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LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period October 1 to December 31, 1976

B. L. Vondra

[redacted]

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LWR FUEL REPROCESSING AND RECYCLE PROGRAM
QUARTERLY REPORT FOR PERIOD OCTOBER 1 TO DECEMBER 31, 1976

B. L. Vondra, Program Manager

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CONTENTS

Page

FOREWORD 1

SUMMARY. 3

1. ASSISTANCE IN SHEAR DEVELOPMENT AND RELATED PROBLEMS 5
   1.1 Consultation with SRO 5
   1.2 ORNL/SRL Joint Program 5

2. HEAD-END STUDIES: VOLOXIDATION AND DISSOLUTION. 7
   2.1 Voloxidation. 7
      2.1.1 Rotary kiln heat transfer studies. 7
      2.1.2 Rotary kiln residence-time distribution studies. . . 8
      2.1.3 Component development. 11
   2.2 Hot-Cell Studies. 13
      2.2.1 Hot-cell dissolution 16
      2.2.2 Radioactivity in off-gas 28
      2.2.3 Insoluble dissolver residue. 32
      2.2.4 Solution stability 34
      2.2.5 Waste concentration. 36
   2.3 Building 4507 Hot-Cell Operations 40
      2.3.1 Development of in-cell equipment 40
      2.3.2 Decommissioning the Curium Recovery Facility (CRF) . 43
      2.3.3 Miscellaneous. 48

3. PUREX PROCESS STUDIES (SOLVENT EXTRACTION) 49
   3.1 Laboratory Studies. 49
      3.1.1 Solvent cleanup. 49
      3.1.2 Ruthenium chemistry. 58
      3.1.3 Solvent extraction kinetics. 59
      3.1.4 Plutonium extraction studies 59
      3.1.5 Analytical development 60
   3.2 Purex Studies with Irradiated Fuels 61
      3.2.1 Purex process studies. 61
      3.2.2 Solvent extraction flowsheet development 64
   3.3 Cold Studies. 66
      3.3.1 Mixer-settler extraction studies 66
      3.3.2 Modifications for the mixer-settler system 70

4. OFF-GASES - FLUOROCARBON ABSORPTION STUDIES. 71
   4.1 Fluorocarbon Absorption Process Development 71
      4.1.1 Pilot-plant operation. 71
      4.1.2 Process application. 76
   4.2 Chemical Studies of Contaminants in LWR Off-Gas Processing. 79

5. FINISHING PROCESSES - MOX FUEL FABRICATION 85

Page

6. URANIUM HEXAFLUORIDE CONVERSION 86

7. ECONOMIC STUDIES. 87

8. RADIOLOGICAL TECHNIQUES FOR ENVIRONMENTAL IMPACT ASSESSMENTS OF THE LWR FUEL CYCLE 88
   8.1 Introduction 88
   8.2 Description of the Model 88
   8.3 Results of Parameter Sensitivity Studies 89
      8.3.1 Internal dose reduction factors 90
      8.3.2 External dose reduction factors 91
   8.4 Conclusion and Future Plans. 93

9. OFF-GASES - THE EXPERIMENTAL INVESTIGATION OF THE FIXATION OF ^{14}C-CONTAMINATED CO_2 IN A GAS-LIME SLURRY CONTACTOR. 95
   9.1 Introduction 95
   9.2 Prior Results. 95
   9.3 Possible Application Points in the LWR Fuel Reprocessing Flowsheet 97
   9.4 Progress 97

10. REFERENCES. 100

LIST OF TABLES

		Page
Table 1.	Experimental conditions and results for 18-in.-diam kiln RTD tests	10
Table 2.	Radioisotopes in dissolver and dissolver/cladding rinse solutions	18
Table 3.	Radioisotopes associated with cladding (Ci/MTU charged)	22
Table 4.	Distribution of ^{129}I during fuel dissolution: runs 1-6	29
Table 5.	Distribution of ^{14}C during fuel dissolution: runs 1-6	30
Table 6.	Distribution of tritium during fuel dissolution: runs 1-6	33
Table 7.	Solids from waste concentration (Extraction raffinate evaporated to ~100 gal/MTU; solids washed with concentrated HNO_3)	37
Table 8.	Irradiated solvents used in preliminary solvent cleanup studies	50
Table 9.	Plutonium retention in aged, irradiated Purex solvent: effects of aqueous washes	52
Table 10.	Plutonium and uranium retained in nonaged, irradiated Purex solvent after preliminary cleanup treatments	54

LIST OF FIGURES

Figure		Page
1	Gamma spectrum of cladding with GeLi detector.	25
2	Gamma spectrum of cladding with NaI detector.	26
3	Intercell transfer port installed in shielding wall between Cells 2 and 3, Bldg. 4507.	44
4	Filter plenum (right) and work tray supports in Cell 3, Bldg. 4507, at early stage of installation.	45
5	Work tray supports, sample chute, and part of alpha barrier in Cell 3, Bldg. 4507, at early stage of installation.	46
6	Portion of electrical and other services installed in Cell 3, Bldg. 4507.	47
7	Adsorption of plutonium from simulated Purex solvent on MP-50 macroreticular resin as a function of acid concentration.	57
8	Analysis of mixer-settler run (run HD-6, strip column) using SEPHIS calculations.	65
9	Overall view of mixer-settler equipment.	67
10	Closeup of extraction and scrubbing stages during run R-2. Feed stage = 25.	68
11	Absorber krypton DF as a function of absorption factor and pressure.	73
12	Primary process concentration factor as a function of fractionator operation.	75
13	Schematic of the modified selective absorption process.	77
14	CH_3I distribution data.	80
15	Illustration of NO_2 monomer-dimer (N_2O_4) equilibrium in the vapor phase as a function of temperature and pressure.	82
16	Phase diagram for N_2O_4--R-12 system.	83

FOREWORD

Seven tasks under the LWR Fuel Reprocessing and Recycle Program have been assigned to UCC-ND with major efforts centered at the Oak Ridge National Laboratory. Because of the close relationship of the reprocessing activities with the on-going LMFBR Fuel Reprocessing Program at ORNL, these tasks will be managed within a combined LWR/LMFBR Fuel Reprocessing Program under the direction of W. D. Burch, Program Director. B. L. Vondra, as LWR Program Manager, will coordinate all activities reported here. Responsibility for the coordination and collation of reports of all work at Oak Ridge was assigned to ORNL by SRO/SRL, who is designated as the lead organization for the LWR Fuel Recycle Program.

Projects for which budget and work plans have been established are as follows:

F-OR-02-001 SRO/LWR: Assistance in Shear Development and Related Problems

F-OR-02-002 SRO/LWR: Head-End Studies: Voloxidation and Dissolution

F-OR-02-003 SRO/LWR: Off-Gases Fluorocarbon Absorption Studies

F-OR-02-004 SRO/LWR: Purex Process Studies (Solvent Extraction)

F-OR-02-006 SRO/LWR: Uranium Hexafluoride Conversion

F-OR-02-008 SRO/LWR: Radiological Techniques for Environmental Assessments of the LWR Fuel Cycle

F-OR-02-009 SRO/LWR: Off-Gases - The Experimental Investigation of the Fixation of ^{14}C

Tasks F-OR-02-005 and F-OR-02-007 have been deferred because of budget limitations. Task F-OR-02-009, Off-Gases - The Experimental Investigation

of the Fixation of ^{14}C, has been initiated. Progress for each task will continue to be reported under the corresponding numbered section, as in previous issues in this series.

SUMMARY

This is the fourth quarterly report issued on the LWR Fuel Reprocessing and Recycle Program at ORNL as part of the national program administered by Savannah River Operations - Savannah River Laboratory.

Two additional dissolutions were performed using irradiated fuel from the H. B. Robinson II reactor. Analyses for the first six dissolution runs are essentially complete. Characterization of the solids is continuing, and the results to date are reported.

All bids received for the procurement of a voloxidizer were nonresponsive. Therefore, a revised bid package has been prepared and issued. Bids are expected to be received in January 1977. It is still projected that a voloxidizer will be received during this fiscal year.

Removal of plutonium, uranium, and organic degradation products from hot-cell-generated Purex solvent is being studied. In a series of tests, both 1 M Na_2CO_3 and 0.1 M hydrazine solutions (equal-volume wash) were found to remove greater than 99% of the unstrippable plutonium from the solvent. Anion resin A-26* (1 g of resin plus 5 ml of solvent) removed greater than 90% of the plutonium.

Rutheniumnitrosyl hydroxide labeled with ^{106}Ru has been prepared. A chromatographic support containing 51% TBP was prepared by adsorbing TBP on dry macroreticular nonionic resin (XAD-2*).

A gas chromatograph for developing analytical techniques for nitrogen oxide mixtures has been ordered. Components for a liquid chromatography

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*Rohm and Haas.

system for developing analytical techniques for organic degradation products and fission product species have also been ordered.

As a part of the continuing development of the fluorocarbon process, tests have been initiated (under campaign 4) to further define the process disposition of various feed gas components. Current tests with krypton have explored the consequences of using lower absorption pressures (i.e., 100 psig vs 300 psig).

1. ASSISTANCE IN SHEAR DEVELOPMENT AND RELATED PROBLEMS

C. D. Watson (Chemical Technology Division, ORNL)

1.1 Consultation with SRO

As part of the joint ORNL/SRL program, consultation was provided on several occasions to SRO in reviewing the Boeing Construction Company's mechanical head-end proposal for a new LWR shear system. As a result of these reviews, the recommendations contained in a recent study[1] of the unresolved shearing and related head-end problems were incorporated into the Boeing proposal. Included in the SRO activities was a visit to the Allied-General Nuclear Services (AGNS) plant at Barnwell, South Carolina. Unfortunately, shakedown testing was in progress at that time, and a tour of the mechanical head end was not permitted.

1.2 ORNL/SRL Joint Program

A planning session was held at each of the two sites in order to arrive at a joint shear assistance program in support of the 3000-MT/year plant design concept now being developed by DuPont Engineering at Wilmington, Delaware, and Savannah River. Basically, the program segments to be performed at ORNL are:

1. Acquire LWR prototype fuel material and fabricate four 3-ft-long PWR prototypes by March 1, 1977: two to be embrittled (to simulate irradiated fuel), and two to be prepared with standard unembrittled materials.

2. Shear prototypes at 6 strokes/min into 3/4-in.- and 2-in.-long segments; this includes cutting the prototype into grids and straddling grids (mid-March 1977).
3. Characterize the sheared product into fractions of various sizes, sample and characterize overhead fines; determine holdup in the shear, measure packing density, determine the population density of dislodged Zircaloy-4 (Zr-4) fines; and perform a neutron activation analysis on Zr-4 fines (first week of April 1977).
4. Prepare a final report with appropriate support data from the ORNL shear system instrumentation (mid-May 1977). Also included will be a videotape recording of selected cuts, along with some selected photographs.
5. Continue present design effort on the ORNL shear in order to acquire new shear tooling specially contoured for LWR fuels (PWR/BWR).

The program just outlined is an ambitious one to be accomplished in the scheduled time frame. The entire program depends on finding a source of grids and the successful development of a hydrogen embrittlement recipe that simulates radiation-hardened Zr-4. ORNL has already acquired ~53,000 linear ft of reject PWR Zr-4 fuel tubes and has ordered 670,000 ceramic pellets to fill them. The tubing is being kept in a special "bill of materials" storage area under strict control to prevent any of it from inadvertently finding its way back into genuine fuel manufacturing channels.

A review of the program is planned at midyear. Some 189 proposals will be prepared based on the recommendations contained in ORNL/TM-5651.

2. HEAD-END STUDIES: VOLOXIDATION AND DISSOLUTION

2.1 Voloxidation

M. E. Whatley (Chemical Technology Division, ORNL)

The voloxidation process is currently being developed as a head-end method for removing tritium from the fuel prior to aqueous processing. Based on experimental work, it appears that this objective can be met by heating the oxide fuel to ~450°C in flowing oxygen or air. Volatilization of tritium and, to a lesser extent, some of the other fission products is effected as the UO_2 becomes restructured during oxidation to U_3O_8. Early removal of tritium from the fuel into a relatively small volume is desirable in order to avoid extensive dilution of the tritium with water in the subsequent fuel dissolution step.

During this report period, the investigation of the applicability of rotary kilns to the voloxidation process was continued by performing tests that extend residence time distribution (RTD) studies to include kiln tubes of larger diameter. Efforts to procure a larger-scale voloxidizer for study and testing are also described.

2.1.1 Rotary kiln heat transfer studies

T. D. Welch (Chemical Technology Division, ORNL)

An understanding of the heat transfer phenomena in rotary kilns is fundamental for voloxidizer development since the voloxidation process is extremely sensitive to temperature.

The rotary kiln used in preliminary heat transfer tests[2] has been decontaminated and transferred to the Fuel Recycle Facility where heat transfer studies will be continued. These studies will determine the

fundamental modes of heat transfer, including the influence of particle RTD on these phenomena. Presently, upcoming experiments are being designed and improved temperature-measurement instrumentation is being investigated. Active data collection will begin early next quarter.

2.1.2 Rotary kiln residence-time distribution studies

T. D. Welch and M. E. Whatley (Chemical Technology Division, ORNL)

The RTDs and associated dispersion numbers (Peclet number) have been obtained for prototypical sheared fuel in an 18-in.-diam rotary drum.

The RTD of process material in the kiln is necessary in order to accurately predict kiln performance for design purposes. If all particles had the same residence time, the kiln could be characterized as a plug flow system. In actual practice, however, significant deviations from idealized plug flow occur, and there is a distribution or range of particle residence times. The RTD can be compared to the axial dispersion occurring in a tubular gas-liquid or liquid-liquid reactor. The amount of tritium removed from sheared fuel by the voloxidation process will depend on the RTD in the kiln as well as on reaction rate information. One purpose of the current tests is to determine the effect of kiln diameter on the RTD.

The experimental equipment consists of a vibratory feeder which feeds 1-in. (0.0254-m)-long prototype fuel to an 18-in. (0.457-m)-diam, 7-ft (2.134-m)-long rotating drum. The drum contains six equally spaced 3-in. (0.0762-m)-wide axial flights that lift, tumble, and transfer material. Rotation is provided by rollers that are powered by a 1/4-hp variable-speed electric motor.

The stimulus-response procedure used consists of disturbing the system and then examining its response to this stimulus. In these tests,

the stimulus is a tracer input of marked hulls, whereas the response consists of a time record of the weight fraction of the tracer leaving the vessel. Both a pulse and a step change input were used, but the pulse signal was found to be more convenient.

Tests were performed under seven operating conditions; in each case, the drum slope was 0.25 in./ft (0.021 m/m). The kiln rotational rate was varied from 0.66 to 4.0 rpm, and the mass feed rate ranged from 0.40 to 1.80 kg/min. At least two replicate runs were made under each condition in order to establish confidence limits. A summary of the experimental conditions, as well as three experimentally determined parameters, is given in Table 1.

The holdup, or inventory, is the total amount of material in the drum at steady state; it is proportional to the mass feed rate and inversely proportional to the rotational rate and the slope of the kiln. As the loading is increased, deviations from the simple model become more significant and the residence time decreases due to a change in the material transfer mechanism.[3] All runs were made at relatively low loadings.

The mean residence time, shown in the fifth column of Table 1, is calculated from the first moment of the experimental RTD (approximately equal to the holdup divided by mass feed rate) and is in excellent agreement with mean times generated by regression fits of the experimental data to dispersion models. This parameter is found to be inversely proportional to the kiln diameter, rotational rate, and slope. It is a fundamental performance measure and must be known accurately for design purposes.

Table 1. Experimental conditions and results for 18-in.-diam kiln RTD tests[a]

Run number	Rotational rate (rpm)	Mass feed rate (kg/min)	Holdup (kg)	Mean residence time (min)	Dispersion number
18-1	2.0	0.90	19.23	22.3	0.019
18-2	4.0	0.90	10.41	11.2	0.020
18-3	4.0	1.80	22.00	12.3	0.018
18-4	2.0	1.80	42.10	23.5	0.017
18-5	1.0	1.80	75.84	39.9	0.017
18-6	0.66	0.70	49.65	71.6	0.018
18-7	1.0	0.40	16.29	42.7	0.023

[a]Slope = 0.021 m/m.

The final parameter shown in Table 1 is the dispersion number (Peclet number) - a dimensionless number which arises from the differential equations and is a measure of the RTD spread. This dispersion number is defined as

$$D/\bar{u}L,$$

where

D = dispersion coefficient, m^2/min;

$\bar{u}$ = average linear velocity, m/min;

L = kiln length, m.

The dispersion number is a manifestation of the kiln flow patterns, and its calculation is an integral part of determining the conversion (release of tritium) and the kiln heat transfer requirements. As shown, the dispersion numbers for the 18-in.-diam drum are on the order of 0.02.

Progress has been made in obtaining fundamental design information, but additional work is needed. Tests will be continued next quarter to determine the effect of diameter on the RTD. The RTD of fines and the effects of feed composition, and flight design will also be studied.

2.1.3 Component development

M. E. Whatley and D. C. Hampson (Chemical Technology Division, ORNL)

In an effort to procure a larger-scale rotary kiln voloxidizer for study and testing, a bid package of specifications and criteria for design and fabrication was prepared and issued to candidate suppliers. This unit, sized to handle 1/2 metric ton of fuel per day, must be sufficiently flexible, both in construction and in heating capability, to provide latitude in operation and in modification necessary for development. After extending the deadline for bid submissions from mid-September to mid-October, and then to mid-November, one response was finally received.

This bid, for various technical and legal reasons, was not acceptable. We now recognize that our original intention to purchase a unit from a commercial vendor, which would be essentially prototypical of a voloxidizer and might be used in a fuel reprocessing plant, is not practical; thus we must consider alternative paths to procurement. The most attractive of these alternatives seems to be the drafting of a new set of specifications which would:

1. remove the requirement that the purchased unit incorporate certain features which would make the unit prototypical for radiochemical plant service; and
2. relieve the vendor of his responsibility for performance under our specific conditions of operation.

This course of action is possible now for the following reasons:

1. It is realized that design for remote operation and maintenance must ultimately be the responsibility of ORNL.
2. Experimental data and analysis performed during the months in which the bid package was being processed have given us more confidence in the suitability of a relatively simple kiln design to perform as an effective voloxidizer.

We have received assurance, both from our purchasing department and from discussions with possible vendors, that a bid package based on the revised specifications can be handled rapidly and will result in acceptable responses.

The auxiliaries, such as the feeding system and the off-gas treatment system, are not part of the above purchase but will be developed at ORNL.

2.2 Hot-Cell Studies

D. O. Campbell, S. R. Buxton, R. L. Beatty, and W. L. Pattison
(Chemical Technology Division, ORNL)

An experimental program centered around hot-cell tests of fuel reprocessing operations was initiated in January 1976. Although a variety of LWR fuels will be used, most work to date has been done with fully irradiated PWR fuel cooled approximately two years. A single experiment was made with a highly irradiated LMFBR test element. The work is supported by "cold" experiments with synthetic solutions which are similar in composition to true process solutions.

The ORIGEN calculations are tailored to the specific irradiation history of each fuel included in the tests, using the best data we can obtain, with the valuable assistance of A. G. Croff. An error, which was found and corrected, indicated an incorrect calculation of the xenon isotopes. It should be recognized that the ORIGEN program is continually evolving as new data become available.

Two fuel dissolutions (runs 7 and 8) were carried out during this report period, and experimental work on the first six runs was essentially completed. Run 7 was made with a 10.7%-burnup LMFBR test rod, while run 8 was made with clad, full-burnup H. B. Robinson reactor fuel. Each experiment involves the study of most or all of the following operations: fuel dissolution; off-gas scrubbing with special attention to the behavior of ^{3}H, ^{14}C, and ^{129}I; dissolver solution clarification and stability; rinsing of the dissolver vessel, cladding, and undissolved residue; solvent extraction of the uranium and plutonium; evaporation of raffinate to produce a waste concentrate; aging of process solutions to study solution stability;

characterization of any solids formed; and, finally, waste partitioning studies that are reported elsewhere. Two areas presently receiving particular attention are the continuing appearance of solids in the dissolver solution and the accurate determination of the amounts of fission products and actinides associated with fuel cladding after dissolution.

Analytical results are essentially complete for the first six runs. Most of the radiochemical data are available for the seventh and eighth runs, but other data for these runs are incomplete. A major effort continues to be directed toward data analysis and interpretation, and the results reported previously are being modified as necessary. (All results published in this series of reports supersede previously presented data; any discrepancy must be resolved in favor of the most recent document.) In general, changes have been of a minor magnitude, and tentative conclusions reported in previous quarterly reports have been either reinforced or confirmed. In most cases, quantitative data are now available from several experiments; thus we hope to derive some statistical basis for our results.

Approximately 0.2 to 0.3 wt % of the irradiated UO_2 in LWR fuel is insoluble during dissolution in HNO_3. This fraction was much higher for the high-burnup mixed oxide fuel used for run 7, as expected from previously reported data. The residue, which consists primarily of ruthenium, palladium, rhodium, molybdenum, and technetium, is extremely radioactive due to the fission product ruthenium. This material will require attention in a

reprocessing plant because of its heat generation properties. The residue from LWR fuel contains very little uranium or plutonium, and leaching with HNO_3 reduces the actinide content to a few thousandths of a percent of the total present.

