Dissolution of spent nuclear fuel in carbonate–peroxide solution

Chuck Soderquist *, Brady Hanson

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

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ABSTRACT

This study shows that spent UO_2 fuel can be completely dissolved in a room temperature carbonate–peroxide solution apparently without attacking the metallic Mo–Tc–Ru–Rh–Pd fission product phase. In parallel tests, identical samples of spent nuclear fuel were dissolved in nitric acid and in an ammonium carbonate, hydrogen peroxide solution. The resulting solutions were analyzed for strontium-90, technetium-99, cesium-137, europium-154, plutonium, and americium-241. The results were identical for all analytes except technetium, where the carbonate–peroxide dissolution had only about 25% of the technetium that the nitric acid dissolution had.

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1. Introduction

Spent fuel is normally dissolved (for analysis or for reprocessing) in hot nitric acid, typically in the range of 8–12 M. The hot nitric acid oxidizes the UO_2 to UO_2^{2+}, dissolving the fuel matrix and nearly all the fission products. Nitric acid works well for dissolving spent fuel, and the nitric acid solution that results is suitable for reprocessing using the Purex process.

As the UO_2 fuel dissolves in hot nitric acid, a large volume of NO and NO_2 gases are formed and are sent up the exhaust stacks. The noble gas fission products xenon and krypton are completely released and sent up the exhaust stacks. Fission product iodine and bromine also appear in the stack gases, but the iodine is radioactive (I-129 in aged fuel) and must be captured – not released to the countryside [1]. Part of the ruthenium evaporates (presumably as RuO_4) and can condense in the stacks [2,3]. Early Hanford operations had trouble with ruthenium in dissolver off-gases [4,5]. Tritium (from ternary fission) is expelled up the stacks [6]. After the fuel has dissolved, a fine black residue usually remains undissolved. This black residue is normally assumed to be a metallic phase of Mo, Tc, Ru, Rh, and Pd, leached somewhat by the nitric acid. The actinides and all the other fission products are in solution at this point.

Uranium(IV) oxide dissolves readily in an oxidizing carbonate solution. Carbonate solutions have been used for extracting uranium from uranium oxide minerals since the 1950s [7]. The solubility of uranium in carbonate solution was the basis of certain older analytical separations [8]. This suggests an improved means of dissolving spent fuel for reprocessing or for analysis. If the spent fuel were dissolved in a carbonate–peroxide solution instead of nitric acid, then stack emissions could be greatly reduced. No NO or NO_2 gases would be generated. The noble gases would still be released, but because the carbonate solution is slightly basic (pH about 10), iodine, bromine, and ruthenium would not be volatile. Because the dissolution takes place at room temperature, most of the tritium would not be lost from the dissolver solution. The noble metal fission product phase should be essentially unattacked by a carbonate–peroxide solution. The fission products and actinides that form insoluble carbonates (the majority of the fission products and actinides) should re-precipitate, leaving the uranium in solution with only a few other elements.

After dissolving the UO_2 in carbonate–peroxide solution, we expect most of the fission products and actinides to be in a readily acid-soluble form. The original UO_2 fuel would have been essentially insoluble in any dilute acid, but freshly precipitated carbonates and hydroxides are easily soluble in a dilute acid. Of the fission products, only the noble metal phase (metallic Mo, Tc, Ru, Rh, Pd) should remain acid-insoluble.

In spent UO_2 fuel and [U, Pu]O_2 fuel, the fission products Mo, Tc, Ru, Rh, and Pd are known to form a metallic precipitate, which remains behind as a fine black suspension after the fuel has been dissolved for reprocessing. Many authors have reported the particle size and chemical composition of this phase [9–15]. The reported composition is variable, but tends to be largely Mo and Ru with smaller amounts of Tc, Rh, and Pd. According to Davies and Ewart [16] and Kleykamp [17], the oxidation potentials of technetium, ruthenium, rhodium, and palladium are low enough that these elements should exist as metals, not oxides, in the spent fuel. As the fuel fissions, uranium is slowly replaced with fission products, some of which do not readily form oxides, and the fuel becomes more oxidizing. The potential for molybdenum is such that molybdenum can exist as either MoO_2 or Mo metal and serve

as an oxygen sink. As the burnup increases, an ever-increasing fraction of the molybdenum oxidizes to take up the extra oxygen made available by the disappearance of uranium. According to this mechanism, the metallic phase should become richer in the other four metals as burnup increases [17]. Also, as burnup increases, more of the fission products come from fission of the heavier actinides such as Pu-239. The heavier actinides have a higher fission yield for Ru, Rh, and Pd than U-235. Since Ru, Rh, and Pd are less chemically active than Mo and Tc, the metallic phase should become more unreactive as the burnup increases and the metallic phase becomes richer in these three metals. However, Adachi et al. [15] chemically analyzed this phase from fuels of widely varying burnup and found no great correlation between composition and burnup.

