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Nuclear Technology —
Materials

RECOVERY OF COATED URANIUM DICARBIDE PARTICLES FROM GRAPHITIZED REACTOR FUEL

E. G. Laggis

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Nuclear Division

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With the US Atomic Energy Commission

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ABSTRACT

Pyrolytic carbon-coated particles were recovered, for possible reuse, from Rover reactor fuel elements cured in fabrication to graphitization temperatures. A process was developed for electrolytically disintegrating the high-cured fuel which was inert to the acid digestion used for disintegrating extrusion and low-cured fuel scrap. A particle-recovery pilot-plant system was operated which contained an electrolytic cell where graphitized fuel elements containing approximately 20 weight percent enriched uranium were completely disintegrated anodically in a 3.5 to 7.5-molar nitric acid solution at an average rate of 0.63 gram/ampere hour. A total direct current of 190 amperes was supplied to a bank of elements by means of a titanium rod inserted into a fuel coolant channel of each element. The disintegration products were separated by filtration, water elutriation, and screening procedures, and consisted of fine graphite and electrolyte (both of which were low in uranium content), +70 mesh oversize solids, and -70 mesh recovered particle solids. The particle solids contained 67 percent of the uranium input to the system and consisted of discrete particles diluted by approximately 14 weight percent fuel-matrix graphite, including occlusions on the particle surface. Minimizing the generation of oversize solids in the disintegration process was anticipated to increase the particle recovery yield and decrease fuel processing costs for the pilot-plant system projected as a production unit operating at a maximum throughput capacity.

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SUMMARY

A process was developed to recover pyrolytic carbon-coated uranium dicarbide particles, for possible reuse, from Rover reactor fuel elements cured to graphitization temperatures of 2,500° C. Fuel scrap from the high-cure phase of element fabrication had previously been found inert to acid-digestion techniques which had been used to recover the particles from extrusion and low-cure (< 450° C) source scrap. An alternative method was, therefore, investigated to electrolytically disintegrate graphitized fuel to a slurry of its carbon and particle constituents from which the particles could be separated. The mechanics of fuel disintegration and effects of electrolytic cell parameters on the rate and particle quality were determined in laboratory studies to provide process data for the design of a pilot-plant system. Subsequent processing of 63 graphitized fuel elements, containing fully enriched uranium, in the prototype system provided data for evaluating the technical and economic aspects of the recovery process. Results of the investigations demonstrated the following:

1. Development of a suitable fuel/anode configuration allowed essentially complete disintegration of graphitized fuel at a rate dependent only on the applied current load when using 1 to 8.7-molar nitric acid, but the amount of unusable coarse fragments increased markedly using 14.2-molar nitric acid. (Figure 2 and Table 1)

2. Yield of disintegrated fuel solids in the -70 mesh particle-size range and containing particles of minimum graphite inclusion was best in nitric acid solutions of moderate concentration. A lower current density and electrolyte temperature were best for producing finer-sized solids. (Tables 1 and 2)

3. The pilot-plant processing of 63 graphitized fuel elements confirmed the system capability for 99 percent disintegration of the fuel at an overall rate of 0.625 gm/amp hr using 3.5 to 7.5-molar nitric acid. (Figure 4 and Table 3)

4. Pilot-plant procedures for separating constituents of the disintegration cell slurry yielded fine graphite and electrolyte streams that were very low in uranium content, and recovered up to 67 percent of the enriched uranium as 12 kilograms of -70 mesh particle solids. Generation of +70 mesh oversize solids accounted for most of the remaining uranium and prevented higher particle recovery yields. (Tables 4, 5, and 6)

5. Chemical and radiographic analyses of the recovered particle solids showed that fuel-matrix graphite was contained, not only as fragments, but also as occluded material on the particle surface, which somewhat diluted the uranium content of the particle solids. Presence of the surface graphite was indicated due to the premature severance of some particles before electrolytic removal of the surrounding graphite was complete. (Figures 5, 6, and 7, and Tables 7 and 8)

6. Recovery process evaluation of the pilot-plant processing campaign provided a basis for a projected maximum throughput operation of the system as a production-scale unit. Total fuel-processing and particle-recovery costs were determined, both of which would be influenced by the uranium composition of the fuel and a potential improvement in the particle recovery yield. (Figures 8 and 9, and Table 9)

INTRODUCTION

Reactor fuel elements are fabricated from pyrolytic carbon-coated uranium dicarbide particles which are dispersed in carbon. The dispersion is extruded, then heat treated to graphitizing temperatures. Recovery of the enriched uranium from various forms of fabrication scrap can be achieved by conventional or specialized(1) techniques which solubilize the contained uranium from the particular scrap matrix.

In addition, development studies have been directed to recover the uranium as intact particles for possible reuse. A method utilizing nitric acid digestion and carbon-particle separation techniques was demonstrated on a pilot-plant scale for recovering particles from extrusion and low-temperature(< 450° C)-cured scrap.(2) However, scrap derived from higher-temperature curing operations (450 to 2,500° C) was found to be inert to this processing method. Limited experimental work indicated, though, that electrolytic treatment would disintegrate this type of scrap to a particle/graphite slurry.

Further studies were, therefore, needed to provide a process for recovering particles from high-temperature-cured scrap. The objectives were to: (1) verify the initial tests utilizing electrolytic techniques to disintegrate the fuel; (2) define those parameters that affect both the processing rate and properties of the generated solids; (3) evaluate the developed process in terms of recovered particle yield, disposition of uranium-bearing waste streams, and other factors affecting operating costs of the proposed process; (4) provide recovered particles in kilogram quantities for future evaluation of their reuse.

An extensive laboratory and bench-scale investigation was needed to develop a mechanical method for achieving complete disintegration of the fuel, then the evolved technology would be applied to the design and operation of a pilot-plant system. Operational and analytical data would form the basis for designing process flow sheets and to estimate operating costs. Factors affecting potential improvements in particle yield and quality would also be derived from operational observations and laboratory experimental data.

DEVELOPMENT OF THE PARTICLE RECOVERY PROCESS

INTRODUCTION

Laboratory and pilot-plant studies were needed to derive and evaluate a process for recovering coated particles from graphitized fuel element scrap. An acid digestion method used for particle recovery from extrusion and first-cure(250° C)-type scrap had been found to be ineffective on high-temperature-cured(>450 to 2,500° C)-type scrap.(2) However, brief tests had indicated that the high-cured matrix could be electrolytically disintegrated to its carbon and coated-particle components.(2) The two phases of the subsequent work based on this technique are described in this report. Laboratory studies were to deal with the disintegration of the fuel and some associated parameters affecting the quality of the particle solids, but the studies primarily provided a suitable electrolytic cell design. These data and known particle-separation techniques(2) were then to be utilized in the design and operation of a pilot-plant system. Pilot-plant processing of a large number of graphitized fuel elements should furnish the basic data to evaluate the factors pertinent to the potential application of the particle recovery process.

LABORATORY STUDIES

Introduction

Development work was directed toward obtaining the design criteria that were needed to construct a production pilot-type particle recovery system and to resolve the problems which were indicated by the original bench-scale work.(2) Although short pieces of fuel elements had been electrolytically disintegrated, the fuel portion that was held in the electrode clamp above the liquid interface remained intact. Since short pieces (2 to 4 inches long) constitute the principal form of fabrication scrap, total processing of these scrap pieces would be desirable. A means, therefore, was needed for supplying electric current to the scrap which could be completely submerged in nitric acid. A second problem was the removal of residual graphite from particles electrolytically recovered from graphitized scrap.

Electrolytic Disintegration of the Reactor Fuel

Various methods were studied for providing DC power to a body of graphitized fuel pieces submerged in nitric acid. The fundamental obstacle to the complete disintegration of the charge was found to be a concentrated attack at the anode contact areas which led to a disruption of the current flow. This problem was ultimately solved by using a fuel-piece length of tantalum rod as the anode to supply a constant current flow. The reliability of this device was demonstrated in twelve bench runs.

Feed material for the initial laboratory work consisted of sheared lengths from fuel element fabrication or broken pieces of reject fuel elements from curing operations (450 to 2,500° C). In later work, finished-length 60-inch elements which had been graphitized (2,500° C) were obtained to provide feed material of known history and composition. The hexagonal cross section of the reactor fuel measured approximately 3/4 inch across the flats and contained 19 full-length coolant channels that were approximately 100 mils in diameter. Although the channels and a portion of the outer element surface are later coated with niobium carbide, the studies were confined to graphitized but uncoated reactor fuel specimens. Essentially all of the high-temperature-cured scrap routinely generated is in the graphitized, uncoated form. One brief test was also made, however, using a coated element section.

Testing of Various Fuel/Anode Configurations

Supplying DC power to the fuel-element segments proved more difficult than was anticipated. Tantalum, one of the few metals inert to anodic attack by nitric acid, was used extensively in various mechanical configurations in an attempt to obtain a continuous electrical contact, but the electrical continuity between the anode and fuel was repeatedly disrupted or incompletely established in several tests.

The first approach to the problem was an attempt to perform initial disintegration and secondary acid treatment of the particles in the same vessel. A perforated tantalum basket (3" D x 18" L) was inserted as the anode into a stainless steel vertical pipe (4" D x 18" L), which served as the cathode. A Pyrex reducer (4" to 1") below the stainless steel pipe served as a product reservoir from which the particle/graphite slurry could be drained through a polyvinyl chloride valve. The reducer also held a tantalum coil, one end of which extended through the wall of the drain valve to the power supply.

Sections of fuel, totaling 1.8 kilograms, were both randomly placed and regularly stacked in the basket. In both cases, current flow was erratic over the range from 0 to 15 amperes, and electrical contact between the basket and charge was visibly poor. Severe arcing burned the fuel and basket at the points of contact. Similar results have been reported in the electrolytic dissolution of nichrome-uranium alloys in this type of dissolver.(3) This procedure was temporarily abandoned in favor of forcing two twisted, 0.040-inch tantalum wires through the center hole of the fuel pieces suspended in the dissolver. A current of 20 to 22 amperes at three volts was passed through seven elements for 16.1 hours of run time. This action disintegrated 726 grams or 41 percent of the element weight at an overall rate of 2.20 grams per ampere hour. However, the fuel pieces were corroded in a preferential, nonuniform manner. Some pieces were unaffected, some partially attacked, and others were almost completely corroded, leaving a cylinder loosely strung on the electrode wire. Electrical contact apparently varied, being nonexistent, poorly distributed, or disrupted at various times in the course of the run.

