

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES



3 4456 0515740 6

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

2

ORNL-4204
UC-4 - Chemistry

UNIT OPERATIONS SECTION
QUARTERLY PROGRESS REPORT

APRIL - JUNE 1967

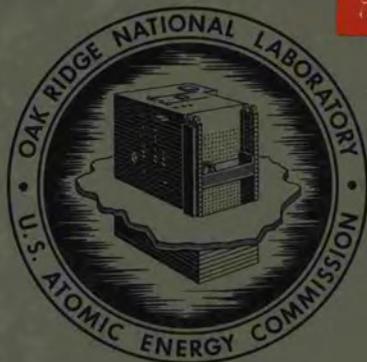
OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this
document, send in name with document
and the library will arrange a loan.

UCN-7962
03-3-67



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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

LEGAL NOTICE

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

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

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

ORNL-4204

Contract No. W-7405-eng-26

UNIT OPERATIONS SECTION QUARTERLY PROGRESS REPORT

April-June 1967

M. E. Whatley

P. A. Haas

L. E. McNeese

A. D. Ryon

J. C. Suddath

C. D. Watson

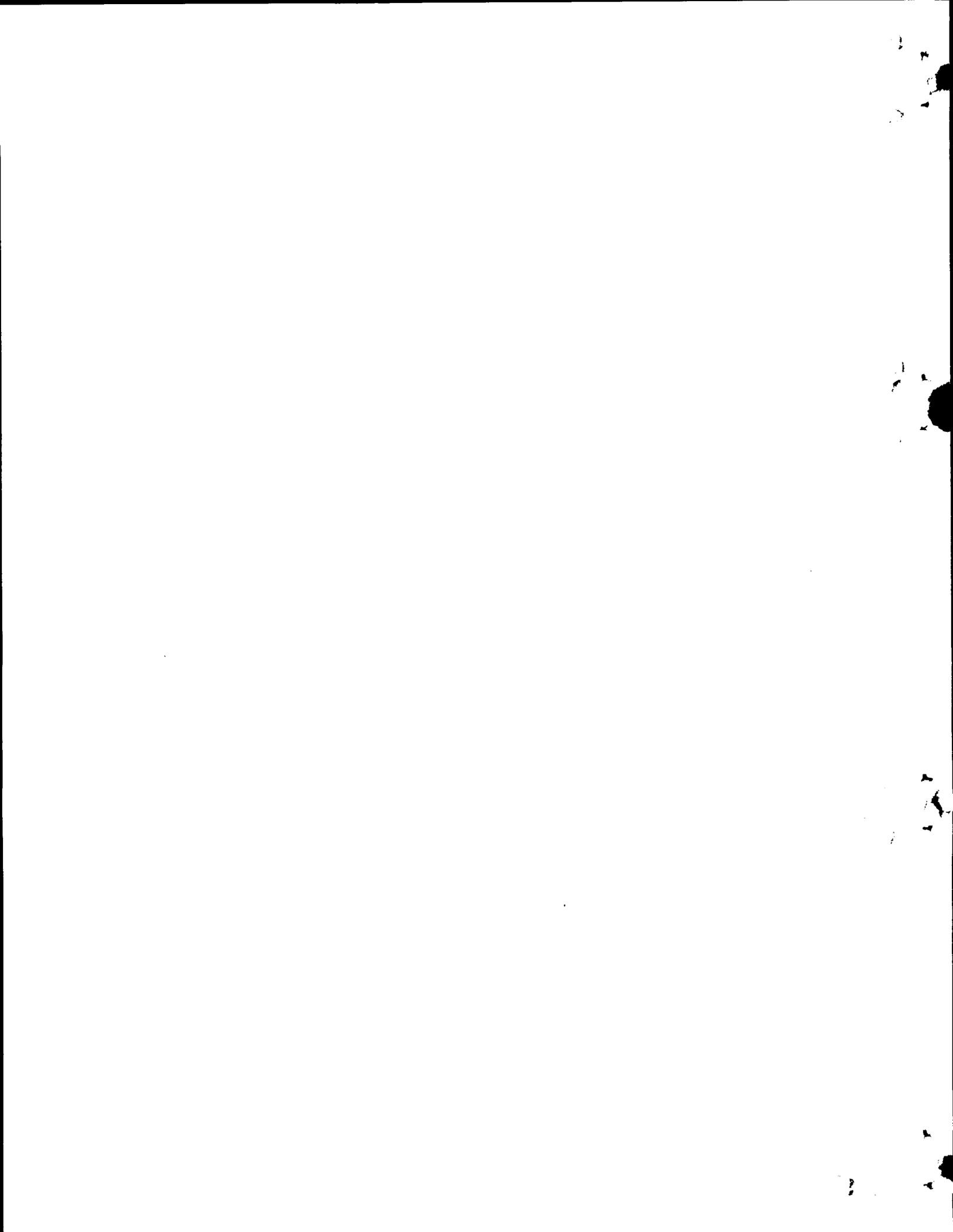
MAY 1968

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES

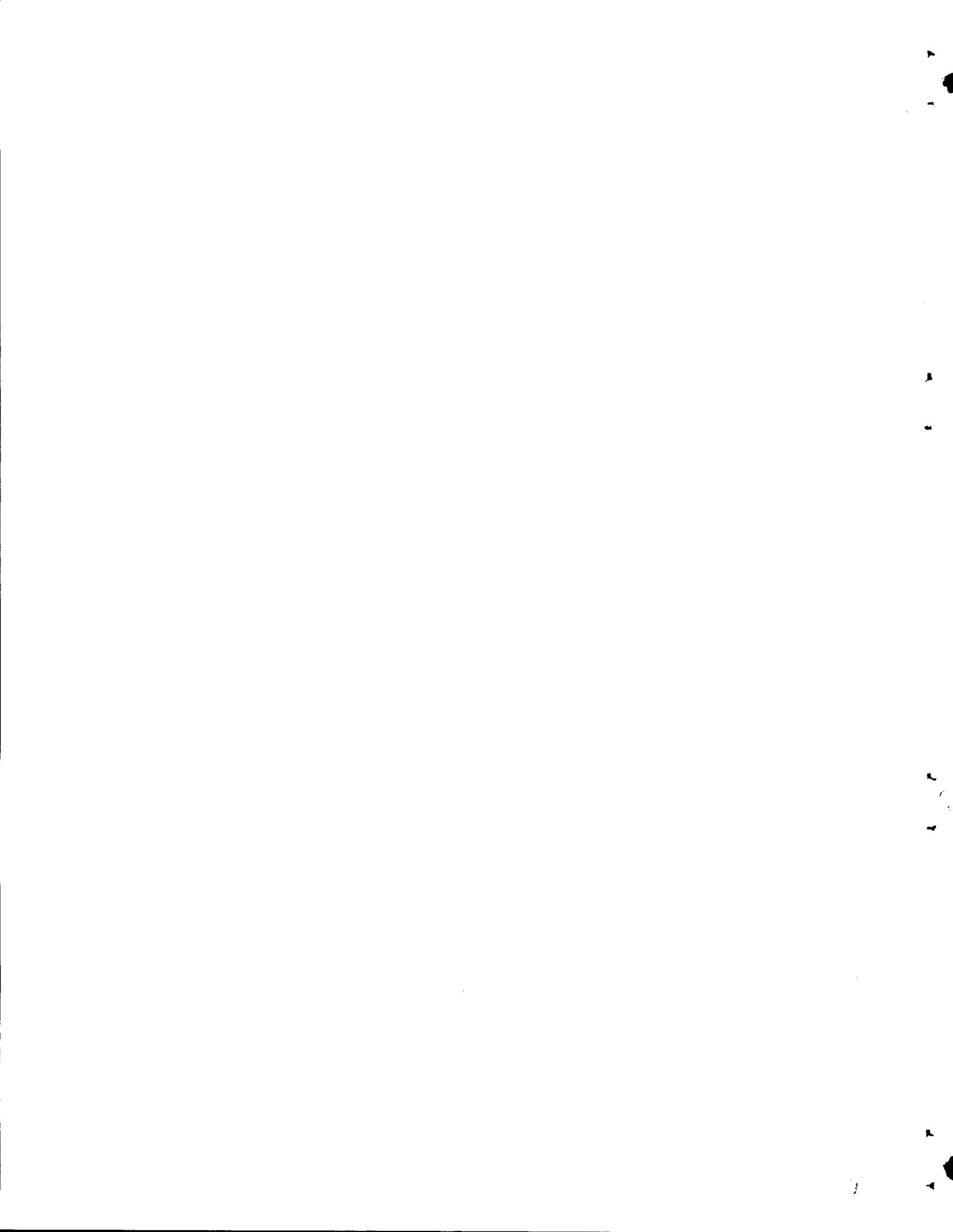


3 4456 0515740 6



CONTENTS

	<u>Page</u>
ABSTRACTS	1
Previous Reports in This Series	3
1. CHEMICAL ENGINEERING RESEARCH	4
1.1 Stacked-Clone Contactor.	4
2. ENGINEERING SEPARATION OF MACROMOLECULAR BIOLOGICAL SUBSTANCES	16
2.1 Production of Mixed Transfer Ribonucleic Acids	16
2.2 Separation of Specific tRNA's	17
3. SOL-GEL PROCESS DEVELOPMENT	22
3.1 Continuous Washing of Urania Precipitates.	22
3.2 Studies of Continuous Peptization and Evaporation Methods in the Preparation of UO ₂ Sols	27
3.3 Microsphere Preparation Development.	33
3.4 Firing of Urania Microspheres.	35
4. THORIUM FUEL-CYCLE STUDIES.	40
4.1 Preparation of Microspheres in the Coated Particle Development Laboratory	40
5. POWER REACTOR FUEL PROCESSING	46
5.1 Shear-Leach.	46
5.2 Grind-Leach.	47
5.3 Jet Evulsion of Fuel Particles	49
6. FAST-BREEDER REACTOR FUEL PROCESSING.	52
7. MOLTEN-SALT REACTOR PROCESSING.	60
7.1 Molten-Salt Distillation Studies	60



ABSTRACTS

1. CHEMICAL ENGINEERING RESEARCH

The 18-stage prototype solvent-extraction stacked-clone contactor, which was designed for radiochemical use, has been further tested with the light phase continuous by maintaining the interface either within the contactor or in an external settler. Operation with an internal interface reduces solution inventory, but is not practical with certain chemical systems. Batch dispersion break times were measured for several systems that have potential for light-phase-continuous operation. The break time varied greatly with the phase ratio. When measured at the proper phase ratio, break times of very finely divided dispersions can be used to aid in the detection of chemical systems that will exhibit significant flows in the stacked-clone contactor.

2. ENGINEERING SEPARATION OF MACROMOLECULAR BIOLOGICAL SUBSTANCES

A mixed tRNA feed was reprocessed by isopropanol precipitation to remove DNA. The reprocessed feed was then treated with DEAE (in a column) to remove ribonuclease. A new form of DEAE and new operating techniques made this operation practical.

A number of runs were made, using isopentyl acetate reversed-phase columns, to determine the effects of column support material, type and lot of amine that was used as the organic phase, and the source of the mixed tRNA feed.

3. SOL-GEL PROCESS DEVELOPMENT

In the washing of precipitated uranous hydroxide, stage efficiencies of a set of mixer-decanters were as high as 89%. A 12-ft countercurrent wash column had an HTU (height of a transfer unit) of 2.3 to 3.6 ft. Dilute sols made in the P²C²D apparatus were successfully concentrated to desirable concentrations by continuous vacuum evaporation. The forming of satisfactory gel microspheres required a Span 80:Ethomeen

S/15 volume ratio of 4:1 in the 2-ethylhexanol. This concentration was maintained by continual additions of the two surfactants during operation. Fired microspheres were found to be more dense and to contain less carbon when the dried gel spheres were exposed to air overnight before firing and then further exposed to air until the temperature of the furnace reached 100°C.

4. THORIUM FUEL-CYCLE STUDIES

Numerous improvements have been made in the equipment in the Coated Particle Development Laboratory to eliminate operational upsets and to improve the clarity of the 2-ethylhexanol. Four pumps and three control valves have been eliminated, and modifications have been made to prevent vessel overflows.

5. POWER REACTOR FUEL PROCESSING

5.1 Shear-Leach

The 250-ton shear has been modified prior to shearing 10- by 10-in. power-reactor fuel prototypes; the operability of this new version has been tested, on a preliminary basis, by shearing oak timbers.

5.2 Grind-Leach

We have successfully demonstrated the use of a hacksaw for reducing large graphite fuel blocks to a feed that is suitable for a hammer mill or a roll crusher.

5.3 Jet Evulsion of Fuel Particles

The high-pressure hydraulic system has been installed and is being tested.

6. FAST-BREEDER REACTOR FUEL PROCESSING

We have prepared a conceptual layout of the mechanical head-end procedure (disassembly, canning, shearing, and leaching) that is needed

for reprocessing fast-breeder fuels. This layout is the basis for an economic study of the costs of reprocessing short-cooled fuels. A model for handling the fuel pins was built and operated to verify its feasibility. Temperatures to be encountered during disassembly and shearing were estimated by using the computer code BIGDEAL.

7. MOLTEN-SALT REACTOR PROCESSING

The relative volatilities of several rare-earth fluorides (REF's) in the ternary system $\text{LiF-BeF}_2\text{-REF}$ have been measured; all except PrF_3 were lower in this system than in the binary system LiF-REF .

Previous Reports in This Series for the Year 1967

January-March

ORNL-4139

1. CHEMICAL ENGINEERING RESEARCH

1.1 Stacked-Clone Contactor

W. S. Groenier

The 18-stage prototype stacked-clone solvent-extraction contactor gave low scrubbing efficiencies when it was tested with solutions used to simulate a ^{233}U recovery process.¹ Since the flow ratio (heavy phase:light phase) in the scrubbing zone of the contactor was much less than 1 for this process (and hence in a region of flow ratios known to be less than optimum for efficient operation), we felt that higher scrubbing efficiencies would be obtained if the contactor were operated with the light phase continuous. Higher flow capacities in the extraction zone should also result from this type of operation.

Previously, an experimental stacked-clone contactor had been operated successfully with the light phase continuous by using various chemical systems, including the following: (1) [0.08 M nitric acid]--Amsco, (2) [66 wt % glycerine]--Amsco, (3) [38 wt % dextrose]--Amsco, (4) [1.7 M aluminum nitrate, 0.2 M acid deficient]--Amsco, and (5) [1 M sodium nitrate]--[5 vol % tributyl phosphate (TBP) in Amsco].² An external phase separator was used in all these runs. By maintaining the interface inside the contactor, the system [0.08 M nitric acid]--Amsco was operated with the light phase continuous without the use of an external settler.

To obtain satisfactory light-phase-continuous operation with the experimental contactor, using an external settler, extensive modifications of the geometry of the contactor and the settler were required; also, a special hydroclone with a very high induced-underflow rate was

¹M. E. Whatley et al., Unit Operations Section Quarterly Progress Report, January-March 1967, ORNL-4139.

²M. E. Whatley et al., Unit Operations Section Quarterly Progress Report, January-March 1966, ORNL-3995.

designed for use in the last stage so that the light-phase portion of the dispersion in the settler could be effectively returned to the contactor. The geometry of the prototype contactor is not amenable to modifications, however, and the light phase must be recycled through a throttling valve and a rotameter to the light-phase feed stage (Fig. 1.1). Hence the results obtained by operating the current prototype contactor (which was designed for heavy-phase-continuous operation) in the light-phase-continuous mode cannot be expected to be the same as those that would be derived from a contactor specifically designed for this type of operation.

The first light-phase-continuous operations of the prototype were made with the system [0.5 M aluminum nitrate, 0.1 M nitric acid]-- [diethylbenzene (DEB)].¹ The flow capacity with an internal interface at a heavy-phase:light-phase flow ratio (A/O) of 0.5:1 was 2.31 liters/min. The flow capacity obtained this quarter by using the system [0.1 M nitric acid]--DEB either with an internal interface or with the interface in an external settler, as shown in Fig. 1.1, was 1.98 liters/min (A/O = 0.5:1).

Flooding data were also obtained by operating with the light phase continuous and by using an external settler for systems containing TBP or di-sec-butyl phenylphosphonate (DSBPP) as the extractant. At an A/O of 0.5:1 the flow capacities were 0.96 and 1.91 liters/min for 14.5 and 5.5 vol % TBP in Amsco, respectively, and 0.96 liter/min for 10 vol % DSBPP in DEB. The aqueous phase was 0.1 M nitric acid in each case. Additional data are presented in Table 1.1 and Fig. 1.2. Flow capacities for the heavy-phase-continuous operation of several of the systems are also presented for comparison. Table 1.2 lists the physical properties of the solutions; batch dispersion break times are given in Table 1.3.

For the systems tested, the flooding rates decreased sharply as the concentration of extractant in diluent was increased. No significant flows could be obtained with the light phase continuous when the extractant concentration was higher than about 15 vol % TBP in Amsco or about 10 vol % DSBPP in DEB. (Attempts were made with 20 vol % TBP and 16 vol

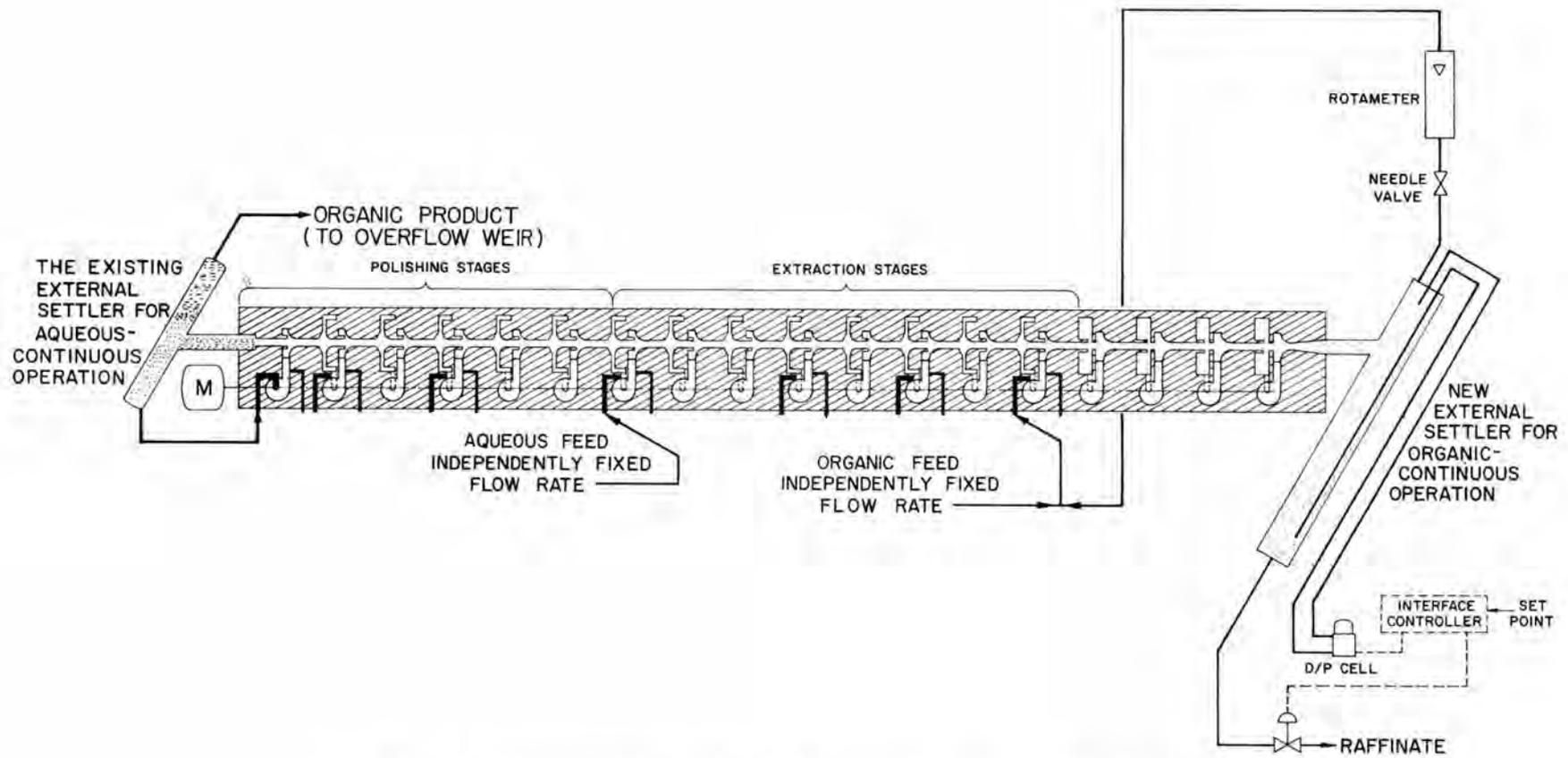


Fig. 1.1 Arrangement of the Prototype Stacked-Clone Contactor to Allow Light-Phase-Continuous Operation.

