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LABORATORY DEVELOPMENT OF  
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THE MTR-RaLa PROCESS FOR THE

PRODUCTION OF BARIUM-140

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Copy 6 of 40, Series A.

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

Laboratory Section

LABORATORY DEVELOPMENT OF THE MTR-RaLa

PROCESS FOR THE PRODUCTION OF BARIUM<sup>140</sup>

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1.0 Abstract

This report presents the laboratory development of the MTR-RaLa Process for the production of barium<sup>140</sup> from Materials Testing Reactor assemblies.

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2.0 Introduction

Kilocurie amounts of barium<sup>140</sup> have been produced in the Oak Ridge National Laboratory RaLa plant since 1945, using a precipitation process. (1,2) Originally, ORNL slugs were used as the raw material, but, as the required amount of product increased, it became more economical to utilize Hanford slugs. The RaLa plant was revised in 1950-51 to increase the safety of the equipment and to increase the plant capacity to 10,000 curies of barium<sup>140</sup> per batch. (3,4) In addition, the latter part of the RaLa precipitation process was replaced with an ion-exchange procedure to increase the purity of the product and to facilitate the handling of small amounts of material by remote control. (5-8)

Subsequently the consumer requested an increase in batch size to a minimum of 30,000 curies. Assemblies from the Materials Testing Reactor were proposed as the source for the production of the larger batches because of their high specific activity. An MTR assembly is composed of an aluminum-uranium<sup>235</sup> alloy, clad with pure aluminum, which after irradiation for 20 days would contain  $3.88 \times 10^4$  curies of barium<sup>140</sup>. An economic survey (9) indicated that it would be cheaper to produce the larger batches in the ORNL RaLa plant using Hanford or Aiken slugs if the required production period was only two to three years. For a longer production period it was probably advantageous to install new RaLa processing facilities at the site of the Materials Testing Reactor.

In order to utilize MTR assemblies for the production of barium<sup>140</sup> it was necessary to develop a new RaLa process. The laboratory study of four possible chemical schemes is presented in this report. The development experiments were performed to scale in both glass and stainless steel equipment with 10- to 20-g transverse sections of a natural uranium MTR assembly, thus assuring the proper ratios of uranium and aluminum to silica and other impurities. The sections were irradiated in the X-10 graphite reactor to provide radioactivity for tracing the cations in the process. Inactive cations were added in the proper concentrations to represent the fission product masses. Cerium, or a mixture of cerium and lanthanum, was used to simulate the rare earths. The final process was chosen on the basis of chemical yield and purity of product, ease of recovery of uranium<sup>235</sup>, simplicity of equipment, and overall time required for processing. Studies of the unit operations in the proposed process and design considerations for a pilot plant and final processing plant are presented in separate reports. (10,11)

3.0 Summary

A process for the production of 30,000-curie batches of barium<sup>140</sup> from Materials Testing Reactor assemblies was developed and successfully demonstrated on a laboratory scale. The barium yield was greater than 97.0% and the product met or exceeded all purity specifications. The process showed good reproducibility and operability with an overall operating time of approximately seventeen hours. The waste solution is suitable for the recovery of the uranium<sup>235</sup> in the "25" solvent extraction process. A

study of the irradiation characteristics of the materials used in the process indicated adequate stability at the anticipated radiation level.

The MTR RaLa Process consists of the dissolution of the assembly in caustic, the recovery of the uranium-barium precipitate from the aluminate solution by filtration, and the purification of the barium both by precipitation of barium nitrate from 85% nitric acid and by an ion exchange separation.

Three additional schemes were developed and evaluated for the dissolution of the assembly and the elimination of the bulk constituents, aluminum and uranium. These schemes utilize a caustic, nitric acid-mercuric ion, or sulfuric acid-hydrogen peroxide-mercuric ion system for the dissolution step and the precipitation of barium sulfate or barium nitrate for the bulk separation step. It was concluded that these processes were less desirable in terms of equipment simplicity, ease of recovery of uranium<sup>235</sup> from the waste stream, or radiation stability of the required chemicals.

Ion exchange and the precipitation of barium chloride from concentrated hydrochloric acid were studied as alternate methods for the separation of barium from the micro-contaminants. The ion-exchange method was selected on the basis of high yield, purity of product, and reliability.

#### 4.0 Physical Considerations

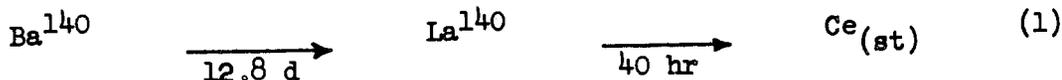
##### 4.1 Composition of an Irradiated Assembly

The final operating schedule for the MTR reactor had not been fixed at the time the MTR RaLa Process was developed, thus preventing an accurate calculation of the composition of the irradiated assemblies to be used in the process. As a result it was necessary to develop a flexible process which could handle one or two assemblies with irradiation times of 12 to 37 days. Assemblies with longer or shorter irradiation periods could be processed with a slightly modified procedure.

An assembly irradiated for 12 days would contain  $2.96 \times 10^4$  curies of barium<sup>140</sup>  $\approx$  0.94 g of barium; 135-204 g of uranium, depending on the amount of uranium<sup>235</sup> present; and approximately 0.76 g and 4.8 g of strontium and rare earths respectively. Irradiation for 20 or 37 days would produce  $3.88 \times 10^4$  curies of barium<sup>140</sup>  $\approx$  1.4 g of barium, or  $4.4 \times 10^4$  curies  $\approx$  2.1 g of barium, respectively. The latter figure represents the maximum amount of barium<sup>140</sup> activity which can be produced in an assembly. (11) Since the consumer's minimum requirements are  $3.0 \times 10^4$  curies per batch, it will be necessary to process two 12-day assemblies or one 20- or 37-day assembly. From the consumer's viewpoint, the 12-day material is preferable because the shorter irradiation results in a lower mass ratio of barium<sup>138</sup>/barium<sup>140</sup>.



The barium decay scheme



must also be considered in estimating the total curies needed for the production of  $3.0 \times 10^4$  curies. For all practical purposes, the barium<sup>140</sup> decay amounts to 5% per day. Thus, a 20-day irradiation, equivalent to  $3.88 \times 10^4$  curies, should be sufficient and would permit a 20% processing loss, although the anticipated losses amount to only 5% for decay and 3% for chemical processing. The assembly will be processed about four hours after it is discharged from the reactor, thus making the initial decay loss negligible.

The total energy produced by radioactivity in the assembly will decrease from  $1.3 \times 10^3$  kw<sup>(29)</sup> at discharge to 5.0 kw<sup>(11)</sup> after four hours of cooling, at which time the barium will represent only 3-5% of the total.

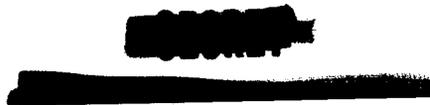
The amount of uranium in an irradiated assembly will vary considerably but will have little bearing on the barium yield in the MTR RaLa Process. Consequently, the development runs were made assuming 150 g of uranium per assembly and no effort was made to investigate other concentrations. The percent uranium loss per run will vary with the total amount of uranium present, but the actual weight loss should be relatively constant. The weight of aluminum was assumed to be 4.37 kg per assembly, which corresponds to the calculated amount remaining after removal of the end boxes<sup>(11)</sup>. The calculated compositions of assemblies irradiated for 12, 20, and 37 days are listed in Table 1 and a nomograph for the calculation of the specific activity of each fission product at discharge time is given in Figure 1.

4.2 Product Specifications

The product specifications as supplied by the consumer are listed below. The aluminum specification was not stated but was derived from a knowledge of the consumer's process. The quantities represent the minimum barium<sup>140</sup> content and the maximum impurity content per batch.

RaLa Product Specifications

Barium <sup>140</sup>	3.0 x 10 <sup>4</sup> curies
Barium <sup>140</sup>	} 2.0 g total (100 curies strontium)
Barium <sup>138</sup>	
Strontium <sup>89, 90</sup>	
Iron	500 mg
Chromium	10 mg
Nickel	10 mg
Aluminum	100 mg



[REDACTED]

An additional specification is that the last separation of barium and rare earths be made just prior to shipment and that the shipment be in the consumer's hands within two days. This precaution is necessary to prevent the build-up of a large amount of cerium, thus rendering the product less valuable (see equation (1)). The final step in the MTR RaLa Process, the fuming nitric acid precipitation, provides the necessary separation of barium from lanthanum and cerium.

#### 4.3 Recovery of Uranium

It was assumed that the uranium waste solutions from an MTR-RaLa Process would be combined with the feed solutions in the "25" Process\* for the recovery of the enriched uranium. This procedure, however, places serious limitations on the type of chemicals used in the RaLa Process, since the waste solution must be compatible with the "25" solvent-extraction feed. An initial survey indicated that organic chemicals were not acceptable but that moderate amounts of sodium sulfate or sodium nitrate could be tolerated. Solutions of nitric acid were completely satisfactory in that the nitric acid concentration can be lowered to any desired level by evaporation.

One of the processes investigated, the Caustic-Sulfate Process, required the use of 400 moles of sulfate per assembly for the precipitation of barium (see Section 6.0). A sample of the uranium sulfate from this process was run through the "25" Process solvent-extraction cycle. The results showed that the efficiency of uranium extraction was lowered to a dangerous degree when the "25" feed solution contained more than 5% by volume of the sulfate waste solution.<sup>(12)</sup> In view of its effect on solvent extraction, together with other considerations (see Sections 4.41 and 6.2), the use of sulfate was abandoned in favor of nitric acid.

In the proposed MTR RaLa Process >99.6% of the uranium appears in a nitric acid waste solution from which it is easily recovered. The total uranium loss per assembly in the caustic dissolver solution and caustic wash solution filtrates will vary from 0.44 to 0.82 g depending on the irradiation and recycle conditions (see Table 2). These values correspond to uranium<sup>235</sup> losses of 0.37 and 0.49 g respectively. It was assumed that it would not be economical to recover so small an amount of uranium from the caustic waste solution.

#### 4.4 Radiation Stability

##### 4.41 Process Chemicals

Versene, a chelating agent with the formula ethylene diamine tetraacetic acid, was proposed initially as a reagent for the dissolution of barium sulfate in an MTR RaLa Process. Previous experience at the 1500<sup>(8)</sup>

\*The "25" Process is the process for recovery and decontamination of uranium from MTR assemblies by solvent extraction.<sup>(13)</sup>

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and 15,000-curie (ORNL RaLa Run 44) level had shown no significant decomposition of Versene by radiation. ORNL RaLa Run 45 at the 21,000-curie level, however, showed that Versene was not stable to prolonged irradiation. The Versene solution in this case was subjected to a total of 0.0404 watt-hr/g, of beta radiation, over a period of 13.5 hours during the feed solution pH adjustment and column feed operations. This irradiation caused a rise in pH at the rate of 0.5 pH unit/hr,  $\approx$  0.17 pH unit/milliwatt-hr/g, and resulted in the precipitation of 35% of the barium. Subsequently, the ORNL RaLa Process was revised to replace Versene in the "hot" feed solution with acetate, which had shown a higher degree of radiation stability. (14)

A program was initiated to study the radiation stability of sodium Versenate using a 3000-curie cobalt<sup>60</sup> source. A synthetic ORNL RaLa Versene feed solution containing barium, strontium, cerium, lead, and nitrate, along with tracer barium<sup>140</sup>, strontium<sup>90</sup>, and cerium<sup>144</sup>, was irradiated at the rate of  $2.18 \times 10^{-3}$  watt/g for 66.5 hours. Air, saturated with water vapor, was bubbled continuously through the solution to maintain its oxygen content in equilibrium with the air. At the end of this period, corresponding to a total energy absorption of 0.155 watt-hr/g, 56%, 74.8%, and 42% of the barium, strontium, and cerium, respectively, had precipitated. Other effects on the solution were a rise in pH from 6.3 to 8.5; a rise in nitrite concentration from zero to 0.13 M; and a change in color from water white to yellow.

In a similar experiment two aliquots of a sodium Versenate-sodium nitrate solution were irradiated at different rates and sampled periodically for analysis. A plot of the millimoles of Versene decomposed versus the total amount of energy absorbed indicates that the Versene is decomposed initially at a rate of 0.69 millimole/watt-hr in an  $8.40 \times 10^{-4}$  watt/g field and at 0.55 millimole/watt-hr in a  $2.18 \times 10^{-3}$  watt/g field. These values are being checked to see if their difference is actually due to the rate of irradiation or to a possible difference in their equilibrium oxygen content. The loss in chelating power of the Versene during irradiation thus accounts for the precipitation of the cations, probably as their carbonates or as oxalates or succinates formed with Versene decomposition products. After 0.2 watt-hr/g of irradiation the concentration of the Versene had decreased by ~60% and its apparent rate of decomposition had approached zero. It has not been determined as yet whether the organic decomposition products are selectively oxidized in the later stages of irradiation and thus protect the Versene or if the decomposition products absorb in the same spectrophotometric range as Versene and are thus mistaken for Versene. The pH of the solutions rose from 6.3 at an approximate rate of 0.06 pH unit/milliwatt-hr/g to the range of 8.5 to 9.5 and then remained constant. The rise in pH is attributed to the formation of weak acids and strong bases (amines) as Versene decomposition products (see Figure 2).

It was concluded that Versene should not be used for the dissolution of barium sulfate in an MTR RaLa Process because of its limited radiation stability. The time required for the pH adjustment of this solution, prior to its use as the ion-exchange column feed, would undoubtedly expose

the Versene to excessive radiation.

The precipitation of barium chloride from ethyl ether-hydrochloric acid is a standard radiochemical separation technique and was used in the ORNL RaLa process at levels up to 4000 curies of barium<sup>140</sup>. A number of RaLa products were black in color, however, rendering the radiation stability of the ethyl ether suspect. It was subsequently shown by I. R. Higgins that irradiation of an ethyl ether-hydrochloric acid solution to 0.14 watt-hr/g by a cobalt<sup>60</sup> source caused the formation of colloidal black decomposition products.<sup>(15)</sup> Consequently ethyl ether was not considered as a process chemical.

Other process chemicals such as sodium nitrate, sodium hydroxide, and nitric acid have been used extensively for the dejacketing and dissolution of irradiated slugs and were assumed to be essentially stable to radiation.

#### 4.42 Ion Exchange Resin

ORNL RaLa Runs 45 and 46 were studied in detail to determine the radiation stability of Dowex-50 resin under actual process conditions. The solutions entering and leaving the column were analyzed for barium<sup>140</sup>, strontium<sup>89</sup>, cerium<sup>141, 144</sup>, and gross beta. Using these analyses, the average residence time of the activity on the column and the total beta energy absorbed by the column system was calculated. It was assumed<sup>(16)</sup> that the gamma radiation damage was negligible and that the beta damage was proportional to

$$E \text{ (average)} = (0.4) E \text{ (maximum)}. \quad (2)$$

Run 45 contained 12,500 curies of barium<sup>140</sup>, 1740 curies of strontium<sup>89</sup>, about 1000 curies of lanthanum<sup>140</sup>, and 500 curies of cerium<sup>141, 144</sup>. The resin system absorbed 0.23 kwh of beta radiation energy per kilogram of oven-dry H<sup>+</sup> form resin, or 0.11 kwh per liter of H<sup>+</sup> form resin, over a period of eighteen hours. Run 46 contained 30,000 curies of barium<sup>140</sup>, 1250 curies of strontium<sup>89</sup>, about 8000 curies of lanthanum<sup>140</sup>, and 700 curies of cerium<sup>141, 144</sup>, amounting to 0.27 kwh per kilogram of oven-dry H<sup>+</sup> form resin over a period of fourteen hours. The resin capacity loss in the latter case should approximate only 2-4% based on results reported I. R. Higgins<sup>(17)</sup>. This work showed a resin capacity loss of 10-15%/kwh/kilogram of resin from radiation produced by cerium<sup>144</sup> in column operations or by irradiation of resin in glass ampules by a cobalt<sup>60</sup> source. This work also showed that anion resins are less stable to radiation than cation resins. Consequently anion resins were not considered for use in the MTR RaLa Process.

The irradiation of the resin columns in ORNL Runs 45 and 46 did not impair the efficiency of the systems for barium purification. It is therefore assumed that ion exchange will be suitable for the MTR RaLa Process and will be well within radiation safety limits since the resin irradiation time in this case will be lower by a factor of three than in the ORNL RaLa Process.

The resin column should be charged with new resin for each RaLa run to avoid a build-up of radiation damage.

#### 4.5 Choice of Separation Methods

The MTR RaLa Process can be divided into three major steps: assembly dissolution; separation of barium from the bulk constituents, uranium and aluminum; and separation of the barium from the fission products.

Nitric acid, sulfuric acid, and caustic were studied as reagents for the dissolution of the assembly. Caustic dissolution was selected for the MTR RaLa Process because of its efficiency and because it afforded an excellent method for the separation of the barium from the aluminate solution by filtration.

Precipitation and ion exchange were considered as methods for the separation of the bulk contaminants. The precipitation method was chosen because it provided a fast, efficient separation whereas ion exchange would require large volumes and a relatively long operating time. In addition, the sulfuric acid used for the separation of barium from uranium by cation exchange<sup>(18)</sup> would not be acceptable in the process used to recover the uranium<sup>235</sup> (see Section 4.3). From a stability standpoint, there was no certainty that the resin could withstand the tremendous amount of radiation of the dissolver solution where the barium furnishes only 3.5% of the total energy from radioactivity. The precipitation method, however, would be stable to radiation and would eliminate a large fraction of the fission products. Thus the level of radiation would be lowered to the point where it is known that the resin can be used effectively and would permit the use of ion exchange for the succeeding purification step (see Section 4.42).

Ion exchange was selected for the separation of barium from strontium and other fission products. This method is excellent for processing small amounts of material by remote control and produces a pure product in high yield. ORNL RaLa experience has demonstrated the effectiveness of ion exchange for the purification of barium<sup>140</sup>. Purification of barium by a hydrochloric acid precipitation process was not satisfactory in that the barium loss was high, the separation from strontium uncertain, and the small volumes required would be difficult to handle by remote control (see Section 9.0).

#### 5.0 MTR RaLa Process

The recommended MTR RaLa Process consists of the following steps: (1) dissolution of the assembly in caustic and separation of the aluminate solution from the uranium-barium precipitate by filtration; (2) dissolution of the precipitate in nitric acid and the precipitation of barium nitrate by the addition of fuming nitric acid; (3) purification of the barium by ion exchange; and (4) final purification and volume reduction by a fuming nitric acid precipitation (see flowsheets, Figures 3 and 4, and Table 2).

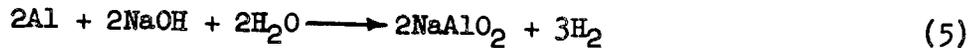
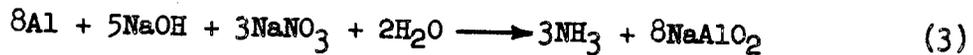
5.1 Assembly Dissolution

5.11 Dissolution Rate

Dissolution of assembly sections in sodium hydroxide and sodium nitrate produces a very vigorous reaction. The fast evolution of gas causes foaming and a resultant increase in solution volume of about 100%. It was necessary to control the reaction by adding the caustic slowly over a period of 1/2 hour. Dissolution was complete in 1 to 2 hours when the mole ratio of NaOH/Al was 1 or greater. Any substantial reduction in this ratio resulted in incomplete dissolution and unstable solutions. Only the higher concentrations of aluminum (1.8 to 5.0 M) were considered in this study in order to limit the dissolver solution volume and consequently the total uranium loss as soluble uranium.

5.12 Off-gas Composition

Sodium nitrate is added to the dissolver solution to oxidize the hydrogen formed during the dissolution of aluminum by sodium hydroxide and thus reduce the explosion hazard. The following equations describe the reactions involved:



A maximum of 60.7 moles of ammonia would be evolved per assembly if the reaction proceeded according to equation (3) alone. Actually the reaction is a combination of the three equations.

The composition of the off-gas was studied as a function of the initial mole ratios of Al : NaNO<sub>3</sub> : NaOH and the final Al concentrations. It was found that the amount of hydrogen in the off-gas varied directly with the initial NaOH concentration at constant Al and NaNO<sub>3</sub> concentrations; and indirectly with the initial NaNO<sub>3</sub> concentration at constant Al and NaOH concentrations. At the recommended flowsheet conditions of mole ratios of Al : NaNO<sub>3</sub> : NaOH of 1 : 0.5 : 1 at 5.0 M Al, the hydrogen evolution did not exceed 2 ml per gram of MTR assembly (see Figure 5). This value agrees very well with that reported by A. T. Gresky(19) for the caustic dissolution of P-10 slugs. At this rate, the dissolution of one assembly would produce about 9.0 liters of hydrogen, which is considered well within safe limits.

The ratios of the final concentrations of NO<sub>2</sub> to Al were plotted as a function of sodium molarity as a convenient method for presenting several variables. The curves show that the fraction of the aluminum dissolved by equation (4) varies directly with the initial NaNO<sub>3</sub> concentration at constant Al and NaOH concentrations, and indirectly with the initial NaOH concentration at constant Al and NaNO<sub>3</sub> concentrations. In plotting the percent of aluminum dissolved by equation (4), it was assumed that the ratio

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of the rate of production of  $\text{NO}_2^-$  to the rate of Al dissolution was constant throughout the dissolving period (see Figure 6). At the recommended flowsheet conditions, approximately 5.0% of the aluminum was dissolved according to equation (3), corresponding to the evolution of 58 moles of ammonia.

### 5.13 Uranium Solubility

The solubility of uranium in the caustic dissolver solution was studied as a function of the initial mole ratios of Al :  $\text{NaNO}_3$  : NaOH and final Al concentrations. Assembly sections were dissolved, and the solution was filtered through both the regular "H" porosity sintered stainless steel process filter using asbestos filter aid, and subsequently through No. 42 quantitative paper. It was arbitrarily assumed for development purposes that all uranium passing through both filters was in solution although some was undoubtedly colloidal. The solutions were neutralized with acid prior to analysis to dissolve any solids. This additional dilution lowered the uranium concentration to about 1 microgram/ml or less, resulting in an analytical accuracy of  $\pm 10\%$ .

Representative results were plotted as a function of sodium molarity as a convenient method for the presentation of several variables. It was assumed that the only cation present was sodium and that all of the ions were monovalent. The uranium solubility varied indirectly with the  $\text{NaNO}_3$  concentration and directly with the NaOH concentration at constant Al concentration, and indirectly with Al concentration at constant  $\text{NaNO}_3$  and NaOH concentrations (see Figure 7).

