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# DISSOLUTION OF METAL OXIDES AND SEPARATION OF URANIUM FROM LANTHANIDES AND ACTINIDES IN SUPERCRITICAL CARBON DIOXIDE

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*This paper investigates the feasibility of extracting and separating uranium from lanthanides and other actinides by using supercritical fluid carbon dioxide (sc-CO<sub>2</sub>) as a solvent modified with tri-n-butylphosphate (TBP) for the development of a counter current stripping technique, which would be a more efficient and environmentally benign technology for spent nuclear fuel reprocessing compared to traditional solvent extraction. Several actinides (U, Pu, and Np) and europium were extracted in sc-CO<sub>2</sub> modified with TBP over a range of nitric acid concentrations and then the actinides were exposed to reducing and complexing agents to suppress their extractability. According to this study, uranium/europium and uranium/plutonium extraction and separation in sc-CO<sub>2</sub> modified with TBP is successful at nitric acid concentrations of less than 6 M and at nitric acid concentrations of less than 3 M with acetohydroxamic acid or oxalic acid, respectively. A scheme for recycling uranium from spent nuclear fuel by using sc-CO<sub>2</sub> and counter current stripping columns is presented.*

## I. INTRODUCTION

Using supercritical fluid carbon dioxide (sc-CO<sub>2</sub>) as a solvent for the dissolution of spent fuel offers a number of advantages compared with conventional nitric acid-organic solvent extraction processes.<sup>1</sup> Minimizing secondary liquid waste generation, rapid separation of solute from solvent, and containment of volatile fission products in a closed system are some unique features that this novel extraction technique can offer for the nuclear industry. However, little is known regarding separation of uranium from lanthanides and other actinides in sc-CO<sub>2</sub>, a knowledge which is essential for real nuclear waste related applications. In this paper we present our recent results regarding separation of uranium from lanthanides and from some actinides including neptunium and plutonium by manipulating redox chemistry and ligand exchange strategy in sc-CO<sub>2</sub>.

Strong inorganic acids such as nitric acid are typically not soluble in sc-CO<sub>2</sub> because carbon dioxide is

a linear triatomic molecule with no dipole moment. However, phosphorus-containing organic compounds such as tri-n-butylphosphate (TBP) and tri-n-octylphosphine oxide (TOPO) are highly soluble in sc-CO<sub>2</sub>. These CO<sub>2</sub>-soluble Lewis bases can serve as carriers to bring inorganic acids into the supercritical fluid phase for chemical reactions. This mechanism has been used to introduce nitric acid into sc-CO<sub>2</sub> phase for oxidation and dissolution of metal oxides.<sup>2</sup> Using TBP as a carrier for nitric acid is of particular interest because lanthanides and actinides form nitrate-TBP complexes which are often soluble in CO<sub>2</sub>. One TBP-nitric acid complex of the form TBP(HNO<sub>3</sub>)<sub>1.8</sub>(H<sub>2</sub>O)<sub>0.6</sub> has been shown to be an effective reagent for dissolution of oxides of the f-block elements including UO<sub>2</sub>, PuO<sub>2</sub> and lanthanide sesquioxides (Ln<sub>2</sub>O<sub>3</sub>) directly in the supercritical fluid phase in one step.<sup>3,4</sup> The TBP-nitric complex is easily prepared by mixing concentrated nitric acid with TBP according to the literature.<sup>5</sup> The sc-CO<sub>2</sub> dissolution process is different from the PUREX process because the latter involves two steps, i.e. it dissolves the oxides in nitric acid (~3 M) first followed by dodecane extraction with TBP into the organic phase. The distribution coefficients of lanthanides between dodecane and 3 M nitric acid are very small and hence UO<sub>2</sub><sup>2+</sup> and Pu<sup>4+</sup> are extracted into the organic phase as nitrate-TBP complexes whereas lanthanide ions remain in the acid solution. In contrast, in the CO<sub>2</sub> dissolution process with TBP(HNO<sub>3</sub>)<sub>1.8</sub>(H<sub>2</sub>O)<sub>0.6</sub>, the oxides of all lanthanides and actinides are dissolved in the CO<sub>2</sub> phase as their nitrate-TBP complexes. Recovery of uranium from lanthanides and other actinides in the CO<sub>2</sub> stream must be accomplished by on-line stripping techniques. One industrial process known in the literature<sup>6</sup> for separation of a lanthanide (gadolinium, Gd) from uranium dissolved in the sc-CO<sub>2</sub> phase is the AREVA process (Fig. 1) which uses a counter-current stripping technique with a nitric acid solution to remove the lanthanide from the CO<sub>2</sub> stream followed by stripping uranium with water. This separation process is based on the fact that the distribution coefficient of gadolinium between sc-CO<sub>2</sub> and 3M nitric acid is very small compared to that of uranium. Therefore