Table 1.1 Flooding Data for the Prototype Stacked-Clone Contactor

Temperature: ~ 42°C

Aqueous Phase	Organic Phase	Continuous Phase	Flow Capacity at Flooding (liters/min)							
			A/O = 1/20	1/10	1/5	1/3	1/2	1	2	3
0.5 <u>M</u> Al(NO ₃) ₃ , 0.1 <u>M</u> HNO ₃	DEB ^a	Aqueous ^b					0.97	1.05	1.19	1.36
		Organic ^c			2.28	2.39	2.31	2.06		
0.1 <u>M</u> HNO ₃	DEB	Aqueous ^b						1.25	1.65	
		Organic ^{c,d}		1.85	1.95	2.03	1.98	1.68	1.40	
0.1 <u>M</u> HNO ₃	10% DSBPP ^e in DEB	Organic ^d				1.08	0.96	0.78	0.66	0.61
0.1 <u>M</u> HNO ₃	5.5% TBP in Amsco	Aqueous ^b					1.76	2.11		
		Organic ^d	2.28	2.21	2.11	2.00	1.91	1.74	1.60	
0.1 <u>M</u> HNO ₃	14.5% TBP in Amsco	Aqueous ^b					1.29	1.54		
		Organic ^d				1.08	0.96	0.78	0.66	0.61
0.1 <u>M</u> HNO ₃	20% TBP in Amsco	Aqueous ^b					1.29	1.54		

^aDiethylbenzene.^bAqueous-phase-continuous operation: Aqueous feed to stage 2, organic feed to stage 14; interface in external settler is controlled by pressure developed by stage 1 pump.^cOrganic-phase-continuous operation: Aqueous feed to stage 4, organic feed to stage 10; interface is controlled internally between stages 10 and 12 by pressure developed by stage 10 pump.^dOrganic-phase-continuous operation: Aqueous feed to stage 7, organic feed to stage 14; interface in external settler is controlled by liquid-filled probes.^eDi-sec-butyl phenylphosphonate.

ORNL Dwg. 68-822

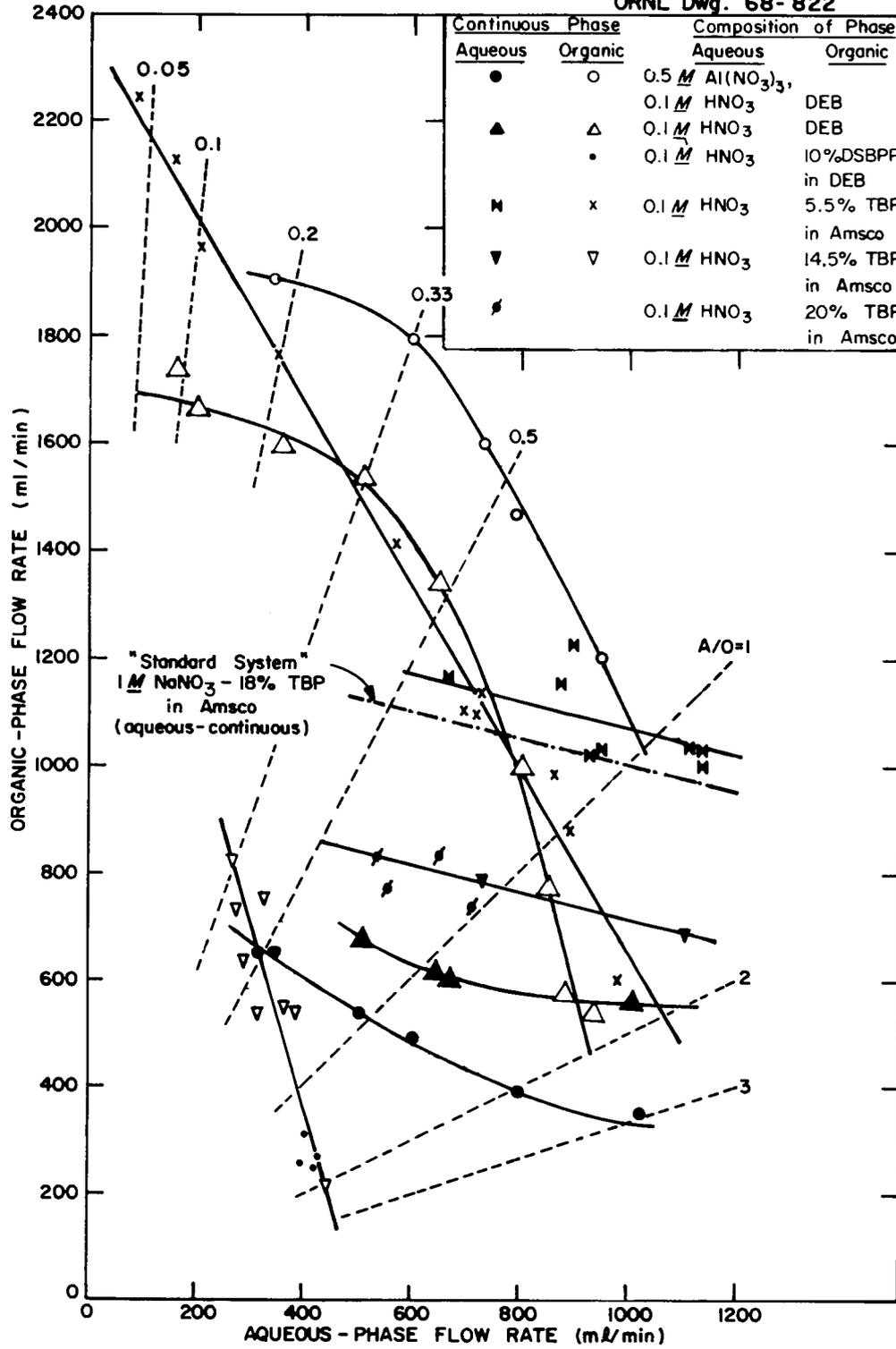


Fig. 1.2 Flooding Data for the Prototype Stacked-Clone Contactor.

Table 1.2 Physical Properties of the Solutions

Solution	Density (g/cc)		Viscosity (centipoises)		Interfacial Tension ^a (dynes/cm)
	25°C	40°C	25°C	40°C	
A. 0.5 M Al(NO ₃) ₃ , 0.1 M HNO ₃	1.066	1.060	1.15	0.94	----
B. 0.1 M HNO ₃	0.998	0.993	0.89	0.66	----
C. DEB	0.858	0.857	0.79	0.73	----
D. 10% DSBPP in DEB	0.874	0.869	0.94	0.83	----
E. 5.5% TBP in Amsco	0.764	0.753	1.33	1.09	----
F. 14.5% TBP in Amsco	0.784	0.773	1.44	1.16	----
G. 20% TBP in Amsco	0.797	0.787	1.52	1.21	----
Solution Pair					
A - C	----	----	----	----	27.4
B - C	----	----	----	----	23.4
B - D	----	----	----	----	19.0
B - E	----	----	----	----	14.9
B - F	----	----	----	----	11.8
B - G	----	----	----	----	10.6

^aAt 25°C.

Table 1.3 Batch Dispersion Break Times

Aqueous phase: 0.1 M HNO₃
 Temperature: ~ 25°C

Organic Phase	Organic Phase Continuous		Aqueous Phase Continuous	
	Phase Ratio ^a	Dispersion Break Time (sec)	Phase Ratio ^a	Dispersion Break Time (sec)
Amsco	1	20.3	1	21.7
	4	15.7	4	24.5
	10	13.5	10	21.9
	15	29.9	15	23.4
2.5% tributyl phosphate (TBP) in Amsco	10	17.5		
5% TBP in Amsco	1	24.4	1	40.3
	4	15.0	4	26.6
	10	22.0	10	20.9
	10	23.7	15	19.3
	15	27.9		
10% TBP in Amsco	1	40.4		
	2	33.7		
	4	29.2		
	10	50.0		
	10	51.5		
	15	86.5		
14.5% TBP in Amsco	1	47.3	1	30.1
	4	39.6	4	24.7
	10	52.0	10	21.0
	15	62.0	15	17.3
20% TBP in Amsco	0.5	44.4	1	30.0
	1	41.8	4	25.3
	4	42.7	10	16.6
	10	80.2		
	15	115		
30% TBP in Amsco	1	53.0	1	24.7
	2	47.0	2.4	24.4
	4	47.7	4	22.2
	10	101	8	18.9
	15	141	15	17.7
Diethylbenzene (DEB)	1	26.5	1	44.4
	4	24.0	4	29.4
	10	30.7	10	29.0
	10	30.4	15	27.5
	15	40.0		
2.5% di-sec-butyl phenylphosphonate (DSBPP) in DEB	0.5	15.6		
	1	20.5		
	4	17.4		
	10	26.0		
	15	44.4		
10% DSBPP in DEB	0.5	43.4	1	43.4
	1	42.3	4	30.2
	4	35.3	10	21.6
	10	60.0		
20% DSBPP in DEB	1	52.1	1	50.1
	4	41.2	4	45.0
	10	64.0	10	35.0
	15	131	15	33.0
CCl ₄	1	16.9	1	23.7
	4	15.4	4	20.3
	10	15.3	10	20.4
	15	27.5	15	24.1
10% DSBPP in CCl ₄	1	20.3	1	28.2
	4	20.4	4	22.8
	10	22.5	10	26.4
	15	32.2	15	37.0
20% DSBPP in CCl ₄	1	26.7	1	32.0
	4	23.4	4	23.8
	10	27.5	10	32.5
	15	43.7	15	41.7
30% TBP in hexane	0.5	26.9	2	13.2
	1	24.0	4	11.3
	4	19.1	10	10.9
	10	28.9	20	11.1
	15	47.3		
30% TBP in heptane	0.5	26.3	2	11.7
	1	24.1	4	10.9
	4	18.9	10	10.9
	10	28.0	20	13.2
	15	49.0		
30% TBP in octane	0.5	34.0	1	12.9
	1	29.9	2	13.1
	4	25.0	4	12.3
	10	30.5	10	11.5
	15	44.0	15	12.4
30% TBP in decane	0.5	41.8	1	19.5
	1	35.5	2	17.9
	4	31.0	4	16.2
	10	41.6	10	14.3
	15	67.5	15	18.1
30% TBP in dodecane	0.5	49.0	1	18.9
	1	45.6	2	18.5
	4	39.5	4	18.1
	10	61.2	10	16.2
	15	94.5	15	18.7

^a Ratio of volume of continuous phase to volume of dispersed phase.

% DSBPP.) When an internal interface was used, the extractant concentrations above which reasonable flows could not be obtained were even lower (about 14.5 vol % TBP in Amsco or 10 vol % DSBPP in DEB) because, even at modest flow rates, the interface could not be contained within a span of four stages. At 5.5 vol % TBP in Amsco the flow capacity was 5 to 10% less with an internal interface than with an external settler.

To simulate contactor operation in instances where the settler must be separately shielded, both external settlers were moved to positions 5 ft from the body of the contactor. Some coalescence of the dispersion in the connecting lines was noted, but flow capacities were unaffected for the system [0.1 M nitric acid]--[14.5 vol % TBP in Amsco].

Dispersion break times were measured for several TBP and DSBPP systems in order to determine their dispersion-breaking characteristics and, possibly, to explain why the systems having the higher extractant concentrations performed unsatisfactorily in the light-phase-continuous mode. All these tests were made in the usual manner, with a 2-in.-diam six-bladed turbine, driven at 1200 rpm, that was enclosed in a 500-ml tall-form beaker fitted with four glass baffles and a stopcock at the bottom. Measurements were made over a wide range of phase ratios, with both the light and heavy phases continuous. Results of these tests are presented in Table 1.3 and Figs. 1.3 and 1.4.

Perhaps the most startling result was that break times of light-phase-continuous dispersions were much greater for dilute dispersions (those with light-phase:heavy-phase volume ratios of 10:1 to 15:1) than for dispersions with more nearly equal phase volumes. When the stacked-clone contactor is operating with the light phase continuous, the internal phase ratios (determined from mixed-phase samples drawn from a pump loop) are nearly equal to those that show the high break times. Generally, when systems that have break times in excess of 60 sec at a phase ratio of 10:1 are used, the flow capacity of the contactor is much less than 1 liter/min.

To determine the effect of the diluent on dispersion breaking, a few dispersion break time tests were made with systems containing 30

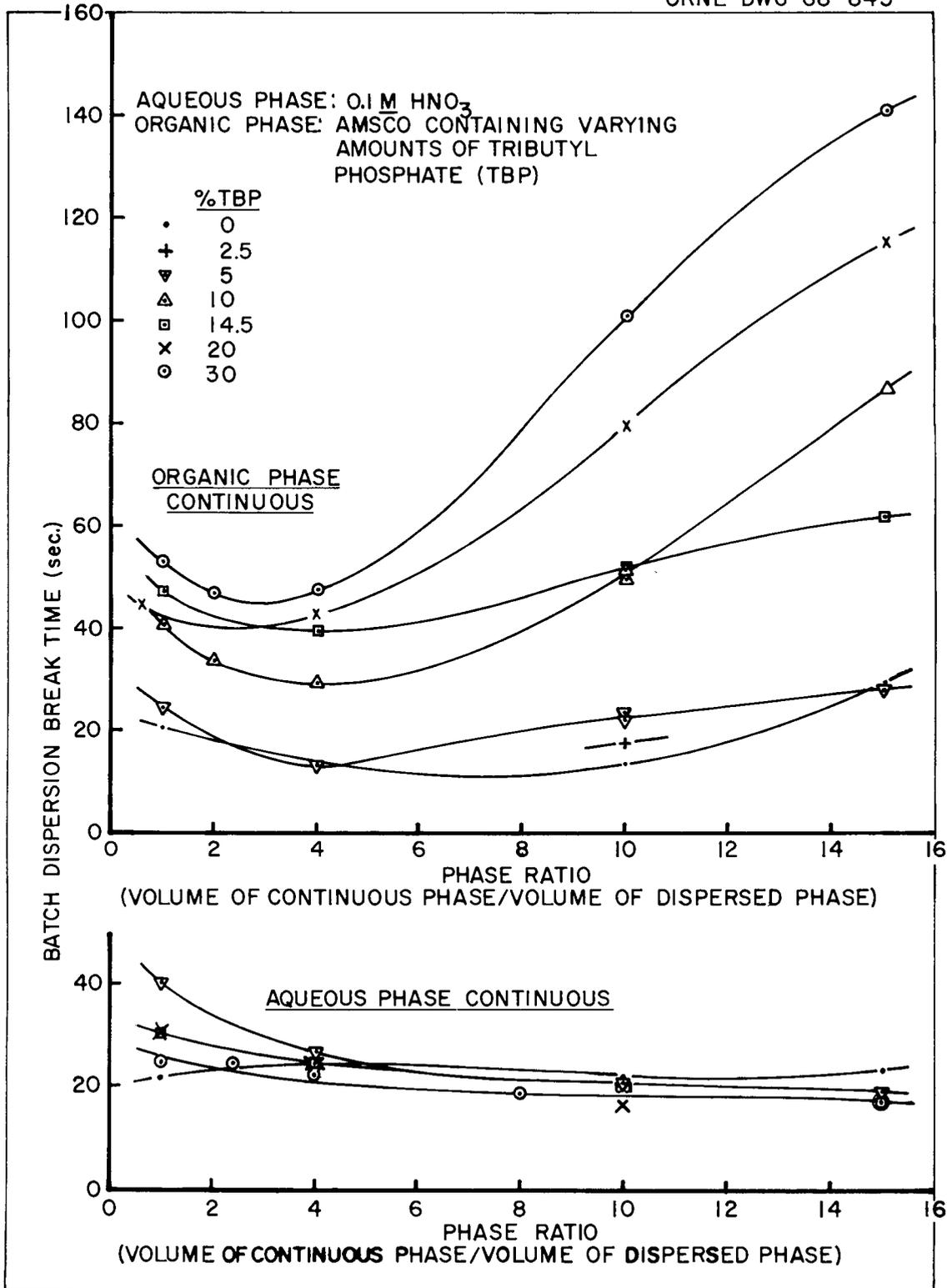


Fig. 1.3 Dispersion Break Test Results for TBP-Amsco Systems.

