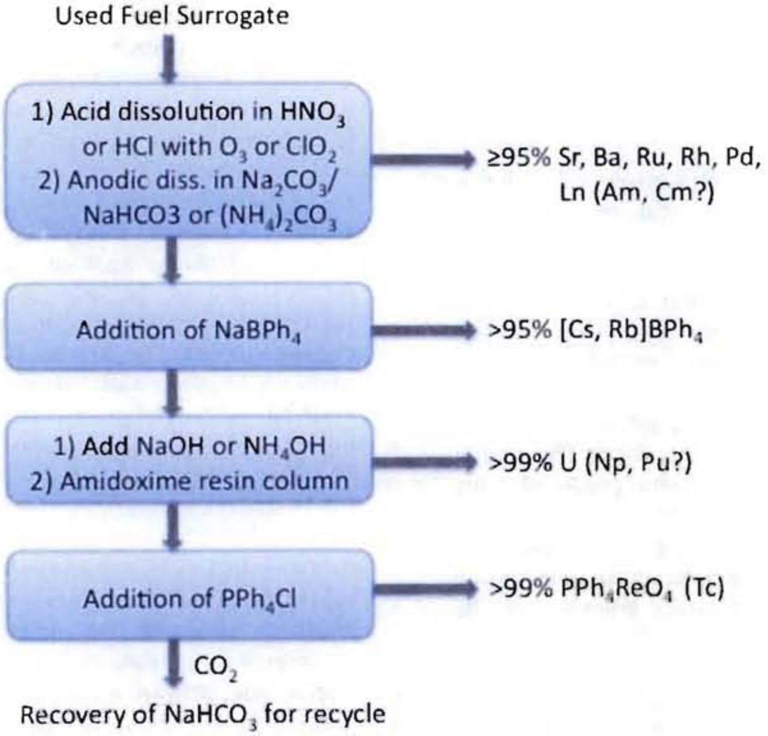

Figure 1. Schematic of separation processes in carbonate solution proposed for used nuclear fuel and partially tested with surrogate materials in Japan [3-5].

The lanthanides, Y, Sr, Ba, Rh Te (all >95%), Zr (~75%), Mo (~40%), Ru (~75%), and Pd (~60%) were found in the precipitate from the carbonate addition. Trivalent Am and Cm were assumed to accompany the lanthanides, but this was not verified. Washing with a dilute acid solution (pH 6-7) was proposed to dissolve the Sr and Ba away from the other elements in the precipitate, but no test results were reported. Methods for recycle of the carbonate solutions were not discussed.

In a later paper, a separation process was proposed that occurred completely in $Na_2CO_3/NaHCO_3$ solution, reduced the number of filtration/centrifugation steps, and considered potential recycle of the carbonate [4]. A schematic of this variation is also shown in Figure 1. For testing of the conceptual flowsheet, simulated pellets of used fuel were employed consisting of UO_2 with 13 fission product elements incorporated in the appropriate atomic ratios for a used fuel. The relatively volatile fission product elements Cs, Rb, Re (for Tc) and Te were not present because they would have been lost during the sintering of the pellet material at 1700 °C.

The process began with an electrochemically-driven oxidation of the UO_2 into a 0.5 M Na_2CO_3 and 0.5 M $NaHCO_3$ solution at 2 V relative to the normal hydrogen electrode [4,6]. As the U dissolved, a precipitate containing the fission product elements formed. The anodic oxidation of the UO_2 solid was continued until the U(VI) approached 0.3 M. In these tests, precipitates were collected on a filter disk of nominal 0.45 micron pore size. The overall precipitation behavior of the fission product elements resembled that measured in the previous work when a nitric acid solution was mixed with $Na_2CO_3/NaHCO_3$ solution [3]. The anodic potential was predicted to produce Np(VI), Pu(VI), Am(III) and Cm(III), but this was not tested experimentally.

The precipitation of Cs (containing Cs-137 as a tracer) with sodium tetraphenylborate was tested using a simulated dissolved fuel solution with U (containing U-237 as a tracer) and 17 fission product elements [4]. The precipitation was essentially quantitative and the precipitate contained very little U. In the conceptual flowsheet it was assumed that sodium tetraphenylborate could be added to the solution after anodic dissolution and the $CsBPh_4$ (and $RbBPh_4$) precipitate filtered off with the other insoluble fission product and TRU elements to eliminate a filtration step.

