MASTER

IDO-14445
Chemistry-Radiation and
Radiochemistry
TID-4500(14th Ed.)

31

LABORATORY DEVELOPMENT OF A PROCESS
FOR SEPARATING BARIUM-140 FROM MTR FUEL

E. L. Anderson
R. S. MacCormack
C. M. Slansky

March 27, 1959

AEC RESEARCH AND DEVELOPMENT REPORT

PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
(UNDER CONTRACT NO. AT (10-1)-205)
IDAHO OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION

PRICE \$2.50

Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

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

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

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

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

DISCLAIMER

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

DISCLAIMER

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

LABORATORY DEVELOPMENT OF A PROCESS FOR SEPARATING BARIUM-140 FROM MTR FUEL

by

E. L. Anderson
R. S. MacCormack
C. M. Slansky

Work done by:

R. L. Andelin	C. R. McMullen
E. L. Anderson	W. H. McVey
G. K. Cederberg	R. F. Murray
K. T. Faler	R. C. Paulus
E. J. Fuller	R. H. Perkins
B. J. Garrick	C. M. Slansky
T. L. Hoffman	M. A. Wahlgren
R. S. MacCormack	R. D. Fletcher

Date work completed:

January 1955

Chemical Development Section
CPP Technical Branch

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
AT(10-1)-205

IDAHO OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

LABORATORY DEVELOPMENT OF A PROCESS FOR SEPARATING BARIUM-140 FROM MTR FUEL

by

E. L. Anderson, R. S. MacCormack, C. M. Slansky

A B S T R A C T

The results of all laboratory research and development on the process for separation of barium-140 from MTR fuel elements are presented. The steps include caustic dissolution, separation of barium and strontium with fuming nitric acid and removal of strontium by the chromate-acetate method. The results of laboratory and pilot plant corrosion investigations and high radiation level flowsheet tests in the Multicurie Cell are also included.

Due to the press of other duties, completion of this report was set aside temporarily. It is issued to record the bench-scale development work that preceded production operations.

TABLE OF CONTENTS

	<u>Page No.</u>
1. SUMMARY	13
2. PREVIOUS PROCESS DEVELOPMENT.	14
2.1 General History.	14
2.2 Status on Date of Phillips Takeover - Oct. 1, 1953 . . .	15
3. NATURE OF PHILLIPS PETROLEUM COMPANY RESPONSIBILITIES . . .	16
3.1 Scheduling	16
3.2 Product Specifications	16
3.3 Basic Assumptions on Flowsheet Development	17
4. OUTLINE OF PROCESS.	17
4.1 Starting Material.	19
4.2 Dissolution of Assembly and Aluminum Separation. . . .	19
4.3 Isolation of Barium and Strontium.	19
4.4 Separation of Barium and Strontium	20
4.5 Conversion to Nitrate Product Form	20
5. EXPERIMENTAL BASIS OF PROCESS STEPS	21
5.1 Fission Product Heat and Acitivity Considerations. . .	21
5.11 Shielding Considerations	23
5.12 Phase Separation Problems.	23
5.13 Radiation Damage to Process Reagents	23
5.2 Dissolution of Assembly and Aluminum Separation. . . .	23
5.21 Chemistry of the Dissolution	23
5.22 Optimization of Dissolvent Composition	24
5.221 Dissolving and Separation Time.	24
5.222 Centrifugation of Dissolver Solutions . . .	27
5.223 Supernate Stability	27
5.224 Uranium Losses.	27
5.225 Residue Washing	29
5.23 Fission Product Distribution	29
5.24 Barium Losses.	32
5.25 Residue Composition and Explosion Hazard	33
5.251 Residue Composition	33
5.252 Explosion Hazard	34
5.26 Caustic Waste Neutralization Technique	34
5.261 Caustic Aluminate Solution.	34

5.3	Crude Barium Separation.	35
5.31	Historical	35
5.32	Residue Dissolution.	36
5.33	Aluminum and Strontium Decontamination	36
5.4	Barium-Strontium Separation.	40
5.41	Historical	40
5.42	Summary of Radiation Damage Effects.	40
5.43	Wash Procedure	41
5.44	Optimization of Barium-Strontium Separation.	42
5.441	Barium Loss	42
5.442	Strontium Decontamination	46
5.443	Summary	46
5.45	Second Barium-Strontium Separation	46
5.5	Metathesis of Chromate to Nitrate.	50
5.51	Product Solution Evaporation	51
5.6	Overall Process Results.	51
5.61	Extraneous Impurity Decontamination.	51
5.62	Fission Product Decontamination.	52
6.	ALTERNATE PROCESS STEPS DISCARDED	53
6.1	Caustic Nitrate Dissolution.	53
6.2	Barium-Strontium Separation as Nitrates.	54
6.3	Barium-Strontium Separation Using Hydrochloric Acid.	55
7.	DISSOLVER CORROSION	57
7.1	Problem.	57
7.2	Plant Tests.	58
7.21	Materials and Procedure.	58
7.22	Results.	62
7.3	Service Tests.	62
7.31	Procedure.	62
7.32	Results.	62
7.33	Recommendations.	66
8.	CENTRIFUGE CORROSION.	67
8.1	Corrosion Studies on Stainless Steel in Chromate Pre- cipitation Solutions	68

	<u>Page No.</u>
8.11 Preparation of Samples	69
8.12 Description of Equipment	71
8.13 Procedure.	71
8.14 Results.	75
8.2 Corrosion in Very Concentrated Nitric Acid	77
8.3 Examination of Pilot Plant Centrifuge Bowl	79
8.4 Conclusions and Recommendations.	80
9. IODINE EVOLUTION.	80
9.1 Iodine Evolution During Caustic Waste Neutralization	80
10. STRONTIUM-90 RECOVERY.	81
10.1 Justification.	81
10.2 Flowsheet.	81
11. MULTICURIE CELL TESTS OF BARIUM-140 RECOVERY FLOWSHEET	83
11.1 Introduction	83
11.2 Design of Experiment	83
11.3 Iodine Monitor	87
11.4 Flowsheet Tested	92
11.5 Starting Material.	92
11.6 Operation.	92
11.7 Supplementary Data	93
11.71 Iodine Monitor Results.	94
11.72 Discussion of Barium Losses	95
11.8 Conclusion	95
BIBLIOGRAPHY.	96
APPENDIX I.	97
APPENDIX II	103

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1	Assumed Feed Material Composition	19
2	Calculated Ba and Sr Content of Irradiated MTR Fuel (168 gm)	21
3	Heat Generated by Barium and Strontium Isotopes	22
4	Total Dissolution and Filtration Time-Hours Required as a Function of Caustic and Mole Ratio	25
5	Effect of Sodium Hydroxide Concentration on Cast Slug Wafer Dissolution Rate.	26
6	Effect of Sodium Aluminate Concentration on Rate of Dissolution of Cast Slug Wafers.	26
7	Uranium Losses in Filtration.	28
8	Distribution of Fission Products and Transuranics in Caustic Dissolution of a Slug Wafer.	31
9	Percent of Initial Individual Fission Product Activity Present in Caustic Supernate from MTR Wafer Dissolu- tion	32
10	Caustic Dissolution Residue Composition from 168 gram Elements	33
11	Initial Composition of Synthetic Nitrate Solutions.	37
12	Barium Recovery and Decontamination from Uranium and Gross Fission Products	37
13	Barium Recovery and Decontamination from Uranium and Gross Fission Products	38
14	Final Nitrate Concentrations Under Boildown Conditions.	38
15	Barium Recovery and Decontamination from Uranium and Fission Products	39
16	Decontamination of Ba-140 Product from Metallic Impuri- ties	51
17	Effect of Total Nitrate on Barium Nitrate Losses.	54
18	Barium Recovery and Strontium Decontamination Factor as Function of Nitrate Precipitant Concentration.	55
19	Corrosion Tests Under Chloride-Type Ba-140 Processing Conditions	56
20	Summary of Amount of Materials Added During a Ba-140 Pilot Plant Dissolution, and Dissolver Solution Composition.	58
21	Summary of Heat Treatment and Stress Given Stainless Steel Type 347 (Cb-Ta) Specimens	59
22	Corrosion Rate of Stainless Steel Type 347 (Cb-Ta) Stressed Specimens Totally Immersed in Ba-140 Fuel Dissolvent Solution at 200°F for 44.5 Hours.	63
23	Exposure of Pilot Plant Dissolver During Pilot Plant Development of the Ba-140 Process.	66
24	Potential of Stainless Steel Type 347 in Chromate Pre- cipitation Solutions at Approximately 25°C	69
25	Ba-140 Process Time Schedules	70

LIST OF TABLES - Con't.

<u>Table No.</u>		<u>Page No.</u>
26	Potentials of Stainless Steels in Chromate Precipitation Solutions	73
27	Potentials of Stainless Steels in Chromate Precipitation Solutions	74
28	Corrosion Rates of Stainless Steels in Chromate Precipitation Solutions	76
29	Corrosion Rates of Stainless Steels in Chromate Precipitation Solutions	76
30	Corrosion of Stainless Steels in Boiling 73 Percent Nitric Acid.	79
31	Strontium-90 Recovery Flowsheet	81
32	Results of Ba-140 Medium Level Flowsheet Tests.	93
33	Final Product Impurities Scaled to Full Level	93

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	Schematic Flowsheet of Ba-140 Recovery Process.	13
2	Laboratory Apparatus for Determination of Fission Pro- duct Distribution in Caustic Dissolution	30
3	Ba-Sr Separation. Effect of pH	43
4	Ba-Sr Separation. Effect of Chromate Concentration	44
5	Ba-Sr Separation. Effect of Inert Ba on Ba ¹⁴⁰ Loss	45
6	Ba-Sr Separation. Effect of pH Strontium Separation.	47
7	Ba-Sr Separation. Effect of Chromate Concentration Strontium Decontamination.	48
8	Ba-Sr Separation. Effect of Inert Barium Carrier on Strontium Decontamination.	49
9	Pilot Plant Fuel Dissolver T-2.	61
10	Stainless Steel Type 347 Stressed Hoops, Compressed Rings, and a Plan View of Stressed Bars After Immer- sion in 20 Ba-140 Dissolver Runs	64
11	Stainless Steel Type 347 Stressed Hoops, Compressed Rings, and a Section View of Stressed Bars After Immersion in 20 Ba-140 Dissolver Runs.	65
12	Apparatus for Measuring the Corrosion of Stainless Steels in Chromate Precipitation Solution.	72
13	Corrosion Loss of Stainless Steel Coupons in Boiling Percent Nitric Acid.	73
14	Jacketed MTR Fuel Dissolver with Condenser.	78
15	Filtration Unit for Multicurie Cell Evaluation of Ba-140 Flowsheet.	84
16	Burettes for the Remote Delivery of Reagents to Ba-140 Test Equipment	85
17	General View of Multicurie Cell Interior.	86
18	Close-Up Showing Receiver in Manipulator Jaws Transfer- ring Liquid Into Filter Can.	88
19	Exterior of Multicurie Cell Showing Chemist Operating Equipment Remotely by Means of Controls on Console	89
20	Monitoring Device for Iodine in Dissolver Off-Gas	90

LABORATORY DEVELOPMENT OF A PROCESS FOR SEPARATING BARIUM-140 FROM MTR FUEL

by

E. L. Anderson, R. S. MacCormack, C. M. Slansky

1. SUMMARY

Chemical flowsheet studies are described for the development of a process for the production of kilocurie quantities of radiobarium-140 from two-day-cooled fuel elements from the Materials Testing Reactor.

An aluminum - highly enriched uranium- 235 fuel assembly is dissolved in boiling five molar sodium hydroxide; the uranium, silica, barium-140, and most of the fission products remain as a residue.

The residue is separated from the gelatinous silica by dissolution in six molar nitric acid and centrifugation. The acid solution is concentrated by evaporation, and barium and strontium nitrates precipitated by the addition of fuming nitric acid.

Barium and strontium are separated by a simple chromate precipitation after the solution is adjusted to a pH of 4.3 with sodium acetate. Sodium bromide may be added to protect the chromate ion from radiation decomposition, but bromide may be omitted if the time of processing is short.

Barium chromate precipitate is washed, dissolved in warm, dilute nitric acid and reprecipitated as the chromate as before for further purification.

Final product is prepared as the barium nitrate by metathesizing the chromate in fuming nitric acid and filtering. Satisfactory product decontamination from strontium, other fission products, aluminum, iron, copper, chromium, manganese, and nickel is obtained.

Flowsheet tests have been made at high radiation levels in the ICPP Multicurie Cell.

Corrosion studies are described on materials of construction for the process dissolver and centrifuge.

A flowsheet for the recovery of by-product strontium is included. The enriched uranium of the MTR fuel element is left in a form suitable for recovery by a standard ICPP solvent extraction process.

2. PREVIOUS PROCESS DEVELOPMENT

2.1 General History

Radioactive lanthanum-140, daughter of barium-140 has been used as an intense radiation source for a number of years. Historically, a need has developed for increasing batches of the barium-140 source material with additional emphasis on increasing specific activity of the barium. The increasing demand resulted in inadequacy of facilities of the original barium producer, the Oak Ridge National Laboratories. The more recent availability of high specific activity fuel from the Materials Testing Reactor indicated the desirability of locating production facilities in conjunction with that reactor. In fact, a RaLa production cell was provided for the ICPP in the original design of the Chemical Processing Plant by ORNL. The popular term "RaLa Process" is a misnomer since the research, development, and production is centered around the isotope barium-140.

Original requests were for 500 to 2000-curie batches of barium of very high purity with the restriction imposed that no barium was permitted other than that actually produced by fission. This requirement severely limited the number of feasible process schemes, the small mass of barium necessitating very high product recoveries and special plant facilities capable of handling one or two grams of exceedingly radioactive final product. A facility was installed at the Oak Ridge National Laboratory in 1945. The source material at that time was slugs from the Oak Ridge graphite reactor, but later requests for increased production made the use of Hanford slugs more economical. Development work had been carried on at ORNL on a lead-barium sulfate precipitation process in which the precipitated sulfates were separated and metathesized to carbonates followed by electrolytic separation of the lead carrier material.

In 1951, ORNL, using a redesigned facility, was producing approximately 10,000-curie batches. At this time, ORNL commenced the development of a process, based on irradiated MTR elements as feed material, capable of consistently yielding batches of at least 30,000 curies. The new process as proposed utilized no carrier barium. This process involved dissolution of MTR assemblies in a sodium hydroxide-sodium nitrate solution, leaving a precipitate of sodium diuranate and fission products. The precipitate was dissolved in nitric acid and barium and strontium nitrates precipitated by the addition of fuming nitric acid. Strontium was separated from the barium by contact with an ion exchange resin and the product was repurified by nitric acid precipitation. Cells L and M of the Idaho Chemical Processing Plant were originally planned to contain the process.

Pending the installation of facilities at the Idaho Chemical Processing Plant, ORNL had been attempting production of 30,000-curie batches. The Oak Ridge facility was operating at far higher levels of activity than originally designed and was considered inadequate for continued production without major modification.

In October 1952, a decision was made to proceed on a long-range RaLa production program at the Idaho Chemical Processing Plant with essentially no limits anticipated on the amounts of material desired. At this time, American Cyanamid Company was given responsibility for the engineering and operation of the process. Originally, the basic flowsheet proposed by ORNL was considered, but in November 1952, an alternate flowsheet was suggested, based on the development of a new type fuel pin, whose design would obviate the need for extensive development work on the problem of uranium-aluminum separation brought about by the use of MTR elements. The difficulty of separating the caustic-nitrate aluminum supernate from the uranium residue by a filtration technique was a major factor favoring the pin-type fuel. Development work on the flowsheet began in the Works Laboratory at the ICPP in June, 1953. Preliminary experiments soon showed the feasibility of straight caustic dissolution and the acceptability of MTR fuel as the source of the radiobarium.

The original ORNL process for MTR elements was in the meantime discarded because of its use of resins which, it was believed, led to contamination of the product with organic irradiation-decomposition residues. Since a limited addition of carrier barium was also considered feasible, two new flowsheets using MTR elements were under consideration, the major emphasis being placed on one in which the separation of strontium was accomplished by selective precipitation of barium chloride in a hydrochloric acid medium. The second flowsheet involved separation of strontium by selective precipitation of barium chromate.

At the termination of the American Cyanamid contract on September 30, 1953, Phillips Petroleum Company was given responsibility for RaLa development.

2.2 Status on Date of Phillips Takeover, 10-1-53

On October 1, 1953, the following questions were unresolved:

- 1) Were either of the proposed barium-strontium separation steps; i.e., the chloride method or the chromate method, satisfactory substitutes for the ORNL proposed ion exchange separation? Some information was available on the general chemistry but none as to the importance of radiation damage effects, relative engineering feasibility, product purities and recoveries, corrosion, etc.
- 2) The suitability of straight caustic dissolution was still in question.
- 3) The proposed operations had not been demonstrated on a pilot plant scale.

3. NATURE OF PHILLIPS PETROLEUM COMPANY RESPONSIBILITIES

3.1 Scheduling

As of October 1, 1953, Phillips Petroleum Company accepted responsibility for the development of a satisfactory flowsheet with timing such that by July 1, 1954, all data necessary for the initiation of the design of a production facility were to be available. It was understood that additional data and process improvements of a minor nature would be developed during the design stages and, if necessary, during plant startup operations. Thus, the tight scheduling precluded complete investigation of all process steps by the deadline date. It was especially understood that flowsheet proof was to be confined to cold testing with as much simulated radiation data provided as was possible under the circumstances. Final proof of the flowsheet was to depend on experiments performed with actual pieces of high burnup MTR element in the ICPP Multicurie Cell scheduled for completion in middle 1955.

This qualification on the proof of the flowsheet was due to the known difficulty of extrapolating dissolution reactions or unirradiated material to those of irradiated, high burnup material and to the problems of simulating with laboratory reagents, the proper chemical species of various fission products produced by irradiation.

Full radiation level pilot plant testing of the process was to be omitted from the program. Such testing was allowed in the startup of the actual production unit.

3.2 Product Specifications

Product specifications upon which the original design by Phillips was based were as follows:

Original Product Specifications

Ba ¹⁴⁰	30,000 curies - 100,000 curies on arrival
Ba(NO ₃) ₂	Maximum of 9.5 g. (5 g. as Ba)
Rare Earths	Not to exceed amount produced by decay since last separation
Silicates	Maximum - 10 mg. as SiO ₂
Organics	None - product to be grey-white
Sulfate	None
Sr ⁸⁹ and Sr ⁹⁰	Maximum - 100 curies
Iron	Maximum - 500 mg.
Chromium	Maximum - 10 mg.
Nickel	Maximum - 10 mg.
Aluminum	Maximum - 100 mg.

These specifications were later revised in view of the anticipated ICPP flowsheet. These changes were:

- 1) Ba^{140} was to be greater than 30,000 curies if possible.
- 2) Sr^{89} , Sr^{90} combined activity was to be less than 10 curies, the lower the better.
- 3) The specifications on Fe, Cr, Ni, and Al were changed to "no more than 50 milligrams of total metallic impurities are to be soluble in 75 ml of 70 percent nitric acid (lanthanum-140 and cerium-140 to be excepted)."

3.3 Basic Assumptions on Flowsheet Development

In designing the flowsheet, the following ground rules were assumed:

- 1) No process was to be considered proven until demonstrated under plant conditions with actual feed material.
- 2) Emphasis was to be placed on development of a rugged process capable of consistent production even if high yield had to be sacrificed.
- 3) Mechanical manipulation in the plant was to be minimized.
- 4) Uranium solution "wastes" from the process were to be compatible with ICPP feed streams.
- 5) The process was to be adaptable to changing MTR element compositions and burnups due to the experimental nature of the MTR. Continued effort was to be put on increasing size of production batches and minimizing impurities of all description.
- 6) Analytical control of the process was to be minimized due to the extreme radioactivity of the solutions. Direct pH measurements were regarded as undesirable.