The secondary electrolytic treatment of the disintegrated sections in the conical bottom part of the apparatus was tried with little success. An impression of 25 volts on the anode coil produced zero current flow. The nonconductivity of the settled particle/graphite slurry was confirmed by a beaker test in which electrodes were imbedded in the slurry one-half inch apart with the same result.

Alternative methods for processing the four-inch-long fuel pieces were investigated. A two-inch length of 0.125-inch tantalum rod was tapered and forcibly rammed into the nominal 0.100-inch center hole of a fuel piece. Current flow to the immersed piece was initially constant, then fluctuated to zero. Although the outer surface had been uniformly corroded, pitting at the fuel rod/anode junction had mechanically loosened the electrode sufficiently to cause poor electrical contact.

Since the work strongly indicated the necessity of an applied force to maintain constant fuel rod/anode contact, the original battery clip-type fixture was restored. In order to prevent rapid dissolution of the clip, tantalum jaw extensions were bolted to it. A rack of 14 such clips, each holding three 4-inch-long fuel pieces, was made and suspended over a nuclearly safe, 2-inch-wide, 48-inch-long vertical tank. Tank depth was sloped from four inches on the ends to ten inches in the center to allow for the accumulation and drainage of solids through a one-inch stainless steel valve. The rack was loaded with 42 four-inch pieces (2.3 kilograms total) and lowered so that the recirculating acid level was 1/4 inch below the junction of the holding clip and fuel element. The objective was to disintegrate the major portion of the fuel, then lower the rack and finish the submerged "tails".

A constant current of 290 amperes at six to seven volts was applied during the first hour of the initial run, and uniform corrosion of the fuel was noted. The run was terminated, however, after 1.3 run hours due to severe arcing at the clip/fuel contact zone. Nitric acid had wetted the fuel surface from the liquid level up to the clip contact line, causing concentrated element attack and subsequent poor electrical contact and severe arcing. Disintegration of 619 grams or 27 percent of the charge was nevertheless achieved during the abbreviated run. As a result of these experiments, it was concluded that the exclusion of nitric acid from the anode/fuel juncture, or an improved mechanical clamp design, would be required.

Another device that was tested proved that essentially total disintegration was possible by incorporating both of the design conditions that were defined by the experimental work. A spring-loaded piston (Figure 1) was improvised which constantly forced the fuel section against a tantalum-strip anode with one face in constant contact for its full length. The polyvinyl chloride cap on the piston and a sheet of Teflon behind the anode electrically insulated the fuel from the cathodic portion of the system. A constant current flow of 21 amperes produced uniform corrosion of the piece except in two areas—the piston/fuel interface and the diametrically opposed portion of the fuel/anode interface. The mechanical pressure evidently sealed these two areas from nitric acid. Consequently, a thin, horizontal, cylindrical piece of fuel element remained that was propped between the piston and anode. This piece

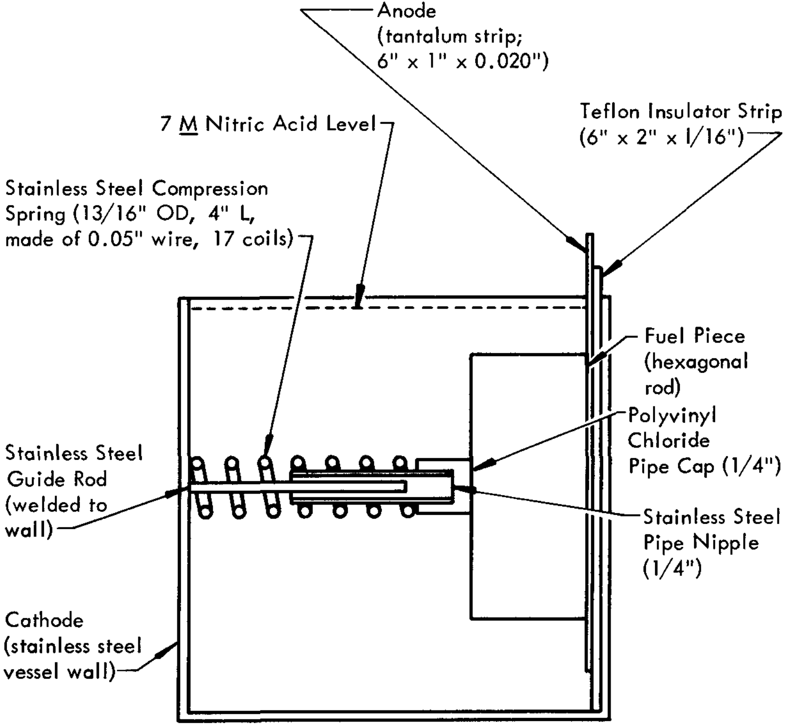


Figure 1. AN IMPROVISED, PISTON-TYPE FUEL-HOLDING TEST DEVICE.

was finally corroded until it broke, releasing the spring. Movement of the piston, however, trapped the fragments against the anode. Current flow dropped to three amperes, then ceased. Thus, the piece was totally disintegrated except for a minute sliver found in the slurry product. Various spring-loaded holding devices were built similar to the one that was previously tested, but modified to permit installation in the two-inch slab geometry dissolver. The first successful performance of the original design was never fully duplicated in the tests because of current-flow interruption before the fuel element was disintegrated.

At the same time, electrolytic disintegration of an entire element was studied. The element was vertically suspended in seven-molar nitric acid and held by an electrical clip which supplied direct current to the dry end. This test showed that fuel disintegration was concentrated at one to two inches below the acid level. In repeated tests, the element was corroded at this zone which reduced the cross section to the point of breakage. These results inferred that electrical current should be applied along the entire length of the element to promote uniform fuel disintegration. Also, electrolytic attack was shown in the various tests to be a surface phenomenon in that the element diameter was progressively reduced as the fuel matrix was disintegrated, but only on the surface. Therefore, the optimum site for power application to the fuel would be the terminal zone of electrolytic attack—the coolant channel located exactly in the center of the fuel element cross section. Previous attempts at supplying power to the channel zone had, as just described, not been wholly successful. However, the deficiencies of those configurations were overcome by the channel-rod anode design which excluded nitric acid from the fuel/anode contact area and applied constant power to the full length of the element.

Performance of a Channel-Rod Anode Device

Fuel-element pieces from 4 to 15 inches long were disintegrated by applying current through a metal rod inserted into and through the center coolant channel of the fuel pieces. Initially, stainless steel and aluminum welding rods, 3/32 inch (0.0937") in diameter, were inserted into the nominal 0.095-inch center hole of graphitized fuel pieces, which were then disintegrated by applying 20 amperes of current to the metal rod. The metal rod heated up and apparently expanded sufficiently to exclude nitric acid from the contact surface; however, both types of rods dissolved above and below the fuel element. This corrosive condition was corrected by changing the rod material to tantalum which performed satisfactorily without corroding.

Performance of the tantalum-rod anode device was verified in 12 runs (Table 1) using fuel sections that were 4 to 15 inches long. From 90 to 100 percent (97.84% average) of each fuel section was disintegrated by applying a constant DC power of 10 to 50 amperes, or 0.14 to 0.56 ampere per gram of initial fuel weight. The 0.093-inch-diameter tantalum rod appeared to be unaffected in the 12 runs and could carry 60

Table 1

ELECTROLYTIC DISINTEGRATION OF GRAPHITIZED FUEL PIECES

		Run Conditions				Disintegration Effectiveness		
			Applied DC Power					
						Amount of	Rates	
Run Number	Fuel Weight (gms)	Electrolyte	Average Current	Amps/Gm Fuel	Total Amp Hrs	Disintegration (wt %)	(gms/hr)	(gms/amp hr)
1	70	14.2 $\underline{M}$ HNO_3	20	0.286	8.6	90	146.5	7.33
2	56	7.2 $\underline{M}$ HNO_3	20	0.357	72.4	96.4	14.9	0.75
3	57	8.7 $\underline{M}$ HNO_3	20	0.351	51.6	100	22.1	1.10
4	68	7.3 $\underline{M}$ HNO_3	20	0.294	94.0	98.6	14.3	0.71
5	66	7.1 $\underline{M}$ HNO_3	36.9	0.558	73.7	99.2	32.8	0.89
6	197	6.6 $\underline{M}$ HNO_3	48.8	0.248	330.0	99.7	29.0	0.60
7	72	7.3 $\underline{M}$ HNO_3	10	0.139	100.0	97.9	7.1	0.71
8	49	3.8 $\underline{M}$ HNO_3	19	0.388	47.5	99.6	19.5	1.03
9(1)	59	1.8 $\underline{M}$ HNO_3	19.5	0.333	74.6	99.2	15.3	0.79
10	177	2.4 $\underline{M}$ HNO_3	45.7	0.258	160.0	95.2	48.1	1.05
11	59	1.0 $\underline{M}$ HNO_3	16.8	0.285	117.3	100	8.4	0.50
12	58	1.0 $\underline{M}$ KNO_3	19.8	0.341	102.5	100	11.2	0.57
	988 (total)					97.8 (overall)		0.79 (average, excluding Run 1)

(1) Electrolyte was cooled to 30° C; all others to 70° C.

amperes at 8 volts, or 480 watts. A higher power input caused overheating, oxidation, and eventual burnout.

Effects of the Disintegration Process Variables

The 12 runs also provided a measure of the variables that affected the disintegration rate and an indication of the properties of the generated solids, although the mechanism of fuel disintegration was not precisely investigated. An overall disintegration rate was determined for each run using various concentrations of nitric acid. Rates of 0.50 to 1.10 gram per ampere hour were achieved in 1 to 8.7-molar nitric acid, and the rate was determined to be linearly dependent on the applied current load (Figure 2). A 14.2-molar nitric acid concentration increased the disintegration rate sevenfold (Table 1, Run 1), but the solids consisted of unusable coarse graphite fragments containing embedded fuel particles. In Run 12, a one-molar potassium nitrate solution was substituted with no apparent advantage over nitric acid. All fuel feed stock for these runs was derived by breaking two graphitized (2,000 - 2,500° C) fuel elements into various lengths.

One test run was also made using a graphitized fuel specimen containing niobium carbide (NbC)-coated coolant channels. Although the fuel was electrolytically disintegrated, the niobium carbide was not dissolved. The disintegrated solids contained large flakes and partially oxidized white fragments of the niobium carbide liner material.