The selection of flowsheet dissolver conditions as mole ratios of Al :  $\text{NaNO}_3$  : NaOH of 1 : 0.5 : 1 at 5.0 M Al, was based on uranium solubility and solution stability (see Section 5.15). Under these conditions the uranium solubility is 5.7 mg/liter and the soluble uranium loss in the dissolver filtrate should approximate 183 mg, or 0.12%, per assembly.

The effect of  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  on the solubility of uranium was studied. Dissolver solutions which were made up to 0.3 M in  $\text{CO}_3^{2-}$  or up to 0.07 M in  $\text{Ca}^{2+}$  did not show any appreciable increase in uranium solubility.

### 5.14 Barium Solubility

The caustic dissolution of an irradiated MTR assembly selectively leaches the aluminum from the uranium-aluminum alloy, leaving the uranium as a precipitate. It was found that very little of the gross activity, other than the aluminum, appeared in the caustic filtrate. This observation leads to the conclusion that the fission products are not free to leave the precipitate. Thus the uranium acts as a carrier for the barium and permits the separation of barium from aluminum by filtration.

The average barium loss in the caustic filtrate for a series of nine experiments was 0.18% using irradiated natural uranium, MTR assembly sections. Barium carrier was not added in these experiments. A portion of this loss is undoubtedly due to barium associated with colloidal uranium.

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particles which pass through the filter. These experiments showed only that barium remained quantitatively with the uranium in the case of low level irradiation. In the MTR, the uranium mass will be depleted by 10-30%. Under these conditions a proportionate amount of barium may be free to go into solution. However, experiments, using barium<sup>140</sup> tracer and barium carrier corresponding to 1, 5, and 10% of the total theoretical mass of barium, showed that the maximum barium loss in the caustic filtrate was 0.12%. It was therefore concluded that any barium which separates from the uranium crystals would be precipitated, probably as the carbonate, and retained on the filter.

### 5.15 Dissolver Solution Chemical Stability

The chemical stability of the sodium aluminate dissolver solution is of the utmost importance since under operating conditions an appreciable delay might occur between the dissolution and filtration steps. A voluminous, white, difficultly soluble precipitate of hydrous aluminum oxides forms in unstable solutions. Consequently, it was arbitrarily established that the solution must be stable for a least 24 hours at 20-100°C. In addition the solution must be stable after a 20% dilution with water since such a dilution will occur when the solution is transferred by steam jet.

In general the solutions were more stable at higher Al and NaOH concentrations and at lower NaNO<sub>3</sub> concentrations. Precipitates formed within 2 hours in solutions which were 3.6 M in Al and contained mole ratios of 1:0.5 - 1.0:1.0 of Al:NaNO<sub>3</sub>:NaOH. Dilution with water caused immediate precipitation. The solutions were very unstable at mole ratios of 1 : 0.6 : 0.8 for 5.35 and 7.4 M Al. The stability requirements were met when the solution was 5.0 M in Al at a mole ratio of 1 : 0.5 : 1 or 3.6 M in Al at 1 : 1 : 1.5. An increase in the NaNO<sub>3</sub> concentration over these amounts resulted in unstable solutions.

A small amount of flocculent brown precipitate formed in the caustic filtrate within a few hours after filtration when the Al and NaOH concentrations were high (~5.0 M). It was soluble in strong caustic, and leaching with aqua regia caused the formation of an insoluble white precipitate, probably silica. A spectrographic analysis of the precipitate showed that it was a silicate containing aluminum, calcium, chromium, iron, magnesium, and manganese. It was determined that the material was derived from the asbestos filter aid rather than from impurities in the assembly or corrosion of the stainless steel filter or stainless steel dissolver. It is assumed that the precipitate will not affect the process since it does not contain uranium or barium and is formed in small quantities.

### 5.2 Separation of Barium and Uranium from Aluminum

The uranium is present in the caustic dissolver solution as a precipitate which can be separated from the solution either by centrifugation or by filtration using asbestos filter aid and an "H" porosity sintered stainless steel filter at 90-100°C. The latter method was selected for the MTR-RaLa Process because of its simplicity.

5.21 Filtration

Without Filter Aid

The solutions filtered rapidly and did not plug an "H" stainless steel filter but it was necessary to recycle the solution to obtain a clear filtrate. The uranium loss was 0.5 - 1.0%.

Celite Filter Aid

Celite filter aid was tried in an effort to reduce the uranium loss and eliminate the recycle. The caustic solution attacked the Celite, however, making its use impractical.

Asbestos Filter Aid

Asbestos, with the formula  $\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$ , proved to be a satisfactory filter aid. It is reasonably stable in caustic solutions, possesses good filtration characteristics, and is stable to heat. The latter point is of interest because of the large amount of heat derived from the radioactive precipitate. The system cannot tolerate too great an addition of calcium or strontium, and the barium addition should not exceed  $\sim 0.2$  g. The following series of tests was run to determine the impurities that would be added to the RaLa system from the use of this filter aid: A sample of medium-fiber, acid-washed, and ignited asbestos was refluxed for three hours with 3.0 M caustic in a stainless steel container and subsequently leached for three hours with boiling 6 M nitric acid as a pretreatment purification step. The leachings were then repeated to simulate process conditions. The asbestos samples were dried for twenty-four hours at  $110^\circ\text{C}$  and weighed before and after the second caustic and acid treatments, and the total weight loss was determined as  $\sim 3.0\%$ . The caustic solution contained 0.25 and 22.6% of the weight of the asbestos as silica and total alkaline earths, respectively, and the acid leach 0.6 and 0.03%, respectively. Barium was not detected by gravimetric analysis in either solution. These results indicate that the amount of impurities derived from the asbestos would not be excessive, since only those contained in the acid solution enter the RaLa system.

The efficiency of asbestos as a filter aid was determined on the basis of uranium loss as solids and on filtration rate. The solid uranium loss was defined as that uranium which passed through the asbestos-"H" stainless steel filter but which was retained by No. 42 quantitative paper. It was shown that an asbestos precoat was necessary but that 1.28 g of asbestos precoat per square inch of filter was no more efficient than  $0.64 \text{ g/in.}^2$  for retaining uranium particles. The solid uranium loss was lowered by a factor of 4 by increasing the amount of filter aid from 2.5 to 5.0 g/liter, but any further increase resulted in an excessive loss in filtration rate. The average solid uranium loss for twelve runs using  $0.64 \text{ g/in.}^2$  of precoat and 5.0 g/liter of asbestos filter aid was 0.06% with individual variations ranging from 0-0.1%. Increasing the Al concentration from 3.6 to 5.0 M and variations in the mole ratio of  $\text{Al} : \text{NaNO}_3 : \text{NaOH}$  made little difference in the solid uranium loss.

The average filtration rate for seven runs which were 3.6 M aluminum was 1.4 liters/in.<sup>2</sup>/hr at 90-100°C and 5 cm Hg vacuum using 5 g. of asbestos per liter of solution and 0.64 g/in.<sup>2</sup> as a precoat. The individual variation was from 1.56 to 1.06 liters/in.<sup>2</sup>/hr. Varying the concentration of NaNO<sub>3</sub> from 1.8 to 5.2 M or increasing the precoat to 1.28 g/in.<sup>2</sup> made little difference in the filtration rate. Increasing the Al concentration to 5.0 M decreased the rate to 1.0 liter/in.<sup>2</sup>/hr. In all cases the rate was essentially constant during any one run and the maximum batch filtration time was fifteen minutes.

It was concluded from these experiments that the commercial medium-fiber, acid-washed, and ignited asbestos should be boiled for three hours in both 3 M NaOH and 6 M HNO<sub>3</sub> prior to its use as filter aid, that the filter should be precoated with 0.64 g/in.<sup>2</sup> of asbestos, and that the dissolver solution should contain 5 g/liter of asbestos as filter aid. The filter aid should be added to the dissolver solution as a slurry in 6 liters (full scale) of 3.0 M NaOH just prior to filtration. A direct scale-up of laboratory conditions indicated that a filter 14 in. in diameter would be required on full scale.

#### 5.22 Centrifugation

Centrifugation was shown to be a satisfactory method for the separation of the uranium precipitate from the aluminate solution. Caustic dissolver solutions centrifuged for one hour at 750 G or 1500 G showed total uranium losses of ~2.3 and ~0.13%, respectively, indicating that the latter figure represents the minimum centrifugation conditions. Increasing the centrifugation period to two hours at 1500 G did not decrease the uranium loss.

These results agree with those reported for both the laboratory<sup>(20)</sup> and pilot plant<sup>(21)</sup> centrifugation of the caustic solution of P-10 slugs. The latter work used a 12 in. bowl centrifuge in batch experiments at 1450 G for one hour. A personal communication from the authors indicated that the process could be adapted to continuous operations.

A serious disadvantage of centrifugation in this case is the convection currents set up in the bowl as the result of radioactive heat. It is assumed that these currents would tend to stir up the precipitate and thus impair the efficiency of the separation.

#### 5.23 Caustic Wash

The caustic wash serves two purposes: (1) it washes the dissolver tank and effects a quantitative transfer of uranium precipitate from the dissolver to the filter; and (2) it washes the aluminum from the uranium precipitate. In the laboratory experiments, the precipitate was washed four times with volumes of 0.5 M sodium hydroxide which were equivalent to 5 liters on full scale. The washes contained on the average 4.0, 0.5, 0.15, and 0.05% of the total amount of aluminum in the system. These results indicate that the last two washes could be eliminated if they are not required as tank washes.

The caustic wash filtration rate was approximately the same as that of the dissolver solution. The use of water as a wash is not recommended since it caused a marked decrease in filtration rate and increased the uranium loss by a factor of ten.

The uranium loss was constant for each caustic wash and totaled 0.11% as an average of twelve runs. The uranium loss in the wash solutions did not vary appreciably when the sodium hydroxide concentration was increased to 8.0 M or when the original dissolver solution was 3.6 or 5.0 M in aluminum.

### 5.3 Dissolution of Barium and Uranium

The uranium precipitate obtained from the caustic filtration would not dissolve quantitatively in 1 M nitric acid at a total mole ratio of  $\text{HNO}_3/\text{U}$  of 8.0. Dissolution was fast and complete, however, in excess 6 M nitric acid.

### 5.4 Separation of Barium from Uranium

The barium is separated from the uranium and the bulk of the fission products by the precipitation of barium nitrate from 85% nitric acid. Under these conditions the solubility of barium is only 0.86 mg/liter while the uranium is very soluble (see Figure 8). In this step the nitric acid solution of the uranium cake is evaporated to constant boiling nitric acid (equivalent to ~55% nitric acid in this case due to the salting action of the dissolved salts), cooled to 25°C, and 91% nitric acid added as precipitant. After the solution has been agitated for fifteen minutes, the precipitate is recovered by filtration, washed with 85% nitric acid, and finally dissolved in water to form the crude product solution.

Laboratory demonstration runs were made to scale using irradiated natural uranium assembly sections which had been cooled five hours and to which fission product carrier masses corresponding to 12 or 37-day irradiations were added. The crude product solution contained 99.5% of the barium and strontium but only ~3.5% of the total gross beta activity and <0.04% of the uranium for both irradiation conditions. The rare earth content of the crude product solution, however, varied from 2.0% for a 12-day irradiation to 25% for a 37-day irradiation. The separation of aluminum from barium in this step was very poor because of the low solubility of aluminum in 85% nitric acid (~0.3 g/liter). The nitric acid solution of the uranium cake contained ~0.15% (~6.5 g) of the total aluminum in the assembly, and approximately 45% of this aluminum appeared in the crude product solution (see Table 3).

The evaporation of the nitric acid solution will undoubtedly result in the dehydration and precipitation of silicic acid derived from the caustic dissolution. In order to prevent the silica from plugging the filter, the latter was precoated with 1.0 g/in.<sup>2</sup> of analytical grade Celite filter aid, and 2.0 g of Celite was added per liter of solution as filter aid. The filtration rate was adequate under these conditions. A disadvantage of this procedure is the relatively large amount of acid held up in the pores of the filter aid. This acid is subsequently washed out during the

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dissolution of the crude product and appears in the ion-exchange column feed where a high nitric acid content is not desirable (see Section 5.5). Pulling air through the filter for ten to fifteen minutes did not reduce the nitric acid hold-up below a minimum value of 0.018 mole per gram of filter aid. It is recommended, therefore, that the total amount of filter aid on full scale be limited to approximately 40 g, 20 g as precoat and 20 g as filter aid. A direct scale-up of laboratory conditions indicated that a 5-in.-diameter, "G" porosity, stainless steel filter would be satisfactory for full-scale operations.

### 5.5 Purification of Barium by Ion Exchange

The purification of barium by ion exchange consists in the adsorption of the barium and other cations on a resin column from the crude product solution (see Section 5.4), selective elution of impurities with sodium citrate and sodium Versenate, and elution of the purified barium in 9 M nitric acid.

#### Resin Column Specifications

Laboratory demonstration runs were performed on a resin column 13 in. in height by 0.71 in. in diameter which represented 1/34 of full process scale. A column 13 x 4 in. containing 2.67 liters of resin, is recommended for full-scale operations. The resin volume should be measured under water in its settled, sodium-form.

The process resin is chemically pure, 60-100 mesh, 12% cross-linked, sodium-form Dowex-50 (Nalcite HCR). It is cleaned and converted to the sodium form by washing in sequence with 3.5 M HCl, 3.0 M NaNO<sub>3</sub>, and 1 M NaOH. The resin preparation procedure for a full-scale column is given in Table 4.

The flow rates for the resin column solutions vary from 1.2 - 6.8 ml/min per square centimeter of column cross section. The slower flow rates are used only when operation at near equilibrium conditions is required. The stepwise process flow rates are given in Table 2.

Demonstration runs, performed in a 316 stainless steel column, indicated that this was a suitable construction material for the ion-exchange column.

#### Product Adsorption

The water solution of the crude barium product (see Section 5.4) contains acid derived from residual solution in the filter cake and on the walls of the fuming nitric acid filter tank. It is partially neutralized with sodium hydroxide and passed through the column where the barium and other cations are adsorbed. The presence of sodium in this solution prevents the conversion of the sodium-form resin to the hydrogen form by the acidic feed. The acid content of the feed solution should approximate 1.0 mole since significantly larger amounts cause the barium to be adsorbed at a lower point on the column. Thus a portion of the barium would be eluted prematurely and lost during the succeeding impurity elutions. A

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demonstration run containing 5.0 moles of nitric acid in the feed solution showed a total barium loss of 1.8%.

The feed solution is followed by water which washes the feed tank and displaces the last of the feed solution from the column.

#### Contaminant Elution

Approximately 2.9 g of aluminum, 0.1 to 3.3 g of rare earths, and 0.7 to 2.0 g of strontium are adsorbed on the resin column as contaminants along with the barium. The aluminum and rare earths are selectively removed by elution with 0.5 M sodium citrate at pH 3.2 and the strontium is removed by selective elution with 0.07 M sodium Versenate at pH 6.3. Previous work has shown that the latter conditions are optimum for the separation of barium and strontium. (5,6)

Sodium citrate has been used at pH's ranging from 2.7(22) to 6.0(23) for the elution of rare earths from Dowex-50 resin. Experiments on the MTR RaLa system, however, showed that elution at pH 3.5 was more efficient than at pH 3.0, 6.0, or 7.0. Aluminum, on the other hand, was more efficiently eluted at pH 3.0 than at higher pH. A compromise pH of 3.2 proved to be a satisfactory operating condition for the elution of both rare earths and aluminum. It was also shown that 12.0 g of aluminum and 5.3 g of rare earths could be successfully eliminated by using the flowsheet conditions, indicating that the capacity of the process for aluminum decontamination is not limited to the expected 2.9 g.

The selective elution of aluminum with sodium hydroxide(24), oxalic acid(24), and Versene was also studied. Sodium hydroxide derives its efficiency through the formation of the anion  $AlO_2^-$  which is not adsorbed by the cation resin. The formation of this anion requires hydroxyl ions, and consequently the pH of the solution decreases. In order to prevent a decrease in pH to 10 or less, with a resultant precipitation of aluminum hydroxide in the resin column, the initial bulk removal of aluminum is accomplished with 1.5 M sodium hydroxide. The balance of the aluminum is then eluted with 0.5 M sodium hydroxide. The use of the less concentrated solution is preferable from a selective elution standpoint since its effect on the barium is directly proportional to the square of the  $Na^+$  concentration. Sodium hydroxide proved to be an efficient aluminum eluting agent, but its use was precluded by its adverse effect on the rare earths. The latter were apparently precipitated in the resin particles, thus preventing their subsequent quantitative elution at finite rates by complexing agents. Versene at pH 6.3 and oxalic acid at reagent pH 0.78 proved to be less efficient than sodium citrate at pH 3.2 for aluminum elution. Sodium oxalate at pH 2.5 eluted aluminum efficiently but precipitated the rare earths in the resin particles.

#### Product Elution

The barium product is eluted with an excess of 9 M nitric acid. A small volume of 2 M nitric acid is passed through the column first, however, to elute the bulk of the sodium from the resin and prevent the precipitation

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of sodium nitrate in the column during the elution with 9 M nitric acid. Experience in the ORNL RaLa Process has shown that the last traces of barium are desorbed with difficulty from highly irradiated Dowex-50 resin but that the use of excess acid effects a quantitative barium elution. The volume of acid shown in the MTR RaLa flowsheet represents a three to fourfold excess over that required for a nonirradiated system (see flowsheet, Figure 4). The 2 M nitric acid and the first portion of the 9 M acid are passed through the column at a fast flow rate to strip off the bulk of the barium as fast as possible and thus minimize the irradiation of the resin. The bulk of the acid is then passed at a lower flow rate, approximating equilibrium conditions, to elute the balance of the barium.

The stability of Dowex-50 resin was studied in 6, 9, and 12 M nitric acid. About 20 g of clean resin was shaken for 24 hr with 75 ml of nitric acid, the phases were separated by filtration, and the filtrate was analyzed for sulfate and total solids. The resin was washed with water and its capacity was determined by titration with 0.1 M sodium hydroxide. The resin moisture content was determined by weight loss in a 105°C oven, and the final capacity results were reported on an oven-dry basis.

The results showed that the resin is quite stable even in 12 M nitric acid, in which the capacity loss was 0.74% as determined by the solution sulfate analysis. This analysis is considered more accurate than the resin titration method which showed a capacity loss of zero. The chemically pure resin was apparently more stable than the technical grade and there was no appreciable difference in the stability of the 8 and 12% cross-linked technical grades of resin (see Table 5).

The relative efficiencies of 6, 9, and 12 M nitric acid for the elution of barium from a Dowex-50 resin column were also determined. Batch equilibrations had shown barium distribution coefficients of 1.0 and 0.5, respectively, for 6 and 9 M. It was expected that 12 M nitric acid would be the most efficient eluting agent due to its higher  $H^+$  concentration and activity coefficient. Column runs showed, however, that the 9 M acid was only about 20% more efficient, and that the 12 M was actually less efficient than the 6 M acid (see Figure 9). A possible explanation of this phenomenon would be the precipitation of barium nitrate in the resin particles due to the high  $H^+$  and  $NO_3^-$  concentrations in the resin phase. The flat appearance of the elution curve suggests the redissolution of a precipitate.

#### 5.6 Final Purification and Volume Reduction

The final volume reduction and separation of barium from its daughter, lanthanum, and other impurities is accomplished by the precipitation of barium nitrate from 85% nitric acid. The 9 M nitric acid ion-exchange column eluate is evaporated to constant boiling nitric acid, and barium nitrate is precipitated by the addition of 91% nitric acid. The precipitate is recovered by filtration, dissolved in a small volume of water, and sent to the shipping cone for evaporation to dryness. The barium loss is  $\approx 1.0\%$  and the product meets the specifications listed in Section 4.2. The final precipitation tank and filter should be constructed of

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tantalum to ensure the purity of the product.

The product from the ion-exchange column will contain a large amount of sodium, derived from the sodium-form resin column, and small amounts of rare earths, strontium, aluminum, and stainless steel corrosion products. A study of the fuming nitric acid precipitation step showed that all these impurities, with the exception of strontium, are separated from barium by the precipitation of the latter from 10 liters of 85% nitric acid. The separation of barium and strontium by ion exchange, therefore, must meet specifications since no further separation of these cations is attained during the fuming nitric acid precipitation. Approximately 1.0 g each of aluminum and rare earths can be separated from the barium by this precipitation, but any significant increase over that amount exceeds their solubilities. The results of representative experiments are listed in Table 6.

The elimination of sulfate and other resin irradiation decomposition products by a fuming nitric acid precipitation was also studied, since an equipment failure or other operational difficulty may allow the radioactivity to remain on the column an inordinate length of time and result in excessive decomposition of the resin. Five grams of Dowex-50 and 1.9 g of  $Ba(NO_3)_2$  were dissolved in 30%  $H_2O_2$  and 16 M  $HNO_3$ , and the barium was subsequently precipitated by the addition of fuming nitric acid. The precipitate was white and completely soluble in water, indicating that the sulfate and colored organic impurities were completely eliminated.

ORNL RaLa development work showed that sulfate could be quantitatively eliminated from the product system by one fuming nitric acid precipitation where the mole ratio of  $SO_4^{=}/Ba$  in the solution is  $\frac{1.0}{2.5}$ , and that two precipitations would eliminate any amount of sulfate. These results were confirmed using the MTR RaLa flowsheet conditions.

The procedure for a second precipitation is to dissolve the product of the first precipitation in 10 liters of 9.0 M nitric acid and repeat the flowsheet conditions for evaporation and precipitation.

## 6.0 Caustic Sulfate Process

The Caustic Sulfate Process was studied as an alternate MTR RaLa process. The process steps include: (1) dissolution of the assembly in caustic and recovery of the uranium-barium precipitate by filtration (see Sections 5.1 and 5.2); (2) dissolution of the precipitate in nitric acid, precipitation of barium sulfate, and recovery of the latter by filtration; and (3) dissolution of the barium sulfate in Versene or nitric acid and purification of the barium by ion exchange. In a variation of this process the caustic dissolver solution is neutralized with excess sulfuric acid. This procedure results in the simultaneous dissolution of the uranium and the precipitation of barium sulfate. The latter is recovered by filtration and treated as indicated in step (3) above (see flowsheets, Figures 10A, 10B).