4. OUTLINE OF PROCESS

A very condensed project terminal report was issued on July 8, 1954,⁽¹⁾ based on the original specifications as outlined above. On July 9, 1954, several changes were made in the official specifications and flowsheet. The flowsheet of Figure 1 outlines the process as of the latter date (Appendix 1), the major changes being in increased barium-140 and lower total strontium activity per batch. A report on the development of the Ba-140 flowsheet was presented at the Nuclear Engineering and Science Congress at Cleveland, Ohio, on December 12, 1955.⁽²⁾

FIGURE 1
SCHEMATIC RaLa CHEMICAL FLOWSHEET

*DOES NOT INCLUDE WATER FROM CENTRIFUGE COOLING
**DOES NOT INCLUDE INACTIVE CARRIER STRONTIUM

NOTE: PERCENTAGE VALUES REPRESENT
PERCENT OF COMPONENT INITIALLY
PRESENT IN FUEL ASSEMBLY

CPP-S-952

4.1 Starting Material

For flowsheet purposes, the fuel element composition shown in Table 1 was assumed.

Table 1

Assumed Feed Material Composition

Basis: 1 "200 gm" MTR element
20 day irradiation, 21.6% burnup, 2 day cooling

<u>Nuclide</u>	<u>Grams Per Element</u>	<u>Curies Per Element</u>
Aluminum	3818	
Uranium (highly enriched)	157	
Barium-138	1.221	
Barium-140	0.750	5.5×10^4
Strontium-88	0.492	
Strontium-89	0.568	1.6×10^4
Strontium-90	0.810	115
Strontium-91	10^{-4}	2.4×10^3

Assuming processing takes one day, about 50,000 curies of barium-140 would be shipped.

The assembly also contains about 30 grams of the silicon used in the braze, 16 grams of iron, 4 grams of copper, and milligram quantities of manganese, nickel, magnesium, and titanium.

4.2 Dissolution of Assembly and Aluminum Separation

The assembly is dissolved in 5M sodium hydroxide, forming sodium aluminate solution containing 99.5 percent of the aluminum and leaving a residue of greater than 99.5 percent of the uranium. Fission products, including barium and strontium, remain with the residue with the exception of cesium, the rare gasses, and part of the iodine. The dissolution is accompanied by the release of about 4800 liters of hydrogen at STP. The off-gas will probably include the rare gases and some of the iodine.

4.3 Isolation of Barium and Strontium

The residue from caustic dissolution is dissolved in 1.5 liters of 6M nitric acid. All residue components dissolve with the exception of silica which remains as a semi-gelatinous material. The off-gas contains nitric oxide, nitrogen dioxide and a portion of the fission product iodine. After centrifugation of the silica, additional barium is added as a carrier, making the total barium present approximately 5 grams. The solution is now

boiled down to 1.0 liter and 0.50 liter of fuming nitric acid is added. This procedure selectively precipitates barium and strontium nitrates. The exact degree of boildown and/or quantity of fuming nitric acid added determines the quantitateness of the barium precipitation and the degree of separation from aluminum and strontium. The conditions described result in barium losses of 1.5 percent, and precipitation of 90 percent of the strontium and essentially no aluminum.

4.4 Separation of Barium From Strontium

The nitrate precipitate is dissolved in 0.50 liter of water and 0.050 liter of 4.0M sodium acetate is added to "neutralize" the nitric acid expected to be held up in plant equipment from the previous step. To this solution 13 grams of sodium dichromate dihydrate and 8.8 grams of sodium bromide are added followed by the addition of 225 milliliters of 4.0M sodium acetate. As pH 3 is approached, barium chromate begins to come down, the precipitation being essentially complete at pH 4.3. Under these conditions the observed strontium decontamination factor is ca 150 and barium losses are below 1 percent.

The purpose of the bromide is to protect the chromate ion from extensive radiation decomposition. Due to process vessel corrosion problems, the bromide will not be added in this step unless found to be essential in the process. The two-step addition of sodium acetate prevents the loss of bromide ion, by chromate oxidation followed by volatilization, from the initially high acid solution. Laboratory experience shows that the highest decontaminations are achieved by changing pH rather than by adding chromate to an already buffered solution.

The supernate from this precipitation is saved for eventual recovery of strontium-90.

Control of pH is not necessary in this step due to the buffering action of sodium acetate in the pH range 4.0 - 4.5. While decontamination decreases at higher pH, even the poorest d.f. reasonably attainable is satisfactory in this first barium-strontium separation step.

After washing, the barium chromate precipitate is dissolved in 1.0 liter of 0.2M nitric acid and heated to 80°C. After cooling, inert strontium is added as strontium nitrate to isotopically dilute the remaining strontium activity. Barium chromate is again separated using essentially the same technique as before, except that final pH is much less dependent on possible acidic solution holdup in plant equipment due to the fact that water is the solution used immediately prior to the precipitation rather than very concentrated acid. Under these circumstances, it is easy to maximize decontamination, still without acidity measurement.

4.5 Conversion to Nitrate Product Form

The barium chromate from the previous step is now metathesized with 250 milliliters of fuming nitric acid heated to 70°C. The very nearly pure barium nitrate is separated from the chromic acid and redissolved in 250 milliliters of water. Addition of 50 milliliters of fuming nitric acid precipitates the final barium nitrate product.

5. EXPERIMENTAL BASIS OF PROCESS STEPS

The following discussion of experimental data is based primarily on the assumption of 168-gram uranium element feed material rather than the 200-gram element whose use was assumed in the flowsheet outlined in Section 4. These slight differences appear only in the first two process steps; namely the dissolution-aluminum separation and the isolation of barium and strontium and involve only such things as ratios of trace impurities to uranium, total quantity of aluminum and uranium, and slight differences in relative amounts of fission product isotopes at a given barium-140 curie level.

The current choice of 200-gram elements is due to a change in MTR operation made after flowsheet development had been essentially completed.

5.1 Fission Product Heat and Activity Considerations

Calculations were made of the amounts of barium and strontium isotopes present in irradiated MTR assemblies under various irradiation and cooling conditions. Due to uncertainties as to MTR operating conditions that are expected several years in the future, two sets of assumptions were considered; one assumption was very conservative with respect to total barium produced per element whereas the other was a more probable condition. For both cases, a 3 x 6 lattice configuration in the MTR pile, and a twenty-day irradiation cycle for elements originally containing 168 grams of uranium-235, were assumed. For the conservative basis, a 17 percent uranium burn-up was assumed, whereas for the more probable case, a 24 percent burn-up was assumed. The results of these calculations are given in Table 2.

Table 2

Calculated Ba and Sr Content of Irradiated MTR Fuel (168 g)

Nuclide	For 17 Percent Uranium Burn-up				For 24 Percent Uranium Burn-up			
	Curies at Shutdown	Grams After Cooling			Curies at Shutdown	Grams After Cooling		
		0 Days	1 Day	2 Days		0 Days	1 Day	2 Days
Ba ¹³⁸	Stable	0.910	0.910	0.910	Stable	1.30	1.30	1.30
Ba ¹⁴⁰	38,800	0.530	0.500	0.480	55,600	0.763	0.751	0.685
Sr ⁸⁸	Stable	0.340	0.340	0.340	Stable	0.49	0.49	0.49
Sr ⁸⁹	10,200	0.370	0.365	0.361	14,600	0.530	0.522	0.520
Sr ⁹⁰	91	0.456	0.456	0.456	137	0.69	0.69	0.69
Sr ⁹¹	48,000	0.014	0.003	0.000	68,800	0.020	0.004	0.001

Using the data in Table 2, calculations were also made on heat load due to beta energy adsorption in the chromate step of the process. It was assumed that beta rays were completely absorbed, whereas gamma energy absorption was negligible in comparison. The average energy of a specific beta decay was taken as 1/3 of the maximum energy. A fuel burn-up of 24 percent was assumed. The results of these calculations are given in Table 3 for one and two-day cooled material.

Table 3

Heat Generated by Barium and Strontium Isotopes

Per 168-g. MTR fuel element; 20-day irradiation cycle; 24% burn-up

Nuclide	Curies After		Mean Energy, Mev.	Beta Energy, Cal/Sec, After	
	1 Day	2 Days		1 Day	2 Days
Ba ¹⁴⁰	53,800	50,000	0.33 (70%) 0.17 (30%)	17.5 3.9	16.3 3.6
Sr ⁸⁹	14,400	14,200	0.5	10.2	10.1
Sr ⁹⁰	137	137	0.2	0.04	0.04
Sr ⁹¹	12,400	2,250	1.07 (60%) 0.4 (40%)	11.3 2.8	2.04 0.51
Total Heat				45.74	32.59

A comparison of the above data shows that if the barium-strontium separation is made any sooner than two days after shutdown, there will be a sharp increase in energy absorption (heat load) due to strontium-91 activity. In engineering terms, one-day cooling leads to heat loads of the order of 650 Btu per hour while two-day cooling decreases this to 465 Btu per hour. In terms of radiation damage to process solutions, this difference might be significant.

A calculation by W. L. Chase indicated a total fission product heat emission of approximately 6,200 Btu per hour due to beta and 8,300 Btu per hour due to gamma after two days of cooling. These data were determined by individual isotope summation. A total heat per element calculated from the Untermeyer-Weill curves⁽³⁾ is about 19,350 Btu per hour. Both of these calculations assumed elements slightly different in history from those mentioned here, but the results are fairly comparable and indicate, within 25 percent, the gross heat load problem.

The effects of high burn-up and very short cooling are of great importance processwise.

5.11 Shielding Considerations

The fission product lanthanum-140 is essentially shielding determining at cooling periods of up to 100 days. Thus, the entire process area and the shipping containers must be shielded for the worst shielding conditions that have yet arisen in processing irradiated fuel.

5.12 Phase Separation Problems

The heat load in process solutions involving the gross fission products was expected to be large enough to preclude the use of ordinary centrifugation-decantation techniques. Convection currents and bubbling caused by irradiation-decomposition of aqueous solutions would almost certainly cause enough agitation to redisperse the solid phase immediately. While process development was under way, Los Alamos tried centrifuging with decantation on a source of about 10,000 curies. The results were exactly as expected.

Under these conditions, filtration or continuous centrifugation with liquid skimming was felt to be the only feasible method of phase separation. Early in the development, Phillips decided on continuous centrifugation. Pilot plant development has been described in (4).

5.13 Radiation Damage to Process Reagents

A complete report on "Radiation Damage Problems in the ICPP Barium-140 Separation Process" by R. L. Andelin⁽⁵⁾, has been issued as IDO-14348. Specific problems will be outlined briefly in the following discussion.

5.2 Dissolution of Assembly and Aluminum Separation

In selecting optimum conditions for caustic dissolution of the MTR element, a compromise had to be made between the desirability of a complete investigation of all process variables and limitations due to manpower availability and an early deadline. Most of the work described was completed before July 1, 1954. Since that time, both this laboratory and ORNL have extended investigations of caustic dissolution into the general field of aluminum fuel element processing, in particular to the possibilities of continuous rather than batch dissolution. Some of the work reported herein was performed under other development programs at the ICPP. An extensive program of investigation has recently been reported by Wymer, et al⁽⁶⁾.

5.21 Chemistry of the Dissolution

The reaction of aluminum with sodium hydroxide can be expressed as:

Additional reactions may be involved such as:

and equilibria with excess caustic can presumably lead to formation of species like $\text{HA}1\text{O}_3^\pm$ and $\text{AlO}_3^\pm$. Hydrogen is released to the extent of 1-1/2 moles per mol of aluminum. With an MTR element, this corresponds to approximately 4800 liters STP. The amount of hydrogen was not felt to be a major concern inasmuch as dissolution control and dilution could be utilized to minimize explosion hazard. Comparable quantities of hydrogen, for example, will be released in the STR processing plant already installed at ICPP. Excess caustic is needed to keep the aluminum in solution, for without it, hydrated aluminum oxide precipitates. Wymer, et al, have shown by X-ray analysis that the oxide is the trihydrate as either gibbsite or bayerite. The overall reaction is:

The reaction is quite temperature sensitive and may exhibit an induction effect due to the difficulty of penetration of the skin of oxide on the surface of the aluminum.

The uranium and most fission products remain as a residue after dissolution, presumably as partial oxides. Traces of the original aluminum also remain. This residue is crystalline, dense, and not easily compressed.

5.22 Optimization of Dissolvent Composition

Original concepts of RaLa design were based on batch dissolution followed by filtration. In optimizing dissolution conditions, it was felt necessary to 1) obtain minimum combined dissolution-filtration times, 2) minimize uranium loss, and 3) be assured of solution stability for at least 24 hours.

5.221 Dissolving and Separation Time. In order to determine what dissolving technique would give the minimum total dissolving and filtration time, it was necessary to study the effect of increasing the amount of caustic per unit amount of assembly and the range of initial caustic concentration. The quantity of caustic in excess of the stoichiometric amount for reaction was varied from 25 percent excess to 100 percent excess and from 2.5M sodium hydroxide to 8.0M sodium hydroxide. The results of these experiments showed that the optimum dissolving and filtration conditions were with 50 to 100 percent excess of 5.0M sodium hydroxide. The data are summarized in Table 4.

The dissolving was done at boiling temperature with all condensables refluxed to the dissolver. The filtration was done on grade H and grade G sintered stainless steel filters at 22 inches of mercury pressure difference and at 80 to 90°C. The filter area was 1.23 square inches. Before each experiment, the filter was cleaned by back washing and thorough washing with hot 4.0M sodium hydroxide and 16M nitric acid and finally with water to have approximately the same water rate for each experiment. All comparisons were based on the time necessary to completely dissolve and filter 45 grams of MTR element leaf.

Table 4

Dissolution and Filtration Time as a
Function of Caustic Concentration and Mole Ratio

<u>Mole Ratio, NaOH/Al</u>	<u>Time, minutes, to dissolve and filter using</u>					
	<u>3.0M NaOH</u>	<u>4.0M NaOH</u>	<u>4.5M NaOH</u>	<u>5.0M NaOH</u>	<u>6.0M NaOH</u>	<u>8.0M NaOH</u>
	<u>Time to Dissolve Only</u>					
1.25	---	---	246	240	---	---
1.35	165	140	---	---	---	---
1.50	120	120	114	120	126	120
2.00	---	---	---	120	140	140
	<u>Total Time to Dissolve and Filter</u>					
1.25	---	---	252	255	---	---
1.35	255	192	---	---	---	---
1.50	300	192	140	150	174	300
2.00	---	---	---	135	195	300

Instantaneous filtration rates for these solutions were measured using grade H filters at 80 to 90°C. The instantaneous rates 10 minutes after filtration began were, for 3.5, 4.0, 5.0, 6.0, and 8.0M sodium hydroxide concentrations, 0.89, 1.07, 1.5, 0.5, and 0.32 liter/(hour)(in. sq.), respectively. Increasing filter pore size increases rates but, as will be shown below, uranium losses increase. As residue deposits on the filter, it serves as a filtering medium, limiting the flow rate but probably decreasing uranium losses.

The effect of increasing viscosity at high caustic concentration is evident. Viscosity also is very temperature dependent, rough experiments indicating filter time differences of approximately a factor of 10 between 20 and 90°C. A complete investigation of these variables has been made by ORNL(6).

The studies indicated that a caustic concentration of 5.0M at a caustic to aluminum mole ratio of 1.5 or 2.0 to 1 would give satisfactory results with respect to overall rate.

The trends appearing in the tabulated results appear due to the effect of larger solution volumes on filtration time as caustic concentration decreases contrasted with the increasing viscosity associated with higher concentrations. These effects are superimposed on a dissolution rate nearly independent of concentration at constant mole ratio.

ORNL, in its study, finds a dissolution rate first order with respect to caustic concentration using miniature uranium-aluminum alloy slugs. No effect due to increasing aluminate concentration is observed, nor in their study is the effect of mole ratio differentiated from that of caustic concentration. Excellent correlations have been obtained with miniature plant type continuous dissolvers.

Work at this laboratory (7) on cast slug wafers of uranium-aluminum alloy is indicated in Table 5 to show effect of caustic concentrations at the boiling point.

Table 5

Effect of Sodium Hydroxide
Concentration on Cast Wafer Slug Dissolution Rate

Mole Ratio NaOH: Al = 3.0 - Initial Areas Constant

<u>Sodium Hydroxide, M</u>	<u>Initial Rate in g./min.</u>
1.0	0.169
2.0	0.262
3.0	0.430
4.0	0.856
5.0	1.51

As can be seen, the effect of concentration is somewhat greater than linear. The rate of dissolution at the boiling point is also affected, according to these data, by sodium aluminate concentration as shown in Table 6.

Table 6

Effect of Sodium Aluminate Concentration
On Rate of Dissolution of Cast Slug Wafers

Initial NaOH Concentration: 5.0M; Mole Ratio NaOH : Al = 3.0

Initial Areas Constant

<u>Sodium Aluminate, M</u>	<u>Initial Rate in g./min.</u>
0.0	1.51
1.0	1.29
2.0	1.19
3.0	0.936

With regard to the effect of the nature of the alloy, extruded material was found to dissolve slower in 5M sodium hydroxide than cast alloy, contrary to experience in nitric acid dissolution. For a NaOH : Al mole ratio of 3, an initial rate of 1.51 grams/minute was found for bare cast metal, compared to 0.94 grams/minute for clad cast metal (2S aluminum jacket), and to 0.50 grams/minute for bare extruded material.

No explanation is offered for these apparent discrepancies. The work reported in Table 4 differs from the others in that dissolution was carried essentially to completion and thus area changed gradually. Also, pieces of MTR plate were used which are aluminum-clad sandwiches with a 15-20 percent uranium-aluminum alloy meat. Thus, in this case, two different types of materials were dissolving simultaneously. The second and third workers differed slightly with respect to type of surface area exposed, but both worked at constant or known area. In the ORNL work, dissolution was occurring primarily on the cast or extruded surfaces in contrast to the Phillips work wherein the cross-sectional area was the main surface exposed. It is known that acid dissolution rates are affected by such differences in type of surface exposed.

5.222 Centrifugation of Dissolver Solutions. After the sintered stainless steel plate filtration work had been completed, it was decided to use centrifugation separation. Much of the dissolution and filtration data above was still useful inasmuch as such factors as dissolution time, effect of dissolvent volume and viscosity, etc., are important considerations in optimization of a centrifugation process. The original flowsheet of 5.0M caustic at 2 to 1 mole ratio was maintained. Centrifuge experiments in the laboratory indicated that the resulting slurries could be separated in less than 2 minutes at 90°C using 1500 g's with reasonable uranium losses.

5.223 Supernate Stability. Caustic dissolutions were made using C.P. granular aluminum at sodium hydroxide concentrations of 5.0M and 8.75M and mole ratios varying from 1.75:1 to 3:1. Black insoluble residues were always observed presumably due to impurities in even C.P. reagents. Portions of these solutions were allowed to stand both open to air and in closed bottles. No alumina precipitates were observed in the closed bottles for at least one week. The 5M caustic bottles open to the air exhibited a slight precipitate which may have been associated with evaporation.

Experiments at 1.5:1 mole ratio indicated that in solutions of original caustic concentrations of 2.5, 3.0, and 4.0M, no instability appeared after one day. This fact is important due to the expected plant dilution of caustic supernate with cooling water.

5.224 Uranium Losses. Minimum uranium losses using filtration separation techniques were obtained using either H (5 micron) or G (10 micron) sintered stainless filters. A tabulation of observed losses is presented in Table 7.

Table 7

Uranium Losses in Filtration

<u>M, NaOH</u>	<u>Uranium Loss, Percent, Using Filter of Pore Size</u>				
	<u>H</u>	<u>G</u>	<u>F</u>	<u>D</u>	<u>C</u>
1.0	18.0	--	---	--	---
2.0	11.0	--	---	--	---
3.0	1.7	--	---	--	---
3.5	0.2	0.15	---	--	---
4.0	0.05	0.21	2.8	11.1	6.0
4.5	---	0.08	---	--	---
5.0	0.1	--	---	--	---
10.0	0.89	--	---	--	---

Dissolutions were run to completion insofar as possible. Anomalous results are probably due to the known effect of small differences in digestion time, higher digestion times leading to finer particle size.

An attempt was made to determine the reason for the uranium losses observed, in particular, whether they were due to true solubility or to the presence of near colloidal forms. Experiments were performed on slugs as reported in (7). In an effort to determine the importance of possible carbonate ion complexing of dissolved uranium, 0.50 to 1.0M sodium carbonate was added to a 5.0M caustic dissolving medium. No increased loss was observed, nor was the loss reduced by pre-treatment of the caustic with barium hydroxide to remove carbonate, or by adding barium carbonate, nitrate, or hydroxide to the caustic. Losses were increased by prolonged boiling of the slurry. The latter reagents were expected to precipitate ionic uranium as barium diuranate and possibly to act as coagulants.

