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**DISSOLUTION IN HTGR
FUEL REPROCESSING**

INTERIM DEVELOPMENT REPORT

Prepared under
Contract EY-76-C-03-0167
Project Agreement No. 53
for the San Francisco Operations Office
Department of Energy

AUGUST 1978

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GENERAL ATOMIC COMPANY

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**GENERAL ATOMIC PROJECT 3261
AUGUST 1978**

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ABSTRACT

This interim development report gives the status of the dissolution step involved in reprocessing HTGR reference TRISO-BISO fuels. The information and recommendations presented herein are based on the pilot-plant experimental results obtained at General Atomic Company between September 1975 and May 1978.

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1. SUMMARY

The experimental work on high-temperature gas-cooled reactor (HTGR) fuel dissolution at General Atomic Company (GA) has demonstrated the feasibility of using current equipment design and operating philosophy to dissolve reference TRISO-BISO fuels at a reasonable rate. Significant progress has been shown toward meeting commercial-scale dissolver requirements. At the same time, this study defines more clearly the areas in which additional experimental work is required. Previous dissolution work (Ref. 1-1) was also performed on Fort St. Vrain (FSV) fissile and fertile fuels.

A 40% heel-mode operation was selected for the dissolution of fertile ThO_2 kernels. The heel operation takes advantage of the rapid dissolution rate during the first portion of ThO_2 kernel leaching. By interrupting the normal cycle before complete dissolution is achieved, it is possible to shorten the average dissolution time for several batches. Experimental results show a significant threefold increase in dissolution rate for heel-mode operation compared to normal no-heel dissolution. The flowsheet specification of 1 M $\text{Th}(\text{NO}_3)_4$ solution was obtained in approximately 6 hr in the pilot-plant-scale dissolvers. However, tests have shown that the dissolution rate can vary as much as 2.5 times for different batches of ThO_2 kernels, depending on their physical properties and past history. Decanting of the product solution from the solids heel was successfully demonstrated between batch cycles when using a steam suction jet. Ninety-seven per cent of the product solution was decanted with less than 0.1 wt % of the heel carried over.

The experimental work indicates that the dissolution rate of ThO_2 kernels in Thorex can be further increased by improving liquid-solids mixing in the dissolver. A partially dry solids bed may exist, based on a heat-transfer study which showed the solids temperature to be above the solution

boiling point in the lower part of the bed. Little liquid-solids contact is expected in this lower part of the bed. Additional experimental work, aimed at circulating the solution through this partially dry bed, is recommended.

The dissolution of the weak acid resin (WAR) derived fissile fuel (processed through a secondary burner) in 2 $\bar{M}$ nitric acid was controllable, and no excessive foaming resulted. The fissile dissolver should operate below the solution boiling point during the first part of the dissolution cycle to limit the peak NO_x off-gas concentration. On the other hand, FSV fissile ash was found to require boiling in Thorex acid for complete dissolution, owing to the presence of a significant amount of thorium oxide.

A submerged steam jet was developed to provide reliable and efficient removal of the fissile dissolver product slurries, which contained SiC hulls and whole fuel particles. The selection was based on operational reliability and the capability for remote control maintenance in a commercial reprocessing plant. For an efficient steam jet transfer, the slurry must be cooled to less than 58°C.

REFERENCE

- 1-1. Hutton, A.E., "Dissolution of HTGR Fuel," ERDA Report GA-A13278, General Atomic Company, September 1975.

2. INTRODUCTION

The HTGR developed at GA is a thermal reactor concept which provides high efficiency in electricity generation, improvements in reactor safety characteristics, and the implementation of an additional energy source by the use of thorium. The HTGR uses helium as the coolant and graphite as the moderator and core structural material. One fuel cycle employs 93% high-enriched uranium in U-235 for the initial and makeup fissile material, thorium as the fertile material, and U-233 as the bred material which is recovered for recycle to the reactor. Alternative fuel cycles which offer potential proliferation resistance are being evaluated.

The technology required for the recycle of bred U-233 in the HTGR fuel includes reprocessing steps to extract the valuable fissile materials in the spent fuel from the fission product wastes, and refabrication to manufacture fuel elements containing the extracted U-233. The HTGR Fuel Recycle Development Program, funded by the Department of Energy (DOE), is presently being undertaken by various contractors to develop this technology. The development of technology for reprocessing HTGR fuel is being undertaken primarily at GA.

This report discusses the dissolution development work at GA from September 1975 to May 1978. Prior work (Ref. 2-1) centered on establishing (1) the feasibility of utilizing a Type 304L stainless steel dissolver, (2) the desirability of boiling Thorex acid [$13 \text{ M HNO}_3/0.05 \text{ M KF}/0.1 \text{ M Al}(\text{NO}_3)_3$] to dissolve FSV HTGR fuel, and (3) the effect of variations in fuel physical properties and dissolver operating parameters on fuel dissolution rates. The development work was limited to the dissolution of crushed, burned-back, unirradiated FSV fissile and fertile particles in the 0.13-m and 0.20-m dissolvers. It was also established that the dissolution rate of HTGR fuel is a function of the entire history of the fuel (such as fuel

preparation and reprocessing methods) as well as of the operating parameters of the dissolver.

The current study extends the development work to the dissolution of the reference high-enriched uranium (HEU) TRISO-BISO fuel for HTGRs. The scope of the work includes:

1. Evaluation of dissolution flow sheets for reprocessing of HEU fuels in the HTGR Recycle Reference Facility (HRRF).
2. Development of a reliable device for the removal of dissolver product slurry, with particular emphasis on applicability to HRRF.

This fuel particle dissolution study is also applicable to other reactor fuel cycles containing ThO_2 fuel. For example, the light water reactor (LWR) thorium fuel cycle, which uses ThO_2 fuel in a zirconium-clad pellet form, can reprocess its spent fuel using HTGR fuel reprocessing techniques.

REFERENCE

- 2-1. Hutton, A. E., "Dissolution of HTGR Fuel," ERDA Report GA-A13278, General Atomic Company, September 1975.

3. FUEL AND REPROCESSING FLOWSHEET

3.1. HTGR FUEL

The basic fuel element in the large HTGR is a graphite block 0.793 m (31.4 in.) high with a hexagonal cross section 0.359 m (14.2 in.) across the flats, as illustrated in Fig. 3-1. The graphite block is drilled lengthwise with two sets of holes: one to allow the passage of helium coolant, and the second to contain fuel rods and burnable poison wafers. Fuel rods are formed by molding selected blends of fuel particles with a graphite pitch. Each fuel rod is 63.5 mm (2.5 in.) long and has a diameter of 15.8 mm (0.625 in.). The reference fuel particles used in the HTGR fuel are shown in Fig. 3-2. These fuel particles contain either $UC_3O_{0.5}$ (highly enriched in U-235 or recycle U-233) or ThO_2 . The particles shown in Fig. 3-2 typically have diameters of 500 to 800 μm .

The two particle types used in HTGR fuel are categorized by their coatings (BISO and TRISO coated particles). As shown in Fig. 3-2, BISO particles are coated with a relatively porous buffer layer of carbon and then with a dense coating of pyrolytic carbon. TRISO coatings have, in addition, a silicon carbide coating placed between two layers of pyrolytic carbon. The silicon carbide layer provides a means of separating these particles from the BISO particles in head-end reprocessing operations and also enhances metallic fission product retention in the fissile particles. BISO coatings are used for particles initially loaded only with ThO_2 , while TRISO coatings are used for particles loaded with uranium oxycarbide.

The fuel for the FSV reactor is slightly different. The fissile particle for FSV is comprised of a mixed ThC_2 - UC_2 (4.25 Th/U) kernel which is TRISO coated. The fertile particle has a ThC_2 kernel, which is also TRISO coated. This fuel is depicted in Fig. 3-3.

Fig. 3-1. HTGR standard fuel element

K72654

Fig. 3-2. GA coated particles

<u>FISSILE</u>		<u>FERTILE</u>
(Th,U)C ₂	FORM	ThC ₂
4.25	Th:U RATIO	(ALL Th)
6 YEARS	LIFETIME	6 YEARS
1260°C	TEMPERATURE (MAX)	1260°C
20% FIMA	BURNUP (MAX)	7% FIMA
8.0 X 10 ²¹ N/CM ²	FAST FLUX EXPOSURE (MAX)	8.0 X 10 ²¹ N/CM ²
200 ± 50 μm	PARTICLE SIZE	400 ± 100 μm
50 μm	BUFFER COATING	50 μm
20 μm	ISOTROPIC PyC COATING	20 μm
20 μm	SiC COATING	20 μm
30 μm	ISOTROPIC PyC COATING	40 μm
120 μm	TOTAL COATING	130 μm

Fig. 3-3. Fissile and fertile TRISO coated particles for the Fort St. Vrain HTGR

Other nonproliferable fuel types are also under consideration for HTGRs, including the 20% medium-enriched uranium (MEU) fuel. The development of a dissolution process for MEU fuel would not pose any major problems since the current HEU fuel dissolution techniques would apply.

3.2. REPROCESSING FLOWSHEET

It is necessary to reprocess spent reactor fuel to permit recycle of the valuable bred and unconsumed fissile materials. The crush-burn-leach technique has been selected from several potential processes for reprocessing HTGR fuels.

Separation of fission products from fissile materials is achieved by solvent extraction from a solution of these materials, formed by their dissolution in nitric acid. However, effective dissolution cannot be performed if a significant amount of carbon is present. The reference method of removing this carbon is by combustion in fluidized-bed burners. The burners convert the uranium and thorium to U_3O_8 and ThO_2 , respectively. The head-end steps of the reference TRISO-BISO reprocessing flowsheet for this large HTGR fuel are shown in Fig. 3-4.

Dissolution of the reference HTGR fertile fuel occurs after classification of the fissile and fertile particles obtained from the primary burner. The mother liquor from thorium-containing particles is processed through the feed adjustment equipment prior to entering the solvent extraction process. However, the fissile particles must be crushed and burned in the fluidized-bed crushed fuel particle burner (secondary burner). After burning, the heavy metal oxides are dissolved, and the slurry, consisting of the insolubles and the mother liquor, is transported to a centrifuge which separates the liquid from the solids. The mother liquor is then fed directly to the solvent extraction system. The head-end reprocessing flowsheet for FSV fuel is shown in Fig. 3-5.