After the precipitation of Cs, NaOH was added to the U solution to give a pH of 12-13 to precipitate the U(VI). A recovery of 99.8% was measured. Some Zr and Pd co-precipitated with the U. Np and Pu were presumed to accompany the U in this step.

After recovery of the U, the carbonate solution still contains ReO_4^- (to mimic TcO_4^-), Ru and Mo. The addition of tetraphenylphosphonium chloride was used to precipitate ReO_4^-, the excess tetraphenylborate from the Cs precipitation, and a fraction of the Ru and Mo.

The carbonate solution is now at pH 12-13, but has relatively low radioactivity. The addition of CO_2 to this solution was investigated to precipitate up to 70% of the $NaHCO_3$ for recycle to the anodic dissolution step. The residual solution could be used to wash precipitates or could be concentrated by evaporation to recover a higher yield of $NaHCO_3$.

In another paper in the series by the Japanese team, the anodic dissolution of a simulated UO_2 fuel pellet containing 13 fission product elements was studied in more detail in ammonium carbonate solution instead of Na_2CO_3-$NaHCO_3$ [5]. The proposed separation flowsheet was similar to that in ref. 4, but now an amidoxime resin was used to sorb U (and Pu) directly from the solution from the dissolver without precipitating Cs. The amidoxime resin had been shown in another report to retain U(VI), Pu(VI), and Pu(IV) in 0.5 M Na_2CO_3 and 0.5 M $NaHCO_3$ solution, but not Ru(III), Pd(II), Zr(IV), Mo(VI), or Re(VII) [7]. The sorbed U(VI) was readily eluted from the resin with 0.5 M HNO_3. It was assumed that Pu would behave similarly. Addition of ammonium hydroxide to the nitric acid eluant solution from the column containing U and Pu was proposed to precipitate the U and Pu. These steps were not tested.

The further processing of the effluent from the amidoxime column containing the Cs, Rb, and part of the Zr and Mo was not discussed. Presumably precipitation of the Cs with tetraphenylborate could be considered as described before [4].

The Japanese research team argued that this series of separations using precipitations with filtration/centrifugation and/or a chelating resin column could be simpler and safer than other reprocessing methods. This was estimated to result in a smaller footprint for the facility and thus lower costs.

In recent work at the Korea Atomic Energy Research Institute (KAERI), a separation process has been proposed for used nuclear fuel that uses alkaline peroxide-carbonate solutions to dissolve the fuel and recover U while leaving the TRU elements with the group of initially precipitated fission products (see figure 2) [8]. A surrogate used fuel was prepared by mixing UO_2, NpO_2, oxide powders of 11 fission product elements (Re_2O_7 as an analogue of Tc), and Cs_2CO_3 in the proper molar ratios for a used fuel of 33 GWd/tonne burn-up. The solid mixture was dissolved in various concentrations of Na_2CO_3 and H_2O_2 at a pH of about 12. The behavior of the fission product elements was similar to that observed by the team in Japan with Sr, Ba, Zr, Ru, Pd, and the lanthanides being very insoluble and about 70% of the Mo in the precipitate. The NpO_2 was also very insoluble and Am(III) and Cm(III) were assumed to follow the lanthanides. Cs, Re and Te were observed to be highly soluble along with the U(VI) and about 30% of the Mo was also found.

Sequential addition of $NaBPh_4$ and PPh_4Cl was used to precipitate Cs and Re in high yield with results very similar to the previous work in Japan [4]. Very little of the Mo and Te were observed in the precipitate.

The U(VI) was assumed to be present as a mixed carbonato-peroxo complex, $UO_2(CO_3)(O_2)^{2-2x-2y}$, based on literature reports. After removal of the Cs and Re, this solution was acidified to pH 2-3 with nitric acid and the U precipitated and recovered in high yield as the peroxide complex $UO_2(O_2)\bullet 4H_2O$. The CO_2 released during the acidification was recovered in a gas absorption column using NaOH solution to give a Na_2CO_3 solution suitable for recycle to the dissolution step. More detailed characterization of the precipitates from U(VI) in Na_2CO_3 and H_2O_2 solutions from adding HNO_3 or NaOH are found in another report from this group [9].