In order to compare the above results with those from solutions known to contain ionic and probably colloidal uranium, a suspension was prepared by adding 2.5 grams of uranyl nitrate to 250 milliliters of 5M sodium hydroxide. These slurries were boiled for 30 minutes with and without additives and then filtered, following which losses were determined. Where there were no additives, the loss was 0.67 percent. Boiling the slurry with a barium hydroxide suspension reduced the loss of 0.073 percent, and boiling with barium carbonate gave a loss of 0.18 percent.

These results established that prolonged heating increases losses greatly. Experiments with the synthetic slurry show that the addition of barium hydroxide or barium carbonate should be effective in reducing losses due to ionic uranium. The presence of sodium carbonate probably has no effect on losses. It is reasonable to conclude that losses in slug dissolution are due primarily to colloid formation or to fine particles which pass through filters or are difficult to centrifuge.

Ultracentrifugation at 25,000 g's was used on some samples in an effort to bring down the ultra fines. No decrease in loss was observed though the analytical problems involved in distinguishing significant differences at such low concentration levels may have been responsible.

5.225 Residue Washing. Originally, it was intended that the caustic residue be washed with either water or fresh caustic solution in an attempt to minimize aluminum carry-over from the aluminate supernate. With improved crude barium separation procedures in the nitrate separation step, it became less important to minimize aluminum carry-over and washing was eliminated to simplify plant operation.

5.23 Fission Product Distribution

In order to determine the fate of fission products in caustic dissolution, a wafer cut from a full-level irradiated uranium-aluminum alloy slug was dissolved in 5M sodium hydroxide, and the uranium residue washed with 2M sodium hydroxide solution, and then dissolved in 6M nitric acid. A sketch of the equipment used is shown in Figure 2. Assuming the chemical reaction

twice the calculated stoichiometric amount of sodium hydroxide was used for the caustic dissolving. The experiment was devised to measure the fraction of certain selected fission products and transuranics going into the caustic supernate and the fraction remaining in the residue. Information was also desired on the behavior of the rare gas activity. The purpose of the gas experiment was to determine what portion of the rare gases would be evolved during the caustic dissolving step, and what portion would be evolved during subsequent acid dissolution of the uranium residue. In the gas experiment, only relative measurements were made, with no attempt to measure absolute quantities of rare gas.

The activity of krypton was determined by passing the off-gases from both dissolution steps through a series of appropriate traps and scrubbers, finally absorbing the gas in a liquid nitrogen-charcol trap. The rare gas was then desorbed by warming the trap and was measured by sampling and counting. Absorption measurements were made on each gas sample to establish its identity. The distributions of the ionic fission products and transuranics were determined by radiochemical analyses of samples taken from the caustic supernate and from the acid solution of the residue.

It was found that approximately one hundred times as much krypton-85 activity appeared on the off-gases from the caustic dissolving step as during the acid dissolution of the residue. Absorption curves of the gas samples indicated the presence of a single beta component of 0.7 Mev with gamma radiation present in about one percent of the transitions (energy of gamma not determined).

FIGURE 2

LABORATORY APPARATUS FOR DETERMINATION OF
FISSION PRODUCT DISTRIBUTION IN CAUSTIC DISSOLUTION

LABORATORY APPARATUS FOR DETERMINATION OF
FISSION PRODUCT DISTRIBUTION IN CAUSTIC DISSOLUTION

KEY

COMPONENTS

FUNCTION

A	CAUSTIC ADDITION
B	NITRIC ACID ADDITION
C	DISSOLVER PROPER
D	5-MICRON MICROMETALLIC FILTER
E	REFLUX CONDENSER
F	CAUSTIC SCRUBBER FOR IODINE REMOVAL
G	STORAGE BOTTLE FOR CAUSTIC WASH SOLUTION
H	STORAGE BOTTLE FOR CAUSTIC FILTRATE
I	DRY ICE TRAP FOR REMOVAL OF WATER VAPOR
J	SAMPLE LINE FOR ACID PRODUCT FROM DISSOLVER
K	SAMPLE LINE FOR CAUSTIC WASH SOLUTION
L	SAMPLE LINE FROM CAUSTIC SCRUBBER
M	SAMPLE LINE FROM CAUSTIC FILTRATE
N AND O	LIQUID NITROGEN ACTIVATED CHARCOAL TRAPS FOR ABSORPTION OF RARE GAS ACTIVITY
P	MANOMETER
Q	LIQUID NITROGEN TRAP TO CONDENSE RARE GASES FROM "N" AND "O"
R	GAS SAMPLE BOTTLE

Radiochemical analyses of the solution samples showed that substantially all of the cesium appeared in the caustic-aluminate filtrate, whereas not more than 0.5 percent of any other measured fission product, or of neptunium or plutonium, was accounted for in this fraction. The results are given in Table 8.

Table 8

Distribution of Fission Products and
Transuranics in Caustic Dissolution of a Slug Wafer

<u>Element</u>	<u>Activity of Individual Element in Caustic Filtrate</u> <u>as Percent of Total Activity of That Element in Fuel</u>
Ruthenium	0.10
Strontium	0.10
Cesium	99.5
Technetium	0.49
Neptunium	0.006
Plutonium	0.004
Total Beta	9.1

The uranium loss to the caustic filtrate was 0.10 percent. Of all the activity present in the wafer, a total of less than 0.01 percent (excluding krypton activity) appeared in the off-gases from both the caustic dissolution and subsequent nitric acid dissolution of the uranium residue, as determined by measurements made on the off-gas scrub solution. Ruthenium accounted for about 10 percent of the volatile activity other than krypton, with about nineteen times as much ruthenium coming off during the acid dissolution as during the caustic dissolution. No iodine determinations were made as the remaining iodine-131 was too low for accurate analysis.

Dissolution of a portion of a 120-day cooled MTR element was affected in 5M sodium hydroxide at a sodium hydroxide-to-aluminum mole ratio of 2 to 1. The residue was dissolved readily in hot 6M nitric acid. Analysis of the caustic filtrate and acidified residue solutions for fission product content indicated that significant proportions only of cesium and iodine were contained in the caustic solution as shown in Table 9.

No explanation is known for the unusually high uranium loss (3.08 percent) encountered in this experiment. This loss compares with a uranium loss of 0.10 percent obtained in the caustic dissolution of the irradiated slug wafer reported previously.

Table 9

Individual Fission Product Activity Present
in Caustic Supernate From MTR Wafer Dissolution

<u>Activity</u>	<u>Percent of Initial Isotope Activity Present in Caustic Supernate</u>
Gross Beta	10.7
Ruthenium	0.045
Zirconium	0.53
Niobium	0.89
Iodine	17.1
Barium	0.30
Strontium	0.65
Cesium	96.0
Uranium	3.08

5.24 Barium Losses

Before it was possible to conduct irradiated metal dissolution experiments, the path of barium in caustic dissolution was a matter of concern. Experiments with tracer irradiations indicated losses of the order of a few tenths percent. Under these conditions, it was felt that the barium must have remained with the residue due to adsorption since no applicable chemical solubility product could be exceeded in the solution.

It had been assumed that macro barium fission product would be precipitated as barium carbonate in plant RaLa runs due to ordinary chemical insolubility. Experiments were run in the presence of 0.1M carbonate ion under scaled-down flowsheet conditions to determine whether the predicted low losses (about 0.01%) were actually obtained. Some of the first experiments with macro-barium, using radiochemical analytical techniques, indicated losses approaching 80 percent when the caustic supernate was separated after two hours' digestion as prescribed in the flowsheet. When the slurry stood for several days before supernate separation, losses were approximately 0.8 percent. The data imply that a slow precipitation of barium carbonate occurs in the aluminate solutions.

Additional experiments were run in which barium proportional to that present in the fuel element was added as nitrate and freshly precipitated barium carbonate was added proportional to the amount added as carrier in the flowsheet. The latter was used as a seed, though it would by itself be expected to lower the percentage loss to about 40 percent of that obtained in its absence if complete exchange occurred and there was no change in the amount of barium carbonate precipitated. Losses of about 2 percent were obtained, indicating that additional precipitation did occur, though not quantitatively.

Shortly after these experiments were concluded, the dissolutions with macro irradiated material were run and the above results became only of academic interest in view of the low losses experienced. No explanation for the low losses observed in the irradiated runs is known.

5.25 Residue Composition and Explosion Hazard

5.251 Residue Composition. Early work with 168-gram fuel elements indicated the following residue composition as determined by wet chemical and spectroscopic techniques, as shown in Table 10.

Table 10

Caustic Dissolution Residue Composition from 168-gram Elements

	<u>mg./mg.U</u>
Iron	0.1
Aluminum	0.06
Copper	0.024
Manganese	2.5×10^{-3}
Chromium	8×10^{-4}
Nickel	4×10^{-4}
Titanium	1×10^{-4}
Magnesium	1.2×10^{-5}

Later work with MTR elements showed a considerable variability as to the amount of aluminum retained with the uranium, presumably related to the concentration of caustic used and the digestion time. Similar effects were observed with slugs wherein the average analysis of 20 residues was 0.27 moles of aluminum per mole of uranium with an erratic spread from 0.10 to 0.80.

In the early stages of RaLa work, it was thought advisable to attempt to decrease the aluminum carried over from caustic dissolution to minimize the change of precipitation as aluminum nitrate in the succeeding barium nitrate precipitation step. Two methods were used in attempting to deplete the aluminum.

The first method involved dissolving several pieces of cold MTR assembly containing normal uranium in 6M sodium hydroxide. These pieces of assembly, having both side plates and end plates, were dissolved with 100 percent excess of caustic present and were digested in the sodium hydroxide-sodium aluminate dissolver solution for periods ranging from two to four hours. The normal period was two hours. Analyses of the residues after these digestion times showed that the aluminum was reduced by a factor of three by digestion for four hours. No firm conclusion can be drawn, however, as to possible reduction in mole ratio of Al : U in whole-element experiments because different proportions of MTR element components were used.

The second method involved treatment of pieces of assembly containing only fuel plates for 0.5 hours, 1.5 hours, and 2 hours, followed by separation of aluminate filtrate from the uranium residue and re-treatment of the residue with fresh 6M sodium hydroxide for 1.5 hours, 0.5 hours, and zero hours, such that the total treatment times were 2 hours in all cases. The aluminum-uranium ratio was decreased by the two-step procedure from 0.5 moles of aluminum per mole of uranium to 0.1 to 0.2 moles of aluminum per mole of uranium. Uranium analyses of the sodium hydroxide-sodium aluminate supernates showed that re-treatment of the residue increased the uranium losses from 0.1 percent to approximately 0.5 percent.

5.252 Explosion Hazard. Early in process development, it was feared that the caustic residue might contain metallic uranium or lower valence states that could be pyrophoric under certain process conditions. The residue, for example, would be releasing 10-20,000 Btu/hour of fission product heat from a total mass of only a few hundred grams.

X-ray analysis of typical residues indicated that the material was mainly amorphous but no pattern was obtainable that could be interpreted. There were indications of oxides of uranium but no evidence of metal. However, because of the nature of the pattern obtained, it was felt that X-ray analysis alone was not conclusive evidence for the absence of metallic uranium.

In an effort to settle the question as to possible hazard, experiments were performed in which a piece of residue was heated on a spatula in an open flame until the spatula was dull red. The particles were then plunged into concentrated nitric acid and the effect observed. The same experiment was performed using tiny portions of powdered uranium metal. In the latter case, a small fireworks effect occurred whereas little more than spattering or bubbling was observed in the first case.

On this basis, it was decided that no hazard was associated with the caustic dissolution residue.

5.26 Caustic Waste Neutralization Technique

The caustic supernate solution from element dissolution must be made compatible with the waste storage facilities at the ICPP.

5.261 Caustic-Aluminate Solution. An investigation was made of the best method of neutralization of caustic-aluminate waste solution. It was decided to make the nitric acid concentration of the waste solution the same as that of TBP process first cycle waste solutions; i.e., about 1M. Using this fact and the condition that in the caustic aluminate waste solution the aluminum-sodium mole ration is 3 to 1, it was found that aluminum nitrate will precipitate at room temperature when its concentration is 1.2M or greater. A solution which is 1.1M in aluminum ion, 3.3M in sodium ion, and 1.0M in nitric acid is stable down to 15°C, at which temperature aluminum nitrate precipitates.

Since three moles of sodium hydroxide per mole of aluminum are used to effect the dissolution, the acid requirement just to neutralize the solution will be three moles of the hydroxide ion formed by the aluminum dissolution and three moles for the sodium hydroxide used, or a total of six moles of acid per mole of aluminum regardless of any assumed species in the caustic solution.

Assuming the values for the amount of aluminum and the flowsheet volume of solution, the conditions mentioned above; i.e., a solution 1.1M in aluminum, 3.3M in sodium, and 1.0M in nitric acid, can be attained by the addition of 62.3 liters of 70 percent nitric acid and 3.4 liters of water to the 63.5 liters of sodium aluminate-sodium hydroxide solution.

The flowsheet was changed to a NaOH to Al mole ratio of 2 to 1 from the originally proposed ratio of 3 to 1. Although the neutralized solution formerly suggested is stable, it is quite difficult to obtain a solution of these concentrations due to the formation of a precipitate during neutralization.

A stable solution can be formed with a moderate amount of care which has the final composition of 0.85M $\text{Al}(\text{NO}_3)_3$, 1.7M NaNO_3 , and 0.8M HNO_3 . This neutralization should be carried out below 50°C by adding the appropriate amount of 70 percent nitric acid to the caustic supernate which has previously been diluted with a volume of water equal to that of the original supernate.

5.3 Crude Barium Separation

5.31 Historical

It has long been recognized that barium and strontium could be separated from many metals by precipitation from fuming nitric acid solutions⁽⁸⁾. In the ORNL process⁽⁹⁾ designed originally for this plant, this method was proposed as the main step for separation of barium from uranium and gross fission product contamination. In the Oak Ridge work, several experiments were performed in which small pieces of slightly irradiated MTR element were run through the complete ORNL process. Carrier fission products were added to the uranium dissolver solution to correspond to the 12- or 37-day irradiations anticipated under the original MTR operating schedule. Tracer analysis, using their flowsheets, showed that over 99 percent of each of the components: zirconium, niobium, total rare earths, and uranium appeared in the filtrate from the nitric acid precipitation. This flowsheet used caustic-nitrate dissolution rather than straight caustic, and slightly different nitric acid precipitation conditions; however, the conditions are similar enough to make conclusions valid.

Several minor flowsheet problems were unresolved when this work was undertaken. In addition, no proof of this step had been undertaken in the presence of macro fission products as would be produced by irradiation.

5.32 Residue Dissolution

It has been found experimentally that approximately 10 moles of nitric acid are needed to dissolve one mole of uranium and its accompanying impurities in the caustic residue. The acid consumption is undoubtedly dependent on the ratio of aluminum to uranium obtained under the particular dissolution conditions used. During dissolution, silica precipitates in a flocculent, colorless form. It is difficultly filterable unless a small quantity of a filter aid such as Celite is used. It centrifuges readily, however, and is separated by this method in the current plant flowsheet.

Experience suggests that silica may be somewhat easier to remove if present in a semi-crystalline form rather than the flocculent form produced by residue dissolution. This dehydration is apparently aided by boiling in acid solution and the silica separation was originally made after the nitrate boildown step for barium separation. For plant convenience, it is now being made before the crude barium separation but the procedure could be changed if necessary.

After dissolution, additional barium is added as carrier to increase the total amount present to 5 grams.

5.33 Aluminum and Strontium Decontamination

Early in process development the use of the hydrochloric acid process for barium-strontium separation was still being considered. Preliminary results had been erratic, due presumably to the influence of varying amounts of aluminum carried over from the nitric acid separation. With the decision to use the chromate separation technique, variations in the amount of aluminum carryover became less important but it was naturally felt desirable to minimize the carryover if possible. Original flowsheet specifications for strontium could have been met after one chromate separation; however, it was felt desirable to get any additional strontium decontamination that could be obtained. Careful control of the nitric acid precipitation step permits maximization of barium recovery and minimization of strontium as well as aluminum carryover. The possible variations in recovery and decontaminations arose from the different solubility curves of the three elements with respect to total nitrate concentration and temperature. Total solution volume is a third variable.

In line with development philosophy, no attempt was made to investigate quantitatively the entire range of solubilities of each of the three components as a function of temperature. The earliest work gave satisfactory results using slight modifications of the ORNL flowsheet. Originally, the nitric acid solution of the uranium cake was evaporated to "constant boiling" at about 55 percent nitric acid. Of course under these conditions there is no true "constant boiling" mixture due to the gradually increasing concentration of inert salts and their changing effect on activities of acid and water. After attaining constant boiling, fuming acid was to be added and the solution cooled to precipitate barium nitrate.

Under plant operation, it was felt desirable to avoid cooling to minimize operational steps. The precipitation was therefore effected in two different ways; by evaporation of the solution at 95°C with continuous air sparging and by evaporation at the boiling point of the solution which corresponds to approximately 115°C. Separations were made at solution temperatures by filtration.

Synthetic solutions were used in these experiments, with concentrations of various constituents taken to approximate or substitute for anticipated process concentrations. Compositions are shown in Table 11.

Table 11

Initial Composition of Synthetic Nitrate Solutions

3.3M Acid

<u>Constituents as Nitrates</u>	<u>Concentration mg./ml.</u>
Aluminum	4.0
Sodium	5.3
Uranium as Uranyl	67.2
Barium	2.0
Strontium	0.70
Rare Earths as Lanthanum	3.0
Iron	6.4
Copper	1.6

The results of both methods of precipitation are summarized in Tables 12 and 13.

Table 12

Barium Recovery and Decontamination
From Uranium and Gross Fission Products

Evaporation with Sparging at 95°C - Initial Volume 2.5 Liters

Final Volume (liters)	0.90	0.64	0.32
Barium Precipitated (%)	87.8	92.9	99.5
Strontium Precipitated (%)	28.4	42.2	80.5
Aluminum Precipitated (%)	3.7	6.6	24.1

Table 13

Barium Recovery and Decontamination
From Uranium and Gross Fission Products

Evaporation at Boiling Point - Initial Volume 2.5 Liters

Final Volume (l)	0.70	0.50	0.40
Barium Precipitated (%)	>99.9	>99.9	>99.9
Strontium Precipitated (%)	31.5	54.4	66.0
Aluminum Precipitated (%)	3.5	6.5	7.9

Data in Table 14 indicate the final total nitrate concentrations found as a function of final volume for the experiments run under conditions of evaporation by boiling.

Table 14

Final Nitrate Concentrations Under Boildown Conditions

Initial Volume 2.5 Liters; 4.5M Total Nitrate

Final Volume (ml)	290.0	310.0	330.0	380.0	440.0	560.0	710.0	900.0
Volume as Percent Original	11.6	12.4	13.2	15.2	17.6	22.4	28.4	36.0
Nitric Acid (M)	1.5	1.7	1.9	3.9	4.7	7.3	7.4	9.0
Nitrate from Salts (M)	10.3	9.7	9.1	7.9	6.8	5.4	4.2	3.2
Total Nitrate (M)	11.8	11.4	11.0	11.8	11.5	12.7	11.6	12.2

Though the analysis for acid in these high uranium solutions was difficult, it is significant that total nitrate concentration stays relatively constant as a function of final volume, increasing salt concentration compensating for decreasing acid. Experimental results indicate that acid concentration decreases more or less linearly with degree of boildown from 9 to 1.5M in the range 35 to 10 percent of initial volume. This implies that the acid solution described by ORNL increases in acidity up to the "constant boiling" range of 11 to 12M and then loses acid with continued evaporation due to the influence of dissolved salts. No experiments have been performed to verify this presumed early increase in acid concentration.

From other experiments it is known that total nitrate concentration, essentially additive independent of origin, determines the solubility of the precipitating nitrate compounds. (See section 6.) From the fact that final total nitrate is constant under the boildown conditions considered it can be seen that solubilities should vary linearly with solution volume subject to differences in final temperature, etc. The data from the boildown experiment show this effect; the percent strontium and aluminum precipitated is linear with boildown volume.

The method involving evaporation at the boiling point is the more desirable one since at comparable volumes it yields higher barium recovery and higher strontium and aluminum decontamination factors.