Fig. 3-4. Simplified TRISO-BISO reprocessing flow sheet

Fig. 3-5. HTGR head-end reprocessing flowsheet for Fort St. Vrain fuel

4. REQUIREMENTS

4.1. DISSOLVER DEVELOPMENT REQUIREMENTS

The objective of dissolver development is to define dissolver systems that can be used in a commercial-scale recycle facility. The anticipated requirements for such commercial dissolvers are

1. Reasonable throughput (i.e., good dissolution rate) in minimum cell space.
2. Operational reliability in a highly radioactive environment.
3. Reliability of dissolver product transfer.
4. Adaptability to remote decontamination and maintenance.
5. Automatic operation via remote control.
6. Capability for cleanout to allow material safeguard accountability with minimum material holdup.
7. Dissolver off-gas compatibility with the off-gas treatment system downstream.

4.2. OBJECTIVES

The specific objectives of the dissolution study undertaken since 1975 are

1. Evaluate and optimize the dissolution rate of fertile BISO kernels in Thorex acid solution, and establish an operating cycle for the commercial-scale fertile dissolver.
2. Determine the dissolution characteristics of the fissile secondary burner product in nitric acid, including both WAR-derived and FSV fissile ashes; and establish an operating cycle for a commercial-scale fissile dissolver.
3. Develop a reliable and efficient device for the removal of dissolver product slurry. The device must be adaptable to remote maintenance and allow minimum material holdup in the dissolver.

The process and equipment information obtained from the experimental study was used in the design of a 0.50-m dissolver-centrifuge system, which, when completed, will be integrated with the head-end systems for an HRRF sequential operation demonstration. The same operating cycles derived from the experimental work will be employed to verify operation in an engineering-scale system and to determine scale-up effects.

5. EQUIPMENT

5.1. EQUIPMENT DESCRIPTION

Two pilot-plant-scale dissolvers are installed in the GA reprocessing pilot plant. To simplify identification, the dissolvers were designated 0.13 m and 0.20 m, based on their respective diameters. Each dissolver system is described in detail below. Table 5-1 summarizes the features of the pilot-plant dissolvers.

5.1.1. 0.13-m Dissolver

A schematic of the 0.13-m dissolver system is shown in Fig. 5-1. The dissolver vessel is fabricated from a 1.52-m (5-ft) long, 127.0-mm (5-in.) inside diameter Type 304L stainless steel pipe. A 150-lb flange covers the top end of the dissolver, and a 60-deg cone of 3.2-mm (0.13-in.) thick stainless steel is attached to the bottom end. The bottom cone is surrounded by a stainless steel jacket that has a wall thickness of 3.2 mm and an outside diameter of 130.3 mm (5.13 in.). The jacket has a 12.7-mm (0.5-in.) inlet and outlet coupling for steam supply and condensate return, respectively. A 1-m (40-in.) long water cooling jacket is welded around the top portion of the dissolver. Four tubular band heaters (Chromalox HBT-55, 950 W) are wrapped around the lower portion of the dissolver just above the jacketed cone. The dissolver cooling jacket, steam jacket, and band heaters are insulated.

The dissolver dump valve assembly is shown in Fig. 5-2. The dump valve is air actuated, with a small opening above the valve for the sparge gas inlet. The feed hopper has a volume of 2.0 liters and is separated from the dissolver by a pneumatically operated ball valve.

TABLE 5-1
DISSOLVER OPERATING FEATURES

Feature	0.13-m Dissolver	0.20-m Dissolver
Operating mode	Batch	Batch/semibatch
Heat input	{ Cone (791 kPa steam) Side (4 resistance heaters)	{ Cone (791 kPa steam) Side (3 resistance heaters)
Feed system	Gravity	Gravity
Product removal	Gravity dump	Gravity dump/steam jet
Condenser	Spiral downdraft	Single-pass downdraft
Cooling	Water jacket	Water jacket
Agitation	Nitrogen sparge	Nitrogen sparge
Operating temperature	120°C	120°C
Operating pressure	100.6 kPa (-3 in. H ₂ O)	100.6 kPa (-3 in. H ₂ O)
Material of construction	Type 304L stainless steel	Type 304L stainless steel
Sampling method	Airlift	Airlift
Liquid level	N ₂ -purged dip tubes	N ₂ -purged dip tubes
Specific gravity	N ₂ -purged dip tubes	N ₂ -purged dip tubes

Fig. 5-1. The 0.13-m dissolver system

HALF SECTION OF VALVE BODY

Fig. 5-2. Dissolver dump valve for 0.13-m and 0.20-m dissolvers

The overhead condenser is a spiral heat exchanger from the American Heat Reclaiming Corporation, Type I-V. The condenser is constructed of Type 304L stainless steel and has a total surface area of 0.46 m^2 (5 ft^2).

The dissolver vessel is supplied internally, via the top flange, with two thermocouples, three N_2 -purged dip tubes for liquid level and specific gravity measurement, an acid addition line, a water rinse line, an airlift supply line, and a sample removal line.

5.1.2. 0.20-m Dissolver

A schematic of the 0.20-m dissolver system is shown in Fig. 5-3. The dissolver vessel is fabricated from a 1.07-m (3.5-ft) long, 203.2-mm (8-in.) nominal inside diameter Type 304L stainless steel pipe. The top of the dissolver is covered by a 150-lb flange, and the bottom of the dissolver has a 60-deg cone of 3.2-mm (0.13-in.) thick stainless steel. The bottom cone is surrounded by a steam jacket similar to that for the 0.13-m dissolver. Three tubular band heaters (Chromalox HBT-85, 1425 W) are wrapped around the lower portion of the dissolver just above the cone. A 0.46-m (18-in.) long water cooling jacket surrounds the upper portion of the dissolver just above the band heaters. The dissolver cooling jacket, steam jacket, and band heaters are insulated.

The dissolver dump valve assembly is shown in Fig. 5-2. The sparge gas enters the dissolver through an opening above the dump valve. The feed hopper has a volume of 3.5 liters and is separated from the dissolver by a pneumatically operated ball valve. The condenser is a single-pass, shell-and-tube heat exchanger from the American Standard Company, Model 03024, and has a heat transfer surface area of 5 m^2 (7.3 ft^2).

Internally, the 0.20-m dissolver contains three nitrogen-purged dip tubes, two thermocouples, an acid addition line, a water rinse line, a product decant line, an airlift supply line, and a sample removal line. The product decant line is connected to an external steam jet that discharges to a basket centrifuge. A solenoid valve controls the flow of steam to the steam jet.

Fig. 5-3. The 0.20-m dissolver system

5.1.3. Instrumentation and Ancillary Equipment

Additional vessels common to both dissolvers are the potassium fluoride makeup tank, the aluminum nitrate makeup tank, the Thorex makeup tank, and the distilled water tank. A drawing of a typical storage tank is shown in Fig. 5-4. The KF and $\text{Al}(\text{NO}_3)_3$ tanks are 1.22 m (4 ft) and 1.52 m (5 ft) long, respectively, and each has a nominal inside diameter of 127.0 mm (5 in.). The KF and $\text{Al}(\text{NO}_3)_3$ tanks are fabricated from Schedule 5S, Type 304 stainless steel pipe. The Thorex and distilled water tanks are fabricated from 1.52-m (5-ft) long, 203.2-mm (8-in.) nominal inside diameter, Schedule 40S, Type 304L stainless steel. All storage tanks contain air-purged dip tubes for measurement of liquid level and specific gravity.

The basket centrifuge, from De Laval/ATM Co., has a 304.8-mm (12-in.) diameter and operates on a batch mode. A 1-hp, dc, variable-speed motor provides a g-force range of 0 to 1550 g. Figure 5-5 shows the basket centrifuge.

Nitrogen flow rates for the dip tubes, product samplers, and sparge gas are controlled by Wallace & Tiernan purge meters. Liquid levels and specific gravities in all vessels are monitored by manometers and Barton differential pressure cells and pen recorders. A diagram of the purgator system is shown in Figure 5-6. The temperature of the dissolvers is monitored by a multipoint recorder (Honeywell, Inc.) and a multipoint digital display (Thermoelectric Co.). The instrumentation is remotely operated from a main control unit.

5.2. OPERATING PROCEDURE

Outlined below in simplified form are the steps for a dissolution experiment in the pilot plant dissolver system.

Fig. 5-4. Typical storage tank

Fig. 5-5. Basket centrifuge

Fig. 5-6. Purgator system for determination of liquid level and specific gravity

1. Prepare a predetermined volume of Thorex solution in the Thorex makeup tank.
2. Steam-jet-transfer the required volume of Thorex to the dissolver. Sample the solution.
3. Load the feed hopper with a given weight of feed material and charge it into the dissolver.
4. Set the sparge gas flow rate and turn on the condenser cooling water. Start recorders.
5. Turn on the electric band heaters and open the steam to the bottom heating cone.
6. Take samples of dissolver solution, as required, throughout the run. Analyze the samples to determine the dissolution rate.
7. At the end of the run, turn off the band heaters and shut off the steam to the bottom cone jacket.
8. Turn on the cooling water to the dissolver cooling jacket until the solution reaches a temperature of $<35^{\circ}\text{C}$. Turn off the condenser cooling water.
9. Turn on the centrifuge motor and set the speed at 500 rpm.

Note: Steps 10 and 11 apply to the 0.20-m dissolver only.

10. Begin steam flow to the product transfer jet, allowing the discharge to enter the centrifuge.
11. Stop the steam flow when the decanting operation is completed.

12. Open the dump valve below the dissolver cone, and discharge the remaining solids and solution into the centrifuge.
13. Record the amount of mother liquor and solids collected at the end of the run.
14. Turn off the recorders.

6. DISCUSSION OF RESULTS

6.1. THORIUM OXIDE PARTICLE DISSOLUTION

Fertile thorium oxide kernels are one type of HTGR fuel particle. The term BISO refers to the initial type of coating applied to the kernel, as shown in Fig. 3-2. The spent fuel particles are reprocessed to recover the residual thorium and the bred U-233. The ratio of these heavy metals depends on the extent of their burnup in the reactor. A final mother liquor concentration of 1.0 $\bar{M}$ thorium is recommended to minimize material and handling requirements and to avoid thorium nitrate precipitation.

Optional modes of dissolution under investigation include the normal (no-heel) mode, two-stage dissolution, and the heel mode. Appendix A gives the operating data for the ThO_2 kernel dissolution runs.