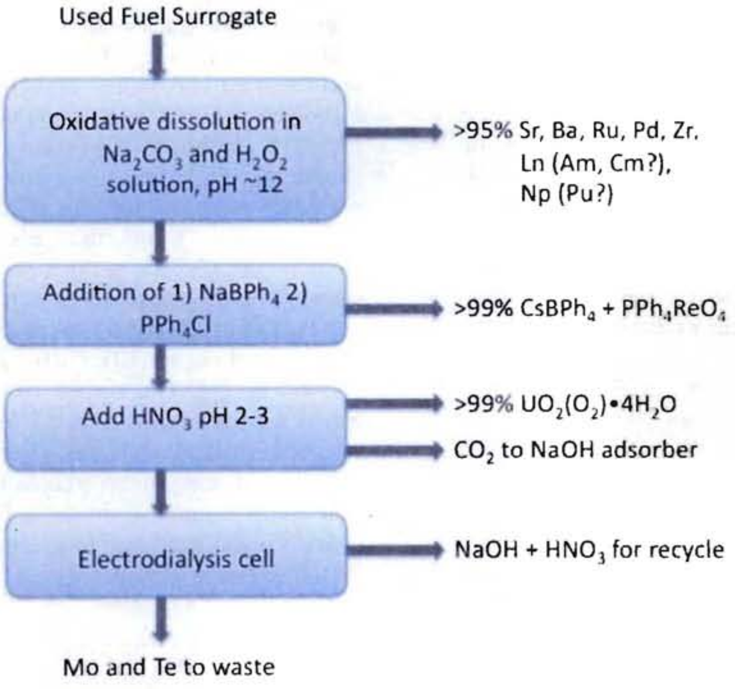

Figure 2. Schematic of separation process in carbonate-peroxide solution proposed for used nuclear fuel and partially tested with surrogate materials at KAERI [8-11].

The filtrate from the U precipitation step contained the remaining Mo and Te in a solution of $NaNO_3$ at pH 2-3. This solution was processed in an electrodialysis cell to yield solutions of NaOH and HNO_3 of about 0.5 M that could be reused in the process. More detailed studies of the electrodialysis process and the equipment developed for this work are found in other reports from the KAERI team [10,11].

In the KAERI work, the fate of the Np, Pu, Am and Cm mixed with a portion of the fission products was not further discussed. The process was considered to have enhanced proliferation resistance, operational safety, and environmental "friendliness" for recycle of the uranium from used fuel.

Alkaline Solution Chemistry of the U, Np, Pu and the Lanthanides

At Los Alamos National Laboratory, a research team has been investigating the fundamental chemistry of the actinides and selected fission products in alkaline solutions to lay the groundwork needed to design separation processes for used nuclear fuel processing. In an early report, the rate of dissolution of UO_2 in carbonate-oxidizer solutions was studied as a function of the cation type (Li^+, Na^+, K^+, NH_4^+) and concentrations of the carbonate and oxidizer (H_2O_2, NaOCl, $K_2S_2O_8$) [12]. The UO_2 was prepared at 500-700 °C and had a BET surface area of 1.17 m^2/g. The fastest rates of dissolution were observed with H_2O_2 and sodium and ammonium carbonates. The dissolution rate increased linearly with H_2O_2 concentration up to about 1 M and then leveled off. Carbonate concentrations much below 0.5 M or above 3 M resulted in precipitation of solids at relatively long times after dissolution. A starting solution of about 0.5 M Na_2CO_3 or NH_4CO_3 and 1 M H_2O_2 appeared optimal for UO_2 dissolution.

The chemistry of U(VI) in carbonate-peroxide solutions has proven to be remarkably complex. At low U(VI) concentrations (~0.5 mM) and low peroxide concentrations in carbonate solution one major species is observed [13]. As shown in Figure 3, addition of aliquots of H_2O_2 to a solution of $UO_2(CO_3)_3^{4-}$ in 0.5 M K_2CO_3 results in the generation of a new species in the UV-Vis spectrum. Even in the presence of the large excess of carbonate, hydrogen peroxide at less than 1 mM rapidly displaces a carbonate ligand to form $UO_2(CO_3)_2(O_2)^{4-}$. Raman and infrared data in solution and solid state and ^{13}C NMR data are all consistent with the formation of the $UO_2(CO_3)_2(O_2)^{4-}$ complex in solution. The apparent formation constant of this complex from the reaction of $UO_2(CO_3)_3^{4-}$ and H_2O_2 was determined to be $\log K' = 4.70 \pm 0.02$ [12]. It is not yet known whether this surprisingly large formation constant is due to more favorable steric or electronic factors or both when the peroxide ligand replaces a carbonate.