The dissolver solution appears to be stable to the formation of the zirconium molybdate compound for at least several days, provided the temperature is maintained below ~60°C and the acidity is not too low. However, there is a very slow formation of an insoluble black material in the dissolver solution, at the rate of 20 to 25 g per day per MTU, which appears to continue for weeks. This material is similar in appearance to the dissolver residue; however, preliminary information indicates that its composition (primarily palladium and rhodium with very little molybdenum) is different.

During dissolution of LWR fuel, ^{129}I is readily released into the off-gas stream. Nitrogen oxides produced during dissolution remove more than 95% of the iodine, and air sparging, either during or following dissolution, will transfer additional iodine to the off-gas. In all experiments with LWR fuel, less than 1% of the ^{129}I was left in the dissolver solution.

The ^{14}C data have been recalculated. The total amount of ^{14}C found is consistent with a nitrogen content in the H. B. Robinson reactor fuel of 6.9 ± 1.1 ppm (average of four runs with standard deviation). Most of the carbon reports to the first caustic scrubber, and there is no evidence for organic carbon.

Plutonium extraction behavior continues to be excellent. Because of the low contents of americium and curium in LMFBR fuel, the plutonium extraction behavior could be measured with less uncertainty; more than 99.99% of the plutonium was readily extracted.

2.2.1 Hot-cell dissolution

Run 7 was made with 111 g (gross) of stainless-steel-clad mixed oxide (20% PuO_2--UO_2) LMFBR fuel from an EBR-2 test rod. One goal of this experiment was to determine whether the hot-cell equipment and analytical procedures developed for LWR studies would also be appropriate for LMFBR tests. The same equipment was used, and the only significant modification in procedure was that the dissolution was carried out at a higher temperature, namely, 100 to 105°C instead of 90 to 92°C.

Dissolution was essentially complete within 1 hr, as indicated by the cessation of nitrogen oxide production. There was a substantial quantity of undissolved residue; however, a longer dissolution time would have reduced this somewhat. In general, the experiment ran very smoothly. The results are reported in detail elsewhere.[4]

Following this dissolution experiment, we continued to centrifuge the remaining portion of the dissolver solution from time to time in order to study the rate of formation and the character of any solids which form in it; this study is still in progress. The largest portion of the dissolver solution was transferred to M. H. Lloyd for solvent extraction studies.

In run 8, 365 g (gross) of clad fuel from the full-burnup region of Rod J-6 of Assembly B05 was dissolved in HNO_3. The rod was cut into nine

pieces, each approximately 2 in. long. After being kept at a temperature in the range of 90 to 92°C for 2 hr, the dissolver solution was removed by vacuum transfer (8D1). The dissolver was then rinsed twice with 1000 ml of 3 M HNO_3 at room temperature, and each rinse solution was removed by vacuum transfer (8D2 and 8D3). Following each rinse, a single piece of cladding was withdrawn. A secondary dissolution was then made with 1000 ml of 3 M HNO_3 for 4 hr at a temperature of 90°C (8D4); the dissolver solution was removed by vacuum transfer, and another piece of cladding was withdrawn. Subsequently, the dissolver and remaining cladding were rinsed again with 3 M HNO_3 (8D5) and a fourth piece of cladding was withdrawn. Finally, a tertiary dissolution was made for 4 hr at 90°C with 7 M HNO_3 (8D6). Five pieces of cladding went through the entire treatment.

Even though no special effort was made to slurry the insoluble residue in the dissolver solution or rinses before they were removed, ~90% of the residue was recovered from the dissolver solution. No measurable residue was recovered in the rinses after the second. In a plant dissolver, agitation should be appreciably more efficient than in this equipment; hence, essentially all the residue would be expected to transfer out of the dissolver with the dissolver solution. In fact, it is possible that some larger particles which still contain undissolved fuel might transfer; therefore, a secondary dissolution of these suspended solids will probably be required.

Analyses of the rinse and dissolver solutions are reported in Table 2. The first rinse (8D2) contained ~0.7% of all the isotopes, while the second (8D3) contained ~0.005% of all the isotopes except ruthenium, which was 0.008%. The secondary dissolution with 3 M HNO_3 (8D4)

Table 2. Radioisotopes in dissolver and dissolver/cladding rinse solutions

	ORIGEN value	Solution designation					
		8D1[a]	8D2[b]	8D3[b]	8D4[c]	8D5[b]	8D6[d]
Volume, ml		690	1000	1000	1000	1000	1000
Uranium, g	250	242	1.57	0.006	0.044	0.003	0.011
		Ci/MTU charged, corrected to 11/1/76					
Gross α		6560	47.7	0.37	5.5	0.044	0.47
5.15-MeV α	837	763	5.9	0.077	3.8	0.025	0.34
5.48-MeV α	2770	2800	20.9	0.15	1.6	0.011	0.12
5.80-MeV α	4300	1980	14.1	0.104	0.05	0.004	0.006
6.11-MeV α	716	1030	6.8	0.041	0.08	0.004	0.005
Plutonium α	2960	3130	22.5	0.15	3.8	0.026	0.37
		Ci/MTU charged, corrected to 2/1/76					
^{106}Ru	1.81E5	6.28E4	494	11.6	346	4.2	20.7
^{125}Sb	6.85E3	<3.7E3	<26	3.0	20.2	0.36	1.01
^{134}Cs	1.33E5	5.85E4	421	3.4	2.2	0.17	0.28
^{137}Cs	1.00E5	8.02E4	572	4.4	5.4	0.23	0.61
^{144}Ce	2.39E5	1.51E5	1099	8.3	<4.7	0.40	1.46
^{154}Eu	1.39E4	3.93E3	24	0.16	<0.3	<0.01	<0.03
^{95}Nb	3.90E3	N.D.[e]	N.D.[e]	0.23	1.7	0.07	0.24

[a] HNO_3 dissolver solution. Conditions: 90-92°C, 2 hr.

[b] 3 M HNO_3 rinse solution. Conditions: room temperature, 1000-ml volume.

[c] 3 M HNO_3 secondary dissolver solution. Conditions: 90°C, 4 hr.

[d] 7 M HNO_3 tertiary dissolver solution. Conditions: 90°C, 7 hr.

[e] N.D. = not detected.

contained much more ruthenium (0.5%) and plutonium (0.12%) but only a few thousandths of a percent of the other major isotopes; apparently, it also contained a larger fraction of the ^{125}Sb. The final dissolution, with 7 M HNO_3 (8D6), similarly contained more ruthenium and plutonium (a few hundredths of a percent) than curium or the other major fission products (less than a few thousandths of a percent).

It is clear that the dissolver residue, which contains a large fraction of the ruthenium, is being attacked, and this accounts for the high ruthenium values in the secondary dissolution. Essentially all of the residue was removed during rinsing prior to secondary dissolution; however, the cladding appeared to be coated with a dull, black material, which was probably a small amount of the residue. A smear of the outside of a piece of cladding (with 400-mesh carborundum paper) showed essentially pure ^{106}Ru-Rh gamma activity, which is characteristic of the dissolver residue.

The behavior of plutonium is less clear, but the data suggest that secondary dissolution recovered primarily ^{239}Pu, relative to ^{238}Pu, americium, or curium. Since LWR fuel contains substantially more activity from ^{238}Pu than from ^{239}Pu, and the LMFBR fuel processed in the previous experiment, run 7, contains almost pure $^{239-240}Pu$, a reasonable explanation is that a small amount of residue from run 7 remained in the dissolver and leaching of this material completely dominated the very small quantity of plutonium associated with the LWR fuel residue. The residue was probably adsorbed on the stainless steel screen in the bottom of the dissolver. These observations suggest that the fine, insoluble plutonium-containing residue from LMFBR dissolution in HNO_3 will probably stick to metal equipment.

Cladding studies. One recognized problem in fuel processing is the demonstration of a suitable method for monitoring cladding hulls after dissolution to ensure that they do not contain a significant quantity of residual undissolved fuel, particularly fissionable material. This has always been of some concern with regard to process recovery, but safeguards considerations have recently elevated this matter to major importance.

A basket of cladding hulls from the AGNS plant, for example, would be approximately 3 ft in diameter by 5 ft high and contain ~250 kg of Zircaloy plus a substantial amount of hardware associated with the fuel elements. The direct approach would be to irradiate the hulls with neutrons and monitor delayed neutrons from fission; unfortunately, this would probably be quite expensive. The favored method at present is to monitor gamma radiation from suitable fission products present in the fuel. This approach clearly requires that these fission products must not dissolve selectively, leaving undissolved fuel which is not "tagged" by associated fission products.

A major purpose of run 8 was to determine more precisely the amount of fission products and actinides associated with cladding and the effects of hull rinsing and secondary dissolution on these factors. Two previous experiments had indicated that more fission products (^{134}Cs, ^{137}Cs, and ^{144}Ce-Pr) than actinides (plutonium, americium, and curium) were associated with cladding, by a factor of ~100; however, the actual quantities of radioisotopes associated with cladding differed by a factor of ~10. In run 6 (full-burnup Robinson fuel), the cladding after dissolution contained 0.14% of the cerium-praseodymium, 0.15% of the cesium, ~0.001% of the plutonium, and 0.002% of the curium. In run 3, reported previously

(an end piece with variable but lower burnup), the quantities of all these isotopes contained in the cladding were approximately ten times greater; on the other hand, the actual values were subject to question because of uncertainty about the neutron exposure. The cladding from run 3 also dissolved less completely in HF, leaving a dark residue which tended to maintain the shape of the original cladding.

The cladding received more careful attention in run 8. The single cladding sections removed after 8D2, 8D3, 8D4, and 8D5 and two of the five pieces removed after 8D6 were rapidly rinsed with 3 M HNO_3 and then dissolved in a 10 M HF--0.05 M HNO_3 solution. Radiochemical analyses of these solutions are summarized in Table 3. There was a significant amount of dark residue from each piece of cladding, and all the residues were combined and dissolved by fusion in Na_2CO_3. Analysis showed the composite residue to contain a small fraction of the total activity in the cladding (~12% of the ruthenium and <5% of the others). This contribution is included in the average values given in the seventh column of the tabulation.

The data summarizing the activity found with the cladding show no clear trend; thus, secondary dissolution apparently had no significant effect on the quantity of either actinides or fission products associated with the cladding. The activity removed in the secondary dissolution (8D4 and 8D6) was largely plutonium, ruthenium, and antimony, which probably originated from insoluble material not directly associated with cladding.

The plutonium content of the five cladding samples was quite variable, with a standard deviation nearly as large as the average content. The average was ~0.003% of the total plutonium present, but the data scatter

Table 3. Radioisotopes associated with cladding (Ci/MTU charged)

	Solution designation						
	8D2	8D3	8D4	8D5	8D6	Average ± S.D.[b]	%
Gross α	0.073	0.165	0.065	0.080	0.154	0.144 ± 0.048	0.0017
Plutonium α	0.030	0.128	0.041	0.031	0.16	0.085 ± 0.064	0.0027
^{244}Cm α	0.026	0.028	0.017	0.015	0.013	0.020 ± 0.007	0.0010
^{106}Ru	183	145	217	147	117	185 ± 39	0.13
^{125}Sb	401	378	372	445	392	400 ± 29	-
^{134}Cs	88	90	72	100	95	92 ± 11	0.16
^{137}Cs	122	118	109	135	122	125 ± 9	0.16
^{144}Ce	51	31	139	37	450	143 ± 180	0.09
^{154}Eu	2.0	1.3	2.2	2.0	5.4	2.6 ± 1.6	0.07
^{54}Mn[a]	10.5	10.4	9.8	11.5	9.8	10.4 ± 0.7	-
^{60}Co[a]	8.2	7.9	7.2	8.5	8.6	8.1 ± 0.6	-

[a]Activation products from manganese and cobalt impurities in Zircaloy-4 cladding.

[b]S.D. = standard deviation.

suggests that this might result from occasional contamination by particles of the LMFBR dissolution residue. The curium content was reasonably constant at ~0.001% of the total present - a fraction which may well be representative of the plutonium originating from run 8, also.

Fission products are present in a much greater proportion than actinides; all show some variation among the five samples. In particular, the cerium and europium contents are much higher in 8D6-clad, and the data for cerium show wide scatter, with the standard deviation being larger than the average. Some of these discrepancies may result from analytical problems in cerium analyses since determinations by radiochemical separations (used in Table 3) differed by factors >2 in some cases, as compared with direct gamma scans.

The average fraction of the fission products found in the cladding, relative to the total in the fuel, was 0.13, 0.16, 0.09, and 0.07% for ruthenium, cesium, cerium, and europium, respectively. The uncertainty is rather large for cerium and europium, probably a factor of 2. In general, the fraction of the fission products associated with cladding is a factor of ~100 greater than the fraction of actinides. This observation, which was common to all three experiments, presumably results from the recoil of fission products into the cladding from that fuel adjacent to the cladding.

The activation products, ^{54}Mn and ^{60}Co, occur in reasonably constant concentrations in all samples, as expected. However, their concentrations were much less than those predicted by ORIGEN for the average core composition because the Zircaloy-4 fuel cladding contains much less cobalt and manganese than some other components. Zircaloy typically contains <10 ppm

of manganese and <1 ppm of cobalt. Other components, including Inconel, stainless steel, and Nicrobraze-50, increase the average cobalt concentration to over 200 parts per million parts of Zircaloy -- hundreds of times that of Zircaloy itself.

The activation products calculated by ORIGEN, therefore, are much higher than the values we find in the cladding. The ORIGEN values for the average fuel composition are 66 and 5920 Ci/MTU for ^{54}Mn and ^{60}Co, respectively. The five cladding samples give 10.4 ± 0.7 and 8.1 ± 0.6 Ci/MTU. Back-calculation yields 11 and 0.29 ppm for the manganese and cobalt concentrations in the H. B. Robinson reactor Zircaloy -- values which are reasonable.

The problem of hull monitoring will be compounded by the high content of cobalt, which may exist largely as a few pieces (e.g., spacer grids) scattered within the basket of hulls; such material is not present in the fuel processed here. Figures 1 and 2 present scans of dissolver cladding (8D6-clad) taken with a GeLi detector and a NaI crystal, respectively. It is clear that several fission product isotopes could be monitored, particularly with the high-resolution GeLi detector; however, in the presence of 500 to 1000 times more ^{60}Co, the problem may be much more difficult.

One possibility seriously considered for application at this time is to monitor the 2.186-MeV gamma ray of ^{144}Pr - a short-lived daughter of ^{144}Ce. The advantage of this gamma ray is its high energy, which results in excellent penetration through the thick layer of cladding and also permits discrimination from the much greater amount of lower-energy radiation by shielding the detector. The major disadvantage is the low

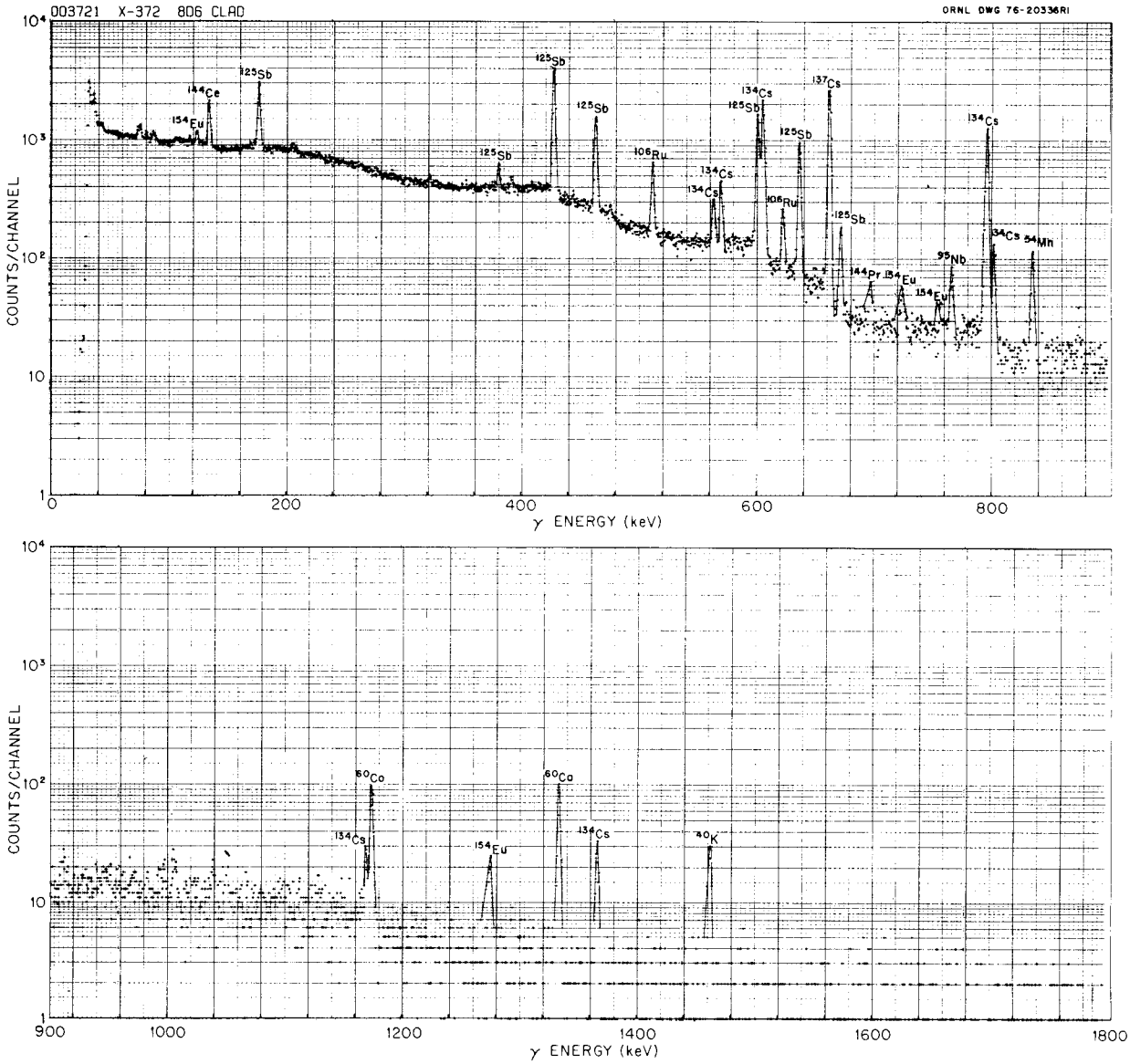

Fig. 1. Gamma spectrum of cladding with GeLi detector.

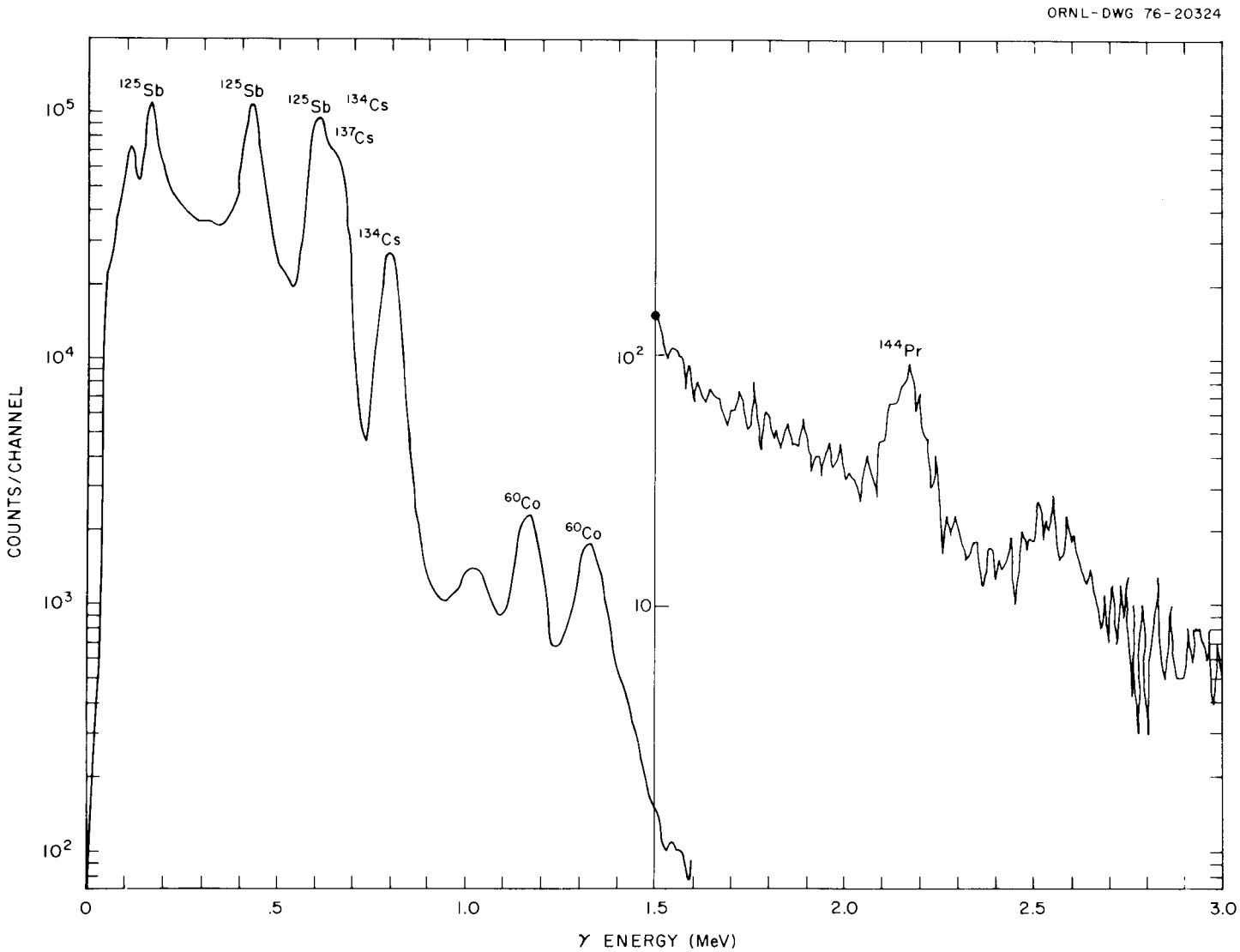

Fig. 2. Gamma spectrum of cladding with NaI detector.

yield - only 0.7% of the decays. This ^{144}Pr gamma emission is clearly visible in the spectrum of 8D6-clad (Fig. 2), which contains 0.29% of the total cerium present. Of course, it might be less conspicuous if the ^{60}Co content was, perhaps, 1000 times higher.