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The Caustic Sulfate Process was rejected because the sulfate was not compatible with the process used to recover the uranium<sup>235</sup> (see Section 4.3). In addition, the dissolution of the barium sulfate precipitate presented difficulties on full scale owing to the limited radiation stability of Versene. Dissolution of the precipitate in nitric acid was not practical because of the large volume of acid required. The principal advantage of the Caustic Sulfate Process was the excellent separation of barium from the bulk contaminants, aluminum and uranium.

#### 6.11 Separation of Barium from Uranium and Aluminum

##### Dissolution of Uranium in Nitric Acid

In this scheme the uranium precipitate is dissolved in nitric acid, and the barium is subsequently precipitated by the addition of sulfuric acid. The efficiency of this separation was determined by studying the quantitative precipitation of barium sulfate and the amounts of cerium, strontium, uranium, and aluminum carried by the precipitate as a function of the barium, nitric acid, and sulfuric acid concentrations. The effects of filtration temperature and digestion in the presence or absence of Celite filter aid were also studied. In each case the solution contained 12 g/liter of analytical grade Celite filter aid and was filtered through an "M" sintered glass disk precoated with 1/4 in. of filter aid; the uranium concentration was 11 g/liter; the solutions were digested fifteen minutes at 90-100°C and cooled to the filtration temperature thirty minutes before filtration; except where noted, the filter aid was added before digestion; the precipitates were washed with 1 M sulfuric acid.

The results of this study, plotted in Figures 11, 12, and 13, showed that the barium loss in the filtrate increased with nitric acid concentration, and decreased with increasing sulfuric acid concentration; and that the amounts of cerium, strontium, aluminum, and uranium carried by the barium sulfate increased with the concentrations of nitric acid, sulfuric acid, or barium, reaching maximums of 12, 80, 45, and 0.15% respectively.

It was concluded that optimum process precipitation conditions were 2.0 M sulfuric acid and 4.0-6.0 M nitric acid. Under these conditions the barium yield was 99% and the precipitate carried approximately 0.05, 0.01, 70, and 4.0% of the uranium, aluminum, strontium, and rare earths, respectively. These percentages were calculated on the basis of the total amounts present in the original assembly.

##### Dissolution of Uranium in Sulfuric Acid

In this variation of the Caustic Sulfate Process, the caustic dissolver solution is neutralized with excess sulfuric acid to dissolve the uranium and simultaneously precipitate barium sulfate. The solution is boiled for two hours to ensure complete dissolution and an additional hour to promote crystal growth. The barium sulfate is recovered by filtration using a 1-in. cake of analytical grade Celite filter aid on a "G" porosity sintered stainless steel filter and washed with 1.0 M sulfuric acid.

The yield and purity of the barium sulfate were studied as functions of the precipitation conditions. Increasing the aluminum or sulfate concentrations above 0.8 or 2.0 M, respectively, lowered the barium yield by 3-5%. It was never determined whether the increase in product loss was due to an actual increase in barium sulfate solubility or was merely the result of poorer crystal formation as the solution approached saturation with aluminum and sodium sulfate and the subsequent loss of the finer particles through the filter. A decrease in the barium concentration to half that expected from a 12-day irradiation resulted in a decrease in yield of 3%, indicating a minimum sensitivity for the precipitation step. The filtration time per batch was reduced from approximately ninety to thirty minutes by increasing the filtration temperature from 25 to 90-100°C. The higher filtration temperature also caused a drop in product yield of 3%. A study of the barium sulfate yield as a function of Celite filter cake depth indicated that the cake must be at least 3/4 in. in depth in order to hold all the particulate barium sulfate that would not pass through a No. 42 quantitative filter paper. Refluxing the solution for two hours instead of 1 to promote crystal growth did not affect the yield appreciably. Representative experiments are listed in Table 7.

It was concluded that the best precipitation conditions were 0.8 M aluminum and 2.0 M sulfate, and that the filtration should be performed at 25°C using a 1-in. cake of analytical grade Celite filter aid and 1.0 M sulfuric acid as a wash. The barium yield under these conditions was 98%, and the precipitate carried 15, 0.02, 0.01, and 50% of the strontium, aluminum, uranium, and rare earths, respectively.

## 6.2 Dissolution of Barium Sulfate

Two reagents, Versene and nitric acid, were considered for the dissolution of the barium sulfate precipitate. Initially Versene appeared to be the most desirable since the solubility of barium sulfate in Versene was known<sup>(6)</sup> and its use in the ORNL RaLa Process had proved its value. Subsequent experiments, however, on the radiation stability of Versene indicated that its use should be limited to lower levels of radioactivity.

The values for the solubility of barium sulfate in nitric acid as listed in the literature<sup>(26)</sup> varied by factors as great as 10. These large variations were presumably due to nonequilibrium experimental conditions. In an effort to obtain more accurate values the solubility was determined using barium<sup>140</sup> tracer. Excess precipitate was shaken for 7 days at 25±2°C with nitric acid solutions which varied in concentration from 0.1 to 6.0 M. The solutions were filtered and both the precipitate and solutions analyzed for barium. The results, plotted in Figure 14, show that the barium sulfate solubility increases linearly with nitric acid concentration up to 4.0 M with a slight increase in dissolution efficiency as the concentration increases from 4.0 to 6.0 M. These figures indicate that a minimum of 24.5 liters of 1.5 M nitric acid would be required for the dissolution of the 3.4 g of barium sulfate expected in the MTR system for a 37-day irradiation. Actually, 63 liters of acid were used in the development program to ensure the solubility of the barium, strontium, aluminum, and fission products.

6.3 Purification of Barium by Ion Exchange

Three ion-exchange processes were developed and evaluated for the purification of the crude barium produced by the Caustic Sulfate Process: (1) The Versene Process; (2) The Nitric Acid Process; and (3) The Nitric Acid-Versene Process. The Versene Process was judged the best in terms of product purity and overall processing time and the poorest in terms of radiation stability (see Table 8). The Versene Process, however, requires a "hot" feed pH adjustment whereas the others do not. As a result, the Nitric Acid-Versene Process is recommended for use at high levels of radiation (see flowsheets, Figures 15, 16, and 17).

All three processes used chemically pure, 12% cross-linked Dowex-50 resin, either in the H<sup>+</sup> or Na<sup>+</sup> form, which had been cleaned and activated by the procedure listed in Table 4. The flow rates were maintained at a maximum of 1.5 ml/min per square centimeter of column cross section for all solutions in which essentially equilibrium conditions are necessary. Wash solutions and the final product elutriant were run at faster flow rates to lower the resin irradiation time. Several column heights were studied for each process, and the column dimensions listed in the following sections represent the best column geometries in terms of product purity and overall operating time.

6.31 Versene Process

The Versene Process steps are: (1) Dissolution of the barium sulfate precipitate in Versene at pH 8.0 to 9.0 and filtration (an appreciable amount of the siliceous filter aid dissolves if the pH rises much above 9.0); (2) adjustment of the pH to 6.3 ± 0.2 and passage of the solution through a sodium-form resin column, 7 in. in height by 4 in. in diameter, where the barium adsorbs and the bulk of the impurities pass through; (3) selective elution of the strontium and rare earths with sodium Versenate at pH 6.3; and (4) elution of the barium and associated sodium in 2 and 9 M nitric acid, respectively (see flowsheet, Figure 15, and Table 8).

6.32 Nitric Acid Process

The Nitric Acid Process was developed to eliminate the use of organic reagents, since the latter are relatively unstable to radiation and require pH adjustment. The process steps are: (1) Dissolution of the barium sulfate precipitate in 1.5 M nitric acid; (2) passage of the solution through a hydrogen-form resin column, 10 in. in height by 6 in. in diameter, where essentially all the cations are adsorbed; (3) selective elution of the strontium and aluminum impurities with 1.5 M nitric acid; and (4) elution of the barium and associated rare earths with 9.0 M nitric acid. The disadvantages of this process are the large volumes of nitric acid required, the poor separation of barium from rare earths, and the long overall operating time (see Table 8, and flowsheet, Figure 16).

The distribution coefficients, K<sub>d</sub>, for barium, strontium, cerium, uranium, mercury, and aluminum were determined for the Dowex-50 resin-HNO<sub>3</sub>

system in an effort to find the optimum conditions for the purification of barium by selective elution with  $\text{HNO}_3$ . The  $K_d$ 's, defined as the  $\frac{\text{mass/gm oven-dry resin}}{\text{mass/ml of solution}}$ , are shown in Figure 18 in a log - log plot as a function of the nitric acid concentration. It is seen that the best separations could be made at 0.1 M  $\text{HNO}_3$  but, since the  $K_d$ 's are so high at this concentration, the time needed for elution would be prohibitively long. The best separation conditions, a compromise between operating time and efficiency of separations, were determined by actual column runs to be 1.5 M  $\text{HNO}_3$ .

Normally, log - log plots of  $K_d$  vs. concentration of complexing agent are straight lines. The curves shown in Figure 18 are attributed to the formation of nitrate complexes at the higher concentrations and hydrolysis of some of the cations at the lower nitric acid concentrations.

### 6.33 Nitric Acid-Versene Process

This process embodies the better features of both the Versene and Nitric Acid Processes from a radiation stability standpoint. Its principal advantage is the elimination of the pH adjustment and consequently the prolonged irradiation of the Versene feed solution. The disadvantages of this process as compared to the Versene Process are its longer operating time and relatively poor separation of rare earths from barium (see Table 8).

The process steps are: (1) Dissolution of the barium sulfate in 1.5 M nitric acid; (2) passage of the solution through a hydrogen-form resin column 14 in. in height by 6 in. in diameter, where essentially all the cations are adsorbed; (3) conversion of the resin to the sodium form with 1 M sodium chloride followed by 1 M sodium hydroxide; (4) selective elution of strontium and the rare earths with sodium Versenate at pH 6.3; and (5) elution of the barium and associated sodium in 9 M nitric acid (see flowsheet, Figure 17).

Approximately 10% of the cerium present in the ion-exchange column feed appeared in the product. The poor separation of cerium was attributed to precipitation of the latter in the resin particles during the sodium hydroxide wash. Experiments in which the cerium was eluted with Versene at pH 4.0 or 5.0 did not show any significant increase in cerium separation efficiency.

### 6.4 Final Purification and Volume Reduction

The sodium, rare earths, and corrosion products are separated from the barium by precipitation of barium nitrate from 85% nitric acid by the procedure described in Section 5.6. The product from the Versene Process requires only one precipitation while the Nitric Acid and Nitric Acid-Versene Processes both require two precipitations to obtain the necessary decontamination of cerium (see Table 8).

## 7.0 Sulfuric Acid Process

The Sulfuric Acid Process utilizes sulfuric acid with hydrogen peroxide and mercuric nitrate as catalyst for the dissolution of the assembly and simultaneous precipitation of barium sulfate. The barium sulfate is separated from the uranium and aluminum by filtration and is subsequently dissolved and purified by the ion-exchange process described in Section 6.3. The Sulfuric Acid Process is capable of producing a pure product in high yield. Its disadvantages are the large amount of sulfate associated with the waste uranium<sup>235</sup> (see Section 4.3); the corrosiveness of the dissolver solution; the large volume of dissolver off-gases as a result of peroxide decomposition; the explosion hazard due to the presence of hydrogen in the off-gas; and the addition of mercury as a contaminant in the system (see flowsheet, Figure 19).

Aluminum is not readily dissolved by pure sulfuric acid as a result of surface passivation. It was found, however, that a 3.0 M boiling sulfuric acid solution containing 0.3% hydrogen peroxide and 2% mercury by weight, as mercuric nitrate, dissolved the MTR assembly test sections in two hours. The final aluminum concentration was 1.0 M. The apparent dissolution cycle mechanism was the amalgamation of the aluminum surface; selective dissolution of the amalgamated aluminum and precipitation of an oxide of mercury; and redissolution of the mercury oxide by the combined action of hydrogen peroxide and sulfuric acid. The nitrate anion enters into the initial reaction but is soon used up and is not an essential component of the system. The peroxide concentration was maintained in the dissolver solution by periodic additions of 30% hydrogen peroxide.

The solution is refluxed for one hour after dissolution is complete to promote crystal growth prior to filtration. Celite-545, Solka Floc (a cellulose derivative), and analytical grade Celite were evaluated as precoat material on an "H" sintered stainless steel filter. The results showed that analytical grade Celite was the best filter aid and that a 1 in. cake would retain about 96% of the barium sulfate. The filtrate from each run was refiltered through No. 42 quantitative paper to distinguish the soluble barium from the small particles of barium sulfate passing through the filter. Any barium passing through the paper was considered as in solution. Representative results are listed in Table 9.

Several experiments were performed in which the assembly sample was dissolved in nitric acid, using mercury as a catalyst, and the barium subsequently precipitated by the addition of sulfuric acid. This procedure was not practical because the excess nitrate ion complexed and prevented the quantitative precipitation of the barium (see Runs S-1 and S-7, Table 9).

## 8.0 Nitric Acid Process

The Nitric Acid Process uses the "25" Process<sup>(13)</sup> dissolving procedure in which the assembly is dissolved in boiling nitric acid, using mercury as a catalyst. Four moles of acid are used for each mole of

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aluminum and 2% mercury by weight as catalyst. The dissolving time is approximately two hours. The aluminum and uranium are separated from the barium by two cycles of precipitation from 70% nitric acid, and the barium is subsequently purified by ion exchange. The overall yield from this process would approximate 95% and the product purity would be adequate. The process is not desirable, however, because of the complexity of the precipitation equipment; the relatively poor separation of aluminum from barium by the crystallization steps; and the addition of mercury as a contaminant (see flowsheet, Figure 20).

In the first cycle, 98% of the aluminum is separated from the barium and uranium by precipitation of aluminum nitrate from 70% nitric acid at  $-15^{\circ}\text{C}$  followed by filtration. This procedure is similar to that reported for the decontamination of aluminum nitrate wastes<sup>(27)</sup> but uses both a higher acid concentration and lower precipitation temperature. In the second cycle, the filtrate from the first cycle is evaporated, and a second and third crystallization are made from 70% nitric acid at  $0^{\circ}\text{C}$  at 1/100 the volume of the first crystallization. Under these conditions, the barium is 100 times more concentrated and precipitates quantitatively, effecting a separation from the soluble uranium. Two crystallizations are necessary in the second cycle to effect a complete separation of uranium from the barium. An investigation of the effect of temperature on the crystallization system showed that  $-15^{\circ}\text{C}$  rather than  $0^{\circ}\text{C}$  was more efficient for the separation of aluminum from barium in the first cycle; and that  $0^{\circ}\text{C}$  was better for the second cycle since the uranium tended to precipitate at lower temperatures under the more concentrated conditions (see Table 10).

Crystallization from 85% nitric acid at  $25^{\circ}\text{C}$  was also studied to eliminate the need for refrigeration equipment. These studies showed that the separation of aluminum from barium under these conditions was not satisfactory since 6-12% of the aluminum remained with the barium. It was also found that the solubility of the barium in the crystallization solution varied inversely with the aluminum concentration and that increasing the barium concentration by a factor of ten resulted in a quantitative precipitation of barium nitrate. This latter phenomenon illustrates the difference in barium solubilities in the first and second cycles, as previously described, where the second-cycle concentration is 100 times greater. Representative experiments are listed in Table 11.

## 9.0 Purification of Barium by Precipitation Methods

Precipitation was considered as an alternate method to replace ion exchange for the separation of barium from the fission products and small amounts of aluminum. A survey of the insoluble compounds of barium indicated that precipitation of barium chromate or barium chloride would be applicable from a chemical point of view since precipitation of these compounds affords an excellent separation of barium from strontium. The chromate precipitation was considered unsatisfactory under process conditions, however, since the precipitation must be carried out at a controlled pH and any aluminum present would also precipitate at this pH.

The precipitation of barium chloride from ethyl ether-hydrochloric acid is a standard analytical separation procedure but appeared undesirable owing to the radiation instability of the ether (see Section 4.41). I. R. Higgins had shown<sup>(28)</sup>, however, that a satisfactory separation of barium from strontium and cerium could be obtained with a 6.1% barium loss under ORNL RaLa final purification conditions by three precipitations of barium chloride from 10.0 M hydrochloric acid. These results indicate that the only function of the ether is to decrease the solubility of the barium. A program<sup>(30)</sup> was initiated to study the efficiency of a hydrochloric acid precipitation as applied to the MTR RaLa conditions. These conditions differ from those in the final ORNL purification step in that the mass of barium is lower by a factor of two to four, the mass of rare earths is greater by a factor of 48-133, and the system contains approximately 6.5 g of aluminum whereas there is no aluminum in the ORNL final precipitation system.

The Hydrochloric Acid Precipitation Process was designed to follow the first fuming nitric acid precipitation (see Section 5.4) and consists of the following steps: (1) Evaporation of the barium nitrate-hydrochloric acid solution; (2) precipitation of barium chloride from 10.5 M hydrochloric acid; and (3) dissolution, evaporation, and recrystallization of barium chloride. The final step is the precipitation of barium nitrate from fuming nitric acid, similar to that described in Section 5.6 (see flowsheet, Figure 21).

The results from demonstration runs of this process, using fission product masses corresponding to 12-, 20-, and 37-day irradiations, showed a total average barium loss of 12.6% for the hydrochloric acid precipitations. The fraction of the original amounts of impurities remaining in the product varied from 0.9-3.0% for strontium, from 0-0.3% for the rare earths and from 2.0-19.0% for aluminum. The corrosion products, iron, chromium, and nickel, were completely eliminated in all cases (see Tables 12, 13, and 14).

The advantages of this process are that it is simple in both equipment and chemicals. Only one chemical, hydrochloric acid, and, in all likelihood, one or two evaporator-precipitator tanks will be required. The system is stable to radiation, and the decontamination of rare earths and small amounts of aluminum is excellent. The overall time cycle should be very low.

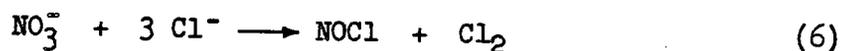
It was concluded, however, that its disadvantages as compared to ion exchange render its use impractical in its present state of development. The disadvantages include a high barium loss, insufficient and erratic strontium decontamination, and insufficient aluminum decontamination in the presence of the higher concentrations of fission products. Also, the tanks and off-gas lines must be stable to the highly corrosive action of boiling aqua regia.

#### Barium Chloride Precipitation Studies

The water solution of the product from the first fuming nitric acid

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precipitation forms the starting material for the chloride precipitation steps (see Section 5.4). This solution of barium, strontium, rare earths, and aluminum nitrates contains up to 1.0 mole of free nitric acid and about 1.2 moles of combined nitrate, which if not removed, decompose an appreciable part of the hydrochloric acid added as precipitant:



Therefore, 1 liter of hydrochloric acid (12 M) is added, and the combined solution is evaporated to the desired precipitation volume. A single evaporation to 100 ml (full scale) removed some 95% of the nitrate but gave a final hydrochloric acid concentration of only 3-5 M. The loss of acid, in excess of that required for the nitrate decomposition, was shown to be the result of the salting out effect of aluminum as the solution became more concentrated during the evaporation.

The volume to which the solution may be evaporated is limited by the mass of the cations present. About 50 ml for a 12-day irradiation system and 100 ml for a 37-day irradiation system were determined as practical minimum volumes. The barium chloride is selectively precipitated by the addition of 0.4 or 0.9 liters of 12 M hydrochloric acid for the 12- or 37-day irradiation systems, respectively, to give a final volume of 0.5 liters per gram of barium. This volume represents a compromise between barium loss and impurity separation. Smaller volumes result in poorer decontamination. In order to minimize supersaturation effects, the precipitate should be allowed to settle and grow for at least one hour. The barium loss in the first precipitation averages 5.7% as compared with a theoretical solubility loss of 3.0%. Undoubtedly the barium solubility is influenced by the high concentration of the other cations since the barium loss in the second precipitation, where the total cation concentration is lower, averaged 4.5%.

The barium chloride precipitate is washed with 0.2 liters of 12 M hydrochloric acid and dissolved in 1.0 liter of water.

The second-cycle precipitation consists of the evaporation of the water solution and a repetition of the first-cycle precipitation and wash procedure.

The final step is the precipitation of the barium from 2.0 liters of 85% nitric acid (see flowsheet, Figure 21).

The solubilities of barium and strontium were determined as a function of the hydrochloric acid concentration (see Figure 22). These data indicate that strontium is 40 times more soluble than barium in 10.5 M acid and on a solubility basis should be completely eliminated in one precipitation. Under the process conditions, however, 5.0 to 27.0% of the strontium coprecipitated with the barium. Apparently the amount of coprecipitation is a direct function of the concentration of aluminum present.

The solubility of aluminum in hydrochloric acid was inversely proportional to the rare earth concentration. For a 12-day irradiation

system, in which the rare earth concentration was low, 2.0% of the aluminum remained with the barium after two precipitations; but for 20- or 37-day irradiation systems 7.5 and 19% respectively, of the aluminum precipitated with the barium. It was also shown that aluminum could be eliminated during the final nitric acid precipitation by making the final nitric acid precipitation from 70% rather than 85% nitric acid and accepting a slightly higher barium loss. The aluminum solubility under these conditions is approximately 12 g/liter.

The complete results of three demonstration runs for 12-, 20-, and 37-day irradiation systems are shown in Tables 12, 13, and 14.

#### 10.0 Acknowledgment

Appreciation is expressed to the ORNL analytical division for its excellent services and cooperation, and in particular to the laboratories of E. I. Wyatt and T. G. Harmon for radiochemical analyses and J. H. Edgerton, L. T. Corbin, and P. F. Thomason for ionic analyses.

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Table 1  
Approximate Composition of an Irradiated MTR-Assembly

Equations:

- (1)  $U^{235}$  content as a function of irradiation time =  $140e^{-\lambda t}$  gm/assembly
- (2) Radioactive fission product mass (gm) =  $(140)(\phi)(\sigma)(0.86)(\text{Fission Yield})(\text{At. Wt}) \frac{(e^{\lambda t} - 1)}{\lambda}$
- (3) Stable fission product mass (gm) =  $(140)(\text{At. Wt})(\text{Fission Yield})(0.86)(1 - e^{-\lambda t})$

$(\phi)(\sigma) = 0.01105/\text{sec}$ ;  $\phi$  = neutron flux;  $\sigma = U^{235}$  cross section;  $\lambda$  = decay constant; 0.86 = fraction of  $U^{235}$  fissioning; fission yields as reported by P. R. Gillette. (28)

Radioactive Energy: At discharge =  $1.3 \times 10^3$  KW (29)  
4 hrs cooling = 5.0 KW (11)  
24 hrs cooling = 1.48 KW

- Assumptions: (1) MTR power level = 30,000 KW  
(2) With the exception of  $Ba^{140}$ ,  $Sr^{89}$ ,  $Ce^{141}$ , and  $I^{131}$ , the decay chains begin and end with the first long-lived product.