6.1.1. Two-Stage Dissolution

Two-stage dissolution is an optional mode of operation for ThO_2 kernel dissolution. The first stage is completed when a 1- $\bar{M}$ thorium nitrate solution is produced after 70% dissolution of the feed batch in boiling Thorex solution. The mother liquor is then transferred to a storage tank, and the remaining 30% heel is in contact with the same volume of fresh Thorex as in the first stage. The second-stage mother liquor has a 0.43- $\bar{M}$ thorium concentration after complete dissolution of the heel.

By using the two-stage dissolution mode, the overall dissolution time per batch can be decreased by about 50% compared with a no-heel dissolution mode (see Fig. 6-1). The disadvantages of this mode, however, are an increase in material handling time between stages and an expected average

Fig. 6-1. Dissolution rates for two-stage versus single-stage operating mode

mother liquor thorium concentration of only 0.72 $\bar{M}$. This low thorium concentration (versus 1 $\bar{M}$) places an extra burden on the solvent extraction feed adjustment system, which must concentrate the mother liquor to approximately 4.0 $\bar{M}$ thorium.

6.1.2. Heel-Mode Operation

Heel operation takes advantage of the rapid dissolution rate during the first portion of leaching of ThO_2 kernels. By interrupting the normal cycle before complete dissolution is achieved, it is possible to shorten the combined dissolution time for several batches. The point at which the cycle is stopped depends on the change in dissolution rate and the inter-cycle time.

6.1.2.1. Bench-Scale Investigations. The initial bench-scale dissolution experiments were conducted in a 500-ml Erlenmeyer flask. A 60-deg conical bottom was attached to the flask for a better simulation of the pilot-plant-scale dissolver geometry (Fig. 6-2). Figure 6-3 compares the dissolution rates achieved for both bench-scale designs and the pilot plant 0.13-m dissolver using a 0% heel operating mode. It is apparent that the flat-bottom dissolver configuration has improved dissolution rates compared with the conical-bottom design. This is most likely due to improved solid-liquid contact on the flat-bottom dissolver. There is, however, a large scale-up factor between the pilot plant dissolver and the conical-bottom bench-scale dissolver which must be considered. This scale-up factor is discussed in Section 6.1.2.2.

A series of bench-scale tests were performed based on 20%, 30%, 40%, and 60% heel-mode dissolution (Ref. 6-1). Figures 6-4 through 6-7 present the results of these tests, which reveal a distinct break in the dissolution rate at a thorium concentration of 1 $\bar{M}$. Figure 6-8 shows the time required to reach a 1- $\bar{M}$ thorium solution versus percent heel for the bench-scale dissolver. Based on a comparison of heel mode capacities, shown in Table 6-1, a 40% heel mode dissolution process would be optimum in the

Fig. 6-2. Bench-scale conical dissolver

Fig. 6-3. Comparison of dissolution rates in the flask, conical dissolver, and 0.13-m dissolver

Fig. 6-4. Bench-scale conical dissolver test with 20% heel

Fig. 6-5. Bench-scale conical dissolver test with 30% heel

Fig.6-6. Bench-scale conical dissolver test with 40% heel

Fig. 6-7. Bench-scale conical dissolver test with 60% heel

Fig. 6-8. Time to reach 1 $\bar{M}$ thorium versus percent heel

TABLE 6-1
COMPARISON OF HEEL MODE-CAPACITIES

% Heel	Bench-Scale Dissolution Time (hr)	Total Pilot Plant Dissolution ^(a) and Handling ^(b) Time (hr)	Capacity per Batch (kg)	No. of Batches per Day	Capacity per Day (kg)
60	1.8	6.9	2.112	3.48	7.35
40	2.2	8.0	3.168	3.0	9.50
30	2.8	9.7	3.696	2.47	9.13
20	3.4	11.3	4.224	2.12	8.95
0	8.2	24.0	5.280	1.0	5.28

(a) The pilot-plant-scale dissolution time is based on a scale-up factor of 2.74 times the bench-scale dissolution time.

(b) The handling time per heel-mode batch is 2 hr. The 0% heel mode handling time is 1.5 hr per batch, since the decanting operation is not required.

pilot-plant-scale dissolvers. A three-cycle dissolution test based on a 40% heel was conducted in the bench-scale conical dissolver. Figure 6-9 shows that the overall dissolution time was 6.6 hr, with an average of 2.2 hr per cycle.

6.1.2.2. Pilot Plant Dissolver Studies. Examination of the ThO_2 dissolution rates in the bench-scale and pilot-plant-scale dissolvers reveals that there is a dissolution rate scale-up factor, which ranges from 2.6 to 2.9, to be considered when comparing the dissolvers. This scale-up factor range is independent of the batch of feed material used, as shown in Table 6-2. The variance in dissolution rates for different batches of ThO_2 kernels can be attributed to their individual physical properties and past histories. Important properties to be considered for each batch of ThO_2 kernels include size distribution, density, and porosity. The method of ThO_2 preparation, the sintering time, the sintering temperature, irradiation, and whether or not the kernels had ever been coated with carbon and "burned-back" are important aspects of the particle history which may influence the dissolution rate.

The bench-scale dissolution rates for three different batches of ThO_2 kernels are shown in Fig. 6-10. The same three ThO_2 batches were tested in the pilot plant dissolvers, and each batch underwent a three-cycle dissolution test. A three-cycle test uses 100% fresh feed for the first cycle and is followed by two runs using a mixture of 40% heel from the previous run and 60% fresh feed. The results of the three-cycle tests in the pilot plant dissolvers are shown in Figs. 6-11 through 6-13.

During commercial operation, the mother liquor will be decanted from the heel, and more Thorex and feed will be added to the dissolver. This cycle will be repeated a number of times until the end of an accountability lot is reached or the insoluble content (crossover fissile particles, SiC hulls, carbon, etc.) arrives at a predetermined level. At this point the remaining ThO_2 kernel heel is dissolved.

Fig. 6-9. Bench-scale conical dissolver three-cycle dissolution test with 40% heel

Fig. 6-10. Bench-scale dissolution tests

Fig. 6-11. Time to reach $1 \bar{M}$ thorium during 3-cycle test (40% heel) for ThO_2 batch No. 10-19-76

Fig. 6-12. Time to reach 1 $\bar{M}$ thorium during 3-cycle test (40% heel) for ThO_2 batch No. 00-QQ-RR

Fig. 6-13. Time to reach 1 $\bar{M}$ thorium during 3-cycle test (40% heel) for ThO_2 batch No. M7-48-5

TABLE 6-2
DISSOLVER SCALE-UP FACTORS

ThO ₂ Batch	Average Dissolution Cycle Time ^(a) (hr)			Scale-Up Factor
	Bench-Scale	0.13-m Dissolver	0.20-m Dissolver	
00-QQ-RR ^(b)	1.6	4.3	--	2.7
10-19-76 ^(c)	2.2	5.8	--	2.6
M7-48-5 ^(d)	3.7	--	10.8	2.9

(a) Based on the average dissolution time of three consecutive 40% heel-mode dissolution cycles.

(b) Average particle diameter = 519 μm ; specific surface area = 12.0 cm^2/g ; density = 9.98 g/cm^3 ; sintering temperature = 1250°C. Made at GA by the sol-gel process.

(c) Average particle diameter = 519 μm ; specific surface area = 11.6 cm^2/g ; density = 9.97 g/cm^3 ; sintering temperature = 1200°C. Made at ORNL by the sol-gel process.

(d) Average particle diameter = 509 μm ; specific surface area = 11.9 cm^2/g ; density = 9.88 g/cm^3 ; sintering temperature = 1250°C. Made at GA by the sol-gel process, coated with pyrolytic carbon, and burned-back in primary burner.

Decanting of the mother liquor solution was tested on a pilot plant scale in the 0.20-m dissolver (Ref. 6-2). A three-cycle test proved steam jet decanting to be a feasible operation for heel-mode dissolution. An average of 97% of the product solution for each run was successfully decanted by steam jet, with less than 0.1 wt % of the heel carried over.

An advantage of 40% heel-mode dissolution over no-heel-mode dissolution is illustrated in Fig. 6-14. Assuming a batch size of 100-kg ThO₂ per cycle, it can be seen that 24 hr can be saved in dissolving 400 kg of material using the 40% heel-mode dissolution method. The benefits of the heel-mode operation are even greater when large campaigns requiring weeks to complete are contemplated. As Figure 6-14 shows, only the final remaining heel of a campaign is required to undergo complete dissolution (no-heel). Another assumption of this figure is that the same dissolver vessel is used for both dissolution modes. Application of this mode of leacher operation to the HRRF is expected to permit size reduction of the leacher equipment.

Fig. 6-14. Required days to dissolve 400 kg of BISO kernels: no heel versus 40% heel

A 6-hr time limit to reach a 1-M thorium solution was selected so that one 40% heel-mode dissolution cycle could be completed per operating shift. This allows a 2-hr down time for transferring the product solution and recharging the dissolver with Thorex and ThO_2 kernels in preparation for the next cycle. A 22.5-hr dissolution time can be expected for complete (no-heel) dissolution per cycle. This time period is based on an 8.2-hr cycle for complete dissolution in the bench-scale dissolver multiplied by an average scale-up factor of 2.74.

A disadvantage associated with the heel operating mode is the nuclear safeguards problem involved in accounting for the Special Nuclear Materials (SNM) remaining as a heel in the dissolver. Since the exact composition of the feed to the dissolver is unknown (only estimated), a material balance around the dissolver cannot be used to accurately account for SNM in the heel. In a fuel reprocessing plant, the first accountability tank is located after the dissolver (Ref. 6-3), enabling an accurate qualitative analysis of SNM. There is also the problem of measuring the crossover TRISO particle buildup in the heel after several dissolution cycles.

6.1.2.3. Pilot Plant Optimization Study. Two variables affecting dissolution rate are sparge rate and heat input. The effects of both variables were examined as a means of improving the ThO_2 particle dissolution rate.

Sparge gas is supplied for two reasons: (1) to induce liquid-solids agitation and (2) to carry off I_2 vapors to the overheads. The effect of various sparge rates were examined for 11 dissolution runs, as shown in Fig. 6-15; a temperature curve of the dissolver solution versus the sparge rate is also included in this figure. Each dissolution run except run 166 had a ThO_2 batch size of 5.28 kg. Run 166 had a smaller batch size of 4.4 kg. The curve for dissolution rate versus sparge rate shows a distinct optimal sparge rate at 3.8 l/min (8 scfh). The fact that run 166 (a 4.4-kg batch) had a sparge rate of 3.8 l/min, yet was below optimum dissolution rate, suggests that different batch sizes have their own optimal sparge

Fig. 6-15. Sparge rate versus temperature and dissolution rate

rates. The degree of agitation and the cooling effect of a given sparge rate seem to be a function of the solids batch size. For run 166 it appears likely that the optimal dissolution rate would be with a sparge rate less than 3.8 l/min. In principle, a series of dissolution rate versus sparge rate curves can be generated for a number of potential batch sizes with their own unique sparge rates for optimal dissolution.

