Page
185
6/29

MASTER

IN-1088
May 1967

RECOVERY OF URANIUM FROM EBR-I CORE 2 MELTED FUEL

M. E. Jacobson, R. R. Mascarenas,
G. F. Offutt, and K. L. Rohde

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

U. S. ATOMIC ENERGY COMMISSION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

H.C. \$ 3.00; MW 65

IN-1088

Issued: May 1967

Chemical Separations Processes
for Plutonium and Uranium

TID-4500

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

RECOVERY OF URANIUM FROM EBR-I CORE 2 MELTED FUEL

By

M. E. Jacobson
R. R. Mascarenas
G. F. Offutt
K. L. Rohde

IDAHO NUCLEAR CORPORATION

A JOINTLY OWNED SUBSIDIARY OF
AEROJET ALLIED
GENERAL CHEMICAL
CORPORATION CORPORATION

U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

A B S T R A C T

The uranium from Core 2 (the melt-down core) of the Experimental Breeder Reactor I was recently recovered at the Idaho Chemical Processing Plant using specially devised procedures. Information on the dissolution and solvent extraction procedures together with the flowsheets is given.

SUMMARY

Core 2 of the Experimental Breeder Reactor I was partially melted in the reactor, and in this condition represented a unique challenge for the recovery of approximately 66 kg of 69-percent-enriched uranium. The melted core material contained uranium, zirconium, and stainless steel from the fuel, as well as sodium and potassium (NaK) from the reactor coolant and bonding agent. Recently this material was reprocessed at the Idaho Chemical Processing Plant (ICPP) by custom dissolution in a shielded cell under direct visual surveillance followed by decontamination of the uranium using conventional solvent extraction techniques. The successful recovery of this uranium at an out-of-pocket cost of well under one dollar per gram suggests that other fuels of unusual composition can also be economically processed with special handling techniques at ICPP.

CONTENTS

	<u>Page</u>
ABSTRACT	ii
SUMMARY	iii
I. INTRODUCTION	1
II. DISSOLUTION	2
1. Safety Aspects	2
2. Development Studies	3
3. Material Balance and Equipment Flowsheet for Production Runs	5
4. Results of Production Runs	5
III. RECOVERY OF URANIUM BY SOLVENT EXTRACTION	6
1. Extraction Tests	6
2. Extraction Flowsheet and Plant Experience	6
3. Extraction Equipment	6
IV. CONCLUSIONS	10
V. REFERENCES	11

LIST OF TABLES

I. Typical Composition for EBR-I Core 2 Fuel	1
II. Chemical Material Balance Flowsheet for Integral Dissolution and Adjustment of EBR-I Core 2 Fuel	4
III. Compositions of Dissolver Product Solutions from the Development Studies	4

LIST OF FIGURES

1. Operating Diagram for Uranium Extraction, EBR-I Core 2 Flowsheet	7
2. Operating Diagram for Uranium Stripping, EBR-I Core 2 Flowsheet	8
3. Extraction Flowsheet for EBR-I Core 2 Fuel	9

I. INTRODUCTION

Occasionally, significant quantities of irradiated highly enriched uranium containing hazardous or insoluble additives become available for reprocessing. The size of the fuel and volume of the dissolver solution are often small enough to allow convenient handling and dissolution in the ICPP Multicurie Cell. In this shielded cell, which is outfitted with remote manipulators and shielding windows and is capable of handling kilo-curie amounts of activity, direct observation and remote handling of the fuel is possible. Under these conditions, liquid metal reactions can be detected and contained, and insoluble residues can be retrieved from the dissolver for further treatment or disposal. Uranium has been recovered in this manner from the melt-down core (Core 2) of the Experimental Breeder Reactor I, from residues from SNAPTRAN destruct tests, and from mold glass from EBR-II. This report presents the results of the EBR-I Core 2 processing.