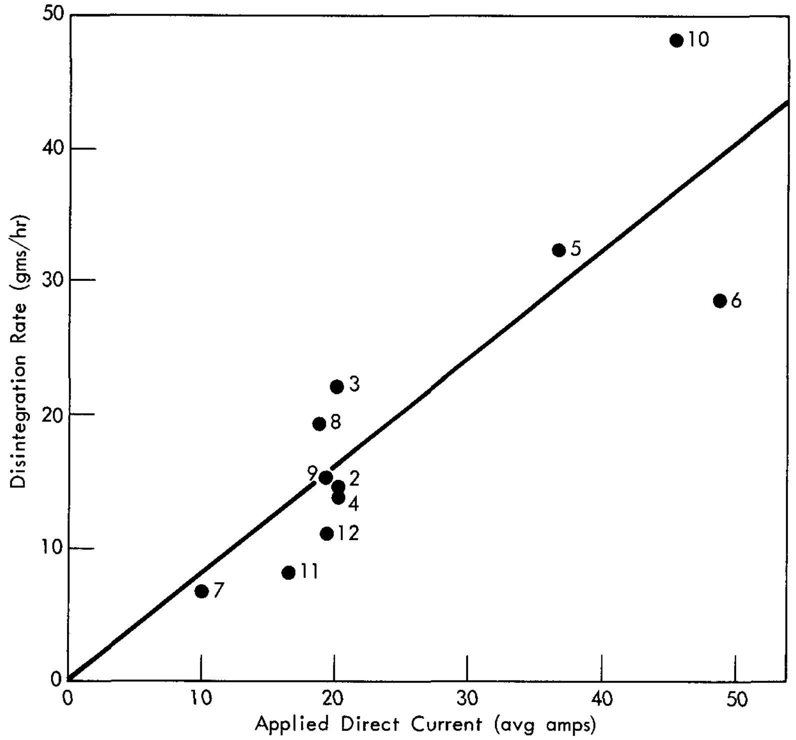


Figure 2. ELECTROLYTE DISINTEGRATION RATE AS A FUNCTION OF THE APPLIED CURRENT. (Numbers by the Datum Points are Run Numbers)

The resultant solids from each of the 12 runs were qualitatively evaluated to determine which set of operating conditions produced the maximum quantity of discrete particles free of surface graphite. Fine carbon was decanted from the slurry product and the remaining solids were dried and screened. Samples of the -70 +80 and -80 +325 mesh screen fractions were examined under a microscope and assigned a relative rank, decreasing in particle quality from 1 to 12. It was concluded from the results (Table 2) that particles of the highest quality were produced in Runs 2, 4, and 7 using 7.1 to 7.3-molar nitric acid and an initial current density of 0.14 to 0.36 ampere per gram. A much higher percentage of oversize (+70 mesh) solids were produced in Runs 3 and 5 (52 and 28 percent, respectively versus 9 to 14 percent in Runs 2, 4, and 7). This increase was due to the high acid concentration (8.7 M) in Run 3. Presumably, the high initial current density of 0.558 ampere per gram in Run 5 was responsible. However, the current density increased in all runs from the initial values given to very high values, since the applied current was kept constant while the fuel or anode area progressively decreased to near zero. No conclusive correlation was evidenced between the initial current density and the solids oversize fraction or particle quality in the runs, other than that indicated in Run 5. Electrolyte concentrations as low as one molar produced variable quantities of oversize solids at initial current densities comparable to those runs using seven-molar nitric acid. There appeared to be some advantage to continuous cooling of the electrolyte as in Run 9 (Table 1) which produced the lowest quantity of oversize solids (Table 2). This effect was to be investigated further in the subsequent pilot-plant work.

Other laboratory tests were also made using other electrolytes to explore the effect on the type of solids generated. No benefication in particle quality was evidenced

Table 2

CHARACTERISTICS OF ELECTROLYTIC SOLIDS PRODUCTS

Run Number	Screen Analysis (wt % in mesh size fraction) + 60	-60 + 70	-70 + 80	-80 + 325	-325(1)	Rank of Particles in Terms of Quality(2)
1	Not Screened - Very Coarse					12
2	10	0	25	65.5	0	1
3	44	8	24	20	4	4
4	14.3	0	25	57.2	3.6	2
5	24	4	24	48	0	8
6	13.3	0	26.3	53.3	6.7	6
7	8.7	0	12.4	49.4	4.9	3
8	4.6	0	18.5	67.8	9.2	5
9	2.8	0	11.1	69.4	16.7	9
10	19	11	19	48	3	10
11	18.4	2	16.3	59.2	4.1	11
12	6.2	0	21.6	67.7	4.6	7

(1) All values are low because fine carbon was first washed off.

(2) Based on visual examination.

by the addition of chromic acid or chromate salts to nitric acid. Similarly, negative results were obtained using low-acid molten aluminum nitrate and 5.3-molar sodium hydroxide as the electrolyte, although the fuel specimens were partially disintegrated. The disintegration rate in 5.3-molar sodium hydroxide was very low (0.1 gm/amp hr) and produced vigorous gas evolution.

In summary, the laboratory work provided a mechanical means for essentially complete disintegration of graphitized reactor fuel. Although the problem of removing surface-adhering graphite from recovered particles was unresolved, the effect of process variables on particle quality and yield was better defined. In addition, data on disintegration rates and electrical power requirements were established to permit sizing of a pilot-plant system.

PILOT-PLANT STUDIES

Introduction

The principal objective in the pilot-plant level of the development work was to test the economic and technical feasibility of a particle recovery process. The pilot-plant system was, in fact, a production-scale prototype unit since criticality considerations in processing enriched uranium necessarily limit equipment and the batch-charge size in a particular geometry. Operational aspects of the pilot-plant system are discussed in the sections that follow, after which an evaluation of the process system as a production-scale unit is given. In addition, results of supporting and concurrent laboratory studies are interjected which elaborate on the disintegration mechanism or pertain to specific problem areas encountered in the pilot-plant work.

System Design and Shakedown Run

Design of the pilot-plant system (Figure 3) was based on the fuel disintegration concepts derived from the foregoing laboratory work, coupled with modifications of known particle separation techniques.(2) Both the disintegration and solids-separation components of the system were mechanically tested in a shakedown run which provided preliminary performance data, but the run also revealed an electrical design deficiency.

Graphitized element sections (up to 26" long) were held suspended in an electrolytic cell by 95-mil tantalum rods that were forced through the element's center coolant channel and clipped to a common bus-bar direct-current power supply. The electrolytic cell (a 30" x 30" x 2" vertical slab tank) was designed to be nuclearly safe for processing up to 2.2 kilograms of enriched uranium, or approximately 9.4 kilograms of bulk weight per charge. The nitric acid electrolyte was continuously cooled and filtered; the generated fine carbon was removed by an external recirculation loop. Product slurry withdrawal was made through a bottom drain for subsequent graphite/particle separation.

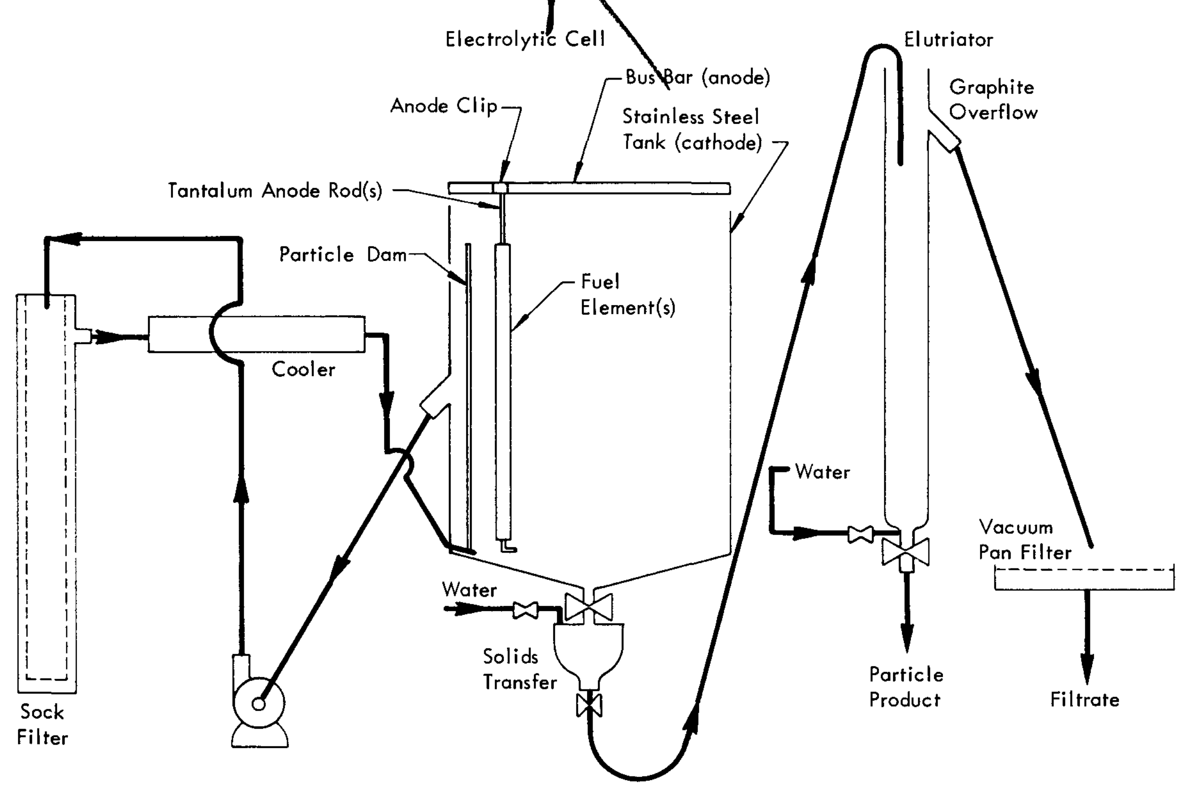


Figure 3. ORIGINAL PILOT-PLANT SYSTEM FOR RECOVERING PARTICLES FROM GRAPHITIZED REACTOR FUEL SCRAP.

A shakedown run was made using a 300-ampere arc welder as a direct-current power supply applied to a 2.3-kilogram charge of seven 26-inch-long sections of finished, but uncoated, fuel elements. The 16-hour run was terminated after 2.04 kilograms, or 88.5 weight percent, of the charge had been disintegrated at an average rate of 0.50 gram per ampere hour. A decrease from 290 to 120 amperes in the applied current load was made necessary as the run progressed. Apparently, as the fuel piece on each of the seven anode rods was consumed, the disparity in the electrical resistance between the anodes increased. Since the seven anodes were in parallel, those elements of least resistance drew the higher current load, sometimes exceeding the 60-ampere capacity of the tantalum rod. The total current load was, therefore, reduced to prevent anode burnup. These facts demonstrated a need for independently controlling the power input to each anode from a central power supply, or by installing a separate power supply to each electrically isolated anode.