In runs 154 and 155, an increase in sparge rate from 8.5 to 17.0 l/min (18 to 36 scfh) essentially produced no change in dissolution rate. However, it is estimated that a fourfold increase in dissolution rate can be obtained by lowering the sparge rate from 8.5 to 3.8 l/min. The solution temperature versus sparge rate curve in Fig. 6-15 indicates that excessive sparging lowers the temperature of the solution, resulting in a decreased dissolution rate. There appears to be a high temperature plateau for the sparge range below 2.4 l/min (5 scfh), followed by a linear decrease in temperature to a sparge rate of 8.5 l/min. The solution temperature then plateaus below 8.5 l/min.

It is therefore suspected that the mechanism for the increase in dissolution rate is the change in solution temperature. The independent work of Shying and Farrell, (described in Ref. 6-4), indicates that the dissolution reaction of sol-gel ThO_2 is kinetically controlled; i.e., the chemical reaction at the ThO_2 surface is the controlling step. Hence, the dissolution reaction rate is a function of the solution temperature.

To verify that solution temperature change rather than the direct effect of sparging (gas-solids contact versus liquid-solids contact) is indeed responsible for the increase in relative dissolution rate, an attempt was made to predict the relative change in dissolution rate based on the available kinetic data in Ref. 6-4. This predicted value was compared with the relative rates obtained from the experiment. Appendix B outlines the theoretical prediction for the dissolution rate in the 0.13-m pilot plant dissolver. The predicted value for the ratio of the dissolution rates at

122° and 117°C was 1.36. The experimental value for the ratio of the dissolution rates for the same temperatures, however, was found to be 4.43. The experimental results do not appear to be as predictable as desired. However, they seem to indicate that a 5°C rise in solution temperature cannot account for the fourfold increase in the experimental result. Based on the activation energy calculation, it would take an ~24°C rise in solution temperature (from 117°C to 141°C) to attain the fourfold rate increase. It is assumed that the higher sparge rate creates more gas channels in the solids bed and therefore decreases the effective liquid-solids contact. However, compared with temperature effects, the gas-solids effect is considered to be a secondary factor in affecting dissolution rate.

The degree of solids-liquid agitation is affected by the amount of heat input and the configuration for supplying the heat input. Heat input to the pilot plant dissolvers is supplied by sidewall resistance heaters and a bottom-cone steam heater. Two water boil-up tests (with and without a ThO₂ solids bed) were performed in the 0.13-m dissolver to determine the effect of the solids bed on heat transfer. In the first test, a 5.28-kg ThO₂ kernel bed was charged to the dissolver and sparged at 3.8 l/min (8 scfh). Steam pressures ranging from 7.9 to 14.5 kPa (40 to 100 psig) were supplied to the bottom cone of the dissolver, and the heat balance around the overhead condenser was determined. An average overall heat transfer coefficient U was calculated to be 397.4 W/m²-K (69.7 Btu/hr-ft²-°F). The values of U at each pressure setting are within 2% error.

The second heat transfer test was accomplished without a ThO₂ solids bed, and it was found that an increase in the steam pressure results in an increase in the heat input and the overall heat transfer coefficient U. The value of U varied from 1032 to 1810 W/m²-K (181 to 318 Btu/hr-ft²-°F) for steam pressures of 6.5 to 14.5 kPa (30 to 100 psig), respectively. The lowest overall value of U obtained without ThO₂ [i.e., 1032 W/m²-K (181 Btu/hr-ft²-°F)] was approximately 2.6 times greater than the constant overall U of 397.4 W/m²-K (70 Btu/hr-ft²-°F) obtained with ThO₂. This

difference in U values indicates that the ThO_2 kernels act as an insulation between the cone heating surface of the dissolver and the bulk solution. This insulation effect deserves consideration in dissolver scale-up when heat-up time to boiling is of importance, particularly if heel operation is employed.

Heel-mode dissolution runs have indicated that the temperature of the ThO_2 solids bed will approach the temperature of the steam supply to the bottom cone. A high solids bed temperature ($>125^\circ\text{C}$) is undesirable, since it might prevent Thorex solution (120°C boiling point) from reaching the lower segment of the bed, thereby decreasing chemical reaction owing to lack of solids-liquid contact. A temperature profile inside a ThO_2 solids bed submerged in water was mapped for the 0.13-m dissolver when the bottom cone was heated with 14.5-kPa (100-psig) steam. The resulting temperature profile of the solids bed is shown in Fig. 6-16. When the steam pressure was lowered, the profile remained unchanged except for a corresponding temperature drop at a depth of 157.5 cm (62 in.). The lower one-third of the bed was above the boiling point of the solution by as much as 10° to 12°C . However, there appeared to be a cooler area at the center of the solids bed, possibly owing to preferential sparge gas channeling along the thermocouple. The temperature adjacent to the cone surface is expected to be close to the steam temperature of 170°C . Conceivably, no solution was present in the lower one-third of the bed. The solids acted like a hot, porous structure which vaporized liquid seeping through the cracks, and it was suspected that no dissolution would occur in this zone because there was no solids-liquid contact.

6.2. FISSILE SECONDARY BURNER ASH DISSOLUTION

Two types of fissile secondary burner ash material [FSV fissile and weak acid resin (WAR) fissile] were examined to determine their uranium solubility rates. The fissile fuel particle for the FSV reactor is composed of a mixed $\text{ThC}_2\text{-UC}_2$ TRISO coated kernel with a Th:U ratio of 4.25.

Fig. 6-16. Temperature profile in solids bed

The WAR fissile particle contains only highly enriched (93%) U-235 as UC_2 , which is TRISO coated. In the pilot plant, TRISO coated particles contain depleted U-238. Figures 3-2 and 3-3 illustrate the WAR and FSV fissile particles, respectively. Appendix A (Section A.2) gives the operating data for the fissile secondary burner ash dissolution runs.

6.2.1. WAR Fissile Ash

6.2.1.1. Bench-Scale Study. The rate of uranium dissolution measured for two batches of WAR fissile material was very rapid (>98% in 1-1/2 hr at 104°C) in 2 $\bar{\text{M}}$ nitric acid (Ref. 6-5). Rapid uranium dissolution rates were also observed for these materials at ambient temperature (>88% in 9 hr at 24°C) in 2 $\bar{\text{M}}$ nitric acid. Uranium dissolution rate curves for WAR-derived secondary burner ash samples are presented in Fig. 6-17.

In preliminary studies, the uranium content of each of the two candidate WAR samples (lot WAR-1, 26.15 wt % uranium and lot WAR-SEQ, 20.37 wt % uranium) was titrimetrically established following complete dissolution in 8 $\bar{\text{M}}$ nitric acid. Each sample was made at GA and was then crushed and burned in the head-end operation of the GA pilot plant. Weighed portions of each material were transferred in separate experiments to the dissolver to yield a final uranium solution concentration of 0.035 $\bar{\text{M}}$ on complete dissolution in 500 ml of $\sim 2 \bar{\text{M}}$ nitric acid. The fissile product specifications are given in Ref. 6-6. Samples were removed as a function of time during the course of each experiment, and uranium dissolution rates were determined for each WAR-derived material at both ambient temperature (24°C) and solution boiling point (104°C).

During secondary burner operations, the uranium oxycarbide core material of WAR fissile particles is converted to finely divided U_3O_8 . The principal reaction in the dissolution is

Fig. 6-17. Bench-scale dissolution of WAR fissile ash

The evolution of nitrogen dioxide in dissolver operations is potentially troublesome because foaming may occur, with resultant handling problems. However, no vigorous reaction or foaming was observed when 2 $\bar{M}$ nitric acid was added to the secondary burner ash charged to the bench-scale dissolver or during subsequent heating to the boiling point (104°C).

6.2.1.2. Pilot-Plant Experiments. As observed in the bench-scale study, there was no foaming in the pilot-plant operation in the 0.20-m dissolver, and the dissolution rate of uranium was very rapid (98% uranium dissolution in 1-1/2 hr) in boiling 2 $\bar{M}$ nitric acid. In addition, at ambient temperature, 84% uranium dissolution can be expected in 7 hr in 2 $\bar{M}$ nitric acid. In the pilot plant experiments, uranium dissolution rate was examined at ambient temperature (19°C) and at the boiling point (103°C). For each run, 0.55 kg of WAR fissile particle ash (21.5% uranium by weight) was charged to the 0.20-m dissolver, followed by addition of 14 liters of 2 $\bar{M}$ nitric acid. The total leaching time as a function of percent undissolved uranium at boiling and ambient temperatures is indicated in Fig. 6-18. Compared with the bench-scale results, these results show that there is little scale-up effect. Figure 6-19 shows the dissolver feed and residue after dissolution; note the unbroken fissile particles among the SiC hulls.

6.2.1.3. Operating Cycle. Based on the pilot-plant study for WAR fissile ash, a batch fissile dissolver operating cycle is proposed. Solids feed to the dissolver should be by batch, and owing to the low bulk density (1.3 g/cm³) of the solids, they should be added before the introduction of dilute nitric acid at ~25°C to avoid poor mixing and prevent rapid foam-producing reactions. Continuous metering of feed could be utilized, but the feed has the potential disadvantage of bridging at the feed chute, especially if the fissile ash is wetted by condensation from boiling nitric acid. The NO_x evolution rate can be controlled by metered addition of the ash to the acid in the dissolver.