EBR-I had several fuel cores of different compositions during its period of operation. Cores 1, 2, and 3 each contained about 50-70 kg of fully enriched uranium. Core 1 was processed at the Idaho Chemical Processing Plant (ICPP) during 1954⁽¹⁾, and Core 3 was processed during the reprocessing campaign at ICPP in 1965⁽²⁾. Large portions of Core 2, which was a 98-percent-uranium, 2-percent-zirconium alloy, NaK-bonded to stainless steel cladding, were melted in the reactor during a transient nuclear excursion. Some of the low-enriched blanket uranium also melted and became mixed with the highly enriched core. The average enrichment of all the melted uranium was about 69 percent. The core was subsequently disassembled and examined, and the pieces of fuel rod and melted material were packaged in small steel cans⁽³⁾. The calculated compositions of melted fuel and unmelted fuel rod pieces are given in Table I. Because

Table I
TYPICAL COMPOSITION OF EBR-I CORE 2 FUEL

Melted Fuel ^(a)			Unmelted Fuel Rods ^(b)		
		Weight Percent			Weight Percent
Fuel Alloy	Uranium	82.0	Fuel Alloy	Uranium	88.3
	Zirconium	1.6		Zirconium	1.8
Stainless Steel	Iron	7.8	Stainless Steel	Iron	6.5
	Chromium	2.2		Chromium	1.9
	Nickel	1.1		Nickel	1.0
NaK	Sodium	0.3	NaK	Sodium	0.1
	Potassium	0.7		Potassium	0.4
O (as oxide)		4.3			
	Total	100.0		Total	100.0

(a) Based on analysis of melt samples⁽²⁾.

(b) Based on geometry of original fuel⁽³⁾, burnup⁽³⁾, and the amount of fuel to be processed.

of the unusual nature of the material, the reprocessing was delayed for several years, but was recently completed at ICPP. Prior to the processing a feasibility study and cost estimate were made wherein it was concluded that custom dissolution of the core in small scale equipment and extraction of uranium in plant equipment was entirely feasible with an estimated out-of-pocket cost well under one dollar per gram of uranium.

II. DISSOLUTION

1. Safety Aspects

Safety problems involving sodium potassium eutectic alloy (NaK), explosive metal reactions, nuclear safety, contamination, and shielding requirements had to be resolved before the fuel could be reprocessed. A preliminary evaluation of these problems led to the conclusion that this fuel should not be dissolved in a routine manner in the plant systems but that it should instead be dissolved on a custom basis in the shielded Multicurie Cell, which has viewing windows and remote manipulators. This allowed direct observation and control of the hazardous anticipated reactions.

1.1 Sodium-Potassium

Analyses of portions of the melt had shown that about 6 to 12 grams of NaK would be present with each kilogram of uranium, which was the anticipated batch size for dissolution. During the core disassembly and packaging operations at Argonne the fuel was handled in an atmosphere of nitrogen containing 1-1.5 percent oxygen at a relative humidity of 1.6-2.1 percent. Metal fires were still occurring when the atmosphere contained as little as two percent oxygen⁽³⁾. However, it was also learned from the observations made during the disassembly that the NaK was distributed in unconnected pockets in the melt; therefore, large amounts could not react suddenly.

Based on this information it was decided that the fuel could be handled in air and dissolved in aqueous reagents. The dissolver was purged with nitrogen to dilute any hydrogen produced by metal-acid reactions and provisions were made for adding the reagent at a slow, metered rate. Equipment for controlling metal fires in air with Metal-X was installed in the cell and could be actuated remotely.

1.2 Explosion of Uranium-Zirconium Alloy

The potential for an explosion of the epsilon phase of zirconium-uranium, which is present in many zirconium-uranium alloys as they are dissolved in nitric acid solutions, was avoided by providing excess fluoride ion in the reagent during the dissolution⁽⁴⁾.