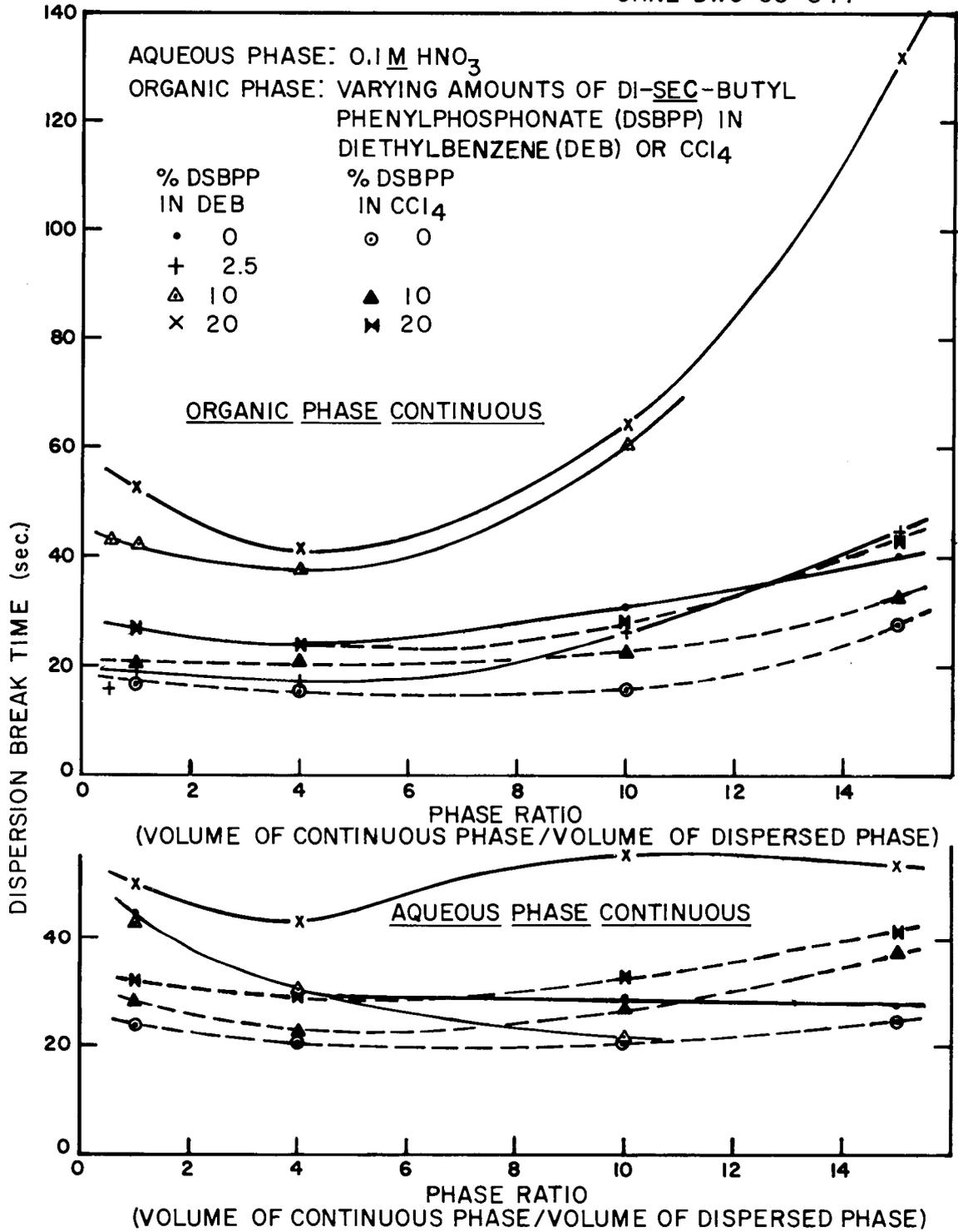


Fig. 1.4 Dispersion Break Test Results for DSBPP-DEB Systems.

vol % TBP in normal aliphatic hydrocarbons. Several of these diluents have been observed to allow higher flow capacities in solvent-extraction equipment than Amsco does,³ and the break time data supported these observations (Table 1.3 and Figs. 1.3 and 1.5). Carbon tetrachloride was also examined as a diluent for DSBPP in two concentrations; this system is unique in that the heavy phase is the organic phase.

On the basis of break time tests, a considerable increase in the flow capacity of a stacked-clone contactor in the light-phase-continuous mode can be expected for TBP systems if light aliphatic diluents such as n-hexane are used. Although higher flow capacities could also be expected for DSBPP in carbon tetrachloride, the latter material may be undesirable in a radiation field. However, it may be possible to find a radiation-stable diluent that has the desirable dispersion-breaking characteristics of carbon tetrachloride and that is compatible with DSBPP and its complexes.

³W. S. Groenier, R. A. McAllister, and A. D. Ryon, Flooding in Perforated-Plate Pulsed Extraction Columns: A Survey of Reported Experimental Data and Correlations, and the Presentation of New Correlations with Physical Properties, Operating Variables, and Column Geometry, ORNL-3890 (March 1966).

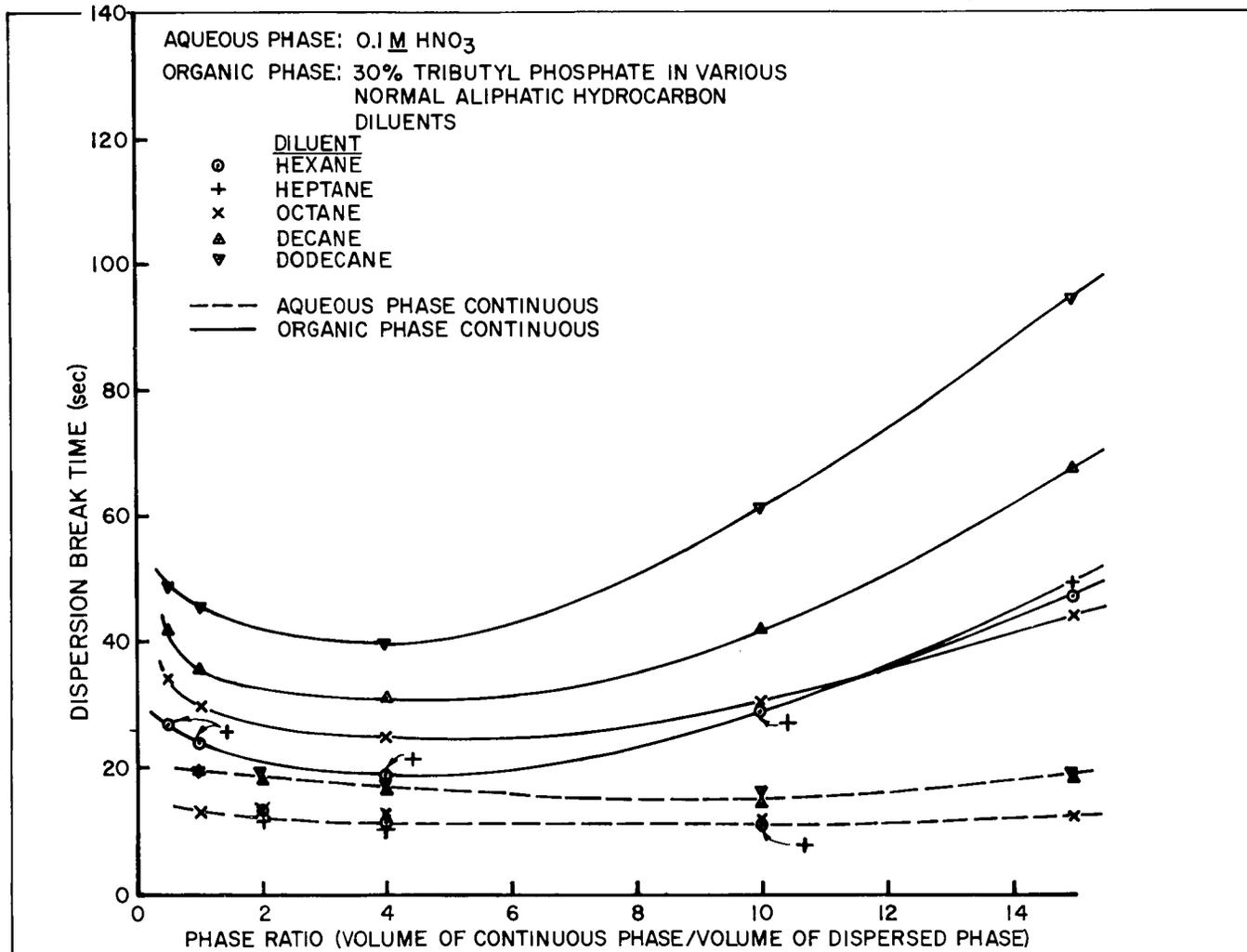


Fig. 1.5 Dispersion Break Test Results for Aliphatic Hydrocarbon Systems.

2. ENGINEERING SEPARATION OF MACROMOLECULAR BIOLOGICAL SUBSTANCES

C. W. Hancher H. O. Weeren

2.1 Production of Mixed Transfer Ribonucleic Acids

The last processing step in the production of mixed transfer ribonucleic acids (tRNA's) is a treatment with (diethylaminoethyl) cellulose (DEAE cellulose) to remove ribonuclease and traces of deoxyribonucleic acid (DNA). Heretofore, batch methods were employed because the form of DEAE cellulose available was not practical for use in a large column. However, new forms of DEAE cellulose have now been obtained, and were tested this quarter in the processing of the final 100 g (dry weight) of the mixed tRNA's (~ 600 g) that had been separated from Escherichia coli B cells last quarter.

Two forms of DEAE cellulose were tested; one had a molecular-sieve type of matrix (Sephadex A-25),* and the other was microgranular (Whatman Chromedia DE-52).** Separation of DNA from the mixed tRNA's was poor with Sephadex A-25, apparently because the ion-exclusion effect opposed the ion exchange effect of the DEAE cellulose. Separation was satisfactory with Whatman Chromedia DE-52, but the column quickly overloaded because of an unexpectedly high DNA content in the feed.

Production commitments could be met by using the Whatman Chromedia DE-52 in either of the following two ways: (1) the column could be loaded repeatedly with very small amounts of material, or (2) the DNA could be removed from the feed by fractional precipitation with isopropanol prior to final purification on the column. The later method was chosen. One part (by volume) of isopropanol was mixed with two parts of feed; the temperature was carefully maintained at 20°C and the pH at 7.0. The precipitate, which is the DNA-rich fraction, contained 380 mg of RNA and 890 mg of DNA per milliliter; the concentrations of specific tRNA's were quite low. The second (RNA-rich)

* Pharmacia Fine Chemicals, Inc., Piscataway, N. J.

** Angel H. Reeve and Co., Inc., Clifton, N. J.

fraction was precipitated by mixing one part (by volume) of isopropanol with three parts of the supernate. The resulting precipitate contained 12 mg of DNA and 6600 mg of RNA per milliliter. Virtually all of the phenylalanine tRNA in the feed was found in this precipitate. This precipitate was redissolved and further purified by passage through a 4-in.-diam by 12-in.-high DEAE cellulose column; loadings were as high as 780,000 optical density units (ODU). The recovery of phenylalanine tRNA was 91%, and the product was free of DNA.

An attempt was made to recover additional tRNA from the first fraction that had been precipitated. The precipitate was dissolved and reprecipitated to give two fractions; the first (rich in DNA) was discarded, and the second (presumably rich in RNA) was analyzed. The latter fraction contained 20 mg of DNA and only 800 mg of RNA per milliliter, with virtually no phenylalanine tRNA. Therefore, further attempts at tRNA recovery from this fraction were abandoned.

A batch of mixed tRNA's obtained from E. coli W is also being reprocessed by isopropanol precipitation and will be treated with DEAE cellulose.

2.2 Separation of Specific tRNA's

We have made a number of runs, using the isopentyl acetate reversed-phase columns, to determine the conditions that will improve the performance of the process. Among the variables investigated were the type of column support, the type and lot number of amine that was used as the organic phase, and the source of the mixed tRNA's used as feed.

The column support used in the reversed-phase columns is diatomaceous earth. Virtually all work to date has been done with 100- to 120-mesh Chromosorb W. This material is relatively fragile, and has a very high void volume (about 90%). Column performance in several runs in which the packing was accidentally pressurized and compacted seemed to be noticeably better than that for uncompact columns. This led to the speculation that perhaps a column support with a smaller void volume might have better flow characteristics, and thus might make better

separations. A few attempts with Chromosorb G (void volume about 70%) showed that its performance was about equal to, or slightly better than, that obtained with Chromosorb W. Therefore, Chromosorb G, which is much less fragile than Chromosorb W, will be used in future work.

In previous experiments, Aliquot 204 (dimethyldilaurylammonium chloride) was used as the organic phase. Recently, however, several runs have been made with Barquat SB-25 (stearyldimethylbenzylammonium chloride) as the organic phase. The resulting chromatograms differed from those obtained with Aliquot 204 in several ways: the tRNA's were eluted over a wider range of salt concentrations, and the separation of various tRNA's appeared to be improved; however, the separation of phenylalanine tRNA and leucine tRNA was much poorer. Since the problem of achieving effective separation of these tRNA's appeared difficult, this line of investigation was discontinued.

In the early work on the separation of tRNA's by reversed-phase columns, phenylalanine tRNA was eluted from the columns with sodium chloride solutions having concentrations as high as 0.80 M. The lot of Aliquot 204 that was received in December 1965 was used in nearly all subsequent runs. In these runs the range of sodium chloride molarities over which the tRNA's were eluted was much narrower than that in the early work (0.5 to 0.66 M compared with 0.6 to 0.92 M); phenylalanine tRNA was eluted at a sodium chloride concentration of 0.62 M. In April 1966, a sample of a new lot of Aliquot 204 was obtained and tested. With this material, the tRNA's were eluted over an even narrower range of sodium chloride molarities (0.53 to 0.64 M) than with the previous lot of Aliquot 204. Although further work with this new lot of amine does not appear to be promising, investigation of the reason for the shift in elution molarity might be enlightening.

A consistent difference has been observed (see Figs. 2.1 and 2.2) in the tRNA elution patterns obtained in runs made with feed prepared from E. coli B and runs made with feed prepared from E. coli W. The tailing-off of optically active material under the phenylalanine tRNA and the leucine tRNA peaks is much more pronounced in the chromatograms

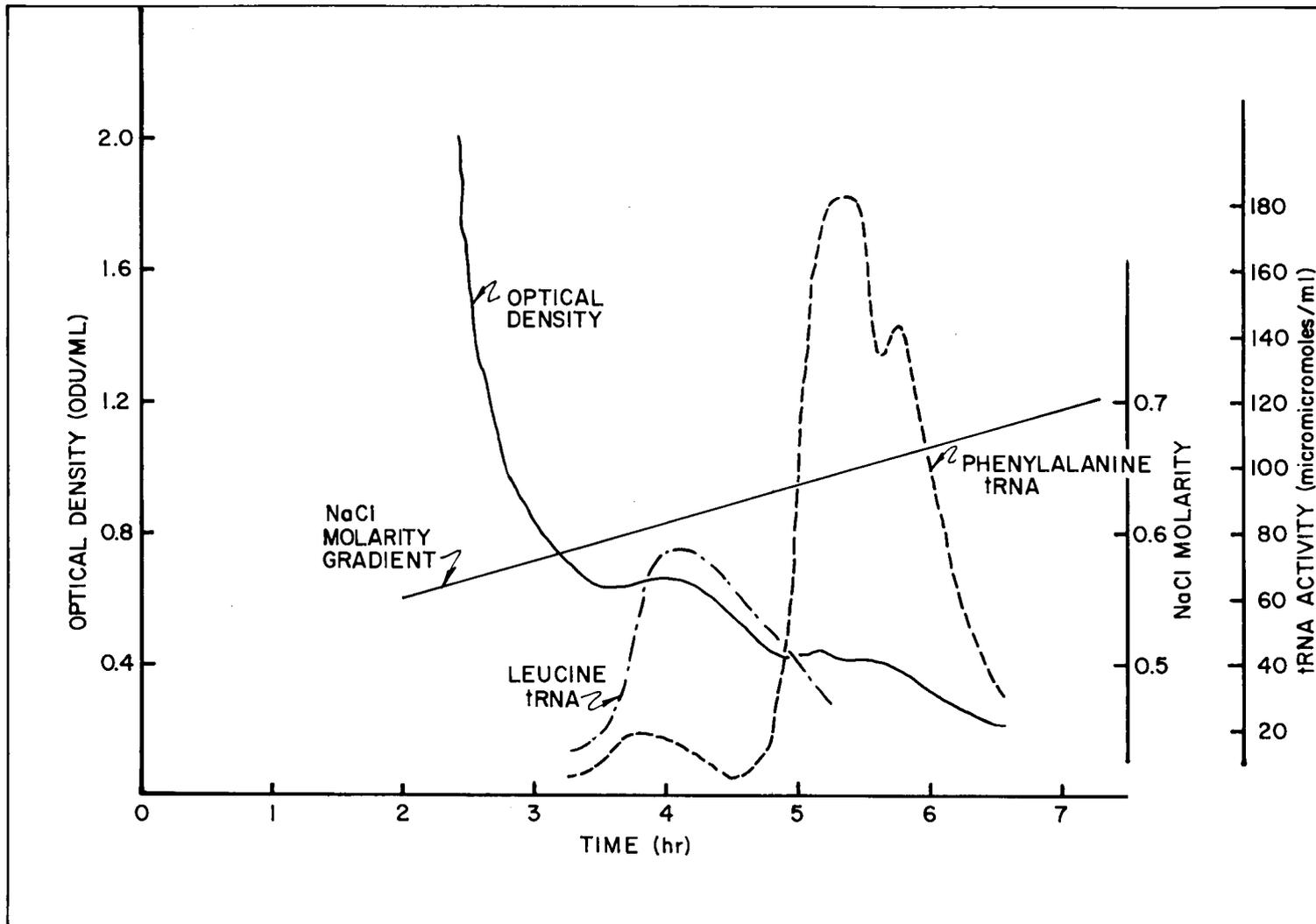


Fig. 2.1 Chromatogram Obtained with Strain B Feed.

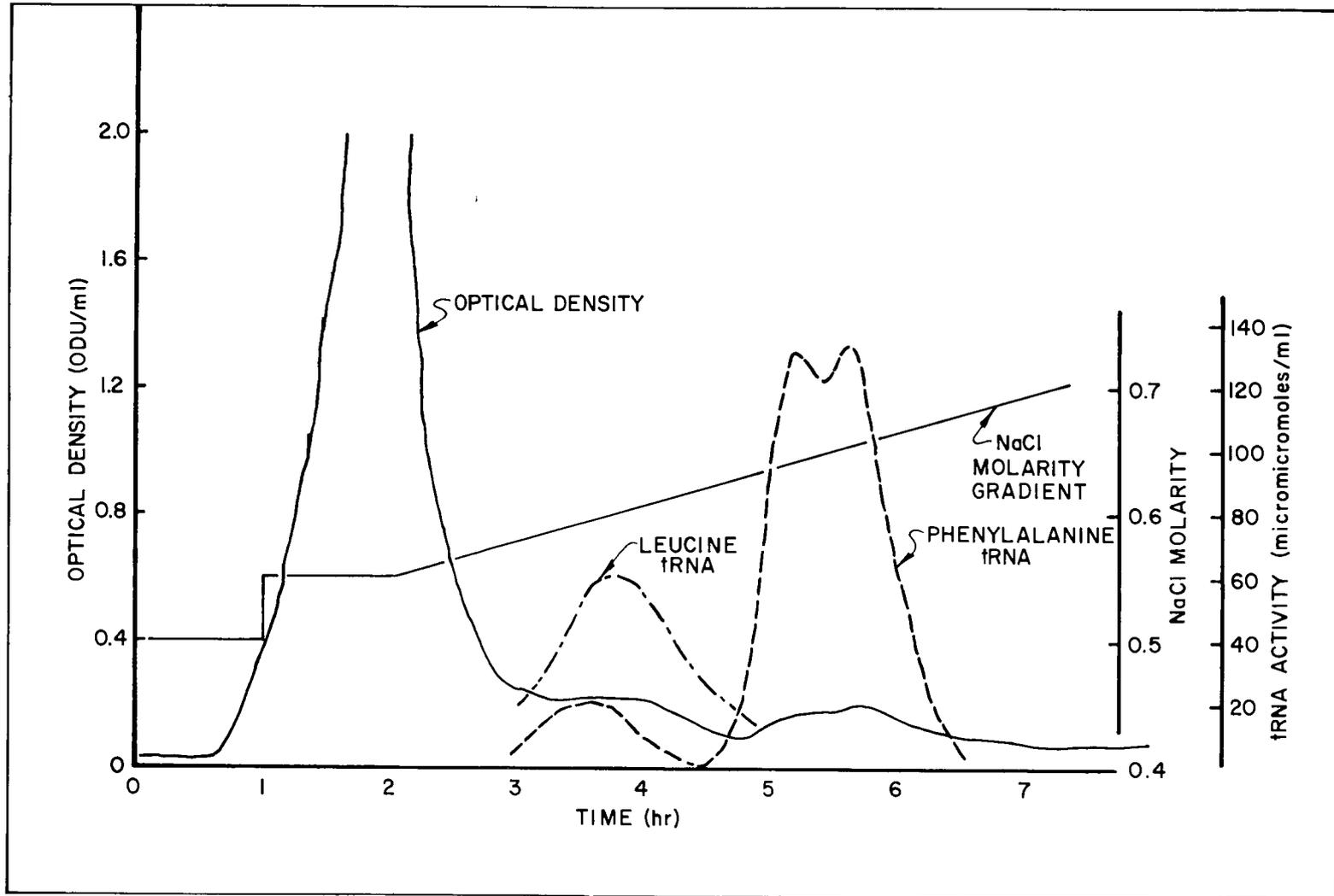


Fig. 2.2 Chromatogram Obtained with Strain W Feed.

obtained from strain B feed than in those from strain W feed. As a consequence, the specific activity of the phenylalanine tRNA from strain B is appreciably lower than that obtained from strain W (580 micromicromoles/ODU vs 870 micromicromoles/ODU). We are now trying to determine the reason for this difference (i.e., whether it is caused by inherent differences in the tRNA that is obtained from different strains of E. coli, or by differences in processing techniques). Two batches of E. coli B that were grown on different media have been obtained from the Grain Processing Corporation.* Batches of E. coli B and E. coli W that were grown locally are also being obtained. All this material will be processed by the same technique, and the mixed tRNA products that are obtained will be compared to determine the differences, if any.

