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SUBJECT: Transuranic Studies Status and Problem Statement

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ABSTRACT

The purpose of the Transuranics Program is to develop separation processes for the transuranic elements, primarily those produced by long term neutron irradiation of Pu-239. The program includes laboratory process development, pilot plant process testing, processing of 10 kg of Pu-239 irradiated to greater than 99% burnup for plutonium and americium-curium recovery, and processing the reirradiated plutonium and americium-curium fractions. The proposed method for processing highly irradiated plutonium is: (1) plutonium-aluminum alloy dissolution in HNO_3; (2) plutonium recovery by TBP extraction; (3) americium, curium, and rare earth extraction by TBP from neutral nitrate solution; (4) partial rare earth removal (primarily lanthanum) by americium-curium extraction into 100% TBP from 15 $\underline{M}$ HNO_3; (5) additional rare earth removal by extraction in 0.48 $\underline{M}$ mono-2-ethylhexylphosphoric acid from 12 $\underline{M}$ HCl; and (6) americium-curium purification by chloride anion exchange. Processing through the 100% TBP--15 $\underline{M}$ HNO_3 cycle can be carried out in the Power Reactor Fuel Reprocessing Pilot Plant. New facilities are proposed for laboratory process development studies and the final processing of the transplutonic elements.

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TRANSURANIC STUDIES STATUS AND PROBLEM STATEMENT

1.0 Objective and Scope

The purpose of the Transuranic Studies Program is to develop and test separation processes for the transuranic elements. At present primary emphasis is placed on development of pilot plant scale processes for recovering plutonium and the transplutonic elements from highly irradiated plutonium. These methods are needed to process 10 kg of plutonium scheduled for irradiation to greater than 99% burnup. The Chemical Technology Division Program includes: (1) laboratory scale development and testing of the process chemistry; (2) pilot plant demonstration and processing of 10 kg of highly irradiated plutonium; and (3) laboratory scale purification and isolation of the transplutonic elements. Associated with this program are the irradiation of plutonium fuel elements in the Oak Ridge Research Reactor to provide development material, development of handling and operating techniques for laboratory scale processing of these hazardous materials, and design and construction of a Transuranic Facility in which process development and product isolation will be carried out.

2.0 Possible Processing Methods

Considerable knowledge of actinide chemistry is available.[1-3] Processes for recovering gram amounts of Am-241 from kilogram quantities of plutonium and nonradioactive lanthanum have been demonstrated at ORNL[4-7] and at Los Alamos.[8,9] Laboratory scale techniques[10] are available for recovering gram quantities of americium and curium from irradiated Am-241, and transplutonic elements have been recovered from gram quantities of highly irradiated plutonium.[11] From this and other available information[12,13] methods for processing 10 kg of highly irradiated plutonium can be outlined. Although the radiation schedule has not been definitely determined, for discussion of the methods it can be assumed that >99% of the Pu-239 will be burned out and that at least 6 months will be allowed for decay. The approximate composition of the highly irradiated plutonium-aluminum alloy is given in Table 1. Considering the present knowledge, the time schedule, and the available processing facilities, the following processing methods are suggested: (1) dissolution of the plutonium-aluminum alloy in 6 $\underline{M}$ HNO_3; (2) extraction of the plutonium with 30% TBP from the acid nitrate solution; (3) extraction of americium, curium, and rare earths with 30% TBP from the neutralized nitrate solution; (4) partial separation from rare earths (primarily lanthanum) by extraction of americium and curium with 100% TBP from 15 $\underline{M}$ HNO_3; (5) other rare earth removal by extraction from 12 $\underline{M}$ HCl with 0.48 $\underline{M}$ mono-2-ethylhexylphosphoric acid; and (6) americium and curium final purification by anion exchange. A schematic outline of these methods with approximate conditions is given in Fig. 1. Many alternative methods are possible, and as development proceeds the flowsheet will be modified to make use of the best conditions. For example, a single cycle in which

Table 1. Approximate Composition pf Plutonium-Aluminum Alloy Irradiated to 99% Pu-239 Burnup

Basis: 10 kg of plutonium as 6% plutonium alloy

Elements	wt, kg
Al	157
Pu	1.6[a]
Am + Cm	0.05[a]
Rare earth fission products	2.3
Gaseous fission products	1.1
Other fission products	5.0

[a] Longer irradiation will convert the higher plutonium isotopes to americium and curium.

