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Consolidated Fuel Reprocessing Program

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D. E. Benker
J. E. Bigelow
W. D. Bond
D. O. Campbell
F. R. Chattin
D. J. Crouse*
R. L. Fellows
L. J. King
F. G. Kitts
J. C. Mailen
R. G. Ross
R. G. Stacy

Oak Ridge National Laboratory**
Oak Ridge, Tennessee 37831

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*Retired.

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HEAD-END AND SOLVENT EXTRACTION STUDIES USING FAST-FLUX TEST FACILITY FUEL*

D. E. Benker, J. E. Bigelow, W. D. Bond, D. O. Campbell, F. R. Chattin, D. J. Crouse (retired), R. L. Fellows, L. J. King, F. G. Kitts, J. C. Mailen, R. G. Ross, and R. G. Stacy (Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831, U.S.A.)

High-burnup mixed oxide fuel pins from the Fast-Flux Test Facility (FFTF) reactor were sheared in a single-pin shear, dissolved in nitric acid, and then used in solvent extraction tests to assist in establishing operating parameters for fuel recycle facilities. The fuel burnups were 2, 36, 55, and 90 MWd/kg for initial cooling times of 2.5, 1.3, 1, and 1 year, respectively. These tests include the first experiments using fuel of approximately the reference burnup (80-MWd/kg peak burnup) irradiated under reference conditions. The FFTF is a sodium-cooled reactor with stainless steel-clad fuel; the oxide fuel, which is of two compositions, has Pu/(U + Pu) ratios of ~0.225 and 0.275. The peak fuel center temperature was about 1640°C, the peak internal cladding temperature was ~530°C, the peak heat rating was ~300 W/cm, and the peak fluence (E > 0.1 MeV) was ~15.7 x 10^{22} neutrons/cm^2.

Head-End Studies

Intact fuel pins were gamma scanned to determine the axial distributions of various isotopes; Cs and Sb demonstrated significant migration toward the ends of the pins and interpellet gaps.

The force required for shearing fuel with a single-pin shear was determined as a function of position along the pin; the relative force is shown in Fig. 1 for 90-MWd/kg fuel. The force varied grossly from values similar to that for unirradiated fuel at either end of the fuel column, where the radiation and temperature were lowest, to a minimum severalfold smaller near the center of the column. The high values of shearing force were observed along the full length of the pins for fuel irradiated to 36-MWd/kg peak burnup. A modest decrease was observed near the center of pins with a peak burnup of 55 MWd/kg. Thus, this effect becomes important only at relatively high burnups. The minimum force required for the high-burnup fuel is even less than that required for simulated fuel pins containing unsintered alumina powder.

The cladding of the 90-MWd/kg fuel was more brittle than that of lower-burnup fuel. A small fraction of the cladding (<20%) was fragmented during shearing, and this fragmentation occurred near the center of the fuel pin. The fraction of fuel dislodged from the cladding (~50%) was greater at the 90-MWd/kg burnup, at least partly because of the fragmentation. The fractions of the mixed oxide free of cladding for the two lower burnups (36 and 55 MWd/kg) were similar, but much smaller (a few percent). In addition, the dislodged fuel from the 90-MWd/kg fuel contained smaller amounts of fine powder. Thus, the behavior of the highest-burnup fuel was significantly

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different from that of the lower-burnup fuels.

The particle size distribution was measured for the fragmented fuel freed from the cladding during shearing. At the highest burnup (90 MWd/kg), only a very small fraction of the fragments were <100 µm; the bulk of the material was around 1 mm or larger. In contrast, at the low burnups of 36 and 55 MWd/kg, roughly equal fractions were <100 µm, 100 µm to 1 mm, and larger than 1 mm. The large size of the oxide fragments from the highest-burnup fuel may be partially due to the brittleness of the stainless steel cladding as well as to a change in fuel properties.