An alternative would be to follow one or more of the gamma emissions from cesium or another fission product with a GeLi detector (Fig. 1). Several are well separated from interferences and are present in sufficient intensity. Although their lower energy is a disadvantage, penetration is probably adequate since the average density of the basket of hulls is rather low. In this case, also, the effect of a much greater concentration of ^{60}Co is not clear.

Two qualitative tests have been made in which different pieces of cladding (8D6-clad) were counted directly with a NaI detector. In one test, the gamma spectrum was measured for a 2-in.-long piece of cladding in a 1-in.-thick lead carrier approximately 8 ft from the detector. In the other test, a small piece of cladding (134 mg) was broken off and counted through 1/2 in. of lead at a more reasonable geometry. Both spectra were qualitatively similar to that of Fig. 2, except that the low-energy portion was suppressed by the lead shielding. It should be mentioned that, when the piece was broken off, any new surface exposed to air momentarily ignited or glowed.

The remaining pieces of cladding from run 8 will be dissolved and analyzed to better define the statistics. Some cladding remaining from the run 3 experiment (in storage) will be similarly processed to verify the

apparently different behavior of that material. There is certainly the possibility of a dilution error, by a factor of 10, in the single determination made for run 3 cladding.

2.2.2 Radioactivity in off-gas

Some additional data have been received for ^{129}I, ^{3}H, and ^{14}C; also, the results for the first six runs have been reviewed and, in some cases, recalculated. New data tables which supersede previously reported data are presented in this section.

The ^{129}I distribution data for the first six runs are summarized in Table 4. Runs 2, 4, 5, and 6, which were made with full-burnup H. B. Robinson reactor fuel, give an average recovery of 81 ± 3.8% of the amount calculated by ORIGEN. Runs 4 and 5, with a long air sparge following dissolution, show substantially less iodine in the dissolver solution and condensate.

In all cases, <1% of the ^{129}I was found in the dissolver solution, and the data indicate that iodine can readily be reduced to a few tenths of a percent. In the projected AGNS operation, the dissolver solution passes through several tanks which are air sparged, with a holdup time that is variable but probably between several hours and a few days. Under these conditions, it is reasonable to expect very little of the iodine to reach the solvent extraction system.

The data for ^{14}C have been recalculated to correct for the ^{14}C resulting from the (n,α) reaction of ^{17}O in the UO_2; the results are summarized in Table 5. Oxygen is a fairly small source of ^{14}C, but it is significant for this fuel because the nitrogen content is apparently low. The ^{14}C resulting from ^{17}O was subtracted from the total found, and the nitrogen content that would produce the remaining ^{14}C was back-calculated

Table 4. Distribution of ^{129}I during fuel dissolution: runs 1-6

Run number	Found		Percent of total found in:			
	g/MTU	% of ORIGEN value	Dissolver solution	Condensate	Scrub 1	Scrub 2
1	118	82	0.52	0.14	99.3	0.08
2	157	84	0.97	1.08	97.4	0.57
3	45	41	0.50	0.90	98.3	0.30
4[a]	149	80	0.20	0.01	98.9	0.80
5[a]	169	84	0.23	0.23	99.4	0.18
6	141	76	0.98	2.89	94.6	1.57

[a]Sparged with air following dissolution.

Table 5. Distribution of ^{14}C during fuel dissolution: runs 1-6

Run number	Ci/MTU found	ppm N calcd[a]	Percent of total found in:			
			Dissolver solution	Condensate	Scrub 1	Scrub 2
1	0.14	~3.6	b	b	99.5	0.5
2	0.27	7.3	b	0.44	97.5	2.1
3	0.15	~6.5	b	0.65	97.5	1.85
4	0.24	5.6	b	0.41	58.7	40.9
5	0.29	8.2	b	0.16	83.2	16.2
6	~0.42	~14.5	b	b	94.4	5.6
Av 2-5		6.9 ± 1.1				

[a]Based on ^{14}C found, corrected for (n,α) reaction on ^{17}O.

[b]Not analyzed thus far.

from ORIGEN data. These results (column 3 of Table 5) are in good agreement for runs 2-5, which were made with H. B. Robinson reactor fuel. The calculated nitrogen content for this fuel is 6.9 ± 1.1 ppm (based on uranium).

Data for run 6 are not yet complete, but a higher ^{14}C content is indicated (0.4 Ci/MTU and 14.5 ppm of nitrogen, respectively). Control was poor during this experiment; consequently, all numbers are subject to considerable uncertainty. The fuel cladding was boiled for considerable time in the dissolver solution, and it is possible that the ^{14}C resulting from nitrogen initially in the air in the fuel rods was dissolved from the surface of the Zircaloy cladding. The H. B. Robinson fuel rods apparently were filled with air at atmospheric pressure and then overpressurized with helium prior to being welded shut. Fission gas analyses reported elsewhere indicate that oxygen and nitrogen were effectively removed; they were probably gettered by the Zircaloy during reactor operation. If so, ^{14}C from the nitrogen in this air (corresponding to ~7 to 12 ppm of nitrogen, based on uranium) would be found on the inner surface of the cladding.

The dissolver solution has not yet been analyzed for ^{14}C because none would be found by the method used. (Carbon dioxide is recovered by acidifying and sparging; this is an essential part of the dissolution process.) Wet oxidation will be used to test for organic material in the dissolver solutions which might contain ^{14}C. Most ^{14}C is found in the first caustic scrubber; on the other hand, fairly large amounts were found in the second scrubber for runs 4 and 5, which involved prolonged air sparging and partial neutralization of the first scrubber.

Tritium recovery for the first six runs is summarized in Table 6. For runs 2-6, which were made with H. B. Robinson reactor fuel, the tritium recovery averaged 62 ± 7% of that calculated to be produced by fission. Nearly all the tritium behaves as water. In run 6, a large fraction of the dissolver solution was distilled to the condensate receiver.

The results for runs 4-6 show that a small fraction of the tritium is not released as water, but probably as elemental gas. Following run 3, a CuO bed was installed between the two scrubbers to oxidize any organic material. In the first three runs (made without the CuO bed), the second scrubber removed <0.01% of the tritium, which is much less than that removed by the first scrubber. After the CuO bed had been installed, the second scrubber removed more tritium than the first. It is likely that ~0.3% of the tritium is released as the element.

2.2.3 Insoluble dissolver residue

The insoluble residue from run 8 constituted 0.24% of the weight of UO_2, which is in good agreement with prior results both here and elsewhere. Analytical work on these solids is continuing; the various methods being used indicate somewhat different results. X-ray fluorescence shows major peaks for ruthenium and molybdenum, with ruthenium substantially greater than molybdenum. Larger particles appear to contain a significant amount of uranium, while smaller, submicron particles contain much less. Unfortunately, this method is unable to resolve the other noble metals.

We are again attempting to use emission spectrographic analysis directly on the solid samples by mixing weighed amounts of the solids with carbon diluent. Duplicate analyses of the residue from run 8 gave

Table 6. Distribution of tritium during fuel dissolution: runs 1-6

Run number	Found		Percent of total found in:			
	Ci/MTU	% of ORIGEN value	Dissolver solution	Condensate	Scrub 1	Scrub 2
1	138	46[a]	98.3	1.29	0.047	0.0009
2	264	53	98.6	1.29	0.11	0.0003
3	201	63[a]	99.0	0.95	0.04	0.006
4	312	61	96.6	2.75	0.17	0.47
5	373	73	96.8	2.81	0.12	0.25
6	310	61	59.0	40.4	0.26	0.29

[a]ORIGEN-value approximations because of uncertain irradiation history.

the following results: 26 to 32 wt % ruthenium, 4 to 5 wt % molybdenum, 9 to 16 wt % palladium, 10 to 21 wt % rhodium, 0.6 wt % zirconium, 0.5 to 5 wt % technetium, and <1 wt % of any remaining components. Although this approach looks reasonably promising, we have encountered problems in the carbon dilution step.

Work continues to improve the accuracy and range of the spark-source mass spectrometry (SSMS) method, but no new results are yet available. The dilution factors are so great for the dissolver residue samples that many elements have been reported as "less than" numbers, which are undesirably large. In addition, tramp material often dominates the sample because of the large dilutions.

2.2.4 Solution stability

A new problem which has received increasing attention is the appearance of black solids in clarified dissolver solution. This material was first thought to be unusually fine solids that were not completely removed during feed clarification by centrifugation. However, repeated centrifugation of the dissolver solution from runs 5-8 over periods of several weeks has shown that new solids continue to appear for at least two weeks; the rate of appearance probably decreases appreciably for longer times. The rate of appearance for these solids corresponds to 20 to 25 g per day per MTU for LWR fuel until ~350 g/MTU has been produced; at this point, the rate of formation appears to decrease sharply. In run 7, which was made with LMFBR fuel, the rate of appearance was appreciably lower, probably because the amount of noble metals that dissolved into the solution was much smaller.

Although these solids resemble the dissolver residue, they appear to be distinctly different in composition. The following results are preliminary. X-ray fluorescence showed major peaks for zirconium and palladium, with a much smaller shoulder for ruthenium. There was no indication of molybdenum, rhodium, or technetium. Emission spectrographic analyses of samples from two successive centrifugations (the second and third, the first of which could include a small amount of dissolver residue) showed 4 and 3 wt % palladium, 10 and 5 wt % ruthenium, 8 and 14 wt % rhodium, 6 and 1 wt % molybdenum, 6 and 0.2 wt % zirconium, and low concentrations of other elements similar to the dissolver residue. The high zirconium peak observed in one of these samples when using the x-ray method is probably an artifact resulting from a nonrepresentative sample.

This secondary precipitate, which appears slowly in clarified dissolver solution, consists of extremely small particles with no particular structure. Similar black residues have appeared in extraction raffinate after standing, and they are probably of similar composition, although zirconium molybdate (white) will also precipitate in some cases. The cause of this precipitation, although not clear, is possibly a radiation effect since such solids do not appear in synthetic process solutions.

The problems related to the formation of solids may be summarized as: (1) a dissolver residue amounting to ~2.5 kg/MTU from LWR fuel and more for higher-burnup fuel, and (2) a secondary solid which appears in clarified LWR process solutions at the rate of about 20 to 25 g per day per MTU for at least two weeks (which would cover any reasonable time for fuel processing). The dissolver residue consists of (in decreasing order): ruthenium, rhodium, palladium, molybdenum, and technetium, and may contain some undissolved fuel;

the secondary solid consists of the same elements, with less technetium and molybdenum. Both are very small-sized particles which, if present in process solutions, will certainly compound the interfacial crud problem.

No additional aging experiments have been completed. The zirconium molybdate that precipitates after aging under appropriate conditions has been observed in various stored solutions, along with a black material which is probably the residue just discussed.

2.2.5 Waste concentration

Solids formed during concentration of the extraction raffinate from run 4 (estimated 96 gal/MTU) were analyzed by radiochemical and SSMS methods. The fractions of the total quantity of several fission product elements which were found to be present are reported in Table 7. The values for the two elements measured by both methods - cesium and strontium - are in good agreement; the other elements were determined by only one method.

The waste concentrate was removed from the evaporator at a temperature of 80 to 90°C as a clear, red solution; most of the strontium and barium crystallized out of this solution as it cooled. The solids remaining in the evaporator contained primarily (in decreasing order): molybdenum, barium, cesium, and strontium. Most, but not all, of the solids left in the evaporator were washed out by rinsing with concentrated HNO_3 and 2 M HNO_3, which also dissolve a fraction of the solids. Thus, the initial solids from evaporation are finally distributed throughout several samples of both solids and liquid solutions.

Table 7. Solids from waste concentration (Extraction raffinate evaporated to ~100 gal/MTU; solids washed with concentrated HNO_3)

Element	% of element in solids	
	α, γ count	SSMS[a]
Cesium	~6	~8
Strontium	~30	~30[b]
Barium	-	~60[b]
Molybdenum	-	~20
Ruthenium	<0.4	
Cerium	<0.2	
Antimony	>20	
Plutonium	0.5	
Americium	0.2	

[a]Analysis also showed larger amounts of calcium, silicon, magnesium, sulfur, and aluminum (in decreasing order).

[b]These numbers depend on temperature. Much of the barium and strontium precipitate on cooling.

Zirconium was not detected in the solids, but substantial amounts of molybdenum did precipitate. Although zirconium molybdate would be expected to precipitate from heated solutions of lower acidities, it apparently does not form during evaporation of waste solutions with concentrations of 8 to 10 M HNO_3. Cesium is often present in solids found in both real and synthetic process solutions. Since most simple cesium compounds are soluble, this probably indicates the formation of double salts. Thus far, we have been unable to identify these materials.

A matter of continuing concern is the loss of HNO_3 during the storage of highly radioactive solutions. The anticipated acid loss under conditions reasonable for high-level waste storage at AGNS (~100 gal/MTU with an air sparge) is as high as 1 mole per liter per day, based on data for a similar but significantly different chemical system. This acid loss results from radiolysis but occurs only if there is a gas sparge to sweep away the radiolysis products. This high rate of destruction of acid might make it difficult to maintain a reasonable acid concentration in the waste.

Several air sparge tests have been carried out with extraction raffinate and waste concentrates, but most have been inconclusive because of analytical problems and changes in solution volume as a result of evaporation. Since the volume of concentrated waste has been small (generally <50 ml), evaporation can be significant over a period of several days with an air sparge. The analytical procedure has been improved; the problem previously encountered was apparently caused by radiation damage to the electrodes used for titration. We are presently analyzing the solutions for alpha- and gamma-emitters at the same time the acid determinations are made, and the radioisotopic determinations are used to correct the acid values for evaporation. These

modifications have removed much of the scatter from the data. Initially, scatter made data interpretation essentially impossible.

The waste concentrate from run 5 (~60 gal/MTU, 9 M HNO_3) was sparged with air for 14 days, and six samples taken during this period showed a consistent acid loss of 1.7% per day (or a 0.15 M decrease in acidity per day). The waste was then diluted to ~150 gal/MTU, 6.5 M HNO_3, and sparged with air for 22 days. Nine samples were analyzed over this interval, and the data for each were normalized by use of the radioisotopic analyses. The results showed an acid loss of ~0.3% per day (or a 0.02 M decrease in acidity per day).

The AGNS projections for acid loss are much greater than these values, as would be expected, for several reasons. The conditions of the experiments reported here differ greatly from the conditions in a large waste tank containing all the radioactivity initially in the fuel. In our experiments, part of the radioactivity was not present, notably ~50% of the ruthenium, which did not dissolve, and most of the strontium and perhaps 10% of the cesium, which was removed in the form of solids following waste concentration. A rough estimate is that approximately 30% of the decay power was not present in the waste concentrate.

An even larger loss in energy deposition in the solution results from the geometry of the experiment, which was conducted in a small bubbler ~2 cm in diameter. Essentially all the gamma radiation and a significant fraction of the beta radiation escaped from the solution. Thus, the net energy deposited in the liquid could be in the vicinity

of, perhaps, 25% of the decay energy. No attempt has been made to calculate this more accurately from the decay schemes or the geometry of the equipment.

In view of these considerations, it is clear that a significant loss of HNO_3 will be sustained in a large, air-sparged storage tank containing concentrated waste from fuel cooled a few years or less. Our data, which are subject to a high degree of uncertainty, indicate a loss probably somewhat less than that calculated but one which is certainly significant; in fact, it could represent a real operational problem. Unfortunately, experimental duplication of the situation corresponding to a large waste tank appears to be a difficult problem.

2.3 Building 4507 Hot-Cell Operations

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2.3.1 Development of in-cell equipment

The decision to use craft labor for the operations involved in refurbishing Cells 3 and 4 this quarter and an increase in hot-cell staffing made it possible for group personnel to reassume many of their designated development responsibilities. Laboratory cold testing and hot-cell shakedowns of the intermediate-scale head-end reprocessing equipment were resumed in preparation for the scheduled hot-cell work.

Trial voloxidations on pieces of stainless-steel-clad, unirradiated UO_2 rods cut in previous fuel shear tests[5] were made under reference LWR operating conditions (480°C) as a test of the burner's operating characteristics. The results of these voloxidations indicate that both the burner (rotary chain-driven) and its furnace will perform mechanically up to expectations; no major apparent difficulties are foreseen under hot operation.

Fuel oxidation performance was also satisfactory. Burner loadings ranged from 100 to 200 g of fuel and cladding. A typical run consisting of a total of approximately 120 g of material contained about 93 g of UO_2. The length of the sheared pieces was either 1 or 1-1/2 in. Typical run conditions were: a burn time of 2 hr after an initial 45-min heatup, an air flow of 300 cc/min, and a moderate tumbling rate (12 rpm). The average increase in the oxide weight was consistently close to the 3.9% theoretical weight gain. At least 75% of the fuel was dislodged as powder from each piece of cladding. Visual inspection revealed no evidence that the fuel remaining within the cladding was sintered. Separate dissolutions could be performed on hulls and dislodged, irradiated fuel powder in any particular hot run to determine whether tritium release had been impaired by sintering.

In subsequent shakedown tests, all of these conditions, including the reaction temperature, have been varied to determine what effect, if any, they might have on performance. Similar runs have been made under reference LMFBR conditions (600°C) as well.

The intermediate-scale, single-rod fuel shear and the voloxidation burner and furnace have been installed in Cell 3 where cold testing is presently under way. This permits new personnel to familiarize themselves with the setup, operation, and handling of the equipment under simulated run conditions using manipulators and helps pinpoint the modifications needed to permit operation under fully remote conditions. More complete checkout of the voloxidizer operating characteristics becomes possible as additional process monitoring and control equipment is installed in the cell. Flow controls are currently being calibrated. Test burns are being

made with oxygen analyzers in the system to more closely follow oxygen utilization (and hence, the conversion of UO_2 to U_3O_8) during the voloxidation runs.

The intermediate-scale dissolver has also been given a comprehensive checkout under LWR reprocessing conditions in the laboratory using voloxidized (and nonvoloxidized) stainless-steel-clad UO_2. Two dissolver systems have been tested. The first system, which was described previously,[6] consists of a steel dissolver pot on a hot plate and uses a rotating basket to contain the hulls and create a slight tumbling action. The other dissolver system consists of a Pyrex resin flask with standard heating mantle and includes a magnetic stirrer. (This system is patterned after D. O. Campbell's apparatus). In this arrangement, the sheared hulls were contained in a stationary basket suspended just above the dissolver floor. The acid solution was stirred directly below the basket.

All runs made to date have been carried out with an air purge and full reflux for 1 to 2 hr. Each dissolution was started with the fuel in 150 ml of water. Sufficient concentrated nitric acid was added over a 30-min period to give a final solution that was 1.3 M in uranium and 3 M in HNO_3. Analyses have shown the uranium dissolution to be complete with only a trace of insoluble material remaining.

Both dissolver systems have performed satisfactorily; however, cold dissolution shakedowns are continuing. Each system has certain advantages that will be incorporated in future cell work.

2.3.2 Decommissioning the Curium Recovery Facility (CRF)

The Curium Recovery Facility (Cells 3 and 4) in Bldg. 4507 has finally been decommissioned. It was not practical to further decontaminate beta-gamma- and alpha-emitters after the cells had been stripped to bare walls, washed extensively, sandblasted twice, and washed extensively again. Even after two coats of epoxy paint had been applied (last quarter), there was some risk of inhalation hazard; thus the final installation was done in protective clothing.