Optimum conditions that were established included evaporation of the gross fission product solution from an original volume of 2.5 liters and an original nitric acid concentration of 3.3M to a final volume of 0.50 liters $\pm$ 0.10 liters followed by centrifugation at a temperature just below the boiling point of the solution.

The above conditions yielded very satisfactory results when the process was run on a laboratory scale. However, unexpectedly high barium losses were encountered in this step in the pilot plant centrifuge, apparently due to the high viscosity of the solution. Because of the barium losses and the change in plans to precipitate strontium more quantitatively at this point for future strontium recovery, the process was modified such that the uranium fission product solution was evaporated from its initial volume of 2.5 liters to a volume of 0.65 $\pm$ 0.10 liters. Then 0.50 liters of 90 percent nitric acid was added to the solution as a precipitant. Results are shown in Table 15.

Table 15

Barium Recovery and Decontamination From Uranium and Fission Products

Modified Procedure - Initial Volume 2.5 liters

	<u>#1</u>	<u>#2</u>	<u>#3</u>	<u>#4</u>
Volume After Boildown (liters)	0.92	0.92	0.68	0.64
Volume 90% HNO ₃ Added (liters)	0.25	0.50	0.40	0.50
Barium Lost (%)	7.81	3.44	2.24	0.93
Aluminum Precipitated (%)	--	5.0	4.0	4.0
Strontium Lost (%)	--	28.1	20.5	8.0

The solution, which is much less viscous than that obtained under previous conditions, is centrifuged at a temperature just below its boiling point. Under run #4 conditions, over 99 percent of the barium and 92 percent of the strontium is precipitated while an aluminum decontamination factor of 25 is obtained across this step. No linearity is expected here because no attempt was made to control final solution temperatures.

This crude barium separation was again modified due to difficulties involved in plant design. It was found necessary to dilute the solution obtained from dissolution of the caustic residue from the original 2.5 liters of nitric acid to 5.0 liters using water. Experimentally, it has been determined that the boildown should proceed as before; i.e., to 650 $\pm$ 100 ml followed by addition of 500 ml of 90 percent acid as a precipitant. Apparently the initial composition of the overhead from the 5.0 liters boildown is too dilute to affect significantly the final nitrate concentrations in the range of final volume and recoveries being considered.

5.4 Barium - Strontium Separation

5.41 Historical

The use of the chromate-acetate process for barium-strontium separation had been considered previously but had been discarded due to possible difficulties with aluminum precipitation in the 4 to 6 pH range. It was found, however, that this precipitation was only observed under conditions where irreversible precipitation was possible. For example, use of sodium hydroxide as a precipitant causes local precipitation under conditions of pH 4 to 6. Use of acetate under buffering conditions rather than hydroxide prevents the original precipitation.

The advantage of the chromate-acetate system is that the influence of varying quantities of aluminum carried over is less than in the hydrochloric acid alternate procedure. Also, the system has a buffering ability to compensate for carryover of nitric acid in the plant equipment from the previous separations step. It was determined that corrosion problems involved with hydrochloric-nitric mixtures would be quite difficult and the acetate system, though dependent on pH, is such that no actual pH control in the sense of measurement for process control is required.

5.42 Summary of Radiation Damage Effects

A complete report on all investigations of "Radiation Damage Problems in the ICPP Barium-140 Separation Process", by R. L. Andelin, has been issued as IDO-14348⁽⁵⁾. As was predicted on a theoretical basis, chromate ions were found to be reduced under the radiation dosages expected in the chromate-acetate separation. It was found that the pH stability is adequate under process conditions but that chromate ion was reduced at the rate of 2.43 ± 0.17 millimoles per kilocalorie of radiation absorbed. Assuming total solution volumes of 1500 milliliters of 0.10M chromate or a total of 150 millimoles, it can be seen that chromate is being destroyed at a rate of approximately 5 millimoles per minute and would be exhausted in the order of 1/2 hour.

At the time of the radiation damage investigations, only one chromate separation was planned and furthermore, there seemed to be an incentive toward slow, dropwise addition of acetate with gradual increase of pH on the basis of higher decontamination observed under these conditions. With these assumptions, it was felt necessary to devise a scheme to protect chromate ion from the effects of radiation reduction. After extensive experiments, it was established that bromide ion is useful in this respect. Using 0.1M bromide ion as an additive to process solutions, the reduction rate of chromate was lowered to 0.3 ± 0.03 millimoles reduced per kilocalorie absorbed. It was also observed that decreasing total acetate concentrations caused decreased chromate reduction but unfortunately this observation was of little value inasmuch as high concentrations of acetate had to be considered to compensate for possible high nitric acid holdups from the previous step. The possibility of continually adding chromate to compensate for the amount consumed by reduction

was also considered. The rate of reduction, even in unprotected solutions was shown to be slow enough to make this procedure possible. Furthermore, it was established that the chromate precipitate, once formed, was not substantially decomposed even in the absence of excess chromate in solution. Some doubt as to the validity of these results should be entered, however, because the experimental assumption that radiation absorbed from external sources is equivalent in effect to that from internal sources is somewhat dubious in the case of solid materials.

Several circumstances caused later revisions in supposedly optimum process conditions. With the increased decontamination required for strontium it became necessary to consider two strontium separations under any conditions. For this reason, less importance was attached to the attempt to maximize decontamination in one step inasmuch as the two steps combined would give ample decontamination under practically any reasonable conditions. The importance of dropwise addition relative to instantaneous addition was then in question, too. Furthermore, investigations of corrosion problems associated with plant equipment indicated that the presence of bromide was probably responsible for the interface and vapor phase corrosion observed in the pilot plant centrifuge. For the above reasons, it was planned to eliminate bromide from consideration if possible. Chromate is added instantaneously and the entire precipitation completed, including phase separation, in 10 to 15 minutes.

A separate item of importance was the problem of carbon or organic contamination of the final barium chromate product and its degree of separation in the succeeding process steps through to the final barium nitrate product. Because the ion exchange process had been rejected for just this reason of carbon contamination, it was necessary to prove the current process was satisfactory in this respect.

Experiments were performed using sodium acetate which had been tagged with carbon-14 in both carbon positions. With the assistance of the MTR Technical personnel, contamination of precipitates was followed during the succeeding process steps using standard carbon-14 counting techniques. Under plant flowsheet conditions, it was found that 10 grams of barium chromate from a typical precipitation would have associated with it 160 milligrams of carbon but that barium nitrate metathesis would reduce the final nitrate product contamination to the order of 0.2 milligrams of carbon. This is considerably below the suggested maximum of 10 milligrams of carbon contaminant.

The rate of radiation induced off-gassing was shown to be negligible.

5.43 Wash Procedure

It has been observed that water washes of precipitated barium chromate lead to barium losses which exceed the equilibrium solubility by a factor of 100. In an attempt to minimize this effect, which was assumed due to peptization, a series of runs was made using wash solutions of different ionic strengths. The observed losses, ranging from

0.12 percent using 0.01N ammonium nitrate to 0.95 percent using distilled water, are still substantially higher than the 0.009 percent predicted and have been rather irreproducible.

These losses were determined in experiments run at proposed plant scale and thus, in the worst case, using water, could lead to 2 to 3 percent losses after three washes.

In pilot plant operation using pure water, cumulative losses never exceeded one percent. For this reason, no additional laboratory work has been performed nor has any explanation of the high losses or differences between laboratory and plant been found.

5.44 Optimization of Barium - Strontium Separation

Laboratory experiments designed to evaluate the effects of several variables during the chromate precipitation step were conducted with the results presented below.

For purposes of comparison, theoretical barium loss curves were calculated on the basis of barium chromate solubility data⁽¹⁰⁾.

The laboratory experiments were run at room temperature using instantaneous acetate addition and a five-minute digestion period with stirring. The solutions were then centrifuged to separate the barium chromate precipitate. The supernate was filtered and the precipitate redissolved in dilute acid for analysis.

5.441 Barium Loss.

(a) pH - The barium loss observed ranged from ca 1% at pH 3.5 to ca 0.1% at pH 4.9 (Figure 3).

(b) Chromate Concentration - The concentration of chromate was varied from 0.5 to 1.5 times the flowsheet concentration. Barium loss appeared to be only slightly affected by the changing chromate concentration in this range (Figure 4).

(c) Inert Barium Carrier - The concentration of inert $\text{Ba}(\text{NO}_3)_2$ carrier was varied to give total barium concentrations of 0.3, 0.65, and 1.0 times the flowsheet concentration. The results (Figure 5) indicate that considerable latitude may exist for increasing the specific activity of the product by decreasing the amount of inert barium carrier added.

(d) Slow Addition of Acetate Buffer - Slow addition of buffer was considered as a possible means of decreasing contamination in the precipitation step. However, the practicality of short reagent radiation exposure time in this step and the reasonable barium recovery obtained with rapid acetate addition have led to tentative acceptance of rapid addition as a process method.

FIGURE 3

Ba-Sr SEPARATION EFFECT OF pH

FIGURE 4
Ba-Sr SEPARATION
EFFECT OF CHROMATE CONCENTRATION

FIGURE 5

Ba-Sr SEPARATION
EFFECT OF INERT BARIUM
ON Ba-140 LOSS

5.442 Strontium Decontamination. The barium loss and the strontium decontamination are plotted for comparison.

(a) pH - (Figure 6) A straight line dependency of log strontium decontamination versus pH was found.

(b) Chromate Concentration - (Figure 7) Strontium decontamination decreases quite rapidly with increasing chromate concentration.

(c) Inert Barium Carrier - (Figure 8) Addition of inert barium as carrier lowers the strontium decontamination somewhat.

(d) Wash Solution - A barium chromate precipitate at pH 4.9 was washed with a chromate solution at pH 4.2. No significant difference was observed in strontium decontamination, indicating that surface adsorption of strontium on barium chromate particles contributes only slightly to the contamination.

(e) Isotopic Dilution of Strontium - Barium chromate precipitations were carried out on two solutions differing in inert strontium, one containing strontium equal to that present at the first precipitation step and the other reduced by ca 10^3 . The low strontium concentration gave a decontamination of 60 while the isotopic dilution of strontium gave a decontamination of 191. This indicates internal adsorption-coprecipitation rather than strontium chromate solubility and accounts for the strontium contamination present in the barium chromate precipitate.

5.443 Summary. Laboratory results indicate that the product specific activity and strontium decontamination can be increased somewhat if desired by the addition of less inert barium carrier. In addition, strontium decontamination may be increased by decreasing the chromate concentration in excess of stoichiometric barium requirements.

5.45 Second Barium-Strontium Separation

In order to enhance decontamination with respect to fission product strontium-89 and strontium-90, a double precipitation of barium chromate was proposed. This involves dissolution of the first barium chromate precipitate in dilute nitric acid, the addition of inert strontium equivalent to that originally present, and re-precipitation of barium chromate under conditions similar to those of the first precipitation. If a strontium decontamination factor of 300 on a gram basis is obtainable after the first precipitation, a strontium decontamination factor of $(300)^2$ or 9×10^4 with respect to strontium-89 and strontium-90 should be obtainable after the second precipitation.

The volume and concentration of nitric acid required to dissolve 9 grams of barium chromate without precipitating barium nitrate was determined. Because of volume limitations, it was desirable to use the least

FIGURE 6

Ba-Sr SEPARATION
EFFECT OF pH ON STRONTIUM SEPARATION

CPP-S-958

possible amount of dilute nitric acid for the dissolution. Experimentally it was found that 0.1 grams of barium chromate would dissolve in 10 ml of 0.6M nitric acid. Therefore, an approximate range was known.

To simulate process conditions, five 0.1-gram samples of barium chromate were precipitated according to flowsheet specifications. The samples were centrifuged and washed. Portions of 0.1, 0.2, and 0.4N nitric acid were added to samples of the precipitate. The solutions were stirred gently and warmed over a flame to aid dissolution. Ten ml of 0.1M acid did not dissolve this amount of chromate completely, whereas 9 ml of 0.2N acid (or 10 ml of 0.4N acid) resulted in complete dissolution. Accordingly, 1 liter of 0.2N nitric acid dissolves at least 12.5 grams of barium chromate. Since flowsheet specifications indicate the presence of ca 9.0 grams of barium chromate, 1 liter of 0.2N nitric acid is adequate for the process.

Because of the wash steps following this first chromate precipitation, no significant holdup of chromate supernate solution is expected. Furthermore, there is no nitric acid holdup as is observed at the start of the first precipitation. Under these conditions, the acid used in cake dissolution is the only acid present and its quantity is known quite accurately. This permits pH control, without measurement, during the second separation and insures maximum decontamination.

Laboratory results indicate a considerably better decontamination can be obtained by the isotopic dilution method proposed than by doing the second precipitation without carrier addition in which advantage would be taken of the very low concentration of strontium relative to barium (Section 5.443 - e).

515 Metathesis of Chromate to Nitrate

Early work on the transformation of barium chromate to barium nitrate indicated that direct metathesis with hot concentrated nitric acid was quite promising. Of the order of 1-2 percent of the chromate remained unconverted, however, which would have given a product considerably out of specifications.

An alternate procedure was considered in which the chromate was dissolved in a small volume of perchloric acid and then precipitated as nitrate using fuming acid. Introducing another component such as perchloric acid had the possible disadvantage of complicating corrosion problems and this alternate was dropped.

The present procedure calls for direct metathesis, dissolution of the primarily nitrate residue in water and a precipitation with fuming acid. The additional step requires very little extra effort in plant processing.

5.51 Product Solution Evaporation

Many of the production plant contamination problems experienced by ORNL have been traced to airborne contamination brought about by the product evaporation technique used. This procedure involves the use of warm air blowing over the solution to assist in slow and controlled evaporation. Much of the heat required is, of course, supplied by radiation heat of the product itself. An advantage of this method is that no electrical heating system is required.

Experiments in this laboratory indicate that the crystals formed by warm air evaporation are small and creep over the product cup surface while the alternate procedure using supplementary electrical heat would appear to aid the growth of larger crystals centered in the bottom of the product cup. This technique has been adopted for plant use despite the slight disadvantage incurred.

5.6 Overall Process Results

5.61 Extraneous Impurity Decontamination

Very early work using less optimum flowsheet conditions than are now known, indicated that the decontaminations shown in Table 16 could be obtained with respect to contaminants not of fission product origin.

Table 16

Decontamination of Ba-140 Product From Metallic Impurities

After	Log Decontamination Factors for					
	Aluminum	Iron	Copper	Maganese	Chromium*	Nickel
Caustic Dissolution	2.6	0.0	0.0	0.0	0.0	0.0
Ba-Sr Nitrate Precipitation	2.6	2.5	2.2	---	---	---
Final Barium Product	7.0	5.0	5.0	4.0	4.8	2.0
Initial Wt. Present, Grams	890.0	3.1	0.19	0.06	1.9	0.01

* Weight present as barium chromate

The decontamination observed, taken in conjunction with the anticipated initial amounts present indicate that product specifications will be easily met.

5.62 Fission Product Decontamination

RaLa process decontamination is based on precipitation equilibria rather than solvent extraction equilibria and as such the decontaminations obtained are concentration dependent. For this reason, investigations based on the ultra-micro quantities of fission products produced in slightly irradiated uranium are subject to misinterpretation. Attempts to experiment with micro quantities comparable to those expected under process conditions are complicated by the difficulty of duplicating the chemical species which would be obtained under actual conditions with laboratory reagents. This problem is important with respect to several of the many fission products, in particular zirconium, ruthenium, niobium, and technetium which are known to have chemistries quite dependent on previous history due to the only slightly reversible formation of hydrated species, polymers, etc.

From chemical reasoning, the information in Willard⁽⁸⁾, and laboratory results it is possible to be completely confident of expected df's for all rare earths, alkali metals, halogens, cadmium, silver, and strontium.

Chemical reasoning strongly suggests that no difficulties will be experienced with zirconium, niobium, ruthenium, platinum metals, and technetium. In the case of these elements, the chemistry of dissolution in nitric acid even during ordinary fuel element reprocessing is not understood inasmuch as reagent grade samples of the first four are not readily soluble in straight nitric acid in the laboratory. For this reason it is difficult to predict if the species that exist in the caustic residue would be completely soluble. However, laboratory experiments performed in the course of the investigation on fission product distribution in caustic dissolution imply that they are. If they do go into solution there is no reason to expect that any of the five is insoluble in nitric acid under the conditions outlined.

Selenium, tellurium, and molybdenum should be present in significant proportions in the process streams but again, no reason exists to suspect their insolubility in concentrated nitric acid solutions if they are originally soluble in dilute acid.

Indium, antimony, and tin are present in almost negligible quantities and in addition the nitric acid chemistry of this group would also appear to be satisfactory.

It is interesting to note that a built-in safety factor exists in the present RaLa process, due to the fact that lanthanum separation uses nitric acid precipitation as one of the processing steps but takes the supernate rather than precipitate as product. In other words, if any of the above elements does follow barium closely through the entire process, it will be similarly insoluble with barium under conditions used in succeeding processing. This consideration is inherent in the

wording of specifications for contaminant metals as "no more than 50 milligrams of total metallic impurities are to be soluble in 75 milliliters of 70 percent nitric acid." Even if the contaminants exhibited the worst possible behavior; i.e., split between precipitate and supernate in the fuming acid precipitations, it is almost certain that the wide range of variables available with respect to temperature, acid concentration, volume, etc., could be utilized in effecting a cleaner separation.

6. ALTERNATE PROCESS STEPS DISCARDED

6.1 Caustic-Nitrate Dissolution

The ORNL process originally proposed used a mixture of sodium hydroxide and sodium nitrate for dissolution of the MTR element. The recommended flowsheet conditions for this caustic-nitrate process were mole ratios of aluminum : sodium nitrate : sodium hydroxide of 1 : 0.5 : 1, at 5.0M final aluminum concentration. Under these conditions, satisfactory filtration rates were observed and the resulting solutions were stable for at least 24 hours at 20 to 100°C.

This process had the advantage of converting much of the hydrogen ordinarily produced to ammonia, leading to a presumably less hazardous off-gas. The residue from this type dissolution was shown to be uranium diuranate rather than uranium oxides and thus, the physical properties of the residue were different from those of the present work.

Experience at the ICPP under American Cyanamid indicated greater difficulty with filtration and solution stability than had been expected and, in conference with an ORNL group in July, 1953, it was decided to pursue an investigation of straight caustic dissolution in the hope of improving these properties. At the termination of the Cyanamid contract, it was stated⁽¹¹⁾ "The straight caustic dissolution produces a black, non-compressible crystalline residue which forms a filter cake that has excellent permeability in contrast to the finely divided, compressible residue of sodium diuranate. The resulting solution from the sodium hydroxide-sodium nitrate dissolution of cold MTR assembly was found to be practically unfilterable a portion of dissolver solution was digested for two hours to insure complete reaction of aluminum with the reagents and then centrifuged for up to 50 minutes at about 1000 G's. Some of the residue settled to the bottom but the supernate was very turbid."

After several months' initial effort on the straight caustic flowsheet, the development work on this alternate was completed.

6.2 Barium-Strontium Separation as Nitrates

An investigation was made as to the possibility of separating barium from strontium and aluminum on the basis of the widely differing solubilities of their nitrates with varying nitric acid concentrations. Product losses of 10 percent would have been acceptable if separations were adequate and easy.

Preliminary experiments indicated that at $7M$ nitrate concentration, substitution of nitric acid by aluminum nitrate caused no significant change in barium losses as shown in Table 17.

Table 17

Effect of Total Nitrate on Barium Nitrate Losses

	<u>Expt. 1</u>	<u>Expt. 2</u>	<u>Expt. 3</u>
Total Nitrate Concentration (M)	7.0	7.0	7.0
Nitric Acid Concentration (M)	7.0	5.0	3.0
Nitrate Concentration due to Aluminum Nitrate (M)	0	2.0	4.0
Barium Nitrate Lost (%)	2.4	2.5	2.6

This experiment implied that nitrate concentration was solubility determining, and that nitrate concentrations could be considered additive without regard to source. The observed results agreed closely (± 10 percent) with the barium nitrate solubilities at the corresponding total nitrate molarity predicted on the basis of the solubility curve for barium nitrate in pure nitric acid.