Dissolution

Dissolution studies were performed to determine linear dissolution rates (the rate at which one edge of a particle recedes) for selected large fuel fragments, the quantity of residue remaining after dissolution of larger fuel samples in nitric acid, the quantity of Pu recovered from the residue by leaching with HNO_3-HF solutions, the fractions of the expected U and Pu recovered, and the behavior of various fission products during dissolution. Linear dissolution rates, determined for 36-MWd/kg fuel, increased only slightly in the range of 1.5 mm/h as the nitric acid concentration increased from 3.1 to 7.25 M. The quantities of U and Pu in the residue after dissolution of the fuel in nitric acid were determined by leaching with HNO_3-HF. At burnups of 36 MWd/kg or greater, the Pu remaining in the fuel residue averaged <0.1% of the initial Pu; higher values were rarely observed. The Pu/(U + Pu) ratio in the residue always exceeded 0.5, a composition range known to be nearly insoluble in nitric acid. The residue weights and the amounts of insoluble Ru after dissolution in nitric acid increased approximately linearly with burnup. Only ~2% of the Ru in the 90-MWd/kg fuel was dissolved in nitric acid; the remainder was present as insoluble residue or as a coating on the stainless steel cladding.

Solvent Extraction Studies

A series of solvent extraction tests was conducted at the Solvent Extraction Test Facility (SETF) to evaluate flowsheets for reprocessing FFTF fuel. Results from these experiments have provided information on fission product decontamination, U and Pu recoveries and separations, evaluation of an in-line photometer analysis system, and general operability of the selected flowsheets and equipment.

The SETF is located in one of the heavily shielded hot cells in the Transuranium Processing Plant at the Oak Ridge National Laboratory. The facility uses three banks of 16-stage mixer-settlers that are fabricated from stainless steel. The settling and mixing chambers hold about 50 and 30 mL of solution, respectively, and the combined solution flow rate of both the organic and aqueous phases ranges from 1.5 to 4 L/h. A water jacket, positioned on the back side of the contactors (adjacent to the mixers), is used to either heat or cool the contactor banks. However, the inlet lines are not jacketed, so there will be some variation in temperature across the contactor if the temperatures of the inlet solutions are different from that of the contactor. Reagents are added from pressurized tanks located in a nonradioactive chemical makeup area; all of these are used on a once-through basis with no recycle.

The processing steps that were done in the SETF include: (1) dissolution of the fuel in nitric acid, (2) clarification of fuel solutions by filtration through diatomaceous earth, (3) adjustment of solution concentrations and Pu valence for solvent extraction, (4) one cycle of solvent extraction with total partitioning of the U and Pu,(5) purification of the Pu by anion exchange, and (6) conversion of the Pu to the oxide by oxalate precipitation and calcination.

One of the first-cycle flowsheets that was evaluated is shown in Fig. 2. This flowsheet, which is similar to the conventional Purex arrangement, includes coextraction and coscrubbing of the U and Pu in the first contactor (A-bank), partitioning of the Pu from the U in the second contactor (B-bank), and recovery of U in the third contactor (C-bank). The organic extractant used in each test was tri-*n*-butyl phosphate (TBP) diluted with a normal paraffin hydrocarbon.

The parameters in which major changes were made in the coextraction-coscrub bank for the different tests included: fuel irradiation and cooling times, arrangement of the scrub and extraction stages, relative solvent loading, and TBP concentration (Table 1). These changes had little effect on the losses of U and Pu to the aqueous raffinate (HAW) or on the decontamination factors (DFs) for Cs, Ce, and Eu. The latter DFs were generally satisfactory under proper operating conditions; however, those for Zr, Nb, and Ru varied significantly, increasing with higher solvent loading, more scrub stages, and lower TBP concentration. With well-chosen and practical conditions, DFs of 10^5 or greater appear to be attainable for Zr and Nb. Although the Ru DF was somewhat smaller, a large additional DF is obtained for Ru in the dissolution process since only a small fraction of this fission product is soluble for high-burnup fuel. In many runs, measured losses of U and Pu were ~0.01% or less.