Recirculation of the electrolyte through a filter was highly successful in removing the fine, suspended graphite which, in earlier work,(2) had presented filtration problems in subsequent separation steps. A total weight that constituted 57.5 weight percent of the consumed charge was collected in the filter. However, the high uranium concentration of 2.62 weight percent indicated a carryover of uranium-bearing or particle solids, in addition to the intended removal of fine (-270 mesh) carbon of approximately 1,000 ppm uranium content. Limiting the recirculation flow to a velocity of less than 0.06 feet per second in the electrolytic cell, and installation of a 270-mesh barrier above the particle dam (see Figure 3), were considered necessary for preventing a particle carryover in future operations. Continuous removal of the fine graphite serves to reduce the weight of solids transfer for elutriation and, at the same time, isolates a potentially discardable waste stream.(2)

Approximately 70 percent of the uranium from the disintegrated fuel was recovered as solids in the -70 +170 mesh particle-size range. The particles were derived from the shakedown operation using 6.3 and 7.7-molar nitric acid cooled to less than 98° F. Although microscopic examination indicated higher-quality particles (less surface graphite) at the higher electrolyte concentration, analysis did not support this appearance. Particle solids analyzed 57.37 and 57.75 percent (58.79 and 57.04 wt %) uranium, respectively, from the 6.3 and 7.7-molar nitric acid phases of the run. By comparison, the virgin particles contained 66 weight percent uranium, which indicates an excess carbon contamination of 8 to 9 percent in the recovered particles.

In summary, the shakedown run verified the capability of the system design for recovering particles of anticipated quality from graphitized fuel elements. Correction of electrical and mechanical defects would be required, however, to permit sustained operation and subsequent process evaluation.

Processing Graphitized Fuel

Modifications were made to the system, as indicated in Figure 4, which permitted trouble-free operation over a one-month period. Principal changes were:

1. Variable 0 to 1-ohm rheostats of 32-ampere capacity were installed to limit the current flow to each anode after measurements had verified that the electrical resistance of each anode differed over a range of 0.12 to 0.26 ohm.

2. To compensate for the reduced current input per anode (< 32 amps), the number of anodes was increased from the original seven to ten, which would utilize the 300 amperes of available power at 30 amperes per anode.

3. The anode rod material was changed from tantalum to titanium for its evaluation, in view of the much lower cost of titanium.

Following these modifications, the modified pilot-plant system was operated to produce ten kilograms of recovered particles to be reused in fuel elements for testing. The results of this system evaluation are discussed in the sections that follow.

System Operation - The processing campaign involved seven operating periods, or runs (Table 3). Each run was terminated to inspect the system or to remove any accumulated solids. The fuel charge for each run consisted of five fuel elements, each broken in half or in several pieces, and loaded on the ten 30-inch-long titanium-rod

Table 3

ELECTROYLTIC CELL DISINTEGRATION OF A REACTOR FUEL
(Summary of Pilot-Plant Data)

Run Number	Cell Operating Time (hrs)	Current Input[1]		Fuel Weight Input		Electrolyte Concentration ($\underline{M}$ HNO_3)		Disintegration Rate (gm/amp hr)	Throughput Rate (kg/hr)
		Average (DC amps)	Total (amp hrs)	(kgs)	(wt % reacted)	Initial	Final		
1	42.39	207	8,768.8			7.5	7.2		
2	25.09	196	4,925.6			7.5	7.2		
3	48.68	185	9,052.5			7.5	7.2		
Totals Runs 1-3	116.16	196	22,746.9	12.837	98.68			0.557	0.111
4	47.12	196	9,237.8			6.1	5.4		
5	94.82	204	19,330.4			5.8	3.5		
6	66.93	181	12,125.6			5.7	4.3		
7	84.93	181	15,391.9			5.7	4.1		
Totals Runs 4-7	293.80	190	51,085.7	37.012	98.96			0.716	0.125
Totals All Runs	409.96	192	78,832.6	49.849	98.89			0.625	0.122

(1) Current density for all runs was 2 amps/cm^2 or 0.05 amp/gram which finally became $\geqq$ 9 amps/cm^2 as fuel was consumed.

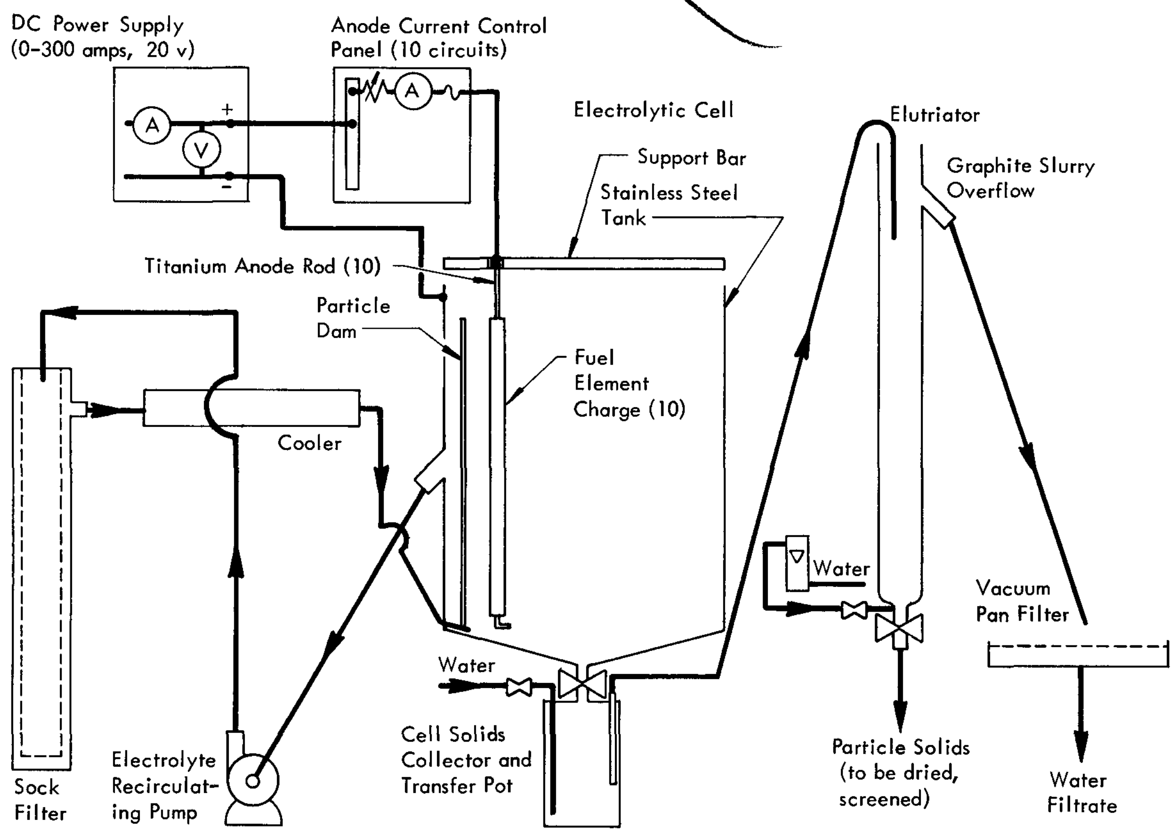


Figure 4. MODIFIED PILOT-PLANT SYSTEM FOR RECOVERING PARTICLES FROM GRAPHITIZED REACTOR FUEL SCRAP.

anodes. It was necessary to provide anode rods of two diameters (0.090 and 0.095") in order to accommodate both the as-graphitized elements and those which had been through the channel-reaming fabrication step. Although most of these rods were reused up to three times, this practice required removal of an oxide coating and is not particularly recommended. The initial weight of the fuel charged in each run varied from 3.5 to 4.5 kilograms, depending on the number of heavier, unmachined fuel elements used. The 63 fuel elements processed in the campaign had all been graphitized, were not lined with niobium carbide, and contained particles produced by a commercial manufacturer. Except for seven elements which contained 10 to 15 weight percent uranium, all elements were fully fueled with between 19 and 21 weight percent uranium.

Disintegration of each fuel charge was conducted in the two-inch vertical-slab electrolytic cell. Applied current was adjusted to 25 - 30 amperes per anode for a total of 250 - 300 amperes at six volts impressed on the 4.5-kilogram fuel charge. After the reliability of the current control was established in Run 1, the cell was operated continuously in subsequent runs through 24-hour periods. Current flow to each anode remained constant at 25 to 30 amperes. Rheostat adjustments were made twice each shift to compensate for resistance differences between the diminishing number of anodes containing an active fuel charge. Consumption time for the individual anode charges varied by several hours, depending on the fuel weight and probably the current efficiency, a factor of anode/fuel contact resistance. Total current input from the constant-voltage-type power supply to the cell decreased as each of the ten anode charges was consumed and the resistance of the parallel circuit increased. Thus, in a 24-hour operating period where, for example, two of the ten anode charges remained, the current input had decreased from approximately 300 to approximately 60 amperes, but still at 25 to 30 amperes per anode. At this point the run was terminated, or new fuel charges were added in the anode positions indicating zero current flow. In Runs 4 through 7, fuel was added at 24-hour intervals until the nuclearly safe cumulative weight limit of 9.4 kilograms had been reached before the system was drained and inspected. The average current input to the cell per run in this batch-type operation was 193 amperes (Table 3), or 64 percent utilization of the maximum available power.

The nitric acid electrolyte was recirculated through a cooler and sock-type filter (Figure 4) to remove generated heat and the fine graphite which formed as a suspension. Although the acid temperature was maintained at 80 to 100° F, satisfactory filtration was not accomplished in the early runs (Runs 1 - 3) due to cloth failure in the 7.5-molar acid. Lower acid concentrations (6 M or less) and cotton cloth were substituted in the later runs (Runs 4 - 7) with excellent results. As the fuel disintegrated, the fine, suspended graphite overflowed the baffle through a 270-mesh screen and was pumped to the filter. The objective was to continuously separate an anticipated high-volume waste stream of low uranium content from the coarser solids which settled to the cell bottom and into the transfer pot below (Figure 4).