1.3 Nuclear Safety

The fuel melts were anticipated to be up to 75 percent by weight uranium-235, and dissolver solutions were anticipated to contain about 200 g/l of uranium-235. Under these conditions strict batch and geometry

limitations were enforced during the storage, sorting, opening, dissolution, and adjustment operations which were involved in the overall dissolution process. As is customary at ICPP the equipment design, flowsheets, and operating procedures were reviewed by the Engineering Safeguards Committee prior to operation.

1.4 Alpha Contamination

Precautions had to be taken during all stages of the processing to prevent alpha contamination because the melted core contained up to ten grams of plutonium⁽³⁾.

1.5 Gamma Radiation

The relatively low burnup and long cooling time (11 years) of the core resulted in only modest radiation fields even from large masses of the melt material. Shielding was still necessary for the dissolution operations, but protection of operating personnel from the chemical hazards described earlier was a large factor in the selection of a remotely operated, well ventilated cell for the dissolution.

2. Development Studies

A tentative material balance for the dissolution and first cycle extraction of the uranium (Table II) was prepared based on the fuel composition calculated in Table I and the knowledge that essentially complete dissolution of the melt could be obtained in nitric-dilute hydrofluoric acid⁽³⁾. To test this flowsheet and to gain direct experience in handling the fuel melt, three of the cans (No. 1/2 size) in which the fuel pieces had been packaged were opened, the contents emptied out, the fuel pieces sorted and examined, and pieces selected for dissolution studies. Slight fuming and some isolated, brief flames were noted as the cans were opened and the fuel pieces and melt were exposed to the moist air of the cell. There was no indication of sustained, exothermic reaction, and it was judged that there was only a small probability of fire. The pieces became sticky very rapidly as moisture from the air reacted with the sodium-potassium oxides on the surfaces.

Dissolution of various small samples of melt and fuel, following the reagent-to-fuel ratio of Table II, proceeded rapidly. It was not necessary to supply heat to initiate or sustain the reaction; the fuel reacted essentially instantaneously as reagent was added. The compositions of the dissolver product solutions from these small scale studies are given in Table III. It was also shown in a separate experiment that the steel can (food product type) in which the fuel was packaged would dissolve rapidly in the reagent. This allowed the option of charging whole cans of fuel to the dissolver.

The results of these tests confirmed the chemical and operational feasibility of the process as envisioned, and firm plans were made for the dissolution on a custom basis. It was concluded that it was safest and most expedient to perforate the lids of the cans and then charge the can and contents to the dissolver for dissolution as opposed to opening

Table II

CHEMICAL MATERIAL BALANCE FLOWSHEET FOR INTEGRAL
DISSOLUTION AND ADJUSTMENT OF EBR-I CORE 2 FUEL

Fuel Charge: 1020 g uranium-zirconium alloy 106 g stainless steel cladding 6 g NaK					
	Dissolution Reagent	Dissolver Product	Adjustment Reagent	Neutralization Reagent	Adjusted Feed
Volume, l	5.0	4.6	5.1	1.4	11.1
H ⁺ , M	12.6	5.5	---	---	0.5
U, g/l	---	218	---	---	90
Zr, g/l	---	4.3	---	---	1.8
Fe-Cr-Ni, g/l	---	23	---	---	9.5
NaK, g/l	---	1.3	---	---	0.5
Al, M	---	---	2.0	---	0.92
NH ₄ ⁺ , M	---	---	---	14	1.8
NO ₃ ⁻ , M	12.0	8.1	6.0	---	6.1
F ⁻ , M	0.6	0.6	---	---	0.3
OH ⁻ , M	---	---	---	14	---

Table III

COMPOSITIONS OF DISSOLVER PRODUCT SOLUTIONS
FROM THE DEVELOPMENT STUDIES

Test No.	U (g/l)	Pu (d/min-ml)	Acid (M)
1	160	4.83 x 10 ⁶	3.08
2	175	6.58 x 10 ⁶	2.78
3	161	3.40 x 10 ⁵	3.18

the cans and sorting and batching the pieces. The tremendous reactivity of the fuel in the reagent made external heating of the large dissolver unnecessary and required that the reagent be added very slowly to control the reaction. These provisions were designed into the equipment and procedures for the final dissolutions. Carpenter-20 stainless steel was selected for the dissolver material, since it has adequate resistance to mixed nitric-hydrofluoric acids⁽⁵⁾. The plutonium content of the dissolver product solutions (Table III) was typical of that usually experienced with highly enriched uranium.