* Grain Processing Corp., Muscatine, Iowa.

3. SOL-GEL PROCESS DEVELOPMENT

P. A. Haas

The objective of these studies is to develop optimum sol-gel processes for preparing ceramic fuel mixtures. All combinations of uranium, plutonium, and thorium as oxides, carbides, or nitrides, and perhaps uranium-plutonium-zirconium oxides, are of interest. The high thorium compositions (more than 75 mole % thorium) are reported separately under the closely related Thorium Fuel Cycle Studies (Sect. 4). The emphasis is presently on the preparation of urania or urania-thoria sols and the use of these sols in the formation of oxide microspheres.

Each of the flowsheets that were developed for preparing UO_2 sols by precipitation requires the same principal operations; only the chemical conditions of the individual operations vary. The principal operations are:

- (1) reduction of uranyl nitrate to uranous nitrate with hydrogen in the presence of a catalyst,
- (2) precipitation of uranous hydroxide with ammonia,
- (3) removal of NH_4NO_3 , NH_4OH , and other solutes by washing,
- (4) dispersion with NO_3^- as the peptizing ion.

Each of these operations has been tested in two or three separate pieces of equipment; hence, a number of flowsheet-equipment combinations have been tested.

3.1 Continuous Washing of Urania Precipitates

P. A. Haas

In the preparation of UO_2 sols by the precipitation-peptization method, the nitrate and ammonium ions that are present after the reduction and the precipitation steps must be removed in order for peptization to take place. Most of these ions are readily washed out

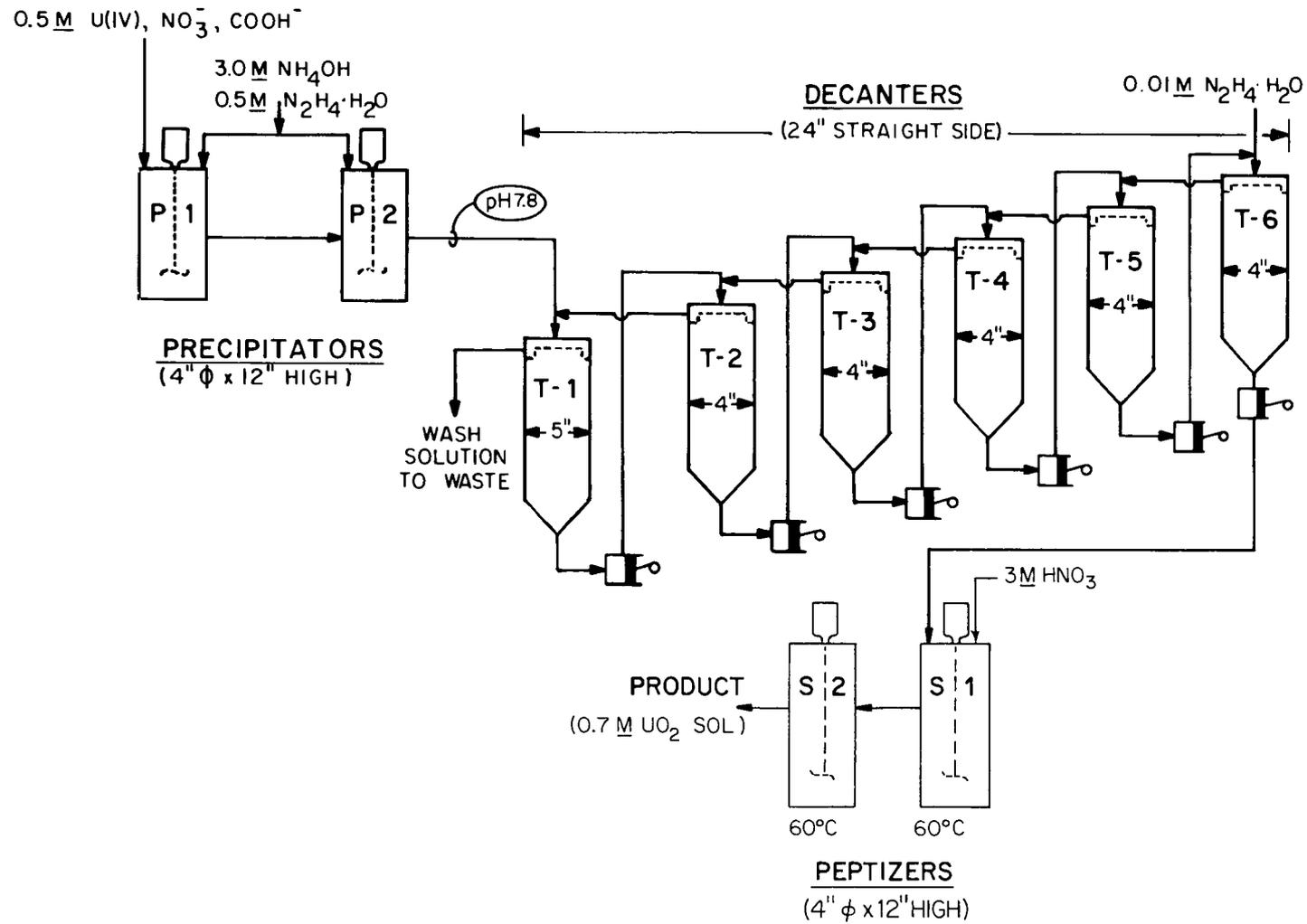
of the precipitate; however, small amounts of nitrate ion (at a pH of less than 7.5) or ammonium ion (at a pH greater than 9) are adsorbed on the precipitate and are not easily removed. Because the precipitate is voluminous unless concentrated by filtration or other treatments, extensive washing is required. For batch preparations, four or five washes, with separation of the supernate by filtration and/or decantation after each wash, are necessary to reduce the $\text{NO}_3^-:\text{U}$ and $\text{NH}_4^+:\text{U}$ mole ratios by factors of 10^2 to 10^3 .

Two types of continuous washing equipment have been tested in an attempt to obtain a more efficient utilization of wash water. One type consists of six countercurrent mixer-decanter stages (Fig. 3.1). The wash water flows by gravity, and the precipitate is transferred by gas-operated (blowcase) pumps. The second type is a 12-ft-high, 4-in.-ID column in which the precipitate and wash solution flow countercurrently. Initial tests of both systems were reported previously.⁴

The chemical flowsheets, precipitators, and peptizer-concentrator equipment are equally applicable to the wash column and the mixer-decanter apparatus. When compared with the mixer-decanters, the wash column is mechanically simpler and causes less accumulation of solids; on the other hand, it has much greater height requirements and provides less positive mixing.

Washing efficiencies can be calculated in terms of stage efficiencies for the mixer-decanters, or in terms of the height of a transfer unit (HTU) for the wash column. These calculations require a knowledge of the volumetric flow rate of the precipitate and of the distribution coefficients of the unwanted solutes between the precipitate and the wash solution. The volume of the precipitate was assumed to be the volume of a static bed of washed precipitate after a short (about 20 min) period of settling. These volumes were equivalent to uranium concentrations of 0.17 to 0.4 M. The NO_3^- and NH_4^+ distribution coefficients were assumed to be 1; that is, the concentrations in moles

⁴M. E. Whatley et al., Unit Operations Section Quarterly Progress Report October-December 1966, ORNL-4094.



24

Fig. 3.1 Precipitation-Peptization-Continuous Countercurrent Decantation (P²C²D) Apparatus for Preparation of UO₂ Sol.

per unit volume in the wash solution and in the precipitate were assumed to be equal. This is a good approximation for the first stage (where the precipitate enters), but it may not be valid at the exit (where the residual NO_3^- or NH_4^+ may be preferentially adsorbed by the precipitate). With these assumptions, the calculations can be made from simple, conventional equations.

For the mixer-decanters, the equation for stagewise operation can be arranged as follows:

$$(V/L)^{n+1} = (X_2/X_1) \left(\frac{V}{L} - 1 \right) + 1 ,$$

where

V = flow rate of wash solution,

L = flow rate of precipitate,

n = number of theoretical stages,

X_2 = concentration of NO_3^- or NH_4^+ in precipitate entering washer,

X_1 = concentration of NO_3^- or NH_4^+ in precipitate leaving washer.

The stage efficiencies for the mixer-decanters (Table 3.1) were 53 to 89%. These efficiencies appear reasonable when the unavoidable backmixing in the transfer pumps is taken into account. The higher efficiencies were obtained in the later runs, when the pump rates were more carefully selected.

For the wash column, the equation is:

$$N = \frac{X_2 - X_1}{(X - Y)_{\ln \text{ mean}}} = \frac{X_2 - X_1}{(X_2 - X_1) - Y_2} \ln \frac{X_2 - Y_2}{X_1} ,$$

where N is the number of transfer units, and Y_2 is the concentration of the ion in the wash solution leaving the washer. For the 12-ft-high wash column (see Table 3.2) 3.3 to 5.2 transfer units, or HTU values of 2.3 to 3.6 ft, are obtained, based on the precipitate phase since the controlling resistance to mass transfer is probably in the precipitate.

Table 3.1 Calculated Stage Efficiencies for Six-Stage Mixer-Decanter Type of Washer

P ² C ² D Test No.	L (liters/hr)	V (liters/hr)	NH ₄ ⁺ Concentrations (M)		Number of Stages (n)	Stage Efficiency (%)
			X ₂	X ₁		
3A	2.6	8.0	1.19	0.010	3.9	65
3B	2.0	9.0	1.19	0.007	3.2	53
4A	1.7	6.5	1.19	0.007	3.6	60
4B	2.0	6.0	1.07	0.004	5.2	87
5	2.0	5.5	0.93	0.006	4.5	75
6	2.0	5.5	0.93	0.003	5.3	89

Table 3.2 Calculated HTU's for 12-ft-high Wash Column

Test	NO ₃ ⁻ Concentrations (M)			Number of Transfer Units (N ^a)	HTU ^a (ft)
	X ₂	X ₁	Y ₂		
WCT-1	0.50	0.015	0.204	5.1	2.4
WCT-2	0.36	0.020	0.141	4.1	2.9
WCT-3	0.50	0.011	0.174	5.2	2.3
WCT-4	0.42	0.062	0.249	3.3	3.6
WCT-5	0.42	0.027	0.234	4.8	2.5
WCT-6	0.46	0.04	0.155	3.3	3.6

^aBased on the precipitate (X) phase, since this is the controlling resistance.

3.2 Studies of Continuous Peptization and Evaporation Methods in the Preparation of UO₂ Sols

P. A. Haas, A. R. Irvine,^{*} A. D. Ryon

The first tests of a Precipitation-Peptization-Continuous Counter-current Decantation (P²C²D) system⁴ showed that material having a suitable uranium concentration could not be obtained unless the washed precipitate was dewatered (by filtration or centrifugation) or the final sol was concentrated by some means. Dewatering on a filter, followed by batch peptization, was shown to be feasible for several precipitates prepared by the P²C²D method. However, a continuous-peptization--concentration operation would be necessary in order to justify the use of continuous washing equipment. Two procedures were demonstrated for concentrating urania sols by forced-circulation vacuum evaporation. The dilute sols from runs P²C²D-3 and -4 were concentrated in an evaporator that had been designed and installed to concentrate sols prepared by a solvent extraction method. No drastic changes occurred in sols that had been stored for two to four months

^{*}Chemical Technology Division, Process Design Section.

before being concentrated in the forced-circulation vacuum evaporator (Table 3.3). After concentration, the first sol was very fluid, but the second and third sols were thixotropic. These three sols were subsequently used to form gel spheres in a column of 2-ethyl-1-hexanol having high surfactant concentrations. Although each sol formed gel particles without difficulty, only the second and third sols yielded a spherical product.

After run 4, a continuous vacuum evaporator was added to the P²C²D system to give sols of suitable concentrations. Although operation appeared satisfactory through two startups with a natural uranous nitrate feed rate of 0.5 mole/hr, run P²C²D-5 had to be terminated each time, after 6 to 10 hr, because of failure of the evaporator pumps. Installation of a centrifugal pump with a double mechanical seal eliminated this problem, and thereafter the evaporator operated with only a slight difficulty. The system was then operated with a uranium feed rate of 0.5 mole/hr for about 70 hr (run P²C²D-6). About 40 liters of sol containing about 7 kg of uranium was produced.

Most of the urania sol analyses for run P²C²D-6 are in the expected ranges (Table 3.4). The variations in uranium concentrations correspond to the upsets in operation. The U(IV):U ratios are satisfactory; the NO₃⁻:U ratios are acceptable. The NH₄⁺ concentrations are in the usual range for sols that are prepared from precipitated UO₂. The HCOO⁻:U and C:U ratios are somewhat high; however, this is an expected result of precipitation at a low pH. The significance of the decrease in x-ray crystallite size is not known. Concentrations of NO₃⁻, NH₄⁺, and HCOO⁻ ions in the supernates (Table 3.5) show that washing was reasonably effective. The unusually low U(IV):U ratios of the feeds (Table 3.6) might explain, to some extent, the anomalous behavior of the sols.

These sols were less attractive for forming spheres (Table 3.7) than most of the UO₂ sols that we have tested. Spheres with only barely acceptable characteristics were formed in fresh 2EH having relatively high surfactant concentrations (0.8 vol % Span 80 and 0.2 vol % Ethomeen S/15). This relatively poor performance is rather difficult to explain

Table 3.3 Analyses of P²C²D-Prepared Sols
Before and After Concentration in a Vacuum Evaporator

Batch No.	Condition	Uranium Concentration (M)	Mole Ratios			(1,1,1) X-Ray Crystallite Size (Å)
			U(IV):U	NO ₃ ⁻ :U	COOH ⁻ :U	
1	As prepared ^a	0.26	0.87	0.17	0.11	85
	Before evaporation ^b	0.198	0.849	0.185	0.275	97
	After evaporation	0.50	0.860	0.220	0.182	102
2	As prepared ^a	0.30	0.86	0.21	0.22	72
	Before evaporation ^b	0.257	0.847	0.266	0.260	70
	After evaporation	0.796	0.840	0.232	0.210	67
3	As prepared ^a	0.38	0.87	0.14	0.12	74
	Before evaporation ^b	0.349	0.855	0.215	0.232	68
	After evaporation	0.810	0.842	0.292	0.211	72

^aAverages for four sols as prepared, before aging (for two to four months) and then combining.

^bAfter aging; a single sol made by combining the four sols of this batch.

Table 3.4 Analyses of Urania Sol Produced in Run P²C²D-6

Batch No.	Concentrations (M)						X-Ray Crystallite Size ^a (Å)	Mole (or Atom) Ratios					
	U	NO ₃ ⁻	NH ₄ ⁺	N	HCOO ⁻	C		U(IV):U	NO ₃ ⁻ :U	NH ₄ ⁺ :U	N:U	HCOO ⁻ :U	C:U
1	0.633	0.128	< 0.006	0.137	0.244	0.236	100	0.877	0.202	< 0.010	0.216	0.38	0.37
2	0.710	0.130	0.0043	0.127	0.271	0.293	102	0.886	0.183	0.006	0.179	0.38	0.41
3	0.603	0.104	---	---	---	---	---	0.885	0.172	---	---	---	---
4	0.502	0.076	< 0.006	0.063	0.244	0.227	82	0.906	0.152	< 0.012	0.126	0.49	0.45
5	0.301	0.073	---	---	---	---	---	0.890	0.242	---	---	---	---
6	0.585	0.110	0.0037	0.122	0.213	0.230	85	---	0.188	0.006	0.208	0.36	0.39
7	0.364	0.084	---	---	---	---	---	0.881	0.230	---	---	---	---
8	0.741	0.149	---	---	---	---	---	---	0.201	---	---	---	---
9	0.772	0.149	---	---	---	---	---	0.878	0.193	---	---	---	---
10	0.585	0.115	0.0043	0.120	0.304	0.295	74	---	0.197	0.007	0.206	0.52	0.50
11	0.928	0.137	---	---	---	---	---	0.889	0.148	---	---	---	---
12	0.911	0.139	---	---	---	---	---	---	0.153	---	---	---	---
13	0.911	0.137	0.009	0.127	0.402	0.410	69	0.888	0.150	0.010	0.140	0.44	0.45
14	0.763	0.126	0.011	0.152	0.324	0.323	68	0.890	0.165	0.014	0.199	0.42	0.42

^a(111) plane.

Table 3.5 Analyses of Supernates in Run P²C²D-6

Stream	Concentrations	Concentrations (M)			
		U	NO ₃ ⁻	NH ₄ ⁺	HCOO ⁻
P-2 ^a Effluent	Material Balance	0.36	0.79	1.0	0.35
T-1 ^a Overflow	Material Balance	~ 0	0.22	0.28	0.095
T-1 ^a Composite	Analyses	0.00009	0.197	0.194	0.038
T-1 ^a Overflow	Analyses	0.00015	0.128	0.133	0.031
T-2 ^a Overflow	Analyses	---	0.098	0.103	0.024
T-3 ^a Overflow	Analyses	---	0.042	0.030	0.008
T-4 ^a Overflow	Analyses	---	0.018	0.0047	0.004
T-5 ^a Overflow	Analyses	---	0.009	0.0014	0.004

^aSee Fig. 3.1 for nomenclature.