In this paper we present the results of dissolution of actual spent fuel using a carbonate–peroxide solution.

2. Experimental

The fuel used in this work was commercial UO$_2$ pressurized water reactor fuel, burnup of 45 GWd/MTU, 23 years out of reactor. This particular fuel, ATM-106, has been extensively characterized for use as a testing material [18].

Samples of spent nuclear fuel were pulverized and sieved into 5-μm and 25-μm sizes for testing. Subsamples of about 50 mg apiece were weighed out in duplicate. One of each size was dissolved in hot 12 M nitric acid, and the other was dissolved in an ammonium carbonate-hydrogen peroxide solution, as described below. The ammonium carbonate, hydrogen peroxide solution of spent fuel was converted to dilute nitric acid for analysis. The fuel solutions that resulted were analyzed for gamma emitters, Sr-90, plutonium, and Tc-99 as described below.

The solution obtained by dissolving fuel in a carbonate–peroxide solution was converted to a nitric acid solution only because the analytical methods that we used require a nitric acid solution. If the dissolved fuel were left in a carbonate solution, then the solution chemistry would be much different from nitric acid. Discussion of the carbonate solution of spent fuel is outside the scope of this paper.

2.1. Carbonate fuel dissolution

Subsamples (50-mg) of each size fuel were placed in 125-mL Erlenmeyer flasks, 20 mL of saturated ammonium carbonate solution was added, and 10 mL of 30% hydrogen peroxide was added. (Reagent grade chemicals from Fisher Scientific were used.) A magnetic stir bar was added and a watch glass was placed over the flask. The mixture was stirred for 1 h, then allowed to stand for 4 days, all at room temperature. The fuel dissolved and made a bright yellow-orange solution, which faded over the next 4 days into something that looked faintly blue through the yellow hot-cell window. No undissolved residue was apparent, and we did not filter the solution. The solution was gently dried on low heat to evaporate off the ammonium carbonate and hydrogen peroxide. The dry residue was dissolved in 5 mL of 12 M nitric acid without heating (it dissolved on contact) and then immediately diluted to 50 mL with 2 M nitric acid. (Nitric acid (12 M) was used to avoid undissolved, but acid-soluble residues that might otherwise skew the results.) The product solution appeared a little dark, with a blue cast, through the yellow hot-cell window.

Note that the final solution from the carbonate fuel dissolution was acidic. Elements that form insoluble carbonates, such as strontium and the rare earths, were ultimately dissolved in the final product solution. The solution was not filtered; any undissolved particles were ultimately transferred to the final solution.

2.2. Nitric acid fuel dissolution

Fifty-milligram subsamples of each size fuel were placed in 125-mL Erlenmeyer flasks and then 15 mL of 12 M nitric acid was added. A magnetic stir bar was added and a glass funnel was placed in the top of the Erlenmeyer to contain spray and cause the nitric acid to reflux, and then the solution was warmed to nearly boiling for an hour, until the fuel had completely dissolved. The solution was not evaporated dry, so that technetium would not be lost to evaporation. (Tc$_2$O$_7$ is moderately volatile in boiling concentrated nitric acid.)

After the bulk of the fuel had dissolved, the solution was centrifuged to separate any undissolved residue. (At this point, no black residue of undissolved material was apparent in these samples through the hot-cell window.) The supernatant liquid was poured to a volumetric flask, and the residue in the bottom of the centrifuge tube (presumably the Mo, Tc, Ru, Rh, Pd phase) was returned to the Erlenmeyer flask and heated again for 3 h with 10 mL of concentrated nitric acid, with the funnel in place to contain spatter and reflux the nitric acid.

After 3 h of heating, the solution was added to the volumetric flask with the previous solution, and then diluted up to 50.0 mL with 2 M nitric acid. The solution was not filtered. Any undissolved particles were ultimately transferred to the volumetric flask with the sample solution.

2.3. Measurement of gamma emitters

The fuel solutions were counted directly for gamma emitters using an intrinsic germanium gamma spectrometer. In these samples we were able to report Cs-134, Cs-137, Eu-154, Eu-155, and Am-241. No other gamma emitters were directly measurable.

2.4. Measurement of Sr-90

Accurate dilutions of the fuel solutions were made, then aliquots were taken for Sr-90 analysis. The aliquots were evaporated dry, then re-dissolved in exactly 1 mL of 8 M nitric acid. Each nitric acid solution was loaded onto an extraction chromatography column of Eichrom SrSpec resin. Strontium loads onto the resin, but not much else does. The column was washed with clean 8 M nitric acid, and then the strontium was eluted with water. The product Sr-90 was counted using a Perkin–Elmer TriCarb model 3100 liquid scintillation spectrometer. (Yttrium-90 does not load onto the column and is separated from the Sr-90, and begins to ingrow again at elution time. The beta count rate must be corrected for ingrown Y-90 to calculate the Sr-90 concentration.)

