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HOT CELL EVALUATION OF THE GRIND-LEACH PROCESS WITH IRRADIATED PYROLYTIC CARBON-COATED SOL-GEL THORIA-URANIA PARTICLES

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ABSTRACT

Duplex pyrolytic carbon-coated sol-gel ThO_2 and $(Th,U)O_2$ particles, irradiated from 15,000 to 17,500 Mwd/metric ton (Th + U) and decayed 10 and 19 months, were ground to -100 mesh to insure fracture of the coatings and, then, were leached with boiling fluoride-catalyzed nitric acid to dissolve the thorium, uranium, and fission products. Recoveries of 99.6% or more of the uranium and 99.9% of the thorium were realized, along with dissolution of more than 86% of the gamma emitters. These results contrast markedly with earlier grind-leach studies, using ground graphite-matrix fuel that contained laminar-coated $(Th,U)C_2$ particles, which gave unacceptable losses of up to 6.9% of the thorium and 4.5% of the uranium to the leached carbon residue. Grinding and leaching may therefore be applicable to HTGR fuels containing coated sol-gel oxide particles, although the feasibility of the process would still be marginal due to the necessity of storing the fission product-contaminated residue as a high - or intermediate-level solid waste.

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Two principal methods have been proposed for the recovery of thorium and uranium from High Temperature Gas-Cooled Reactor (HTGR) fuel elements composed of pyrolytic carbon-coated $(Th,U)C_2$ or $(Th,U)O_2$ particles dispersed in a graphite matrix. With either fuel, the thorium and uranium must be separated from greater quantities of carbon. The proposed burn-leach process involves oxidizing the carbon to CO_2, leaving an "ash" of ThO_2--U_3O_8--fission product oxides to be dissolved in fluoride-catalyzed nitric acid. The concentration of the resulting solution would be adjusted to make feed for a conventional aqueous solvent extraction system. The proposed grind-leach process involves crushing the graphite matrix and fuel particles to expose the thorium- and uranium-containing cores to the leaching action of nitric acid; uranium and thorium are then recovered by solvent extraction.

Hot-cell evaluation of the burn-leach process, with irradiated Peach Bottom Fuel compacts obtained from General Atomics, has been completed and a report is in press.[1] Fission product volatility, the principal unknown prior to the tests, was low and the process appeared applicable to HTGR fuels. However, evaluation of the grind-leach process in the hot-cell[2] with long-decayed Peach Bottom and AVR fuel compacts, containing $(Th,U)C_2$ particles with a single laminar coating, indicated that the leached graphite residues contained excessive thorium (6.9% of the total), uranium (4.5%), and gamma emitters (up to 35%). These results completely contradicted the promises of grind-leach experiments with unirradiated prototype fuel in which recoveries of greater than 99.7% of the heavy metals were realized.

This memo briefly describes grind-leach experiments with duplex-coated sol-gel ThO_2 and $(Th,U)O_2$, and $(Th,U)C_2$ that had been irradiated

as loose particles (no supporting matrix) in the GCR-ORR Loop as Experiments 1-14 and 1-15. A more complete report of these experiments is in preparation.[3] The particles were ground in a food blender to -100 mesh to insure that all the particles had been broken, and then were leached and washed several times using the best procedures developed during earlier leaching experiments.

Table 1 summarizes the results of these leaching experiments. Recovery of the uranium and thorium was satisfactory in all of the tests, and in the longer-decayed material from experiments 1-14, the average retention of the fission product gamma emitters was 1.97% vs 13.66% in 13 earlier experiments with the prototype Peach Bottom and AVR fuels. The residue from the 10-month-decayed Loop 1-15 $(Th,U)O_2$ particles contained 14.08% of the total gamma emitters in the sample. Radiochemical analysis indicated from 4.5 to 8.5% of most of the fission products were in the residue, but that 26.45% of the ^{95}Nb had not been leached. In the case of the $(Th,U)C_2$ particles of Loop 1-15, where 61.23% of the gamma emitters were found in the pyrolytic carbon residue, 96.6% of the ^{95}Nb, 59.7% of the ^{95}Zr, and 67% of the ^{106}Ru were insoluble.

These few experiments indicated that the grind-leach process might be applicable to HTGR fuels containing pyrolytic carbon-coated sol-gel oxide particles. Our data support the post-irradiation metallographic and microradiographic studies and fission product release experiments of the Reactor Chemistry Division which indicated a superiority of coated oxide particles over coated carbide particles. The superiority is due to little or no migration of thorium or uranium into the pyrolytic carbon coating and better retention of fission products. Our experiments showed that the residue from the oxide particles from experiment 1-15 contained (on a

Table 1. Recovery of Thorium and Uranium from Ground (-100 mesh) Pyrolytic Carbon-Coated Oxide and Carbide Particles Irradiated in GCR-ORR Loop No. 1 by Leaching with Boiling 13M HNO_3--0.05M HF--0.1M $Al(NO_3)_3$

Loop Expt. No.	1-14			1-14			1-15			1-15		
Particle Type	ThO_2 + $(Th,U)O_2$			ThO_2 + $(Th,U)O_2$			$(Th,U)O_2$			ThO_2 + $(Th,U)C_2$		
Coating	Duplex			Duplex			Duplex			Duplex		
Mwd/ton (Th + U)	17,500			17,500			15,000			15,000		
Decay - months	19			19			10			10		
Init. wt-g	13.4			15.3			8.9			17.8		
Sample	U	Th	γ	U	Th	γ	U	Th	γ	U	Th	γ
1st Leach-%	99.35	99.66	96.14	99.32	98.67	95.12	99.86	99.69	74.21	83.76[a]	6.03	28.33
2nd Leach-%	0.35	0.30	1.32	0.46	1.21	3.03	0.10	0.23	11.70	15.81	93.88	10.43
3rd Leach-%	<0.01	0.02	0.25	<0.01	0.05	0.20	b	b	b	b	b	b
Final Wash-%	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	b	b	b	b	b	b
Residue-%	0.29	0.02	2.29	0.21	0.06	1.64	0.04	0.07	14.08	0.42	0.09	61.23

[a] 1st leach with 13M HNO_3 only in attempt to preferentially dissolve the $(Th,U)C_2$; 2nd leach 13M HNO_3--0.05M HF--0.10M $Al(NO_3)_3$ for total dissolution.

[b] 3rd leach and washes combined with 2nd leach for analysis

weight basis) one-fifth as much ruthenium, one-third as much zirconium, and one-fourth as much niobium as the residue from the Experiment 1-15 carbide particles. We have evidence that a large fraction of the cerium and cesium in the carbide-core particles had migrated through the pyrolytic coatings into the outer container.

Although the grind-leach process might be used for the recovery of thorium and uranium from HTGR fuels that contain carbon-coated oxide particles, the practicality of the process might still be marginal due to the quantity of fission products retained by the leached carbon residue. Even in the case of long-decayed fuel the residues would have to be treated as intermediate-to high-level solid wastes, which would increase the cost of processing.

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