Table 3.6 Analyses of Feeds: Run P²C²D-6

Sample	Uranium Concn. (M)	Mole Ratios			
		U(IV):U	NO ₃ ⁻ :U	NH ₄ ⁺ :U	HCOO ⁻ :U
5-22-1436	0.47	0.92	2.32	0.013	0.93
5-23-0115	0.47	0.96	2.28	0.018	1.07
5-23-1045	0.50	0.96	2.18	0.006	0.94

Table 3.7 Sphere-Forming Test Results for Sols Prepared in Run P²C²D-6

Sol Batch No.	Test Time	2EH in System			Comments on Operation and Product
		Date In	Span 80 (vol %)	Ethomeen S/15 (vol %)	
11	5-30-1540	5-5-67	0.75	0.35	Severe distortions ("raisins").
11	6-5-1144	6-1-67	0.5	0.2	Excessive sticking, some coalescence; drops that dried were spheres.
11	6-7-1230	6-1-67	1.1	0.2	Poor disperser operation; "raisins".
11	6-7-1425	6-1-67	1.1	0.2	Good column operation; "raisins" or very severe pits.
3	6-8-1108	6-1-67	1.1	0.2	Disperser and column operation satisfactory, but product is not usable.
13	6-8-1500	6-1-67	1.1	0.2	Good disperser and column operation; product ("raisins") not usable but is slightly better than 6-8-1108.
13	6-9-1000	6-1-67	1.1	0.3	Good spherical product, but it exhibits excessive sticking and coalescence.
13	6-14-1550	6-13-67	0.8	0.2	New 2EH; spheres exhibit sticking and clustering to some extent; product, for the most part, was acceptable (spherical).
12	6-19-1408	6-13-67	1.1	0.3	Sol in product collector formed large wet drops; dried particles are spheres; not as good as 6-14-1550; unacceptable operation of equipment.

because the sols were fluid, free of a "heel" or second phase, and had uranium concentrations, $\text{NO}_3^-:\text{U}$ mole ratios, and $\text{NH}_4^+:\text{U}$ mole ratios that were normally acceptable for UO_2 sols prepared by precipitation. Essentially all the previous UO_2 sols that gave such poor results had exhibited obvious undesirable characteristics such as nonoptimum concentrations or a tendency to gel or precipitate after standing. The P²C²D-6 sols contained less "heel" than any other UO_2 sols that we have used.

3.3 Microsphere Preparation Development

P. A. Haas

Surfactants must be added to the 2-ethyl-1-hexanol (2EH) that is used for preparing microspheres in order to prevent coalescence of sol droplets, sticking of droplets to the column walls, or clustering of partially dried drops. The amounts and types of surfactants required for a new type of sol are determined empirically since the effects of the surfactants have no known theoretical basis.

The required initial surfactant concentrations and the quantity of each surfactant that must be added periodically to the 2EH are more difficult to predict for UO_2 sols than for ThO_2 sols. The UO_2 sols are more prone to stick, to coalesce, or to cluster, and thus require more careful control of surfactant concentration. Also, because the urania sols are prepared by several different methods, they have many more composition variables. For example, in the case of thoria sols, the only variables of consequence are the thorium molarity and the $\text{NO}_3^-:\text{Th}$ mole ratio; urania sols, on the other hand, are affected by the uranium molarity and by the $\text{NO}_3^-:\text{U}$, $\text{COOH}^-:\text{U}$, $\text{NH}_4^+:\text{U}$, and $\text{O}:\text{U}$ mole (or atom) ratios.

The forming of satisfactory UO_2 gel microspheres generally requires the simultaneous use of Span 80 and Ethomeen S/15 in the 2EH, with a much higher total surfactant concentration than is needed for making ThO_2 microspheres. About 1 vol % total surfactant, with a Span

80:Ethomeen S/15 volume ratio of 4:1 was quite satisfactory for most UO_2 sols. A concentration of not less than 0.5 vol % Span 80 was necessary to minimize sticking and clustering. A total surfactant concentration (or Span 80:Ethomeen S/15 ratio) that was too high tended to cause the formation of misshapen particles with the appearance of raisins. High Ethomeen S/15 concentrations seemed to produce particles having a deep indentation, or dimple, on one side. For some sols, a high total surfactant concentration seemed to contribute to cracking of the spheres into fragments.

Some UO_2 sols were formed in 2EH that contained 0.8 vol % Span 80 and 0.2 vol % Ethomeen S/15 initially, and to which 10 cc each of Span 80 and Ethomeen S/15 (per liter of UO_2 sol) were added periodically. This schedule of surfactant addition will be further tested in the future by long-term operation with UO_2 sols.

The $\text{ThO}_2\text{-UO}_3$ sols (Th:U atom ratios of 3:1 to 5:1) that had been prepared by solvent extraction methods were formed into gel spheres by using 2EH containing Span 80 and Ethomeen S/15 at volume ratios of about 2:1. The use of Span 80 alone tended to cause wrinkled, or "raisin", surfaces, whereas the use of Ethomeen S/15 alone tended to cause deep dimples. Small-scale tests with freshly prepared sol and fresh 2EH required low total surfactant concentrations (not more than 0.2 vol %) to prevent cracking of the gel spheres into fragments; however, cracking did not occur in spheres prepared from aged sol (stored for 1 to 3 months) and 2EH that had been used 20 to 40 hr and contained as much as 0.8 vol % surfactant. The drying and firing conditions were the same as those for ThO_2 sols having small amounts of uranium added as $\text{UO}_2(\text{NO}_3)_2$ or UO_3 . The analyses of calcined microspheres are given in Table 3.8.

Gel microspheres formed from sols prepared via solvent extraction have, after drying, shown an unexpected heating effect upon exposure to air. Temperature rises of more than 100°C were observed when batches of about 1 kg were poured into alumina trays. One batch of dried gel was kept under argon and transferred to the laboratory for further study. This study is still in progress.

Table 3.8 Analyses of Calcined $\text{ThO}_2\text{-UO}_3$ Microspheres^a
 Formed from Sols Prepared via Solvent Extraction Methods

Sol No.	Surfactant Concentration in 2EH (vol %)	BET Surface Area (m^2/g)	O:U Atom Ratio	Density ^b (g/cc)
EVR-1	0.17	0.015	2.0039	10.05
EVR-2	0.17	0.014	2.0063	10.02
EVR-2	0.62	0.013	2.0054	9.86

^aAll samples had a carbon content of 0.002 wt %.

^bDensities were determined by mercury pycnometer at 5000 psi; maximum change from atmospheric pressure to 10,000 psi was 0.05 g/cc.

3.4 Firing of Urania Microspheres

P. A. Haas

Controlled oxidation is required during the firing of urania microspheres. If a reducing or inert atmosphere is used throughout the drying and firing steps, the carbon content of the fired microspheres will be high (10^3 to 10^4 ppm). Densification is poor for high-carbon material, and the presence of the carbon makes the microspheres unacceptable for some uses. On the other hand, excessive oxidation results in a low-density product. If oxidation is excessive, the UO_2 structure is apparently lost and sintering does not occur at the usual temperature for sol-gel oxides even though the urania is again reduced to UO_2 . The effects of drying and firing conditions on sol-gel urania have been extensively investigated in laboratory studies,⁴ but no universally optimum conditions have been found.

About 3 kg of urania microspheres was used in each of two firing tests. The purpose of these tests was to fire large quantities of urania microspheres, using the muffle furnace and the instrumentation

that is normally employed in the preparation of $\text{ThO}_2\text{-UO}_3$ microspheres. Although more-complex heating cycles (using steam or other atmospheres, and soak periods) would be very effective,⁴ they cannot be tolerated in the available equipment without alterations or additions.

The charge for the first test consisted of four batches of off-specification product from microsphere-preparation tests. The furnace was heated to 1150°C in argon, held for 4 hr in Ar--4\% H_2 , and then cooled to below 100°C in argon. The products had low O:U atom ratios (2.0045 to 2.0059); however, the carbon contents were undesirably high (150 to 980 ppm), and the densities were correspondingly low (Table 3.9).

Table 3.9 Results of UO_2 Firing Test CALC-1

Charge: 600 to 1000 g of gel, less than 1 in. deep in trays.

Firing cycle: argon atmosphere to 1150°C , Ar--4\% H_2 for 4 hr, argon during cooldown to below 100°C .

Batch No.	O:U Atom Ratios	Carbon Content (ppm)	BET Surface Area (m^2/g)	Density ^a Measurements (% of theoretical)	
				Hg Pycnometer	Tap
1	2.0046	150	0.059	91	91
2	2.0059	580	0.224	88	--
3	2.0050	980	0.312	89	91
4	2.0045	520	0.322	90	92

^aBased on theoretical densities of 10.7 g/cc for Hg pycnometer at 100 psi and 6.65 g/cc for tap density.

A second test (Table 3.10) indicated that satisfactory UO_2 microspheres could be made in the muffle furnace by utilizing a simple oxidative pretreatment. This pretreatment, which promotes densification and the removal of carbon, consists in exposing the microspheres to air overnight at room temperature and at temperatures up to 100°C during startup. The smaller-diameter, deeper crucibles used for the second

Table 3.10 Gel Charges for UO₂ Firing Test CALC-2

Sols: UO₂ sols prepared by precipitation-peptization method.

Column conditions: Gel spheres formed, using 2EH that contained both Span 80 and Ethomeen S/15.

Sample Charge	Gel Sphere Samples	Sol Preparation	Estimated Average Diameter (μ)	Comments on Product
2-1A 2-1B 2-1C	5-30-1520 6-7-11230 6-7-1425 6-8-1500	P ² C ² D-6	270	Nonspherical, raisin-like particles
2-2	6-6-1552 6-15-1155	WCT-13 WCT-13	200	Good spheres
2-3	3-22-1200 3-23-1545	WCT-7 WCT-9	270	Good spheres
2-4	Miscellaneous	Miscellaneous	350	Not usable
2-5	3-1-1146 3-9-1545 3-22-1555	WCT-1 WCT-3 WCT-5	260	Some deep dimples
2-7	Miscellaneous	Miscellaneous	220	Some "raisins"
2-8	Miscellaneous	Miscellaneous	300	Some deep dimples

test were less satisfactory than the shallow trays used in the first test. When sufficient gel microspheres were used to fill the crucibles to a depth of 3 in., the densities of the particles in the bottom halves of the charges were 4 to 7% lower than those in the top halves (Table 3.11). The O:U atom ratios were 2.0016 to 2.0072 (average, 2.0034), with no significant variation between top and bottom samples. Analyses of the calcined product showed from less than 10 ppm to 190 ppm of carbon for microspheres recently formed from sol and 50 to 220 ppm of carbon for gel microspheres stored for three months (Tables 3.10 and 3.11), compared with 150 to 980 ppm for the first calcination without deliberate air exposure (Table 3.9). The differences in the carbon contents of the top and bottom samples were not significant. Severe caking occurred in the bottom half of several crucibles, and the fired product could be removed only by gouging with a screwdriver. Even though these cakes broke up into individual spheres during screening, the unloading and screening were made more difficult by the caking. No caking of any consequence took place in the shallow trays that were used in the first firing test.

Table 3.11 Analyses for UO₂ Firing Test CALC-2

Gels: See Table 3.10.
 Charge conditions: About 300 g of gel spheres, sufficient to fill crucibles to a depth of 3 in. Spheres equilibrated overnight with air.
 Firing cycle: Air atmosphere to 100°C, argon to 1150°C, argon--4% H₂ for 4 hr, argon during cooldown to below 100°C.

Sample Code ^a	O:U Atom Ratio	Carbon Content (ppm)	BET Surface Area (m ² /g)	Density ^b Measurements (% of theoretical)	
				Hg Pycnometer	Tap
2-1AT	2.0037	---	---	---	---
2-1BT	2.0032	190	---	---	---
2-1CT	2.0033	---	---	---	---
2-1AB	2.0028	---	---	---	---
2-1BB	2.0016	30	---	---	---
2-1CB	2.0018	---	---	---	---
2-1	2.0021	< 10	0.007	101	106 ^c
2-2T	2.0047	50	0.020	97.9	100
2-2B	2.0072	10	0.035	91.4	93
2-3T	2.0028	170	0.008	93.2	93
2-3B	2.0032	200	0.020	89.4	89
2-4	2.0027	50	---	---	100
2-5	2.0028	200	---	88	90
2-7	2.0046	220	---	90	100
2-8	2.0045	170	---	---	88

^aT and B, as last letters, refer to top half and bottom half, respectively, of the crucibles. Fresh gel samples: 2-1 and 2-2; aged gel samples: 2-3 through 2-8.

^bBased on theoretical densities of 10.7 g/cc for Hg pycnometer at 100 psi and 6.65 g/cc for tap density.

^cNonspherical shape apparently gave greater packing fraction than possible for spheres.

4. THORIUM FUEL-CYCLE STUDIES

P. A. Haas

The objective of these studies is to develop low-cost processes, adaptable to remote operation, for the recycle of thorium and ^{233}U to heterogeneous reactors. The present emphasis is on procedures and prototype equipment for preparing oxide microspheres in the Thorium-Uranium Recycle Facility. These studies seek: (1) to improve and to simplify existing equipment and operations, (2) to obtain data on the reliability and behavior of both the equipment and the process over extended operating periods, (3) to adapt the equipment to the exacting requirements of remote operation, and (4) to provide hundred-kilogram lots of ThO_2 microspheres for use in large-scale pyrocarbon-coating experiments.

4.1 Preparation of Microspheres in the Coated Particle Development Laboratory

C. C. Haws

CPDL Microsphere Preparation

During April, 137 kg of ThO_2 microspheres was prepared by operating the microsphere-forming column on a schedule of six shifts per week. With the multiple (six-needle) two-fluid nozzle, the daily yield in the desired (210 to 250 μ) diameter range varied from 40 to 70%. Most of the microspheres not in this range had diameters of 250 to 297 μ . The combined yield of these two size ranges (i.e., 210 to 297 μ) was consistently greater than 90%.

During May, much of the equipment was cleaned and dismantled to permit completely redesigned microsphere-forming and drying systems to be installed. The existing distillation apparatus and the temperature recorders were retained in the new unit. The purposes of this major modification were:

- (1) to simplify the process flowsheet as much as possible,

- (2) to improve its reliability, and
- (3) to improve operability sufficiently that remote operation would be feasible.

A schematic flowsheet of the new equipment is shown in Fig. 4.1. The features of this new unit (and the basic changes from the old one) are as follows:

- (1) A single canned-rotor pump replaces five conventional pumps.
- (2) Overflow weirs, which control the liquid levels in all vessels, eliminate three control valves and their associated instrumentation.
- (3) All the 2-ethylhexanol (2EH) used in the equipment is returned by gravity to a single surge tank, thereby eliminating two alcohol storage tanks. The equipment is arranged in such a way that 2EH cannot overflow and spill from any vessel.
- (4) A settler between the column overflow and the pump removes undried gel and other suspended matter.
- (5) A new and improved dryer-settler was installed (see Fig. 4.2). Later, a calciner of improved design will be installed.
- (6) All transfers of microspheres between operations are now accomplished by pneumatic or hydraulic methods.

Construction was completed, and preliminary operations were started during this reporting period.

Complexities of the old system, which had led to operational upsets even with direct observation and operation, have been removed. All the equipment is arranged near a common level so that, at liquid-level equilibration (i.e., when the pump is stopped), virtually no change of liquid level occurs in any of the vessels. No piece of equipment can be made to overflow since all flows return to a single surge tank and no vessel has a valve in its discharge line.

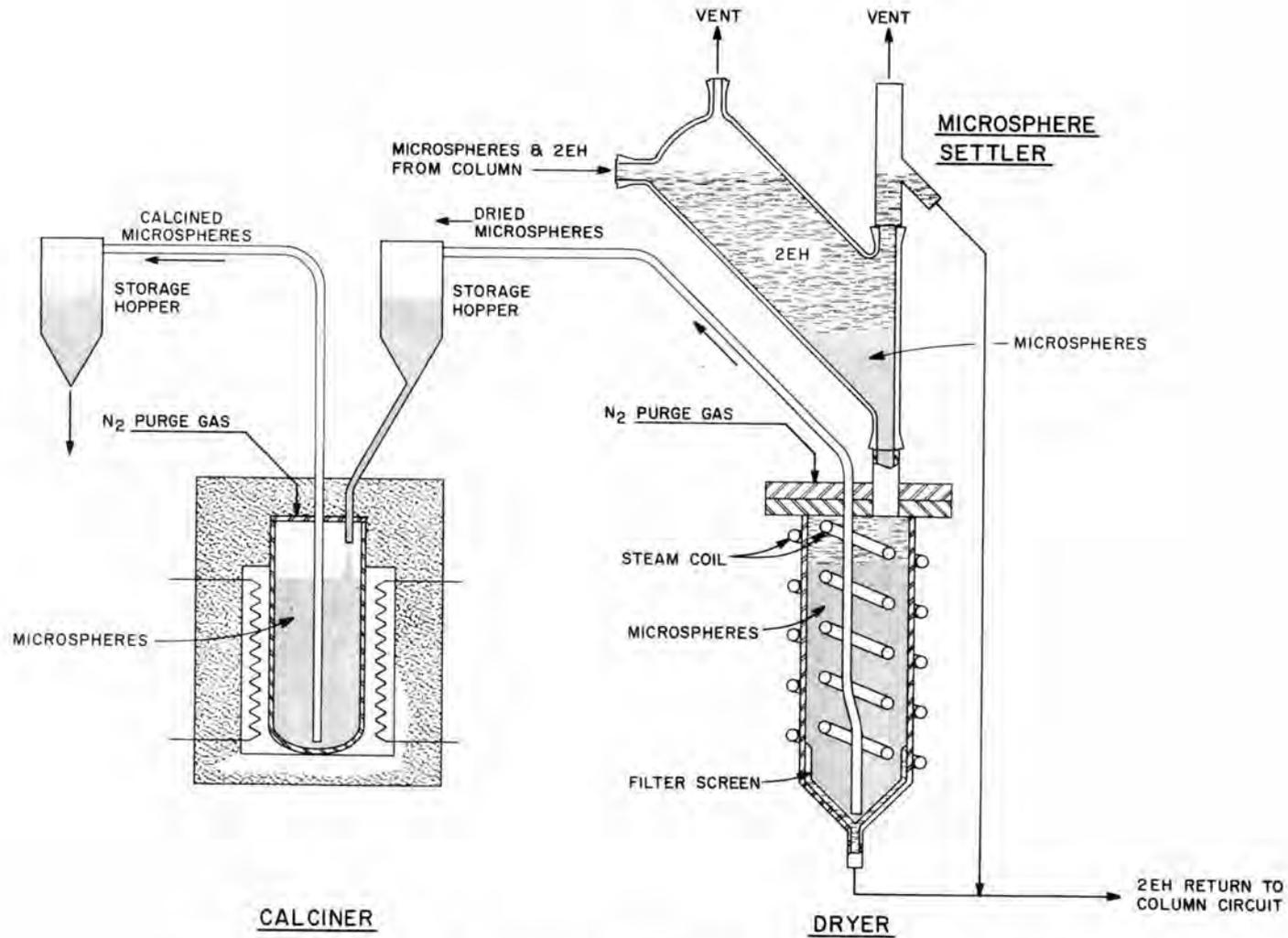


Fig. 4.2 Schematic Arrangement: Microsphere Dryer and Calciner.

Over several six-month periods of operating with different charges of 2EH, very fine ThO_2 particles constituted the only detectable "impurity" that steadily accumulated in the alcohol (Table 4.1). The very fine particles were formed by redispersion of incompletely dried thorium microspheres that were carried into a pump. Turbidity of the 2EH, resulting from this impurity, made observation of microsphere settling difficult, and was the only reason for draining two charges of alcohol from the system.

Table 4.1 Analysis of the 2-Ethyl-1-Hexanol
Used in the CPDL Microsphere Column over a Four-Month Period

Material	Concentration (M)	Comments
Nitrate ion	$(1.5 \text{ to } 4) \times 10^{-4}$	No trend with time
Total nitrogen	$(2.0 \text{ to } 5) \times 10^{-4}$	No trend with time
Amine	$(6.0 \text{ to } 10) \times 10^{-4}$	No trend with time
Thorium	$(2.0 \text{ to } 7) \times 10^{-4}$	Increasing with time

Filters in the original pilot plant effectively removed suspended solids from the 2EH as long as the solids were completely dried. However, the filters plugged immediately when incompletely dried sol entered the pump-filter circuits. (Incompletely dried sol is produced by operational upsets in the sphere-forming column.) Hence, we sought a method that would prevent the thorium from being carried into the pumps. Settlers were suggested for this purpose.