We started the installation of equipment and services for the LMFBR-LWR fuel reprocessing programs by assigning priority to Cell 3, the fuel storage-shearing-voloxidation cell. Equipment that has now been installed in Cell 3 includes the transfer port assembly between Cell 2 (the dissolution cell) (Fig. 3) and Cell 3, the plenum for cell ventilation exhaust filters, supports for the work tray--storage array and the work trays (Fig. 4), a sample removal--fuel charging chute (Fig. 5), and the cask pedestal in the Penthouse. Services installed include: 15- and 100-psig air, 40-psig water, radioactive waste and process waste drain connections, vessel off-gas, building vacuum, 24 thermocouples, power leads for the voloxidizer and other heaters, fire spray nozzle, sump liquid level alarm and sump jet line to radioactive waste, hydraulic lines and pump for the single-rod shear, external gas supply and controls for the voloxidizer, intercom system, electronic balance leads, heated off-gas line leading to Penthouse analytical equipment, and a number of other service and spare lines (Fig. 6).

The cloudy lead glass shielding windows in Cells 2 and 3 were rinsed with an alcohol-toluene solvent to remove the residual oil, the deposits dissolved in glacial acetic acid, the acid removed with more solvent, and

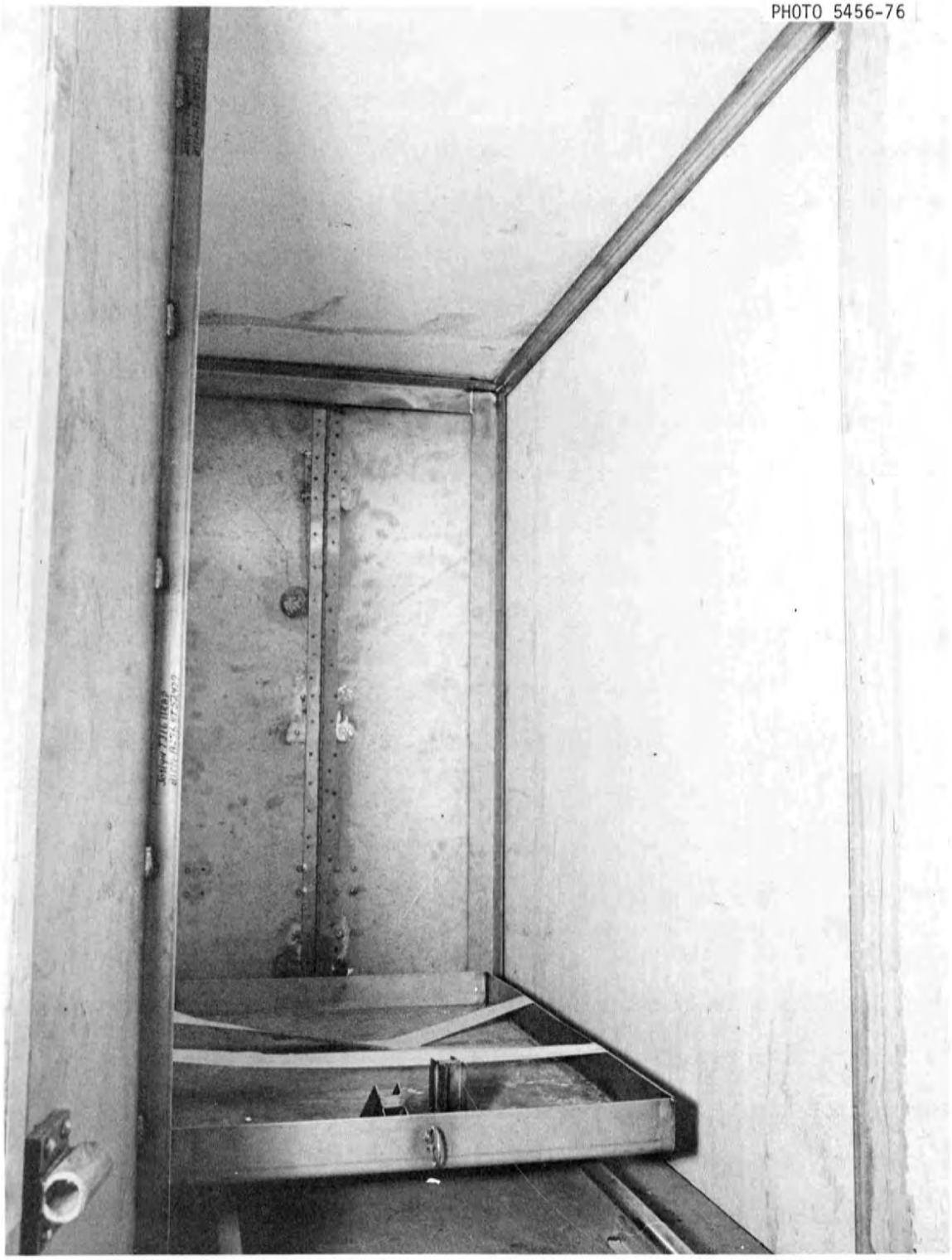

Fig. 3. Intercell transfer port installed in shielding wall between Cells 2 and 3, Bldg. 4507.

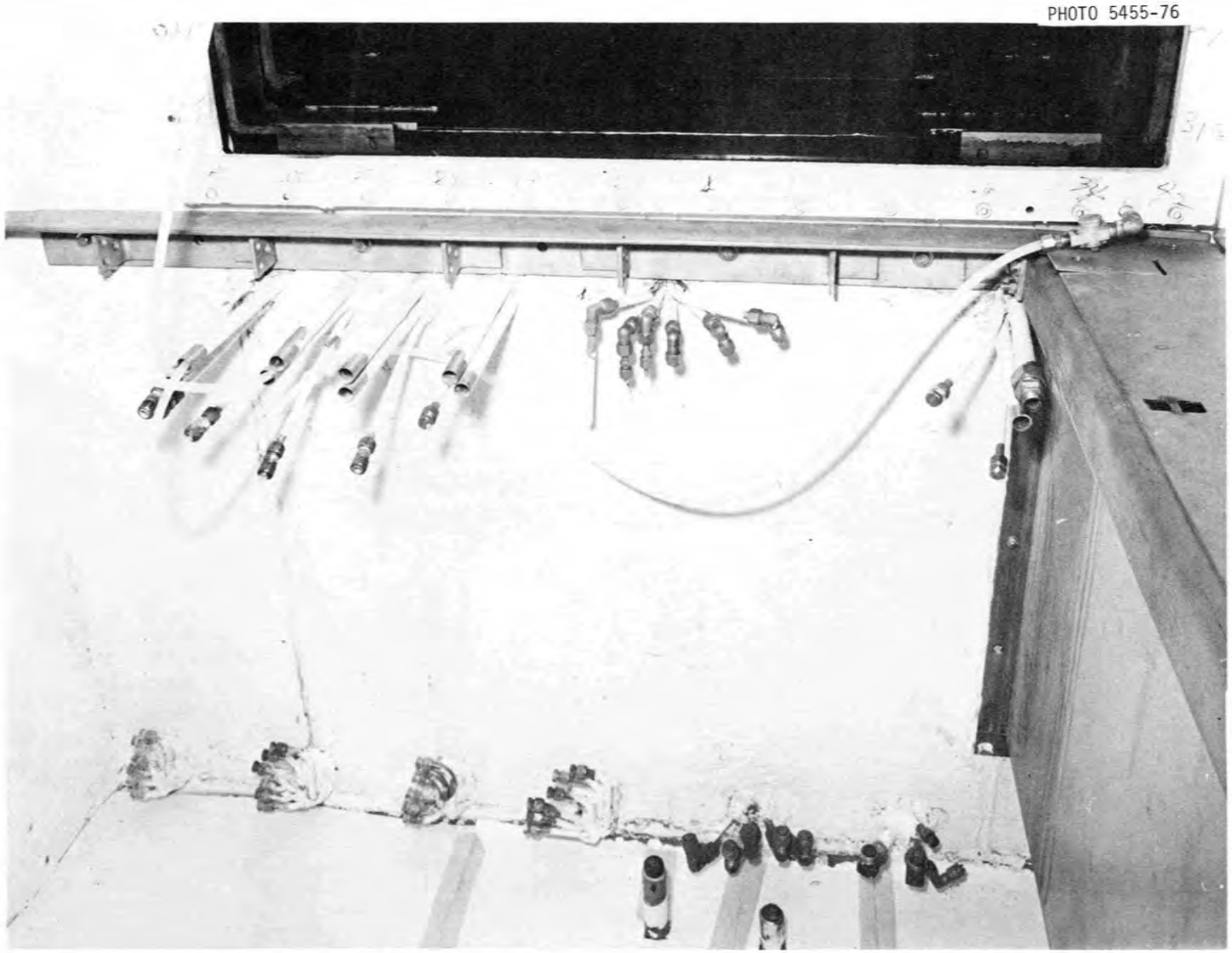

Fig. 4. Filter plenum (right) and work tray supports in Cell 3, Bldg. 4507, at early stage of installation.

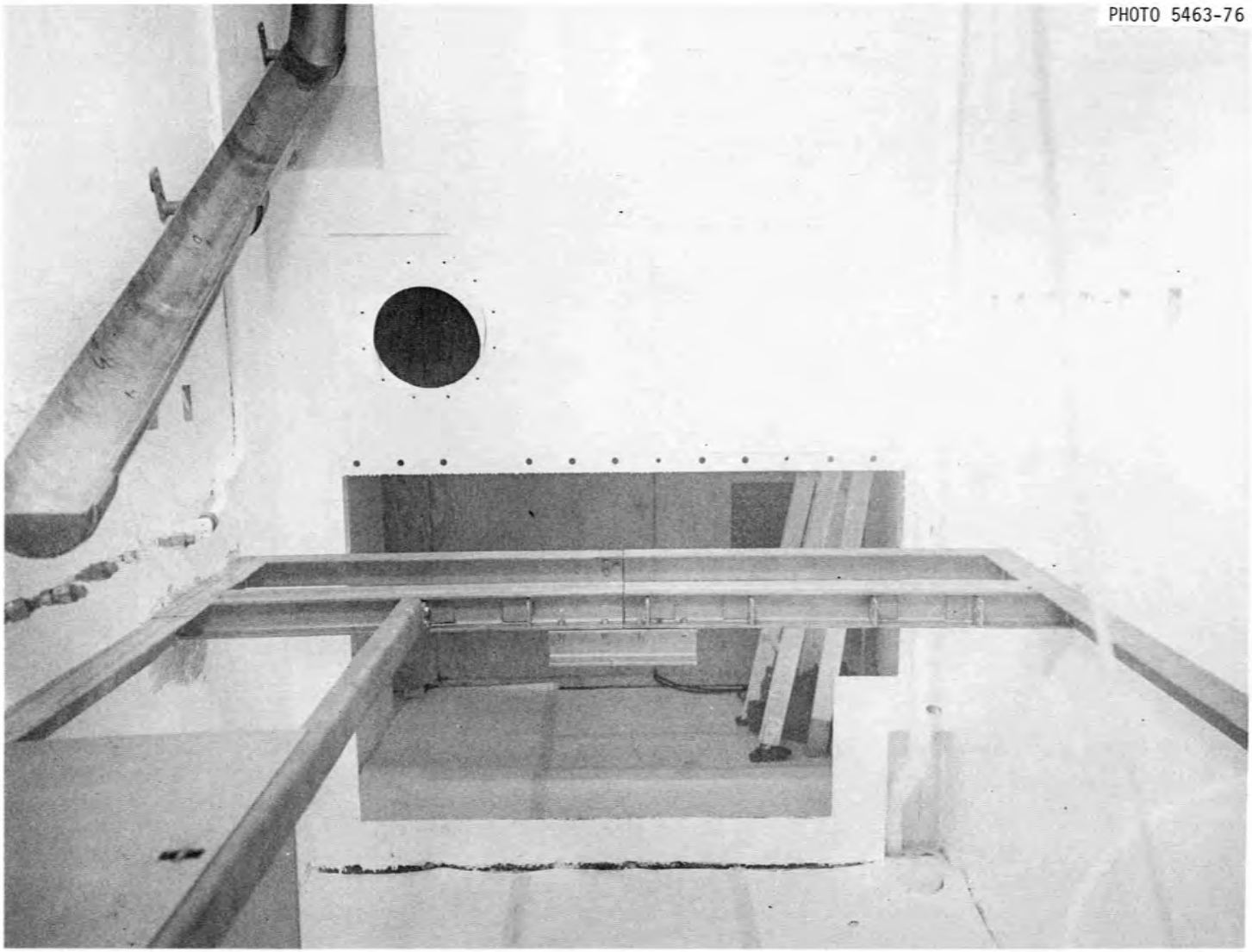

Fig. 5. Work tray supports, sample chute, and part of alpha barrier in Cell 3, Bldg. 4507, at early stage of installation.

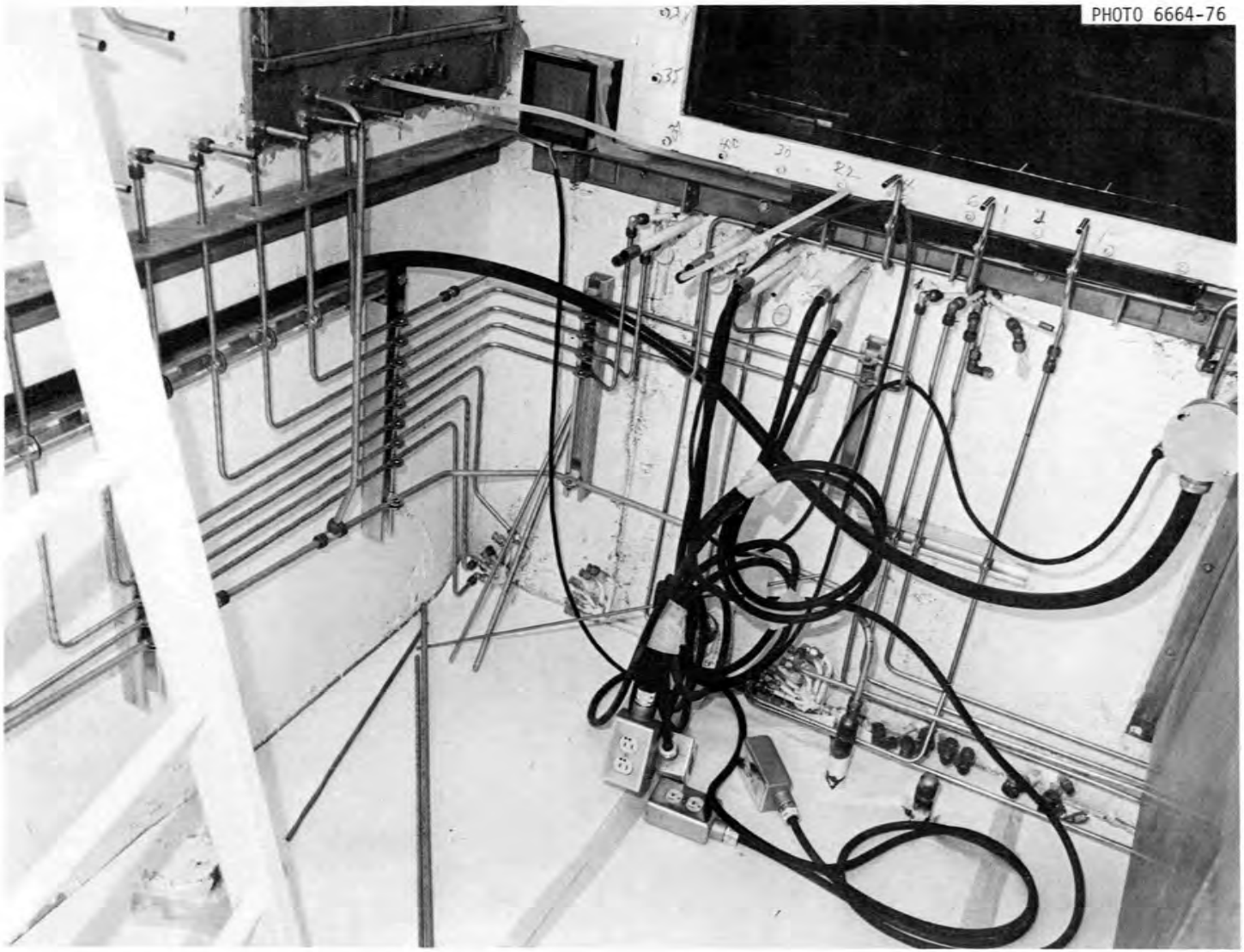

Fig. 6. Portion of electrical and other services installed in Cell 3, Bldg. 4507.

new oil installed. A period of about ten working days was required to clean each window due to precipitation of lead salts from the solvent used to rinse out the acetic acid. Visibility was restored to normal. The mercury lights in Cells 2 and 3 were replaced.

The shear and voloxidizer were installed in Cell 3.

2.3.3 Miscellaneous

The new Equipment Maintenance Glove Box, to be installed above Cells 3 and 4, was designed. A cost estimate is now being prepared. Two shielding plugs for the cell access holes have been fabricated. Concrete shielding plugs for the tops of the fuel storage wells at the Hot Garden were installed.

3. PUREX PROCESS STUDIES (SOLVENT EXTRACTION)

B. L. Vondra (Chemical Technology Division, ORNL)

This program involves the integration of laboratory development studies, flowsheet tests employing synthetic solutions, and confirmatory investigations in a hot-cell system using irradiated LWR fuels.

3.1 Laboratory Studies

J. C. Mailen (Chemical Technology Division, ORNL)

3.1.1 Solvent cleanup

O. K. Tallent and Karen Williams (Chemical Technology Division, ORNL)

The purposes and plans for the study of solvent cleanup methods were discussed in some detail in the last quarterly report.[2] The primary purpose of this work is to develop an improved method for cleanup of Purex recycle solvent. Solid adsorbent work with simulated solvents, which was initiated last quarter,[2] was continued; in addition, work with irradiated solvents was initiated during this report period.

Irradiated solvents. The data obtained on irradiated solvents this quarter in preliminary studies should not be considered to seriously reflect on the merits of a particular Purex flowsheet or solvent cleanup method. They are included here simply to provide general background information which can be useful in planning future experiments.

Specifics about the history of each of three irradiated solvents that were tested are listed in Table 8. For identification purposes, the three solvents have been designated as irradiated and aged, costripped, and reductively stripped.

Table 8. Irradiated solvents[a] used in preliminary solvent cleanup studies

Solvent number	Identification	Type of fuel rod	Hot-cell stripping method	Solvent as received in glove-box facility				Solvent after exhaustive stripping with 0.01 M HNO_3			
				Gross α (counts min^{-1} ml^{-1})	Plutonium (M)	Uranium (M)	β-γ dose rate (R/hr)	Gross α (counts min^{-1} ml^{-1})	Plutonium (M)	Uranium (M)	β-γ dose rate (R/hr)
1	Irradiated and aged	H. B. Robinson reactor	None	3.18×10^{8}	4.0×10^{-3}	0.49	2.0	3.4×10^{7}	4.4×10^{-4}	5.0×10^{-4}	<0.05
2	Costripped	Experimental LMFBR	0.01 M HNO_3	1.40×10^{7}	1.8×10^{-4}	4.2×10^{-4}	<0.06	1.29×10^{7}	1.7×10^{-4}	Not det.	<0.05
3	Reductively stripped	Experimental LMFBR	0.07 M $Fe(NH_2SO_3)_2$--1.4 M HNO_3	1.67×10^{5}	8.8×10^{-6}	>0.10	<0.06	5.01×10^{4}	6.55×10^{-7}	4.6×10^{-3}	<0.05

[a]30% TBP--70% dodecane solvents equilibrated with equal volumes of irradiated fuel dissolver solutions and stripped as indicated.

The irradiated and aged solvent was obtained from D. O. Campbell of the Chemical Technology Division. This solvent (30% TBP--70% dodecane) had been equilibrated with an equal volume of a nitric acid dissolver solution used to dissolve an H. B. Robinson fuel rod in the Bldg. 2026 cell area. Following separation of the phases (contact time, 20 min), the loaded organic solvent had been allowed to stand for about 6 months before 50 ml of the solvent was transferred to the alpha glove-box facility in Bldg. 4501. At the time it was received in the glove-box facility, the solvent had a beta-gamma dose rate of ~2.0 R/hr at contact. The solvent was exhaustively stripped or back-extracted with 0.01 M HNO_3 behind localized lead shielding in a glove box, after which the dose-rate reading decreased to ~60 mR/hr. At this point, the gross alpha count, the plutonium concentration, and the uranium concentration in the solvent were 3.4×10^7 counts min^{-1} ml^{-1}, 4.4×10^{-4} M, and 5.0×10^{-4} M, respectively. Several wash solutions were tested for their effectiveness in removing the retained plutonium from the solvent. The results (see Table 9) showed that 99, 99, 87, and 68%, respectively, of the retained plutonium was removed by individual, equal-volume, 1-hr equilibrations with 1.0 M Na_2CO_3, 0.1 M $N_2H_4 \cdot H_2O$, 0.39 M $UO_2(NO_3)_2$, and 4.0 M HNO_3--0.04 M HF wash solutions.