2.5. Measurement of plutonium

Accurate dilutions of the fuel solutions were made, then subsamples were taken for plutonium analysis. The subsamples were evaporated dry with concentrated nitric acid (to oxidize any Pu(III) to Pu(IV) and Pu(VI)), then dissolved in concentrated hydrochloric acid. The hydrochloric acid solution of each sample was passed through an anion exchange column with BioRad MP-1 resin, 50–100 mesh, chloride form. Plutonium loads onto the resin, along with a large number of other elements. The columns were washed with clean concentrated hydrochloric acid to remove a number of fission products, and then plutonium was eluted off the resin with a solution of ammonium iodide in concentrated hydrochloric acid. The iodide reduces the plutonium to Pu(III), which comes off the resin, leaving the other alpha-emitting actinides (U, Np) still loaded on the resin. The plutonium was mounted for alpha spectrometry by coprecipitating it on 50 μg of NdF$_3$. The NdF$_3$ (with Pu) was mounted onto a 0.1-μm membrane filter by suction, then

attached to a steel counting disk with double-sticky tape. The plutonium was measured by alpha spectrometry. Pu-239 and Pu-240 have nearly identical alpha energies which cannot be resolved with this instrumentation; we report their sum.

2.6. Measurement of technetium

This technetium separation is designed to recover only TcO_4^-, not technetium in other oxidation states. The fuel sample dissolution (both hot nitric acid and alkaline peroxide) would have oxidized any soluble technetium up to TcO_4^-; no soluble technetium would be present in any other oxidation state in these samples.

To measure technetium, the fuel solutions were diluted with water (to reduce the acid concentration), then passed through a hydrogen form cation exchanger (Dowex 50 W-X8, 100–200 mesh) to remove the uranium, plutonium, and most fission products. The technetium is anionic (TcO_4^-) and does not load onto the cation exchanger. After the cations were removed, the solution was made basic with sodium hydroxide, then tetraphenyl arsonium chloride solution was added, and then the solution was shaken with methyl isobutyl ketone. The methyl isobutyl ketone extracts the technetium as tetraphenylarsonium pertechnetate. The mixture was centrifuged to separate the phases, and then the organic phase (with the technetium) was removed and placed in a liquid scintillation vial. The technetium was measured by liquid scintillation (Perkin–Elmer TriCarb model 3100). This technetium analysis gives reliably high recovery of the technetium and excellent decontamination from other beta emitters.

3. Results

The nitric acid fuel dissolution and the carbonate–peroxide fuel dissolution gave the same results for every analyte except technetium (see Table 1). The uncertainty given is total propagated uncertainty at one standard deviation. The analytical results are statistically the same for both fuel dissolutions, within two standard deviations, for all analytes except technetium.

Results are given in Becquerels of analyte per gram of fuel. The two fuel samples are 25 μm and 5 μm sieved samples. "Carb" refers to room temperature ammonium carbonate, hydrogen peroxide fuel dissolution, and "Nitric" refers to hot 12 M nitric acid dissolution.

The fuel clearly broke up and dissolved completely in the carbonate solution. The carbonate solution directly dissolved the UO_2 fuel matrix and several other elements, and left a number of other elements in an acid-soluble form. The cesium, europium, americium, strontium, and plutonium were completely in solution at the end of the carbonate fuel dissolution (in 2 M nitric acid).

4. Discussion

The UO_2 fuel was completely decomposed in a carbonate–peroxide solution, except for the noble metal phase, as expected. All the analytes measured in the fuel were converted to a readily acid-soluble form except technetium, which is known to exist in the fuel as a metallic phase.

The fuel used for this experiment was pulverized to 5 μm and 25 μm. Bigger pieces may dissolve much more slowly. Higher burnup fuel will probably dissolve more slowly than low burnup fuel. Fuel becomes more resistant to oxidation as the burnup increases [19], which we expect will slow down the dissolution process.

The data obtained suggest that under fuel repository conditions, much of the technetium may never dissolve, even after the fuel has completely corroded over geologic time. The primary mechanisms for corrosion of UO_2 fuel involve water, atmospheric O_2, and atmospheric CO_2, assisted by radiolytically produced H_2O_2 [20]. These are chemically equivalent to the conditions we used, although at a much lower concentration. Because we were unable to dissolve much of the technetium in a strong carbonate–peroxide solution, even though the UO_2 completely dissolved, it seems unlikely that the technetium buried in the 5-metal phase would extensively corrode under milder conditions. Technetium metal is only very slowly corroded by wet air [21]. Ruthenium, rhodium, and palladium are impervious to corrosion in wet air and may protect the technetium indefinitely.