Two settlers were needed: one for the column overflow, and one for the transfer line from the column to the dryer. These settlers, which have now been installed, differ considerably in design because of the differences in the rates of flow of 2EH through them and the different sizes of particles that must settle in them. The flow rate to the settler at the column overflow is 20 liters/min, and the particles are usually smaller than 100μ in diameter. The flow rate from the bottom

of the column to the dryer is only 2 to 4 liters/min, with particle diameters ranging from 400-800 μ .

A liquid-liquid separator, which should further help to achieve clarity, was installed in the dryer underflow stream. The purpose of this separator is to remove sol from the 2EH return stream before it can enter a pump. Sol appears infrequently at this point from upsets in column operations.

The new settling equipment described above should greatly improve the clarity of the 2EH.

A change in operating procedure has eliminated plugging of the microsphere transfer jet. The microsphere transfer jet is located at the bottom of the column and transfers the microspheres from the bottom of the column to the dryer. To implement this change, a valve was installed in the discharge line from the jet. During start-up, this valve is closed. The 2EH transfer stream, which flows at the rate of 2 to 4 liters/min, thus flows backward through the jet into the bottom of the sphere-forming column. In this way large, incompletely dried ("gummy") sol droplets are prevented from entering and plugging the transfer jet. Instead, they remain suspended in the column until they are completely dried. Once the column is operating normally, the valve at the discharge of the transfer jet is opened and routine operation begins.

The design features and the physical arrangement of the settler-dryer and the calciner are shown in Fig. 4.2. Microspheres will be transferred from dryer to storage (or calciner) and from calciner to storage by pneumatic means. A criticality-safe dryer has operated satisfactorily with an 18-kg charge. This new dryer system was installed and tested prior to removal of the old microsphere column.

5. POWER REACTOR FUEL PROCESSING

5.1 Shear-Leach

The development and the evaluation of the shear-leach method for recovering fissile and fertile materials from spent power-reactor fuel assemblies are continuing.

Modifications of the 250-ton shear have been completed preparatory to shearing a 10- by 10-in. prototype fuel assembly that simulates a larger power-reactor fuel element. In addition, the shear has been fitted with new gibs of D2 tool steel, with a hardness equivalent to 60C on the Rockwell scale, and with wrought Stellite 6B liners.

The efficiency of operation of the modified shear under reasonable load conditions was evaluated by shearing a 3 x 3 array of 3-1/4 x 3-1/4 x 30 in. oak timbers, which are much less expensive than prototype fuel. Shearing these timbers with a rectangular straight-edged blade required a force of about 90 tons, compared with about 125 tons for prototype fuel. The two bottom gibs were inspected after approximately 30 cuts had been made on the oak timbers, and no scoring or galling could be seen. On two occasions when terminal pieces (about 2 in. long) were being sheared, the vertical row of timbers next to the fixed blade became tightly jammed in the gag guide. This difficulty was caused by a corner, which broke off one of the timbers and subsequently acted as a wedge. In one instance, the timbers were pressed together so tightly that the shaft on which the pusher head is mounted was bent. This shaft has a 1- by 11/16-in. rectangular section with a 1/4-in. dowel hole.

A large prototype fuel assembly is now being fabricated and will be used for the final tests of the shear. Fabrication is approximately 50% complete. The assembly contains 432 stainless steel tubes filled with uranium dioxide. Of these tubes, 327 have a 0.34-in. outside diameter, and 105 have a 0.300-in. outside diameter. The assembly has 10 Westinghouse-type leaf-spring grids on approximately 10-in. centers. Overall dimensions of the assembly are 9-1/8 x 9-3/8 x 105 in.

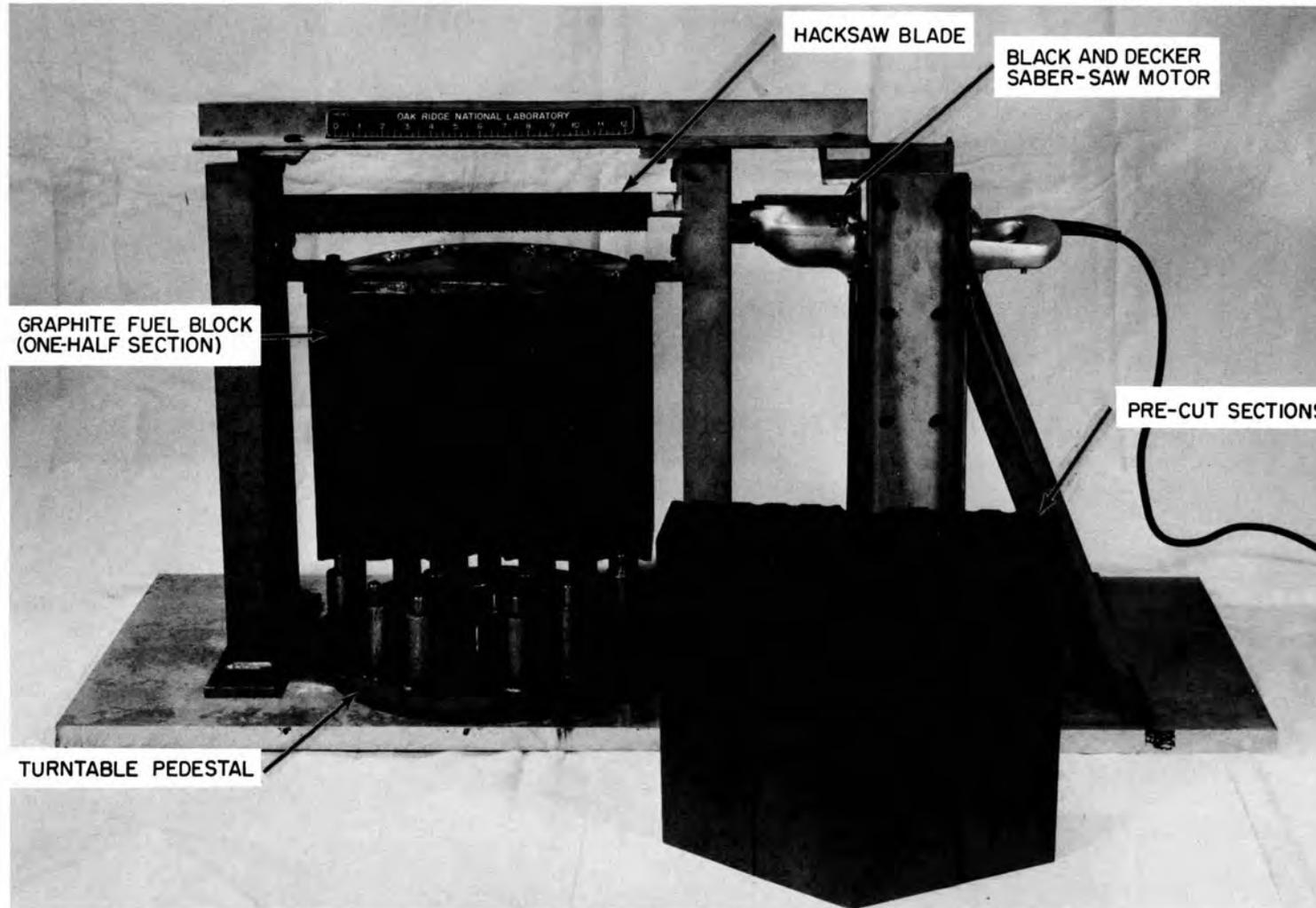
5.2 Grind-Leach

Grind-leach methods for recovering fissile and fertile particles are being evaluated and developed for HTGR fuels. Attention is currently centered on the graphite fuel blocks used in the Public Service of Colorado (PSC) reactor. These fuel blocks - hexagonal cylinders - are 30 in. long and 14 in. wide across the flats. Each block has a large axial hole (for lifting), and numerous smaller longitudinal holes for fuel and coolant. The initial problem in the application of the grind-leach process involves reduction of the blocks to pieces that are small enough to be fed to a hammer mill or a roll crusher.

Our experiments were done on an unfueled prototype block consisting of two 6-in.-long sections cemented together to form a 12-in.-long hexagonal block. A hacksaw reduced these blocks to pieces of the desired size by making three cuts through rows of coolant holes. The six resulting wedge-shaped pieces were 12 in. long and 7.3 in. across the widest dimension (see Fig. 5.1).

Sawing was accomplished by supporting the graphite block, with its long axis in a vertical position, on a turntable pedestal that allowed rotation to the desired position for each cut. The block was also held in place by a clamp (on top), which contained a slot that served to guide the saw blade. Additional guide slots for the blade were located in the supporting framework. The blade was 21 in. long, 1-3/4 in. wide, and 0.088 in. thick, and had six teeth per inch. It was driven by a Black and Decker saber-saw motor that was rated at 115 v and 6 amp and had six speeds in the range of 480 to 2310 strokes/min. The saw was fed to the material by gravity, that is, by using the weight of the saw itself.

At a blade speed of 2310 strokes/min, the saw easily cut through the block in 2.9 min; this is equivalent to a cutting time of 7.25 min for the PSC fuel block.



GRAPHITE FUEL BLOCK
(ONE-HALF SECTION)

HACKSAW BLADE

BLACK AND DECKER
SABER-SAW MOTOR

PRE-CUT SECTIONS

TURNTABLE PEDESTAL

Fig. 5.1 Hacksaw Equipment. Cut sections and one-half of a Public Service of Colorado prototype graphite fuel block are shown.

5.3 Jet Evulsion of Fuel Particles

We are considering the possibility of removing the ceramic fuel particles from the fuel holes of the Public Service of Colorado graphite fuel block by means of a high-pressure hydraulic jet. To evaluate the feasibility of this operation, a high-pressure hydraulic system (Fig. 5.2) has been installed in cell 2 of Building 4505. The system consists of a water pump, a gas pressure booster, a hydraulic accumulator, a solenoid valve, and a pressure switch that functions between preset pressures. Additional details of the equipment are:

Water pump - Noncontaminating pumping unit with a nominal pressure ratio of 150:1 and a nominal capacity of 55 in.³/min at 5000 psi. Sprague* model No. S-44CS-1500SS.

Gas booster - Separated type of gas booster for compressing industrial gases to 5000 psi. Sprague* model No. 79026-50.

Accumulator - Hydropneumatic accumulator; 5-gal capacity; 6000-psi water service. Greer** model No. 60 A-5WS.

Solenoid valve - For liquid service; maximum pressure, 6000 psi. Atkmatic Valve Co., Inc.***; type SLP, Serial No. 194383, catalog No. 7300.

Pressure switch - Barksdale**** pressure-actuated switch; model No. B2T-A65SS; adjustable range, 325 to 6500 psi. Proof pressure, 9750 psi.

All equipment was connected with 3/8-in.-OD annealed stainless steel tubing with a 0.065-in.-thick wall and was rated for a pressure of 7000 psi at 100°F; Swagelok fittings that were fabricated of stainless steel type 316 were used.

*Sprague Engineering Co., Gardena, Calif.

**Greer Hydraulics, Inc., Los Angeles, Calif.

***Atkmatic Valve Co., Inc., Indianapolis, Ind.

****Barksdale Valve Co., Los Angeles, Calif.

ORNL DWG 67-5285 R2

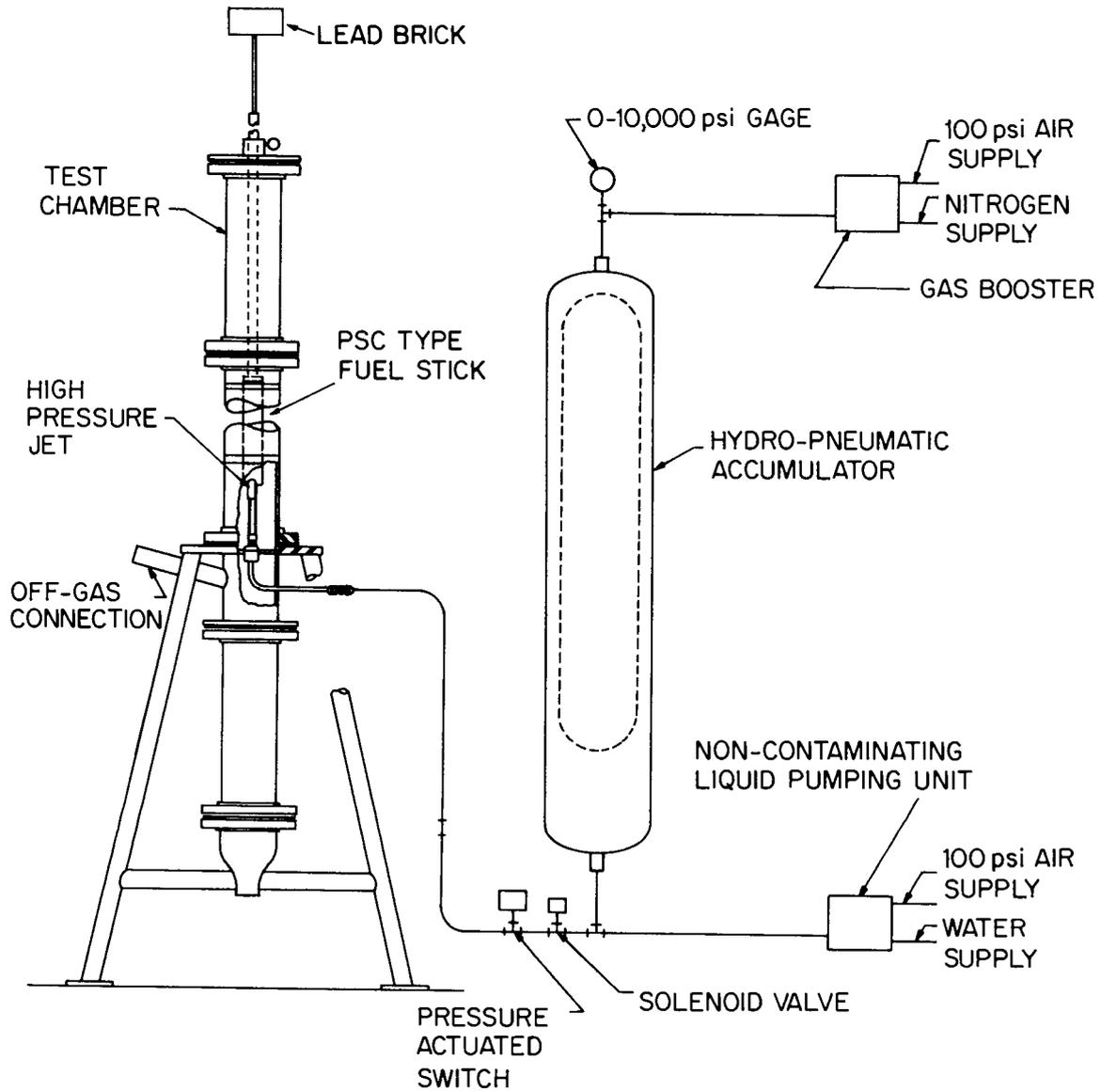


Fig. 5.2 High-Pressure (6000 psi) Hydraulic Test System.

In a preliminary test, 1250 cm³ of water was exhausted from the accumulator in 4 sec while the pressure was decreased from 5900 to 4800 psig; a period of 6 min was required to restore the pressure to 5900 psig by pumping an equal volume of water into the accumulator.

6. FAST-BREEDER REACTOR FUEL PROCESSING

C. D. Watson G. A. West

We have begun the development of a mechanical head-end method (disassembly, canning, shearing, and leaching) for reprocessing short-cooled (30 days) fast-breeder fuels. This work is being pursued in order to supplement the current estimated shipping costs⁵ with the cost of disassembling and canning the fuel pins before they are shipped.

The reference fast-reactor fuel design selected for our study was the General Electric Company's Fast Oxide Breeder because it appears to be within present-day technology, and because it may be the first large fast-breeder reactor in operation. This reactor, which is sodium cooled, has a core consisting of UO_2 - PuO_2 (17.9 at. % fissile plutonium) and axial blankets of depleted UO_2 (0.3 at. % ^{235}U). The hexagonal fuel subassemblies consist of 490 or 546 pins, of which 76.8% in the inner zone and 92.2% in the outer zone are fueled. The unfueled pins contain BeO and must be separated from the fuel pins prior to shearing and leaching. Also, each fuel pin is wrapped by a spiral spacer wire that should be removed before shearing.

We have prepared a conceptual flowsheet and a facility layout for mechanically dismantling a subassembly and removing the BeO pins prior to recanning the fuel pins (Figs. 6.1 and 6.2). We have built and have successfully operated a simple model of the equipment that is required for handling and separating the fuel pins prior to removing the spiral spacer wire. A mechanism for removing the spacer wire has also been designed.

As a basis for our study, the following conditions that influence the handling procedures were assumed, in all possible combinations:

1. A burnup of 50,000 or 100,000 Mwd per metric ton.
2. Specific reactor powers of 75 or 100 w/g.

⁵R. Salmon, Oak Ridge National Laboratory, personal communication, January 12, 1967.

ORNL DWG 67-5265

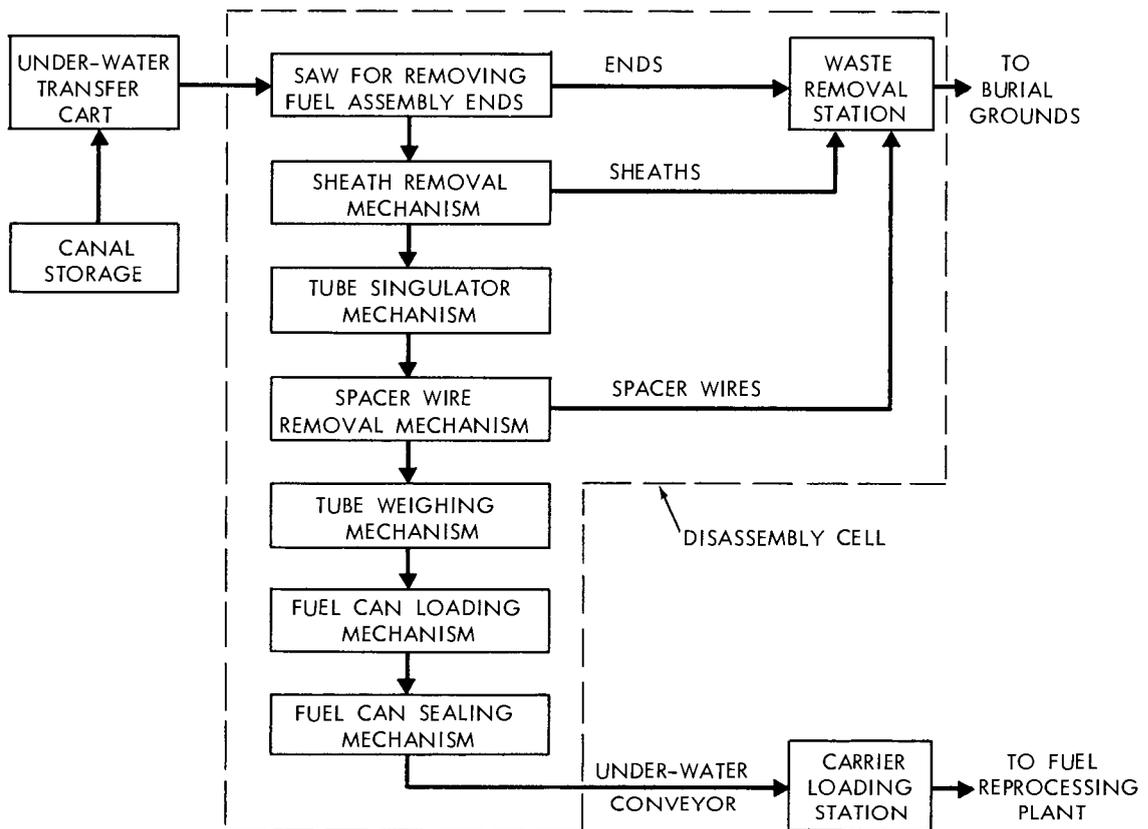


Fig. 6.1 Flowsheet for Disassembling and Packaging Spent Fuel from Fast-Breeder Reactor.