Experiments were then performed in which barium nitrate was precipitated from 1/2-scale flowsheet amounts of barium nitrate, strontium nitrate, and aluminum nitrate at arbitrarily chosen final nitrate concentrations. Assuming nitrate ion additivity, no strontium nitrate should have precipitated from any of the three solutions. Strontium activity, as strontium-89, was added to the solution and strontium determined in the barium precipitate by counting. Precipitations were made by dropwise addition of 90 percent nitric acid at room temperature. Barium recovery ranged from 82 to 95 percent with strontium decontamination factors of 7 to 112, as shown in Table 18.

The results indicate that extensive coprecipitation of barium and strontium occurs. Whether digestion would increase decontamination was not established. In all experiments, actual losses of barium were within 10 percent of those predicted.

Table 18

Barium Recovery and Strontium Decontamination
Factor as Function of Nitrate Precipitant Concentration

	<u>Expt. 1</u>	<u>Expt. 2</u>	<u>Expt. 3</u>
Original barium concentration (M)	0.106	0.0916	0.0786
Original strontium concentration (M)	0.0403	0.0329	0.0286
Original aluminum concentration (M)	0.986	0.856	0.726
Final nitrate concentration (M)	4.30	6.30	8.60
Strontium df observed	112	12	6.8
Strontium df expected	0.0	0.0	0.0
Percent barium recovered (expected)	79.5	87.8	94.3
Percent barium recovered (observed)	81.5	88.7	94.6

Two slightly different techniques were then tried. In the first case, an attempt was made to leach strontium away from barium in the precipitate obtained from the gross fission product solution boil-down. Experiments were run at several concentrations of nitric acid and several different volumes. The solutions were agitated constantly at 95°C for four hours. Strontium decontamination factors ranged from 1.1 to 5.9 and corresponding barium losses were from 2.6 to 5.5 percent. In view of such poor strontium decontamination factors, the leaching experiments were abandoned.

The second series of experiments consisted of dissolving the barium nitrate-strontium nitrate residue in 7M nitric acid and then reprecipitating barium nitrate by evaporation of the solution. On evaporation, the solution became super-saturated with respect to barium nitrate and approximately half of the barium nitrate precipitated all at once. This precipitate carried with it enough strontium to lower the strontium decontamination factor to 5.8. Even when special precautions were taken to assure slow precipitation, the highest strontium decontamination factor was 7.1. The corresponding barium loss was 18.2 percent.

The results obtained implied coprecipitation and mixed crystal formation and as a result, the experiments were abandoned.

6.3 Barium-Strontium Separation Using Hydrochloric Acid

Several alternate processes for barium-strontium separation were proposed by Oak Ridge. Included among them was the separation of barium by precipitation of barium chloride dihydrate from 10.5M hydrochloric acid, a procedure which leaves strontium in solution. Oak Ridge National Laboratory felt that the many advantages of this process would be offset by such disadvantages as the high barium losses observed, the insufficient and erratic strontium decontamination and the possible corrosion problems. American Cyanamid re-examined the process after the ion exchange method had been discarded and extended the data somewhat⁽¹¹⁾.

Preliminary corrosion results were obtained by Phillips for typical process solutions using possible construction materials. These corrosion problems arise due to the presence of metal nitrates in strong hydrochloric acid or conversely to the presence of metal chlorides in the final nitric acid precipitation step; in either case, the solutions would presumably have some of the characteristics of aqua regia.

Simple, short-time, room temperature corrosion tests were run on a number of metals using test solutions representing the most serious conditions anticipated. The results of these tests indicated that only tantalum should remain unattacked, although the rate of attack on platinum (unattacked in nitric acid-rich solution) might also be tolerable considering the short exposures anticipated in the most corrosive solutions. Worthite alloy and zirconium were also subject to limited attack by hydrochloric acid containing nitrates. For pilot plant purposes, considering requirements of availability and ease of fabrication, Hastelloy C, which was lightly attacked by nitric acid containing chlorides and more seriously affected by hydrochloric acid containing nitrates, was felt to be a potentially useable alloy. The results of these corrosion tests are given in Table 19.

Table 19

Corrosion Tests Under Chloride-Type Ba-140 Process Condition

Coupon Areas: 1.3 to 8.0 cm.

Temperature: About 25°C

Metal Tested	Penetration Rate, mils/year					
	In 65% HNO ₃ Containing 0.04M BaCl ₂		In 34% HCl Containing 0.04M Ba(NO ₃) ₂ and 0.013M Sr(NO ₃) ₂			
	After 24 hours		After 24 hours		After 68 hours	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Illium	1.5	--	933	--	--	--
Tantalum	0	0	---	--	0	0
Platinum	0	0	77	73	--	--
Worthite	0	--	173	--	--	--
Zirconium	5.1	1.5	---	--	267	209
Hastelloy C	32	8	476	679	508	712
Haynes Alloy 25	2.8	2.5	---	--	1376	1498
Hastelloy B	Entirely Dissolved		---	--	852	925
Type 347 SS	--	--	---	--	17000	22000

While it was felt that several of the materials had promise due to the short exposures actually expected, it was still obvious that severe difficulties existed.

At this time, the chromate process was established as feasible and the chloride proposal was dropped.

7. DISSOLVER CORROSION

7.1 Problem

In the Ba-140 recovery process, a two-day cooled MTR fuel element is dissolved in boiling twenty percent caustic. The dissolving time for one element is two and one-half hours. Dissolver corrosion life was designed on the basis of probably forty-five batches. In addition, chemical solutions, generally containing appreciable quantities of nitric acid, must be used periodically to decontaminate the process equipment. These chemicals impose an additional requirement upon the dissolver vessel.

Austenitic Type 347 stainless steel appears to be the most suitable alloy for the dissolver. Nickel and Monel are more desirable for caustic than Type 347; however, impractical in nitric acid service. Mild steel suffers stress corrosion cracking in twenty percent caustic at temperatures above 160°F⁽¹²⁾. This observation suggests that the austenitic stainless steels may also suffer stress cracking in boiling twenty percent caustic. If all stress risers are eliminated from the stainless steel dissolver vessel, this possible stress cracking effect will be mitigated.

Corrosion studies were conducted to evaluate general attack and stress corrosion cracking by dissolver solution upon Type 347 stainless steel. The corrosion studies were of two types: plant tests and service tests. Service tests were conducted on the pilot plant equipment used to dissolve the MTR fuel assemblies. For plant tests evaluation, variously stressed specimens were placed within the pilot plant prior to fuel dissolving operations. These specimens were totally immersed in the caustic solution. At the same time, electrical contact was maintained by using stainless steel wires between the simulated fuel assembly and specimens.

The details of the actual dissolving operation in pilot plant equipment may be found in Appendix II. Caustic was added after purging the dissolver with nitrogen gas to remove all oxygen from the system. Hydrogen gas was evolved during the dissolution according to the following reaction:

Nitrogen was employed again at the end of the dissolution period prior to exposing the vessel to the atmosphere. This purge effectively removes the hydrogen gas from the dissolver vessel. The charge to the dissolver and resulting dissolver solution composition are given in Table 20.

Table 20

Summary of Amount of Materials Added During a Ba-140
Pilot Plant Dissolution, and Dissolver Solution Composition

<u>Element</u>	<u>Molar Concentration</u>
Dissolvent, liters	58-60
Fuel Assembly, Kg	4.006-4.070
Dissolution, Average Time	2.26 hrs.
Dissolver Solution	
Specific Gravity	1.26-1.27
Sodium	4.70-5.21
Aluminum	2.31-2.55
Free Hydroxide	2.40-2.74

7.2 Plant Tests

7.21 Materials and Procedure

The Type 347 stainless steel (Cb-Ta) samples used in this study were (a) twelve 7.0-inch x 1.0-inch x 1/8-inch stressed bars, (b) 8 1-1/2-inch high compressed rings cut from 2-inch schedule 10 pipe, and (c) six 1-inch high stressed hoops having 1.5-inch O.D. These samples were stressed and heat treated as shown in Table 21.

The second group, labelled "Compressed Rings", were intentionally stressed before being given the indicated heat treatment. This was accomplished by compressing the rings into ovals 1-3/4 inches wide by 3 inches long. These rings were further compressed by a bolt during exposure.

The third group, shown in Table 21 as "Welded Stressed Hoops", were made from 2.0-inch schedule 10 pipe in the following manner: a longitudinal strip about 1/2" wide was cut from the 2.0-inch pipe, the pipe was vice-closed, welded, and cut into 1-inch long hoops.

Bolting provided a simple means of applying a predetermined stress to the bar and compressed ring specimens. One compressed ring specimen was bolted on each side of the specimen jig. A means for determining the stress level applied to the welded hoops was omitted.

Bar specimens of rectangular cross section were supported at both ends and loaded at the center. The maximum tensile stress occurs in the outermost fibers and this stress is given by the formula: (15)

$$S = \frac{Mc}{I}$$

Table 21

Summary of Heat Treatment and Stress Given
Type 347 Stainless Steel (Cb-Ta) Specimens

Stressed Bars			Compressed Rings			Welded Stressed Hoops		
No. of Spec.	Heat Treatment	External Stress Applied After Heat Treatment PSI	No. of Spec.	Heat Treatment	External Stress Applied After Heat Treatment PSI	No.* of Spec.	Heat Treatment	External Stress Applied After Heat Treatment PSI
2	4 Hrs at 1000°F Water Quench	20,000 ¹	4	4 Hrs at 1000°F Water Quench	20,000 ¹	4	4 Hrs at 1000°F Water Quench	None
2	4 Hrs at 1000°F Water Quench	75,000 ²						
2	1 Hr at 1600°F Water Quench	20,000 ¹	2	1 Hr at 1600°F Water Quench	20,000 ¹	4	1 Hr at 1600°F Water Quench	None
2	1 Hr at 1600°F Water Quench	75,000 ²						
2	As received	20,000 ¹	2	As recieved	20,000 ¹	4	As welded	None
2	As recieved	75,000 ²						

* Use the best two of four specimens.

1. Approaching elastic limit.

2. Approaching yield point.

In this formula, M is the bending moment in lbs., c is the linear distance to the extreme fiber (one-half the thickness) and I is the moment inertia of the cross sectional area about a neutral axis expressed in inch units. For beams freely supported at the ends, span L in inches, carrying a concentrated load P in pounds at the middle, the maximum moment I is given by $\frac{PL}{4}$.

The deflection sigma, in inches necessary to impress a predetermined load, was calculated from the deflection formula: ⁽¹⁴⁾

$$\text{Sigma} = \frac{PL^3}{(48)(E)(I)}$$

In this mathematical expression, sigma equals deflection in inches; P equals pounds of force; L equals length of beam, 6"; E equals modulus of elasticity for stainless steel, 30×10^6 psi; and I equals principal axis of moments through the rectangular centroid $\frac{(\text{base})(\text{height})^3}{12}$

Thus:

$$P = \frac{(\text{sigma})(48)(E)(I)}{L^3}$$

By substituting into the first equation

$$S = \frac{(\text{sigma})(12)(E)c}{L^2}$$

For a measured deflection of 0.1034", S = 64,700 psi; and for a deflection of 0.0275", 17,190 psi. These two levels of stress are just below the elastic limit and yield point and are used to bracket the stress region for determining stress corrosion cracking.

Stress values on the compressed rings did not exceed their elastic limit. The specimens were compressed by tightening a nut and bolt arrangement. Permanent deformation of the specimens was not observed upon complete release of the stress caused by the nut.

A jig was used to accomodate both stressed bars and compressed rings. The jig was suspended from the lid of the pilot plant dissolver by means of a stainless steel wire. The welded stressed hoops were threaded on the stainless steel wire.

The dissolver vessel was fabricated from six feet of 12-inch Type 347 stainless steel Schedule 10 pipe as shown in Figure 9. The lower two feet five and one-half inch part of the vessel, was jacketed with 14-inch Schedule 10 Type 347 pipe. After erecting, the vessel was used in the "as-welded" condition.

Simulated MTR fuel assemblies were made from 2S aluminum sheet stock. Twenty 24-inch x 3-inch sheets were assembled with stainless steel bolts. One-inch square pieces of 2S aluminum sheet were used to separate the fuel plates.

FIGURE 9
PILOT PLANT FUEL DISSOLVER
T-2

IDC-14445
 PAGE 61

CPP-S-961

The completed experimental plant test study involved a total of twenty dissolution runs. The total exposure time was 44.5 hours. Weight change data and microscopic observations at 30X were obtained at the beginning of the experiment and after the last run. From weight change data, general corrosion weights were determined. Prior to recording their weights, all specimens were cleaned in 10 percent nitric acid at 140°F. A micro examination up to 100 diameters was conducted on representative specimens after the last exposure.

7.22 Results

Corrosion rates for the variously heat treated Type 347 (Cb-Ta) stressed specimens after immersion in the Ba-140 dissolver solution are listed in Table 22. Figures 10 and 11 show typical specimens after exposure. Specimens which were heat treated either at 1000°F for four hours, or 1600°F for one hour or left in the "as-welded" condition suffered very mild corrosion. Corrosion damage from pitting was not apparent when the exposed specimens were compared with the original specimens. Variations of stress and heat treatment fail to have any effect upon the corrosion resistance of Type 347 alloy.

These data indicate that Type 347 stainless steel will resist stress corrosion cracking when immersed in the 200°F Ba-140 process dissolver solution. Although projection of this knowledge to other similar alloys is hazardous, all austenitic stainless grades possess a low susceptibility limit toward stress cracking.

7.3 Service Tests

7.31 Procedure

Service test studies were made on the pilot plant dissolver shown in Figure 9. The tests involved a non-destructive examination of the vessel after the first 173 hours of operation (28 runs), and a more complete examination of the sectioned vessel after the additional 44.5 hours described in section 7.2. Various parts of the vessel were exposed to total immersion, alternate drying and wetting, and total vapor conditions. The vessel was in stand-by condition for six months between the 173-hour period and 44.5 hour series.

The time and temperature of exposure of the dissolver to dissolving and to cleanout are summarized in Table 23.

7.32 Results

At the end of the 173-hour Pilot Plant Development Program and six month stand-by, three small cracks were found in the dismantled dissolver by means of "Dy-check". These were confirmed by microscopic examination to be about 2-5 mils deep, and only a few inches long. However, these same cracks could not be found on the sectioned pilot dissolver at the end of the 44.5-hour corrosion study.

Table 22

Corrosion Rate of Type 347 Stainless Steel (Cb-Ta) Stressed Specimens
Totally Immersed in Ba-140 Process Fuel Dissolvent at 200°F for 44.5 Hours

Specimen No.	1000 PSI Stress	Heat Treatment	Mils/Month Corrosion Rate	Average MPM Corrosion Rate
<u>Wrought Welded Stressed Hoops</u>				
253D	30-180	1000°F - 4 hrs in Argon	0.028	0.026
254D	30-180	Water Quench	0.024	
257D	30-180	1600°F - 1 hr in Argon	0.037	0.027
258D	30-180	Water Quench	0.016	
281D	30-180	As-welded	0.026	0.021
262D	30-180	As-welded	0.016	
<u>Wrought Compressed Oval Rings</u>				
230D	< 30	1000°F - 4 hrs in Argon Water Quench	0.011	0.034
231D	< 30		0.004	
232D	< 30		0.061	
233D	< 30		0.061	
234D	< 30	1600°F - 1 hr in Argon	0.012	0.022
235D	< 30	Water Quench	0.032	
236D	< 30	As-Received	+0.003	+0.013
237D	< 30	As-Received	+0.023	
<u>Wrought Stressed Bars</u>				
241D	17.1875	1000°F - 4 hrs in Argon Water Quench	0.005	0.008
242D	17.1875		0.004	
243D	64.6875		0.012	
244D	64.6875		0.011	
245D	17.1875	1600°F - 1 hr in Argon Water Quench	+0.017	+0.008
246D	17.1875		+0.011	
247D	64.6875		+0.005	
248D	64.6875		+0.001	
249D	17.1875	As-Received	+0.007	+0.008
250D	17.1875	As-Received	+0.007	
251D	64.6875	As-Received	+0.010	
252D	64.6875	As-Received	+0.009

Figure 10

Stainless Steel Type 347 Stressed Hoops, Compressed Rings, and a
Plan View of Stressed Bars After Immersion in 20 Ba-140 Dissolver Runs

Figure 11

Stainless Steel Type 347 Stressed Hoops, Compressed Rings, and a
Section View of Stressed Bars After Immersion in 20 Ba-140 Dissolver Runs

Table 23

Exposure of Pilot Plant Dissolver During
Pilot Plant Development of the Ba-140 Process

<u>Temperature °F</u>	<u>Hours During Dissolving Runs</u>	<u>Hours During Jet Tests and Cleanout</u>	<u>Cumulative Total Hours</u>
290-9	0	1	1
280-9	0	2	3
270-9	0	0	3
260-9	0	0	3
250-9	0	1	4
240-9	2	0	6
230-9	5	2	13
220-9	6	1	20
210-9	20	1	41
200-9	35	1	77
190-9	12	6	95
180-9	12	15	122
170-9	6	10	138
160-9	8	4	150
150-9	11	9	170
140-9	2	1	173

Of the 173 hours, 80 were exposed at temperatures above 190°F. This time added to succeeding 44.5 hours totals 124.5 hours exposure in the dissolution solution which is equivalent to 50 runs in the plant dissolver at 2.5 hours per run.

Gates on the Types 304 and 316 stainless steel valves and fittings were slightly worn. Only one shallow, long pit was found on these fittings. This was not visible at 30X, but could be seen at 100X.

7.33 Recommendations

Type 347 stainless steel appears to be a satisfactory engineering construction material for the Ba-140 process head-end dissolver vessel. Both service and plant test data indicate that the alloy resists stress cracking and pitting in the caustic dissolver solution. The general corrosion rate was established at less than 0.1 mils per month and pitting was not observed. For service at the boiling point up to 125 hours, the fabricated vessel may be used in the as-welded condition, or in a post heat treatment at 1600°F for one hour or 1000°F for four hours. By reason of economy, the fabricated vessel should be used in the as-welded condition.

The use of high-purity caustic for the dissolvent to eliminate any chloride would be a means of lessening any tendency for stress cracking. The recommended caustic reagent is American Chemical Society, Chemically Pure grade sodium hydroxide.

8. CENTRIFUGE CORROSION

The centrifuge proposed for plant use performs the following process steps:

1. Separation of aluminum dissolved in hot sodium hydroxide from the insoluble uranium, barium, strontium, fission products, etc., followed by washing the residue with water.
2. Dissolution of uranium, barium, strontium, etc., in 6M nitric acid and their separation from insoluble silica, followed by 6M nitric acid washes.
3. Transfer of silica from centrifuge by water washes.
4. Evaporation of the nitric acid solution, from Step 2 above, to precipitate the barium and strontium nitrates leaving the uranium in solution.
5. Separation of the soluble uranium plus residual aluminum in nitric acid from the insoluble barium and strontium nitrates followed by two washes of 70 percent nitric acid and one of 50 percent nitric acid.
6. Dissolution of barium nitrate and strontium nitrate wet with 50 percent nitric acid by the addition of water.
7. Precipitation of the barium as a chromate by the additions of sodium bromide, sodium dichromate, and sodium acetate which raised the pH from 0 to 4 or 4.5, leaving the strontium almost quantitatively in solution.
8. Separation of strontium from barium followed by water washes.
9. Dissolution of barium chromate in 0.2M nitric acid.
10. Re-precipitation of barium as in Step 7 above, but with the addition of non-radioactive strontium to dilute strontium-89 and strontium-90.
11. Separation of strontium from barium chromate followed by water washes.
12. Metathesis of barium chromate to the nitrate by the addition of 90 percent nitric acid and heating to 90°C.
13. Separation of the chromate in solution from the barium nitrate cake.
14. Recrystallization of the barium nitrate by the addition of water to dissolve, followed by 90 percent nitric acid to re-precipitate.

15. Separation of nitric acid mother liquor from the cake followed by 3 washes of 70 percent nitric acid.
16. Dissolution of the barium nitrate product in water and transfer to the stripping cone.

These procedures are recorded in Appendix I. The most corrosive conditions the centrifuge must withstand include:

1. Hot caustic soda solutions containing 10-15 percent sodium hydroxide plus sodium aluminate.
2. Nitric acid solutions from 0-90 percent at temperatures from room temperature to 110°C.
3. An acid solution, pH 0-4.5, containing bromides, chromates, nitrates, and acetates with sodium, barium, and strontium ions.