at 3 M nitric acid, uranyl can be quantitatively extracted into sc-CO<sub>2</sub> with TBP whereas the extraction of Gd<sup>3+</sup> is negligible under this condition. This separation scheme works for a simple system such as the incinerator ash produced by the light water fuel fabrication process where only enriched uranium and some gadolinium are present in the solid waste. For real nuclear waste applications, separation of uranium from other actinides must also be considered and knowledge of the redox chemistry of actinides in CO<sub>2</sub> becomes necessary for designing their separation schemes.

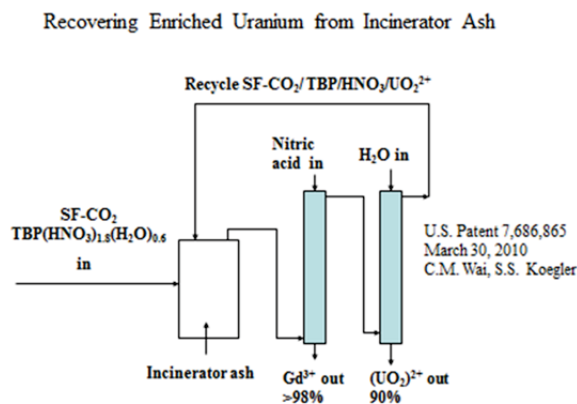


Fig. 1. The AREVA's sc-CO<sub>2</sub> extraction process for recovering uranium from the incinerator ash produced by the light-water nuclear reactor fuel fabrication process.

## II. Experimental Section

### II.A.1. Chemicals and Reagents

Concentrated nitric acid (70%w/w), tri-n-butylphosphate (TBP), Acetohydroxamic Acid (AHA), and dodecane (ReagentPlus) were purchased from Sigma-Aldrich (Milwaukee, WI). Sodium Nitrite and a standard lanthanide stock solution (100 ppm) were obtained from Fischer (Santa Clara, CA). Oxalic Acid was purchased from EM Science (Cherry Hill, NJ). Carbon dioxide (CO<sub>2</sub> liquid) equipped with a full length dip tube for liquid withdrawal was obtained from Norco (Boise, ID). Uranium dioxide (UO<sub>2</sub> 200–325 mesh size) was purchased from Internal Bio-Analytical Industries, Inc. (Boca Raton, FL). Both <sup>242</sup>Pu (7260ppm, 1M HNO<sub>3</sub>) and <sup>237</sup>Np (6162 ppm, 2 M HNO<sub>3</sub>) were obtained from stock solutions on hand at the Idaho National Laboratory (INL).

### II.A.2. Experimental Setup and Instruments

The supercritical fluid apparatus used for this study is shown in Fig. 2. The apparatus is comprised of an ISCO syringe pump (Model 206D, Lincoln, NB) with a series D pump controller connected to a liquid CO<sub>2</sub> tank on one end and valves (Autoclave Engineering, Erie, PA) linking to the high-pressure extraction vessels (home-made) on

the other. There is a check valves in line to relieve pressures if over 34 MPa and a pressure transducer (Omegadyne, Sunbury, OH) measuring the pressure of the system. The lines and valves are wrapped with heating tape (Brisk Heat, Columbus, OH) and the temperatures are measured by thermocouples (Omega Engineering, Stamford, CT) and regulated by a monitor and control device (Omega Engineering, Stamford, CT). At the end of the line there's a micrometer valve (Autoclave Engineering, Erie, PA) assisting the control of the CO<sub>2</sub> flow exiting to the collection vial.

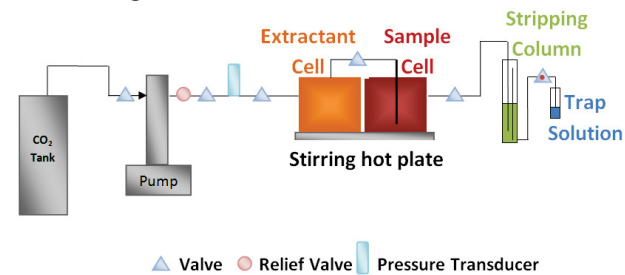


Fig. 2. Supercritical CO<sub>2</sub> extraction apparatus.