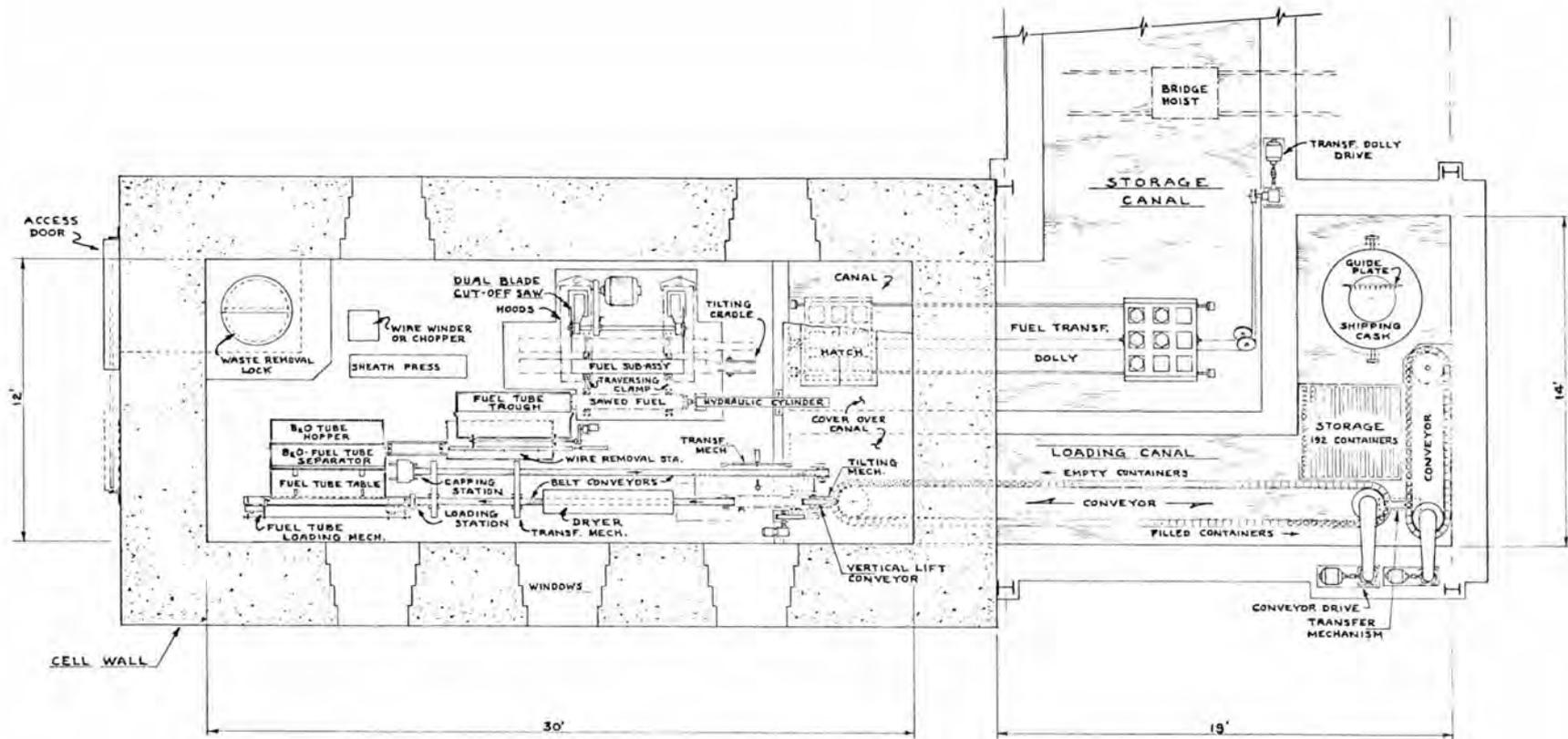


Fig. 6.2 Conceptual Design of a Facility for Disassembling Fast-Reactor Fuel.

3. Storage of spent fuel under water for 13 to 15 days or for 150 days (after it has been removed from the reactor, stored under sodium for 5 to 7 days, removed from the sodium, and cleaned). For the short-decayed case, the carrier load of subassemblies is disassembled and shipped for processing within 30 days from the time the fuel is removed from the reactor.
4. The cell containing the disassembly and canning equipment is located over the reactor canal, or it is offset from it.
5. To make a full carrier load, nine subassemblies (3864 fuel pins) are disassembled, and the pins are recanned in 184 cans made of 5-ft-long sections of standard 2-in.-diam pipe. Each can contains 21 fuel pins.

The methods of handling the reference fuel depend on, among other things, the temperature resulting from the decay heat and on the radioactivity. Computer code BIGDEAL, which is normally used to calculate the decay heat from ^{235}U fissioning, was used to approximate the decay heat from the reference fuel. Since the BIGDEAL code was devised for calculating the heat from a square array of fuel pins, a 21- by 21-pin arrangement was used to simulate the reference fuel (average of 429 pins). Results from these calculations indicate that the subassemblies must be cooled during transit in the carrier and while being disassembled in air. After the pins are separated, forced cooling will no longer be needed. The temperatures in the mechanical disassembly step and in the shear feed envelope will exceed 2000°F for fuel irradiated to a burnup of 50,000 Mwd per metric ton (at a specific power of 75 w/g) and cooled for 20 days. If the fuel is allowed to cool 150 days, the temperatures during disassembly and in the shear envelope (Table 6.1) will be approximately 1384°F and 1480°F , respectively.

Proposed Handling Procedures

The proposed procedures for disassembling the reference fuel and packing it for reshipment are as follows:

Table 6.1 Temperatures for Fast Oxide Breeder Fuel During Head-End Processing^a

Conditions: 21 x 21 tube array
0.265-in.-OD fuel pins on 0.2995-in. centers

Cooling Time (days)	Heat Release Rate [Btu hr ⁻¹ (kg U) ⁻¹]	Calculated Temperatures (°F)			
		Underwater Storage	Mechanical Disassembly In Air	Shear Feed Envelope, Center Tube	5-in.-ID Basket Center Line
Burnup - 100,000 Mwd/ton					
<u>Specific Power - 75 w/g</u>					
20	474.69	180	2097	2194	1773
150	151.67	120	1448	1545	1019
<u>Specific Power - 100 w/g</u>					
20	621.32	202	2282	2377	2006
150	192.36	129	1567	1664	1064
Burnup - 50,000 Mwd/ton					
<u>Specific Power - 75 w/g</u>					
20	450.66	176	2063	2160	1730
150	132.33	115	1384	1480	951
<u>Specific Power - 100 w/g</u>					
20	582.61	197	2236	2332	1948
150	163.45	123	1485	1582	1059

^aCalculated from ²³⁵U fission.

1. The fuel subassembly in the underwater storage canal is loaded onto an underwater dolly and is transported into a disassembly cell.
2. The fuel is picked up from the dolly with a cell hoist that has a latching mechanism, and is placed into a cradle that is then lowered onto the saw table.
3. The adapter end of the subassembly is pushed against a stop plate to index the fuel properly, prior to sawing off each end.
4. The fuel subassembly is held in a pair of clamps that are mounted on a cross-feed mechanism. A water spray is directed onto the subassembly in order to dissipate the decay heat and to keep the temperature at a tolerable level.
5. The fuel is fed into a pair of abrasive wheels that are mounted on a common drive shaft.
6. The sawed fuel is indexed into alignment with a hydraulic cylinder, and the fuel tubes are pushed out of the sheath onto a trough. Two types of pusher heads will be required for the two types of assemblies.
7. Individual tubes are then picked up on a pair of notched wheels, which transfer the tubes to a trough. A hydraulic cylinder, with a stroke of approximately 2 in., pushes the tube through a hole that is sized to permit passage of the tube but to exclude the spacer wire. When the end of the tube passes through the hole, it is forced into a pair of rotating rollers that pull the remainder of the tube through the hole. A pair of rotating fingers clears the spacer wire from the trough.
8. The spacer wires are assembled in a compact bundle, sheared into short lengths, or coiled into rolls in such a manner that they occupy minimum space in the waste-disposal containers.

9. The plenum chamber, end adapter, and spacer wires are stored in a container for subsequent burial. Portions of the sheaths can be loaded vertically into a scrap container, and the void areas can be filled with BeO tubes and other scrap. Unused sheaths should be flattened for burial. Containers are loaded into a shielded carrier that is located in a shielded lock.
10. The tubes then pass through a balancing mechanism that separates the BeO tubes from the fuel tubes. The fuel tubes are discharged onto a conveyor that feeds the tubes into an indexing mechanism; this mechanism loads 21 tubes into a compartmented, 2-in. pipe container.
11. The loaded containers are transferred to a capping station where a positive seal cap is attached. The seal cap can either be welded or mechanically attached. The containers are then lowered onto a second conveyor.
12. The conveyor transfers the container to the tilting mechanism.
13. The tilting mechanism raises the container to a vertical position and lowers it into the canal onto a horizontal conveyor, which, in turn, transfers it to the shipping-cask loading area. Here the containers are transferred to another conveyor, which positions the containers adjacent to the shipping cask in an effort to minimize the time required for final transfer to the cask.
14. The canal bridge crane, which is provided with a special handling tool, picks up the containers by a tool post that is located on the container cap and loads them into the shipping cask. A movable guide plate is inserted into the end of the shipping cask for easier insertion of the containers into the shipping cask grid.
15. After the shipping cask is loaded, the end plug is attached and the cask is ready for removal. When the cask is raised

from the water, it should be thoroughly drained before shipping.

16. A container storage area is provided so that disassembly of the fuel can continue even though a shipping cask is not ready for loading.
17. Reverse procedures are used for unloading empty containers from the shipping cask and transferring them into the disassembly cell. If the containers do not contain seal caps, the water is dumped from each container with the tilting mechanism. The container is then placed on a conveyor that transfers it to a position where it is dried prior to reloading.

NOTES: The above equipment should be automatic or semi-automatic in order to minimize the time required for the disassembly of the fuel and the loading of 184 fuel containers into each shipping cask.

The exposed canal water in the disassembly cell should be provided with a cover having remotely operated, covered hatches for fuel entry.

These procedures are based on the assumption that welded seal caps are used on the 2-in. pipe containers, and that the end of each container is open on the return of the latter from the fuel reprocessing plant. Considerable time could be saved, and a less-complicated design of the cell equipment could be made if a mechanical type of seal cap were used. This would allow the drying station to be eliminated.

7. MOLTEN-SALT REACTOR PROCESSING

L. E. McNeese

A molten-salt breeder reactor (MSBR) will be fueled with a molten ^{233}U -containing fluoride mixture that will circulate continuously through the reactor core (where fission occurs) and through the primary heat exchanger (where most of the fission energy is removed). The reactor will also have a blanket of molten fluorides containing the thorium from which new fuel is produced. A close-coupled processing facility for removing fission products, corrosion products, and fissile materials from the fused fluoride mixtures will be an integral part of the reactor system.

7.1 Molten-Salt Distillation Studies

J. R. Hightower

Distillation continues to appear attractive as a means for removing rare-earth fission products from the fuel stream of an MSBR. Relative volatilities of several rare-earth fluorides (REF's) are needed for designing distillation systems and for evaluating distillation as a processing method. Relative volatilities of several REF's referred to LiF were measured and reported previously;⁶ relative volatilities of some of these REF's in the LiF-BeF₂-REF system are given in this report. With the exception of PrF₃, these REF's had lower relative volatilities in the ternary system LiF-BeF₂-REF than in the binary system LiF-REF.

Experimental Equipment

A diagram of the recirculating equilibrium still used in this work is shown in Fig. 7.1. The vaporizing section consists of a 16-in. length of 1-1/2-in.-diam nickel pipe. The condensing section is made from 1-in. nickel pipe wrapped with cooling coils fabricated from 1/4-in. nickel tubing. Condensate is collected in a trap below the condenser

⁶MSR Program Semiann. Progr. Rept., Feb. 28, 1967, ORNL-4119.

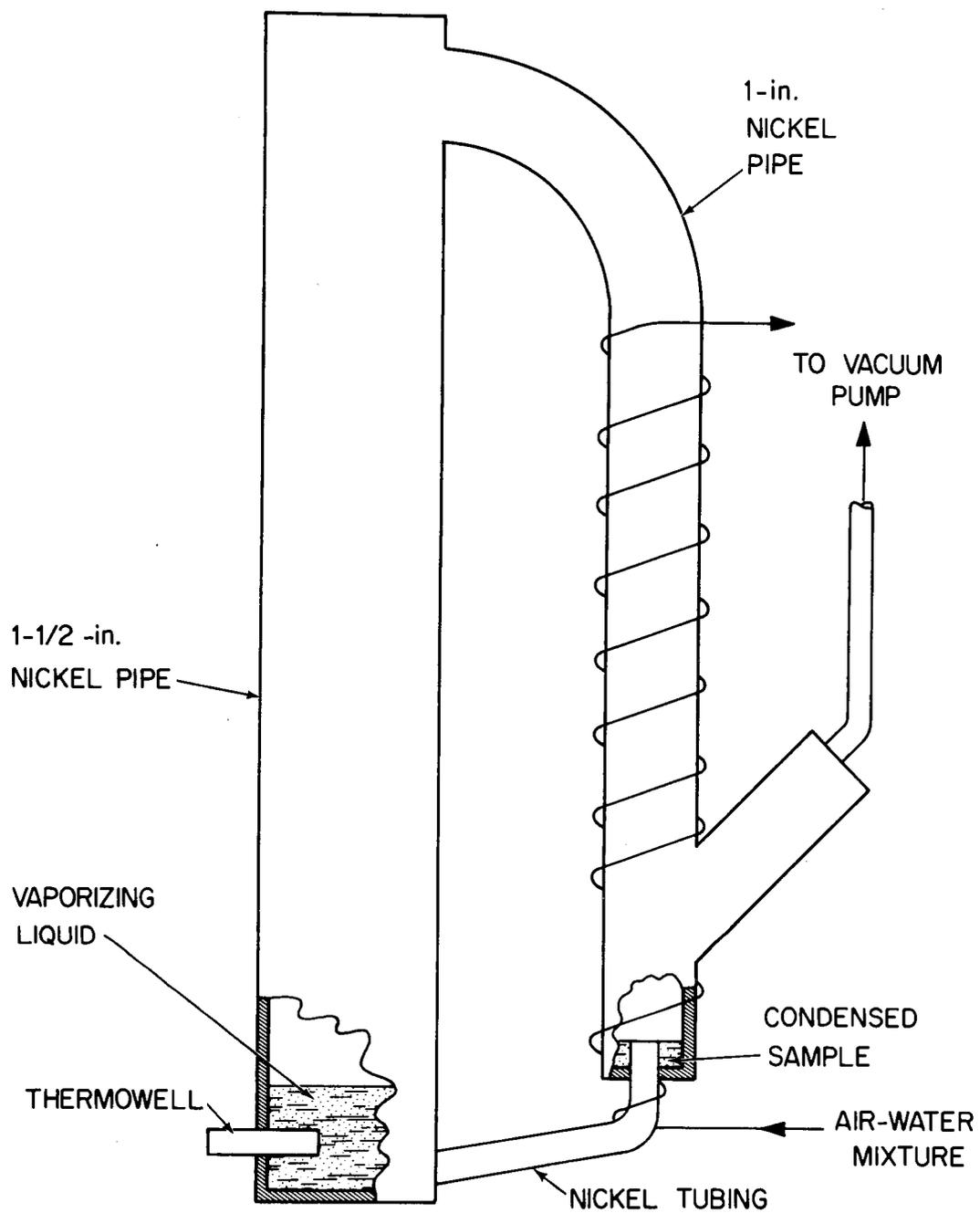


Fig. 7.1 Molten-Salt Still Used for Relative Volatility Measurements.

and overflows a weir before returning to the still pot. A vacuum pump is connected near the bottom of the condenser. Fig. 7.2 is a photograph of a typical still.

A diagram of the pressure-control system is shown in Fig. 7.3. Pressure is measured at a point near the condenser in the line that connects the still and the pump. As there is little or no gas flow from the still, the measured pressure should equal the condenser pressure. The pressure is controlled by varying an argon flow to the vacuum-pump inlet, which changes the pump inlet pressure. The pressure is sensed by a Taylor absolute-pressure transducer with a range of 0 to 6 mm Hg. The signal from the transducer is fed to a Foxboro recorder-controller, which, in turn, operates an air-driven control valve to vary the argon flow. The pressure at the measuring point is also read with a tilting McLeod gage and with an ionization gage.

Experimental Procedures

Because beryllium compounds are toxic when inhaled or ingested, special procedures have been followed to prevent the exposure of operating personnel to BeF_2 . The safety precautions and the experimental techniques pertinent to the vapor-liquid equilibrium measurements are described in this section.