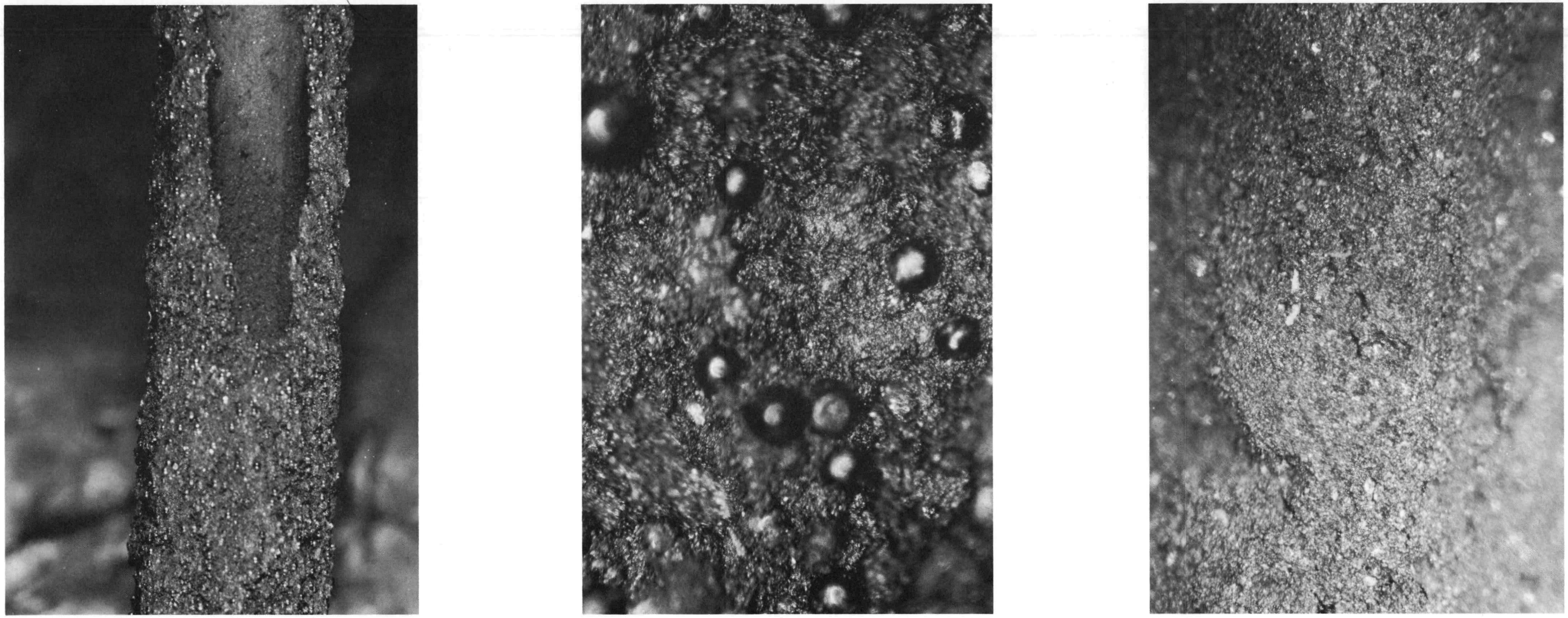
Separation procedures developed in the earlier work(2) were utilized in the processing steps following disintegration. The generated cell solids were water flushed into the elutriator column to remove the free graphite with water at a velocity of 0.06 foot per second. Overflow solids from the elutriator were filtered out, dried, and collected for further processing. The settled particle solids were drained from the elutriator, filtered, and dried for final screening. These procedures were conducted after starting the next disintegration run, since they were independent of the cell operation.

Evaluation of Electrolytic Cell Performance - All but 1.11 weight percent of the 49.849 kilograms of fuel charged to the system was disintegrated. The unreacted fuel consisted of thin, cylindrical shells remaining on some but not all anodes. The nature of the electrolytic attack on the fuel was evidenced on the surface of a fuel-shell specimen (Figure 5). The surrounding graphite matrix has been removed, exposing the particles which were bound to the fuel surface by the graphite (which was finally undercut) and the particles dropped off. The surface of the center channel in contact with the rod anode, Figure 5(a) and 5(c), appears relatively unattacked, as intended. However, some attack on the inner surface does occur in the final stages of disintegration when the fuel charge consists of these 1/4-inch-diameter by 2 to 3-inch-long shells. In some instances, it progressed to the point of poor contact between the anode rod and fuel. In fact, most fuel shells removed from the anode rods were loose and it was obvious the original interference fit had been altered to the point of no electrical contact. There was also evidence of the shells cracking and spalling off where the anode was bowed, either originally or through thermal distortion.

Disintegration rates were determined (Table 3) to be 0.71 gram per ampere hour for Runs 4 - 7 and somewhat lower (0.56 gm/amp hr) for Runs 1 - 3 where the higher acid concentration was used. Both rates fall in the range 0.50 to 1.03 grams per ampere hour achieved in previous work (Table 1) using 1 to 7.3-molar nitric acid and a tantalum anode. However, the lower acid concentration in Runs 4 - 7 all but eliminated the white oxide formation on the titanium rods prevalent in the higher acid of Runs 1 - 3. This difference possibly resulted in a lower anode/fuel contact resistance; therefore, a higher current efficiency could account for the higher disintegration rate. The lower acid concentration is considered preferable for the overall system operation.

The overall solids weight throughput (Table 3) in the processing campaign was 49.8 kilograms in 410 hours of cell operating time, or 0.122 kilogram per hour. However, the nuclearly safe solids capacity of the cell was not utilized. A throughput rate of 0.268 kilogram per hour would be realized by initially charging to the 9.4-kilogram solids limit. This level of operations would require 20 anodes, instead of 10, for which there is space in the 30-inch-wide cell, and an increase in power supply from 300 to 600 amperes. The expected increased throughput rate was calculated using actual values of a 0.71 gram per ampere hour disintegration rate and 64 percent utilization of the available power experienced in batch-type operations.

An increase to the maximum throughput of 0.420 kilogram per hour would be possible through semicontinuous-type operation of the cell; that is, replacement of anode charges on a consumption demand schedule. This procedure would allow 100 percent usage of the available power, or a constant 600-ampere input to the cell. However, this type of operation would require continuous drainage of generated solids from the cell to prevent exceeding the 9.4 kilograms of solids or 2.2 kilograms of uranium for the nuclearly safe limitation. In fact, continuous solids drainage was studied and achieved in Runs 4 - 7. Solids accumulation on the sloped cell bottom was significantly nonexistent where the fine, suspended graphite was being removed by the recirculating stream. In Runs 1 - 3, the recirculating filter was not functioning and the accumulated solids had packed on the cell bottom and were difficult to dislodge. In contrast, the periodic cell inspections in Runs 4 - 7, when 9.4 kilograms had been charged, showed no such accumulation where the fine graphite was being removed. On two occasions, recirculating flow had ceased due to complete solids stoppage of the filter. This condition resulted in a layer of fine and coarse solids mixture on the cell bottom which settled and did not flow through the one-inch drain line. In view of these observations, operation of the cell under the proposed semicontinuous feed conditions is considered mechanically feasible by expanding the recirculating filter capacity and installing a flow meter and sight gage to verify satisfactory recirculating flow conditions.



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(a) Outer Surface of Fuel Shell and Portion of the Inner Channel Surface. (photograph of unmounted specimen; 10X)

S-67-3394-5

(b) Surface of the Fuel Shell Remnant. (100X)

S-67-3394-7

(c) Coolant Channel Surface of the Fuel Shell Remnant. (100X)

Figure 5. SHELL REMNANT OF GRAPHITIZED REACTOR FUEL AFTER ELECTROLYTIC DISINTEGRATION.

Solids and Uranium Distribution in the System - The uranium content was determined for each material component separated from the cell slurry product. These data described the makeup of the cell-generated solids and indicated the effectiveness of techniques used to separate graphite from particles. Distribution of solids and uranium in the system were summarized separately for the two operational phases of the processing campaign. In Runs 1 - 3, Table 4, all generated solids were elutriated and screened; in Runs 4 - 8, Table 5, fine graphite solids were continuously removed, but only the coarser settled solids were elutriated and screened.

Although greater than 98 percent of the fuel was disintegrated, separation of the cell solids showed that high values of uranium were contained in solids coarser in size than the particles and consisting of particles imbedded in the matrix graphite. In Runs 1 - 3, 61.94 weight percent of the cell-generated solids were removed in the elutriator overflow. However, these solids carried only 21.54 weight percent of the total uranium. Part of this apparent high loss was attributed to the presence of the fine graphite which overloaded the column. Slug-flow conditions existed in the short column (3" D x 3' L) being used which led to initially poor disengagement of the solids, possibly causing particle carryover into the overflow stream. Subsequent screening of the settled elutriated solids produced an additional 19.2 weight percent uranium loss to the +60 and +70 mesh oversize solids fractions. Uranium content of the coarser +60 mesh fraction approximated that of the reactor fuel, while the finer -60 +70 mesh fraction contained less graphite and was more concentrated in uranium (0.417 gm/gm U). As a result, the uranium recovered as -70 +170 mesh particle solids accounted for only 56.46 weight percent of the total uranium (as 2.613 kgs of solids which analyzed 0.5812 gm/gm U).

Particle recovery was increased to 67.08 percent in the second phase of the operations (Runs 4 - 7, Table 5). In these runs, greater than 98 percent of the 37 kilograms of the fuel charged to the apparatus was disintegrated, and 7.9 kilograms or 22.12 percent of the total solids were continuously filtered as fine graphite. These solids contained only 0.14 weight percent of the uranium at a 700 to 1,000 ppm uranium concentration. Elutriator efficiency was also improved in that the uranium loss to the overflow was 5.55 percent as opposed to 21.54 percent in Runs 1 - 3. This difference was partially compensated for by a somewhat higher uranium loss to the oversize screened solids (25.3 percent of the total uranium versus 19.2 percent in Runs 1 - 3). However, the overall loss to the separated graphite solids was lower by approximately 10 percent in Runs 4 - 7 (31.12 percent rather than the 40.80 percent in Runs 1 - 3). The particle recovery (67.08 percent) was correspondingly higher in Runs 4 - 7, and 9.290 kilograms of -70 +170 mesh particle solids were collected which analyzed to an average value of 0.5302 gram per gram of uranium.