Constituent	Grams/Assembly		
	Irradiation Time (Days)		
	12	20	37
$Ba^{138}$ $Ba^{140}$	0.54 0.40	0.87 0.53	1.5 0.6
$Sr^{88,89,90}$	0.76	1.2	2.0
$Ce^{140,141,142,144}$	1.6	2.5	4.4
Rare Earths: (Other than Ce; includes $La^{139,140}$ and $Y^{91}$ )	3.2	5.2	8.9
*Inert Gases: $Kr^{83,84,86}$ $Xe^{131,132,134,136}$	0.18 1.1	0.28 1.9	0.48 3.3
Alkali Metals: $Rb^{85,87}$ $Cs^{133,135,137}$	0.23 1.4	0.37 2.2	0.62 3.8
Halogens: * $Br^{81}$ $I^{127,129,131}$	0.008 0.21	0.012 0.28	0.021 0.35
Zinc Group: $Zr^{91,92,94,95,96}$ $Nb^{93}$ * $In^{115}$	1.4 0.36 <0.001	2.3 0.58 0.001	3.9 0.98 0.002
Platinum Metals: $Ru^{101,102,103,104,106}$ * $Pd^{105}$	0.92 0.087	1.5 0.14	2.5 0.24
Arsenic Group: $Se^{78,79,80,82}$ $Te^{126,127,128,129,130}$ $Mo^{97,98,100}$ * $Sb^{121}$ and $Sn^{117,118,119,120,122,123,124,125}$	0.020 0.24 1.1 0.010	0.032 0.39 1.7 0.016	0.055 0.66 2.9 0.028
* $Cd^{111,112,113,114,116}$	0.004	0.007	0.012
* $Ag^{109}$	<0.002	0.003	0.005
* $Tc^{99}$	0.35	0.56	0.96
$U^{235}$ (29) $U^{234,236,238}$	122.6 12.4-81.1	112 13.8-82.5	92.4 16.6-85.3
Al	4,370	4,370	4,370
Si (from welding flux)	35	35	35

\*Not included in synthetic experimental solutions.

Table 2

Operating Flow Rates for the MTR RaLa Ion Exchange Process

See Flowsheet, Figure 4.

Solution	Volume (liters)	Flow Rate (ml/min)	Total Time (hrs)	Average Resin Irradiation Time (hrs)
(1) "Hot" Feed	20	550	0.61	0.32
(2) Wash - H <sub>2</sub> O	2	550	0.06	0.06
(3) Rare Earth & Al Elution: 0.5 M Na Citrate pH 3.2	22	260	1.42	~1.42
(4) Wash: A. H <sub>2</sub> O B. H <sub>2</sub> O	2.5 7.5	260 550	0.16 0.23	0.16 0.23
(5) Sr Elution: 0.07 M Na Versenate pH 6.3	12.0	260	0.77	~0.77
(6) Wash: A. H <sub>2</sub> O B. H <sub>2</sub> O	2.5 7.5	260 550	0.16 0.23	0.16 0.23
(7) Na Elution: 2.0 M HNO <sub>3</sub>	2	550	0.06	0.06
(8) Product Elution: A. 9.0 M HNO <sub>3</sub> B. 9.0 M HNO <sub>3</sub>	5 10	425 100	0.20 1.67	0.10 Negligible
Total:	93	---	5.57	3.51

Table 3

Distribution of Fission Products in the MTR RaLa Process

Conditions:

20g transverse sections of an MTR RaLa assembly were irradiated for sixteen hours in the ORNL pile and processed after five hours.

Carrier fission products were added to the uranium dissolver solution corresponding to 12- or 37-day irradiations in the MTR reactor (see Table 1).

For process conditions see flowsheets, Figures 3 and 4 and Table 2.

12 and 37 day results are reported separately only when significantly different.

Process Step:	% of Total Initially Present at Process Time										
	Gross $\beta$	Ba	Sr	Zr	Cb	Ru	Cs	I	Total R. E.	U	Al
<u>Dissolution:</u> Caustic Waste	2.58	0.2	0.2	-	-	-	-	1.0	*0.1 ~0.2	0.3	>99.8
<u>1st Fuming HNO<sub>3</sub> Precipitation:</u> Uranium Filtrate	93.92	0.3	0.3	~99.9	~99.6	~99.7	~99.3	96.9	*97.9 ~74.8	>99.6	0.08
<u>Ion Exchange:</u> Combined Wastes	-	0.7	>99.1	0.001	0.4	0.06	0.4	1.9	*1.9 24.5	<0.01	0.07
<u>2nd Fuming HNO<sub>3</sub> Precipitation:</u> Final Barium Product	-	>97	<0.3	0.005	0.0	0.0	0.0	0.1	*0.005 <0.03	<0.0003	<0.0006

\*12-Day Irradiation

Table 4

Resin Clean-up and Activation Procedure

Conditions:

Column Dimensions: 4 in. in i.d. by 14 in. in height.

Resin: Dowex-50, C.P., 60-100 Mesh, 12% cross-linked.

Flow Rate: 162 ml/min

Solution	Molarity	Volume (liters)
(a) HCl	3.5	8.0
(b) H <sub>2</sub> O	-	3.0
(c) NaNO <sub>3</sub>	3.0	8.0
(d) NaOH	1.0	1.0
(e) H <sub>2</sub> O	-	4.0
(f) Repeat steps (a) to (e) four times.		

Table 5

Stability of Dowex-50 Resin in Aqueous Nitric Acid SolutionsConditions:

20 g of oven-dry resin shaken for twenty-four hours with 75 ml of HNO<sub>3</sub>.

Phases separated by filtration through No. 42 Whatman Paper; filtrate analyzed for SO<sub>4</sub><sup>=</sup> and total solids.

Resin washed with deionized H<sub>2</sub>O and capacity determined by titration with 0.1 M NaOH.

Resin Sample	Capacity, oven-dry (meq/g)			SO <sub>4</sub> <sup>=</sup> leached out as % of total present in resin*			Total solids in HNO <sub>3</sub> as % of oven-dry resin wt.			
	Original	HNO <sub>3</sub> Concentration			HNO <sub>3</sub> Concentration			HNO <sub>3</sub> Concentration		
		6M	9M	12M	6M	9M	12M	6M	9M	12M
L-2566-11 (c.p. - 12% Cross-Linked)	5.08	5.10	5.10	5.12	0.03	0.03	0.03	-	-	-
L-2647-28 (Tech. -12% Cross-Linked)	5.01	4.95	4.97	4.97	0.19	0.51	0.74	0.07	0.17	0.17
L-2566-47 (Tech. -8% Cross-Linked)	5.03	5.12	5.14	5.13	0.14	0.34	0.50	-	-	-

\*Equivalent to % resin capacity loss.

Table 6

Purification of Barium<sup>140</sup> by Precipitation from 85% Nitric AcidConditions:Precipitation: ~10 liters, 85% HNO<sub>3</sub>, ~517 g of NaNO<sub>3</sub>Wash: 1 liter of 85% HNO<sub>3</sub>Precipitate Dissolution: H<sub>2</sub>OBa<sup>140</sup> and Sr<sup>89</sup> used as tracer for alkaline earths.Ce<sup>144</sup> used as tracer for rare earths.

Separation of Ba from Fe, Cr, and Ni was complete in all cases.

Analyses									
Ba		Sr		Total Rare Earths		Al		Na	
g in Feed	% in Prod.	g in Feed	% in Prod.	g in Feed	% in Prod.	g in Feed	% in Prod.	g in Feed	g in Prod.
0.86	98.1	0.04	100.0	1.98	16.5	0.49	<1.05	137.9	0.156
0.88	98.2	~0.025	> 99	0.13	3.5	2.48	--	137.5	0.156
0.88	98.7	<0.002	~96	0.003	*	0.014	<62.5	~137	0.028
1.89	98.9	0.16 0.19	~99.5	1.52	14.4	5.37	12.6	136.3	0.208
1.93	97.6	0.006	> 99	1.20	8.9	0.42	1.27	--	--
2.0	99.6	0.02	95.2	Tracer Only	5.8	--	--	153.5	0.03
2.0	99.1	0.004	94.3	0.06	3.1	0.5	0.32	--	--
2.04	98.5	<0.003	~73.1	3.64	48.4	0.82	0.64	~137	1.25
2.05	99.4	0.006	~99	0.013	*	0.007	71.4	~137	0.156

\*Background

Table 7

Caustic-Sulfate Process: Effect of Precipitation Conditions on Barium Sulfate YieldCaustic Dissolution:

A natural uranium MTR assembly was sectioned transversely into 10-g samples which were irradiated and dissolved in caustic; dissolving conditions: 3.6 M NaOH, 3.6 M Al, 1.8 M NaNO<sub>3</sub>

Acid Dissolution:

Neutralize with 6 M H<sub>2</sub>SO<sub>4</sub> to: 0.8 M Al, 0.08 M NO<sub>3</sub><sup>-</sup>, 0.2 M H<sup>+</sup> and add barium carrier. Reflux 2 hr; filter, using 1-in. cake of analytical grade Celite filter aid.

Wash: 200 ml of 1.0 M H<sub>2</sub>SO<sub>4</sub>; 200 ml of H<sub>2</sub>O

Precipitation Conditions		Temperature (°C)	Barium Loss (%)		Product Barium Sulfate Yield (%)
Sulfate Molarity	Barium Molarity (x 10 <sup>5</sup> )	Filtration and Wash	Filtrate	Sulfuric Acid Wash	
2.0	1.79	25	3.4	0.46	96.3
2.0	3.58*	25	1.2	0.68	98.1
2.0	3.58*	90-100	3.6	1.36	95.1
2.0	3.58*	90-100	3.8	3.2	92.8
2.5	2.15	25	5.1	1.2	93.9

\*Equivalent to 1.0 g of barium per assembly.

Table 8

Comparison of the Ion-Exchange Processes for Purification of Barium<sup>140</sup>

These procedures are designed to process the BaSO<sub>4</sub> produced by the caustic sulfate precipitation. The percentages represent the fractions of the total present in the MTR Assembly.

Process	Column Size (in.)	Ion Exchange						Estimated Evaporation Time (hr)	Precipitation (85% HNO <sub>3</sub> )		Shipping Cone Evaporation (hr)	Final Product (% of Total)				Total Overall Time (hr)
		Volume (liters)	Column Product (% of Total)			Na (g)	Total Time (hr)		No. of Pptn's	Total Time (hr)		Final Product (% of Total)			gm Na	
			Ba	Sr	Ce							Ba	Sr	Ce		
Nitric acid	6 by 10	34	97	0.2	20	0	20	3	3	3	2	95.5	0.2	0.006*	0	28
Nitric acid-Versene	6 by 14	34	97	0.02	10	3.7	17	3	2	2	2	96	0.02	0.02*	0.01	24
Versene (requires pH adjustment of feed)	4 by 7	8	98	0.02	0.06	85	5.2	1	1	1	2	97	0.02	0.003	0.01	9

\*Calculated, assuming a cerium decontamination factor of 20.0 per precipitation.

Table 9

Sulfuric Acid Process: Separation of Barium Sulfate from Uranium and Aluminum by Filtration

Sample Preparation: A natural uranium MTR assembly was sectioned transversely into 10-g samples which were irradiated and used in dissolving experiments.

- Conditions:
- (1) Dissolve the sample as indicated using 200 mg of  $Hg^{+2}$  as catalyst
  - (2) Add 2.18 mg of Ba and 2.18 mg of Sr
  - (3) Digest 1 hr at boiling point
  - (4) Cool to 25°C and filter, using a filter-aid precoat on a 2.5-in.-diameter, "H" porosity, stainless steel filter
  - (5) Wash with three 30-ml volumes of 1.0 M  $H_2SO_4$  and three, 20-ml volumes of  $H_2O$
  - (6) Dissolve barium precipitate in Versene and draw the solution through the filter
  - (7) Refilter (4) through No. 42 quantitative paper and wash with 1.0 M  $H_2SO_4$  and  $H_2O$ ; dissolve precipitate in Versene

Conditions		Product Analysis - % of Total				
Dissolver	Filter Precoat	Amt. Retained on No. 42 Paper	Amt. Retained on Filter Aid			
		Ba	Ba	Sr	U	Al
Dissolve in 350 ml of 3.0 M $H_2SO_4$ - 0.3% $H_2O_2$ ; final Al = 1.0 M	1/2 in. of Solka-Floc (BW 40)	1.0	>93	7.14	0.19	--
		5.37	96.8	8.45	0.032	0.3
	1/2 in. of c.p. Celite	2.77	~91	--	--	--
		80*	81.8	~2.3	<0.05	--
Dissolve in 300 ml of 4.8 M $HNO_3$ ; add $H_2SO_4$ and evaporate to 2.0 M Al and 1.0 M $SO_4^{=}$	3/4 in. of c.p. Celite	1.38	95.3	5.0	<0.013	0.07
		1/4 in. of Celite-545	1.07	~37	--	--
Dissolve in 294 ml of 2.4 M $H_2SO_4$ - 1.6 M $HNO_3$ ; final Al = 1.0 M	1/4 in. of Celite-545	7.6	71.8	5.0	0.05	--

\*Warm when filtered through Celite filter cake.

Table 10

Nitric Acid Process: Separation of Barium from Aluminum and Uranium  
by Crystallization from 70% Nitric Acid

Sample Preparation: A natural uranium MTR assembly was sectioned transversely into 10-g samples which were irradiated and used in dissolving experiments.

Conditions: 1st Cycle: (1) Dissolve sample in 70% HNO<sub>3</sub>, 4 moles of acid per mole of Al; 200 mg of Hg<sup>2+</sup> as catalyst.  
(2) Add 2.18 mg of Ba and 2.18 mg Sr.  
(3) Evaporate to 86 ml and add 503 ml of 82% HNO<sub>3</sub>, ~0.6 M Al-70% HNO<sub>3</sub>; heat to 80°C; cool and filter through a medium sintered glass filter.  
(4) Wash twice with 196 ml of cold 90% HNO<sub>3</sub>.

2nd Cycle: 1/100 1st Cycle (actual experiments performed on 150-ml scale).

(5) Combine filtrates and evaporate to 0.86 ml.  
(6) Add 5.03 ml of 82% HNO<sub>3</sub>; heat to 80°C, cool, and filter.  
(7) Wash with 1.96 ml cold 90% HNO<sub>3</sub>.  
(8) Repeat steps (6) and (7).  
(9) Dissolve cake in water.

Crystallization Temperature	1st Cycle, Filtrate Analysis (% of Total)				2nd Cycle, Cake Analysis (% of Total)			
	Al	U	Ba	Sr	Al	U	Ba	Sr
Both Cycles: -10°C	1.4	99.4	96.3	96.6	1.4	0.09	95.8	95.7
Both Cycles: 0°C	3.0	99.8	99.4	99.1	2.9	0.08	98.6	98.1
1st Cycle: -15°C 2nd Cycle: 0°C	1.8	99.8	98.5	98.7	1.8	0.03	97.2	97.9

Table 11

Nitric Acid Process: Separation of Barium from Aluminumby Precipitation of Aluminum Nitrate from 85% Nitric Acid

Sample Preparation: A natural uranium MTR assembly was sectioned transversely into 10-g samples which were irradiated and used in dissolving experiments.

- Conditions:
- (1) Dissolve sample in 70%  $\text{HNO}_3$ ; 3.3 moles of acid per mole of Al; 200 mg of  $\text{Hg}^{2+}$  as catalyst.
  - (2) Add 2.18 mg of Ba and 2.18 mg of Sr (theoretical amount) for runs 10C to 18C.  
Add 4.36 mg of Ba and 4.36 mg of Sr for Run 19C.  
Add 21.8 mg of Ba and 21.8 mg of Sr for Run 20C.
  - (3) Add an equal volume of 70%  $\text{HNO}_3$  and evaporate to the desired Al molarity.
  - (4) Add an equal volume of 98%  $\text{HNO}_3$  for Runs 10C to 16C.  
Add 1.57 times this amount for Runs 18C to 20C.
  - (5) Filter through a medium sintered glass filter and wash with an equal volume of 85%  $\text{HNO}_3$ .
  - (6) Dissolve precipitate in water and repeat steps (3), (4), and (5).

Run No.	Molarity of Aluminum at Precipitation	Filtrate Analysis (% of Total)				Ba Material Balance %
		Al	U	Ba	Sr	
18C	0.47	10.3	99.9	71.8	45.7	72.6
10C	0.65	11.0	98.5	81.1	98	83.6
13C	0.9	6.0	99.8	56.7	45.4	87.5
15C	1.25	6.4	99.3	72.4	84.2	86.5
16C	1.5	4.7	99.3	47.8	44.0	113.0
19C	0.47	12.4	99.8	100	92.5	121.8
20C	0.47	12.0	99.8	96.8	97.6	104.1

Table 12

Purification of Barium<sup>140</sup> by the Hydrochloric

Acid Precipitation Process

Conditions: 12-Day Irradiation System - 1/2 Scale

0.47 g of Ba + Ba<sup>140</sup> Tracer                      0.8 g of Ce } + Ce<sup>144</sup> Tracer  
 0.38 g of Sr + Sr<sup>89</sup> Tracer                      1.6 g of La }  
 6.5 g of Al

First HNO<sub>3</sub> Precipitation; 8.0 liters of ~85% HNO<sub>3</sub>.  
 For other conditions see Flowsheet, Figure 21.

1st HNO <sub>3</sub> Separation	Per Cent Distribution			
	Ba	Sr	Ce	Al
Filtrate	(3.0)*	2.5	25	
Wash	(0.8)	3.8	(1.9)	
Precipitate	$\frac{>100}{>100}$	$\frac{>100}{>100}$	$\frac{73}{99.9}$	11.1
1st HCl Separation				
Filtrate	5.7	82	68	3.5
Wash	1.9	4.2	2.0	
Precipitate	$\frac{88}{95.6}$	$\frac{5.0}{91.2}$	$\frac{0.3}{70.3}$	$\frac{7.0}{10.5}$
2nd HCl Separation				
Filtrate	4.6	2.5	0.9	5.0
Wash	1.4	0.0	0.0	
Precipitate	$\frac{87}{93.0}$	$\frac{0.9}{3.4}$	$\frac{0.0}{0.9}$	$\frac{2.0}{7.0}$
2nd HNO <sub>3</sub> Separation				
Filtrate	(0.3)	(0.0)	(0.0)	1.5
Wash	(0.0)	(0.0)	(0.0)	
Precipitate	$\frac{95}{95}$	$\frac{0.1}{0.1}$	$\frac{(0.0)}{0.0}$	$\frac{0.01}{1.5}$

Total barium loss in HCl separations = 13.5%

\*Parentheses indicate disintegration rates <100/min/ml.

Table 13

Purification of Barium<sup>140</sup> by the Hydrochloric

Acid Precipitation Process

Conditions: 20-Day Irradiation System, 1/2 Scale

0.70 g of Ba + Ba<sup>140</sup> Tracer                      1.3 g of Ce }  
 0.60 g of Sr + Sr<sup>89</sup> Tracer                      2.6 g of La } + Ce<sup>144</sup> Tracer

First HNO<sub>3</sub> Precipitation; 8.0 liters of ~85% HNO<sub>3</sub>.

For other conditions see Flowsheet, Figure 21.

1st HNO <sub>3</sub> Separation	Per Cent Distribution			
	Ba	Sr	Ce	Al
Filtrate	(1.0)*	2.5	24.8	--
Wash	(0.1)	0.7	(2.9)	--
Precipitate	<u>100</u>	<u>96.7</u>	<u>73.1</u>	<u>24</u>
	100	99.9	100.8	
1st HCl Separation				
Filtrate	4.1	57	72	9.9
Wash	1.3	10	1.0	1.1
Precipitate	<u>86</u>	<u>29</u>	<u>(0.1)</u>	<u>11.1</u>
	91.4	96	73.1	22.1
2nd HCl Separation				
Filtrate	5.2	11	(0.1)	3.1
Wash	1.2	2.4	(0.0)	1.2
Precipitate	<u>95</u>	<u>3.0</u>	<u>0.3</u>	<u>7.5</u>
	101.4	16.4	0.4	11.8
2nd HNO <sub>3</sub> Separation				
Filtrate	(0.8)	0.0	(0.1)	8.1
Wash	(0.0)	0.0	(0.0)	
Precipitate	<u>84</u>	<u>2.3</u>	<u>(0.0)</u>	<u>0.01</u>
	84.8	2.3	0.1	8.1

Total barium loss in HCl separations = 11.6%

\*Parentheses indicate disintegration rates <100/min/ml.

Table 14  
Purification of Barium<sup>140</sup> by the Hydrochloric  
Acid Precipitation Process

Conditions: 37-Day Irradiation System, 1/2 Scale

1.0 g of Ba + Ba<sup>140</sup> Tracer  
 1.0 g of Sr + Sr<sup>89</sup> Tracer  
 2.2 g of Ce } + Ce<sup>144</sup> Tracer  
 4.5 g of La }

First HNO<sub>3</sub> Precipitation; 8.0 liters of ~85% HNO<sub>3</sub>.

For other conditions see Flowsheet, Figure 21.