The extractant vessel is placed upstream to the sample cell to allow the TBP to be delivered to the sample cell for complex formation. The extraction temperature was 313 K at a pressure of 20 MPa. After the extraction, the aqueous residue leftover in the sample vessel were sent for analysis. The <sup>237</sup>Np liquid phases were  $\gamma$ -counted using a GEM High-Purity Germanium (HPGE) detector (Ortec; Oakridge, TN) to determine the <sup>237</sup>Np distribution ratio ( $D_{Np}$ ). The <sup>238</sup>U, <sup>242</sup>Pu, and <sup>153</sup>Eu liquid phases were subjected to a Thermo X7 ICP-MS to determine distribution ratios of Eu, Pu, and U.

## III. RESULTS AND DISCUSSION

### III.A.1. Supercritical CO<sub>2</sub> Extraction of Lanthanides and Their Separation from Uranium

Fig. 3 shows the extraction of UO<sub>2</sub><sup>2+</sup> and Eu<sup>3+</sup> from nitric acid solutions by sc-CO<sub>2</sub> at different acid concentrations. The experiments were conducted at 313 K and 20 MPa with 1% mole fraction of TBP in the CO<sub>2</sub> phase. Extraction of UO<sub>2</sub><sup>2+</sup> is near quantitative from 3-6 M nitric acid solutions whereas extraction of Eu<sup>3+</sup> is negligible ( $\leq 1\%$ ) even at 6 M HNO<sub>3</sub>. At 8 M nitric acid, about 20% of Eu<sup>3+</sup> can be extracted by sc-CO<sub>2</sub> at the specified experimental conditions. The results confirm the fact that trivalent lanthanide ions are not extractable by sc-CO<sub>2</sub> with TBP at low nitric acid concentrations ( $\leq 6$  M). This implies that the lanthanide nitrate-TBP and uranyl nitrate-TBP complexes dissolved in the sc-CO<sub>2</sub> phase can be separated by stripping the lanthanides with nitric acids at concentrations less than 6 M. Using 3 M nitric acid in a counter-current stripping mode would be a

good condition for separating lanthanides from uranium dissolved in the sc-CO<sub>2</sub> phase.

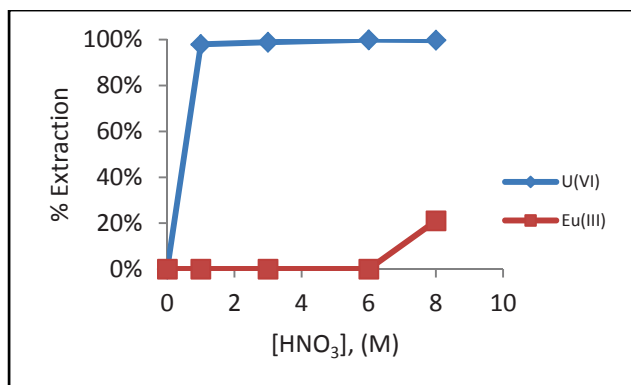


Fig. 3. Extraction of UO<sub>2</sub><sup>2+</sup> and Eu<sup>3+</sup> from nitric acid solutions by sc-CO<sub>2</sub> containing 1 mole % of TBP.

### III.A.2 Supercritical CO<sub>2</sub> Extraction of Pu<sup>4+</sup> from Nitric Acid Solution

The effect of nitric acid concentration on the extraction of Pu<sup>4+</sup> by sc-CO<sub>2</sub> containing 1% by mole of TBP at 313 K and 20 MPa is shown in Fig. 4. In 3 M HNO<sub>3</sub>, the stable oxidation state of plutonium is Pu<sup>4+</sup> and it is over 95% extracted into the sc-CO<sub>2</sub> phase similar to the extraction of UO<sub>2</sub><sup>2+</sup> under the same condition. Complexing agents such as acetohydroxamic acid (AHA) and oxalic acid can affect the extraction of Pu<sup>4+</sup> by sc-CO<sub>2</sub>. In the presence of 0.1 M AHA, Pu<sup>4+</sup> is complexed and its extraction by sc-CO<sub>2</sub> is achieved at higher acid concentrations (> 6 M), where AHA is decomposed. At 3M HNO<sub>3</sub> only a small fraction of the plutonium is extracted. Oxalic acid shows a more pronounced effect on the extraction of Pu<sup>4+</sup> than AHA. At higher nitric acid concentrations, oxalic acid could be protonated so that it is not able to complex with Pu<sup>4+</sup>.