The dissolver solution used in the extraction to prepare the costripped solvent was obtained via the dissolution of an experimental LMFBR fuel rod. This dissolution was carried out in Bldg. 2026 by J. H. Goode (of the Chemical Technology Division), and the dissolver solution was transferred to Bldg. 7920 to M. H. Lloyd (of the Chemical Technology Division). The dissolver solution was extracted in the cell area in Bldg. 7920 with an equal volume of 30% TBP--dodecane, and the TBP-dodecane extractant was

Table 9. Plutonium retention in aged, irradiated Purex solvent:[a] effects of aqueous washes

Aqueous wash solution[b]	Percent plutonium retention
1.0 M Na_2CO_3	<1
0.1 M $N_2H_4 \cdot H_2O$	<1
0.39 M $UO_2(NO_3)_2$	13
4.0 M HNO_3--0.04 M HF	32

[a]H. B. Robinson reactor fuel dissolvent extracted with 30% TBP--dodecane, after which the solvent was allowed to age six months before being exhaustively stripped with 0.01 M HNO_3. The plutonium solvent concentration was 4.4×10^{-4} M.

[b]Organic/aqueous volume ratio = 1.

immediately stripped with three equal volumes of 0.01 M HNO_3 to costrip most of the plutonium and uranium. The solvent was subsequently transferred to the alpha glove-box facility in Bldg. 4501; at this time the beta-gamma dose rate for 50 ml of the solvent was ~60 mR/hr. After exhaustive stripping with 0.01 M HNO_3, the gross alpha count and the plutonium concentration in the solvent were 1.29×10^7 counts min^{-1} ml^{-1} and 1.7×10^{-4} M respectively. The effectiveness of alternative aqueous wash solutions, ion exchange resins, and filtration in removing the retained plutonium from the solvent was investigated. The results showed (see Table 10) that: (1) 1.0-hr equal-volume equilibrations with 1.0 M Na_2CO_3 and with 4.0 M HNO_3--0.04 M HF, respectively, removed 99 and 78% of the originally retained plutonium; (2) 5 ml of solvent equilibrated with 1.0 g of MP-50, MP-1, or A-26 ion exchange resins removed 24, 48, or 92%, respectively, of the originally retained plutonium; and (3) slow filtration of the solvent with a fine glass frit removed ~12% of the originally retained plutonium.

The history of the reductively stripped solvent is similar to that of the costripped solvent except that the former was first stripped with three equal volumes of 0.07 M $Fe(NH_2SO_3)_2$--1.4 M HNO_3 instead of with 0.01 M HNO_3. The plutonium was back-extracted with this reductive strip in a manner similar to that used in the Purex partition column. After the reductive strip, this solvent was exhaustively stripped with 0.01 M HNO_3 to back-extract the uranium as in the Purex "C" column. Following the exhaustive strip, the gross alpha count, the plutonium concentration, and the uranium concentration were 5.01×10^4 counts min^{-1} ml^{-1}, 6.5×10^{-7} M, and 4.6×10^{-3} M (1.1 mg/ml) respectively. The plutonium concentration

Table 10. Plutonium and uranium retained in nonaged, irradiated Purex solvent[a] after preliminary cleanup treatments

Treatment method	Post-treatment retentions		
	Gross α counts min^{-1} ml^{-1}	Pu (M)	U (M)
Wash with equal volume of 1.0 M Na_2CO_3	1.38×10^4	1.8×10^{-7}	$<4 \times 10^{-4}$
Wash with equal volume of 4.0 M HNO_3--0.04 M HF	2.83×10^6	3.7×10^{-5}	$<4 \times 10^{-4}$
MP-50 cation resin[b]	1.03×10^7	1.3×10^{-4}	Not det.
MP-1 anion resin[b]	6.73×10^6	8.8×10^{-5}	Not det.
A-26 anion resin[b]	1.10×10^6	1.4×10^{-5}	Not det.
Filtration through fine glass frit	1.17×10^7	1.5×10^{-4}	$<4 \times 10^{-4}$

[a]Experimental LMFBR-type fuel dissolvent extracted with 30% TBP--70% dodecane after which the solvent was immediately back-extracted with 0.01 M HNO_3. The gross alpha count and the plutonium concentration in the solvent were 1.29×10^7 counts min^{-1} ml^{-1} and 1.7×10^{-4} M, respectively.

[b]1.0 g of resin equilibrated for 1 hr with 5.0 ml of solvent.

retained in this solvent was relatively low compared with that retained in the other two solvents. The plutonium and the uranium concentrations in the solvent were decreased further to 2.1×10^{-7} and 1.26×10^{-4} M, respectively, by equilibrating 5.0 ml of the solvent with 0.50 g of MP-50 cation resin for 1 hr. A sample of this solvent has been submitted to the Analytical Chemistry Division for gas chromatographic and mass spectrographic analyses.

Discussion of irradiated solvent tests. The studies that were carried out using irradiated solvents allow a number of significant observations and conclusions:

1. Even solvents which have contacted fuel solutions for extended periods of time can be easily decontaminated to levels consistent with glove-box studies.
2. Reductive stripping of plutonium from the solvent resulted in a much lower level of "unstrippable" plutonium than was attained by costripping with 0.01 M HNO_3. The apparent mechanism is reduction of complexed Pu(IV) to Pu (III), which forms only weak complexes. The larger quantity of uranium held in the reductively stripped solvent is consistent with the fact that removal of more plutonium from the solvent makes more complexing agent available to complex uranium.
3. Plutonium can be displaced from the complexes by scrubbing with uranyl nitrate solution, as shown in Table 9 for the irradiated, aged solvent, where 87% of the "unstrippable" plutonium was removed by a 0.39 M $UO_2(NO_3)_2$ wash.
4. A 0.1 M $N_2H_4 \cdot H_2O$ wash was as effective as 1 M Na_2CO_3 in removal of plutonium from degraded solvent.

5. The fact that the resin treatments were not as effective in removing plutonium from irradiated solvent as they were in tests using solvent containing only mono- and dibutyl phosphate[2] is evidence for other plutonium complexes or forms in the irradiated solvents. The removal of a small portion of the plutonium by filtration through a fine glass frit demonstrates the presence of some insoluble plutonium species.

Tests with solid adsorbents using simulated Purex solvents. The objective of this particular task is to evaluate, on a laboratory scale, a number of new (or partially new) methods utilizing solid adsorbents for purifying recycle Purex solvents. Information was previously reported[2] on several tests in which plutonium was adsorbed on macroreticular resins from simulated Purex solvents. Additional information has been obtained on the effects of acid concentration in these tests, as discussed below.

The experimental data were obtained in two runs using MP-50 cation resin as the adsorbent and dibutyl phosphate (DPB) and plutonium as the solvent impurities. In each run, 1.00 ± 0.001 g of moist resin was equilibrated with 10 ml of solvent at 25°C for 1.0 hr. The composition of the solvent was 30% TBP--0.0011 M DBP--0.0038 M Pu(IV)--0.03 to 1.0 M HNO_3 in dodecane. Solvent effluent samples were analyzed for plutonium using gross alpha and alpha pulse-height techniques. Plutonium distribution coefficients were calculated by dividing the concentration of plutonium adsorbed per gram of resin by the effluent plutonium concentration per milliliter.

The logarithms of the 1.0-hr distribution coefficients obtained are plotted vs solvent HNO_3 concentration in Fig. 7. The conditions for the two runs are similar except that the reagents were prepared separately and

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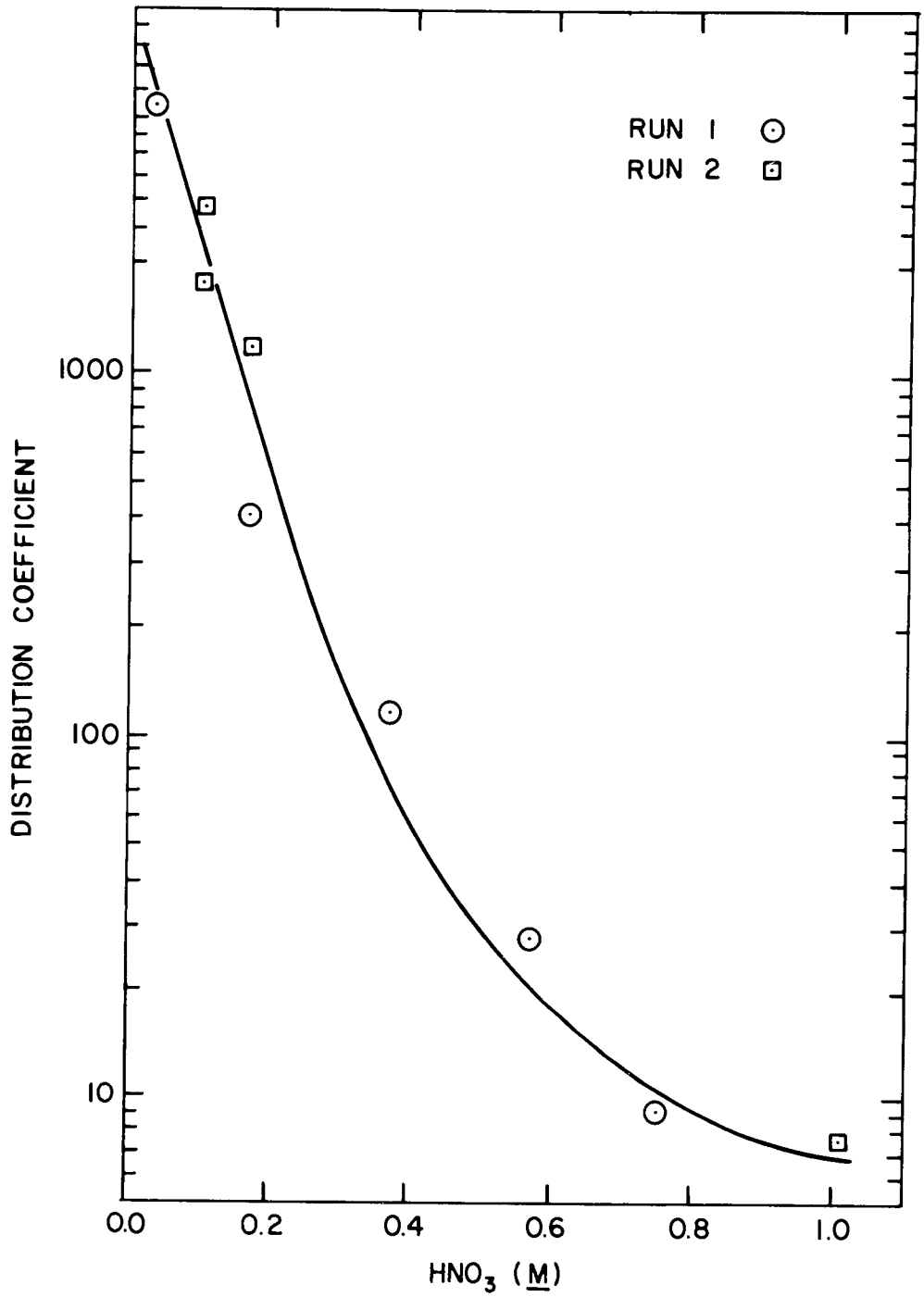

Fig. 7. Adsorption of plutonium from simulated Purex solvent on MP-50 macroreticular resin as a function of acid concentration.

the runs were conducted at different times. The plot clearly illustrates the strong dependence of plutonium adsorption in this system on the acid concentration of the solvent.

3.1.2 Ruthenium chemistry

L. Maya (Chemistry Division, ORNL)

Rutheniumnitrosyl hydroxide labeled with ^{106}Ru was prepared so as to give a final activity of 70 μCi/g. This compound will be used in preparing equilibrium mixtures of nitrosylruthenium nitrates from which the isolation of highly extractable species will be attempted by reversed-phase chromatography. The chromatographic support was prepared by adsorbing TBP on dry macroreticular nonionic resin (XAD-2*). The amount of TBP retained after extensive water washing was equivalent to 51 wt % of the support. This support resembles the commercial product Levextrel, which is used by German workers[7] for column extractions.

A highly extractable ruthenium species was detected by Joon[8] using TBP adsorbed on Celite; however, it could not be desorbed from the column except by elution with 24 N HNO_3. This treatment prevented any further tests on the nature of the species. The use of an organic support, as envisaged for our work, will allow the highly extractable species to be released under much milder conditions. A preliminary test showed that benzene completely desorbs the TBP from the resin. This treatment will allow isolation of the species, determination of their distribution coefficients, and, possibly, their identification by chemical and spectroscopic means.

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*Rohm and Haas.

3.1.3 Solvent extraction kinetics

D. E. Horner (Chemical Technology Division, ORNL)

A topical report summarizing several years of process development of solvent extraction was completed. Publication of this report should provide useful background information for both present and future LWR (as well as LMFBR) processing programs.

Laboratory studies have been initiated to determine the relative kinetics of the distribution of uranium (later, plutonium) and important fission products between organic and aqueous phases. The first set of measurements will utilize a falling and rising drop technique in typical glass equipment. The effects of important process variables such as temperature, TBP concentration, solvent loading, and aqueous composition will be determined. This work will be followed by tests with miniature centrifugal contactors, when available, to demonstrate separations based on any differences in distribution rates determined by the previous technique. The anticipated goal of this work is to increase decontamination factors (DFs) during solvent extraction by taking advantage of possible rate differences.

3.1.4 Plutonium extraction studies

R. H. Rainey, J. T. Barker, and J. H. Paehler (Chemical Technology Division, ORNL)

One area of concern in the Purex process is the possibility that unusual or unexpected conditions might lead to breakthrough of plutonium into the "C" column where low acid conditions exist and polymerization of the plutonium could occur. In order to study this column under such conditions, a plutonium stock solution low in acid content and high in

plutonium concentration is required; normal resin loading and elution techniques do not produce the required solution. Small-scale tests of loading and elution methods are being performed to develop these operations before the bulk of the plutonium stock solution is prepared. Plutonium (IV) nitrate could be eluted more easily from Ionac A-580, a strong base anion exchange resin with quaternary ammonium and pyridinium groups, than from Dowex 1, which has only quaternary ammonium groups. No polymer was found in the plutonium product when HNO_3 concentrations as low as 0.1 M were used as the eluent; however, some disproportionation may have occurred at the lower acidities. These combinations of resin and eluent should be capable of producing the needed plutonium stock solutions.

The data base for the SEPHIS code is being extended; equilibrium extraction data are being accumulated over a wide range of TBP concentrations. The distribution coefficients for uranium and plutonium in nitric acid are being determined for 6% TBP.

3.1.5 Analytical development

D. A. Lee (Analytical Chemistry Division, ORNL)

Gas chromatographic (GC) and liquid chromatographic (LC) equipment have been ordered for the development of analytical methods for the chemical reprocessing flowsheet for LMFBR fuels. The gas chromatograph ordered will be identical to the instruments used by the Chemistry Division (A. D. Kelmers) in the study of Purex processing. It will be used primarily for analyzing nitrogen oxides evolved from various chemical reactions, including plutonium valence adjustment, denitration, waste treatment, and fuel dissolution. The unit is capable of being used in a glove box.

The LC system consists of modular units which may be adapted to several of the analytical chemistry problems associated with the Purex process. Liquid chromatography will be used to quantitatively determine nitrogen-containing species (i.e., NH_4^+, NH_2OH, HN_3, HNO_2, HNO_3, and H_4N_2) in effluents from the reductive stripping of plutonium in Purex processing. It may also be used to analyze for organic degradation products and fission products. The LC units are readily adaptable to glove-box operation.

3.2 Purex Studies with Irradiated Fuels

V. C. A. Vaughen (Chemical Technology Division, ORNL)

Detailed engineering flowsheets have been completed for the Purex flowsheet test facility to be installed in Cell 5 of the TRU facility. Study and estimates are being made of the design, fabrication, and installation of the equipment and instrumentation needed. Fabrication of the mixer-settlers by an outside vendor is essentially complete. Existing flow control instrumentation is being evaluated.

3.2.1 Purex process studies

H. C. Savage, L. J. King, and V. C. A. Vaughen (Chemical Technology Division, ORNL)

The preliminary equipment flowsheet[9] for the Purex solvent extraction system to be installed in Cell 5 at the TRU facility has been upgraded to detailed engineering flowsheets required to install the system in Cell 5. The detailed flowsheets indicate the interconnections with existing service and process lines, auxiliary equipment, and instrumentation. An instrument and controls flowsheet has also been prepared. Instrumentation that has already been installed or is on hand and can be used in the Purex hot-cell

system has been identified, and a tabulation of the additional instrumentation that must be procured has been prepared. Delivery of the three 16-stage mixer-settlers to be used for the extraction, partitioning, and stripping banks in the system is expected during the first week in January.

Study and estimates are being made of the design, fabrication, and installation of the equipment and instrumentation required for the Purex Flowsheet Test Facility (PFTF) in Cell 5 at TRU. The PFTF will be capable of processing LWR fuel through one cycle of solvent extraction at the rate of about 4 kg/day. Each test period will require at least 2 kg of fuel, and the number of tests undertaken in any campaign will be limited by plutonium inventory since the equipment will not be geometrically safe. Major new equipment items include: (1) an equipment rack for mounting the three mixer-settlers; (2) an equipment rack for sampling process tanks located in the Cell 5 tank pit and for converting the first-cycle plutonium product to a form that will be suitable for disposal or storage as solid waste (without further purification at this time); (3) an equipment rack containing a dissolver, feed adjustment tank, feed tank, and feed rate control system; (4) bundles of process lines to connect equipment items in the processing cubicle to tanks in the tank pit; and (5) one stainless steel and seven glass-pipe makeup and head tanks for cold solutions. As part of a cost reduction effort, many of the instruments needed will be salvaged from the CRF, Bldg. 4507. In addition, all seven of the process catch tanks in the tank pits will be spare or excess TRU project tanks made from Zircaloy-2, Hastelloy C, or tantalum. Since these materials of construction are foreign to an LWR reprocessing plant, we cannot use the tanks to store effluent solutions for other studies.

Thus, provisions are being made to collect relatively large samples of effluent streams in temporary containers so that follow-up studies of solvent treatment, waste treatment, plutonium recovery, uranium recovery, and solids handling will not be obfuscated by the presence of contaminants from the existing pit tanks. We plan to fabricate most of the new equipment from 304 or 304L stainless steel or glass. Process solutions will be handled only in stainless steel or temporary plastic lines; however, many Zircaloy-2, Hastelloy C, and tantalum lines presently installed at TRU will be used for off-gas and instrument service.

In order to adequately test flowsheet improvements in the hot-cell Purex solvent extraction system, the flow rates of all input streams to the mixer-settlers must be maintained within relatively narrow limits throughout each run. These limits are being defined. Flow rates of the various feed streams will range between about 2 and 80 cc/min. The desired flow of each input stream will be obtained from pressurized tanks and valves that are controlled and monitored by differential pressure cells equipped with capillary tubes and feedback controllers or other suitable flow control devices. Pneumatic differential pressure cells salvaged from the CRF are to be used for the nonradioactive feed solutions if they will provide the necessary control of flow rates. A differential pressure cell with electronic output is preferred for the 1AF feed system, which is inside the hot cell, since no direct pipes leading outside the cell are required and the electronic control system can be mounted outside the cell for necessary adjustment and maintenance.

Two prototype pneumatic flow control systems have been assembled for testing and evaluation. Each system consists of a pneumatic differential

pressure cell, transmitter, recorder/controller, and a control valve with pneumatic operator. One system was sized for water flow rates in the range of 0 to 40 cc/min using a capillary tube flow element 1/8 in. (3.2 mm) OD x 0.069 in. (1.8 mm) ID by 2 ft (0.61 m) long. The second system was sized for water flow rates of 0 to 15 cc/min using the same type of capillary tube flow element, but 3 ft (0.91 m) long. Testing and calibration of these systems indicated that water flow rates between ~3 and ~40 cc/min could be controlled by either system within less then ±5% of the set point (95% confidence) from a feed tank pressurized to 5 psig (3.5×10^4 Pa). No significant effect was observed when the feed tank pressure was increased to 10 psig (6.9×10^4 Pa). Further tests and calibrations of these two flow control systems are in progress using 30% TBP in n-dodecane (NDD) as the feed solution.