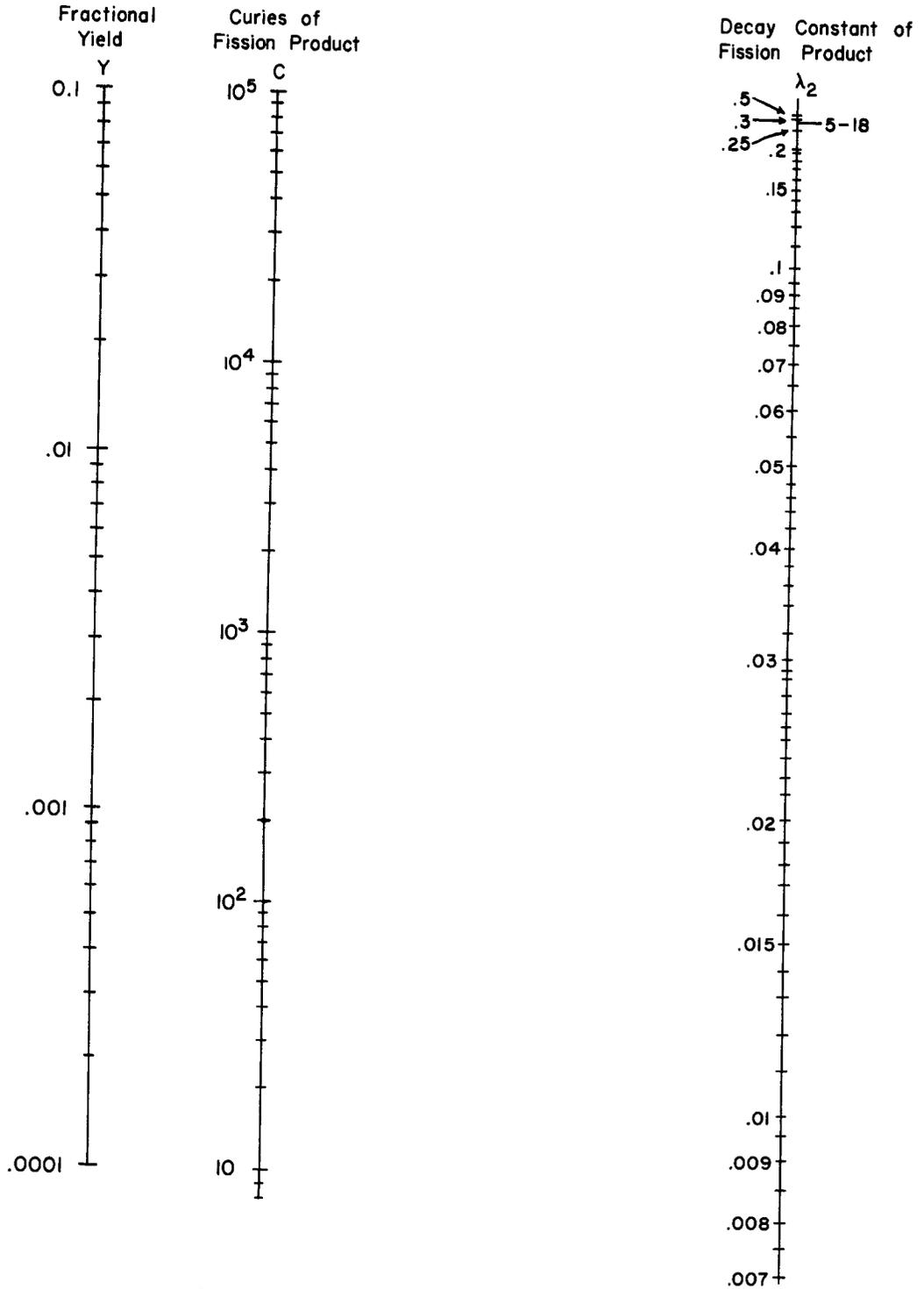
	Per Cent Distribution			
	Ba	Sr	Ce	Al
<b>1st HNO<sub>3</sub> Separation</b>				
Filtrate	(0.8)*	2.3	18.5	
Wash	(0.2)	(0.3)	1.3	
Precipitate	<u>100</u>	<u>97.7</u>	<u>86.5</u>	<u>43</u>
	101.0	100.3	106.3	
<b>1st HCl Separation</b>				
Filtrate	7.3	47.7	82	7.5
Wash	1.1	5.2	2.0	1.3
Precipitate	<u>87.0</u>	<u>27.0</u>	<u>1.4</u>	<u>28</u>
	95.4	79.9	85.4	36.8
<b>2nd HCl Separation</b>				
Filtrate	3.6	36	(0.1)	9.1
Wash	0.7	0.7	(0.0)	1.2
Precipitate	<u>86</u>	<u>1.2</u>	<u>0.3</u>	<u>19</u>
	90.3	37.9	0.4	29.3
<b>2nd HNO<sub>3</sub> Separation</b>				
Filtrate	(0.0)	(0.1)	(0.1)	13
Wash	(0.0)	(0.0)	0.3	1.0
Precipitate	<u>72.5</u>	<u>0.8</u>	<u>?</u>	<u>5.4</u>
	72.5	0.9	<.4	19.4

Total barium loss in HCl separations = 12.7%

\*Parentheses indicate disintegration rates <100/min/ml.

[REDACTED]  
Drawing # 14117

**Figure 1**  
**RADIOACTIVITIES OF FISSION PRODUCTS AT**  
**DISCHARGE PER MTR ASSEMBLY AFTER**  
**12 DAYS IRRADIATION AT 30,000 KW**



$$C = \frac{10^{-14}}{(3.7)(8.64)} \lambda_2 Q$$

Where  $Q = \frac{Y P_0 \lambda_1}{\lambda_2 - \lambda_1} (e^{-12\lambda_1} - e^{-12\lambda_2})$

Figure 2.

UNCLASSIFIED  
Dwg. #14070

Irradiation Decomposition of Versene by Cobalt<sup>60</sup>

Solution: 0.065 M Versenate, pH 6.3; 0.13 M NO<sub>3</sub><sup>-</sup>; 0.33 M Na<sup>+</sup>.

Procedure: (A) Irradiate solutions with Co<sup>60</sup> source, at the indicated rates.  
Bubble water-saturated air through solutions continuously during irradiation.  
(B) Sample and determine Versene concentration and pH:

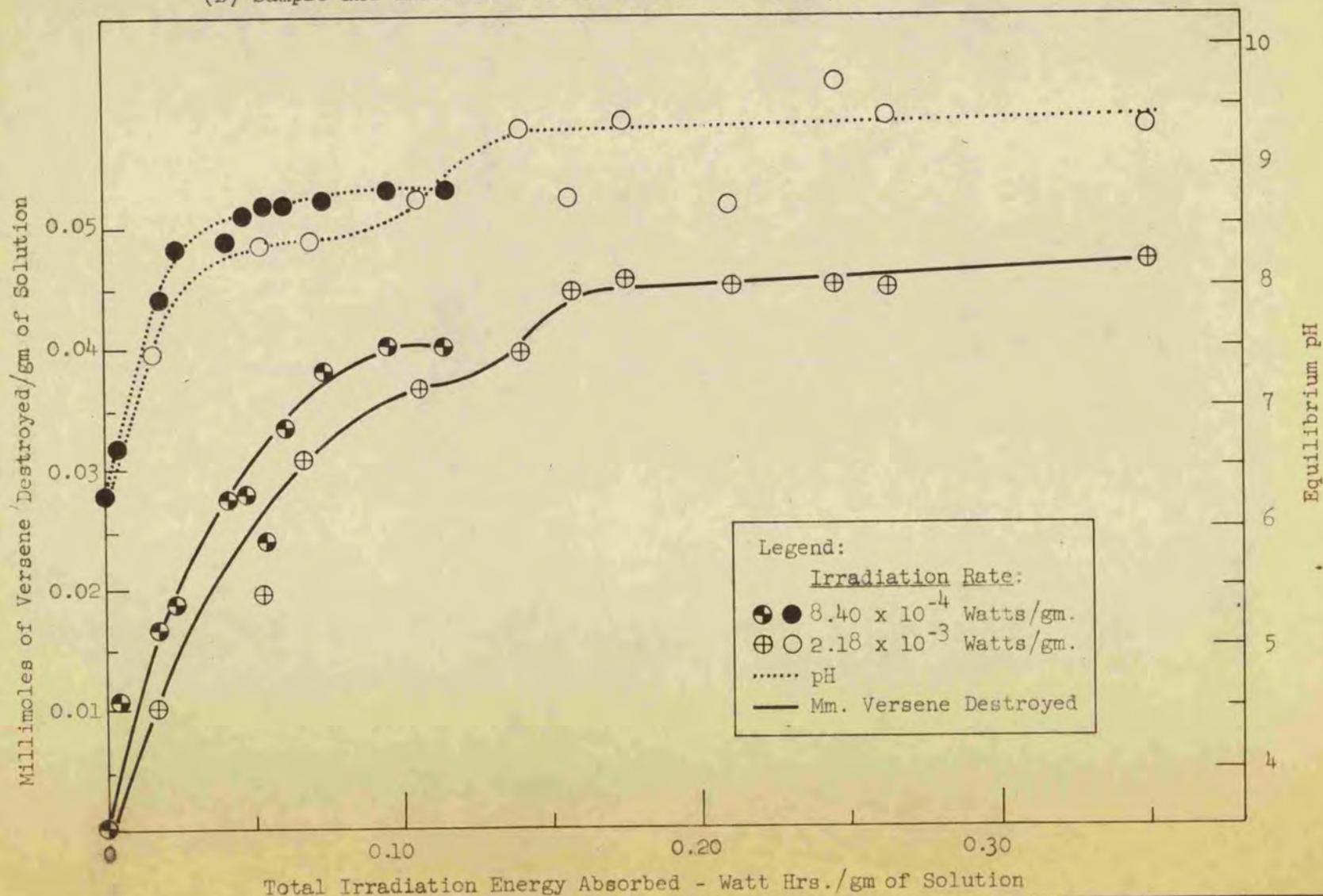


Figure 3

DWG No12795

FLWSHEET: MTR-RaLa PROCESS - Part 1  
PREPARATION OF CRUDE BARIUM<sup>140</sup> BY THE CAUSTIC-NITRATE PROCESS

BASIS: 1 MTR Assembly

162 Moles Aluminum  
 0.63 Moles Uranium  
 $6.8 \times 10^{-3}$  Moles Ba  
 12 day irradiation

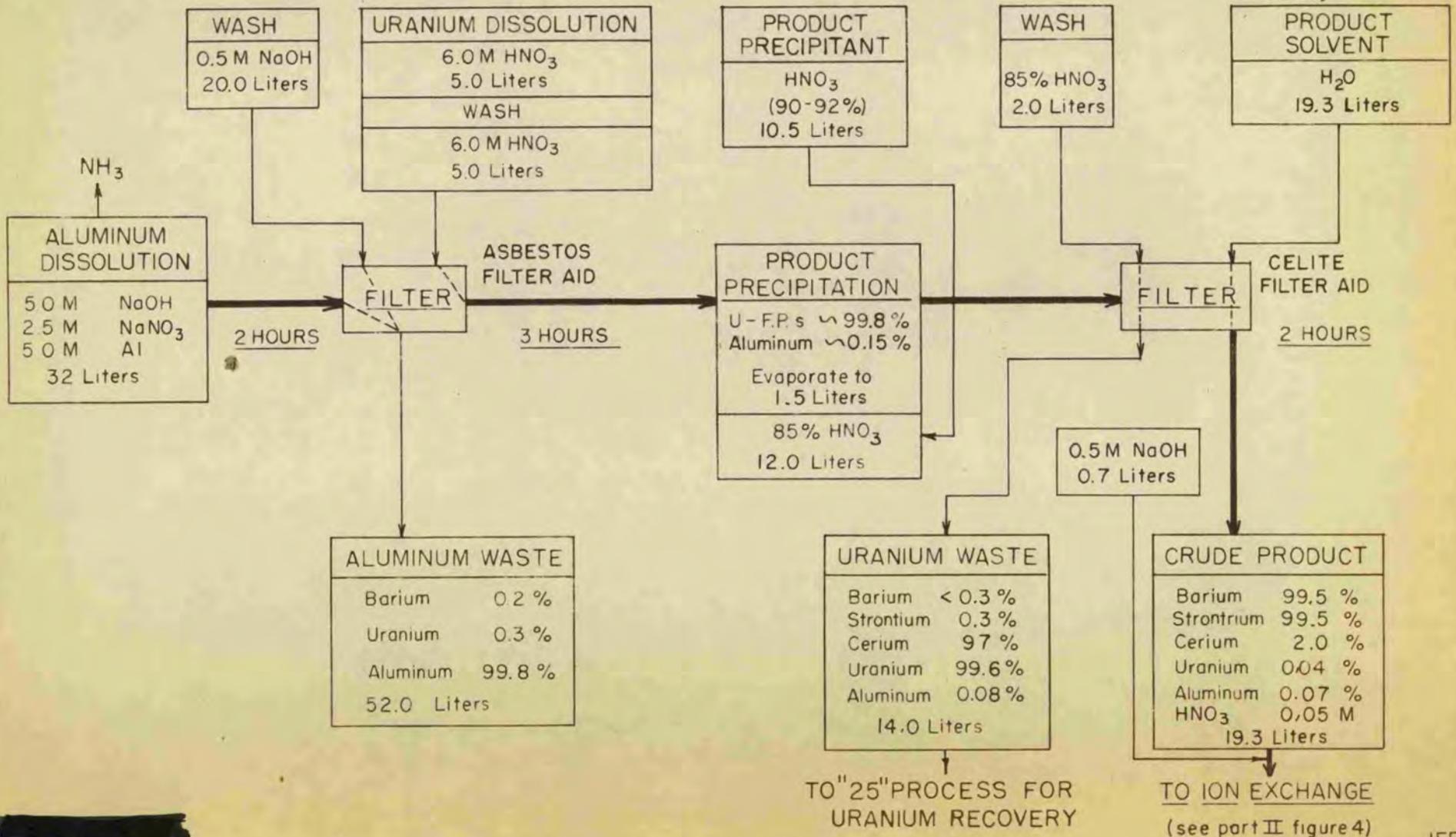
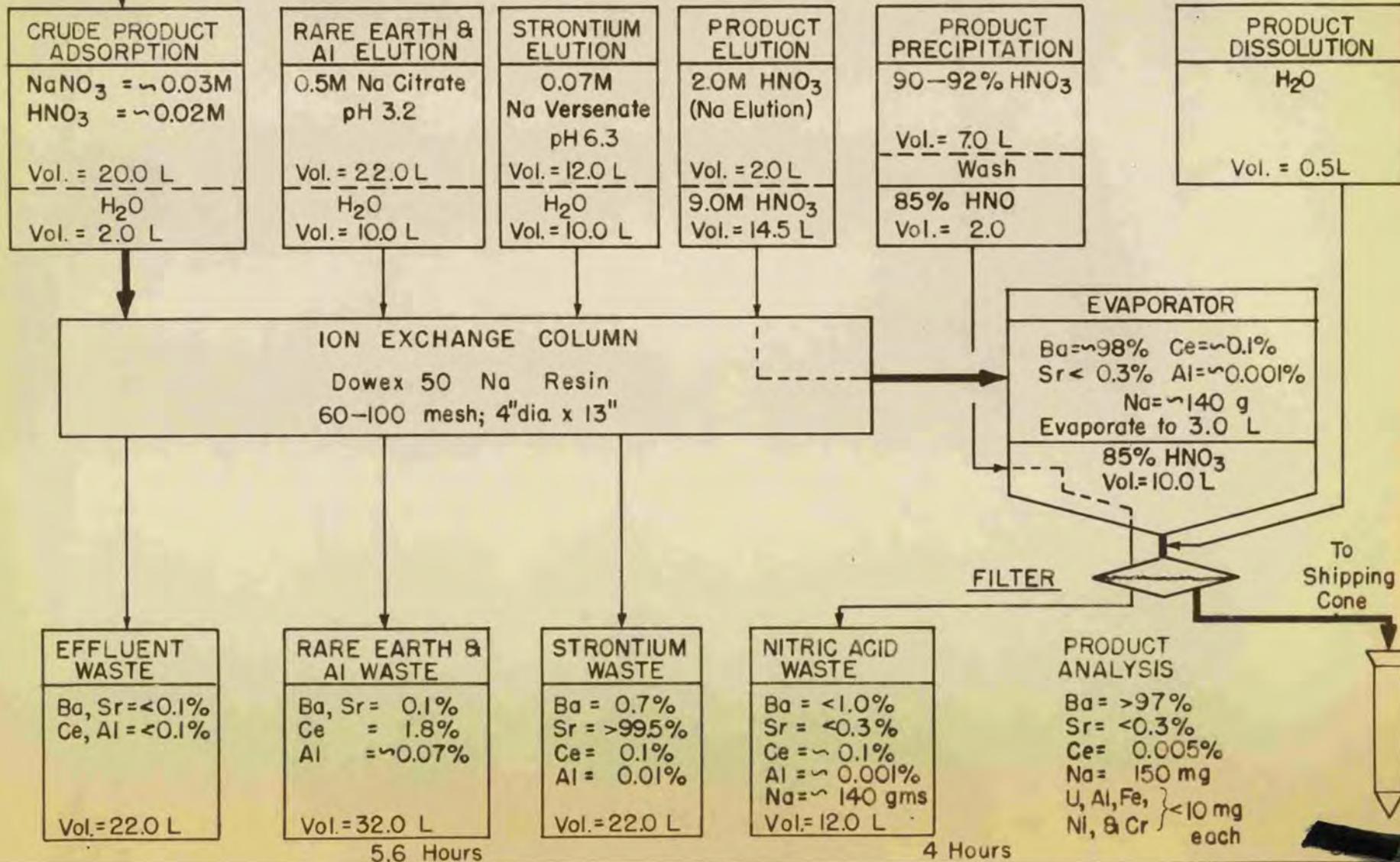


FIGURE 4

FLWSHEET: MTR-RaLa PROCESS-Part II  
PURIFICATION OF BARIUM<sup>140</sup> BY ION EXCHANGE

From Caustic-Nitrate Process (see figure 3)



Dwg. 14581

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Figure 5

HYDROGEN EVOLUTION AS A FUNCTION OF TOTAL IONIC STRENGTH

CONDITIONS: Approximately 20 gm transverse sections of an MTR-Assembly were dissolved in  $\text{NaNO}_3 - \text{NaOH}$  solution. Off gas was collected and analyzed.

KEY: Initial mole ratios are given as  $\text{Al} : \text{NaNO}_3 : \text{NaOH}$ ; Al molarity = final concentration.

LEGEND:

- Function of (NaOH); (Al) and ( $\text{NaNO}_3$ ) constant.
- - - Function of ( $\text{NaNO}_3$ ); (Al) and (NaOH) " "

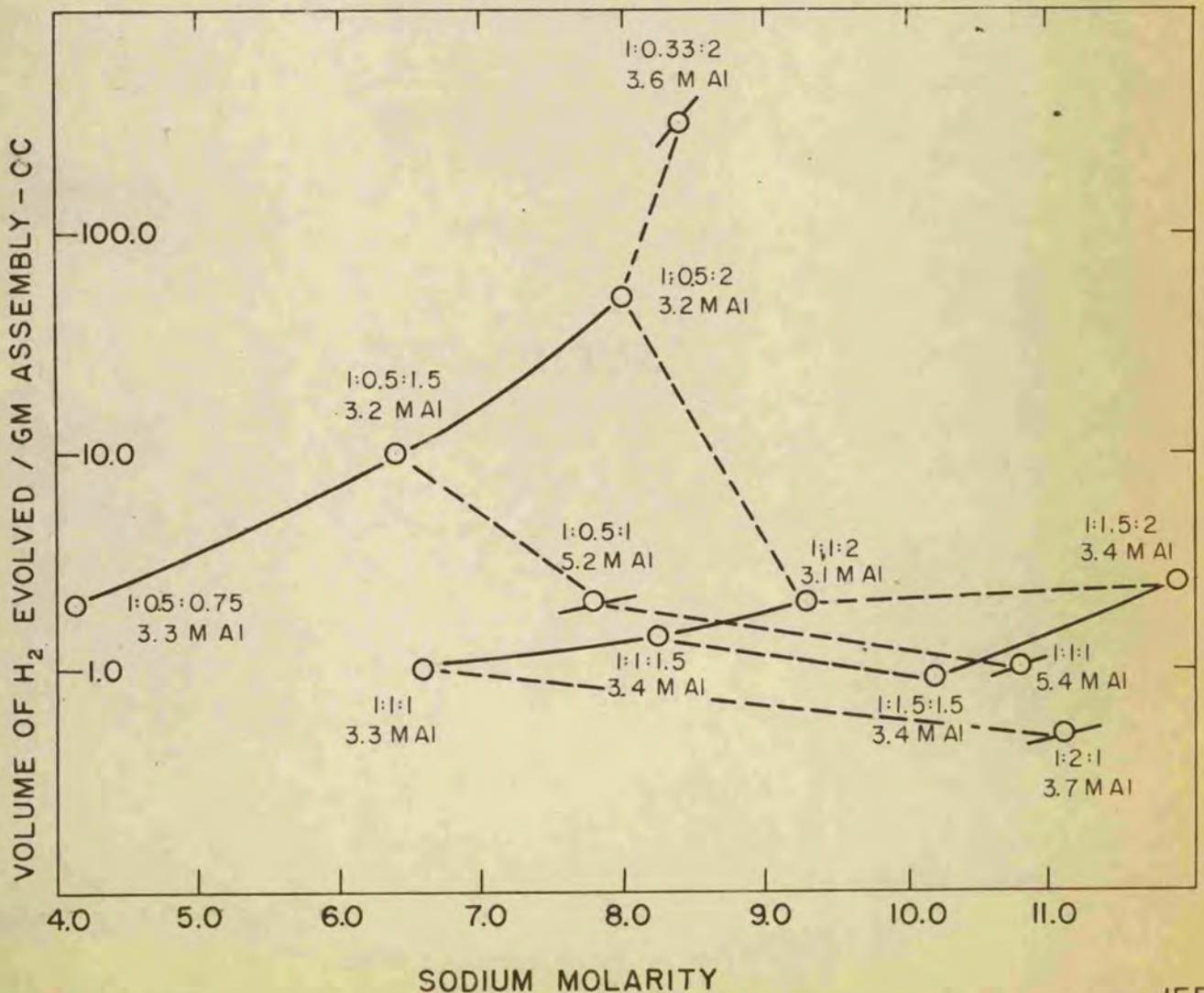


Figure 6

DWG No12794

RATIO OF FINAL NITRITE CONCENTRATION TO ALUMINUM CONCENTRATION AS A FUNCTION OF TOTAL IONIC STRENGTH

CONDITIONS: Approximately 20gm transverse sections of an MTR-Assembly were dissolved in NaOH-NaNO<sub>3</sub> solution.

KEY: Initial mole ratios are indicated as Al: NaNO<sub>3</sub> : NaOH; Al molarity = final concentration.