In actual spent fuel, decay heat generation in the ash will probably cause fissile dissolution to occur above ambient temperature. The estimated

Fig. 6-18. Uranium dissolution rate curves for runs 187 and 188

186-1

500 μm

(a) WAR fissile secondary burner ash before dissolution

186-2

500 μm

(b) WAR fissile dissolver residue after dissolution

Fig. 6-19. WAR fissile dissolver feed and residue

decay heat for WAR fissile (segment 9) fuel is 164 W/FE (560 Btu/hr-FE), which could raise the dissolver solution temperature to 30° to 40°C with no cooling. The projected dissolution rate is in the envelope bounded by the curves at boiling (103°C) and room temperature (19°C). The ambient temperature curve represents the lowest reaction rate. If peak NO_x concentration in the off-gas treatment system NO_x converter must be limited to less than 10,000 ppm (Ref. 6-7), the process should be controlled at a lower temperature (i.e., below boiling), at least in the first few hours of the cycle, to control reaction rate. After the bulk of the uranium is dissolved, the solution temperature can be brought to the boiling point to dissolve as much residue as possible and to volatilize iodine. Since the dissolution curves at ambient and boiling temperature are widely separated, using temperature to control NO_x evolution is relatively effective. Sparge gas is required to promote mixing, especially in the nonboiling portion of the cycle. At the same time, the sparge gas dilutes the NO_x evolved in the reaction. In commercial operation, a soluble neutron poison would be included in the dissolver solution as a criticality precaution. However, the effect of a soluble neutron poison on dissolution rate has not been determined.

6.2.2. FSV Fissile Ash Bench-Scale Study

In tests performed with FSV fissile secondary burner ash, less than 10% of the contained uranium was found to be soluble in boiling nitric acid ranging from 2 to 16 $\bar{M}$ (as expected). The low solubility of uranium measured for this material is due to the presence of ThO_2 following burner operations. The ThO_2 entrains uranium, preventing its complete dissolution in nitric acid. Total recovery of uranium from FSV secondary ash is possible only with Thorex dissolution, and the rate of uranium solubility is a direct function of the ThO_2 dissolution rate. Since the uranium dissolution rate in Thorex for FSV fissile secondary burner ash is moderated by ThO_2 dissolution, no rapid, unmanageable reaction is encountered.

The uranium and thorium concentrations of the FSV secondary burner ash material tested were 8.61 and 36.01 wt %, respectively. The uranium/thorium solubility rate curve for FSV fissile secondary burner ash in boiling

Thorex is shown in Fig. 6-20. Complete heavy metal dissolution occurred in ~4 hr. No significant differences in dissolution rates were found for FSV fissile and fertile particles (Ref. 6-3).

Because the uranium dissolution rate for FSV fissile ash is dependent on thorium dissolution rate, pilot plant studies were centered on the dissolution of thorium oxide in ThO_2 fertile particles. This simplifies the pilot-plant-scale experimental work by concentrating on rate-controlling dissolution steps. The ThO_2 fertile particles have a smaller surface area and therefore a longer dissolution rate.

6.3. STEAM JET TRANSFER OF DISSOLVER PRODUCT

A series of tests was conducted to evaluate methods of transporting dissolver slurries. A reliable and remotely maintainable product removal device is required to transport dissolver slurry to the centrifuge for liquid-solids separation. On the fissile dissolver flowsheet (Ref. 6-8), the slurry contains 87 kg of SiC hulls, ~2 kg of unbroken fissile particles, and ~10 kg of fertile particles from particle crossover as solids. Particular attention was given to selecting a transfer method which has low plugging incidence and is maintenance-free. Among the several alternatives considered for HRRF, steam jet appears to be the most promising. Airlift does not have the suction head required for slurry transfer. The following steam jet configurations were evaluated:

1. Gravity jet.
2. Suction jet.
3. Dilution water concepts for suction jet.
4. Submerged jet.

6.3.1. Gravity Jet

Operating experience with gravity jet transfer of SiC hulls was gained during several transfers made for centrifuge experiments. The gravity jet

Fig. 6-20. Dissolution rate of FSV fissile secondary burner ash in Thorex

configuration and the dump valve needed to isolate the jet from the slurry are shown in Fig. 6-21. This jet plugged repeatedly when the slurry was let into the jet prior to admitting the steam. The details of this operating experience are given in Ref. 6-9. A gravity jet is not recommended for use in the HRRF for the following reasons:

1. The reliability of the slurry transfer is poor.
2. A dump valve is required below the dissolver to keep the slurry out of the jet. This valve would need remote maintenance and could not be removed from a full dissolver.

6.3.2. Suction Jet

Product removal of whole fuel particles is required in the fissile dissolver, and therefore jet transfer tests were performed with SiC hulls and glass beads (to simulate fissile particles). The size of the beads was 420 to 595 microns, and the bead density was 2.6 g/cm^3 , which is similar to the 2.2-g/cm^3 fissile particle density.

Figure 6-22 shows a typical suction jet configuration used in the test. The steam jet was a special Penberthy Houdaille jet (304L stainless steel construction) and the sparge tube was located at the bottom of the tank. Water was used in place of the dissolver solution. This configuration is the most desirable for remote maintenance and minimum corrosion of the jet, which is exposed to the solution only during transfer.

Tests with SiC hulls using the suction jet configuration give a 75% confidence level for avoiding plugging in the suction tube, which is the location most vulnerable to plugging. Although most plugs were cleared by back-pressurizing the suction tube with steam, there was one incident in which the suction tube had to be replaced. A high sparge rate in the tank, which occurred while transferring with the suction jet, interrupted slurry

Fig. 6-21. Gravity-jet transfer configuration

Fig. 6-22. Suction steam-jet configuration

flow. The suction jet transfer tests on glass beads (simulating fuel particles) were inefficient, but no plugging was observed, despite sputtering.

Two types of flow were noticed in the runs. Each run started with sputtering of glass beads and steam with very little liquid. After most of the glass beads were transferred, the flow suddenly stabilized and very good transfer of water began. The sputtering flow noticed during the first part of each run is indicative of inefficient energy transfer from the steam to the slurry in the jet. The cause of the sputtering lies in attempting to transfer a concentrated, packed bed of slurry. (The slurry was packed because the sparge rates used did very little to mix the glass beads and water.) The high total suction lift required to move this packed slurry resulted in very low flow rates. Despite this inefficient transfer, neither the suction tube nor the jet chamber were plugged during the tests, probably because the beads could roll past each, maintaining the low flow rate. The experimental details of suction jet transfer of the glass beads are given in Ref. 6-10.

Several factors affecting jet performance became apparent during these tests. For example, it was seen that a good transfer is one in which the discharge slurry concentration is quickly reduced, indicating a high solids transfer rate and a short sputtering flow period. High solids loading tended to prolong sputtering flow with a slow change of discharged solids concentration. The effects of these variables on performance are summarized below.

6.3.2.1. Sparge Effect. For SiC hull transfer, high sparge rates resulted in low flow rates, high temperature rise, and large dilution of the slurry. Sparge air interfered with the flow of slurry in the suction tube of the steam jet, and SiC hull transfer was uniform immediately after sparging ceased. High sparge rates also interfered with jet transfer of glass beads as air entered the suction tube. Sparging the slurry with low air flow rates did little to mix a bed of glass beads in water.

6.3.2.2. Solution Temperature. Increasing slurry temperature resulted in slightly decreased flow rates. Although a definite correlation between slurry temperature and plugging was not obtained, no plugging occurred in the suction jet configuration at slurry temperatures below 40°C.

6.3.2.3. Solids Loading. As expected, low solids loading gave better and smoother flows. The average SiC hull loadings in these tests were typically 70 to 140 g per liter of water. The average glass bead loadings were from 70 to 194 g per liter of solution. These solids loadings refer to the average solids concentration in the tank, assuming perfect mixing. Instantaneous discharge slurry concentration at the beginning of a jet transfer run varied from 500 to over 1000 g/l.

6.3.2.4. Suction Height. The two suction heights used in the test were 2.44 m (8 ft) and 3.36 m (11 ft), respectively. As expected, better flows were obtained at the lower suction height.

6.3.3. Dilution Water Concept for Suction Jet

The suction jet transfer tests have shown a rather low confidence level of 75% for avoiding plugging of SiC hulls in the suction tubes, and sputtering flow indicates low jet transfer efficiency for glass bead transport. In an effort to find a more reliable transfer method, a dilution water suction jet configuration was evaluated.

The steam jet transfer setup for the dilution water concept is shown in Fig. 6-23. Water was injected at the base of the suction tube using a rotary pump. This liquid diluted the slurry as it entered the suction tube, thereby reducing the potential for plugging, which is characteristic of the transfer of more concentrated slurries. When purge air was used to keep lines clean prior to a test, the discharge valves for the jet and the pump were closed to direct the air into the holding tank.

The slurry used for the tests was made up of about 7 kg of either SiC hulls or glass beads in about 50 liters of water. To demonstrate the most

Fig. 6-23. Steam-jet transfer apparatus for dilution water concept

severe conditions for transfer, the slurry was allowed to settle in the holding tank for several hours prior to most of the tests. Slurry samples of the discharge stream were periodically taken throughout the tests by briefly collecting the entire flow. Detailed operating conditions and performance data are given in Ref. 6-11.

Use of the dilution water concept as an alternate method for leacher product removal via steam jet transfer was found to be unreliable and therefore is not recommended. Although the test conditions were extreme to demonstrate the worst case, the test runs had a reliability of only 50%. A higher confidence level could be expected for more diluted and better mixed slurries. Confidence in the reliability of this concept was lost because of the lack of reproducibility of the results. Varying the dilution water flow rate did not reduce the plugging incidents. One test plugged and another was successful at a dilution water flow rate of 1 l/min (0.26 gpm) (about 12% of the total flow). At a dilution flow rate of 5 l/min (1.32 gpm) (about 62% of the total flow), one test also failed and another was successful.

6.3.4. Submerged Jet

Another approach to minimizing jet plugging is to shorten or eliminate the suction tube of a steam jet. To test this approach, a steam jet was submerged in the bottom of the slurry holding tank. Two submerged steam jet configurations were tested; the suction of one jet was open to the slurry being transferred (Fig. 6-24), and the other jet had a short suction tube to the bottom of the holding tank (Fig. 6-25). The steam-jet transfer setup is shown in Fig. 6-26. Purge air was used to keep the slurry from filling the steam nozzle prior to a test. At the start of a test, the purge air was turned off and motive steam was simultaneously activated.

The slurry used to simulate dissolver product in most runs was made up of 7 kg of either broken SiC hulls or glass beads in 50 liters of water (140 g/l). Only one test used 17 kg of glass beads. To demonstrate the most severe conditions for transfer, the slurry was allowed to settle freely in the holding tank for several hours prior to all tests. Each test

Fig. 6-25. Steam-jet transfer modified jet for submerged, short suction tube service

Fig. 6-26. Steam-jet transfer test apparatus

consisted of removing the slurry from the holding tank using one of the two jet configurations. Slurry samples of the discharge stream were periodically taken throughout the tests by briefly collecting the entire flow. The operating conditions for the open suction jet and the short suction tube jet are given in Tables 6-3 and 6-4, respectively. Variations in the solids concentration of the discharged slurry are given in Table 6-5.