3.2.2 Solvent extraction flowsheet development

R. H. Rainey (Chemical Technology Division, ORNL)

Analyses of the experiments made to determine the effectiveness of the mixer-settlers in the stripping cycle (see Sect. 3.3) have shown that there is sufficient mixing to reach equilibrium. The uranium profile in the system was in close agreement with the concentrations calculated by SEPHIS, but the operating line obtained by stepping off from the profile data did not match the theoretical operating line (Fig. 8). Apparently, some internal recycle (at each stage) decreased the stage efficiency to about 75 to 80%. Analytical errors in the profile data are clearly shown by this plot. In certain cases, the aqueous-phase analyses of samples were obviously too low. The results indicate that it may be possible to use SEPHIS calculations for the equilibrium profile instead of the shakeout

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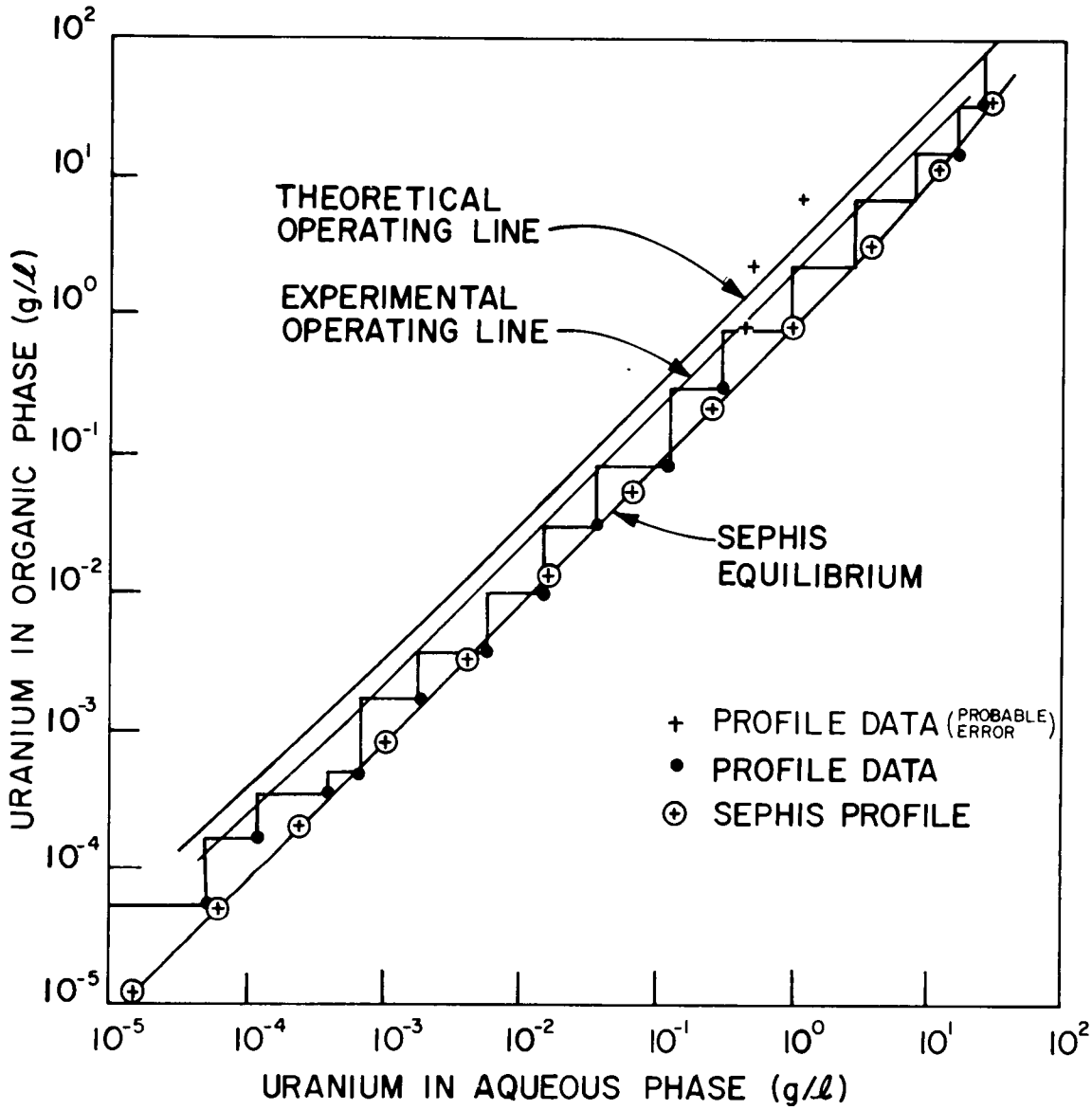

Fig. 8. Analysis of mixer-settler run (run HD-6, strip column) using SEPHIS calculations.

samples usually required for the analysis of this type of experiment. This would save a large amount of time for the operators, eliminate the need for large numbers of analytical samples, and greatly simplify the hot-cell studies. We will continue to use both methods to gain more confidence in the technique. We plan to reduce the number of shakeout samples to a minimum for the redundant confirmation that SEPHIS is being given the proper inputs.

The analysis of similar experiments relative to the uranium extraction cycle using HNO_3 or HNO_3 containing nonradioactive fission product elements in a synthetic LWR feed gave similar performance efficiency results. These studies also showed that the existing pumping system was not capable of attaining long-term flow stability. The runs are reported more fully in Sect. 3.3.

3.3 Cold Studies

W. D. Bond and F. A. Kappelmann (Chemical Technology Division, ORNL)

Work performed this quarter consisted of flowsheet studies using mixer-settlers. Some equipment modifications of the mixer-settler system were also made.

3.3.1 Mixer-settler extraction studies

A second experimental run (R-2) with a uranyl nitrate feed solution containing 284 g of uranium per liter and cold fission products was made using two 16-stage mixer-settler banks. Photographs of the equipment are shown in Figs. 9 and 10. The purpose of the run was to evaluate flowsheet conditions and the mixer-settler units in the extraction and stripping of

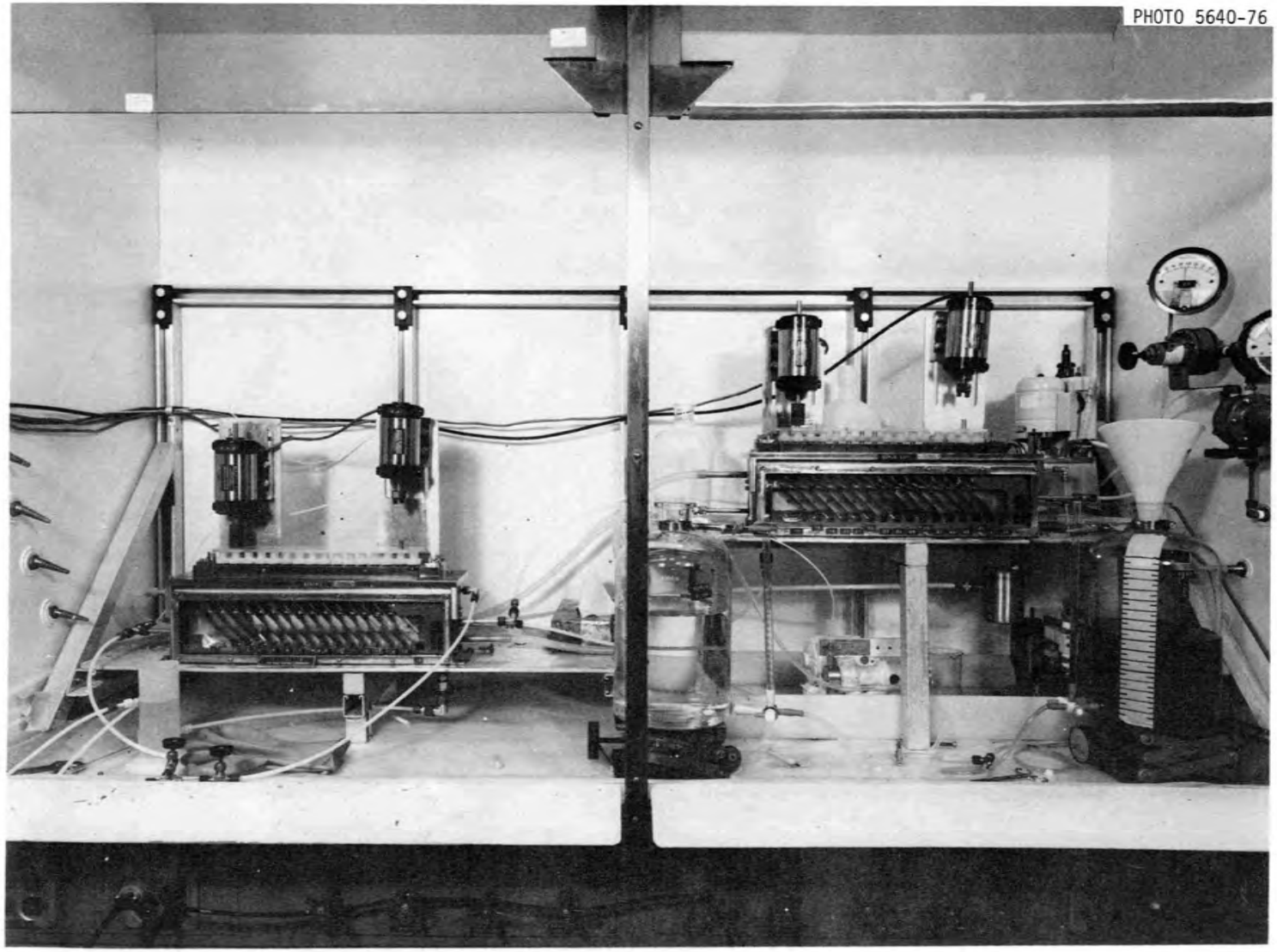

Fig. 9. Overall view of mixer-settler equipment.

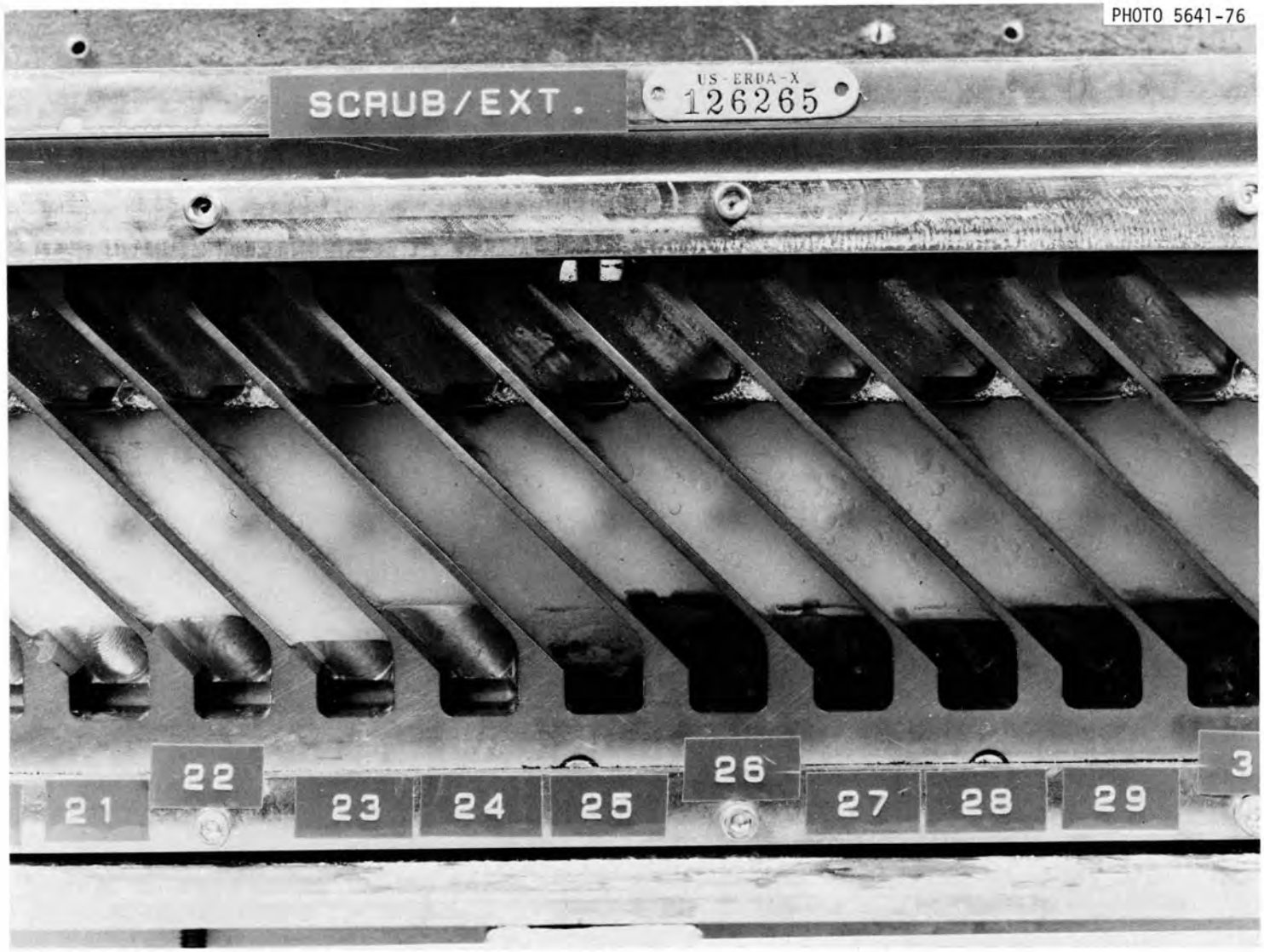

Fig. 10. Closeup of extraction and scrubbing stages during run R-2. Feed stage = 25.

uranium. A temperature of 42 to 43°C was used for each of the mixer-settler units. The flowsheet conditions, which were provided by R. H. Rainey, were as follows:

Extraction Bank - Feed:	284 g of uranium per liter with cold fission products in 2.5 M HNO_3 (at 0.5 liter/hr)
Solvent:	30% TBP--dodecane (at 1.75 liters/hr)
Scrub (8 stages):	3 M HNO_3 (at 0.2 liter/hr)

The organic phase from the extraction bank was stripped with 0.3 M HNO_3 flowing at 4.0 liters/hr. The uranium-laden solvent from the extraction bank entered stage 16 of the stripping bank. To avoid phase disengagement difficulties, the stripping solution was metered to stage 1 at 0.5 liter/hr and to stage 5 at 3.5 liters/hr. Subsequent tests showed that it was not necessary to divide the stripping solution; thus, all of it could be pumped to stage 1.

Operations with both mixer-settler banks were satisfactory. Samples of the exiting aqueous and organic streams were taken for uranium and HNO_3 analyses at intervals of 1 hr during the run (duration, 11.5 hr). On completion of the run, aqueous and organic samples were taken from each stage; in addition, equilibration shakeout tests were performed for each stage. The uranium was found to be distributed in the various exit streams as follows:

Extraction raffinate:	$<0.01\%$
Stripped organic:	0.02%
Aqueous product:	99.97%

Uranium distribution coefficients for each stage of the mixer-settler system were in agreement with SEPHIS calculations. The stage efficiency for each bank of mixer-settlers was about 70%.

Several experimental runs were made to determine stable flow conditions for the stripping bank. In these experiments, the aqueous flow entered stage 1 and the total flow of the organic and aqueous streams was varied. In the first run (duration, 12 hr), the stripping bank operated with the organic phase continuous at an aqueous/organic (A/O) ratio of 2.29 with the solvent flow at 0.875 liter/hr and the aqueous flow at 2.0 liters/hr. The unit operated satisfactorily, and excellent stripping of the uranium was obtained during the run.

In the second run (duration, 10 hr), the stripping bank operated with the aqueous phase continuous at a A/O ratio of 3.08 with the solvent flow at 1.3 liters/hr and the aqueous flow at 4.0 liters/hr. The unit operated satisfactorily, and excellent uranium stripping was obtained during the run.

3.3.2 Modifications for the mixer-settler system

New Milton-Roy pumps and new head tanks were installed for the feed, scrub, extractant, and strip solutions. These modifications should ensure more efficient control of pumping rates and more constant flow rates to the mixer-settler system.

4. OFF-GASES - FLUOROCARBON ABSORPTION STUDIES*

M. J. Stephenson (ORGDP)

This program is concerned with the development of the Krypton Absorption process on an accelerated basis. Funding is provided for expansion of the pilot-plant development, initiation of plant engineering design criteria, performance of a proposed system reliability analysis, and a study of the chemical effects of impurities in the fluorocarbon solvent on the process and equipment.

4.1 Fluorocarbon Absorption Process Development

M. J. Stephenson (ORGDP)

4.1.1 Pilot-plant operation

M. J. Stephenson, R. S. Eby, V. C. Huffstetler, and B. E. Kanak (ORGDP)

The development of the fluorocarbon process is continuing at the selective absorption pilot plant. Tests scheduled under campaign 4 have been initiated to further define the general process disposition of various feed gas components and the effects of these components on the operability and overall performance of the process. Current tests with krypton have explored the consequences of lower absorption pressures (i.e., 100 psig vs 300 psig) and have more accurately defined the fractionation requirements necessary to yield various product concentration factors. The data show that high krypton removals (e.g., 90 to 99%) can still be achieved at the lower absorber pressures but that higher solvent flow rates are required to offset the resulting solubility differences. Fractionation

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*Jointly funded by LWR Recycle and LMFBR Reprocessing Programs.

tests indicate that a wide range of fractionator pressures will yield primary process product concentration factors in excess of 1000; however, this becomes more difficult to achieve as the pressure and, consequently, the temperature of the fractionator are increased.

Results of tests designed to determine the low-pressure operating capability of the fluorocarbon process are summarized in Fig. 11. Here, the absorber DF is plotted against the average absorption factor, kG/L, and column pressure. The relative benefit of a 15-ft column vs the standard 9-ft contactor is also shown. As the average absorption factor was varied from 0.96 to 0.41, the column DF increased from approximately 5 to nearly 1000. Pressure effects on column behavior are predictable. Specifically, higher liquid flows were necessary at the lower pressures to achieve krypton removals comparable to those measured at 300 psig. Physical flow limitation of the equipment forced tests to be conducted in restricted flow ranges. Gas and liquid flows required to achieve higher DFs, especially at the lower column pressures, could not be achieved without changing the trim of various control valves.

Whether more contacting stages will significantly improve the performance of the absorber depends on the kinetics of the particular system as established by the selected operating conditions and, consequently, the location in the column where the mass transfer is taking place. Increasing the column packed height from 9 ft to 15 ft generally increased the krypton removal capability of the column. As can be seen in Fig. 11, use of the longer column resulted in a substantial improvement in some cases. However, when the average absorption factor was less than 0.5 or greater than 0.9, the improvement was only marginal. Descriptive absorber column concentration

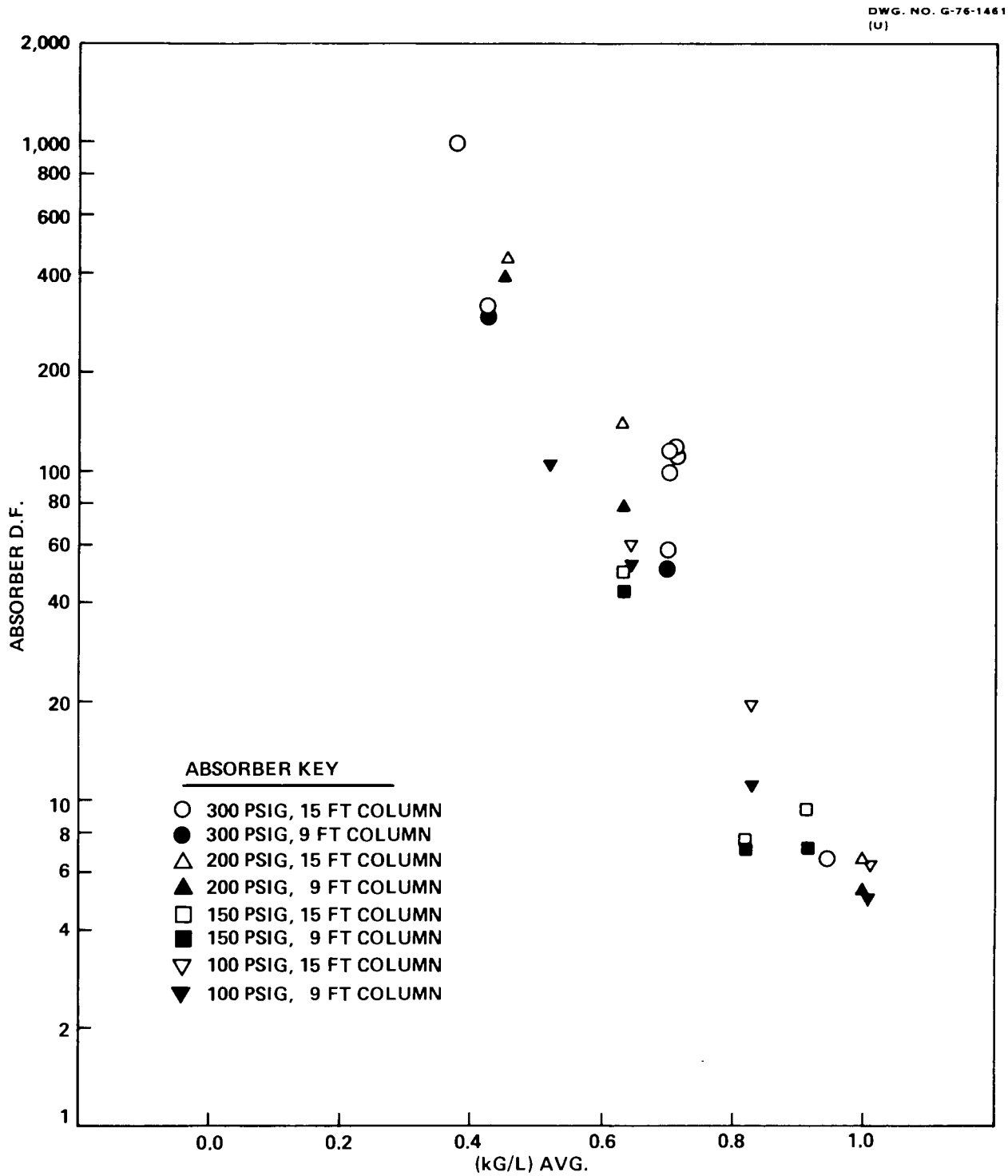

Fig. 11. Absorber krypton DF as a function of absorption factor and pressure.

profiles have been obtained for each of the runs using a scanning gamma scintillation technique and are now being analyzed to provide design and operating guidelines. These data and accompanying interpretation will soon be available.