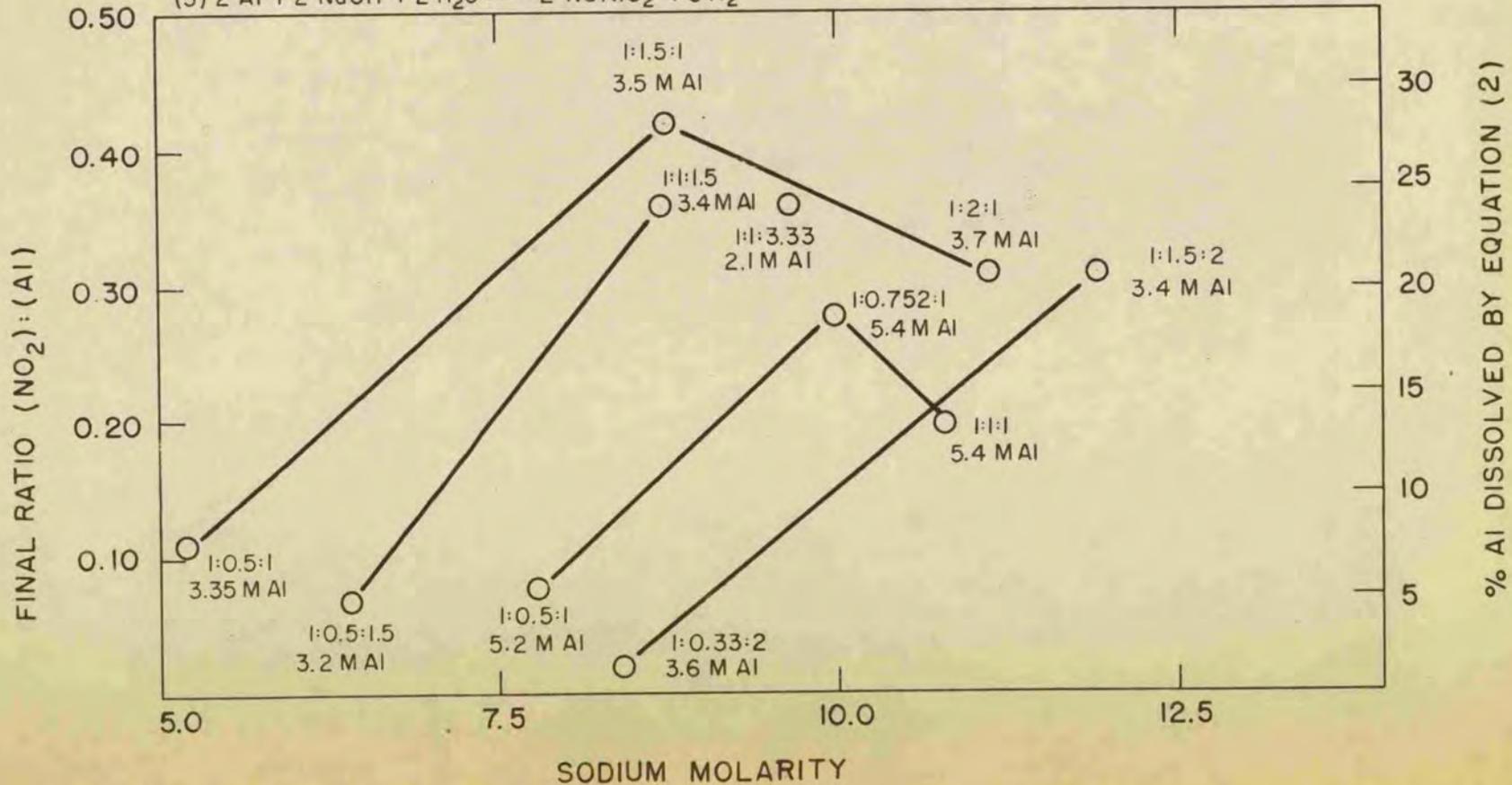
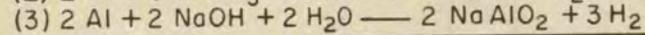
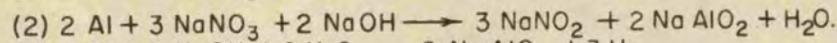
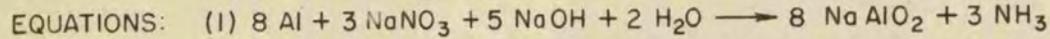


Figure 7

### URANIUM SOLUBILITY AS A FUNCTION OF TOTAL IONIC STRENGTH

CONDITIONS: Approximately 20gm transverse sections of an MTR-Assembly were dissolved in  $\text{NaNO}_3$ -NaOH solution.

KEY: Initial mole ratios are indicated as Al:  $\text{NaNO}_3$ : NaOH; Al molarity = final concentration.

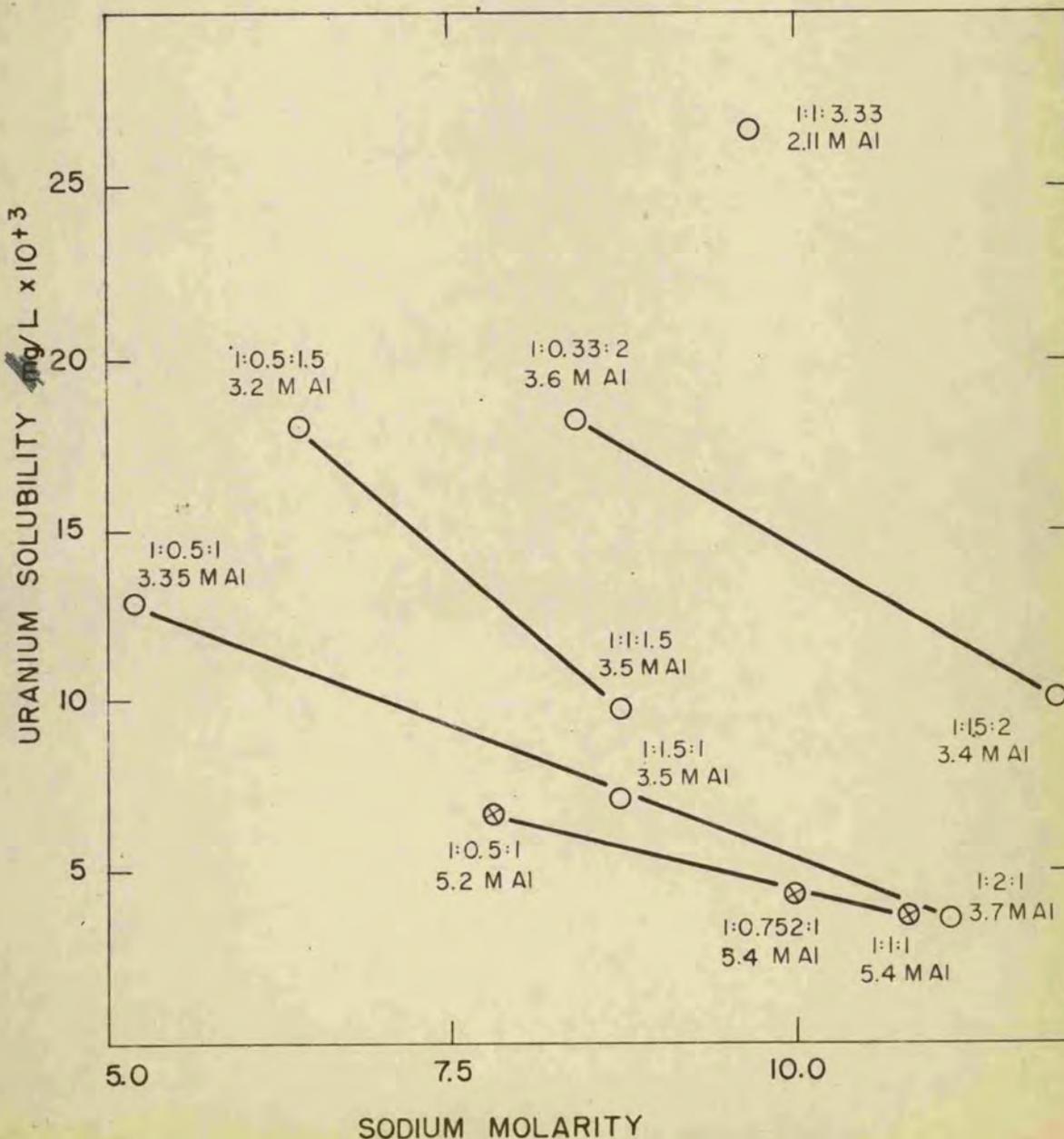


FIGURE 8

SOLUBILITY OF BARIUM NITRATE IN NITRIC  
ACID AT 24.88° C

(Greene, CH, JACS., 59, 1186 - 1188, 1937)

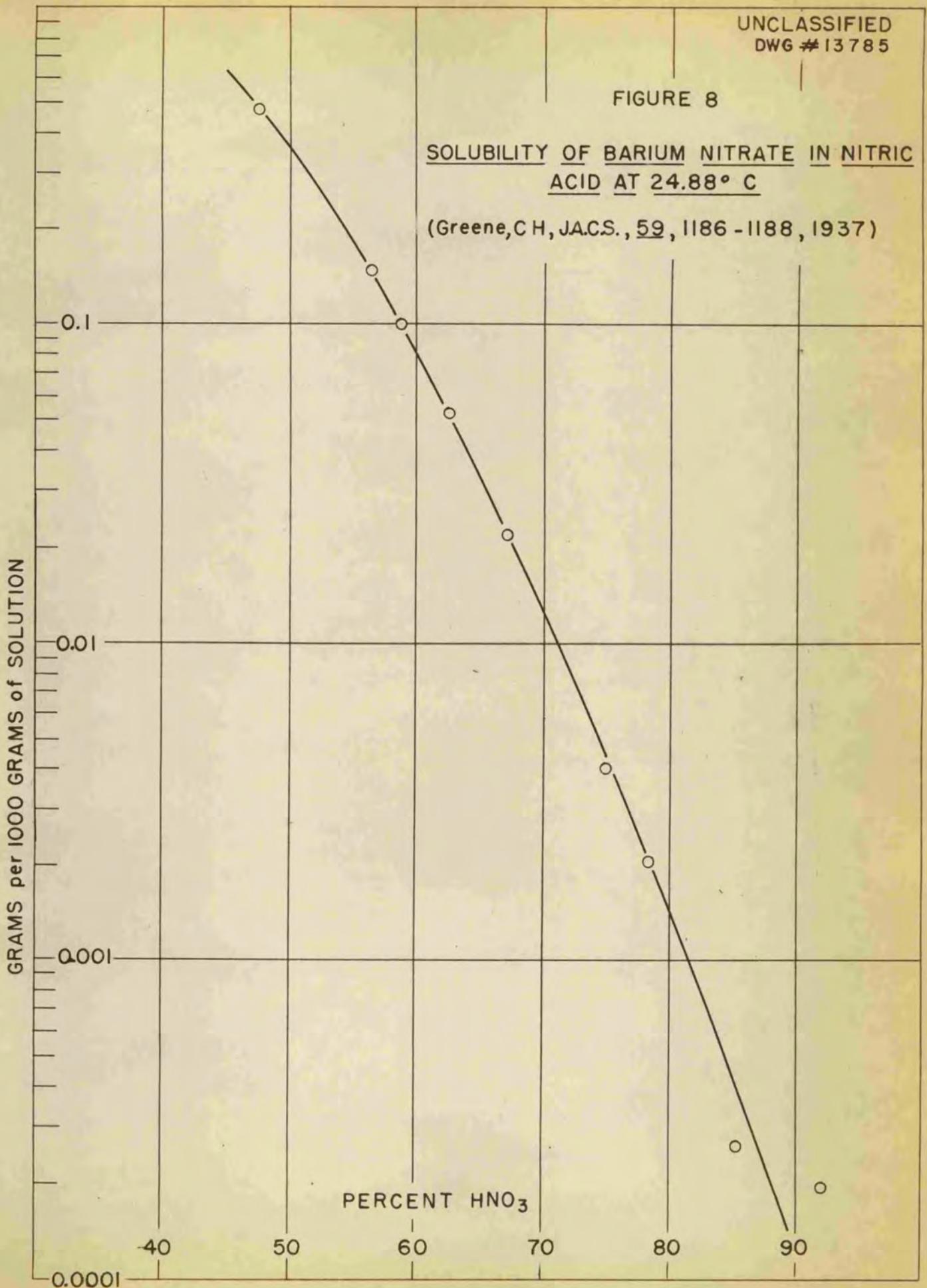


Figure 9

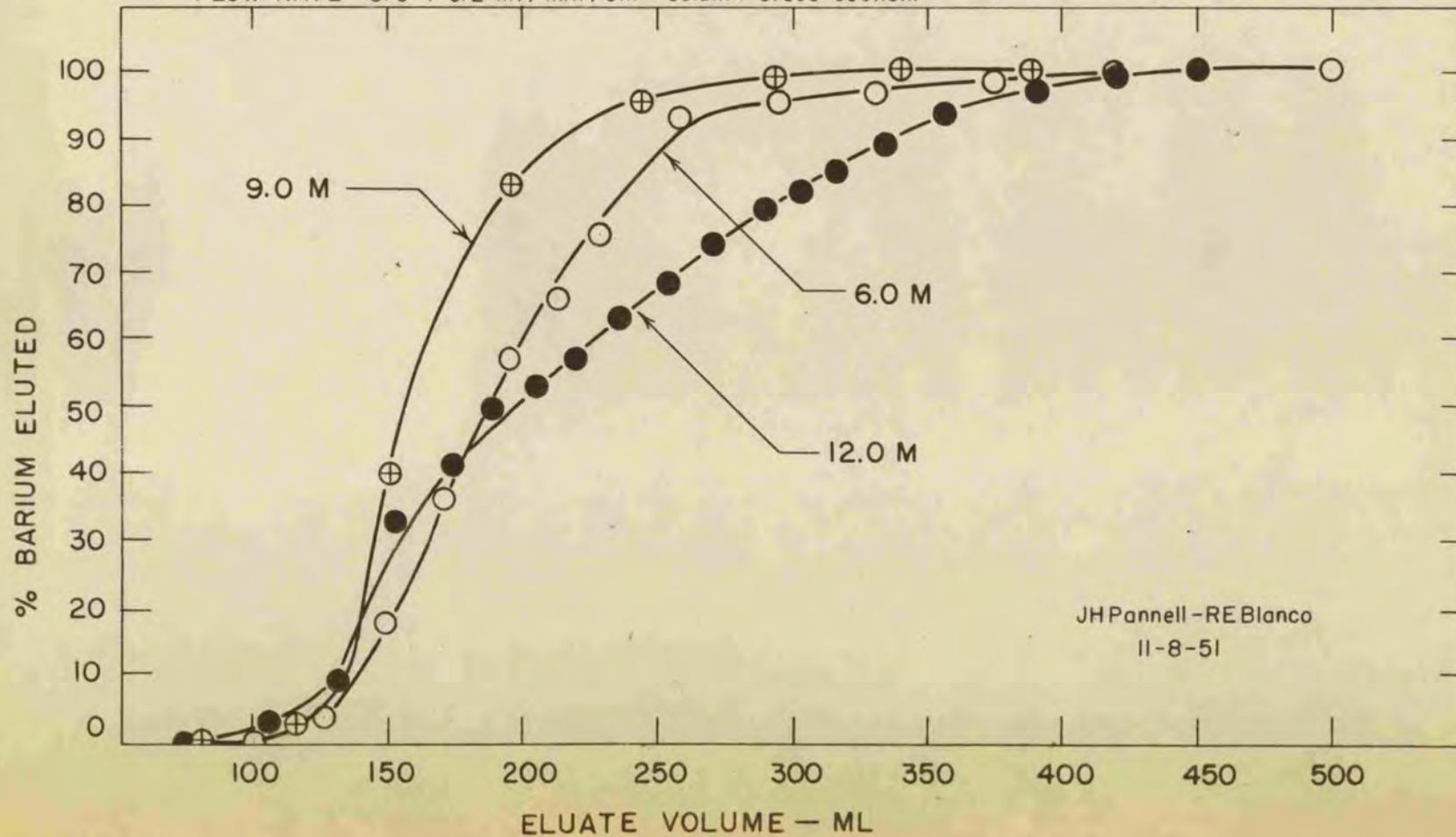
ELUTION OF BARIUM FROM DOWEX-50 RESIN WITH NITRIC ACID

COLUMN: 2.3 cm x 53.7 cm  
Dowex-50-H<sup>+</sup> Resin  
60-100 mesh

ADSORPTION: 10mg Ba + Ba tracer / 50 ml 0.5 M HNO<sub>3</sub>.

ELUTION: HNO<sub>3</sub> (concentration as shown.)

FLOW RATE: 0.3 ± 0.2 ml/min/cm<sup>2</sup> column cross-section.



JHPannell-REBlanco  
11-8-51

FIGURE 10-A  
 FLOWSHEET: MTR-RaLa PROCESS — Part I  
 PREPARATION OF CRUDE BARIUM BY THE CAUSTIC SULFATE PROCESS  
 Basis: 1 MTR Assembly

DWG No 11601

162 Moles Aluminum  
 0.63 Moles Uranium  
 $1.46 \times 10^{-2}$  Moles Barium

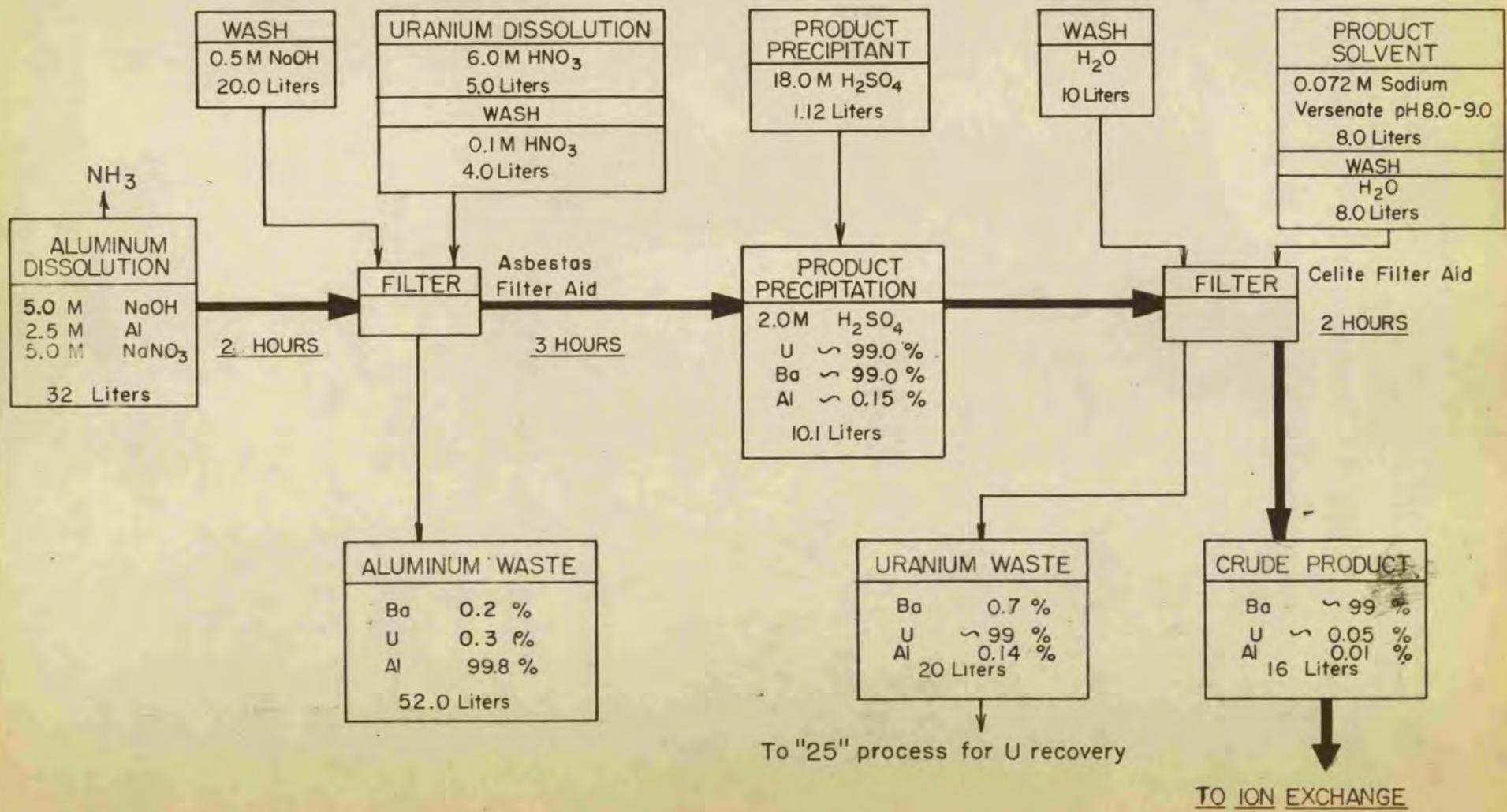
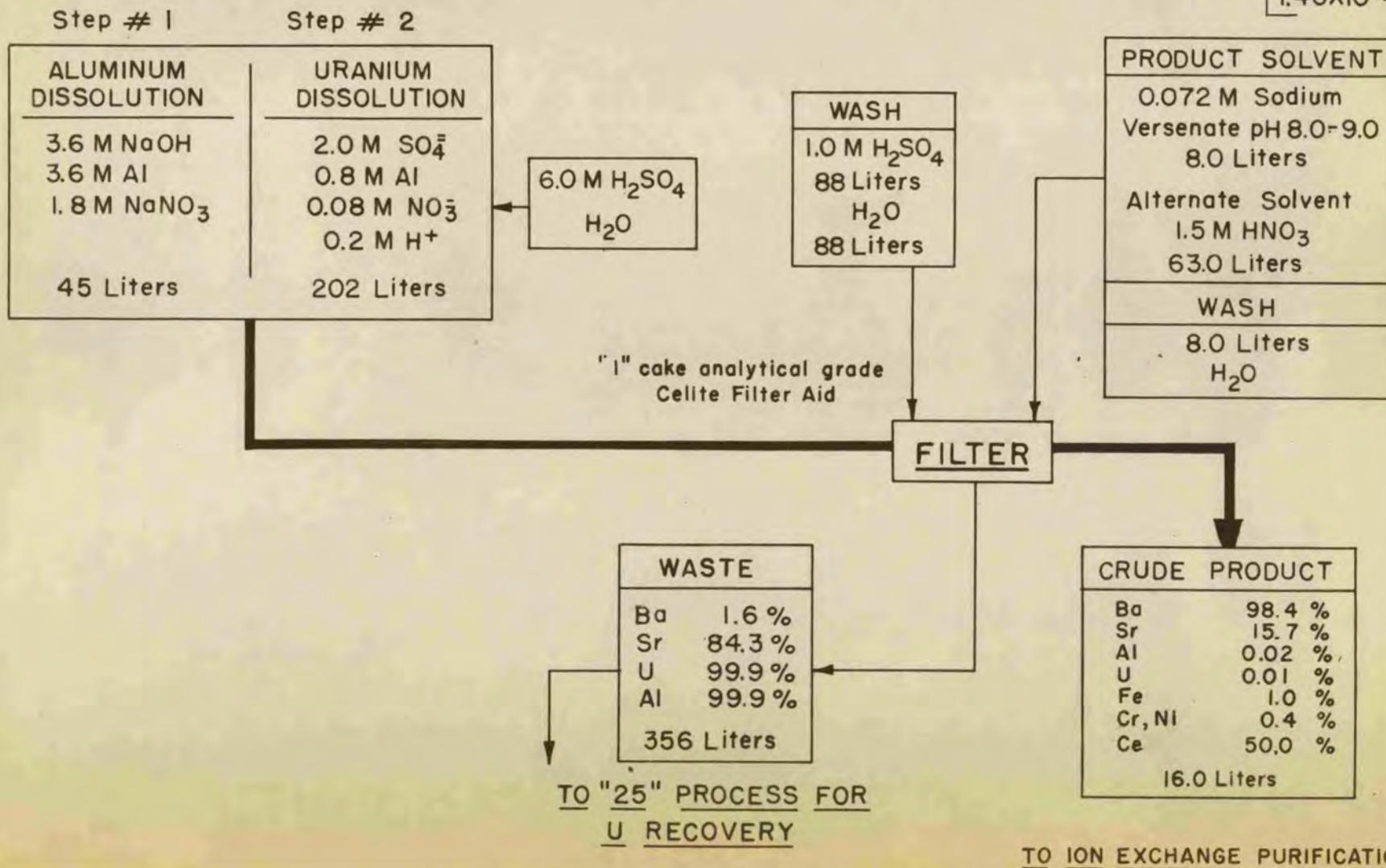
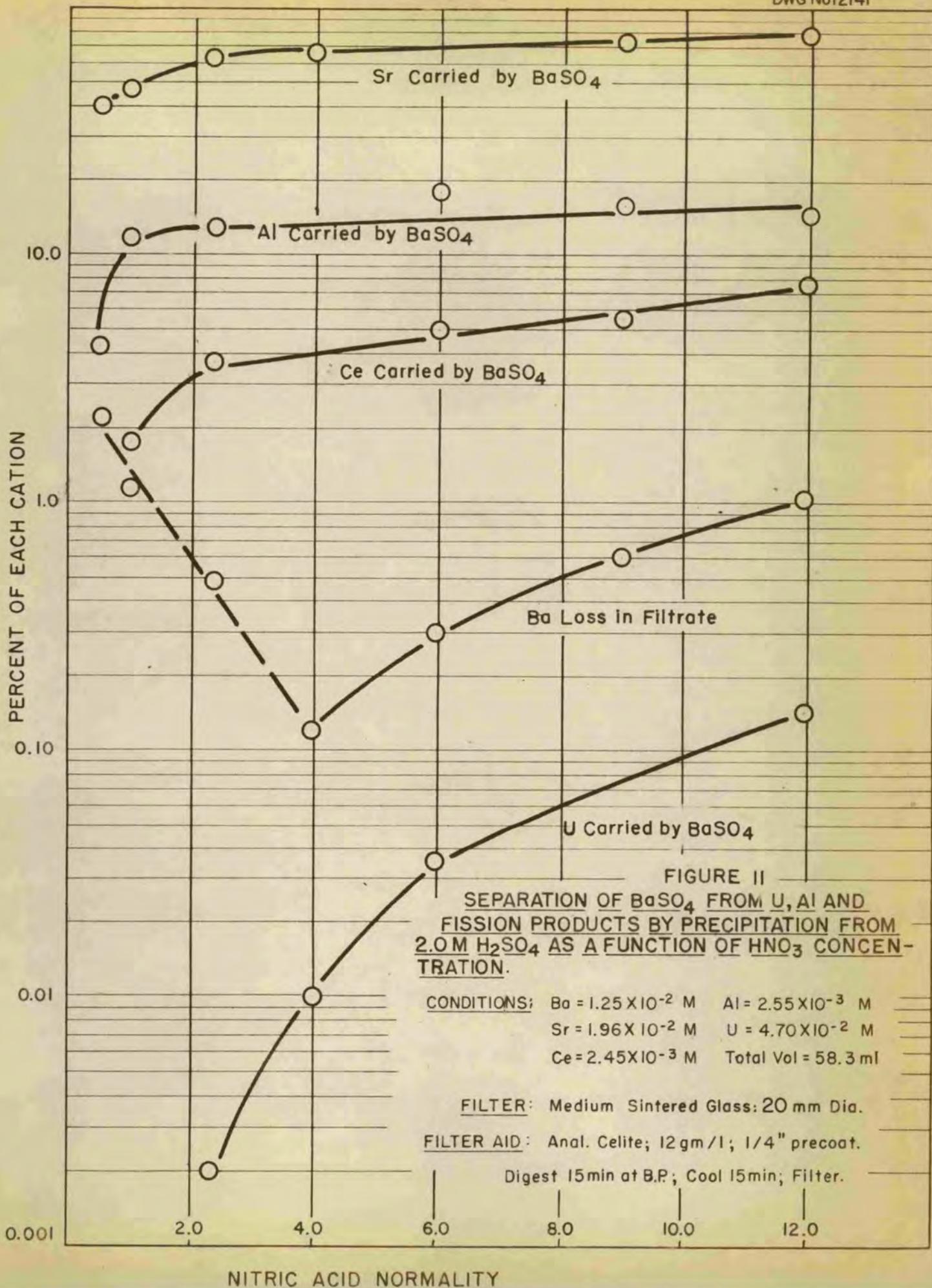