6.3.4.1. SiC Hull Slurry Transport. Slurries of SiC hulls in water were transported with good flow characteristics using either the open suction or the short suction tube jet. Under similar conditions, the open suction jet produced a flow rate of 14.6 l/min (3.86 gpm) and a temperature rise of 10°C, and the short suction tube jet produced a flow rate of 11.9 l/min (3.14 gpm) with a temperature rise of 13°C. Although there is a little additional resistance to flow with the short suction tube, it has the significant advantage of easily and completely removing the slurry and is therefore attractive for transferring SiC hull slurries typical of the product from the fissile dissolver on the HRRF flowsheet (Ref. 6-8).

It was observed that SiC hulls in water could be transferred if the slurry temperature was less than 58°C at the start of the run. According to the manufacturer's performance curves, the suction capacity of the jet should decrease as the slurry temperature increases. However, the opposite trend was observed, as illustrated in Fig. 6-27. It is possible that heat transferred from the submerged steam supply line to the slurry caused more condensation when the slurry was colder. The efficiency of a jet was lowered when the resultant wet steam was used.

Varying the motive steam pressure for the steam jet caused an approximately linear variation in the resulting slurry flow rate, as shown in Fig. 6-28. Steam pressures of 790 and 308 kPa (100 and 30 psig) gave flow rates of 15 and 5 l/min (3.96 and 1.32 gpm), respectively. As steam pressure decreased, steam consumption of the jet also decreased. Therefore, the product slurry flowing at lower rates was not greatly diluted by large amounts of steam. The temperature rise of the slurry (an indication of the amount of steam dilution) was 8°C for 790 kPa (100 psig) and 14°C for 308 kPa (30 psig).

TABLE 6-3
OPERATING CONDITIONS AND TRANSFER CHARACTERISTICS OF OPEN-SUCTION, SUBMERGED JET RUNS

Run	Slurry Temp (°C)	Steam Press		Solids (in 50 l)	Transfer Time (min)	Flow Rate (l/min)	Temp Rise (°C)	Solids Holdup (g)
		(kPa)	(psig)					
62	60	777	98	7 kg SiC	(a)			
63	52	777	98	7 kg SiC	3.5	14.6	10	853
64	62	790	100	7 kg SiC	(b)			
65	49	790	100	7 kg SiC	3.6	14.9	10	1036
66	52	790	100	7 kg SiC	3.5	15.1	8	864
68	21	584	70	7 kg SiC	5.1	10.4	11	886
70	38	446	50	7 kg SiC	5.6	9.2	10	892
72	20	308	30	7 kg SiC	9.9	5.1	14	1070
76	33	722	90	7 kg beads	4.1	13.3	9	434
79	18	722	90	16.8 kg beads	6.6	8.5	10	324

(a) Stopped transfer 1 min after start because only steam was flowing.

(b) Stopped transfer after 26 sec because only steam was flowing. A very high solids concentration slurry was transferred 5 sec after start of run.

TABLE 6-4
OPERATING CONDITIONS AND TRANSFER CHARACTERISTICS OF SUBMERGED, SHORT-SUCTION TUBE JET RUNS

Run	Slurry Temp (°C)	Steam Press		Solids (in 50 l)	Transfer Time (min)	Flow Rate (l/min)	Temp Rise (°C)	Solids Holdup (g)
		(kPa)	(psig)					
67	16	722	90	7 kg SiC	6.8	7.8	21	--
69	30	722	90	7 kg SiC	4.8	10.4	18	--
71	39	722	90	7 kg SiC	4.3	11.3	16	--
73	50	722	90	7 kg SiC	4.5	11.9	13	--
74	58 ^(a)	722	90	7 kg SiC	4.2	12.2	13	--
75	16	722	90	7 kg beads	(b)			
77 ^(c)	19	722	90	7 kg beads	(d)			
78 ^(e)	18	650	95	7 kg beads	7.8	6.4	15	3276
80 ^(f)	18	722	90	7 kg beads	(g)			

- (a) First attempt to run at 60°C failed. Slurry cooled to 58°C and transfer was successful.
- (b) Flow was sporadic with lots of glass beads and steam. Transfer stopped after 7.8 min because slurry in holding tank was heating up too much.
- (c) The 13-mm-o.d. short suction tube was replaced with an equal length of 19-mm-o.d. tubing.
- (d) High concentration of glass beads was transferred for 30 sec, then flow stopped and run was terminated.
- (e) Short suction tube removed from jet.
- (f) 19-mm-o.d. short suction tube replaced after shortening it by 13 mm.
- (g) Flow would not start.

TABLE 6-5
DISCHARGE SLURRY CONCENTRATIONS OF SUBMERGED JETS
[SOLIDS CONCENTRATION OF DISCHARGE SLURRY (g SOLIDS/1 H₂O)]

Run	Time After Start of Run (min)									
	0.1	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Open Suction Jet (SiC Hulls)										
62	1054	282								
63	344	190	112	--	77	--	21			
64	1783									
65	208	176	100	--	85	--	20			
66	304	327	159	--	73	--	62			
68	654	301	213	241	173	119	67	44	--	
70	331	305	250	196	91	93	62	11		
72	1785	3013	1005	182	176	352	198	179	205	63
Open Suction Jet (Glass Beads)										
76	1678	1708	219	29	13	8	5	0		
79	1287	1348	1284	779	0	0	600	435	63	36
Short Suction Tube Jet (SiC Hulls)										
67	807	1994	--	374	190	224	4	0		
69	256	269	409	258	237	67	1	0		
71	158	220	185	306	337	35	2	2		
73	1109	688	354	213	5	4	3	2		
74	500	316	477	488	40	2	0	0		
Short Suction Tube Jet (Glass Beads)										
75	--	798	1153	1015	1037	1414	1163	1114		
77	1473									
78	1297	1364	174	70	69	33	21			
80

Fig. 6-27. Effect of slurry temperature on suction capacity of submerged steam jet

Fig. 6-28. Effect of steam jet pressure on suction capacity of submerged jet

The efficiency of the jet will be affected by using steam pressures which are different from those the jet was designed for. Normally, the manufacturer would not recommend jet transfer at a steam pressure less than 515 kPa (60 psig). However, varying the steam pressure of a jet can provide some control over slurry flow rates.

6.3.4.2. Glass Bead Slurry Transport With Submerged Jets. Slurries of glass beads and water, simulating slurries of whole fuel particles typical of product from the fissile fraction leacher on the HRRF flowsheet, were transported with both the open suction and short suction tube jets. Transfer with the open suction jet was very smooth and efficient, even with twice the amount of glass beads used in the short suction tube tests. However, transfer with the short suction tube jet resulted in sputtering of steam and glass beads. This sporadic flow is indicative of inefficient entrainment of slurry with motive steam within the jet. Apparently, small restrictions to slurry flow on the suction side of the jet prevent good entrainment of steam and slurry in the jet diffuser. In an attempt to reduce frictional losses, the diameter of the short suction tube was increased from 13 to 19 mm (0.5 to 0.75 in.). This did not prevent a sputtering discharge flow.

The disadvantage of the open suction jet configuration is that about 450 g of glass beads are held up in the bottom of the 60-deg cone. Considering density differences, this corresponds to about 600 g of whole fissile fuel particles, which corresponds to about 17% of the fissile particles in an initial makeup fuel element. Since the fissile fraction dissolver on the HRRF flowsheet is to process 43 elements per batch (Ref. 6-8), the holdup would be about 0.39% of the batch. There are about 250 fuel elements to be processed in each accountable process lot. The error in accountability for the process lot (six batches) due to a holdup of 600 g would be 0.07%. This holdup is therefore considered tolerable, but should be minimized by designing the jet and leacher with the optimum configuration.

6.3.4.3. Conclusions of Submerged Jet Tests. The following conclusions can be drawn from the submerged jet tests:

1. Slurry of SiC hulls can be efficiently transported using a submerged jet.
2. A short suction tube can be provided to minimize slurry holdup in the tank.
3. There is a maximum slurry temperature above which a submerged jet cannot pump. For SiC hulls and water, this temperature is 58°C. As the slurry temperature increases, the capacity of a submerged jet can increase slightly.
4. Varying the motive steam pressure to a submerged jet can provide some control of jet flow capacity. However, the jet manufacturers will not normally recommend a steam pressure of less than 515 kPa.
5. Slurries of glass beads and water could not be efficiently transferred using a submerged jet with a short suction tube. However, an open suction submerged jet would provide efficient transfer.

6.3.5. Jet Recommendation for Engineering-Scale Dissolver

Table 6-6 presents a summary of the performance of the four jet configurations. Of all the jet configurations tested, the submerged jet is the most reliable and remotely maintainable dissolver product removal device for the HRRF. In particular, the short suction tube submerged jet configuration is especially attractive for transporting SiC hull slurries typical of product from the fissile dissolver. It also enables almost complete removal of slurry from the fissile dissolver.

TABLE 6-6
COMPARISON OF THE PERFORMANCE OF FOUR JET CONFIGURATIONS

	Short Suction Tube Sub- merged Jet	Open Suction Submerged Jet	Suction Jet	Dilution Water Suction Jet
SiC hull slurry transfer	100% reliable	100% reliable	75% reliable	50% reliable
Glass bead slurry transfer	Inefficient (sputtering)	100% reliable	Inefficient (sputtering)	50% reliable
Solids holdup (after transfer)	None	600 g	None	None
Slurry temperature rise (°C)	13	10	20 to 78 ^(a)	22 to 39 ^(a)
Maximum slurry operating tem- perature (°C)	58	58	40	34

(a) Temperature variations were due to sputtering of steam.

Although there are disadvantages inherent in the short suction tube jet in the HRRF dissolver, its reliability and complete transfer of slurry outweigh its slight drawbacks. The two disadvantages are

1. Corrosion. The corrosive environment could require jet replacement; however, remote replacement of submerged jets from the dissolver top penetrations should be relatively simple.
2. Inefficient transfer of whole fissile particles. Slurry transfer of whole fissile particles (simulated by glass beads) is not as efficient with a short suction tube jet as with an open jet. However, the conditions used in the glass bead transfer test with the short suction tube jet were severe. One HRRF fissile dissolver batch will contain 87 kg of SiC hulls but only an estimated 2 kg of whole fissile particles. Therefore, solids loading of whole particles will not be as severe as in the glass bead transfer test.

