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Dissolution of uranium dioxide in supercritical fluid carbon dioxide

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Uranium dioxide can be dissolved in supercritical CO_2 with a CO_2-philic TBP–HNO_3 complexant to form a highly soluble $UO_2(NO_3)_2 \cdot 2TBP$ complex; this new method of dissolving UO_2 that requires no water or organic solvent may have important applications for reprocessing of spent nuclear fuels and for treatment of nuclear wastes.

A key chemical process in the nuclear industry is the extraction and purification of uranium in the initial production of fuel for nuclear reactors and in the reprocessing of spent nuclear fuel. The most commonly used commercial process to achieve this objective is the Purex (Plutonium Uranium Extraction) process, which involves the dissolution of spent nuclear fuel in strong nitric acid and the subsequent solvent extraction of uranium and plutonium from the acid solution using tri-*n*-butylphosphate (TBP) as an extractant.[1,2] The extracted uranium and plutonium nitrate TBP complexes are further separated by chemical steps to yield pure uranium and plutonium dioxide. The Purex process, though highly efficient, has the inherent drawbacks of liquid–liquid extraction including generation of aqueous and organic liquid wastes. The large volumes of high level wastes accumulated from the weapons build-up program during the Cold War period are one example of the nuclear waste problems facing the USA.[3] Spent fuels from commercial nuclear power plants are still reprocessed today using the Purex process to recover unused uranium for recycling by several countries excluding the USA. Developing techniques for effective treatment of the wastes generated in the past and for reprocessing of spent nuclear fuels in the future has been one of the most actively pursued research areas by nuclear scientists all over the world. In evaluating any acceptable new techniques for reprocessing of spent nuclear fuels in the future, reduction of waste generation is an important criterion for consideration.

The possibility of using supercritical fluid carbon dioxide as a solvent for reprocessing of spent nuclear fuels was suggested recently in the literature.[4] Supercritical CO_2 is considered a green solvent because it is non-toxic and environmentally benign. Carbon dioxide is also cheap, readily available in relatively pure form, and has moderate critical constants (T_c = 31.3 °C, P_c = 72.8 atm and ρ_c = 0.45 g cm^{-3}). A major advantage of using supercritical CO_2 for reprocessing spent nuclear fuels is the possibility of eliminating the acid and organic solvent required in the conventional Purex process. Since the solvation strength of a supercritical fluid depends on the density of the fluid phase, selective dissolution and separation of solutes may also be possible in supercritical CO_2. Rapid separation of the dissolved metal complexes can be easily achieved by reduction of the fluid pressure to cause precipitation of the solutes, and the gas can be recycled for repeated use. This approach does not directly contribute to global warming, as the CO_2 used in this process is generated as a by-product from other chemical processes. A major problem for developing this new process is to identify a complexing agent that will effectively dissolve the main component of the spent nuclear fuel, basically uranium dioxide, in supercritical fluid CO_2.

The hexavalent uranyl ion $(UO_2)^{2+}$ is known to form CO_2-soluble complexes with a number of complexing agents including TBP and β-diketones.[5] In an earlier report, we showed that uranyl ions in strong nitric acid solutions could be extracted by supercritical CO_2 containing TBP.[6] The extracted uranyl complex $UO_2(NO_3)_2 \cdot 2TBP$ has an unusually high solubility in supercritical CO_2, of the order of 4.2×10^{-1} mol L^{-1} at 40 °C and 200 atm.[7] In another report, we demonstrated that uranium trioxide UO_3 could be dissolved in supercritical CO_2 with a fluorinated β-diketone thenoyltrifluoroacetylacetone (Htta) and TBP forming the uranyl complex $UO_2(tta)_2 \cdot 2TBP$ which has a solubility of 7.5×10^{-3} mol L^{-1} at 40 °C and 200 atm in supercritical CO_2.[8] This reaction, however, is not effective for dissolution of tetravalent uranium dioxide UO_2. In our previous experiments regarding the extraction of uranyl ions from nitric acid solutions, we noticed that HNO_3 could also be extracted by TBP forming a highly soluble complex in the supercritical CO_2 phase.[9] Our recent experiments show that this CO_2-philic TBP–HNO_3 complexant can oxidize UO_2 to the hexavalent state leading to the formation of the highly soluble $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2. This paper describes the initial results obtained from our laboratory regarding the direct dissolution of uranium dioxide in supercritical CO_2 using the TBP–HNO_3 complexant as an extracting agent.