In our laboratory we have found that milligram amounts of freshly precipitated $TcO_2 \cdot nH_2O$ oxidize very quickly on exposure to air under slightly basic conditions. Gram quantities of massive, dry, crystalline TcO_2 dissolve easily in $NH_4OH + H_2O_2$ at room temperature. Because most of the technetium in the fuel did not dissolve, clearly most of it does not exist in the fuel as interstitial TcO_2.

The reason for the chemical inertness of the 5-metal phase is probably the ruthenium and rhodium. Massive ruthenium and rhodium metal are impervious to all mineral acids, including aqua regia. At room temperature, ruthenium and rhodium can be dissolved only when they are finely divided, regardless of the reagent mixture. Ruthenium is best dissolved by an oxidizing alkaline fusion, such as sodium peroxide. Rhodium is not attacked by an alkaline fusion. It is best dissolved by a pyrosulfate fusion, under conditions where ruthenium is unattacked [22]. Adachi et al. [15] used hydrochloric acid and nitric acid $(9 + 1)$ under pressure at 180 °C for 20 h to dissolve the 5-metal phase that remained after fuel was dissolved in 3 M nitric acid.

The technetium concentrations given in Table 1 for the fuel dissolved in nitric acid are probably slightly low, because hot nitric acid does not normally dissolve all the of the 5-metal phase. ORIGEN predicts that this fuel should have 5.36E + 5 Bq Tc-99 per gram of fuel [18]. Our results for the 5-μm fuel agrees with that, but we found only 4.33E + 5 Bq/g in the 25-μm fuel.

Part of the technetium found in the carbonate–peroxide dissolution may have been dissolved by the nitric acid, not the carbonate–peroxide solution. The carbonate–peroxide dissolution was converted to nitric acid solution before analysis, which may have leached some amount of technetium out of the noble metal phase. If so, then the fraction of technetium which resides in the noble metal phase is higher than the data in Table 1 indicates.

Table 1
Analytical data, Bq/g of fuel ±1 s uncertainty.

Fuel sample	Cs-134		Cs-137		Eu-154		Eu-155		Am-241	
25 μm Carb	3.65E + 6	±4%	3.19E + 9	±3%	4.66E + 7	±2%	7.55E + 6	±9%	1.14E + 8	±4%
25 μm Nitric	3.46E + 6	±4%	3.03E + 9	±3%	4.56E + 7	±2%	7.70E + 6	±8%	1.10E + 8	±4%
5 μm Carb	3.60E + 6	±4%	3.12E + 9	±3%	4.33E + 7	±2%	7.84E + 6	±9%	1.05E + 8	±4%
5 μm Nitric	3.60E + 6	±4%	3.12E + 9	±3%	4.26E + 7	±2%	8.07E + 6	±15%	1.01E + 8	±4%
	Pu-239 + 240		**Pu-238**		**Sr-90**		**Tc-99**			
25 μm Carb	3.19E + 7	±4%	1.53E + 8	±3%	1.74E + 9	±3%	1.81E + 5	±3%		
25 μm Nitric	3.10E + 7	±2%	1.59E + 8	±2%	1.70E + 9	±3%	4.33E + 5	±3%		
5 μm Carb	3.01E + 7	±4%	1.50E + 8	±3%	1.68E + 9	±3%	1.71E + 5	±3%		
5 μm Nitric	3.11E + 7	±3%	1.58E + 8	±2%	1.70E + 9	±3%	5.37E + 5	±3%		

A carbonate–peroxide dissolution should be a good way to dissolve fuel for analysis of volatile elements. The halogens are not lost when fuel is dissolved in a carbonate–peroxide solution (pH around 10). This would be a good dissolution method for analysis of fuel for bromine and iodine, which would otherwise be lost up the exhaust stacks if the fuel were dissolved in nitric acid.

5. Conclusions

We have shown that a carbonate–peroxide solution will effectively dissolve pulverized spent nuclear fuel and give results comparable to nitric acid dissolution. Parallel tests of fuel dissolution in carbonate–peroxide and dissolution in nitric acid, followed by analysis for several radionuclides, gave the same results for all radionuclides measured except technetium.

The carbonate dissolution is done under moderately basic conditions (pH around 9–10) at room temperature and has several advantages over hot nitric acid dissolution. Certain fission products that are volatile in boiling nitric acid are much less volatile at room temperature and pH 10 (bromine, iodine). The carbonate–peroxide dissolution uses milder conditions than nitric acid, and no NO_x is generated. The noble metal phase is apparently unattacked, because most of the technetium does not dissolve in the carbonate–peroxide solution.

The fuel is completely attacked and broken up in the carbonate–peroxide solution, other than the noble metal phase. The uranium in the fuel dissolves directly in the carbonate solution, forming an orange-yellow solution, which fades to yellow over several hours. The strontium, europium, plutonium, and americium are left in a readily acid-soluble form.

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