The two remaining system streams accounted for 0.97 percent of the total uranium dissolved in the electrolyte and elutriation water combined, and less than 0.01 percent in the -170 mesh screen fraction. Since the solids output of the system was below

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Table 4

SOLIDS AND URANIUM DISTRIBUTION IN THE PILOT-PLANT SYSTEM

(Runs 1 through 3)

	Solids		Uranium Content		
System Operation and Material Type	Weight (kgs)	Percent of Output	Concentration (gm/gm)	Weight (gms)	Percent of Output
Input					
Fuel Elements to Disintegration Cell	12.837	-	0.1996 (avg)	2,691[1]	-
Output					
1. Disintegration, Unreacted Fuel	0.169	1.32	0.2042	34.33	1.27
2. Electrolyte Filtration, Fine Graphite	0	0	-	0	0
3. Elutriation, Graphite Overflow	7.942	61.94	0.072 (avg)	579.52	21.54
4. Screening					
+60 Mesh Coarse Graphite	1.709	13.33	0.2241(avg)	382.98	14.24
-60 +70 Mesh Coarse Graphite	0.324	2.53	0.417	134.86	5.01
-170 Mesh Fine Graphite	0.064	0.50	0.000723	0.04	0.01
Total of Steps 2 through 4	10.039	78.30		897.40	40.80
-70 +170 Mesh Particle Product	2.613	20.38	0.5812	1,518.68	56.46
5. Dissolved Uranium in Electrolyte	-	-	0.000407 (avg)	39.64	1.47
Total Output	12.821	100	-	2,690.05	100

(1) Sum of in-process uranium values assigned to each element.

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Table 5

SOLIDS AND URANIUM DISTRIBUTION IN THE PILOT-PLANT SYSTEM

(Runs 4 through 7)

	Solids				Uranium Content				
	Weight (kgs)		Percent of Output		Concentration (gm/gm)	Weight (gms)		Percent of Output	
Input									
Fuel Elements to Disintegration Cell		37.012		-	0.2094 (avg)		7,751(1)		-
Output									
1. Disintegration, Unreacted Fuel		0.386		1.08	0.2042		78.82		1.07
2. Electrolyte Filtration, Fine Graphite	7.916		22.12		0.00134 (avg)	10.61		0.14	
3. Elutriation, Graphite Overflow	10.631		29.71		0.0383	407.17		5.55	
4. Screening									
+60 Mesh Coarse Graphite	5.499		15.37		0.2241 (avg)	1,235.62		16.83	
-60 +70 Mesh Coarse Graphite	1.515		4.23		0.417	631.76		8.60	
-170 Mesh Fine Graphite	0.545		1.52		0.000723	0.04		0.01	
Total of Steps 2 through 4		26.106		72.95			2,285.20		31.12
-70 +170 Mesh Particle Product		9.290		25.96	0.5302 (avg)		4,925.85		67.08
5. Dissolved Uranium in Electrolyte		-		-	0.000407 (avg)		53		0.72
Total Output		35.782		100	-		7,342.87		100

(1) Sum of in-process uranium values assigned to each element.

the input, a composite sample of the acid electrolyte was analyzed for dissolved carbon. This value was found to be a negligible 120 ppm carbon, or representing 27 grams of total dissolved carbon. Material balance closures (Table 6) of 97.70and 96.08 percent for solids weight and uranium, respectively, were achieved in the processing campaign.

Table 6

PILOT-PLANT MATERIAL BALANCE

	Bulk Weight (kgs)	Uranium Content (gms)
Input		
Reactor Fuel Elements	49.849	10,442(1)
Output		
Unreacted Fuel Shells	0.555	113.15
Separated Graphite	35.590	3,069.45
Particle Product	11.903	6,444.53
Solutions(2)	566	92.64
Total Output	48.703	10,032.92
Weight Percent of Input	97.70	96.08

(1) Sum of in-process uranium values assigned to each of 63 elements.
(2) Combined volumes of acid electrolyte, elutriate, and wash water.

Composition of the Recovered Particle Solids - Analysis of the recovered particle solids showed an average composition of 0.5415 gm/gm U, equivalent to 82.05 weight percent as particles and 14.09 weight percent as excess fuel matrix graphite. The particle solids were collected in seven batches which were sampled and analyzed for uranium and carbon (Table 7). The difference in batch concentration of uranium, all below the 67 weight percent uranium of virgin particles, was due to dilution by graphite in two forms, loose fragments and graphite bound to the particle surface. These types are evident in the typical radiographs (Figures 6 and 7) taken to verify the uranium content as a coated particle form. The inclusion of graphite solids in the same size range as the particles was a known circumstance of the separation procedures used. In previous work(2) such solids, derived from the acid digestion of low-temperature cured scrap, were not completely removed by elutriation and screening and remained at concentrations of 0 to 10 weight percent. The graphite bound to the particle surfaces is also evident from the radiographs, primarily as columnar projections which probably constituted terminal support of particles to the fuel body. Particles were also prematurely severed from the fuel body while bound to it by a larger graphite mass attached over a wider area of the particle surface (see Figure 7).

Various methods in exploratory-type tests have been used in attempting to remove the excess graphite from recovered particle solids. Electrolytic treatment to remove surface graphite has not been accomplished in bench-scale equipment, nor in later work using tantalum, platinum, or graphite as anodic receptacles for monolayer or deep-bed

Table 7

COMPOSITION OF THE RECOVERED PARTICLE SOLIDS

Batch Number	Batch Weight (kgs)	Pilot Plant Run Number Source	Solids Composition (gm/gm)				
			Analyzed Uranium	Equivalent Particles$^{(1)}$	Equivalent Carbon$^{(2)}$	Analyzed Carbon	Excess Carbon$^{(3)}$
A	2.613	1, 2, 3	0.5812	0.8806	0.2994	0.3945	0.0951
B	1.556	4	0.5468	0.8285	0.2817	0.4243	0.1426
C	1.749	5	0.5258	0.7967	0.2709	0.4362	0.1653
D	1.816	5, 6, 7	0.5627	0.8526	0.2899	0.4054	0.1155
E	1.659	7	0.4814	0.7294	0.2480	0.4791	0.2311
F	1.109	5, 6, 7	0.5387	0.8162	0.2775	0.4441	0.1666
G	1.401	5, 6, 7	0.5264	0.7976	0.2712	0.4562	0.1850
Total	11.903						
	Weighted Averages		0.5415	0.8205	0.2790	0.4199	0.1409
Composite Sample of All Samples			0.5587	0.8465	0.2878	0.4193	0.1315

(1) Values calculated from uranium analysis and uranium content of particles as 0.67 gm/gm.

(2) Values calculated from carbon content of particles as 0.33 gm/gm.

(3) By difference; analyzed carbon minus particle equivalent carbon.

particle solids. In all cases, no current flow was established through the solids beds at a maximum of 40 volts.

Other methods were also tried to remove surface graphite. Additional runs were made to verify earlier work in which refluxing 70 percent nitric acid was used to apparently improve the quality of a mixture of particle solids derived from various electrolytic test runs. However, results of the more recent work using refluxing 70 or 90 weight percent nitric acid and also cold nitrogen dioxide (N_2O_4) for treating particles of known graphitized fuel origin were negative and no improvement was evidenced. Mechanical removal of the surface graphite was also briefly examined by rolling 400 grams of particle solids at 75 rpm for 48 hours inside a can lined with 200-mesh stainless steel wire cloth. Microscopic examination revealed no significant improvement in the surface quality.

Removal of the loose graphite present in the particle solids is considered a potentially lesser problem. Test work was conducted using Freon 114B2 ($CBrF_2$-$CBrF_2$) as a sink-float medium (ρ = 2.33 gms/cc) to separate the loose graphite from the particles. Although complete separation was not achieved due to agglomeration of graphite and particles in this particular medium, evidence of benefication was noted by microscopic examination. The technique appeared promising but would require further work in formulating the proper liquid medium.

More rigid control of factors affecting the basic disintegrative mechanism might be expected to provide a higher ratio of particles comparatively free from surface graphite.