Although the normal suction tube jet is not suitable for SiC slurry transport, it is well suited to decant dissolver solution from a heel-mode-operated fertile dissolver between dissolution cycles.

REFERENCES

- 6-1. "Thorium Utilization Program Quarterly Progress Report For the Period Ending November 30, 1976," ERDA Report GA-A14214, General Atomic Company, December 1976.
- 6-2. "HTGR Fuel Recycle Development Program Quarterly Progress Report For the Period Ending February 28, 1978," DOE Report GA-A14878, General Atomic Company, March 1978.
- 6-3. "Coordinated Safeguards For Material Management in a Fuel Reprocessing Plant," ERDA Report LA-6881, Vol. 1, Los Alamos Scientific Laboratory, September 1977.
- 6-4. Hutton, A. E., "Dissolution of HTGR Fuel," ERDA Report GA-A13278, General Atomic Company, September 30, 1975.
- 6-5. "HTGR Fuel Recycle Program Quarterly Progress Report for the Period Ending November 30, 1977," DOE Report GA-A14738, General Atomic Company, December 1977.
- 6-6. Holder, N., and L. Abraham, "Reprocessing Yields and Material Throughput - HTGR Recycle Demonstration Facility," ERDA Report GA-A14320, General Atomic Company, August 1977.
- 6-7. Park, U. S., General Atomic Company, private communication, May 15, 1978.
- 6-8. Holder, N., and L. Abraham, "Reprocessing Flowsheet Review and Material Balance," General Atomic unpublished data, December 1976.

- 6-9. "Thorium Utilization Program Quarterly Progress Report for the Period Ending August 31, 1975," ERDA Report GA-A13593, General Atomic Company, September 30, 1975.
- 6-10. "Thorium Utilization Program Quarterly Progress Report for the Period Ending November 30, 1975," ERDA Report GA-A13746, General Atomic Company, December 31, 1975.
- 6-11. "Thorium Utilization Program Quarterly Progress Report for the Period Ending February 29, 1976," ERDA Report GA-A13833, General Atomic Company, March 31, 1976.

7. ENGINEERING SCALE DISSOLVER

The experimental work presented in this report has demonstrated the feasibility of the current dissolver design to handle the reference TRISO-BISO fuels, and has shown significant progress toward meeting the commercial-scale dissolver requirements. Based on these experimental results, an engineering-scale 0.5-m dissolver has been designed and built and has gone through initial shakedown tests.

Figure 7-1 shows the major components and the main piping of the 0.5-m dissolver-centrifuge system. Figure 7-2 shows the 0.5-m dissolver, which has a capacity of 200 liters solution per batch. The dissolver design features, resulting from the development work reported herein, are described in the following paragraphs.

Continuous- and batch-mode operating cycles developed from the experimental work can be used in the 0.5-m dissolver. The 40% heel-mode option is selected for the thorium particle campaign, and batch dilute nitric acid operation is selected for the fissile ash. In the thorium campaign, the product mother liquor can be decanted from the solids heel with a suction tube steam jet. For removal of slurry from a fissile campaign, a submerged steam jet is used. This method of slurry transfer permits the location of the centrifuge at a level above the dissolver, thus relieving the height constraint on equipment arrangement.

The dissolver has a 90-deg conical bottom to enhance steam jet transport and to reduce material holdup. A steam jacket surrounds the bottom cone, and a jacket surrounding the main section of the vessel provides steam heating or water cooling to maintain solution temperature in the dissolver. As observed in the steam jet tests, cooling of the dissolver solution to less than 58° C is required for proper slurry transfer.

Fig. 7-1. The 0.5-m dissolver centrifuge system

1 ASSEMBLY

- NOTES:
- 1 SOURCE: GYROLON INC., MOORE INC., CHESBROUGH, LOCKHART, CASTLE CONTROLS INC., CHAMBERLAIN, CO.
 - 2 SOURCE: TPI-CLOVER INC., LADSON CO., BENDIS, WISCONSIN
 - 3 SOURCE: WAP REFRACTORY PRODUCTS, MT. PROSPECT, ILL.
 - 4 SEE COG ENGINEER FOR DESIGN CENTER
 - 5 ALL WELDED CONSTRUCTION U.S.
 - 6 ROD WILL SUPPLY THE FOLLOWING ITEMS:
1) AIR LIFT SAMPLE ASSY, ITEMS 19 & 20
2) STERN JET ASSY, ITEMS 18 & 15
 - 7 ALL MATERIALS IN VESSEL WELDMENT TO BE 304L, EXCEPT FOR INSULATION JACKET, ITEM 6
 - 8 DESIGN CONDITIONS:
DISSOLVER VESSEL, -0.4 PSIG TO +5 PSIG
170°C (338°F)
CONTENTS: 300 LBS MAX
CORROSION ALLOWANCE: .078 INCHES
STERILIZING JACKET: 30 PSIG STERN
170°C (338°F)
 - 9 DESIGN & STAMP PER ASME SECTION VIII DIV. I, CORROSION TEST PER ASTM A-467-70
 - 10 MAKE PROVISION FOR EXPANSION BETWEEN INSULATION JACKET & PENETRATIONS
 - 11 ADD TO SUPPLY INSULATION AFTER VESSEL INSTALLATION ON PLATFORM
 - 12 ALL MATERIAL THICKNESSES SHOWN IN B/M ARE APPROX. ONLY & SUBJECT TO DETAIL DESIGN CALC.
 - 13 TOLERANCES TO BE ASSIGNED IN ACCORDANCE WITH FABRICATOR'S STANDARD MANUFACTURING PRACTICES

ITEM	DESCRIPTION	DATE
1	28	CAP, WELDING T
2	27	ROUND 2" DIA
3	26	INSULATION (REMOVABLE)
4	25	TUBE 1/2 O.D. x .042 WALL
5	24	TUBE 3/8 O.D. x .032 WALL
6	23	FLAT 5/8 x 2 1/2
7	22	ROUND 1 1/2 DIA
8	21	FLAT 5/8 x 1 1/2
9	20	ANGLE 3 x 3 x 1/2
10	19	CONNECTOR, MALE 3/8"
11	18	CONNECTOR, MALE 1/2"
12	17	CLAMP - SCH 5
13	16	FERRULE - WELD ON TYPE
14	15	CAP 1" SCH 5
15	14	PIPE 1 1/2" SCH 40
16	13	PIPE 4" SCH 40
17	12	WELDING FL-40" SCH. TYPE 6"
18	11	PIPE 2" SCH 40
19	10	WELDING FL-40" SCH. TYPE 1"
20	9	PIPE 1" SCH 40
21	8	ELLIPTICAL DISH 18"
22	7	STERN JACKET 18 PIPE
23	6	INSULATION SHELL 206" (205)
24	5	WATER JACKET
25	4	BRFFLE
26	3	CONE
27	2	BODY 20" DIA
28	1	ASSEMBLY

Fig. 7-2. Dissolver vessel

The dissolver gravity feed hoppers are located above the dissolver and are equipped with load cells for material accountability and safeguard. To control potential high NO_x concentration in the off-gas, a rotary valve is installed to keep the option of metering the fissile feed. Thoria fuel is fed in batches. Feed lines to the dissolver consist of heated tubes for gravity solids addition. Distilled water, Thorex acid, and nitric acid are transferred via gravity from their storage tanks to the dissolver. To satisfy commercial-scale dissolver requirements, all process and instrument lines penetrate the top of the dissolver.

8. CONCLUSIONS

8.1. FERTILE BISO DISSOLUTION

1. Two-stage dissolution can reduce the overall dissolution time per batch by 50% when compared with the no-heel dissolution mode. However, an average thorium concentration in the product solution of only $0.72 \bar{M}$, as well as the increased material handling time between stages, is a disadvantage.
2. A 40% heel operating cycle is practical to obtain a $1 \bar{M} \text{Th}(\text{NO}_3)_4$ solution within a 6-hr cycle. This is a significant threefold improvement in dissolution rate over the no-heel operating mode. Ninety-seven percent product solution decanting was feasible using a suction tube steam jet. The decanted solution only contained less than 0.1 wt % solids carryover.
3. A scale-up factor ranging from 2.6 to 2.9 times longer dissolution time can be expected for the pilot-plant scale dissolvers when compared with the bench-scale. This scale-up factor is independent of the feed material.
4. The dissolution rate varies for different batches of feed material.
5. Sparge rate will affect dissolution rate through gas-solids contact and temperature effects. For a given batch size, there is a corresponding optimum sparge rate to ensure maximum dissolution rate.

6. A partially dry solids bed is suspected in the dissolver based on the heat transfer study. Heat transfer coefficient measurement shows a constant overall heat transfer coefficient U of $400 \text{ W/m}^2\text{-K}$ ($70 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$) over a range of heat inputs, indicating the solids create a thermal insulation between the solution and the heating surface. Liquid-solids contact in the lower portion of the solids bed is expected to be poor.

8.2. FISSILE SECONDARY BURNER ASH DISSOLUTION

1. The dissolution of WAR fissile ash in 2 M nitric acid is controllable and causes no excessive foaming. It is recommended that the fissile dissolver be operated below the boiling point in the first part of the batch cycle to limit the peak NO_x concentration in the off-gas.
2. The FSV fissile ash should be dissolved in boiling Thorex solution. The uranium dissolution rate is the same as that for the thorium oxide present in the ash. The operating cycle developed for the FSV fertile ash is directly applicable for the FSV fissile ash.

8.3. STEAM-JET TRANSFER OF DISSOLVER PRODUCT

1. Gravity jet is not recommended for dissolver slurry removal due to its high number of plugging incidents.
2. Suction jet is neither reliable for SiC hull transfer nor efficient for fissile particle transfer. The suction tube is most susceptible to plugging. However, the suction jet proves to be an efficient and reliable device in decanting solution from a fertile dissolver that uses a heel-mode operating cycle.

3. Dilution water suction jet is not reliable for either SiC hulls or fissile particle slurry transfer.
4. A submerged jet with short suction tube is most suited for the complete removal of SiC slurry from the dissolver. However, it is not efficient in transferring whole fissile particles under extreme test conditions.
5. A submerged jet with open suction is efficient in transferring both SiC hulls and whole fissile particles provided the slurry temperature is less than 58°C. However, it cannot empty out a dissolver completely due to its open suction configuration.
6. The minimum required dilution of the SiC slurry for jet transfer has not been established. However, 140 g solids per liter of water (assuming perfect mixing before the transfer) was used for all the successful submerged jet tests. This averaged solid concentration should be distinguished from the instantaneous discharge slurry concentration, which could vary from 150 to over 1000 g solids per liter of H₂O in the initial few minutes of the transfer.