The preparation of the salt charge for an experiment, and the sampling of liquid and condensate after a run, were carried out in an enclosed hood fitted with glove ports. The preparation of the still for operation and the actual experiment were done in a metal walk-in hood having absolute filters and beryllium air monitors. Salt charges for the still were prepared by melting lumps of $2\text{LiF}\cdot\text{BeF}_2$, additional LiF , and a REF in a graphite-lined crucible, and mixing the resulting material by means of an argon sparge. After cooling, the resulting salt ingot could then be loaded into the still with little danger of contaminating the laboratory in which the beryllium hood is located. After the salt charge was placed in the still, the outside of the still was cleaned and the cap of the still was backwelded to produce a leak-tight system. The condenser section of the still was then insulated,

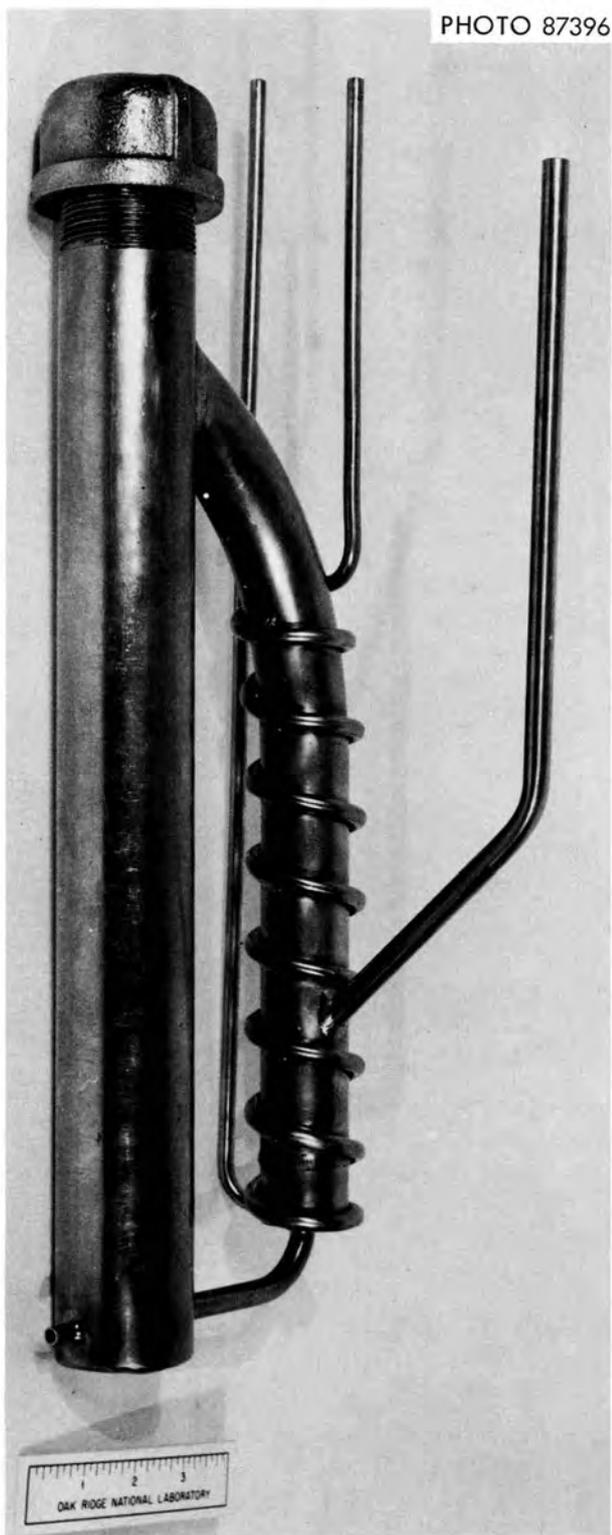


Fig. 7.2 Molten Salt Equilibrium Still.

ORNL DWG. 68 - 833

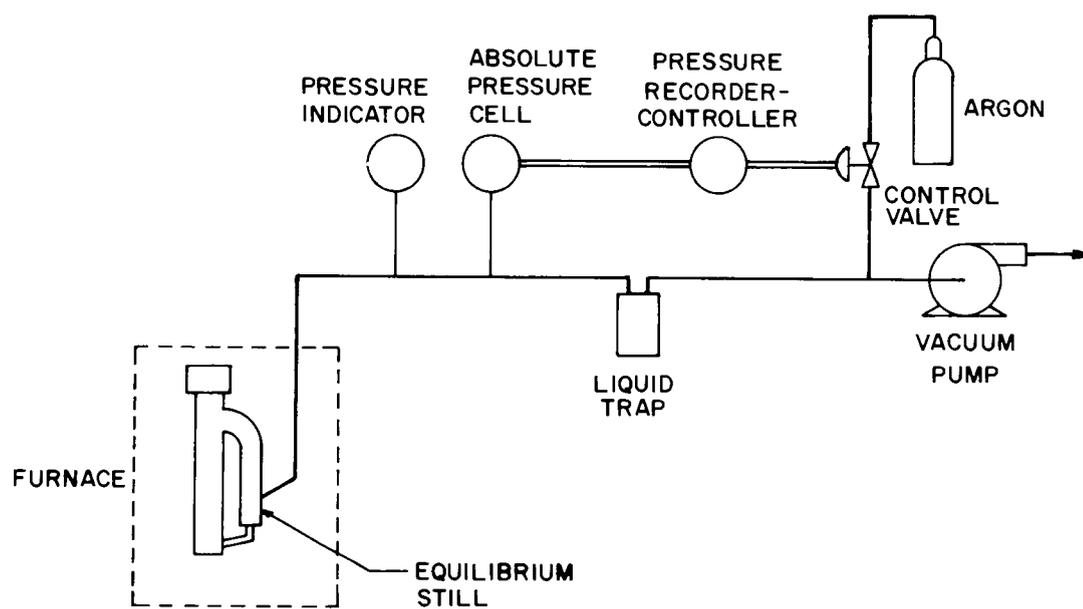


Fig. 7.3 Pressure-Control System for Molten-Salt Equilibrium Still.

and the still was suspended in the furnace. After the system was checked for leaks, it was repeatedly evacuated and filled with argon to remove oxygen. The pressure of the still was then decreased to 1.5 mm Hg, the furnace temperature was increased to 1000°C, and cooling was applied to the condenser, which had an outlet temperature of 675° to 700°C. These conditions were maintained for approximately 30 hr, after which the system was cooled to room temperature. Smears were made of the still and the vacuum line to determine beryllium contamination, and the still was then transported to the beryllium hood and cut apart for examination and sampling. Salt from the still pot and from the condensate trap was then analyzed for lithium, beryllium, and rare earth.

Experimental Results

Relative volatilities of five REF's, zirconium tetrafluoride, beryllium fluoride, and yttrium trifluoride were measured with respect to LiF in the system just described. All measurements were made at 1000°C and 1.5 mm Hg with a liquid mixture containing approximately 85-10-5 mole % LiF-BeF₂-REF. Table 7.1 presents these measurements, along with the previously reported values obtained in the binary system LiF-REF at 1000°C and 0.5 mm Hg. Except for PrF₃ (and possibly SmF₃), the rare earths have relative volatilities that are somewhat lower when BeF₂ is present. Calculations, using these relative volatility data, show that, in a single-stage distillation system, rare-earth fluorides will be adequately removed; however, the extent of removal of zirconium tetrafluoride will be insignificant.

Table 7.2 summarizes all experiments with the LiF-BeF₂-REF system and gives complete chemical analyses of liquid and vapor samples. Numbers in the columns labeled "Material Balance" give an indication of the consistency of each analysis. Since the concentration of each material was determined independently, a large deviation of these values from 100% indicates a poor analysis.

Table 7.1 Relative Volatilities of Rare-Earth Trifluorides, ZrF₄, and BeF₂ at 1000°C

Compound	Relative Volatility in	
	LiF-BeF ₂ -REF Mixture ^a	LiF-REF Mixture ^b
CeF ₃	3.3×10^{-4}	3×10^{-3} (ref. c)
LaF ₃ (ref. d)	1.4×10^{-4}	3×10^{-4} (ref. c)
NdF ₃	$< 3 \times 10^{-4}$	6×10^{-4}
PrF ₃	1.9×10^{-3}	6.3×10^{-4} (ref. e)
SmF ₃	$< 3 \times 10^{-4}$	2.3×10^{-4}
ZrF ₄ (ref. f)	1.4, 0.76	---
BeF ₂ (ref. g)	4.71	---
YF ₃ (ref. d)	3.4×10^{-5}	---

^a Pressure was 1.5 mm Hg; composition of liquid was ~ 85-10-5 mole % LiF-BeF₂-REF.

^b Pressure was 0.5 mm Hg; composition of liquid was ~ 95-5 mole % LiF-REF except as noted.

^c Liquid composition was 98-2 mole % LiF-REF.

^d One value from two experiments reported; the other value was questionable.

^e Not previously reported.

^f Two widely different liquid compositions were used. See Table 7.2.

^g Average of 14 values.

Table 7.2 Summary of Molten-Salt Experiments

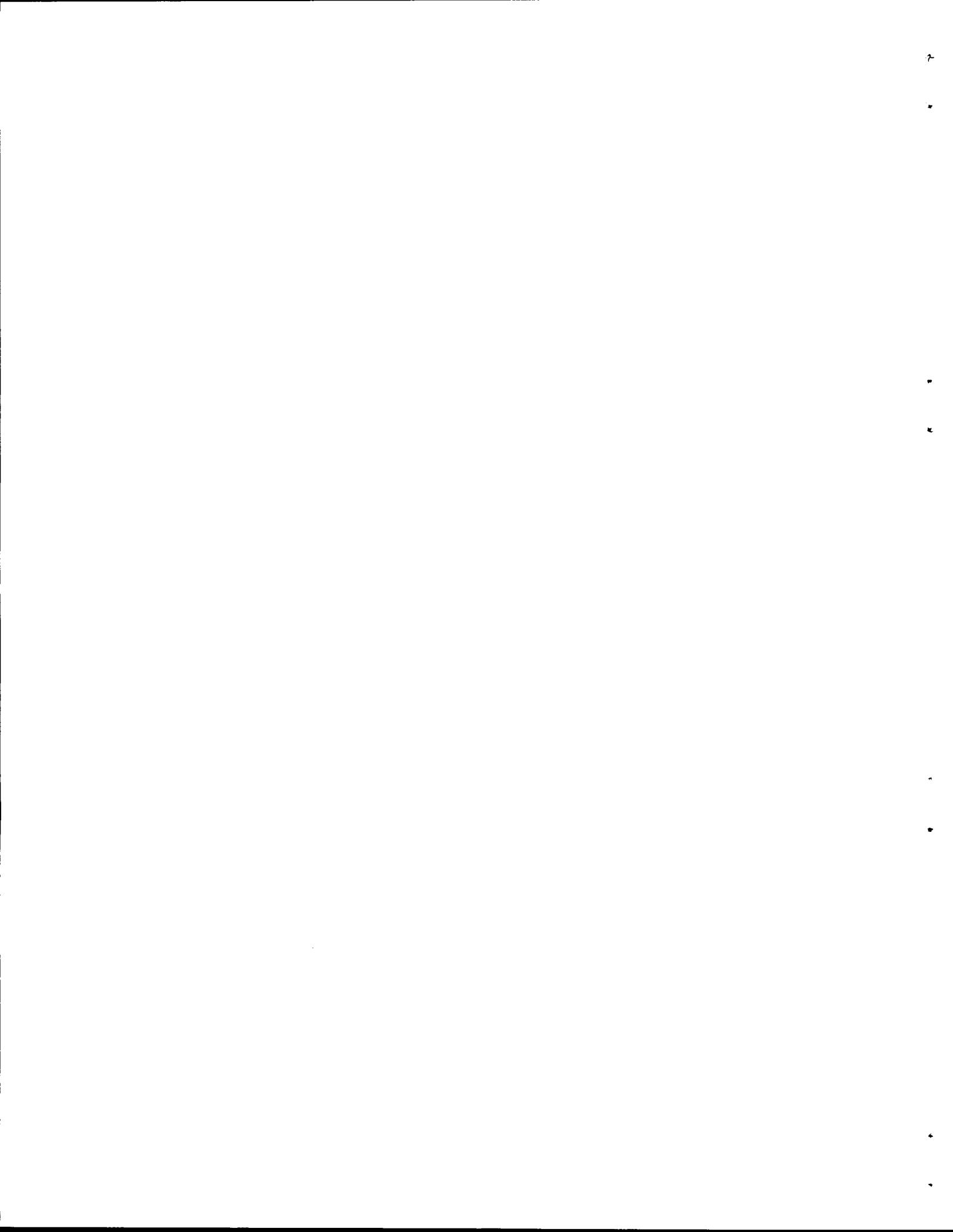
Run No.	Mole Fraction in Liquid			Material Balance (%)	Mole Fraction in Vapor			Material Balance (%)	Relative Volatility of Third Component	Relative Volatility of BeF ₂
	LiF	BeF ₂	Third Component		LiF	BeF ₂	Third Component			
Be-1Sm-1	0.848 ^a	0.103	SmF ₃ : 0.049	Ref. b	0.669 ^a	0.330	Ref. c	Ref. d	---	4.05
Be-2Sm-2	0.846	0.104	SmF ₃ : 0.05	96.2	0.653	0.347	< 1.07 x 10 ⁻⁵	94.8	< 3 x 10 ⁻⁴	4.32
Be-1Zr-3	0.893	0.097	ZrF ₄ : 0.0096	97.0	0.667	0.323	0.010	99.9	1.4	4.46
Be-1Nd-4	0.840	0.101	NdF ₃ : 0.060	93.3	0.636	0.364	< 1.22 x 10 ⁻⁵	92.2	< 3 x 10 ⁻⁴	4.76
Be-2Nd-5	0.849	0.098	NdF ₃ : 0.053	96.8	0.624	0.376	< 1.3 x 10 ⁻⁵	90.0	< 3 x 10 ⁻⁴	5.22
Be-1Pr-6	0.836	0.110	PrF ₃ : 0.056	100.0	0.651	0.349	9.59 x 10 ⁻⁵	98.5	2.46 x 10 ⁻³	4.07
Be-2Pr-7	0.842	0.1047	PrF ₃ : 0.055	98.5	0.625	0.375	5.26 x 10 ⁻⁵	91.2	1.30 x 10 ⁻³	4.81
Be-1La-8	0.802	0.102	LaF ₃ : 0.096	96.7	0.605	0.395	1.03 x 10 ⁻⁴	98.0	1.42 x 10 ⁻³	5.14
Be-2Zr-9	0.878	0.120	ZrF ₄ : 0.0003	106.0	0.602	0.396	1.6 x 10 ⁻⁴	95.9	0.763	4.80
Be-1Ce-10	0.836	0.112	CeF ₃ : 0.053	100.1	0.609	0.392	< 2.4 x 10 ⁻⁵	101.9	< 6.2 x 10 ⁻⁴	4.81
Be-2La-11	0.845	0.1035	LaF ₃ : 0.051	106.6	0.625	0.375	5.1 x 10 ⁻⁶	94.2	1.36 x 10 ⁻⁴	4.90
Be-2Ce-12	0.843	0.107	CeF ₃ : 0.051	103.6	0.625	0.375	1.26 x 10 ⁻⁵	96.1	3.33 x 10 ⁻⁴	4.71
Be-1Y-13	0.865	0.1002	YF ₃ : 0.0357	95.7	0.643	0.357	9.1 x 10 ⁻⁷	96.7	3.43 x 10 ⁻⁵	4.80
Be-2Y-14	0.865	0.105	YF ₃ : 0.0298	96.3	0.602	0.398	4.51 x 10 ⁻⁶	100.4	2.18 x 10 ⁻⁴	5.44

^aBy difference.

^bAll analyses were not independent.

^cContaminated sample.

^dNot applicable.



ORNL-4204
UC-4 - Chemistry

INTERNAL DISTRIBUTION

- | | |
|-------------------------------------|----------------------------------|
| 1. Biology Library | 73. D. M. Lang |
| 2-4. Central Research Library | 74. C. E. Larson |
| 5-6. ORNL - Y-12 Technical Library | 75. R. E. Leuze |
| Document Reference Section | 76. R. B. Lindauer |
| 7-41. Laboratory Records Department | 77. H. G. MacPherson |
| 42. Laboratory Records, ORNL R.C. | 78. G. M. Marrow (Y-12) |
| 43. R. E. Blanco | 79. J. L. Matherne |
| 44. J. O. Blomeke | 80. J. P. McBride |
| 45. R. E. Brooksbank | 81. W. T. McDuffee |
| 46. K. B. Brown | 82. W. H. McVey |
| 47. F. R. Bruce | 83. E. L. Nicholson |
| 48. W. D. Burch | 84. F. L. Parker |
| 49. W. H. Carr | 85. J. R. Parrott |
| 50. G. I. Cathers | 86. J. H. Pashley (K-25) |
| 51. J. M. Chandler | 87. F. S. Patton, Jr. (Y-12) |
| 52. W. E. Clark | 88. R. H. Rainey |
| 53. K. E. Cowser | 89. J. T. Roberts |
| 54. F. L. Culler, Jr. | 90. A. D. Ryon |
| 55. W. Davis, Jr. | 91. W. D. Schaffer, Jr. |
| 56. D. E. Ferguson | 92. M. J. Skinner |
| 57. L. M. Ferris | 93. Martha Stewart |
| 58. J. R. Flanary | 94. J. C. Suddath |
| 59. H. E. Goeller | 95. D. A. Sundberg |
| 60. J. M. Googin (Y-12) | 96. W. E. Unger |
| 61. H. B. Graham | 97-117. Unit Operations Section |
| 62. A. T. Gresky | 118. C. D. Watson |
| 63. P. A. Haas | 119. A. M. Weinberg |
| 64. F. E. Harrington | 120. M. E. Whatley |
| 65. R. W. Horton | 121. R. H. Winget |
| 66. G. Jasny (Y-12) | 122. R. G. Wymer |
| 67. H. F. Johnson | 123. E. L. Youngblood |
| 68. W. H. Jordan | 124. P. H. Emmett (consultant) |
| 69. S. H. Jury | 125. J. J. Katz (consultant) |
| 70. L. J. King | 126. J. P. Margrave (consultant) |
| 71. B. B. Klima | 127. E. A. Mason (consultant) |
| 72. E. Lamb | 128. R. B. Richards (consultant) |

EXTERNAL DISTRIBUTION

129. E. L. Anderson, Atomic Energy Commission, Washington
130. A. L. Babb, University of Washington
131. F. P. Baranowski, Atomic Energy Commission, Washington
132. R. G. Barnes, Union Carbide Corporation, New York
133. W. G. Belter, Atomic Energy Commission, Washington
134. S. Bernstein, Union Carbide Corporation, Paducah
135. J. A. Buckham, Idaho Chemical Processing Plant

136. J. T. Christy, Richland Operations Office
137. C. R. Cooley, Pacific Northwest Laboratory, Richland, Washington
138. C. B. Deering, Atomic Energy Commission, Oak Ridge
139. E. R. Gilliland, Massachusetts Institute of Technology
140. W. W. Grigorieff, Assistant to the Executive Director, Oak Ridge
Associated Universities
141. M. J. Harmon, Pacific Northwest Laboratory, Richland, Washington
142. L. P. Hatch, Brookhaven National Laboratory
143. O. F. Hill, Pacific Northwest Laboratory, Richland, Washington
144. C. H. Ice, Savannah River Laboratory
145. E. R. Irish, Pacific Northwest Laboratory, Richland, Washington
146. B. M. Legler, Idaho Chemical Processing Plant
147. J. A. Lieberman, Atomic Energy Commission, Washington
148. B. Manowitz, Brookhaven National Laboratory
149. J. A. McBride, Idaho Chemical Processing Plant
150. J. W. Nehls, Atomic Energy Commission, Oak Ridge
151. C. M. Nicholls, AERE, Harwell, England
152. E. O. Nurmi, Babcock and Wilcox Company
153. H. Pearlman, Atomics International
154. A. M. Platt, Pacific Northwest Laboratory, Richland, Washington
155. G. L. Plotz, Knolls Atomic Power Laboratory
156. J. W. Pollock, Idaho Operations Office
157. K. L. Rohde, Idaho Chemical Processing Plant
158. C. A. Rohrman, Pacific Northwest Laboratory, Richland, Washington
159. C. M. Slansky, Idaho Chemical Processing Plant
160. M. Smutz, Ames Laboratory, Ames, Iowa
161. C. E. Stevenson, Argonne National Laboratory, Idaho Falls
162. K. G. Steyer, General Atomic
163. J. A. Swartout, Union Carbide Corporation, New York
164. C. D. Tabor, Goodyear Atomic
165. V. R. Thayer, Du Pont, Wilmington
166. R. C. Vogel, Argonne National Laboratory
167. E. E. Voiland, Pacific Northwest Laboratory, Richland, Washington
168. G. H. Wagner, General Electric Company, Santa Clara, California
169. Laboratory and University Division, AEC, ORO
- 170-422. Given distribution as shown in TID-4500 under Chemistry category
(25 copies - CFSTI)