Many metals were considered for the construction of the centrifuge, but few could qualify. Platinum would be resistant except possibly to the bromides in the presence of nitric acid, but its softness was a disadvantage. Duriron was rejected because of its low tensile strength and its low resistance to caustic. Tantalum also has a low resistance to caustic. Stainless steels had disadvantages but appeared to be the best candidates since a pilot plant centrifuge had withstood several runs without serious evidence of damage. Corrosion rates of stainless steels in caustic were known to be low and stress corrosion cracking was considered to be improbable since the concentration would be only 10-15 percent sodium hydroxide. A laboratory study was made on stainless steels in the chromate precipitation solutions, and in the very concentrated nitric acid. Further, the pilot plant centrifuge bowl of Type 316 stainless was examined for attack as runs progressed.

8.1 Corrosion Studies of Stainless Steels in the Chromate Precipitation Solutions

The media present during the chromate precipitation step are too complex to allow prediction of corrosion rates. As a preliminary step, a sample of Type 347 stainless steel was exposed to a series of solutions at room temperature and its potential versus a calomel half cell was recorded. The data of Table 24 show that the stainless steel was passive in 12 percent nitric acid, the addition of acetate caused little change, the bromide caused the potential to become quite negative and strongly indicated a breakdown of passivity, and the dichromate made the potential very positive. Since dichromate is such a strong oxidizing agent this last positive result does not necessarily prove that corrosion had been halted by the chromate. It could still be proceeding in pits at an accelerated rate with the chromate present. In addition, the presence of chromate in a stronger (65 percent) nitric acid at its boiling point is known to accelerate the corrosion of stainless steels.

Table 24

Potential of Type 347 Stainless Steel in Chromate
Precipitation Solutions at Approximately 25°C

<u>Time in Minutes</u>	<u>Chemicals Added</u>	<u>Potential in mv., Versus Sat. Calomel Cell</u>
0	610 cc, 12% HNO_3	- 40
4		140
8		200
13	60 cc, 4M $\text{NaC}_2\text{H}_3\text{O}_2$	160
14		140
17		255
18	200 cc, 30% NaBr	300
30		- 290
32	290 cc, 25% $\text{Na}_2\text{Cr}_2\text{O}_7$	
33		830
36		870
39		720
41		805
44		850

Further tests were made on various stainless steels in a series of solutions intended to simulate the chromate precipitation step. The time intervals were taken from a typical pilot plant run (see Table 25), and these intervals were multiplied by one hundred. The solutions were then added to the test media after 100 times the normal interval. This procedure has drawbacks, but it allowed the tests to be run unattended for long periods. Weight losses, potentials, pitting, and intergranular attack were measured.

The tests were run in two parts, the first on Types 304, 316, and 347 stainless steels at roughly 46°C, and later on Type 347 versus Type 309 Cb (with small samples of Type 310 weld wire for potentials only) at about 60°C.

8.11 Preparation of Samples

Pieces, 24-inch by 5-inch by 1/16-inch, of Type 304, 309Cb, 316, and 347 stainless steels were obtained from stock. Analyses were run to confirm the composition. A weld bead with the proper rod was made lengthwise down the center of each metal piece by the heliarc method. Then each metal was sheared into 1-inch by 5-inch coupons, numbered and stressed. Some of the coupons were heat treated at 1250° F to sensitize the metal, and others at 2050°F for solution heat treatment. The coupons were then de-scaled in 2 percent HF plus 10 percent nitric acid at 140°F, followed by a passivation treatment with 10 percent nitric acid.

Table 25

Ba-140 Process Time Schedules

The following time schedule is based on Pilot Plant Run No. 19, in which a mock MTR fuel element was used. The latest RaLa flowsheet was followed.

<u>Step I</u>	<u>Pilot Plant Time</u>
A. Fuel Dissolution	1 hr. 30 min.
B. Slurry Transfer and Sparge	29 min.
C. First Centrifugation (Dissolver Solution)	1 hr. 51 min.
D. Dissolver Cake Wash	1 hr. 40 min.
<u>Step II</u>	
A-B Spike Addition and Dissolver Cake Dissolution	20 min.
C. Second Centrifugation (Silica Separation)	11 min.
D. Silica Cake Wash	30 min.
<u>Step III</u>	
A. Silica Removal	30 min.
<u>Step IV</u>	
A-B U-Ba-Sr Transfer from T-6 to T-4 and Carrier Addition	15 min.
C. Evaporation and Transfer to Centrifuge	30 min.
D. Precipitant Addition and Cooling	22 min.
E. Third Centrifugation (Uranium, Separation)	8 min.
F. Nitrate Cake Wash	35 min.
<u>Step V</u>	
A. Nitrate Cake Dissolution	40 min.
B-C First Chromate Precipitation and Buffer Addition	37 min.
D. Fourth Centrifugation (Series 1 Strontium-Separation)	7 min.
E. Chromate Cake Wash	25 min.
FGH Chromate Cake Dissolution and Second Precipitation and Buffer Addition	40 min.
I. Fourth Centrifugation (Series 2 Strontium-Separation)	5 min.
J. Chromate Cake Wash	22 min.
<u>Step VI</u>	
A. Metathesis	35 min.
B. Fifth Centrifugation (First Nitrate Separation)	52 min.
<u>Step VII</u>	
A. Final Product Precipitation	41 min.
B. Sixth Centrifugation (Second Nitrate Separation)	16 min.
C. Product Cake Wash	25 min.
<u>Step VIII</u>	
A. Product Cake Dissolution	35 min.
B. Product Solution Transfer and Drying	3 hr.

Total Pilot Plant operation time for one run is 18 hours.

8.12 Description of Equipment

The container for the test samples was a cylindrical pyrex vessel. The samples were held vertically by small cubes of teflon resting on the bottom. The vessel was placed on a magnetic agitator with a teflon coated stirrer. A thermometer was immersed in the solution.

This vessel was part of a circulating and heating system for the corrosion process liquid. A constant level overflow discharged liquid to a 5-gallon pyrex carboy which served as a reservoir. An air lift raised the liquid to another pyrex vessel. This vessel was wound with an electric heating element. From here the solution syphoned back to the test vessel. The bath temperature was manually controlled by a variac on the heating element line.

The samples were partially immersed to about 0.5 inches above the weld, except some short samples of 309 Cb which were completely submerged. On a maximum of eight samples a wire was attached through a selector switch and to a Beckman vacuum tube volt meter. The reference electrode was a saturated calomel cell placed in a beaker of salt solution at room temperature and connected to the test vessel by a salt bridge filled with glass wool to prevent diffusion. A reversing switch in the circuit was used for convenience because of frequent changes in the relative polarity of the samples versus the calomel cell.

Teflon covers were made to fit the heating vessel and the reservoir in order to reduce evaporation. The test vessel was uncovered. See Figure 12 for a partial view of the apparatus.

8.13 Procedure

The fluid circulating system was started with water in an amount required in the dilute nitric acid. Samples were placed in the test container, and potential readings were taken to check the circuits. Strong nitric acid was added to the reservoir and further potentials were taken. Additions of sodium acetate, sodium dichromate, sodium bromide and more sodium acetate were made over a period of days. Potential, temperature, and pH measurements were recorded. Extra water was added daily to make up for evaporation losses, and near the end of the run, some nitric acid was added to make up for evaporation losses of acid.

In the beginning of the first run, a hot plate was used for heating and the control was difficult. Temperature varied from 30°C to 70°C. Later, when a wound heating element was adopted, temperatures were held from 45-50°C. In the second run, the temperature was controlled from 58-61°C.

Some details of the procedure may be found in tables of data together with the potential results (see Tables 26 and 27).

Figure 12

Apparatus for Measuring the Corrosion of Stainless Steels
in Chromate Precipitation Solution

Table 26

Potential of Stainless Steels in Chromate Precipitation Solutions

	Type 347		Type 304			Type 316					
Heat Treatment	2D 1250°F and Water Quench	11D 2050°F Annealed	V50 1250°F	V51 1250°F	V60 2050°F	Y50 1250°F	Y61 2050°F	Y62 2050°F			
Date and Time	Potential Vs-Saturated Calomel Cell-Millivolts								pH	Temp.	Remarks
July 13, 1954											
1615	-80MV	-105MV	-120MV	-95MV	-120MV	-55MV	-120MV	-155MV	45°C	Water	
1618	-80MV	-100MV	-110MV	-80MV	-120MV	-50MV	-110MV	-145MV	45°C	Add HNO ₃ , 300 cc of 70% HNO ₃ + 5LH ₂ O at 1620	
1625	+150MV	+315MV	+485MV	+490MV	+160MV	+430MV	-85MV	-90MV	46°C		
1650	+295	+560	+565	+590	+370	+570	+20	-40	44°C		
1735	+500	+500	+580	+605	+445	+695	+635	+230	43°C		
1900	+605	+445	+585	+580	+430	+615	+655	+525	70°C		
1925	+625	+450	+560	+555	+420	+685	+715	+650	60°C		
July 14, 1954											
0830	+655	+495	+600	+620	+496	+645	+695	+605			
0930	+630	+490	+585	+580	+490	+605	+635	+550	38°C	Add NaAc, 500 cc 4M NaAc at 0935	
1000	+570	+435	+575	+575	+445	+560	+570	+500	0.6	41°C	
1105	+540	+415	+590	+585	+420	+545	+530	+460		40°C	Add NaBr, 200 gr 34% NaBr at 1120
1125	+840	+825	+830	+840	+815	+835	+845	+830		38°C	Add Na ₂ Cr ₂ O ₇ , 800 gr 25% Na ₂ Cr ₂ O ₇ at 1120
1230	+855	+845	+840	+845	+845	+845	+850	+845	1.3	37°C	
1500	+860	+620	+845	+850	+867	+855	+535	+860		58°C	
1535	+855	+580	+850	+855	+875	+860	+340	+865		58°C	Cooled overnight at 30°C
Note: Levels of liquid were marked and then in morning, water was added until level was up to account for evaporation.											
July 15, 1954											
0950	+465	+105	+860	+855	+735	+865	+305	+825		59°C	
1050	+320	+55	+855	+850	+605	+860	+335	+785		55°C	
1150	+305	+5	+860	+865	+460	+870	+285	+755		50°C	
1300	+300	+35	+860	+865	+165	+870	+265	+730		49°C	
1415	+240	-100	+860	+870	+160	+865	+270	+690		49°C	
1600	+180	-140	+860	+860	+110	+865	+265	+680		49°C	
July 16, 1954											
0830	+95	-235	+855	+785	-45	+865	+190	+190		48°C	
0915	+85	-240	+855	-50	+865	+200	+170	+775	0.6	48°C	At 0920 NaAc, 500 cc 4M NaAc was added
1015	+50	-230	+800	-45	+815	+205	+150	+705			
1115	+75	-170	+795	-15	+795	+200	+160	+690		11°C	
1410 (Air was off and run was at a standstill.)	+95	-205	+800	-55	+810	+210	+185	+735	0.6	49°C	At 1415 NaAc, 500 cc 4M NaAc was added over weekend
1500	+5	-270	+570	-145	+580	+70	+55	+560		50°C	
1545	-80	-170	+530	-130	+560	+30	+5	+30	3.3	50°C	
July 19, 1954											
1010	-65	-200	+490	+105	-70	+295	+75	-20	3.8	47°C	
1120	-110	-215	+380	+50	-115	+150	+45	-75	4.8	48°C	
1615	-120	-230	+365	+45	-120	+160	+50	-90			1250 cc 4M NaAc at 1025
July 20, 1954											
0930	-120	-140	-20	-110	-175	-10	+105	-40	4.9	49°C	Enough HNO ₃ added to bring pH to 4.5 (120 cc)
1100	-70	-145	-105	-155	-120	+25	+190	-45	4.5		
1550	-100	-16-	+160	-20	-120	+150	+235	-65		47°C	
July 21, 1954											
0848	-60	-65	+130	-65	-70	+165	+200	-100	4.7	43°C	Temporary shutdown last night

Table 27
Potentials of Stainless Steels in Chromate Precipitation Solution

Time Hr:Min	Additions	pH	Temp °C	Potentials Versus Sat. Calomel Cell, in mv.					
				310		309-309Cb		347	
				Sens.	S.H.T. **	Sens.	S.H.T.	Sens.	S.H.T.
0:00	Water		57	115	150	150	100	115	45
0:05	Nitric Acid								
0:25		0.7	60	450	235	450	200	115	200
4:40		0.9	60	565	340	470	425	255	400
4:45	4M NaAc								
5:15		1.0	60	445	345	490	375	230	320
5:25	NaBr-Na ₂ CrO ₄								
5:40		1.0	60	770	780	790	765	795	790
23:15		1.3	58	840	850	845	845	850	845
23:30	4M NaAc								
24:10		1.6	58	815	820	810	780	820	795
24:30	4M NaAc								
25:00		2.2	58	750	745	735	690	745	720
25:30	4M NaAc								
26:20		4.2	60	540	525	540	80	475	120
27:55	4M NaAc								
28:30		4.9	61	450	220	440	255	430	-200
28:45	Nitric Acid								
29:00		3.5	61	630	660	620	480	600	- 80
49:00		3.9	60	200	430	365	30	355	-165
70:25		4.1	58	410	440	400	50	250	-150
96:30		4.2	60	445	470	200*	85	480	- 90
114:00	Run Ended								

* The alternate sample C-22 of 309 was reading -70 mv. at 96:30.

** Solution Heat Treated at 2050°F.

8.14 Results

The potentials of the 18-8 samples are presented in Table 26.
A summary of the variations in potentials is as follows:

<u>Date</u>	<u>Time</u>	<u>Media</u>	<u>Range of Potentials, mv</u>	<u>Remarks</u>
7/13/54	16:15	Water	-155 to - 55	
7/13/54	19:25	Dilute Nitric Acid	+425 to +715	Passivated
7/14/54	10:00	Plus Sodium Acetate	+435 to +575	No great effect caused by acetate or acetic acid at pH = 0.6
7/14/54	11:15	Plus Bromide and Dichromate	+815 to +845	Inhibition by chromate possibly indicated in spite of bromide, at pH = 1.3
7/14/54	15:35	Nothing further added	+340 to +875	Breakdown of two samples indicated by bromine probably
7/15/54	14:15	Same solution	-100 to +870	Five samples breaking down
7/20/54	9:30	pH - 4.9 Same Solution with higher pH due to acetate additions	-175 to +105	All eight samples had lost passivity

The data in Table 27 of potentials with the 18-8 versus higher alloy stainless showed that Type 310 had the highest positive potential and apparently retained its passivity best.

Weight loss results showed no correlation with heat treatment of composition (see Tables 28 and 29). Apparently most of the weight loss occurred at the meniscus as pits under the crust of salts, and as smaller pits in the vapor phase. Apparently the most important factor in weight loss was the location of the samples relative to the hood draft. The front side of the samples had few pits; the back side had many in general. Only the completely submerged samples, which were tested with only Type 309 Cb, had consistently low weight losses. Microscopic observation for pits confirmed the above results.

Metallographic results showed that sensitized Type 304 had severe intergranular attack and both Type 316 and 309 Cb had some intergranular attack in the sensitized condition. Only Type 347 resisted intergranular attack in the sensitized condition. All four types resisted intergranular attack in the solution heat treated condition.

Table 28

Corrosion Rates of Stainless Steels
In Chromate Precipitation Solutions

Exposure: 114 hours at about 46°C in duplicate, partially submerged.

<u>Type of Stainless Steel</u>	<u>Rate, ipy</u>	<u>Metal Appearance</u>	
		<u>Liquid Phase</u>	<u>Vapor Phase</u>
347 Sensitized	0.003, 0.003	OK	Pitted
347 Solution Heat Treated	0.002, 0.001	OK	Pitted
316 Sensitized	0.001, 0.002	Intergranular	Pitted
316 Solution Heat Treated	0.001, 0.003	OK	Pitted
304 Sensitized	0.004, 0.003	Intergranular	Pitted
304 Solution Heat Treated	0.001, 0.003	OK	Pitted

Table 29

Corrosion Rates of Stainless Steels
In Chromate Precipitation Solutions

Exposure: 114 hours at 60°C, in duplicate.

<u>Type of Stainless Steel</u>	<u>Submergence</u>	<u>Rate, ipy</u>
347 Sensitized	Partial	0.002
347 Solution Heat Treated	Partial	0.0002
309 Cb Sensitized	Partial	0.002
309 Cb Solution Heat Treated	Partial	0.003
309 Cb Sensitized	Complete	0.0001
309 Cb Solution Heat Treated	Complete	0.0000

Above Corrosion rates are calculated from weight losses, based on submerged areas only.

The low corrosion rates of less than 4 mils per year were encouraging. The lack of pitting in the liquid phase was also encouraging. The pitting at the meniscus and in the vapor should not be a problem in the centrifuge because precipitated salts will not form or will not stay for a long time at the meniscus and the high speed will blow the vapors away. The laboratory test was probably more severe than the real environment in the process. The long duration of several days in the laboratory tests would allow bromine to be formed by air oxidation to a greater degree than in the plant centrifuge and hence, less corrosion is expected in the plant. The radiation induced formation of bromine was discussed in Section 5.42.

Because of the lack of intergranular attack on Type 347, this metal is superior to Types 304, 316, and 309 Cb in this service. Low carbon or stabilized Type 310 might be superior to Type 347, but coupons were not available for tests and a recommendation cannot be made on the basis of weld wire potentials.

Both the potential measurements and the vapor phase pitting indicate that the bromide is the most aggressive component of these solutions.

8.2 Corrosion in Very Concentrated Nitric Acid

In the precipitation of barium nitrate from aqueous solution by the addition of 90 percent nitric acid and in the metathesis step, nitric acid often becomes more concentrated than 70 percent. Temperatures were often as high as boiling in the planned procedure for these steps. The use of Type 347 stainless steel is not normally recommended at temperatures above 175°F with nitric acid concentrations above 60 percent. A short study was done to investigate corrosion during the metathesis step and the final product precipitation.

Coupons of Types 347 and 309 Cb in both the sensitized and solution heat treated conditions were immersed in duplicate in boiling 73 percent nitric acid for 12 days. Every 1 to 3 days the samples were weighed and the solution was replaced with new solution.

As shown in Figure 13, the corrosion rate appeared to be constant or decreasing rather than increasing. Final corrosion results are given in Table 30.

Since the centrifuge was to be welded, the rates in the sensitized condition are important. Type 347 was judged to be superior to Type 309 Cb. Rates were not considered to be excessive since the exposure time at elevated temperatures will be short.

FIGURE 13

CORROSION LOSSES OF STAINLESS STEEL
COUPONS IN BOILING 73% HNO₃

ACID CHANGED EACH TIME DATA TAKEN.

WEIGHT LOSS IN GRAMS

AREA 309Cb = $3\frac{1}{4}$ in²

AREA 347 = $4\frac{1}{4}$ in²

AREA NOT COMPENSATED,
IN THIS TABLE

Table 30

Corrosion of Stainless Steels in
Boiling 73 Percent Nitric Acid

Test Duration: 12 Days

<u>Type 347 Stainless Steel</u>	<u>Corrosion Rate, In/Yr.</u>	<u>Appearance</u>
Sensitized 1250°F one hour	0.0299	Dark grey
Solution heat treated, 2000°F	0.0105	Light grey
<u>Type 309 Cb Stainless Steel</u>		
Sensitized 1250°F one hour	0.0525	Black
Solution heat treated, 2000°F	0.0048	Metallic white

8.3 Examination of Pilot Plant Centrifuge Bowl

The pilot plant centrifuge bowl was constructed of Type 316 stainless steel. It was 8 inches in diameter by 3-1/2 inches deep. It was welded at the hub in the center of the bottom, at the top and bottom of the side wall, and up a seam in the side.

The bowl was examined three times during sixteen pilot plant runs, partial or complete. These runs are equivalent (except for caustic exposure) to 11 complete plant runs, 7 with single chromate precipitations and 4 with double chromate precipitations. It was exposed to caustic only five times.

After the runs, the surface was generally in very good condition. General corrosion was practically nil; the original fine machine marks were present over most of the surface. Near welds the metal was etched and corroded, apparently through intergranular attack in the sensitized zone. In the welds, a few pits and several cracks were present and appeared to become slowly worse.