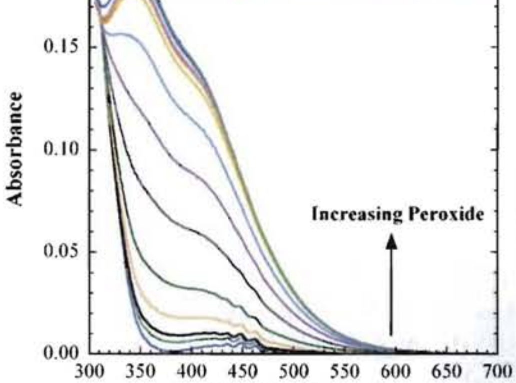

Figure 3. Spectral changes on titration of 0.21 mM U(VI) in 0.5 M K_2CO_3 with H_2O_2 [11].

At higher U(VI) concentrations the speciation of U in carbonate-peroxide solutions is much more complex. The presence of oligomeric species is suggested by ^{13}C NMR studies. For example, in Figure 4 ^{13}C NMR spectra of U(VI) in 0.5 M K_2CO_3 with an excess of H_2O_2 relative to the U(VI) are presented as a function of time. Initially there is only the signal of the free carbonate near $\delta \sim 164$ ppm and the U(VI) is presumably present as the peroxo complex $UO_2(O_2)_3^{4-}$ that is NMR silent. Peroxide decomposes continuously in alkaline solution and as the peroxide concentration drops over 224 hours new species are observed in the NMR spectrum. The shifts for $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2(O_2)^{4-}$ are well-established at $\delta \sim 168.5$ and ~167.9, respectively. Combined UV-Vis and NMR studies suggest that the ^{13}C-NMR resonance at 167.8 ppm (the left ? near the peak for $UO_2(CO_3)_2(O_2)^{4-}$) is due to a novel dimeric

U(VI) peroxo-carbonato solution species with a proposed formula of $(UO_2)_2(O_2)(CO_3)_6^{6-}$. However, this species has so far eluded attempts to crystallize and characterize the solid by single crystal x-ray diffraction. Recent extended x-ray absorption fine structure data of these solutions will hopefully provide further structural data on this dimeric species. The peak noted with the other question mark in the spectra of Figure 4 is currently an unknown species. The complexity and dynamics of the $U(VI)-H_2O_2-HCO_3^{-}-CO_3^{2-}$ system have proven very challenging to unravel and interesting new chemistry is expected to be revealed in future work.

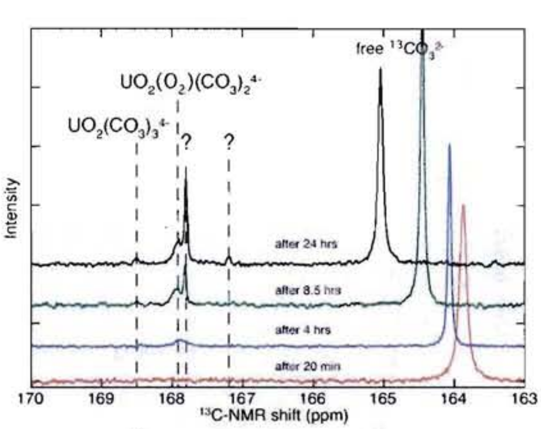

Figure 4. ^{13}C NMR spectra of a solution of U(VI) plus initially excess H_2O_2 in 0.5 M K_2CO_3.

Neptunium in various oxidation states in peroxide-carbonate solutions exhibits complex redox reactions and Np(V) species appear to be the final products in most cases. For the Np(VI) complex, $NpO_2(CO_3)_3^{4-}$, in 2 M K_2CO_3 addition of near stoichiometric amounts of H_2O_2 gives reduction to the Np(V) complex, $NpO_2(CO_3)_3^{5-}$, but additional of excess H_2O_2 causes the precipitation of an amorphous brown solid. The Np(IV) complex in 2 M K_2CO_3 solution is oxidized to $NpO_2(CO_3)_3^{5-}$ as well by near stoichiometric amounts of H_2O_2, but higher ratios of peroxide leads to formation of a brown color indicating at least one more presently unidentified species.