FIGURE 10-B  
 FLOWSHEET: MTR-RaLa PROCESS-Part I  
PREPARATION OF CRUDE BARIUM BY THE CAUSTIC-SULFATE PROCESS

Basis: 1 MTR Assembly

162 Moles Al  
 0.63 Moles U  
 $1.46 \times 10^{-2}$  Moles Ba





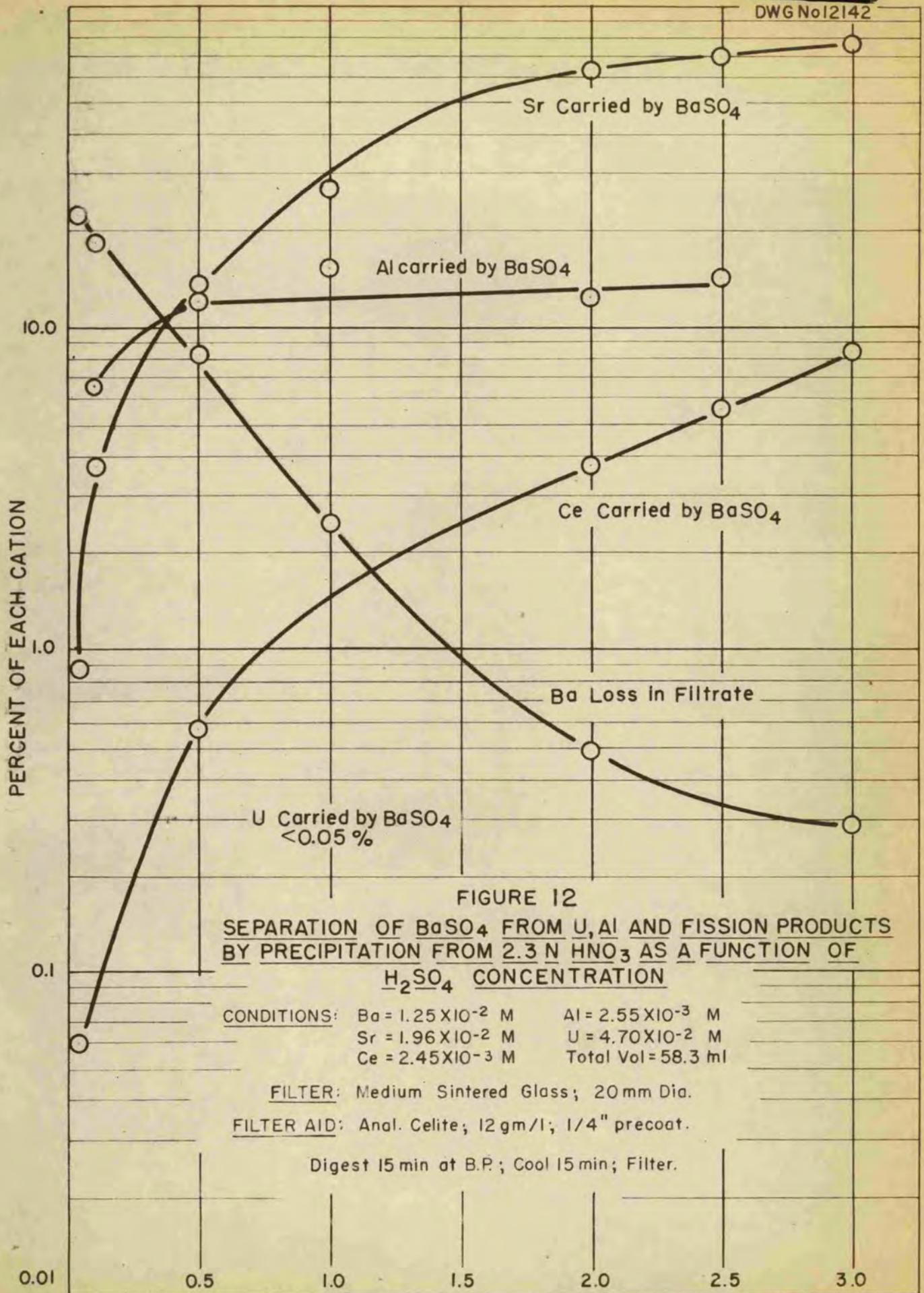


FIGURE 12  
 SEPARATION OF BaSO<sub>4</sub> FROM U, Al AND FISSION PRODUCTS  
 BY PRECIPITATION FROM 2.3 N HNO<sub>3</sub> AS A FUNCTION OF  
 H<sub>2</sub>SO<sub>4</sub> CONCENTRATION

CONDITIONS: Ba = 1.25 X 10<sup>-2</sup> M      Al = 2.55 X 10<sup>-3</sup> M  
 Sr = 1.96 X 10<sup>-2</sup> M      U = 4.70 X 10<sup>-2</sup> M  
 Ce = 2.45 X 10<sup>-3</sup> M      Total Vol = 58.3 ml

FILTER: Medium Sintered Glass; 20mm Dia.

FILTER AID: Anal. Celite; 12 gm/l; 1/4" precoat.

Digest 15 min at B.P.; Cool 15 min; Filter.

SULFURIC ACID MOLARITY

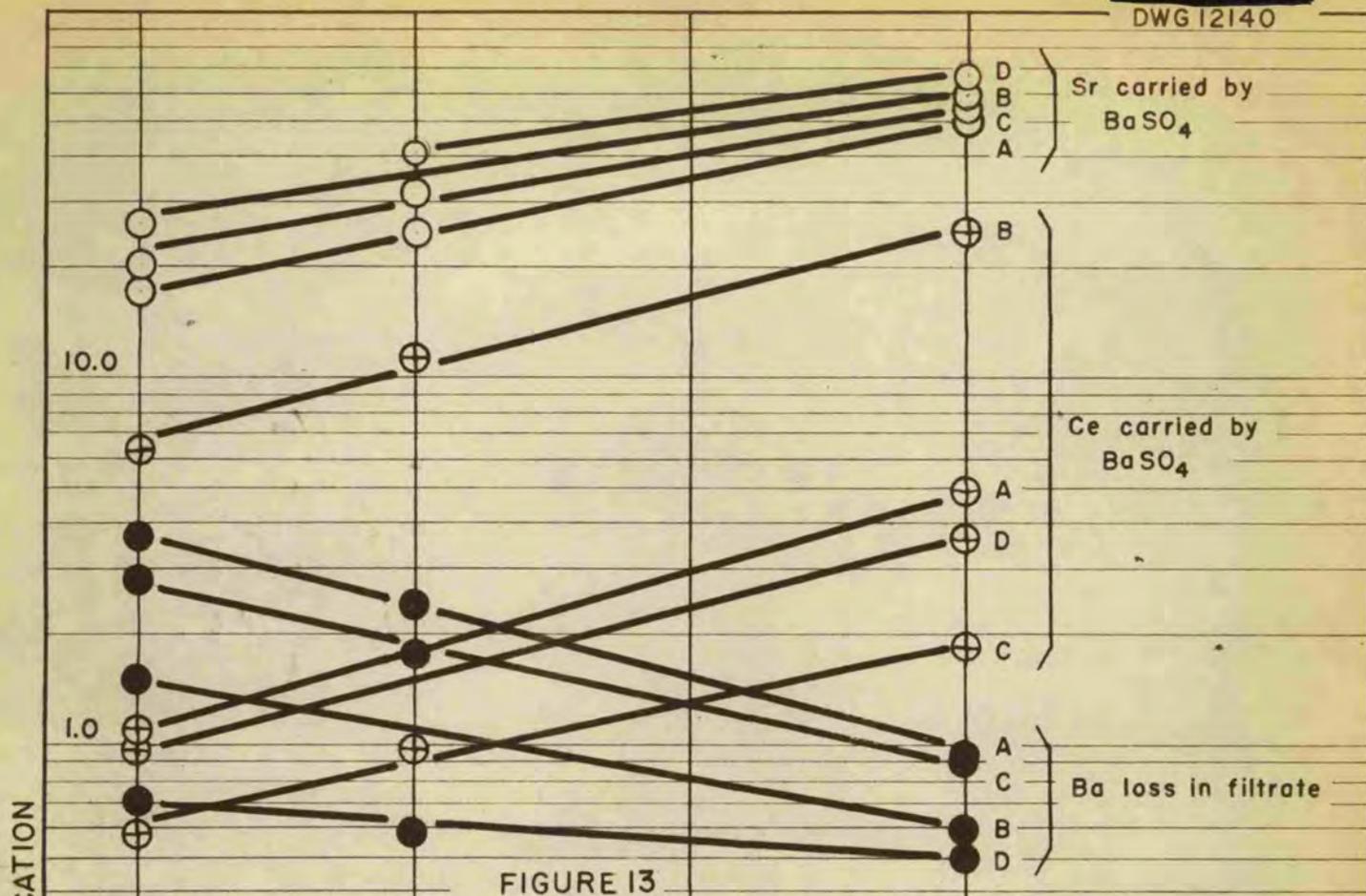


FIGURE 13

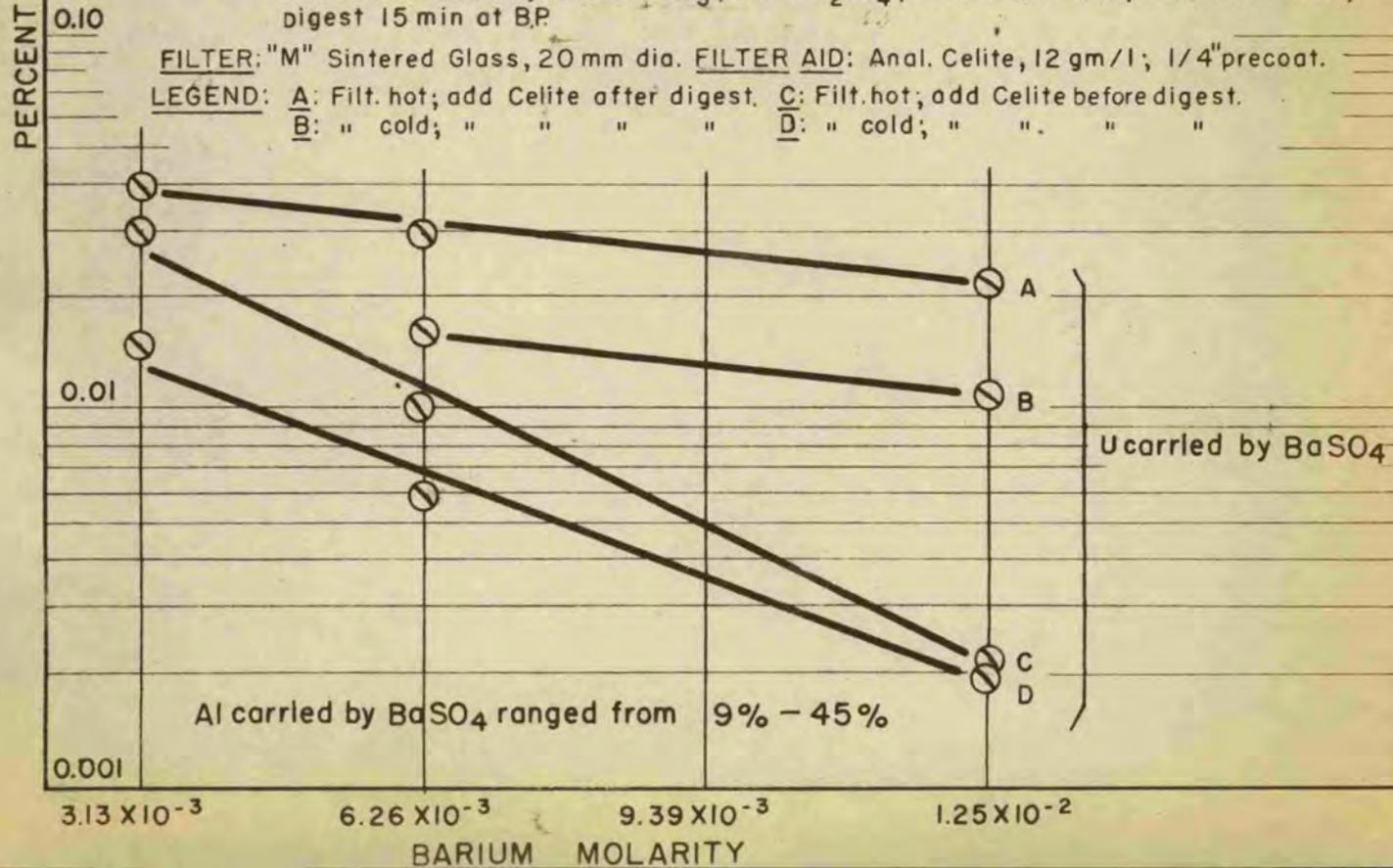
SEPARATION OF BaSO<sub>4</sub> FROM U, Al AND FISSION PRODUCTS BY PRECIPITATION FROM AN HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> SYSTEM AS A FUNCTION OF TEMPERATURE AND BARIUM CONCENTRATION

CONDITIONS: Mole Ratio of Ba, Sr, Ce = 0.728:1.141: 0.143; Vol = 58.3 ml.  $3.13 \times 10^{-3}$  M Ba  $\approx$  0.5 gm Ba / M.T.R Assembly. 2.31 N HNO<sub>3</sub>, 2.0 M H<sub>2</sub>SO<sub>4</sub>,  $4.70 \times 10^{-2}$  M U,  $2.55 \times 10^{-3}$  M Al; digest 15 min at B.P.

FILTER: "M" Sintered Glass, 20 mm dia. FILTER AID: Anal. Celite, 12 gm/l; 1/4" precoat.

LEGEND: A: Filt. hot; add Celite after digest. C: Filt. hot; add Celite before digest.

B: " cold; " " " " " D: " cold; " " " " "



Al carried by BaSO<sub>4</sub> ranged from 9% - 45%

Figure 14  
 SOLUBILITY OF  $\text{BaSO}_4$  IN AQUEOUS SOLUTIONS OF  $\text{HNO}_3$

UNCLASSIFIED  
 DWG. 15784

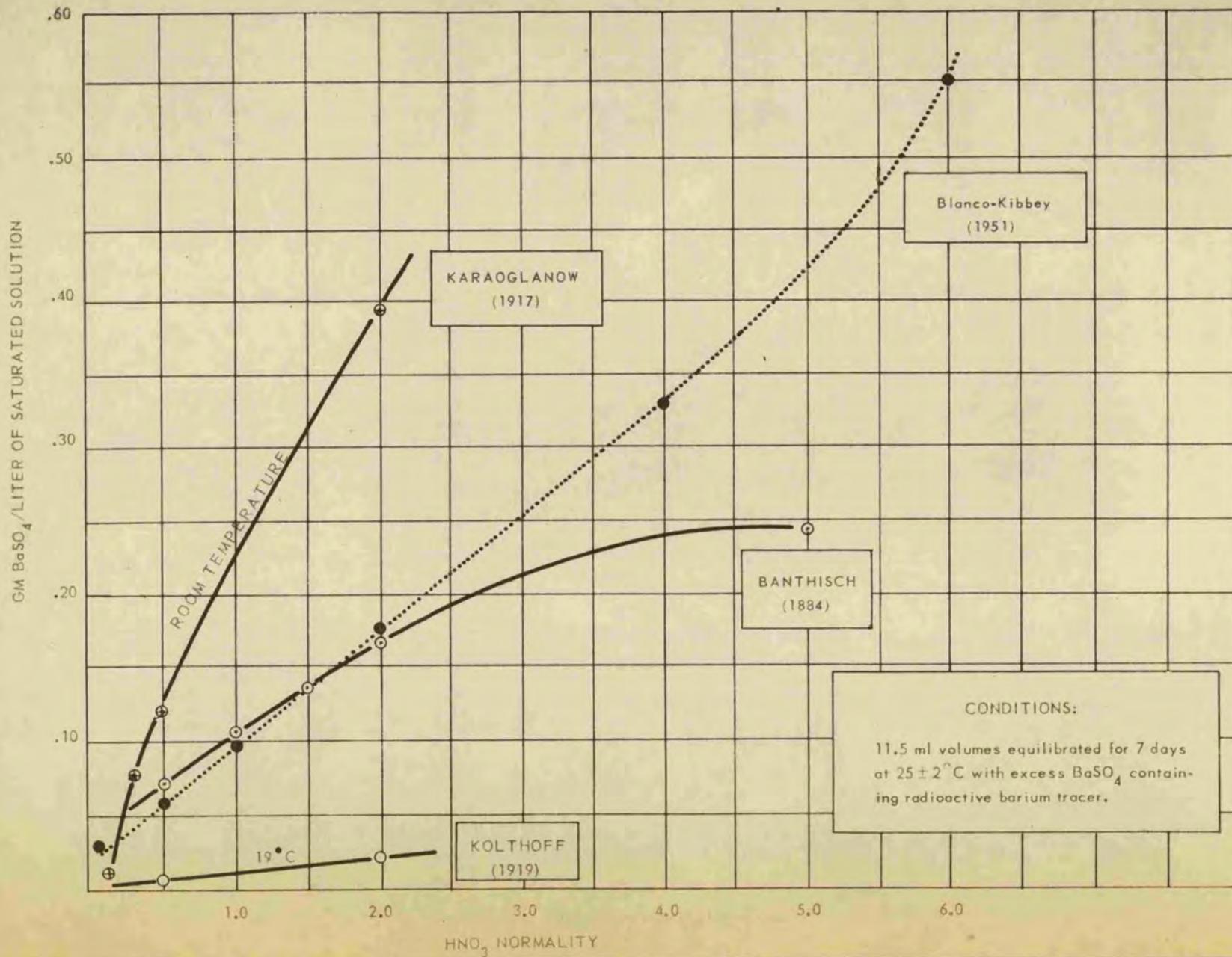


FIGURE 15  
FLWSHEET: MTR-RaLa PROCESS - Part II  
PURIFICATION OF BARIUM BY THE VERSENE ION EXCHANGE PROCESS

DWG 11617

From Caustic Sulfate Process (see figure 10A)