3. Material Balance and Equipment Flowsheet for Production Runs

The chemical material balance shown in Table II was used for the processing runs. The equipment for dissolution consisted of a nitrogen-purged, geometrically safe dissolver made of Carpenter-20 stainless steel and a calibrated glass vessel for volume measurement. After dissolution the dissolver product solution was adjusted with aluminum nitrate in the dissolver. The aluminum nitrate adjustment reagent, added to complex free fluoride ions, made the final adjusted feed about one molar in aluminum. The solution was transferred batchwise by gravity from the adjustment vessel into a plant storage vessel where the product solution was accumulated; after neutralization, the input measurement was made. Standard operating procedures which embodied all of the safety considerations mentioned earlier were prepared and followed for the 87 dissolutions which made up the campaign.

4. Results of the Production Runs

The production-scale dissolutions proceeded smoothly with two batches of fuel, each containing about one kg of uranium, being dissolved each eight-hour shift. The dissolver product solution from the first production batch was analyzed with the following results:

uranium:	240 g/l	acid:	4.4M
iron:	46 g/l	fluoride:	0.7M
potassium:	0.7 g/l		

Considering the non-homogeneous nature of the fuel material, this was regarded as adequate adherence to the material balance (Table II) and no further detailed analyses were made. The higher iron content of the solution as compared to the material balance is due to the steel can, which was dissolved but not shown in the original chemical material balance.

The complexed and adjusted dissolver product was transferred to plant storage vessels for scheduled processing through two cycles of solvent extraction using Hexone.

III. RECOVERY OF URANIUM BY SOLVENT EXTRACTION

1. Extraction Tests

Consistent with usual practice at ICPP, experimental work was done in the laboratory to determine if uranium extraction in a Hexone solvent would be satisfactory. Two simple and inexpensive tests were performed. The first test was designed to determine the distribution coefficients for either extraction or stripping. Three stages of extraction and two of stripping were performed in a test using appropriate plant feed, solvent, and scrubbing and stripping reagents. Figures 1 and 2 show operating diagrams based on laboratory data for extraction and stripping, respectively. Based on these tests, uranium losses for three stages of extraction and two stages of stripping were estimated to be under 0.01 percent for each column; actual losses in the plant were about 0.001 percent from each column.

The second test was designed for detection of possible flooding problems in the plant columns. This test is known as a dispersion-coalescence test and involves mixing equal aliquots of the aqueous and organic phases by means of a perforated plate agitator which moves vertically across the interface. The quantitative measurement consists of observing the time required to achieve a given degree of dispersion of both phases with a given power input to the agitator. Then, with a standard energy input to the system, the time required for coalescence is noted. The test performed on the EBR-I Core 2 solution indicated that dispersion-coalescence times were sufficiently short for good column operation. This was confirmed during plant extraction.

2. Extraction Flowsheet and Plant Experience

The extraction flowsheet written based on the laboratory work is shown as Figure 3. Full rates were not achieved during the run because a pump used to empty the evaporator between the two extraction cycles was not operating properly. However, extraction efficiency was very good; only about three grams of uranium were lost to the raffinates out of 65,800 grams processed.