Table 1. Comparison of flowsheet conditions for the coextraction-coscrub contactors

Run	Fuel burnup (MWd/kg)	Stages[a]	Solvent saturation[b] (%)	TBP concentration (vol %)
7-1	2	3/3/10	~60	30
7-2	2	4/4/8	~65	30
8-1	36	4/5/7	~50	30
8-3	55	4/5/7	~90	30
9-2	90	4/5/7	~90	30
9-3	90	4/5/7	~80	10

[a] Low-acid scrub/high-acid scrub/extraction stages.
[b] Peak saturation.

The high solvent loading and consequent low raffinate losses achieved in Runs 8-3, 9-2, and 9-3 were the result of using an in-line photometer system to measure the U and Pu concentrations at an intermediate stage in the extraction section. The photometer system provided the data necessary to adjust the solvent (HAX) addition rate to maintain a relatively high solvent loading while still achieving low aqueous losses. The optical unit of the system was located outside the hot cell (away from the highly radioactive materials), and the light signals were transmitted via fiber-optic cables that penetrated the concrete shielding. The same instrument was used to provide signals for testing of automatic process control.

One of the partitioning methods that was used in the SETF accomplished the U-Pu separation by reducing the plutonium to Pu(III) with hydroxylamine nitrate (HAN). (Another method that uses no reductant is described in another paper at this conference.[1]) Although satisfactory products were obtained with HAN, a relatively large excess of the reagent was required. The excess is apparently needed in this case to overcome a plutonium reoxidation problem in the scrub section of the contactor. The necessity for excess reductant, which varies in degree depending on the particular system and conditions, has been generally observed and reported.[2]

The addition of hydrazine helped to mitigate the reoxidation problem, but the best result in minimizing plutonium reoxidation was obtained by decreasing the acidity of the aqueous strip solution and by lowering the operating temperature of the contactor. Partitioning with HAN reduction has generally given satisfactory U and Pu product concentrations and mutual DFs. With an initial Pu/(U + Pu) ratio of 0.2 to 0.25, cross-contamination in the products has generally been <200 ppm U in the Pu and <20 ppm Pu in the U.

REFERENCES

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2. Y. Sze and J. A. Gosselin, "Oxidation of Pu(III) by Nitric Acid in Tri-n-Butyl Phosphate Solutions. Part II. Chemical Methods for the Suppression of Oxidation to Improve Plutonium Separation in Contactor Operation," <u>Nucl. Technol. 63</u>, 431 (1983).

Fig. 1. Relative force required for shearing FFTF fuel pins with peak burnups of 90 MWd/kg. The squares, crosses, and diamonds are data for three fuel pins.