The purpose of the fractionator is to remove the bulk of the coabsorbed carrier gas from the solvent leaving the absorber prior to noble gas and ^{14}C collection in the stripper off-gas. The intermediate step is necessary to achieve the desired fission product purity. The results of a series of pilot-plant tests designed to more accurately quantify the operation of this important piece of equipment are summarized in Fig. 12. In this figure, the krypton concentration factor is plotted as a function of heat input and operating pressure. Various fractionation parameters, including column pressure drop and inlet solvent temperature, were examined to establish parametric dependencies. In two series of runs (i.e., the runs conducted at 50 and 100 psig), a large variation in fractionator operation was achieved and krypton concentration factors varied by a factor of 3 in each case. Significantly more heat was required per pound of solvent being treated to achieve DFs in excess of 1000 for those runs conducted at 100 psig as compared with the tests conducted at 50 psig. This is because more heat was needed to warm the incoming solvent from the feed temperature of near -25°F to the boiling point of the solvent at the higher column pressure. For example, the boiling point of refrigerant-12 (R-12) is about 52°F at 50 psig, but increases to 88°F at 100 psig.

It should be noted that the primary process concentration factors given in Fig. 12 do not represent process limits but only the results obtained by operation of the pilot plant within certain defined limits.

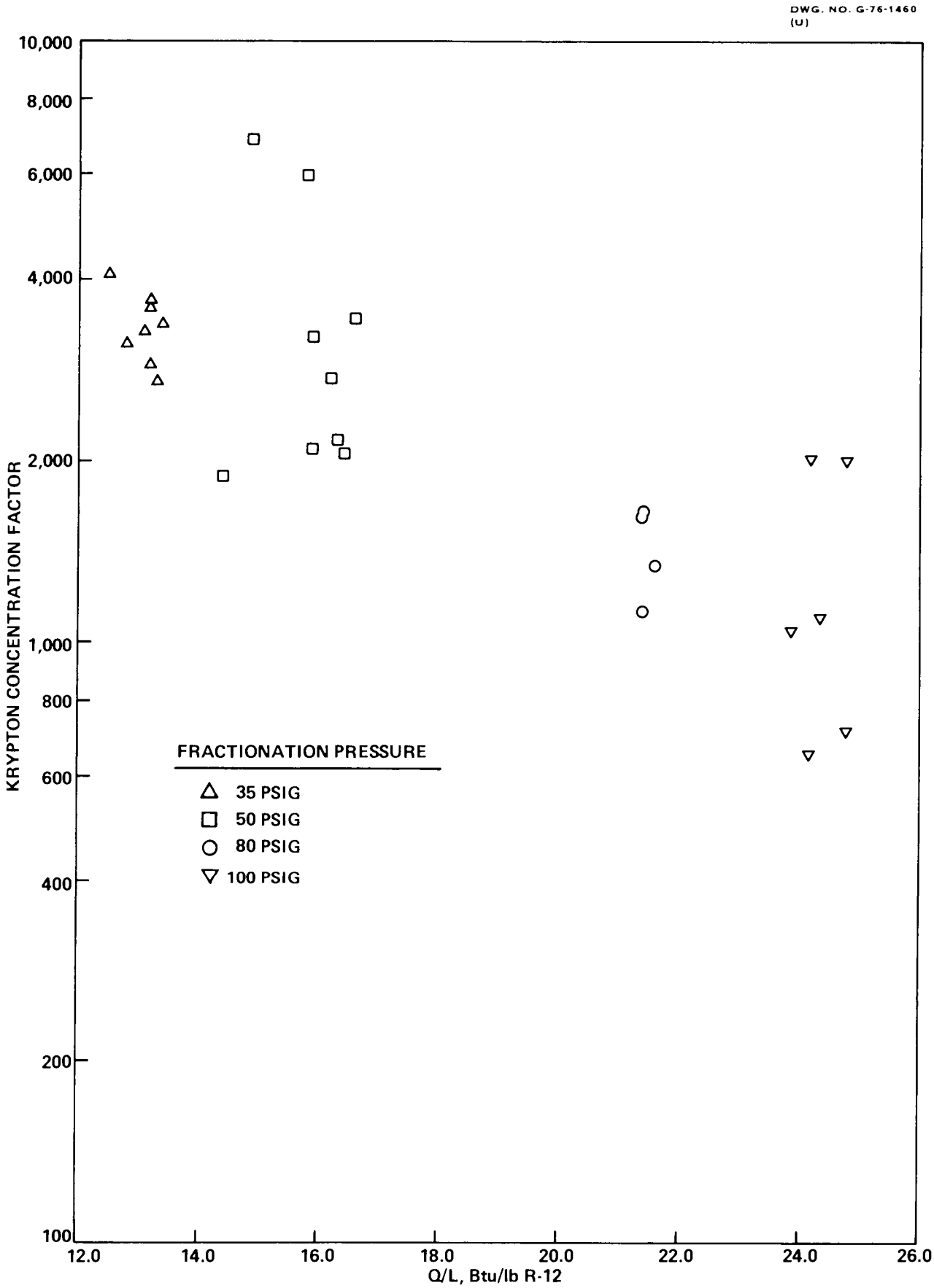

Fig. 12. Primary process concentration factor as a function of fractionator operation.

Also, the concentration capability of the process is dependent on the concentrations of other soluble feed gas components in the process feed gas such as xenon and carbon dioxide. These components were not present in any significant quantities during the tests described here. Significantly higher concentration factors are expected once the product purification equipment is installed, even in the presence of all expected soluble feed gas components.

The pilot-plant work with xenon scheduled under campaign 4 has been completed, but all analytical data have not been received. These data will be summarized in the next report. Currently, absorption studies are being conducted with carbon dioxide. Following completion of this work, a series of tests with nitrogen dioxide, iodine, methyl iodide, and water will be initiated.

4.1.2 Process application

One of the objectives of this work is to identify flowsheet options and simplifications that might lead to a more economical or reliable process. Previous work suggests that a significant flowsheet simplification can be proposed at this point. Specifically, data obtained in successful absorption and fractionation runs conducted at 100 psig with similar solvent flow rates strongly support the idea that a combination absorber-fractionator can be designed and operated at the conditions necessary to achieve both a specified DF and simultaneous product concentration. Figure 13 is a schematic of the modified selective absorption process. Although this combination was not previously obvious, the operational and economic advantages look attractive for fuel reprocessing plant applications.

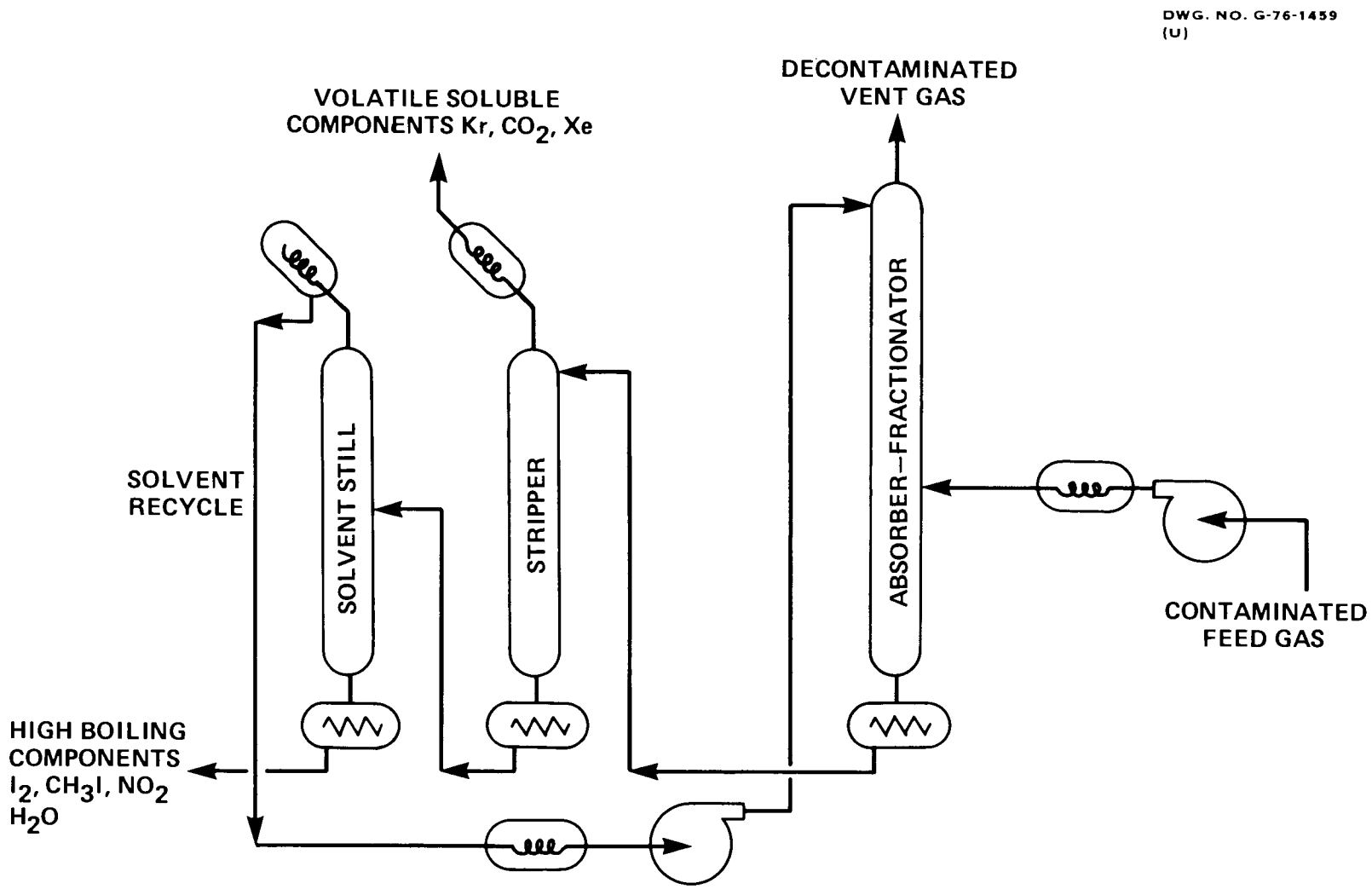

Fig. 13. Schematic of the modified selective absorption process.

A combined unit will contain no external fractionator recycle stream; consequently, the requirements for the process gas compressor will be substantially reduced. (This is particularly true at the lower absorption pressures favored by the absorber-fractionator combination, e.g., 100 psig.) Also, recycle solvent vapor will not be mixed with the incoming process gas prior to cold trapping. Consequently, the nitrogen dioxide, water, and iodine removed in the feed gas cooler will be free from cross-contamination, making it possible for the nitrogen dioxide and water to be recycled to the nitric acid makeup system for the reprocessing plant. Another advantage is that the fractionator flash unit and condenser can be eliminated. This reduction will, of course, serve to decrease process equipment costs. The number of process flow controls can also be reduced, thereby improving the reliability of the resulting process. The modified flowsheet does not require fractionator off-gas recycle instrumentation, condenser refrigeration controls, or an absorber liquid-level system. From an operational standpoint, elimination of the liquid control valve between the absorber and fractionator is desirable since this valve tends to plug when large amounts of free water are introduced into the system. Finally, the modified process will require less space.

Additional data will be available next quarter to further support the modified flowsheet and, hopefully, identify other process simplifications.

4.2 Chemical Studies of Contaminants in LWR Off-Gas Processing

L. M. Toth, D. W. Fuller, and J. T. Bell (Chemistry Division, ORNL)

Further analysis of the CH_3I distribution coefficient data led to the following expression for the distribution of CH_3I between the liquid and vapor phases of R-12:

$$\log_{10} D = 1.868 + 712.1/T,$$

where

T = temperature, in °K,

$$D = \frac{A^L_{CH_3I}}{\ell_L \cdot \rho_L} \quad \frac{\ell_V \rho_V}{A^V_{CH_3I}} ,$$

A = the optical absorbance for CH_3I in the liquid or vapor phase,

ℓ = the pathlength,

ρ = the density of R-12 in the liquid or vapor phase,

L, V = superscripts or subscripts designating liquid and vapor phase, respectively.

This expression supersedes the one given earlier[2] and is valid for CH_3I concentrations in liquid R-12 concentrations up to 0.27 wt %. These data are shown in Fig. 14 for the 20 to -40°C region.

Corrosion of the type 304 L stainless steel cell as a result of its contact with CH_3I was studied by adding up to 220 ppm of water to the CH_3I solution. No corrosion of the stainless steel or loss of CH_3I from solution was observed, in agreement with the results of the liquid CO_2 KALC studies.[10]

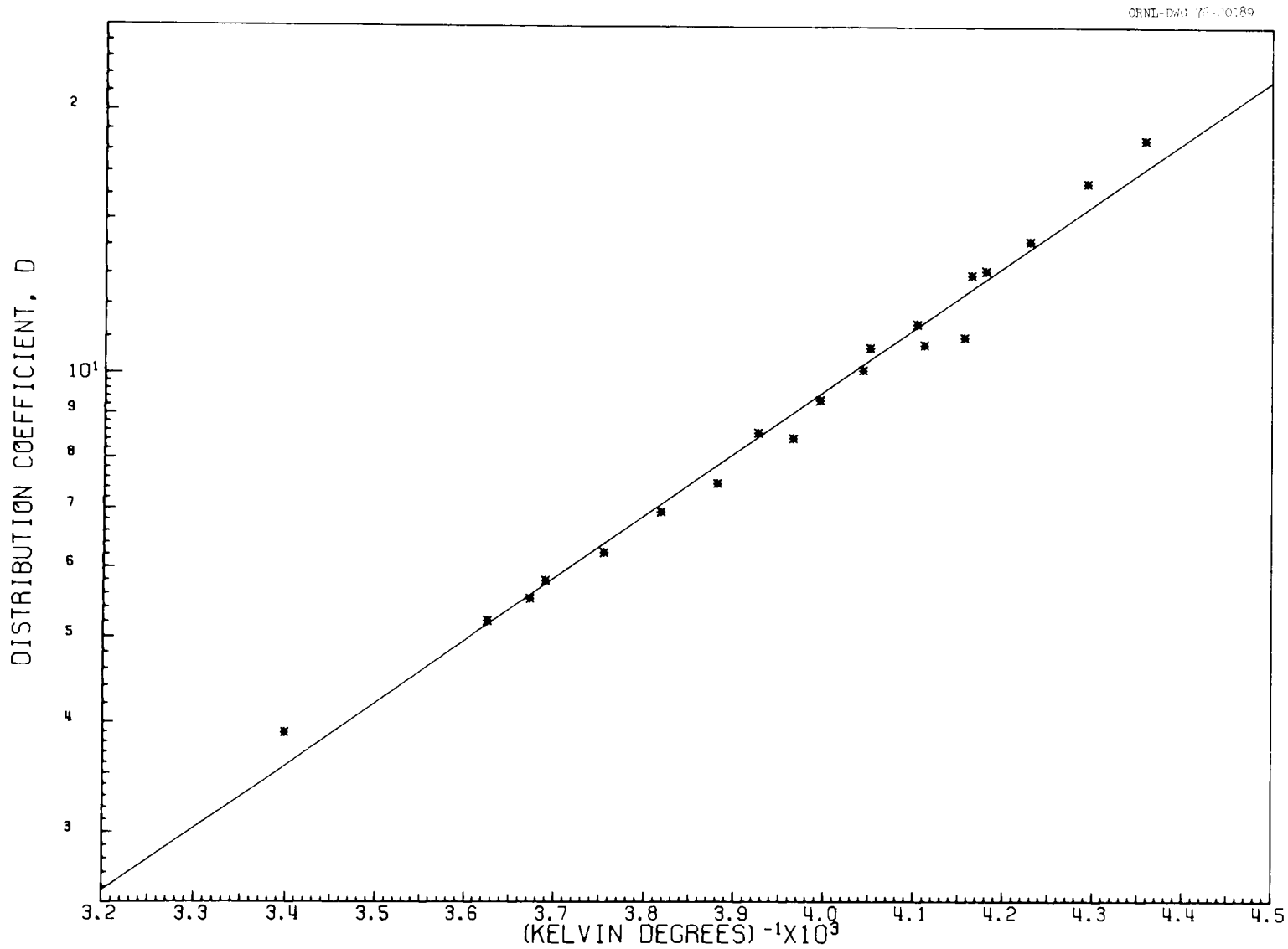

Fig. 14. CH_3I distribution data.

Because of pressing needs for nitrogen oxide--R-12 solution data in support of pilot-plant operations, our attention was turned to a study of these solutions. Nitrogen dioxide exists in the liquid and vapor phases as an equilibrium mixture of monomer (NO_2) and dimer (N_2O_4), with an equilibrium constant:

$$\log_{10} K = 9.191 - 2.983 \times 10^3/T,$$

where

$$K = (NO_2)^2/(N_2O_4).$$

The amount of NO_2 in the vapor as a function of temperature and pressure as determined from the above expression is illustrated in Fig. 15. The left-hand terminus of each line represents the condensation point for that pressure (i.e., the equilibrium vapor pressure over solid or liquid N_2O_4 - so named because, in the condensed phase, most of the nitrogen dioxide exists as the dimer.)

Nitrogen dioxide was observed to be miscible in R-12 in all proportions from 20 to -9°C. Below this temperature, N_2O_4 crystals separate as a primary phase in the N_2O_4--R-12 binary system, the temperature depending on the molar concentration of N_2O_4. A crude phase diagram of this system (see Fig. 16) was determined by visually observing the temperature at which N_2O_4 crystals separated from solution for various mixtures of the two components. It was assumed that no volume change occurred when these two components were mixed since the determination of molar quantities had to be made solely on the basis of measured volumes of the two liquids.

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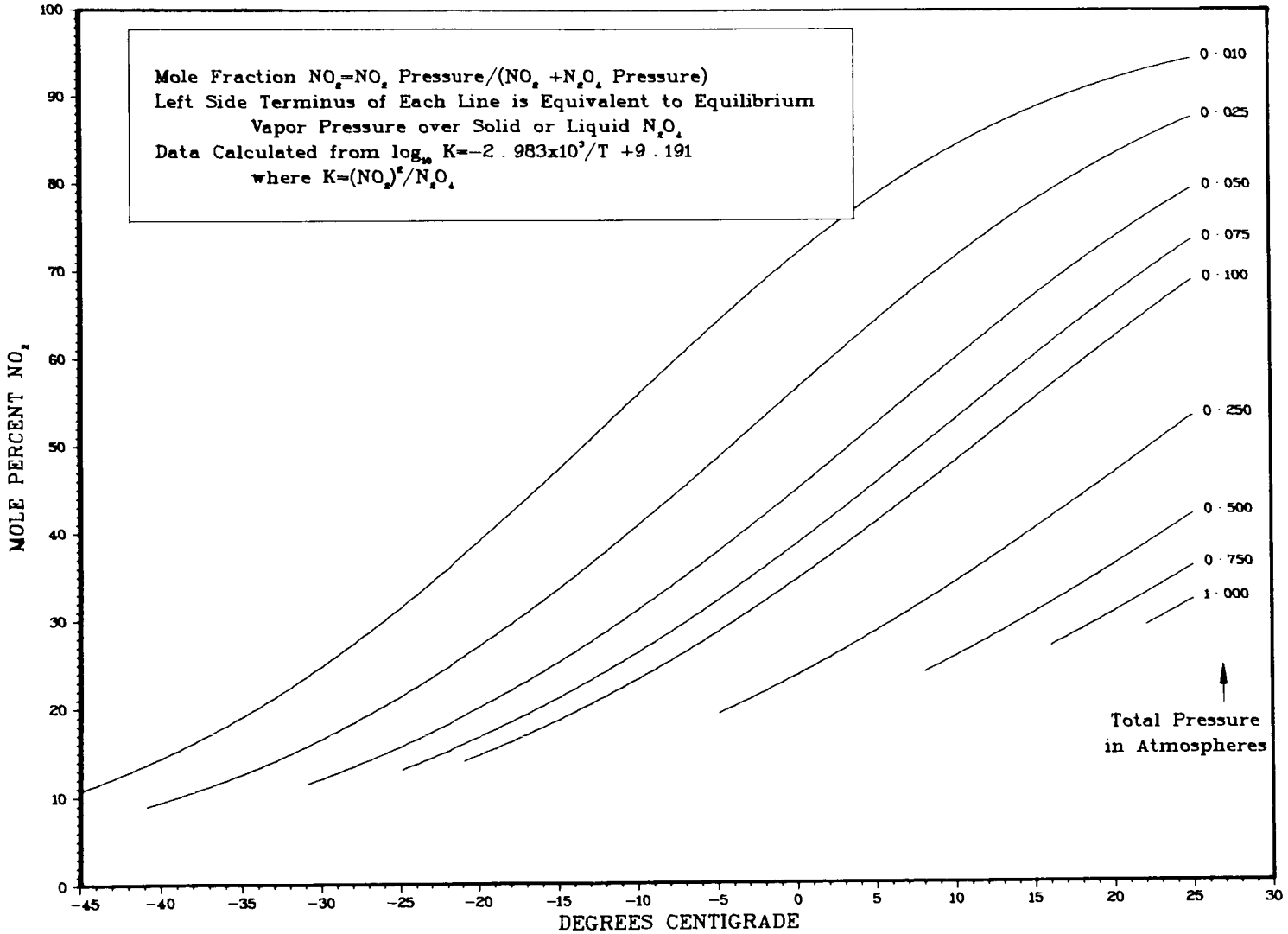

Fig. 15. Illustration of NO_2 monomer-dimer (N_2O_4) equilibrium in the vapor phase as a function of temperature and pressure.