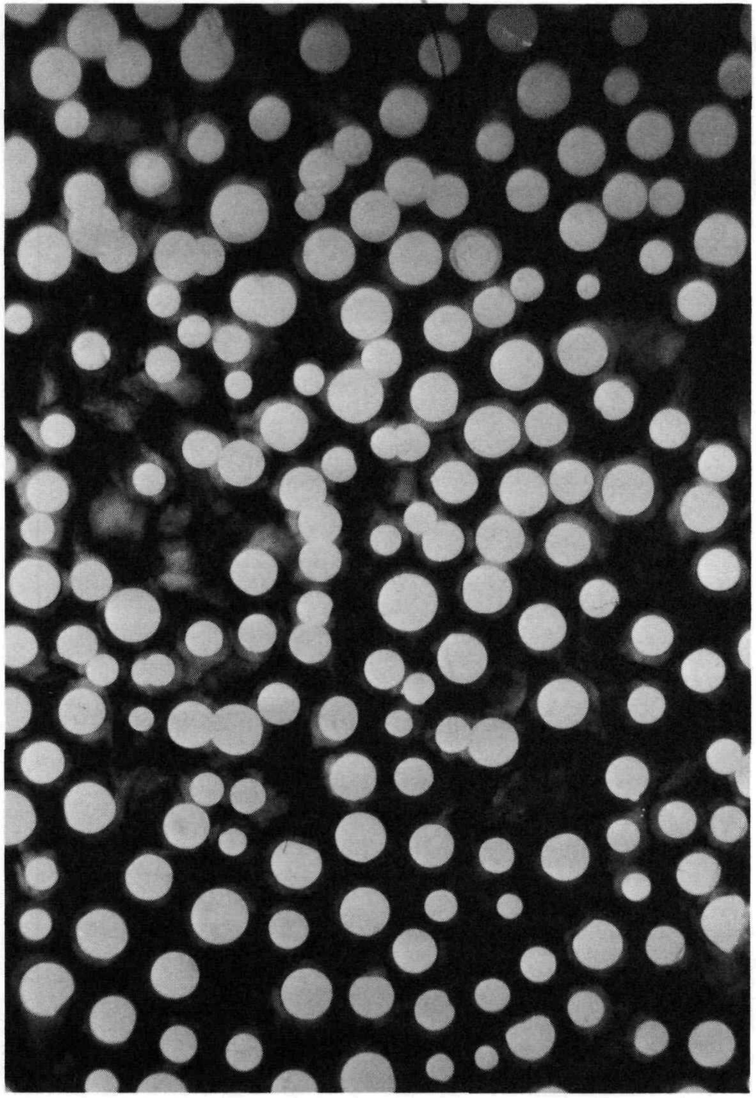

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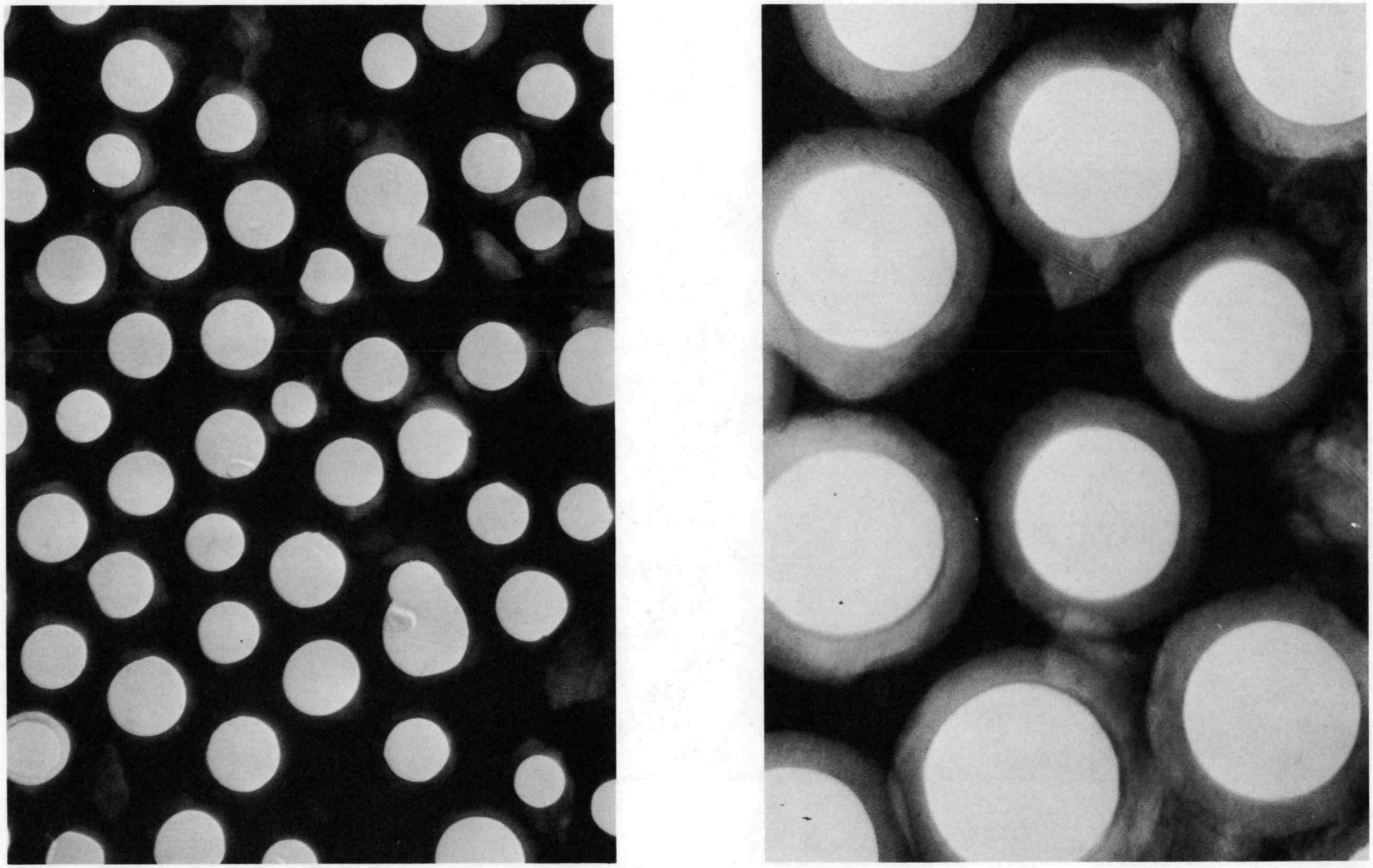
Figure 6. RADIOGRAPH OF RECOVERED PARTICLE SOLIDS FROM PILOT-PLANT OPERATIONS. (50X)

Cell operating conditions for converting reactor fuel ideally to only fine graphite and particles would also simplify the separation procedures and permit much higher recovery yields from graphitized fuel. More intensive work in the area of current density control and possibly in the choice of electrolyte would appear warranted in efforts to improve particle quality and yield. Further pursuit of these topics depends largely on reuse evaluation of the recovered particles and, consequently, the anticipated demand for additional quantities. Objection to the presence of the excess graphite depends on the end use of the particle solids. For recycle into the fuel fabrication stream, the compatibility of graphite with carbon and binder to produce satisfactory elements would seem important. At least, the excess graphite creates sampling difficulties. For instance, a composite sample taken from riffle fractions of each particle



(a) 100X S-68-0035-2

(b) 250X S-68-0035-3

Figure 7. RADIOGRAPHS OF RECOVERED PARTICLE SOLIDS FROM PILOT-PLANT OPERATIONS. (Examples of Excess, Surface-Bound Graphite)

batch contained 55.87 weight percent uranium, or almost two weight percent higher than the weighted average from an analysis of each batch (Table 7).

Spectrographic analyses were made of the recovered solids and compared (Table 8) to typical virgin particles and fuel elements, to reflect the contribution of the excess fuel graphite. Corrosion of the stainless steel equipment and titanium anodes increased the levels of iron, chromium, and titanium to some degree. More severe was the contamination by calcium, magnesium, and sodium. Whether the source of these contaminants was external or represents soluble impurities that were incompletely washed from the solids before drying was not immediately determined.

Table 8

IMPURITY CONTENT OF RECOVERED PARTICLE SOLIDS
(All Values in ppm on a Metal Basis)

	Spectrographic Analyses (ppm)				
	Recovered Particle Solids				
	Samples of 7 Batches				
Chemical Element(1)	Range	Average	Composite Sample from 7 Solid Batches	Virgin Particles(2)	Fuel Elements, Range(3)
Al	6 - 8	7	6	6	5 - 10
Ca	175 - 500	317	400	10	20 - 40
Cr	< 2 - 70	35	10	4	< 2 - 10
Cu	1 - 8	3	4	2	< 1 - 5
Fe	250 - 400	313	200	75	135 - 200
K	< 6 - 15	< 8	< 6	< 6	< 5
Mg	45 - 175	86	30	< 2	< 2
Mn	< 1 - 10	4	< 1	< 1	2 - 4
Mo	20 - 45	29	10	20	40 - 80
Na	10 - 60	20	30	< 1	< 1 - 4
Ni	8 - 30	15	10	20	2 - 10
Si	60 - 200	137	100	10	60 - 100
Ti	20 - 65	41	15	6	10 - 15
V	15 - 20	18	15	6	5 - 10

(1) Major constituents selected from 40 elements; pyrospectrographic reports.
(2) Two-lot cross-blend analysis; picked at random.
(3) Analyses of fuel elements; picked at random.

RESULTS OF THE STUDY

Process Evaluation and Application to Graphitized Fuel

Aside from considerations of the particle recycle to a specific reactor fuel, the pilot-plant work demonstrated a means for the nondestructive concentration of uranium as particles from reactor fuel. In order to evaluate the process and ascertain the recovery costs, the capability of the pilot-plant system was depicted (Figures 8 and

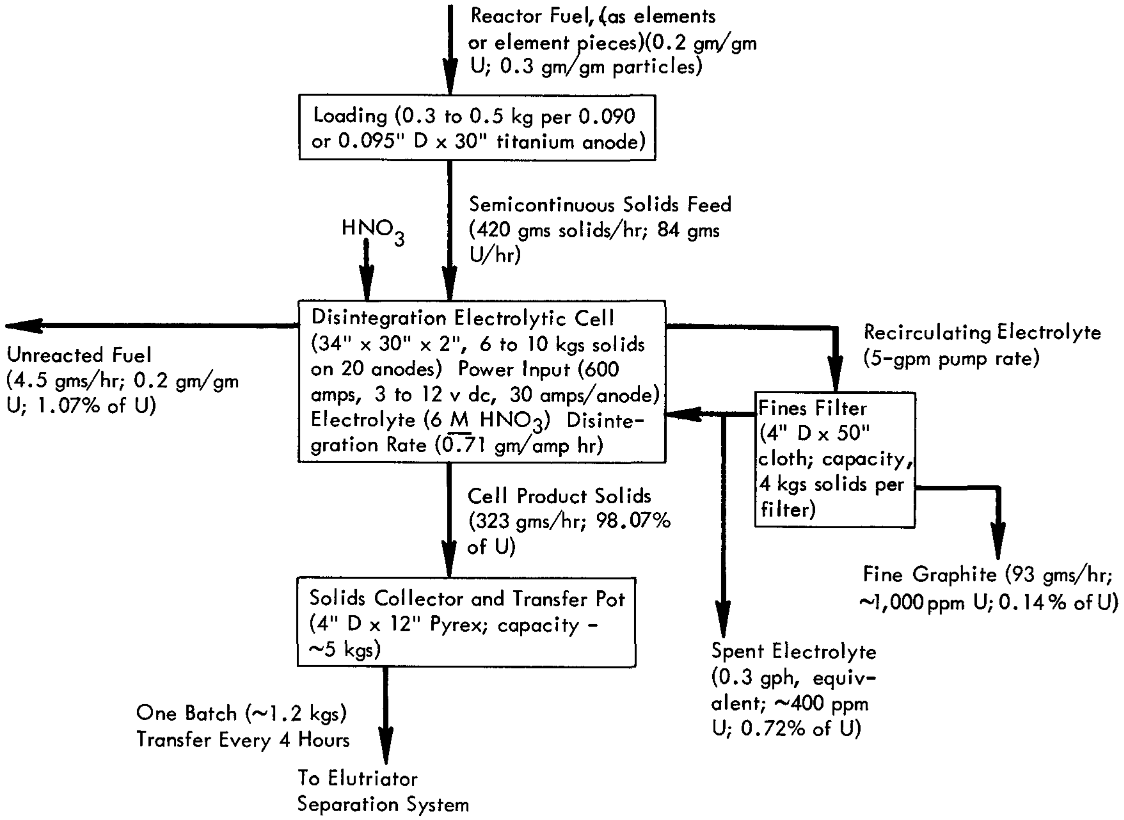


Figure 8. PILOT-PLANT DISINTEGRATION OF GRAPHITIZED REACTOR FUEL AT MAXIMUM THROUGHPUT CONDITIONS.