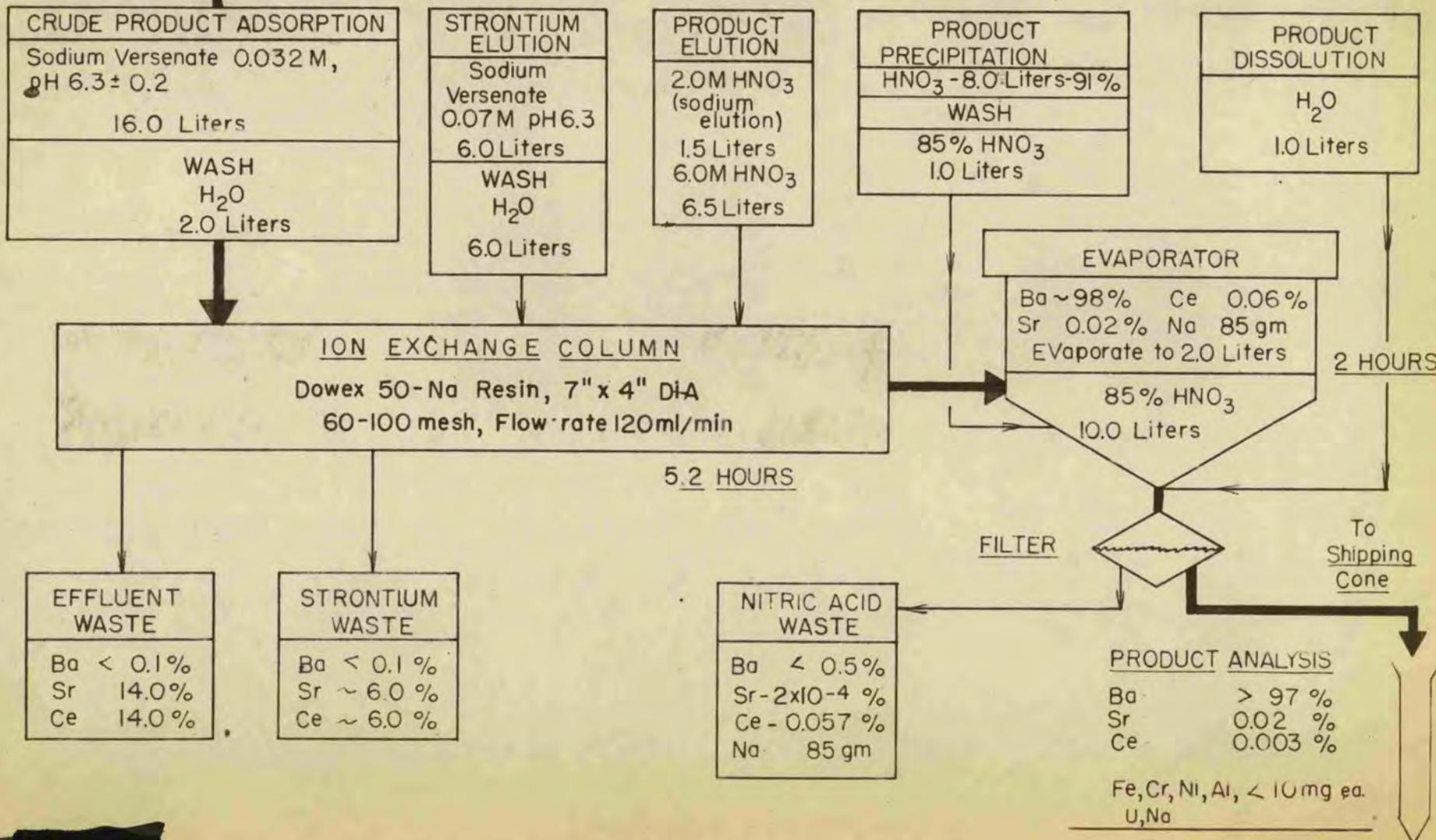


FIGURE 16

DWG No 14217

FLWSHEET: MTR RaLa PROCESS - Part II  
PURIFICATION OF BARIUM BY THE NITRIC ACID ION EXCHANGE PROCESS

From Caustic Sulfate Process  
 (see figure 10B)

CRUDE PRODUCT ADSORPTION
1.5 M HNO <sub>3</sub> 63.0 Liters
H <sub>2</sub> O WASH 2.0 Liters

STRONTIUM ELUTION
1.5 M HNO <sub>3</sub> 225.0 Liters

PRODUCT ELUTION
9.0 M HNO <sub>3</sub> 34.0 Liters

ION EXCHANGE COLUMN Dowex 50 - H <sup>+</sup> Resin 60-100 mesh 10" X 6" Dia. Flow rate = 273 ml/min. Total time 20 hours
--

WASTE
Ba - Sr - Ce - Al < 0.01 % ea.

STRONTIUM WASTE
Ba 1.0 %
Sr 20.0 %
Ce < 0.1 %
Al 0.36 gm

PRODUCT
Ba 97 %
Sr 0.2 %
Ce 20 %
U 0.02 mg
Al 80 mg

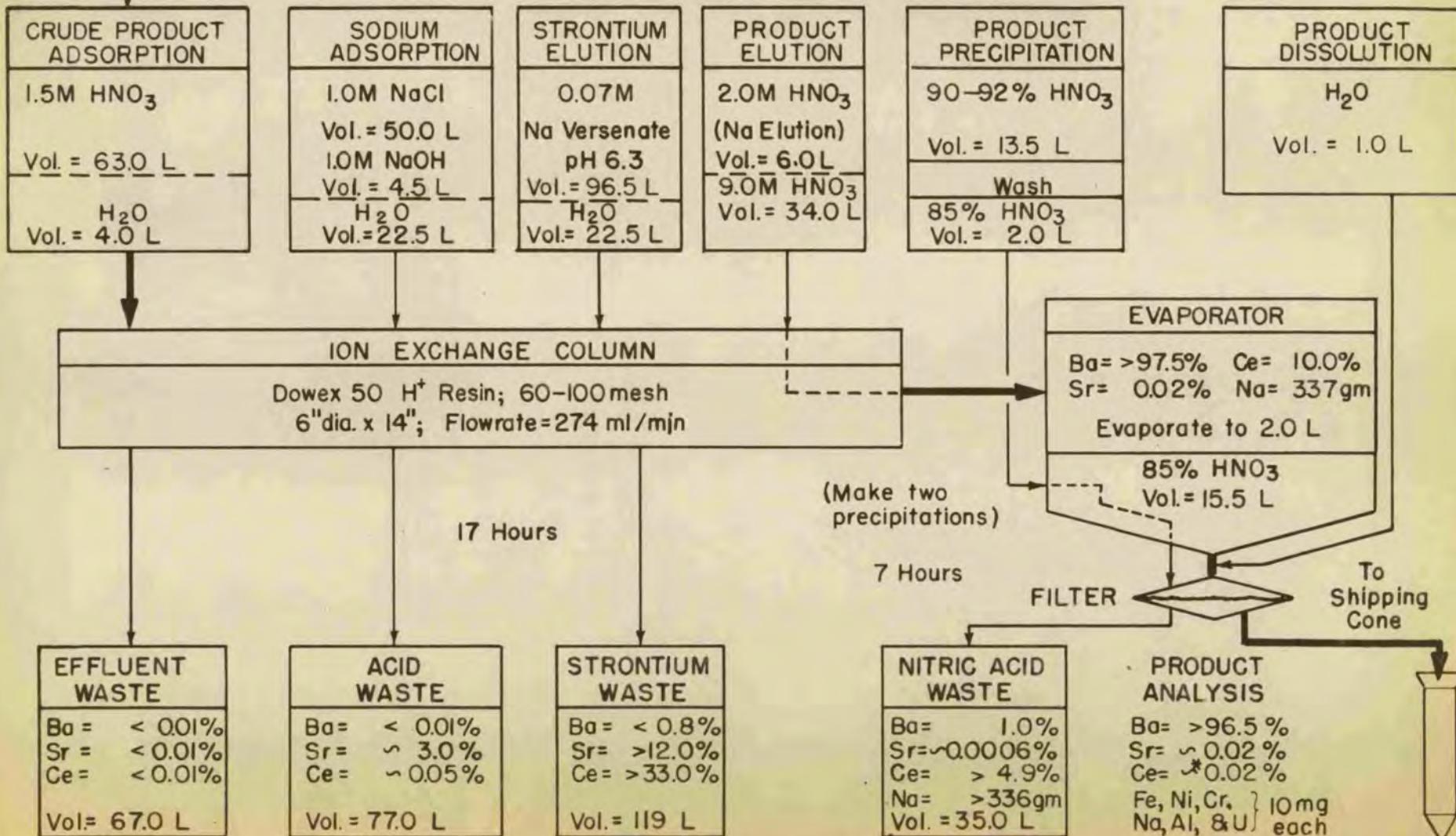
TO FUMING NITRIC ACID  
 PRECIPITATION

- 64 -

FIGURE 17

**FLWSHEET: MTR-RaLa PROCESS-Part II**  
**PURIFICATION OF BARIUM<sup>140</sup> BY THE**  
**NITRIC ACID-VERSENE ION EXCHANGE PROCESS**

From Caustic-Nitrate Process (see figure 10B)



\*Calculated

Figure 18

Ba, Sr, U, Al, Hg, AND Ce DISTRIBUTION COEFFICIENTS IN A DOWEX-50-H<sup>+</sup> RESIN-NITRIC ACID SYSTEM AS A FUNCTION OF NITRIC ACID CONCENTRATION

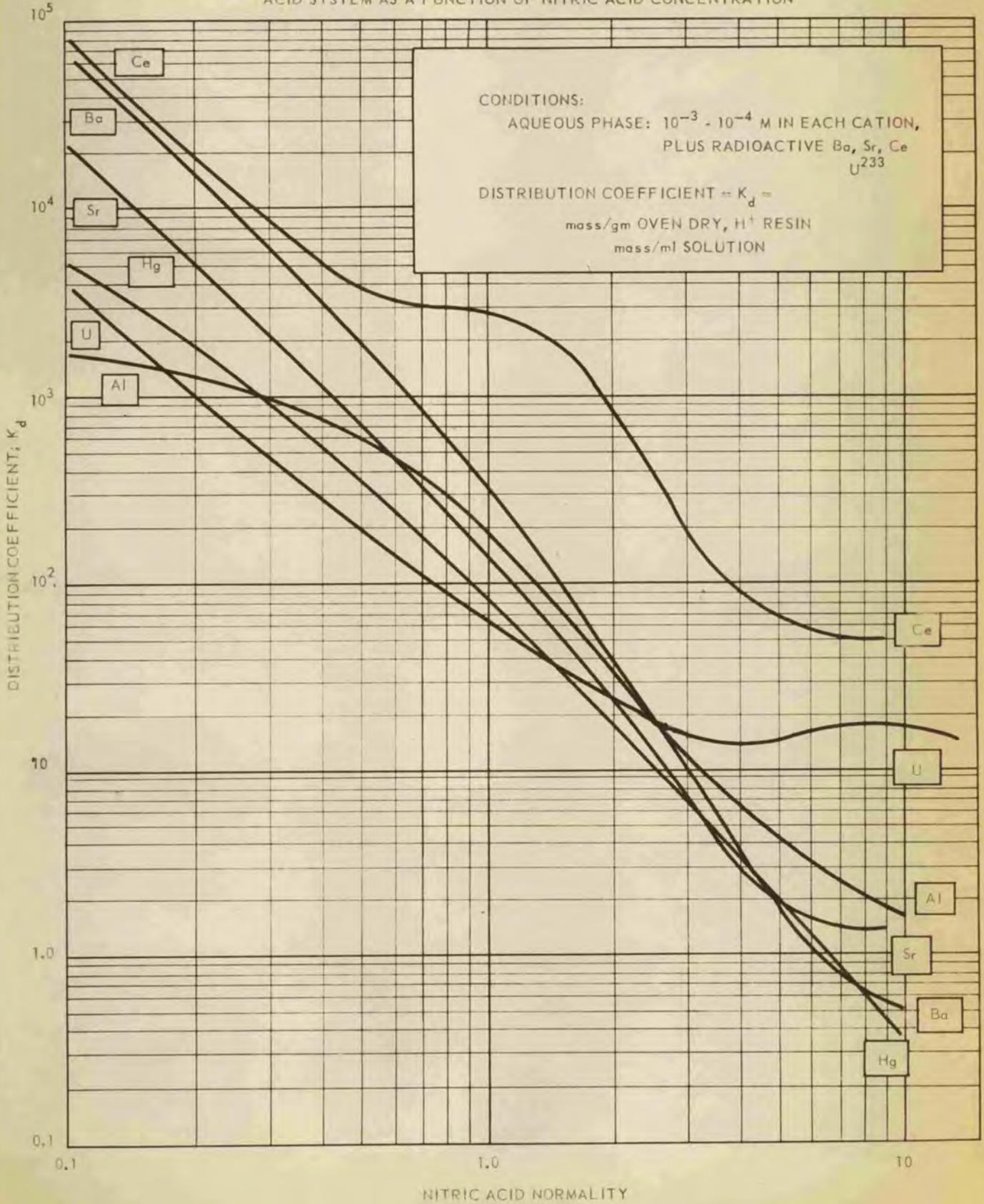


FIG. 19.

FLWSHEET : MTR-RALA PROCESS

PREPARATION OF CRUDE BARIUM BY THE SULFURIC ACID PROCESS

BASIS: 1 MTR ASSEMBLY -  $\left\{ \begin{array}{l} 162 \text{ Moles Al.} \\ 0.63 \text{ Moles U} \\ 7.28 \times 10^{-3} \text{ Moles Ba.} \end{array} \right.$

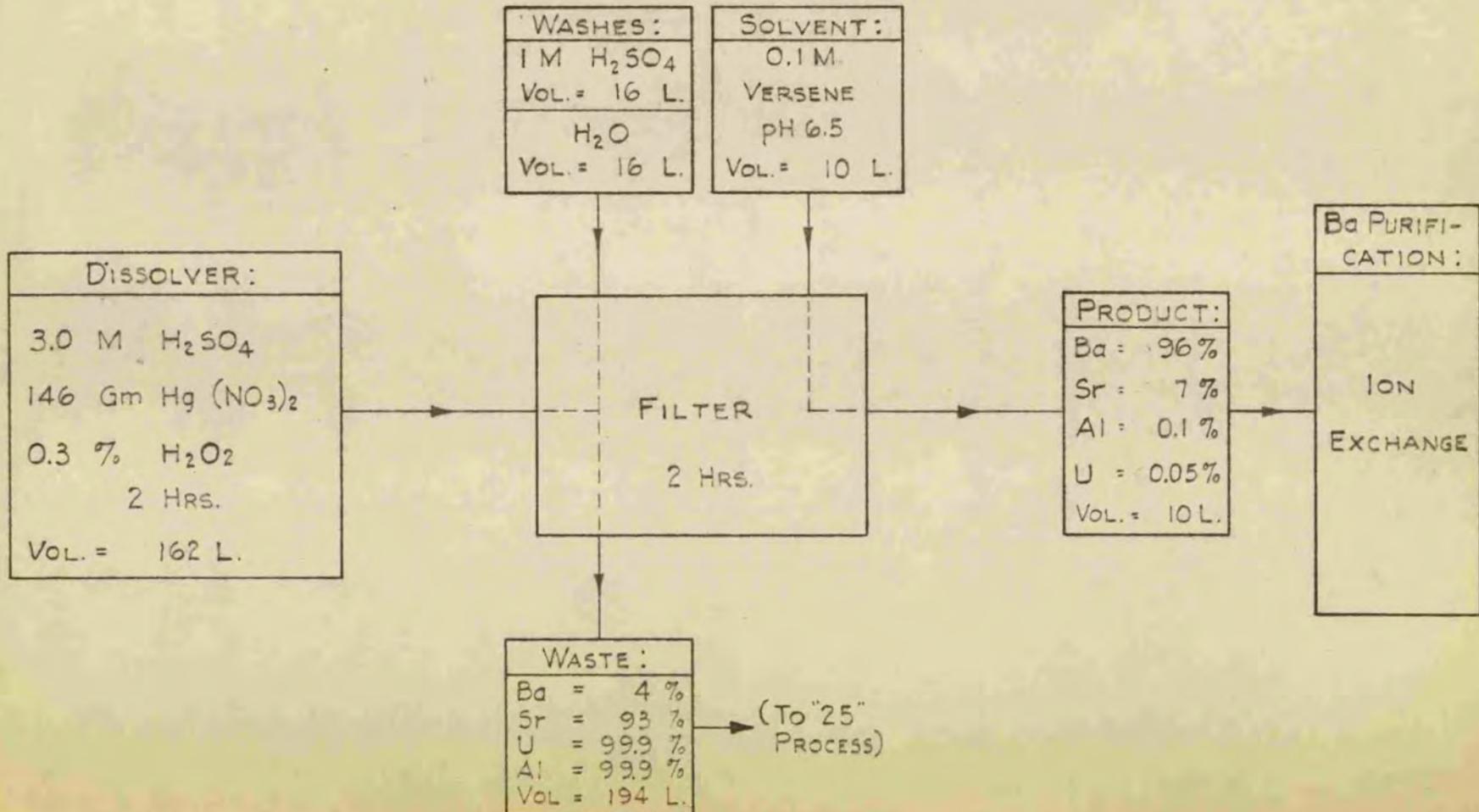


FIG. 20

FLWSHEET: MTR-RALA PROCESS  
 PREPARATION OF CRUDE BARIUM BY THE NITRIC ACID PROCESS

BASIS: 1 MTR ASSEMBLY -  $\begin{cases} 162 \text{ Moles Al.} \\ 0.63 \text{ Moles U} \\ 7.28 \times 10^{-3} \text{ Moles Ba.} \end{cases}$

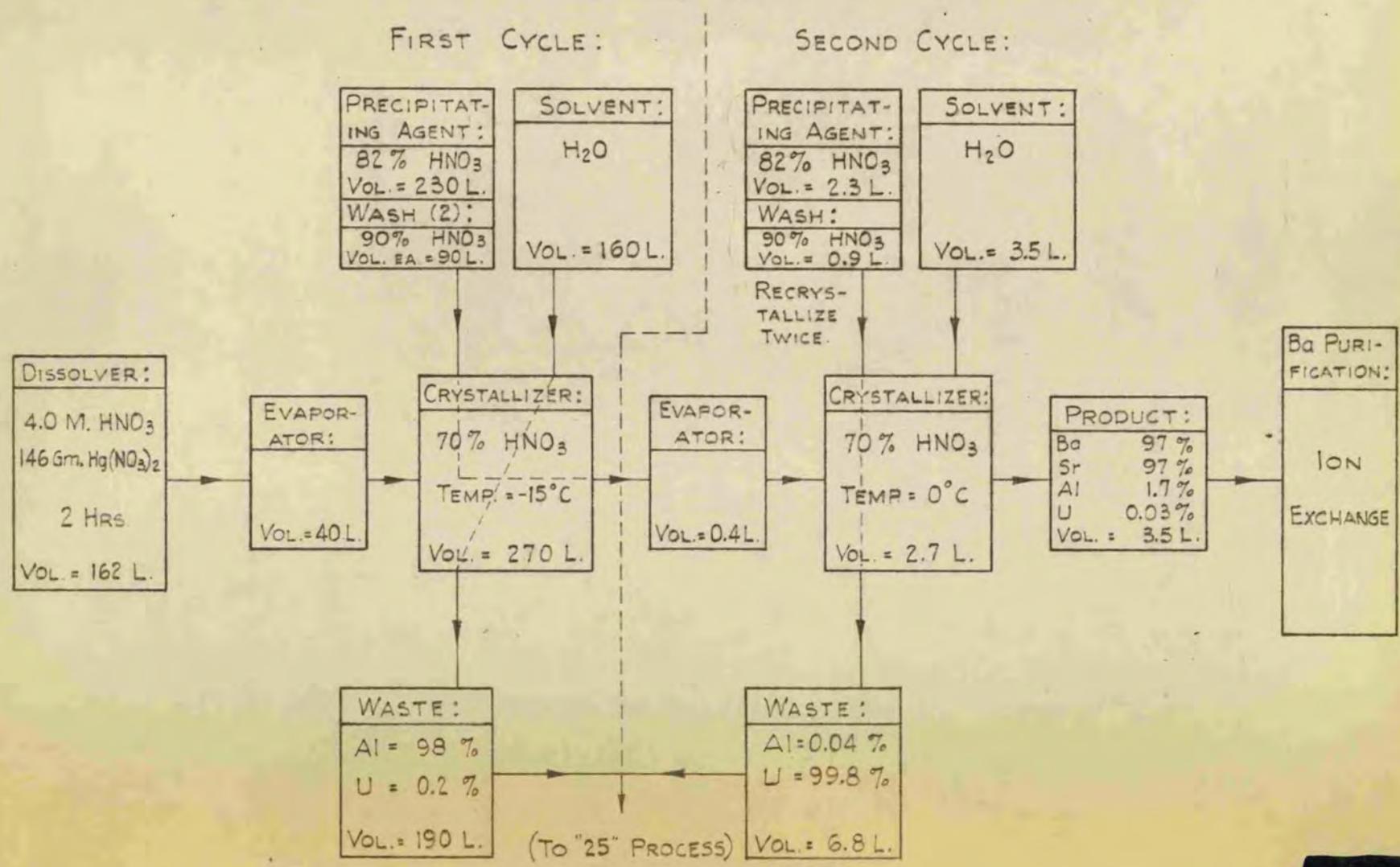


FIGURE 2I

FLWSHEET: MTR-RaLa PROCESS — Part II

DWG No 14212

PURIFICATION OF BARIUM BY THE HYDROCHLORIC ACID PRECIPITATION PROCESS

(FOR PART I SEE FIGURE 3)

From Caustic-Nitrate Process  
(see figure 3)