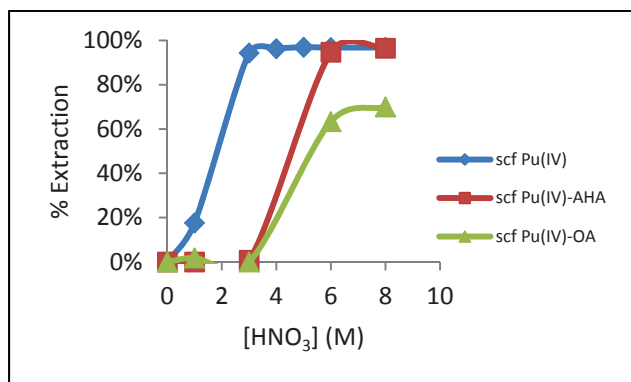


Fig. 4. Extraction of Pu<sup>4+</sup> from nitric acid solutions into sc-CO<sub>2</sub> phase containing 1 mole % TBP in the presence and absence of complexing agents.

Table 1 shows the extraction results for a mixture of UO<sub>2</sub><sup>2+</sup> and Pu<sup>4+</sup> in 3M nitric acid using 1 mole % TBP modified sc-CO<sub>2</sub> in the presence of AHA or oxalic acid (OA). The results indicate that it is possible to separate uranium from a mixture of uranium and plutonium in 3M nitric acid by sc-CO<sub>2</sub> extraction. The results suggest that uranium and plutonium dissolved in sc-CO<sub>2</sub> may be separated by stripping with 3M nitric acid containing AHA or oxalic acid.

TABLE 1. Extraction efficiency of UO<sub>2</sub><sup>2+</sup> and Pu<sup>4+</sup> in the absence and presence of AHA or OA in 3M nitric acid

3M HNO <sub>3</sub>	% U extracted	% Pu extracted
U/Pu untreated	98.8	94.3
U/Pu + AHA	97.9	7.5
U/Pu + OA	96.8	0

### III.A.3 Supercritical CO<sub>2</sub> Extraction of Neptunium from Nitric Acid Solution

The reduction of Np(VI) is measured by absorption spectroscopy as shown in Fig. 5. The appearance of a tail in the range of 400 to 450 nm is associated with Np(VI). When an appropriate amount of NaNO<sub>2</sub> is added to the acid solution, the growth of the absorbance band at 990 nm and disappearance of the tailing in the range of 400-450 nm indicates Np(VI) is reduced to Np(V). The reduction of Np(VI) to Np(V) is sought after because Np(V) is not extractable by TBP.

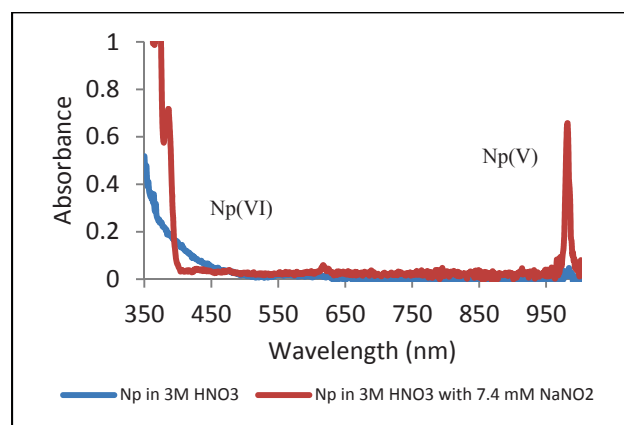


Fig. 5. UV-Vis absorption spectra of Np species in 3M HNO<sub>3</sub>

The extraction efficiencies of  $\text{NpO}_2^{2+}$  at various nitric acid concentrations and with different reducing or complexing agents are shown in Fig. 6. With 1 M nitric acid,  $\text{NpO}_2^{2+}$  is about 50% extracted by sc- $\text{CO}_2$  containing 1 % by mole of TBP. At 3 M  $\text{HNO}_3$ , the extraction of  $\text{NpO}_2^{2+}$  is lowered from about 62% to 32% with the addition of 0.1 M AHA. This would give a uranium/neptunium separation factor of about 3. This factor may be sufficient for separating neptunium from uranium in a counter-current stripping process. Sodium nitrite and oxalic acid do not show much effect on neptunium extraction compared with AHA. Further studies to achieve better separation of uranium from neptunium in sc- $\text{CO}_2$  are currently in progress.