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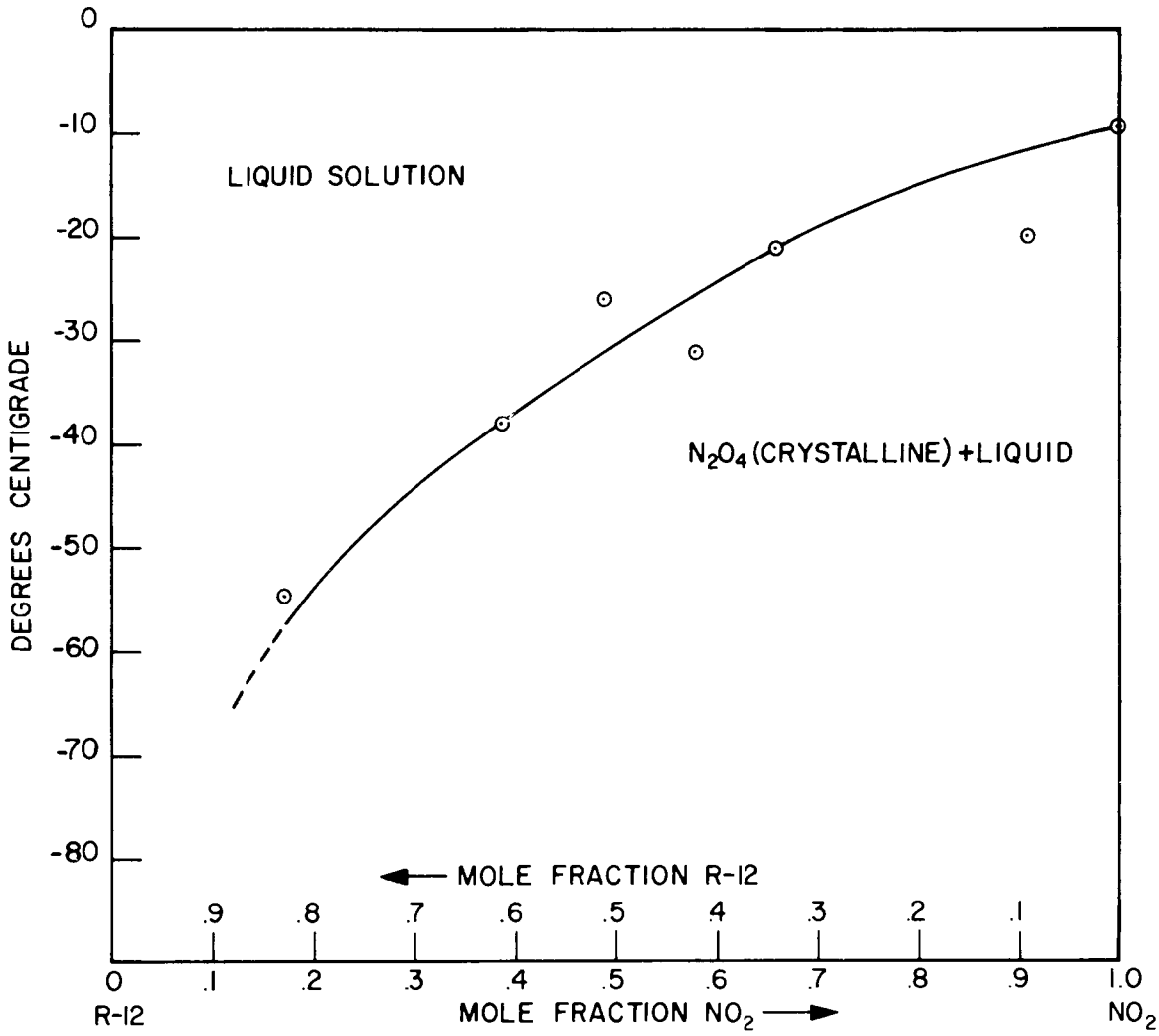

Fig. 16. Phase diagram for N_2O_4--R-12 system.

These data, nevertheless, suffice to illustrate the operational characteristics of the solution and suggest that N_2O_4 might be more effectively separated as a primary phase from R-12 in the final stages of concentration instead of using the currently intended distillation process.

Distribution coefficient data have been obtained for NO_2 as was done for I_2 and CH_3I. These spectral data, which are complicated by the NO_2 monomer-dimer equilibrium phenomena in both liquid and vapor phases, are still being analyzed. Concentrations of NO_2 up to 0.37 wt % have been studied.

5. FINISHING PROCESSES - MOX FUEL FABRICATION

This task has been canceled.

6. URANIUM HEXAFLUORIDE CONVERSION

J. H. Pashley (ORGDP)

Collection of available general information on conversion processes was completed, and an internal memorandum was issued. This information will form a part of a general evaluation report.

Currently, evaluation of two dry processes for converting denitrated UO_3 to UF_6 is planned. The first would involve additional heating to reduce the nitrate content of the oxide to near zero, followed by direct fluorination to produce UF_6. The second uses reduction with hydrogen and conversion of the UO_2 to UF_4 with HF prior to fluorination to remove nitrates and reduce the need for costly fluorine.

7. ECONOMIC STUDIES

This task has been canceled.

8. RADIOLOGICAL TECHNIQUES FOR ENVIRONMENTAL IMPACT ASSESSMENTS OF THE LWR FUEL CYCLE

D. C. Kocher (Environmental Sciences Division, ORNL)

8.1 Introduction

The model we have developed to study the effects of simple building structures on population doses resulting from routine releases of radionuclides to the atmosphere was described previously.[11] During the present quarter, our work has progressed in three areas: (1) simplification of the model in order to reduce the number of input parameters and the complexity of the calculations; (2) careful checks of the computer code in order to eliminate programming errors and verify the correctness of the calculations; and (3) performance of parameter sensitivity studies for the significant radionuclides for the LWR Fuel Recycle Program.

8.2 Description of the Model

Our model[11] estimates the effect of simple building structures on internal dose from inhaled radionuclides and on external dose from airborne and surface-deposited radionuclides. The model was simplified by assuming that all building structures can be approximated by a hemispherical shell of uniform wall thickness. Compared with the previous assumptions,[11] this simplification results in small changes in the calculated external dose rates from activity deposited on the ground and on the roof and outside walls of the structure.

For a given radionuclide, we assume an infinite, uniform, and time-independent distribution in the atmosphere at a concentration of 1 pCi/cm^3. The reduction factor for internal dose[11] then depends on the following parameters (symbol in parentheses):

Building radius (a),

Air ventilation rate (λ_v),

Deposition velocity on floor (V_{df}), and

Deposition velocity on inside walls (V_{dw}).

In addition to these parameters, the reduction factor for external dose depends on the following parameters:

Deposition rate on ground and outside walls (F_s),

Height of reference position aboveground (Z),

Wall thickness (t) and building construction material,

Frequency of removing activity from floor (τ_f), and

Frequency of removing activity from inside walls (τ_w).

For activity deposited on the ground and outside walls, we use a fixed value of the accumulation time of 50 years.

8.3 Results of Parameter Sensitivity Studies

Parameter sensitivity studies were performed for radionuclides of importance for the LWR Fuel Recycle Program.[12] Of primary importance are ^{3}H, ^{14}C, ^{85}Kr, ^{90}Sr, and ^{129}I. Of lesser importance are ^{131}I, $^{134,137}Cs$, $^{238,239,240,241}Pu$, ^{241}Am, and $^{242,244}Cm$. For each radionuclide, we chose three representative values for most of the parameters, one "average" value and two extreme but nonetheless reasonable values, and performed the calculations for all possible combinations of parameter values.

8.3.1 Internal dose reduction factors

For internal dose, the radionuclides can be divided into three categories: those with no net deposition on inside surfaces, the iodine isotopes, and the remaining radionuclides that are assumed to be in particulate form.

Tritium, ^{14}C, and ^{85}Kr are three of the most important radionuclides for the LWR Fuel Recycle Program. Since krypton is an inert gas, it does not deposit on surfaces. We assume that ^{3}H and ^{14}C are in the form of tritiated water vapor and carbon dioxide, respectively. We then assume that an equilibrium is attained between the rate of deposition and the rate of removal on inside surfaces so that there is no net deposition of these molecules. Therefore, since the air ventilation rate is much greater than the radioactive decay constants, we conclude that a building structure provides no protection for internal dose for ^{3}H, ^{14}C, and ^{85}Kr (i.e., the reduction factor is unity).

For iodine and particulates, we assumed the following parameter values:

$a = 2, 5, 10$ m,

$\lambda_v = 0.2, 1.0, 5.0\ hr^{-1}$,

$V_{df}, V_{dw} = 0.001, 0.03, 1.0$ cm/sec (iodine), and

$V_{df}, V_{dw} = 0.01, 0.05, 0.30$ cm/sec (particulates).

The calculated internal dose reduction factors for iodine span the range 0.0025 to 1.0. The values for particulates are 0.04 to 1.0. The reduction factor has roughly equal sensitivity to each of the parameters. In general, the protection provided by a building structure against inhaled radionuclides is greater for smaller values of a and λ_v and larger values of V_{df} and V_{dw}.

8.3.2 External dose reduction factors

External dose reduction factors were calculated for those radionuclides which are photon emitters. The assumed values for a, λ_v, and V_{df}, V_{dw} are given above. For the height of the reference position aboveground, only the single value Z = 1 m, which is characteristic of a one-story structure, was used.* The building structural material was assumed to be concrete.** For the remaining parameters, we assumed the following values:

F_s = 0.01, 0.15, 2.1 pCi cm^{-2} sec^{-1} (iodine),

F_s = 0.01, 0.10, 1.0 pCi cm^{-2} sec^{-1} (particulates),

t = 3, 10, 30 cm, and

τ_f, τ_w = 7 days, 1 year, 50 years.

It is not reasonable to allow the exterior deposition rate, F_s, to vary independently of the interior deposition velocities, V_{df} and V_{dw}. In our calculations, we always used the average value of one parameter with the average value of the other, etc.

An important result of our calculations is that, for any set of parameter values for any of the radionuclides, the external dose rate is dominated by the contribution from the activity deposited on the ground and exterior and interior surfaces of the structure. This is a consequence of the assumed 50-year accumulation time for the buildup of activity exterior to the structure and the assumed values of τ_f and τ_w

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*One-story structures are, by far, the most common in the vicinity of the Savannah River Plant; see FHA Homes 1970: Data for States and Selected Areas, HUD SOR-3 (1970).

**Brick, stone, and concrete block construction are the most common in the vicinity of the Savannah River Plant; see FHA Homes 1970: Data for States and Selected Areas, HUD SOR-3 (1970).

inside the structure. For low-energy photon emitters in particular, the contribution from airborne activity inside and outside the structure is negligible.

Representative results of parameter sensitivity calculations for the external dose reduction factor are discussed below.

The radionuclides ^{129}I and ^{131}I yield contrasting and illuminating results. Iodine-129 is characterized by a very long half-life and the emission of low-energy photons. Consequently, the reduction factor is essentially proportional to the parameters τ_f and τ_w describing the buildup of activity on inside surfaces of the structure. The reduction factor is also very sensitive to smaller values of the wall thickness but rather insensitive to larger values much greater than the photon mean free path. Since deposition on inside surfaces is so important, the reduction factor is also quite sensitive to the parameters a, λ_v, and V_{df}, V_{dw}. For ^{129}I the reduction factor covers the range 2.7×10^{-7} to 0.16, a variation of almost six orders of magnitude for reasonable values of the input parameters. On the other hand, ^{131}I has a relatively short half-life and emits higher-energy photons. Consequently, the reduction factor varies over a much smaller range, 0.013 to 1.0, only about a factor of 80. Furthermore, the reduction factor is insensitive to the values of τ_f and τ_w. Because of the higher-energy photons, the wall thickness is, by far, the most sensitive parameter. The reduction factor shows moderate sensitivity to the parameters a and λ_v but very little sensitivity to F_s, V_{df}, and V_{dw}.

The radionuclides ^{134}Cs and ^{137}Cs are similar in that they have half-lives of less than 50 years and a preponderance of high-energy photons.

Consequently, the only two parameters to which the reduction factor is significantly sensitive are the wall thickness and the building radius. The reduction factors for these radionuclides cover the range 0.03 to 1.25. It is noteworthy that, for certain parameter values, the presence of a building structure can increase the external dose rate compared with no structure present.

The transuranic radionuclides are all low-energy photon emitters and, in most cases, have moderately long half-lives. Therefore, the parameter sensitivity calculations give results similar to those for ^{129}I. For example, for ^{238}Pu the reduction factor is quite sensitive to all parameters except the wall thickness. The reduction factor covers the range 9.0×10^{-7} to 1.1, a variation of more than six orders of magnitude.

Since the radionuclides of interest have a wide range of half-lives and photon spectra, it is difficult to formulate vigorous generalizations concerning the dependence of the reduction factor on variations of the input parameters. However, it is apparent that the protection provided by a building structure against external photon radiation is greater for smaller values of λ_v, τ_f, and τ_w and larger values of t, F_s, V_{df}, and V_{dw}. For larger values of the building radius, the protection is increased for higher-energy photon emitters but decreased for low-energy photon emitters.

8.4 Conclusion and Future Plans

The calculations performed thus far using a coarse grid of input values provide a simple but crude parameter sensitivity analysis. However, examining only the change in reduction factor for a relatively large change in a given input parameter can give deceiving results since the

functional dependence can be highly nonlinear. A good example is the dependence on the wall thickness for low-energy photon emitters. In addition to calculating the reduction factor for each set of input parameters, a more rigorous approach would be to also calculate the partial derivatives of the reduction factor with respect to each input parameter. This approach would more accurately assess the sensitivity to each parameter for any set of parameter values. At present, we are contemplating the incorporation of calculating partial derivatives into our computer code. However, the time required to make extensive changes in the code and the severalfold increase in computing time may be prohibitive.

The overall objective of this study is to assess the effect of building structures on population doses. Toward this end, we have obtained data on the distribution of building types and structural materials*,** and on the distribution of time use[13] between indoor and outdoor environments throughout the United States. Work on estimating the reduction in population doses for the radionuclides of interest will proceed during the next quarter.

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*One-story structures are, by far, the most common in the vicinity of the Savannah River Plant; see FHA Homes 1970: Data for States and Selected Areas, HUD SOR-3 (1970).

**Brick, stone, and concrete block construction are the most common in the vicinity of the Savannah River Plant; see FHA Homes 1970: Data for States and Selected Areas, HUD SOR-3 (1970).

9. OFF-GASES - THE EXPERIMENTAL INVESTIGATION OF THE FIXATION OF ^{14}C-CONTAMINATED CO_2 IN A GAS-LIME SLURRY CONTACTOR

D. W. Holladay (Chemical Technology Division, ORNL)

9.1 Introduction

As presently designed, LWR fuel reprocessing plants may emit to the atmosphere, through stack gases, as much as 2.6 Ci of ^{14}C (incorporated in CO_2) per day, assuming a N_2 impurity level of 25 ppm in the fuel.[14,15] For a typical 5-metric ton U/day plant in which the majority of the CO_2 arises from the inleakage of air, the proposed process of removing CO_2 by fixation with a slaked lime slurry would result in the daily production of about 17 kg of $CaCO_3$ for total removal of all CO_2. Two bench-scale process techniques are being developed to remove the ^{14}C-contaminated CO_2 from different candidate streams in the LWR fuel reprocessing flowsheet. The simpler process consists of the application of an agitated gas-lime slurry contactor as a single process treatment for both the separation and the fixation of CO_2. The second process consists of initial application of molecular sieves to remove CO_2 from the contaminated LWR off-gas streams, followed by utilization of the gas-slurry contactor to process the preconcentrated sieve effluent.

9.2 Prior Results

Prior bench-scale studies[16] in the Experimental Engineering Section of the Chemical Technology Division have shown that molecular sieve columns (Linde 5A) can be used to reduce the CO_2 concentration from 90% in the feed gas to less than 10 ppm in the effluent when the composition

of the feed is 93-5.5-1.5% in CO_2-O_2-Kr, respectively. It is reasonable to assume from these results that a fairly high DF is possible for the removal of CO_2 from a gas stream containing 300 ppm of CO_2 (approximately the composition of normal air).

In a recently completed study,[17] bench-scale experiments were conducted to determine the feasibility of the application of a stirred-tank contactor filled with a gas-lime slurry for the fixation of CO_2 produced in the burning of fuel elements during the reprocessing of spent HTGR fuels. The mechanism of CO_2 interaction with the slaked-lime slurry should be the same, regardless of whether the stream is produced from HTGR or LWR fuel reprocessing, although the CO_2 compositions of candidate streams may vary. Further, if the fixation process for LWR off-gas processing is applied at some point where NO_x gases are present in considerable quantity or where there is a high-activity radionuclide (I_2 or Kr), then interference with the CO_2-$Ca(OH)_2$ reaction could possibly occur; in such cases, it could become necessary to restrict the operation of the fixation process to a high-level containment facility.

Results for the fixation of CO_2 from gas streams with CO_2 concentrations in the 10 to 90% range (balance as O_2 or air) have been very promising. The process is gas-phase- and interfacial-area-limited, with a direct relationship between total CO_2 mass transfer and both agitation speed and efficiency of agitation. In a 7.72-in.-ID x 14-in. contactor, DFs as high as 3600 were achieved for a single pass of 90% CO_2--10% O_2 gas at a flow rate of 4 liters/min. By utilizing two contactors in series, it was possible to achieve DFs for CO_2 as high as 25,000.

9.3 Possible Application Points in the LWR Fuel Reprocessing Flowsheet

The following compositions are representative of the gas streams present in the LWR fuel reprocessing plant which are candidate streams for removal of CO_2 and fixation as $CaCO_3$:

1. Off-gas consisting of I_2, CH_3I, Kr, Xe, Ar, N_2, O_2, and NO_x with a CO_2 content approximately equivalent to that of standard air. This is the direct dissolver off-gas to be studied in both molecular sieves and the gas-lime slurry contactor.
2. Gas consisting of Kr, Xe, Ar, N_2, O_2, H_2, CO_2, and traces of NO_x and I_2. This is the dissolver off-gas and vessel off-gas, after iodine and NO_x removal, to be studied in both molecular sieves and the gas-lime slurry contactor.
3. Gas containing primarily 60 to 80% CO_2, Kr, Xe, O_2, and N_2. This is reprocessing off-gas, after I_2, NO_x, and Kr removal (such as after silver zeolite columns or after the FASTER krypton removal process), to be studied in the gas-slurry contactor.

9.4 Progress

The bench-scale molecular sieve equipment with beta detector is in the process of being relocated and adapted to our operating conditions. Results concerning the simple operation of concentrating CO_2 from normal air should be available in the very near future. Blended gases with compositions similar to that described in item (1) in Sect. 9.3 will then

be studied for CO_2 removal. Larger-scale studies will be made in a 6-in.-ID x 6-ft-high molecular sieve column which has been designed but not yet fabricated.

The availability of the gas-slurry contactor made it possible for us to undertake exploratory studies relative to the fixation of CO_2 from a normal, dry air stream. Data obtained in previous studies had shown that, for a fixed total gas flow rate, the DF for CO_2 removal decreased as the mole fraction of CO_2 decreased. However, for flow rates in the vicinity of 20 liters/min, the DF for a 5% CO_2 feed was about 20, while the DF for air, although containing only 0.03% CO_2, was about 20 to 30. A DF of 50 was obtained for a 5% CO_2 feed with a total gas flow of 10 liters/min and agitation at 800 rpm, while the removal of CO_2 from air under the same operating conditions was so efficient that CO_2 could not be detected in the effluent gas by chromatography.

In summary, it appears that the CO_2 was removed more easily from normal air than from a stream of 5% CO_2 at the same total gas flow. This is in contradiction to previous trends observed for DFs achieved in processing gases containing 100, 80, 30, and 5% CO_2. A sensitive beta detector will soon be available to allow further elucidation of the DFs achievable in the gas-slurry contactor for removal of CO_2 from air. Additionally, another agitated contactor is being constructed. The new contactor will be twice as large as the previous contactor and will be fitted with an improved impeller seal for processing radioactively traced simulated gases.

For air flow through the contactor in the absence of mechanical agitation, the DF at 10 liters/min was about 7 as compared with values in excess of 50 when agitation at 800 rpm was provided. As the air flow rate increased with no mechanical agitation, the DF effectively leveled out at about 1.0 for flow rates ranging from 30 to 50 liters/min.

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