An important fact discovered during these examinations is that very strong acid will remain in the pits in spite of four good water washes. This holdup could do two things, cause further corrosion of the stainless steel enlarging the pits between runs, and cause impurities from the beginning of the run to contaminate the product or succeeding steps. Pits and cracks in welds in the new plant bowl should be tolerated and an adequate washing procedure should be developed before runs begin with radioactive solutions.

8.4 Conclusions and Recommendations

Although Type 347 is far from perfect, it appears to be the best material for the centrifuge bowl in terms of corrosion resistance, strength, hardness, and availability.

A recommendation has been made to omit the bromide from the chromate precipitation step if possible. This should reduce the corrosion rate and the pitting tendency and also the possibility of stress corrosion cracking of the bowl. Its effect on the storage tank for strontium solution is probably even more important.

A recommendation was made to precipitate the barium nitrate at the end of the initial evaporation step by the addition of cold strong nitric acid rather than through straight evaporation.

A recommendation was made to limit the temperature during the metathesis step with nitric acid to 160°F rather than allow it to reach 194°F as was initially proposed.

A recommendation was made to precipitate the final product by the addition of 90 percent nitric acid while cooling rather than while heating. Surface temperatures of the metal became important in the consideration.

9. IODINE EVOLUTION

9.1 Iodine Evolution During Caustic Waste Neutralization

As a part of the experiment to follow the path of fission products, it was desired to know the extent of iodine evolution during the neutralization of a caustic supernate which had been diluted fifteen-fold and thirty-fold. In all cases, the caustic solution, after being diluted, was acidified to 0.5N^A using 6N nitric acid.

The results indicate a difference in the behavior of iodine between the two different solutions. In the case of the caustic solution diluted thirty-fold, the maximum amount of iodine trapped from the off-gas was 0.93 percent. Material balances were good. With the caustic solution diluted only fifteen-fold, the amount of iodine trapped averaged about 1 percent. Material balances, however, were poor, generally ranging between 70 percent and 90 percent. It was discovered that this iodine had been adsorbed on the walls of the glass and tygon apparatus. It may be assumed that in the neutralization of the fifteen-fold diluted caustic waste, as much as 30 percent of the iodine present may be evolved and then adsorbed on the walls of the apparatus a short distance from the neutralization vessel.

10. STRONTIUM-90 RECOVERY

10.1 Justification

The barium-140 recovery process carries the great majority of radio-strontium along with the barium through the uranium separation and first decontamination cycle. The separation of barium and strontium by chromate results in a chromate waste which is relatively pure Sr-90, can be recovered with high yields and is amenable to the chemistry and equipment developed for Ba-140. A minimum of experimental work was performed to set down the necessary, but not optimum, steps in recovering Sr-90. The rate of recovery of strontium from this process would be coupled to barium production and is scarcely a significant source of Sr-90. Occasionally gram quantities could be recovered in this way at a minimum of new equipment or expense.

10.2 Flowsheet

A standard chromate waste stream was treated with potassium oxalate to precipitate strontium oxalate which was filtered, washed, and then converted to $\text{Sr}(\text{NO}_3)_2$ by metathesis with dilute nitric acid. $\text{Sr}(\text{NO}_3)_2$ was crystallized from concentrated nitric acid, washed, transferred to a shipping cone, and evaporated to a solid. The experimental results are incorporated into the Sr-90 recovery flowsheet of Table 31. On the basis of one MTR fuel element, 91% of the Sr-90 is recovered or 105 curies in a total of 2.58 g $\text{Sr}(\text{NO}_3)_2$.

Table 31

Strontium-90 Recovery Flowsheet

I. MTR Assembly - 21.6 Percent Burn-Up

Strontium-88	0.492 grams
Strontium-89	0.568 grams
Strontium-90	0.810 grams
Strontium-91	Negligible

Note: Assume that 90 percent of the strontium is contained in the RaLa chromate waste solution. Also, assume that strontium-89 is allowed to decay before processing.

II. Chromate Waste

1.225 liters of the following composition:

Sr	1.17 grams
$\text{CrO}_4^{=}$	0.1M
Ac^-	1.23M

Solution pH is 4.0 - 4.5

(Continued on following page)

Table 31 - Continued

III. Precipitation of Strontium Oxalate

- A. Add 23.07 g $K_2C_2O_4 \cdot H_2O$ dissolver in 100 ml. water
- B. Allow solution to stand for approximately 30 minutes before centrifugation.

IV. Separation of SrC_2O_4 From the Oxalate Solution

- A. SrC_2O_4 Cake (holds up approximately 0.030 liters of solution) containing:

98.5% of Sr (1.15 grams)

- B. Oxalate Waste

1. Initial Supernate	1.325 liters	0.5% of Sr
2. First wash	0.200 liters H_2O	0.5% of Sr
3. Second wash	0.200 liters H_2O	0.5% of Sr

containing:

1.5% of Sr

Note: During washes the solution should be cooled to approximately 20°C to avoid high Sr losses.

V. Metathesis of SrC_2O_4 to $Sr(NO_3)_2$

- A. Add .020 liters of 90% HNO_3 and stir. Cool to 5 - 20°C

Note: Laboratory procedure calls for the addition of 35 ml. 6N HNO_3 to dissolve the SrC_2O_4 but since approximately 0.030 liters of H_2O are held up in the centrifuge bowl, the above conditions will accomplish the dissolution satisfactory.

- B. Add .075 liters of 90% HNO_3 to precipitate $Sr(NO_3)_2$

VI. Separation of $Sr(NO_3)_2$ by Centrifugation

- A. $Sr(NO_3)_2$ Cake

91.0% of Sr (1.07 grams)

- B. Nitric Acid Waste

1. Initial Supernate	.095 liters	4.5% of Sr
2. First Wash	0.10 liters	1.5% of Sr
3. Second Wash	0.10 liters	1.5% of Sr

containing:

7.5% of Sr

(continued on following page)

VII. Dissolution of $\text{Sr}(\text{NO}_3)_2$ for Transfer to Shipping Cone

- A. Add 0.10 liters of H_2O , skim to product cone. Evaporate to a small volume.
- B. Add 0.05 liters of H_2O to centrifuge, skim to product cone, evaporate further.
- C. Add 0.05 liters of H_2O to centrifuge, skim to product cone.
- D. Add 0.05 liters of H_2O to centrifuge, skim to product cone.

VIII. Evaporation of $\text{Sr}(\text{NO}_3)_2$ in Product Cone

A. Evaporated water	0.25 liters
B. $\text{Sr}(\text{NO}_3)_2$ product	91% 105 curies strontium-90. (1.07 grams strontium or 2.58 grams strontium nitrate)

11. MULTICURIE CELL TESTS OF Ba-140 RECOVERY FLOWSHEET

11.1 Introduction

It has been mentioned that one of the ground rules assumed in designing the Ba-140 flowsheet was that no process was to be considered proven until demonstrated under plant conditions with actual feed material. Although this philosophy was still considered appropriate, it was only natural to attempt a proof of the flowsheet with medium level runs before full level plant runs. In addition, it was hoped that medium level runs could shed some light on three important questions:

1. What is the barium loss to the caustic in the first dissolution?
2. What is the radiochemical purity of the Ba-140 product?
3. What is the path of iodine during the two dissolutions?

The first two problems had been recognized in the course of development of the cold flowsheet, and the design of the warm flowsheet test was made with the solution of them in mind. The problem of iodine evolution was added after the design of the Multicurie Cell experiment had been completed and only minor modifications were made in the attempt to answer this question.

11.2 Design of Experiment

The Multicurie Cell facility in which the medium level tests of the flowsheet were made has been described elsewhere (IDO-14386)(16). The equipment used inside the cell consisted primarily of a dissolver (Figure 14), a filtration unit (Figure 15), and a rack of burettes for reagent addition (Figure 16). The dissolver is capable of handling four MTR fuel plates and all equipment was designed for an experiment using this quantity of starting material.

Figure 14

Jacketed MTR Fuel Dissolver with Condenser

Figure 15

Filtration Unit for Multicurie Cell Evaluation of Ba-140 Flowsheet

Figure 16
Burettes for the Remote Delivery of Reagents to Ba-140 Test Equipment
Sample Access Plug is Visible Directly Under the Burette Rack

It was decided to use filtration rather than centrifugation in the experiments because of the small volumes of solutions involved. In addition, it was felt that the experiment should not be tests for scaled-down plant equipment. Filtration was considered to be easier from the standpoint both of fabrication and remote operation.

The filtration unit (Figure 17) used was fabricated almost completely of Type 347 stainless steel. It consisted of five filters of 5 μ porosity, each equipped with a strap heater. These filters were supported on a movable turntable so that each filter could be positioned over a receiver. Seven receivers were placed on another movable turntable so that a filtration could be made into any of the available receivers. The hoists which supported the receivers were also equipped with heaters. By means of vacuum and air, solutions could be either filtered or held up in filters while a precipitation was being made. Solutions could also be poured from receivers into filters as shown in Figure 18.

Reagents were added directly to the receivers and filters from burettes. The burettes were controlled from the front of the cell and liquid levels read with the aid of binoculars.

The filtration unit was also fitted with a sampling station so that samples could be taken at each step of the process. In addition, the unit contained stirrers and lines for drawing solutions from the dissolver and sending other solutions to either plant waste streams or uranium recovery streams. The entire operation of the filtration unit, with the exception of pouring solutions, was carried out remotely from a console at the front of the cell (Figure 19).

11.3 Iodine Monitor

In the first experiment the iodine monitor consisted of a scintillation detector placed inside the cell next to the dissolver off-gas line and shielded from background radiation by a minimum of four inches of lead. This arrangement was modified for the second test by rerouting the off-gas line so that it passed in front of the cell wall plug holes (Figure 20). The end of the hole was then fitted with a four-inch lead plug with a 1/4-inch diameter hole through it. This allowed the scintillation detector to be placed any distance desired behind the lead plug so as to be able to maintain practical counting rates. This arrangement also made it possible to remove the scintillator in order to calibrate the photopeak position.

The spectrometer was calibrated with cesium-137. The calibration was made with a sample inside the cell, with the detector in place, and with a small cesium source outside the cell. This gave the shift of the 663 Kev photopeak with increasing source to detector distance. With these data, it was possible to set the voltage correctly for any source to detector distance.

Figure 17

General View of Cell Interior Showing the Filters and
Receivers Mounted on the Turntable. Polyethylene Film Covers
the Wall, Windows, and Sodium Vapor Lights.

Figure 18

Close-Up Showing Receiver in Manipulator Jaws Transferring
Liquid into Filter Can. The Filter is Mounted on the Turntable
and has a Heater Strap on its Exterior.

Figure 19

Exterior of Multicurie Cell Showing Chemist
Operating Equipment Remotely by Means of Controls on Console

FIGURE 20

11.4 Flowsheet Tested

The flowsheet tested was with one modification, the one to be used in production runs. The change was made in the step where barium and strontium are separated as nitrates from uranium and the fission products. The production flowsheet called for evaporation of the solution to a volume reduction of approximately 70 percent followed by nitric acid addition. Since it was extremely inconvenient to follow the volume of this solution during evaporation in the warm tests, this step was altered to eliminate the evaporation and effect the precipitation with a greater quantity of nitric acid. Cold laboratory tests showed that under ideal conditions, a loss of approximately 8 percent could be expected.

11.5 Starting Material

The starting material used for each experiment consisted of four MTR fuel plates approximately three years old and containing a total of 27.5 g uranium. Each group of fuel plates was then reirradiated for a period of two hours at an average flux of 2×10^{12} n/cm² to provide radioactive barium and iodine. The calculated quantities of active barium and iodine were 0.622 curies and 0.475 curies respectively at discharge. A two-week period was allowed for decay of the short-lived activities. Sufficient inactive barium and long-lived iodine were present in the fuel plates to assume the presence of macro quantities of these elements. This was important in order to trace the barium loss in the caustic dissolution and the iodine distribution in the two dissolutions.

11.6 Operation

The four fuel plates were removed from an MTR charging cask and placed in the dissolver. The dissolver was charged with a quantity of 6.0N sodium hydroxide such that the mole ratio of sodium hydroxide to aluminum was 2:1. In the first experiment the temperature of the dissolver solution was held at 140°F for five hours and then boiled for one hour. In the second run, the dissolver solution was held at boiling for three hours and the dissolution at a lower temperature was eliminated. The solution was then filtered through a $5/16$ filter and sampled to determine barium and uranium losses, iodine distribution, and major activity in the caustic solution.

The remaining residue consisting of uranium and fission products was then treated with 6.0N nitric acid, the solution boiled, transferred to the filtration unit and sampled. The analysis of this sample gave further information on iodine distribution as well as the input for barium and strontium.

All succeeding operations were carried out in the filtration unit and samples taken at each point to determine barium loss and strontium decontamination. The final product was analyzed for metallic impurities as well as radioactive contaminants.

The results of the two experiments are summarized in Tables 32 and 33.

Table 32

Results of Ba-140 Medium Level Flowsheet Tests

Operation	Run 1		Run 2	
	Barium Loss	Strontium Decontamination	Barium Loss	Strontium Decontamination
Caustic Dissolution	< 0.01		0.2	
Uranium-Fission Product Separation	21.3		18.4	
First Chromate Precipitation	34.9	640	1*	460
Second Chromate Precipitation	0.9	270	0.9	8
Nitric Acid Metathesis	7.8		0.03	
Barium Nitrate Reprecipitation	3.5		14.5	
Total Barium Losses	68.4		35.0	

* This barium loss was not determined directly but was estimated from the corresponding strontium decontamination and pH measurements taken during the experiment.

Table 33

Final Product Impurities Scaled to Full Level

Specifications		Run 1	Run 2
Strontium 89-90	10 curies	< 1 curie	4 curies
Aluminum	*	< 4.5 mg.	5.8 mg.
Chromium	*	4.5 mg.	< 2.7 mg.
Copper	*	< 0.9 mg.	0.9 mg.
Iron	*	22.6 mg.	8.3 mg.
Nickel	*	< 4.5 mg.	< 5.4 mg.

* No more than 50 mg. of metallic impurities are to be soluble in 75 ml. of 70 percent nitric acid. In these experiments, the total impurities were less than 50 mg.

11.7 Supplementary Data

The uranium losses to the caustic dissolver solution observed in the two experiments were 0.21 percent and 1.26 percent. It should be noted that the corresponding barium losses in this step were lower by a factor of six. In both experiments, greater than 95 percent of the activity in the caustic solution was due to cesium.

A gamma scan of the final product solution showed only peaks due to the 140 chain. Since the strontium decontamination was adequate, the product was presumably sufficiently free of all radioactive contaminants.

Large quantities of ruthenium were found with the silica residue after it had been removed from the process stream. The silica precipitate was washed several times with nitric acid and the silica dissolved in a mixture of nitric acid and hydrofluoric acid. This solution was analyzed for ruthenium and zirconium. The residue remaining after the nitric acid-hydrofluoric acid treatment was then subjected to aqua regia. This solution was then analyzed for ruthenium and other fission products.

The aqua regia solution consisted of greater than 99 percent ruthenium. Of the remainder, antimony-125 made up the larger share with a trace of zirconium and niobium also present.

The nitric acid-hydrofluoric acid solution contained only 0.3 percent as much ruthenium as the aqua regia solution and even less zirconium.

Ruthenium was also found during the cleanup following the first run when a smear was taken from the inside of the off-gas line. This smear also showed the presence of cesium. It is unknown whether the ruthenium was volatilized during the dissolution or appeared in the off-gas line as a result of liquid entrainment.

11.71 Iodine Monitor Results

The experiment to determine the path and distribution of iodine was unsuccessful. In the first run 47.1 percent of the calculated iodine was found in the caustic filtrate and 59.3 percent in the acid dissolver solution. (106.4 percent material balance). In the second run 17.9 percent of the calculated iodine was found in the caustic and less than 1 percent in the acid solution.

In neither case was it possible to determine any iodine in the off-gas line with the scintillation detector in place. During the first experiment, when the detector was inside the cell, the counting rate increased suddenly during the caustic dissolution to a point which exceeded the counting rate of the spectrometer.

It was hoped that the installation in the second run (Figure 20) would correct this deficiency and reduce the counting rate to a point where gamma spectra could be obtained.

During the second run, the counting rate at the 364 Kev iodine photopeak was observed to increase gradually, in contrast to the first run where the counting rate was observed to increase suddenly to an excessive rate.

Periodically, the spectrometer was set to scan the gamma spectrum from 0 to approximately 1.2 Mev. No definite conclusions could be drawn from these results because of the extremely high general background. Any activities which may have been in the off-gas were completely masked by the high scattered background.

11.72 Discussion of Barium Losses

Several steps in the process showed unexpected, large barium losses. The average loss in the uranium-fission product separation step was 19.8 percent. This is appreciably higher than the 8 percent loss expected under optimum conditions but seems only to indicate that insufficient nitric acid was added to precipitate all the barium nitrate and strontium nitrate.

A loss of almost 35 percent was observed in the first chromate precipitation of the first run. This was undoubtedly due to the presence of excess acid held up from the previous precipitation step. This resulted in a low pH for the chromate precipitation solution which in turn caused high barium losses and excellent strontium decontamination.

Other barium losses were close to the expected values of slightly higher.

11.8 Conclusions

The warm flowsheet tests verified the low barium loss during caustic dissolution and the radiochemical purity of the product. The tests also indicated that ruthenium showed up in some unexpected places. The experiments did not provide the answer to the problem of iodine evolution during the two dissolutions.

BIBLIOGRAPHY

1. Anderson, E. L., and Weech, M. E., Development of the RaLa Process for Installation in the ICPP, IDO-14307, July 8, 1954
2. Anderson, E. L., and Slansky, C. M., Laboratory Development of a Process for Preparation of Kilocurie Quantities of Ba¹⁴⁰-La¹⁴⁰, Phillips Internal Report, July 15, 1955
3. Untermeyer, S., and Weills, J. T., Heat Generation in Irradiated Uranium, ANL-4790, February 25, 1952
4. Legler, B. M., Pilot Plant Development of a Process for Separating Ba¹⁴⁰ from MTR Fuel, IDO-14344, September 1, 1955
5. Andelin, R. L., Radiation Damage Problems in ICPP Barium-140 Separation Process, IDO-14348, November 1, 1955
6. Wymer, R. G., Helton, D. M., Kibbey, A. H., and Land, J. F., Caustic Dissolution: Preliminary Studies, ORNL-1782, January 28, 1955
7. Stevenson, C. E., Quarterly Progress Report, Technical Branch, ICPP IDO-14324, 1954
8. Willard, H. H., and Goodspeed, E. W., Ind. Eng. Chem. Anal. Edition 8, 414-418, 1936
9. Blanco, R. E., Laboratory Development of the MTR-RaLa Process for the Production of Barium-140, ORNL-1148, August 19, 1952
10. Beyer, G. L., and Rieman, W., III, J. Am. Chem. Soc., 65, 971: 1943
11. Cederberg, G. D., Erhart, A. E., Garrick, B. J., Lemon, R. B., Status of RaLa Process Development Studies at the Termination of American Cyanamid's Contract, ACCO-3650, September 30, 1953
12. Schmidt, H. W., Gegner, P. J., Heinemann, G., Pogacar, C. F., Wyche, E. H., Corrosion, 7 No. 9, 295, 1951
13. Uhlig, H. H., The Corrosion Handbook, Page 794, J. Wiley and Son, Inc. New York, 1953
14. Timoskenko, S., and MacCullough, G. H., Elements of Strength of Materials, Pages 112, 182, 122, D. Van Nostrand Co., Inc., New York, June 1949
15. Fletcher, R. D., and Slansky, C. M., A Multicurie Facility for High Level Chemical Process Research, IDO-14386, September 17, 1956

APPENDIX I

The following represents the process design basis agreed to by the Process Advisory Committee to the Ba-140 process. It assumes 10 curie total strontium contamination of barium and includes losses taken from both laboratory and pilot plant experience.

Ba-140 PROCESS FLOWSHEET

1. MTR Assembly Note 1.
21.6% burn-up - 2 days cooled

<u>Nuclide</u>	<u>Grams Per Element</u>	<u>Curies Per Element</u>
Aluminum	3818	
Uranium	157	
Barium-138	1.221	
Barium-140	0.750	5.5×10^4
Strontium-88	0.492	
Strontium-89	0.568	1.6×10^4
Strontium-90	0.810	115
Strontium-91	10^{-4}	2.4×10^3

Note 1: Processing of the assembly should begin 2 days after discharge, with the barium nitrate product ready for shipment the 3rd day after discharge.