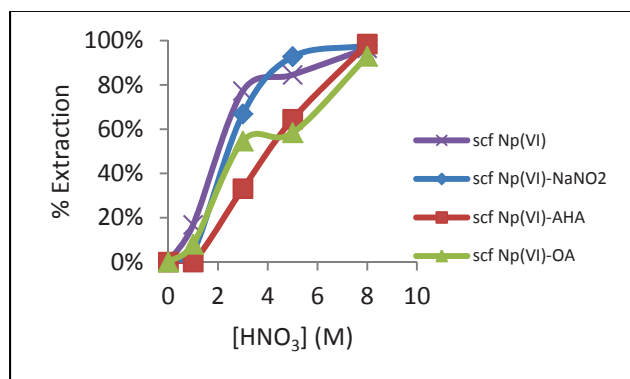


Fig. 6. Extraction of  $\text{NpO}_2^{2+}$  from nitric acid solutions into sc- $\text{CO}_2$  phase containing 1 % by mole of TBP in the presence and absence of reducing and/or complexing agent.

#### III.A.4 Recycling Uranium from Spent Fuel in Supercritical Fluid Carbon Dioxide

A schematic diagram illustrating the concept of recycling uranium from spent fuel in sc- $\text{CO}_2$  is given in Fig. 7. The process begins with the dissolution of actinides, lanthanides, and fission products from spent fuel pellets by  $\text{TBP}(\text{HNO}_3)_{1.8}(\text{H}_2\text{O})_{0.6}$  carried by sc- $\text{CO}_2$  in a pressure vessel at 40°C and 20 MPa. All lanthanides and actinides are dissolved and fission products such as Sr and Cs which are not soluble in sc- $\text{CO}_2$  should remain in the dissolution cell. Uranium and the other f-block elements together with the volatile fission products are carried by sc- $\text{CO}_2$  to flow through a sorbent to remove the latter from the remaining species. The first counter-current stripping column utilizes 3M  $\text{HNO}_3$  to strip lanthanides from the sc- $\text{CO}_2$ . Next the actinides excluding uranium are stripped from the sc- $\text{CO}_2$  by a counter-current stripping column holding a reducing and/or complexing agent in 3M  $\text{HNO}_3$ . Lastly  $\text{UO}_2^{2+}$  is recovered by stripping with water and the sc- $\text{CO}_2$  carrying the TBP- $\text{HNO}_3$  complex is recycled.

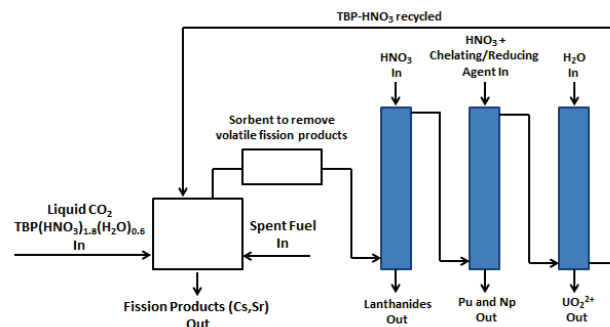


Fig. 7. Schematic diagram illustrating the concept of recycling uranium from spent fuel by using sc- $\text{CO}_2$  and counter-current stripping columns.

## IV. CONCLUSION

The results given in this paper suggest the feasibility of developing a counter-current separation scheme for isolation of uranium from lanthanides and other actinides using supercritical fluid carbon dioxide as a solvent. The dissolution of uranium dioxide and lanthanide sesquioxides in sc- $\text{CO}_2$  with a TBP-nitric acid complex is a well-established technology. Combining the supercritical fluid dissolution method with the lanthanide/actinide separation conditions given in this paper, a concept for recycling uranium from spent fuel is presented in Figure 7. This supercritical fluid-based dissolution and separation technology may be a more efficient and environmentally sustainable technology for treating nuclear wastes and for recycling uranium from spent fuel compared with the conventional liquid-liquid extraction processes. There are still a number of unknowns in the proposed supercritical fluid dissolution/separation process including the behaviors of some fission products such as technetium and volatile radioisotopes. Further research along this direction is needed.

## ACKNOWLEDGEMENT

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