9. RECOMMENDATIONS FOR FUTURE WORK

The following recommendations are made for future work:

1. The dissolution step of fertile and fissile fuels should be demonstrated in the engineering-scale dissolver to look for scale-up effects and to verify pilot-plant experimental results. Actual dissolver solution should be used for the jet transfer of dissolver slurry to a continuous centrifuge, where the insolubles are separated. The rinsing of SiC hulls to recover occluded heavy metals should also be studied.

After individual component testing, the engineering-scale system should be integrated with the dry head-end system to demonstrate the HRRF head-end sequential operation starting with loaded fuel elements.

2. Improvement is needed in the dissolution rate of ThO_2 with heel-mode operation. The goal is to approach the bench-scale results. Methods should be developed to provide better solution mixing in the solids bed.
3. The volatility of iodine and ruthenium during dissolution of ThO_2 fuel should be studied. To isolate iodine in the off-gas treatment system, complete volatility of iodine from the dissolver is preferred. On the other hand, volatility of ruthenium during dissolution will complicate isolation of this highly radioactive fission product. Preliminary bench-scale work (Ref. 9-1) indicates the need of nitric oxide sparge to aid iodine volatility. The verification and optimization of nitric oxide sparge in pilot-plant dissolvers

should be carried out. The impact of the extra nitric oxide on the off-gas treatment system, especially the NO_x converter, should be evaluated.

4. Due to the significant crossover of fertile particles (estimated at 10 kg) in an HRRF fissile dissolver, steam jet transfer of these high density particles (9.9 g/cm^3) from the fissile dissolver to the centrifuge should be demonstrated. The reliability of submerged jet transfer and potential particle breakage should be examined.
5. The effects of soluble neutron poison on dissolution should be determined when the poison concentration is defined. A criticality analysis is required to help define this concentration.
6. The reference Thorex for the LWR-thorium cycle uses zirconium in place of aluminum salt to complex the fluoride present. The effect on HTGR fuel dissolution using such zirconium-containing Thorex should be determined. There is a potential benefit of isotopic dilution of zirconium fission product by such addition in the HTGR reprocessing waste.

REFERENCE

- 9.1. "HTGR Fuel Recycle Development Program Quarterly Progress Report for the Period Ending February 28, 1978," DOE Report GA-A14878, General Atomic Company, March 1978.

10. ACKNOWLEDGMENTS

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APPENDIX A
PILOT-PLANT DISSOLUTION RUN DATA

A.1. BISO KERNEL RUN DATA

The operating conditions for the BISO kernel dissolution runs are given in Table A-1. All runs, with the exception of run 157, were made using a 40% heel operating mode.

A.2. FISSILE ASH RUN DATA

Table A-2 shows the operating parameters for the WAR fissile ash dissolution runs performed in the pilot-plant 0.20-m dissolver.

TABLE A-1
OPERATING DATA FOR ThO₂ (BISO KERNEL) DISSOLUTION RUNS

Run No.	Dissolver Diameter (cm)	ThO ₂ Feed (g)	Fresh ThO ₂ in Feed (%)	Heel in Feed (%)	Thorex (l)	Gas Sparge Rate (l/min)	Dissolution Time to Reach 1M Th(NO ₃) ₄ (hr)
154	13	5280	100	0	11.8	8.5 ^(a)	17.0
155	13	5280	100	0	11.8	17.0	22.0
156	13	5269	100	0	12.1	5.7	6.5
157	13	3960 ^(b)	100	0	12.0	5.7	11.0
158	13	5280	100	0	12.0	5.7	5.8
159	13	5280	66.5	33.5	12.0	5.7	5.2
160	13	5280	60	40	12.0	5.7	6.5
161	13	5280	100	0	11.9	3.8	3.0
162	13	5280	63	37	12.1	5.7	5.3
163	13	5280	68	32	11.9	0.9	4.6
164	13	5280	100	0	12.0	2.4	4.2
166	13	4400	100	0	10.7	3.8	3.9
170	13	5280	100	0	12.3	3.8	5.2
173	20	5280	100	0	12.4	3.8	11.8
175	20	5280	44.5	55.5	11.8	5.7 to 7.6	13.0
176	20	5280	40.3	59.7	12.0	5.7	10.6
177	20	5280	54.2	45.8	11.9	7.6	10.0

(a) Raised to 15.0 l/min after 3.5 hr of dissolution.

(b) 20%-heel operating mode.

TABLE A-2

OPERATING PARAMETERS FOR WAR FISSILE ASH DISSOLUTION

	Run 187	Run 188
Dissolver diameter, m	0.20	0.20
Ash weight, kg	0.55	0.55
2 M HNO_3 volume, l	14.0	14.0
Sparge rate, l/min	3.8	3.8
Operating temperature, °C	19.0	103.0
Time to reach 84% dissolution, hr	0.3	7.0

APPENDIX B
THEORETICAL PREDICTION OF ThO_2 DISSOLUTION RATE

The purpose of this analysis is to determine whether the apparent activation energy for ThO_2 dissolution, obtained from the kinetic studies (Refs. B-1 and B-2) described in Hutton's report (Ref. B-3) can be used to predict the relative change in dissolution rates as a function of solution temperatures. When established, the relative dissolution rate ratio from the Arrhenius equation can be estimated.

Hutton showed that thorium dissolution rate in the region of 8 to 13 $\overline{\text{M}}$ HNO_3 is

$$\text{rate}_{\text{Th}} = \frac{dM_{\text{Th}}}{dt} = 1/4 \ k S C_{\text{H}} \quad (1)$$

where M_{Th} = quantity of thorium in solution (moles),
k = reaction rate constant (moles/hr),
S = surface area for reaction (m^2)
 C_{H} = H^+ concentration (moles/l),
t = time (hr).

This relationship is true in our experiment only in the initial straight portion of the dissolution curve (Fig. B-1) when the H^+ concentration is relatively high, the particle size has not decreased, the thorium concentration is low, and the free fluoride is unhindered by thorium complexing.

From Eq. 1:

$$\log \text{rate}_{\text{Th}} \propto \log k + \log (S C_{\text{H}}) \quad (2)$$

Fig. B-1. Sol-gel ThO_2 dissolution curves for 40% heel operation (0.13-m dissolver)

The last term, SC_H , is a constant once the geometry of the vessel, particle size, density, and concentration are fixed--a condition which is representative of the straight portion of the dissolution curve. Equation 2, therefore, is a linear plot, with an intercept determined by the surface area and acid concentration. The Arrhenius equation for activation energy is expressed as

$$k = k_o \exp (-\Delta E/RT) \quad (3)$$

where $\Delta E \equiv$ activation energy for thorium dissolution,

$k_o \equiv$ a constant,

$T \equiv$ absolute temperature (K).

Substitution of Eq. 3 into Eq. 2 gives

$$\log \text{rate}_{\text{Th}} \propto \frac{-\Delta E}{2.303 RT} + \text{constant}, \quad (4)$$

which is a form of the Arrhenius plot.

Figure B-2 represents the results of Farrell and Shying and the GA experiment in the form of Eq. 4. Farrel's ThO_2 powder dissolution was done in 13 $\bar{M}$ HNO_3 /0.05 $\bar{M}$ HF over a range of 70° to 115°C. Shying conducted his study of ThO_2 powder in 2 to 6 $\bar{M}$ HNO_3 over 25° to 50°C range. However, the results were essentially identical in both cases and were expected, as explained in Eq. 4. The apparent activation energy is 18 to 19 kcal/mole, which means that the two lines had the same slope but were displaced, as expressed by the constant in Eq. 4.

From this comparison, it has been established that the activation energy obtained from Farrell or Shying can be used to predict the GA experimental dissolution rates. This comparison can be made despite the higher temperature, the particle surface area, and the acid concentration, all of

Fig. B-2. Effect of temperature on dissolution rate of ThO_2

which shift the curves but not the slope, as explained by Eq. 4. Therefore, by integrating Eq. 3 from T_1 to T_2 , we obtain

$$\log \left(\frac{\text{rate}_2}{\text{rate}_1} \right) = \log \left(\frac{k_2}{k_1} \right) = \frac{\Delta E}{2.303 (1.987)} \left(\frac{T_2 - T_1}{T_1 T_2} \right) ,$$

$$\log \left(\frac{\text{rate}_2}{\text{rate}_1} \right) = \frac{(19 \times 10^3)}{2.303 (1.987)} \left(\frac{T_2 - T_1}{T_1 T_2} \right) .$$

For $T_2 = 395 \text{ K (122}^\circ\text{C)}$ and $T_1 = 390 \text{ K (117}^\circ\text{C)}$,

$$\left(\frac{\text{rate}_2}{\text{rate}_1} \right)_{\text{predicted}} \cong 1.36 ,$$

while the GA experimental results showed

$$\frac{\text{rate @ 122}^\circ\text{C}}{\text{rate @ 117}^\circ\text{C}} = \left(\frac{\text{rate}_2}{\text{rate}_1} \right)_{\text{experimental}} = \frac{0.31 \text{ wt \% min}}{0.07 \text{ wt \% min}} \approx 4.4 .$$

The analysis is based on two assumptions:

1. The dissolution curve (log % versus time) is a straight line, at least in the initial phase, so that a constant dissolution rate can be taken.
2. The limited amount of temperature and dissolution data points are representative within the experimental accuracy attainable.

REFERENCES

- B-1. Shying, M.E., T.M. Florence, and D.J. Carswell, "Oxide Dissolution Mechanisms - II, Mechanism for the Thoria/Nitric/Hydrofluoric Acid System," J. Inorg. Nucl. Chem. 34, 213 (1972).
- B-2. Farrell, M.S., and S.R. Isaacs, "Laboratory Development of the Grind-Leach Process for the H.T.G.C.R. Fuel Cycle, Part 1. Dissolution of Urania/Thoria Fuel Particles in Nitric Acid Solutions," Australian Atomic Energy Commission Research Establishment Report AAEC-E143, September 1965.
- B-3. Hutton, A.E., "Dissolution of HTGR Fuel," ERDA Report GA-A13278, General Atomic Company, September 30, 1975.