3. Extraction Equipment

Except for a Clarkson feeder, the extraction equipment was the same as that used previously⁽⁶⁾. The Clarkson feeder is a small variable-speed water wheel with cups attached which meters the uranium-containing feed solution to the second cycle (hexone) extraction system. Previously remote head pumps were used which often gave erratic flowrates which caused the extraction columns to be unstable. The Clarkson feeder appears to have solved this problem; the exceptionally smooth operation of the system during this run was due in part to the feeder.

OPERATING DIAGRAM FOR URANIUM EXTRACTION
EBR-1 CORE-2 FLOWSHEET

Figure 1.

OPERATING DIAGRAM FOR URANIUM STRIPPING
FROM EBR-1 CORE-2 FLOWSHEET

Figure 2

Figure 3

EXTRACTION FLOWSHEET FOR EBR-I CORE 2 FUEL

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
DESCRIPTION	II AF	II AX	II AS	II AP	II AR	II BX	II BP	II BR	SECOND CYCLE PRODUCT	III AX	III AS	III AP	III AR	III BX	III BP	III BR	PRODUCT
FLOW, l/batch	18	45	30	45	48	20	20	40	4.6	17	12	17	16.6	10	10	17	4.6
FLOW, l/hr	1.36	0.80	1.31	0.87	1.26	1.00	1.11	0.80	1.48	0.80	1.31	0.94	1.23	1.00	1.22	0.80	1.48
SP GR	1.36	0.80	1.31	0.87	1.26	1.00	1.11	0.80	1.48	0.80	1.31	0.94	1.23	1.00	1.22	0.80	1.48
EXTRACTANT	Hexone		Hexone				Hexone		Hexone		Hexone				Hexone		
Al(NO ₃) ₃ , M	0.97		2.00	1.61						2.00		1.45					
HNO ₃ , M	0.52				0.04	0.04		0.17				0.18	0.04	0.04			0.09
H ₂ O, M		0.5		0.12						0.32							
H ₂ SO ₄ , M	1.78			0.86								0.05					
Fe(NH ₄ SO ₄) ₂ , M		0.05		0.04													
F, M	0.16			0.06													
U, g/l	90		36	0.001		81	0.001	350				95	0.001	162	0.001	350	

IV. CONCLUSIONS

The uranium from EBR-I Core 2, the meltdown core, was successfully reprocessed at ICPP with no difficulty in spite of the unusual condition of the core. The ease of handling this material and the small cost incurred give evidence that other non-standard fuel materials can be economically and safely recovered in a versatile facility, like ICPP, without hazard or interference with production schedules. The residues from SNAPTRAN⁽⁷⁾ tests and the uranium on mold glass from EBR-II⁽⁸⁾ are fuel materials of this class which have also been handled successfully at ICPP.

V. REFERENCES

1. A. E. Erhard, et al, Processing of the Core Fuel Used Initially in the Experimental Breeder Reactor (EBR-I), IDO-14331 (December 1955).
2. G. F. Offutt, et al, First Zirconium Alloyed Fuel Reprocessing Campaign Using Soluble Nuclear Poison, IN-1091 (to be published).
3. J. H. Kittel, M. Novick, and R. F. Buchanan, The EBR-I Meltdown--Physical and Metallurgical Changes in the Core, ANL-5731 (November 1957).
4. T. A. Gens, Explosive Reactions During Reprocessing of Reactor Fuels Containing Uranium and Zirconium or Niobium, ORNL-CF-58-11-31, (1958).
5. G. S. Adams and J. J. Bordeaux, Corrosion of Alloys in Aqueous Hydrofluoric-Nitric Acid Solutions, IDO-14516 (July 1960).
6. R. E. Griffin, Solvent Extraction of Enriched Uranium, IDO-14556 (April 1956).
7. J. R. Bower (ed.), Chemical and Process Development Branch Annual Report, Fiscal Year 1966, IDO-14680 (October 1966).
8. J. R. Bower (ed.), Chemical Technology Branch Annual Report, Fiscal Year 1967, IN-1087 (to be published).