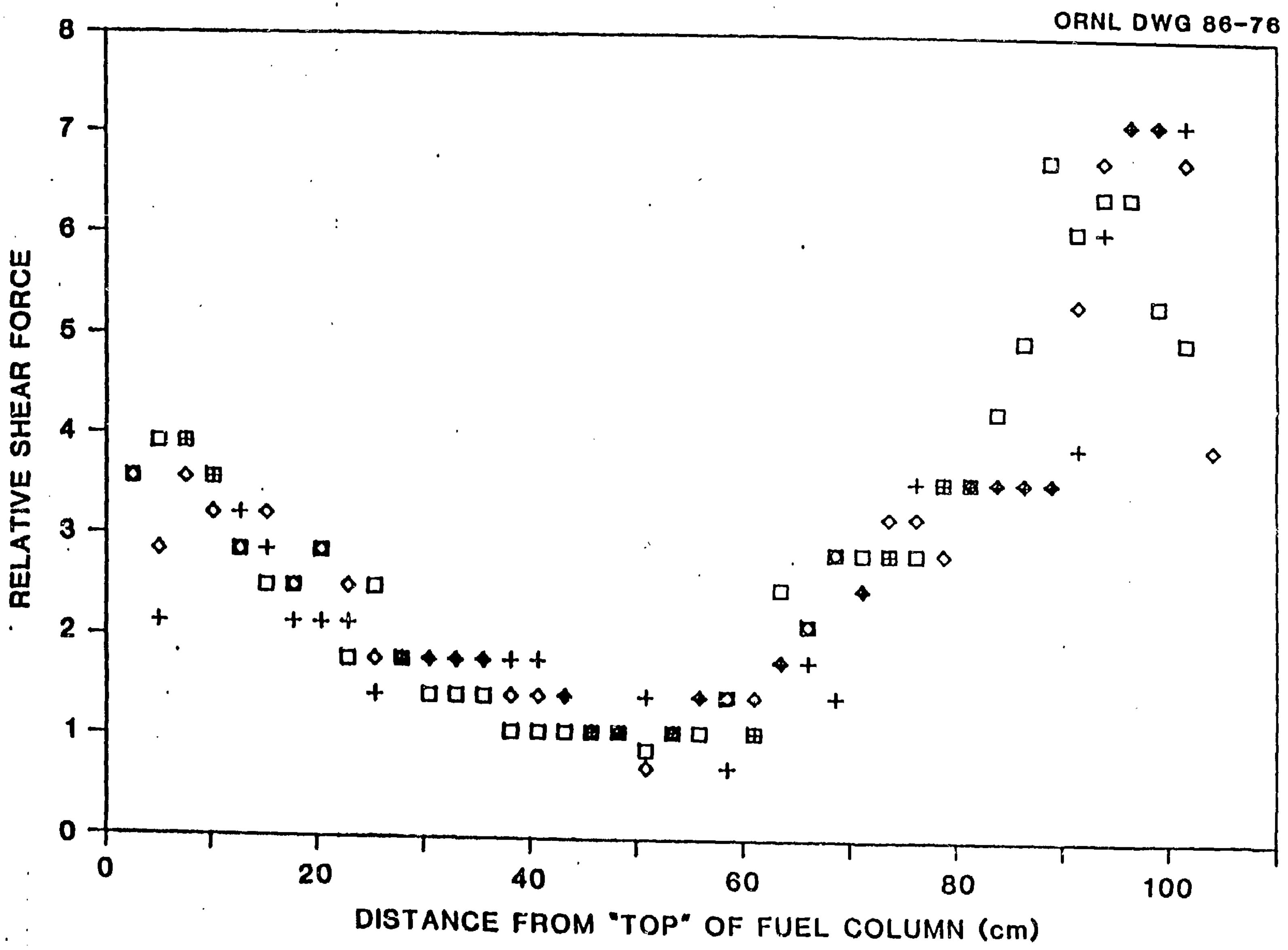
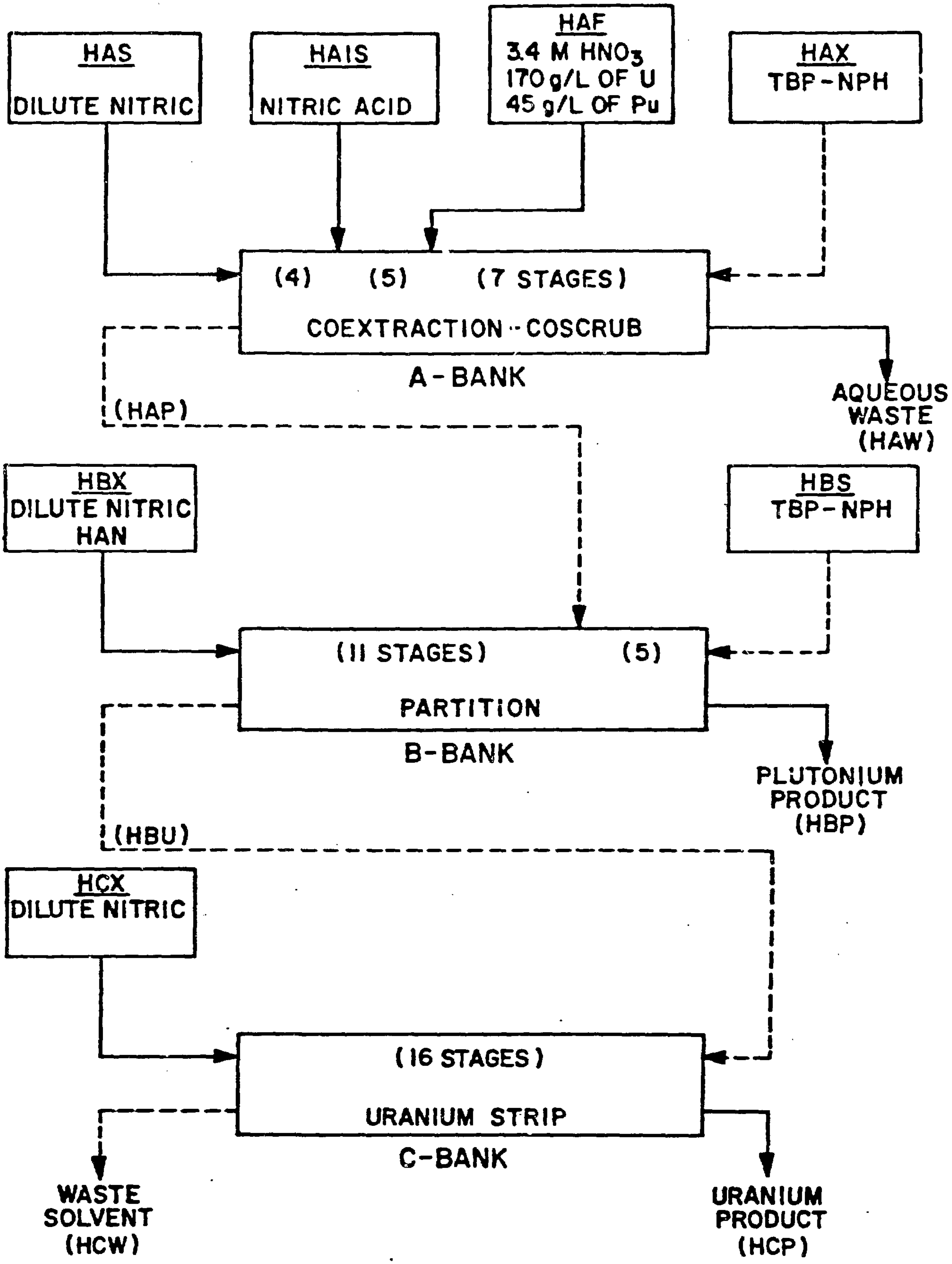

ORNL DWG 86-76
RELATIVE SHEAR FORCE
0
1
2
3
4
5
6
7
8
DISTANCE FROM "TOP" OF FUEL COLUMN (cm)
0
20
40
60
80
100

Fig. 2. Solvent extraction flowsheet used in the SETF with the organic backscrub method for partitioning.


HAS
DILUTE NITRIC
HAIS
NITRIC ACID
HAF
3.4 M HNO_3
170 g/L OF U
45 g/L OF Pu
HAX
TBP-NPH
(4)
(5)
(7 STAGES)
COEXTRACTION - COSCRUB
A-BANK
AQUEOUS
WASTE
(HAW)
(HAP)
HBX
DILUTE NITRIC
HAN
HBS
TBP-NPH
(11 STAGES)
(5)
PARTITION
B-BANK
PLUTONIUM
PRODUCT
(HBP)
(HBU)
HCX
DILUTE NITRIC
(16 STAGES)
URANIUM STRIP
C-BANK
WASTE
SOLVENT
(HCW)
URANIUM
PRODUCT
(HCP)