9), at its present stage of development, as a production unit operating at the proposed maximum throughput conditions. The flow of solids and the uranium distribution in the system are based on the pilot-plant data given in Table 6. Other details such as acid usage, filter capacities, and solids transfer schedules, are also based on pilot-plant operating experience. In the flow sheet of Figure 9, an existing three-inch-diameter by six-foot-high elutriator column and pressure filter have been substituted for the lower-capacity column and vacuum filter used in the pilot-plant work.

Fuel Disintegration Flow Sheet

The disintegration, or head-end processing of the reactor fuel (Figure 8), would include a bank of three filters in the recirculating stream so that continuous cell operation could be maintained. The cell power supply could be one 600-ampere, or two 300-ampere, rectifier banks feeding the 20 anodes through separate rheostat controls, or 20 independent 30-ampere power supplies. The latter would seem preferable in regard to space, current efficiency, and operating factors. The acid electrolyte in the system would be either completely drained from the system and replenished once every 32 hours, or continuously adjusted to six molar manually or by automated density and liquid-level controls. The four-kilogram solids capacity of the sock filter would be

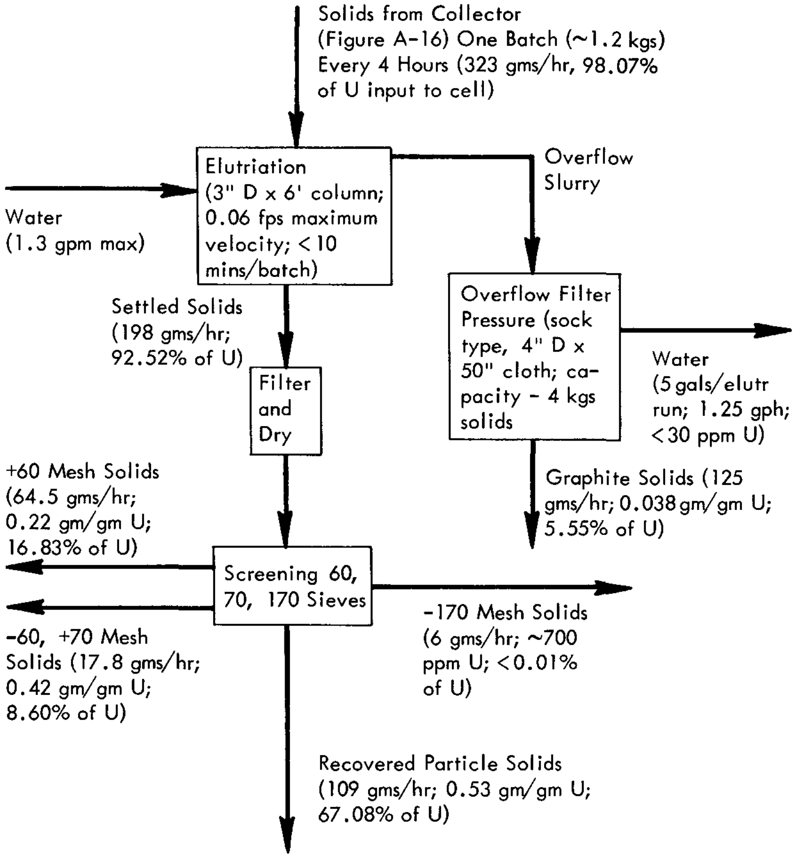


Figure 9. PILOT-PLANT BATCH-TYPE SEPARATION OF CELL SOLIDS. (Equivalent Mass Flow Rates are Shown per Hour of Cell Operating Time)

reached in approximately 40 cell operating hours, at which time one of the two standby filters would be valved in and the full filter sock removed and replaced. The generated coarse solids would leave the cell and accumulate in the four-inch-diameter Pyrex collector at a rate of 323 grams per hour. Since the collector's solids capacity is approximately five kilograms, it would accommodate solids generated from 16 hours of cell operating time. However, solids would be transferred from the collector at four-hour intervals. By this method, 1.2 kilograms of solids would be collected and transferred to the elutriator column for graphite/particle separation.

Solids and Particle Separation Flow Sheet

The solids-separation phase of the system (Figure 9) involves a five to ten-minute period for elutriation of the 1.2-kilogram solids batch, followed by handling of low-volume, but highly concentrated solids. The elutriated solids would be collected in compliance with standard nuclearly safe procedures and processed by drying and screening methods using laboratory-sized equipment. The filtered, elutriate water effluent would be stored in safe tanks for disposal. The uranium content of the water was not measured in the pilot-plant work since it was combined with the acid electrolytes for analysis. However, from previous work,(2) values of 0 to 30 ppm uranium would be expected. Particle solids would be accumulated at a rate of 109 grams per hour of cell operating time and would average 53 weight percent uranium.

Estimated Fuel Processing Costs

Costs to operate the system and process the waste streams were determined by applying Y-12 unit costs to the material flow data of Figures 8 and 9. The low-throughput and particle-yield aspects of the process are reflected in the relatively high estimated recovery costs (Table 9).

Table 9

OPERATING COSTS OF PILOT-PLANT PARTICLE RECOVERY SYSTEM

Type Cost(1)	Cost $/Kg Solids Input		$/Kg Recovered Particles
A. Labor (12 manhours per 8-hour shift)	71.40		
B. Material (titanium anodes, filter cloth, nitric acid)	0.79		
Total Labor and Material Cost		72.19	
C. Disposal or Processing(2) of Waste Streams			
1. Sample and Discard Elutriation Water	12.80		
2. Recover Uranium from Acid Electrolyte	9.42		
3. Sample and Discard Fine Graphite Solids	1.08		
4. Recover Uranium from Coarse Graphite Solids	14.57		
Total Waste Treatment Cost		37.87	
D. Total Processing Cost		110.06	
Minus Cost to Process Reactor Fuel by Standard Method		7.15	
E. Net Processing Cost to Recover Particles		102.91	
At Actual 67.1% Recovery Yield		102.91	511
At Theoretical 100% Recovery Yield		82.83	276

(1) Bases for calculating costs: (1) material flows as per Figures 8 and 9; (2) Y-12 unit operating cost as of January 1, 1968.

(2) Processing of materials through organic, primary extraction step.

Although operating manpower for the system could be shared, 12 manhours per shift or 1.5 manhours per hour of cell operating time were assigned to maintain the accelerated semicontinuous throughput rate of 0.420 kilogram per hour. By comparison, the pilot-plant work required approximately 0.7 manhour per hour of cell time (but, for a lower throughput), or 5.5 manhours per kilogram of solids compared to 3.6 manhours per kilogram in the proposed system. Total operating cost for labor and such things as titanium wire and acid would total $72.19 per kilogram of solids input to the cell.

Solids, other than the recovered particles, and solutions generated by the system would require disposal or further processing to reclaim the contained uranium. Uranium content of the elutriation water (< 30 ppm uranium) and the fine graphite solids (1,000 ppm uranium) would not justify further processing and would be sampled and discarded. The electrolyte (marginal at 400 ppm uranium) and coarse graphite solids containing percentage concentrations of uranium would be processed by standard techniques. The cost for treating the waste streams in this manner was calculated to be $37.87 per kilogram of solids input to the pilot-plant system. Therefore, total cost for processing the reactor fuel would amount to $110 per kilogram of solids input. The unit cost to otherwise destructively process this type of reactor fuel to recover the uranium is $7.15 per kilogram. The net cost for particle recovery over this standard treatment is, therefore, the difference, given in Table 9, or $102.91 per kilogram of input.

The cost per kilogram of recovered particles is, of course, much higher since only approximately 30 percent of the solids input to the system consists of particles. Using the 67.1 percent yield experienced in the pilot plant, the overall processing cost is calculated to be $511 per kilogram of recovered particles. At the theoretical 100 percent particle recovery yield, labor costs would remain constant, but all waste streams would be discarded at a lower cost. Under these circumstances, processing costs would drop to $82.83 per kilogram of input or $276 per kilogram of recovered particles. These minimum values might be approached if, as mentioned, the disintegration mechanism were improved to produce only fine graphite and particles. Even so, the minimum cost values for fully loaded fuel (20 wt % U) are quite high. Processing a reactor fuel of decreased uranium loading would increase the costs, per kilogram of particles, to correspondingly higher, possibly unacceptable, levels. The operating cost data do not include the capital investment for equipment. This value was estimated to be $45,000 to $55,000, including adequate safe tankage and a ventilated hood for handling the solids. The electrolytic system is similar to that used for processing low-cured scrap.(2) It is anticipated that one system, with options of heat input or cooling and electrical power input, could be designed to process both types of scrap. Such a system would share common elutriation and separation equipment at a savings on the capital investment.

PROCESS APPLICATION TO OTHER FUELS

Potential of the electrolytic process to particle recovery from intermediate-cured scrap (1,000° C) was not evaluated in pilot-plant work since very little scrap is generated from this phase of the fabrication cycle. However, the limited amount of laboratory work(2) indicated a higher (threefold) disintegration rate and recovery of graphite-free particles. Although further work to verify these data would be required, application of the process to this type of fuel at conceivably much lower cost than the graphitized fuel would be considered attractive.

On the other hand, the processing of niobium carbide-lined or coated reactor fuel poses an additional separation problem. Since one test run indicated that the niobium carbide was not dissolved, leaching of the particle solids from electrolytic disintegration of such fuel in a hydrofluoric-nitric acid solution(1) would probably be required to remove niobium contamination from the recovered product.

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The feasibility of electrolytically processing reactor fuels other than the Rover type would depend on the particle-coating material, suitability of the element geometry for electrical power input, and fuel matrix composition. Success of the process in recovering particles from Rover reactor fuel, of course, depended on the imperviousness of the pyrolytic carbon coating to chemical and electrolytic attack, whereas the graphite matrix was disintegrated. However, electrolytic treatment of graphite reactor fuel could conceivably be used to simultaneously disintegrate and dissolve dispersed but uncoated uranium particles where disadvantages of combustion/dissolution procedures prevail. The fact that many metals and alloys are anodically dissolved using an acid electrolyte might be applicable to metallic-coated particles. Conversely, other electrolytes could be utilized to prevent the dissolution of metallic constituents. The reaction of a particular reactor fuel to electrolytic attack can be determined very quickly using a simple apparatus. The validity of several electrolytic processing options could, therefore, be tested with minimum effort. Since electrolytic reaction rates are, in general, comparatively low, such processes would probably be most economically applicable to the recovery of specialized fuel particles or the recovery of enriched uranium from matrices unyielding to conventional techniques.

[redacted]

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