The limiting complex species for Pu(IV) and Pu(VI) in carbonate solutions are known to be $Pu(CO_3)_5^{6-}$ and $PuO_2(CO_3)_3^{4-}$, respectively [14]. The $Pu(CO_3)_5^{6-}$ complex in carbonate solution is reduced by H_2O_2 to Pu(IV) [15]. The Pu(IV) carbonate species has a characteristic absorption band in 2 M Na_2CO_3 at 485.5 nm. On titrating with H_2O_2 and new band grows in at 495.5 nm that is characteristic of the dimeric Pu(IV) anion, $Pu_2(O_2)_2(CO_3)_6^{8-}$ [16]. Crystals of the sodium salt of this complex can be readily formed from the aqueous solution by addition of methanol. The single crystal x-ray diffraction structure of $Na_8Pu_2(O_2)_2(CO_3)_6 \cdot 12H_2O$ has been determined. The dimer unit exhibits two $\mu^2,\eta^2-O_2^{2-}$ ligands bridging the Pu(IV) ions and three bidentate carbonate dianions bound to each Pu (Figure 5). The solution spectrum of this species shows remarkable agreement with the solid state diffuse reflectance spectrum of $Na_8Pu_2(O_2)_2(CO_3)_6 \cdot 12H_2O$, indicating that solution species is the dimeric Pu(IV) peroxo-carbonate anion.

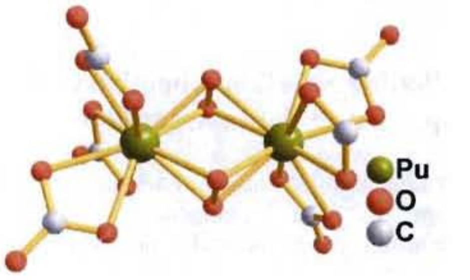

Figure 5. Ball and stick representation of the crystal structure of the anion $Pu_2(O_2)_2(CO_3)_6^{8-}$ [15].

When molar ratios of H_2O_2 higher than 1:1 are added to Pu(IV) solutions in carbonate, a new species in addition to $Pu_2(O_2)_2(CO_3)_6^{8-}$ is indicated by new peaks in the UV-Vis spectrum. At much higher peroxide ratios precipitation of Pu(IV) occurs. The composition and structure of the new solution species and the solid precipitate have yet to be resolved.

The study of the speciation of key fission product elements is also under investigation. The limiting species for the light trivalent lanthanides in carbonate solutions is $Ln(CO_3)_4(H_2O)^{5-}$ [17]. Spectrophotometric studies upon addition of H_2O_2 to lanthanide carbonate solutions show greatly reduced solubility of the lanthanides (Figure 6) and yet no indication even at very high mole ratios (100:1) of any shifts in the lanthanide absorption bands of the residual Ln(III) in the solution. The amorphous precipitated solid contains peroxide and carbonate, but no details of the structure of these solids are known [18]. Addition of peroxide also appears to reduce the solubility of Sr and Ba in carbonate solution. These solid phases need further study as well.

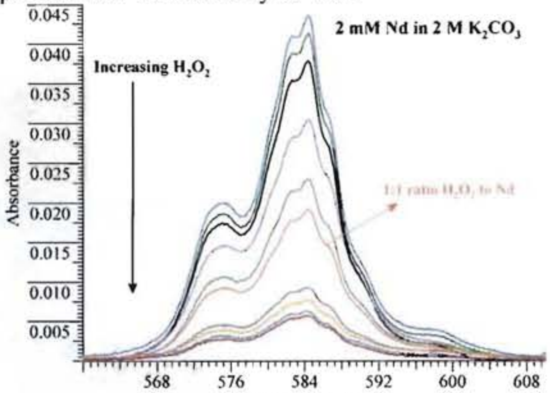

Figure 6. Precipitation of 2 mM Nd(III) in 2 M K_2CO_3 upon addition of aliquots of H_2O_2.

Conclusion

The processing of used nuclear fuel in alkaline solution provides potentially useful new selectivity for separating the actinides from each other and from the fission products. The work to date has focused on carbonate or carbonate-peroxide solutions and principally selective precipitation methods. There are many other combinations of ligands that could provide additional selectivity patterns. An array of additional separation methods could be deployed in alkaline solutions and the experiments with chelating resin sorption and electrodialysis that were briefly referenced above provide examples.

The chemistry of the actinides and fission products in alkaline solution requires extensive investigation to more carefully evaluate its potential for developing useful separation methods for used nuclear fuel. Most of the coordination chemistry in alkaline solution has been studied under conditions where only one major anionic species is present. The complexity already encountered in examining the chemistry of the early actinides in carbonate-peroxide solution give an indication of the magnitude of the challenge ahead.

Acknowledgements. The authors would like to thank the Laboratory-Directed Research and Development Program and the G.T. Seaborg Institute at Los Alamos National Laboratory for support of this work and our co-workers noted in the papers for their many contributions.

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