Note 2: An assembly also contains approximately 30 g of Si used in the braze, approximately 16 g of Fe, 4 g of Cu and milligram quantities of Mn, Ni, Mg, and Ti.

2. Dissolution of Assembly
 - a. Assembly Solvent
52 L. of 27% NaOH
 - b. Off-gas
4760 L. of H₂ at STP (428.1 g. H₂)
3. Separation of the Uranium and Fission Product Residue from the Aluminate Solution by Centrifugation
 - a. Uranium, F.P. residue
 - 99.9% of total U
 - 99.9% of Ba
 - 99.9% of Sr
 - 95% of other F.P. (approximately)
 - 1% of Al

b. NaAlO_2 - NaOH Waste

- (1) Initial supernate (52 L.)
- (2) Rinse of Dissolver and Holdup Tank (10 L. of H_2O)
- (3) 1st Wash - 0.5 L. of H_2O
- (4) 2nd Wash - 0.5 L. of H_2O
- (5) 3rd Wash - 0.5 L. of H_2O

containing:

99.0% of Al
0.1% of U
0.1% of Ba
0.1% of Sr
5.0% of other F.P. (approximately)

Note: Percent values are the percent of the specific component initially present in the assembly, except that after carrier Ba is added, the percent values then refers to the amount initially present plus the added quantity.

4. Dissolution of Uranium - F.P. Residue

- a. Residue Solvent
1.5 L. of $\underline{6\text{M}}$ HNO_3
- b. Off-gas
8.0 L. of NO_2 at S.C.
8.0 L. of NO at S.C.
 1.37×10^5 curies of Kr, Xe, and I

Note 1: Assume that residue is composed of uranium oxides and reacts as U_3O_8 ;

Note 2: Assume that all Kr, Xe, and I come off in this step.

5. Separation of Insoluble Particulates

a. Uranium Solutions

- (1) Initial supernate - 1.5 L.
- (2) 1st Wash ($\underline{6\text{M}}$ HNO_3) - 2 L.
- (3) 2nd Wash ($\underline{6\text{M}}$ HNO_3) - 2 L.
- (4) 3rd Wash ($\underline{6\text{M}}$ HNO_3) - 2 L.

containing:

99.9% of U
99.9% of Ba
99.9% of Sr
95% of other F.P. (approximately)
1.0% of Al

Note 1: Assume 0.3 L. of 6M HNO_3 are needed to transfer uranium solution from hold-up tank to centrifuge.

b. Insoluble Particulates

Approximately 30 g of Si in the particulates

- (1) 0.5 L. of H_2O to transfer particles from centrifuge
- (2) 0.5 L. of H_2O to complete centrifuge washing

6. Evaporation of the uranium-containing solution to salt out $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$

a. Add 2.9 g of Ba as 5.49 g of $\text{Ba}(\text{NO}_3)_2$ in 100 ml of solution

b. Evaporate the solution to 0.500 ± 0.100 l. and centrifuge at about 110°C . (Initial solution volume approximately 2.5 L.)

7. Separation of $\text{UO}_2(\text{NO}_3)_2$ solution from $\text{Ba}(\text{NO}_3)_2$

a. $\text{UO}_2(\text{NO}_3)_2$ solution

(1) Initial supernate (0.450 L.)	0.5% of Ba
(2) 1st Wash (70% HNO_3) 0.30 L.	0.1% of Ba
(3) 2nd Wash (70% HNO_3) 0.30 L.	0.1% of Ba
(4) 3rd Wash (50% HNO_3) 0.30 L.	0.2% of Ba

containing

99.9% of U
0.9% of Ba
30 % of Sr
0.8% of Al
95 % of other F.P. (Approximately)

b. $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$

99.0% of Ba (4.87 g of Ba)
70.0% of Sr
0.2% of Al

8. Dissolution of $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ Cake
(Assume a hold-up of 30 ml of 50% HNO_3)

Add 0.50 L. of H_2O and heat if necessary and then cool.

9. Precipitation of BaCrO_4

- Add 50 ml of 4.0M NaAc to "neutralize" a portion of the 30 ml of 50% HNO_3 which was held up in the precipitate.
- Add 11.36 g of $\text{Na}_2\text{Cr}_2\text{O}_7$ and 8.79 g of NaBr in 50 ml of H_2O
(The NaBr acts as a protecting agent to minimize radiation damage to reagents.)
- Add 0.225 L. of 4.0M NaAc with stirring over a period of 5 minutes. Agitate for 20 minutes more before centrifuging.

Final solution has the following concentrations:

0.1M NaBr
0.1M CrO_4^{--}
1.23M NaAc
Solution pH is 4.0 - 4.5

10. Separation of BaCrO_4 from the chromate solution

- BaCrO_4 Cake (holds up approximately 30 ml of solution) containing 97.9% of Ba (4.769 g) and 35 curies of Sr-89 (approximately 4 mg of Sr)

- Chromate Waste

(1) Initial Superate	0.825 L.	0.6% of Ba
(2) 1st Wash	0.2 L. of H_2O	0.3% of Ba
(3) 2nd Wash	0.2 L. of H_2O	0.1% of Ba
(4) 3rd Wash	0.2 L. of H_2O	0.1% of Ba

containing:

1.1% of Ba
70% of Sr

Note 1: Wash is tentatively a water wash but may be changed to a combination of NaBr, NaAc, and $\text{Na}_2\text{Cr}_2\text{O}_7$

Note 2: The solution will be reserved for Sr-90 recovery.

11. Dissolution of BaCrO_4 prior to a second BaCrO_4 precipitation
Add 1.0 L. of 0.2M HNO_3 and heat to approximately 70°C. Cool.

12. Re-precipitation of BaCrO_4

- a. Add 0.050 L. of 4.0M NaAc
- b. Add 4.25 g of $\text{Sr}(\text{NO}_3)_2$ (to dilute Sr-89 and Sr-90), 16.5 g of $\text{Na}_2\text{Cr}_2\text{O}_7$, and 12.86 g of NaBr in 50 ml of solution
- c. Add 0.20 L. of 4.0M NaAc with stirring over a period of 5 minutes. Agitate for 20 minutes before centrifuging.

Composition of the final solution is:

0.1M Br^-	
0.1M CrO_4^{--}	pH is 4.0 - 4.5
0.64M Ac^-	

13. Separation of BaCrO_4 prior to the Metathesis

- a. BaCrO_4 precipitate (assume a 30 ml hold-up of solution on the precipitate)

97.0% of Ba (4.72 g)
0.12 curies of Sr-89 (approximately 4 mg of Sr)

- b. Chromate Waste

(1) Initial supernate	1.25 L.	(0.5% of Ba)
(2) 1st Wash	- 0.2 L. of H_2O	(0.1% of Ba)
(3) 2nd Wash	- 0.2 L. of H_2O	(0.1% of Ba)
(4) 3rd Wash	- 0.2 L. of H_2O	(0.1% of Ba)

Note 1: Water wash may be changed to a combination of NaBr, Na_2CrO_7 , and NaAc.

Note 2: This chromate waste will not be processed for Sr-90 recovery.

14. Metathesis of BaCrO_4 to $\text{Ba}(\text{NO}_3)_2$

Add 0.250 L. of 90% HNO_3 and heat to 90°C. Cool.

15. Separation of $\text{Ba}(\text{NO}_3)_2$

- a. $\text{Ba}(\text{NO}_3)_2$ Cake
96.7% of Ba (4.71 g)
- b. Nitric acid - chromic acid waste
Initial supernate

16. Dissolution of $\text{Ba}(\text{NO}_3)_2$

Add 0.250 L. of H_2O ; heat to 90°C, and then cool to room temperature.

17. Precipitation of $\text{Ba}(\text{NO}_3)_2$ to eliminate occluded chromate
Add 0.50 L. of 90% HNO_3
18. Separation of $\text{Ba}(\text{NO}_3)_2$ from HNO_3 Waste
 - a. $\text{Ba}(\text{NO}_3)_2$ Cake
96.1% of Ba (4.68 g)
 - b. Nitric Acid Waste
 - (1) Initial supernate - 0.75 liters (0.2% of Ba)
 - (2) 1st Wash - 0.2 L. of 70% HNO_3 (0.2% of Ba)
 - (3) 2nd Wash - 0.2 L. of 70% HNO_3 (0.2% of Ba)
 - (4) 3rd Wash - 0.2 L. of 70% HNO_3 (0.2% of Ba)
19. Dissolution of $\text{Ba}(\text{NO}_3)_2$ for transferring to shipping cone.
Add 0.30 L. of H_2O (heat if necessary) containing 96.1% of Ba (4.68 g) and 4 mg of Sr.
20. Evaporation of $\text{Ba}(\text{NO}_3)_2$ solution in the shipping cone.
 - a. Evaporated water 0.3 liters
 - b. $\text{Ba}(\text{NO}_3)_2$ Product
 5.3×10^4 curies of Ba as 8.91 g of $\text{Ba}(\text{NO}_3)_2$
0.12 curies of Sr-89 and 1.1×10^{-4} curies of Sr-90 as 0.01 g of $\text{Sr}(\text{NO}_3)_2$.

APPENDIX II

The following is a slightly revised flowsheet on the basis of newer laboratory, pilot plant, and plant design data. Changes relative to the previous flowsheet (Appendix I) are:

1. The method of adding the sodium hydroxide during the process has been changed and the moles of sodium hydroxide in excess of the moles of aluminum have been changed.
2. Approximately 99 percent of the xenon and krypton are released during the caustic dissolution. This was determined experimentally.
3. The washing of the uranium-fission product residue has been omitted.
4. The final volume of the concentrated uranium solution during the first barium nitrate separation has been increased, followed by the salting of the barium nitrate by the addition of 90 percent nitric acid.

The gram quantities of barium entered refer to the approximate total grams present as barium during that process step.

Ba-140 PROCESS FLOWSHEET

1. MTR Assembly - 21.6 Percent Burn-up, 2 Days Cooled

<u>Nuclide</u>	<u>Grams per Element</u>	<u>Curies per Element</u>
Aluminum	3818	
Uranium	157	
Barium-138	1.221	
Barium-140	0.750	5.5×10^4
Strontium-88	0.492	
Strontium-89	0.568	1.6×10^4
Strontium-90	0.810	115
Strontium-91	10^{-4}	2.4×10^3

Note 1: Processing of the assembly should begin 2 days after discharge with the barium nitrate product ready for shipment the third day after discharge.

Note 2: An assembly also contains approximately 30 g of silicon used in the braze, approximately 16 g of iron, 4 g of copper, and milligram quantities of manganese, nickel, magnesium, and titanium which will stay with the residue.

2. Dissolution of Assembly (194°F - 248°F)

a. Assembly Solvent

- (1) Add 23 L. of water to the dissolver to just cover the assembly in the dissolver.
- (2) Add 25.6 L. of 32.66% NaOH continuously to control the reaction rate.

b. Off-gas

- (1) Hydrogen
4760 l. H₂ at STP (428.1 g) (STP defined as 0° C. at 1 atm.)
- (2) Rare Gases
99% of Xe and Kr

Note: 99% of Xe and Kr was experimentally obtained in the off-gas during the caustic dissolving by R. C. Paulus and J. M. Scarborough.

3. Separation of the Uranium and Fission Product Residue from the Aluminate Solution by Centrifugation (176.0°F - 221°F)

a. Uranium and Fission Product Residue

98% of total U
98% of Ba
98% of Sr
0.5% of Al
1% of Xe and Kr
95% of other fission products

b. Sodium aluminate-sodium hydroxide waste

- (1) Initial supernate (48.6 L.)
- (2) Rinse of dissolver and hold-up tanks (10 L. of H₂O, 70°F to 180°F) containing:
99.5% of Al
2% of U
2% of Ba
2% of Sr
5% of other fission products (approximately)

Note: Percent values are the percent of the specific radioisotope initially present in the assembly.

4. Dissolution of Uranium-Fission Product Residue (120°F - 180°F)

a. Residue Solvent

1.5 L. of 6M HNO₃

b. Off-gas

2.62 L. of NO₂ at STP (0°C, 1 atm.) 3.505 g

2.62 L. of NO at STP (0°C, 1 atm.) 5.374 g

Note 1: An operational change during processing may include 5 L. more of solvent to effect dilution for heat transfer to the cooling medium in the supernate tank jacket.

Note 2: Assume that the residue is composed of uranium oxides and reacts as U₃O₈;

5. Separation of Insoluble Particulates (80°F - 120°F)

a. Uranium Solution

(1) Initial Superates	1.5 L.
(2) 1st Wash (<u>6M</u> HNO ₃)	0.2 L.
(3) 2nd Wash (<u>6M</u> HNO ₃)	0.2 L.
(4) 3rd Wash (<u>6M</u> HNO ₃)	0.2 L.
(5) Add 2.5 L. H ₂ O for heat transfer	

containing:

98% of U
 98% of Ba
 98% of Sr
 95% of other fission products (approximately)
 0.5% of Al

b. Insoluble Particles (room temperature to 120°F) containing approximately 30 g of Si.

- (1) Add 5 L. of water slowly through sprays and remove water continuously by jet to waste tank.
- (2) Add 0.5 L. of H₂O to transfer particles from centrifuge.
- (3) Add 0.5 L. of H₂O to complete centrifuge washing.

6. Evaporation of the Uranium-Containing Solution to Salt out Ba(NO₃)₂ and Sr(NO₃)₂.

- a. Add 2.9 g of Ba as 5.49 g of Ba(NO₃)₂ in 0.10 L. of solution.
- b. Evaporate the solution to 0.650 L. $\pm$ 0.1 L.; transfer to centrifuge.
- c. Add 0.50 L. of 90% HNO₃ to solution in centrifuge.

7. Separation of $\text{UO}_2(\text{NO}_3)_2$ Solution from $\text{Ba}(\text{NO}_3)_2$ (230°F)

a. $\text{UO}_2(\text{NO}_3)_2$ Solution

(1)	Initial Supernate	1.5 L.	0.5% of Ba
(2)	1st Wash (70% HNO_3)	0.30 L.	0.5% of Ba
(3)	2nd Wash (70% HNO_3)	0.30 L.	0.1% of Ba
(4)	3rd Wash (50% HNO_3)	0.30 L.	0.4% of Ba

containing:

98% of U
1.5% of Ba
10% of Sr
0.5% of Al
95% of other fission products (approximately)

b. $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ Cake

96.5% of Ba (4.70 g)
90% of Sr
Negligible Al

8. Dissolution of $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ Cake (Assume hold-up of 0.030 L. of 50% HNO_3 .)

a. Add 0.50 L. of H_2O and heat to 150°F if necessary, then cool to 80°F - 150°F.

9. Precipitation of BaCrO_4 (80°F - 150°F)

a. Add 0.050 l. of 4.0M NaAc to "neutralize" a portion of the 0.030 L. of 50% HNO_3 which was held up in the precipitate.

b. Add 12.92 g of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 8.79 g of NaBr in 0.050 L. of H_2O (The NaBr acts as a protecting agent to minimize radiation damage to reagents.)

c. Add 0.225 L. of 4.0M NaAc with stirring over a period of 10 - 30 seconds. Agitate for 1 to 5 minutes before centrifuging. Final solution has the following concentration:

0.1M Br^-
0.1M CrO_4^{--}
1.23M Ac^-
Solution pH is 4.0 - 4.5

10. Separation of BaCrO_4 from the Chromate Solution ($80^\circ\text{F} - 150^\circ\text{F}$)a. BaCrO_4 Cake (holds up approximately 0.030 L. of solution)

containing:

95.84% of Ba (4.67 g) and 68 curies of Sr-89 (approximately 4 mg of Sr total.)

b. Chromate Waste

(1)	Initial Supernate	0.825 L.	0.6% of Ba
(2)	1st Wash	0.2 L. of H_2O	0.03% of Ba
(3)	2nd Wash	0.2 L. of H_2O	0.03% of Ba

containing:

0.66% of Ba
90% of Sr

Note 1: Wash is tentatively a water wash but may be changed to a combination of NaBr, NaAc, and $\text{Na}_2\text{Cr}_2\text{O}_7$.

Note 2: This solution will be reserved for Sr-90 recovery.

11. Dissolution of BaCrO_4 Prior to Second BaCrO_4 Precipitationa. Add 1.0 L. of 0.2M HNO_3 and heat to approximately 180°F .b. Cool to $80^\circ\text{F} - 150^\circ\text{F}$.12. Re-Precipitation of BaCrO_4 ($80^\circ\text{F} - 150^\circ\text{F}$)

a. Add 0.050 L. of 4.0M NaAc

b. Add 4.25 g of $\text{Sr}(\text{NO}_3)_2$ - to dilute Sr-89 and Sr-90, 18.77 g of $\text{Na}_2\text{CrO}_7 \cdot 2\text{H}_2\text{O}$ and 12.86 g of NaBr in 0.050 L. of solution.

c. Add 0.20 L. of 4.0M Ac with stirring over 10 - 30 seconds.

d. Agitate for 1 - 5 minutes before centrifuging.

Composition of the final solution is:

0.1M Br^-
0.1M CrO_4^{--} pH is 4.0 - 4.5
0.64M Ac^-

13. Separation of BaCrO_4 Prior to the Metathesisa. BaCrO_4 precipitate (assume a 0.030 L. hold-up of solution on the precipitate)

95.18% of Ba (4.64 g)
0.39 curies of Sr-89 and 3.1×10^{-3} curies of Sr-90 (approximately
4 mg of Sr total)

b. Chromate Waste

(1)	Initial Supernate	1.25 L.	0.6% of Ba
(2)	1st Wash	0.2 L. of H_2O	0.03% of Ba
(3)	2nd Wash	0.2 L. of H_2O	0.03% of Ba

Note 1: Water wash may be changed to a combination of NaBr, $NaCr_2O_7$, and NaAc.

Note 2: This chromate waste will not be processed for Sr-90 recovery.

14. Metathesis of $BaCrO_4$ to $Ba(NO_3)_2$

a. Add 0.250 L. of 90% HNO_3 and heat to 160°F. Cool to 80°F - 120°F.

15. Separation of $Ba(NO_3)_2$ by Centrifugation (80°F - 120°F)

a. $Ba(NO_3)_2$ Cake
94.68% of Ba (4.61 g)

b. Nitric Acid - Chromic Acid Waste
Initial supernate 0.5% of Ba

16. Dissolution of $Ba(NO_3)_2$

a. Add 0.250 L. of H_2O , heat to 194°F.

17. Precipitation of $Ba(NO_3)_2$ to Eliminate Occluded Chromate

a. Add 0.50 L. of 90% HNO_3 over a 5 minute interval with the temperature at 160°F. Cool to 80°F.

18. Separation of $Ba(NO_3)_2$ from HNO_3 Waste

a. Agitate for 5 minutes; centrifuge at 80°F or less.

(1) $Ba(NO_3)_2$ Cake
93.88% of Ba (4.57 g)

(2) Nitric Acid Waste

(a)	Initial Supernate	0.75 L.	0.2% of Ba
(b)	1st Wash (70% HNO_3)	0.2 L.	0.2% of Ba
(c)	2nd Wash (70% HNO_3)	0.2 L.	0.2% of Ba
(d)	3rd Wash (70% HNO_3)	0.2 L.	0.2% of Ba

19. Dissolution of $\text{Ba}(\text{NO}_3)_2$ for Transferring to Shipping Cone

- a. Add 0.30 L. of H_2O (heat if necessary), skim to product cone. Evaporate to a small volume.
- b. Add 0.20 L. of H_2O to centrifuge, skim to product cone, evaporate further.
- c. Add 0.20 L. of H_2O to centrifuge, skim to product cone.
- d. Add 0.20 L. of H_2O to centrifuge, skim to product cone.

20. Evaporation of $\text{Ba}(\text{NO}_3)_2$ Solution in the Shipping Cone

- a. Evaporated water 0.9 L.
- b. $\text{Ba}(\text{NO}_3)_2$ Product
 - 93.88% (4.57 g Ba) or 8.70 g $\text{Ba}(\text{NO}_3)_2$
 - 5.1×10^4 curies of Ba-140
 - 0.387 curies of Sr-89
 - 3.13×10^{-3} curies of Sr-90