TBP is known to form complexes with aqueous HNO_3, and the 1:1 and 2:1 (TBP:HNO_3 mole ratio) complexes are the predominating species when formed with 3 M or lower molarity nitric acid solutions.[10] The TBP–HNO_3 complexes also contain water with different hydration numbers.[10] In this study, the TBP–HNO_3 reagent was prepared by adding 5.0 mL of TBP to 0.82 mL concentrated nitric acid (69.5%, ρ = 1.42 g cm^{-3}) in a glass tube with a stopper. This mixture of TBP and HNO_3 (about 1:0.7 mole ratio) was shaken vigorously for 5 min followed by centrifuging for 20 min. After centrifugation, 3 mL of the TBP phase was removed for supercritical fluid experiments. The density of the TBP phase was measured to be 1.035 g cm^{-3}. The remaining aqueous phase was found to have a pH about 1 after 20 times dilution in water, indicating most of the HNO_3 had reacted with TBP to form the TBP–HNO_3 complex. Upon addition of the TBP–HNO_3 complex to $CDCl_3$, small water droplets were formed in the solution indicating the water in the complex would precipitate in the organic solution. A 300 MHz proton NMR spectrum of the TBP–HNO_3 complex was taken by placing D_2O in an insert separated from the complex sample in a regular NMR tube. The D_2O in this case was used to lock the NMR spectrum. The NMR spectrum showed a resonance peak at 10.28 ppm which is attributed to HNO_3 and other peaks at 4.26 ppm (dt), 1.86 ppm (qnt), 1.61 ppm (sext) and 1.14 (t) ppm for TBP. The peak areas of TBP and HNO_3 indicated a proton ratio close to 27:2 for the TBP–HNO_3 complex. The HNO_3 proton NMR peak suggests a hydrated HNO_3 species complexed with TBP. The solubility of this TBP–HNO_3 complex in liquid CO_2 at room temperature and 80 atm is about 0.38 mL/mL CO_2. The TBP–HNO_3 complex (about 3 mL) was placed in a 10.4 mL stainless steel cell which was connected upstream to a 3.47 mL extraction cell containing about 40–60 mg of a uranium oxide. Liquid CO_2 was added to the cells using an ISCO model 260D syringe pump and the system was heated in an oven at a desired temperature. Uranium

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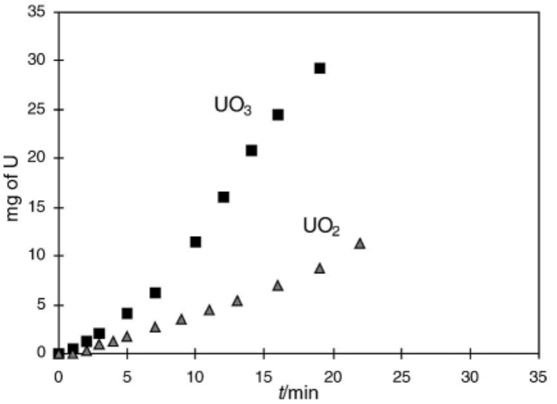

Fig. 1 Cumulative mass of uranium extracted from UO_3 and UO_2 with time by supercritical CO_2 containing the TBP–HNO_3 extractant (60 °C, 150 atm, flow rate = 0.4 mL min^{-1}).

dioxide in a powder form with size < 0.15 mm in diameter was obtained from Alfa Aesar (Ward Hill, MA). Uranium trioxide was also obtained from Alfa Aesar with a size of about 0.15–0.25 mm.

The uranium oxide dissolution experiments were performed with supercritical CO_2 containing TBP–HNO_3 flowing through the system at a rate of 0.4 mL min^{-1} measured at the pump. The dissolved uranium complex was collected in chloroform followed by back extraction with 8 M HNO_3 and washed by deionized water twice. The combined acid-water solution was analyzed by spectrophotometric method[11] and by ICP-AES for uranium determination. UV–VIS spectroscopy showed that the trapped uranium complex had an identical absorption spectrum to that reported for $UO_2(NO_3)_2{\cdot}2TBP$.[7] Fig. 1 shows the dissolution of UO_2 and UO_3 in supercritical CO_2 with the TBP–HNO_3 complexant at 60 °C and 150 atm (ρ = 0.613 g cm^{-3}). The results are expressed as the cumulative mass of uranium (in mg) found in the collection solution with time. The amount of the TBP–HNO_3 complexant dissolved in the CO_2 phase during the dynamic extraction process was determined by measuring the volume change of the complexant before and after the experiment. The amount of the TBP–HNO_3 complexant in the supercritical CO_2 stream was determined to be about 0.08 mL/mL of CO_2 at 60 °C and 150 atm. The amount of the TBP–HNO_3 complexant was in excess with respect to UO_2 in our dynamic extraction experiments. Direct dissolution of UO_2 in supercritical CO_2 under the specified conditions apparently occurred rapidly. Dissolution of UO_3 in supercritical CO_2 under the same conditions was more effective than that of UO_2. This is expected because UO_3 is in the hexavalent oxidation state which is ready to form the CO_2 soluble $UO_2(NO_3)_2{\cdot}2TBP$ complex. The dissolution of UO_2 may be represented by eqn. (1) assuming the TBP–HNO_3 complex has a 1:1 stoichiometry:

$$UO_2(\text{solid}) + 8/3\ \text{TBP–}HNO_3 \rightarrow UO_2(NO_3)_2{\cdot}2TBP + 2/3\ NO + 4/3\ H_2O + 2/3\ TBP \quad (1)$$

Similar equations can be written for the 2:1 and other TBP–HNO_3 complexes with different stoichiometry.

Dissolution of UO_2 in liquid CO_2 was slow relative to that observed in the supercritical CO_2 experiments (Fig. 2). Because oxidation of UO_2 was required in the dissolution process, diffusion of the oxidized products in the liquid phase could be a factor limiting the dissolution rate. The diffusion coefficient of supercritical CO_2 is typically an order of magnitude higher than that of the liquid. Under the same liquid CO_2 conditions, dissolution of UO_3 was about the same as that in the supercritical phase perhaps because oxidation was not required in this case.

The density of supercritical CO_2 is known to influence the solvation strength and hence solubility of solutes in the supercritical fluid phases. The dissolution of UO_2 in supercritical CO_2 increased rapidly with the density of the fluid phase as shown in Fig. 3. The amount of UO_2 dissolved in the supercritical CO_2 phase at density 0.7662 g cm^{-3} was about an order of magnitude higher than that at density 0.6125 g cm^{-3} after 12 minutes of dynamic extraction. The density effect could be partly due to the increased amount of the TBP–HNO_3 complex in the supercritical CO_2 stream caused by the increase in density of the fluid phase. This strong dependence of UO_2 dissolution on supercritical CO_2 density may be used as a parameter for selective dissolution and separation of UO_2 in supercritical CO_2. The direct dissolution of uranium dioxide demonstrated in this study suggests a possibility of dissolving spent nuclear fuels in supercritical CO_2 without the use of conventional acid and organic solvents. This new technique could offer many benefits for the 21st century nuclear industry including reduction in waste generation and improved efficiency of chemical processing.

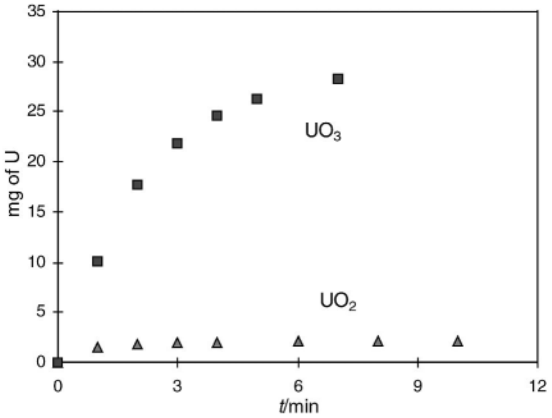

Fig. 2 Cumulative mass of uranium extracted from UO_3 and UO_2 in liquid CO_2 containing the TBP–HNO_3 extractant (21 °C, 80 atm, flow rate = 0.4 mL min^{-1}).

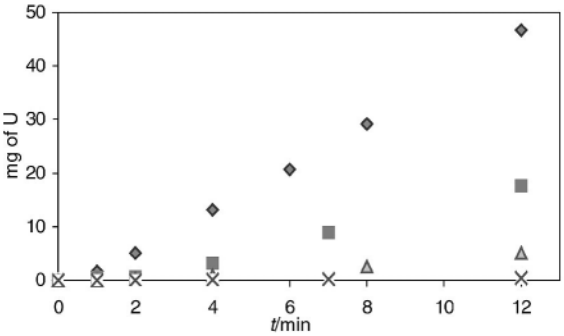

Fig. 3 Cumulative mass of uranium extracted from UO_2 by supercritical CO_2 with the aid of the TBP–HNO_3 complexant at different densities (g cm^{-3}). (◆) 0.766 (65 °C, 250 atm), (□) 0.732 (60 °C, 200 atm), (△) 0.613 (60 °C, 150 atm), (×) 0.378 (60 °C, 110 atm).

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