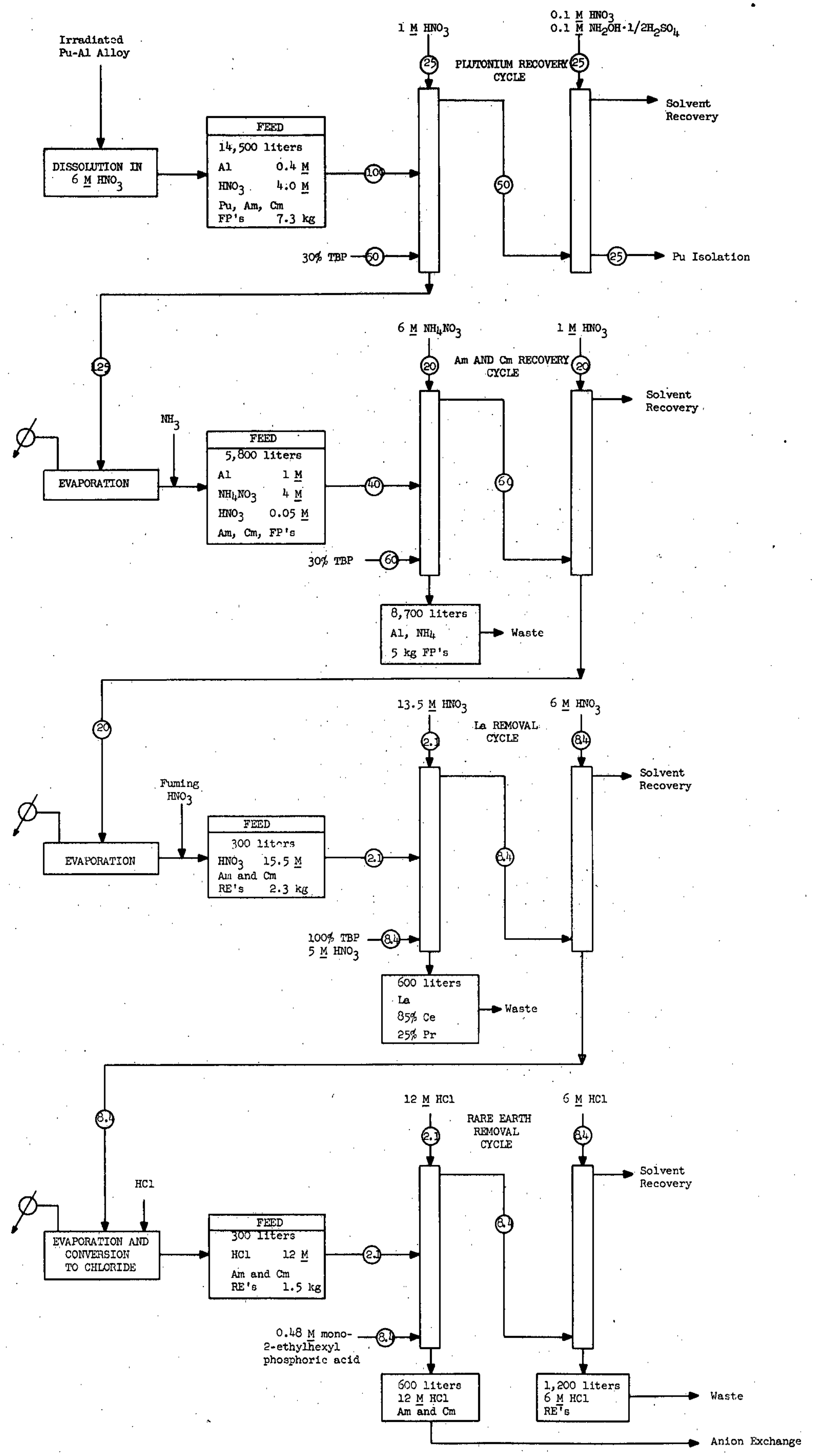

Fig. 1. Transplutonic element recovery flowsheet. Basis: 10 kg of plutonium as 6% plutonium-aluminum alloy irradiated to >99% burnup of Pu-239. Numbers in circles indicate relative flow volumes.

plutonium, americium, curium, and rare earths are extracted in the first column and americium, curium, and rare earths are separated from plutonium in the second column (see Fig. 2) may replace the first two extraction cycles shown in Fig. 1.

A detailed flowsheet for the plutonium recovery cycle must be prepared for pilot plant operation. There is no difficulty in obtaining good plutonium recovery, but careful adjustment of conditions is required to give high decontamination factors. It has been suggested by Hart[14] that 5% TBP be used and that conditions be set to approach saturation of the organic phase at the feed plate, thus improving decontamination. An alternative procedure is to use more concentrated TBP but to add uranium to the feed in order to saturate the organic phase. These variables will be considered in preparing and testing the flowsheet.

The americium and curium recovery cycle was demonstrated in the Metal Recovery Pilot Plant during processing of plutonium metallurgical waste[5] and the Clementine[15] fuel elements. However, optimum conditions for this particular application should be determined. Since these conditions will also quantitatively extract the rare earths, there will be no need to set optimum conditions for decontamination of other fission products.

The lanthanum removal cycle was tested in the Metal Recovery Pilot Plant[7] in separating gram quantities of Am-241 from kilogram quantities of nonradioactive lanthanum. Some operational difficulties were encountered, and salts precipitated from the concentrated nitric acid feed. These difficulties must be resolved, and the effect of the presence of other rare earths must be determined. Calculations based on the distribution coefficients in Fig. 3 indicate that lanthanum can be effectively removed and cerium and praseodymium can be partially removed by processing in existing equipment. The Power Reactor Fuel Reprocessing Pilot Plant has a solvent column that provides for 17 ft of extraction and 17 ft of scrub. This is equivalent to approximately 6 scrub and 6 extraction stages. For the flowsheet conditions given in Fig. 1, it can be calculated that this column will extract 99.5% of the americium and >99.5% of the curium, with only 0.2% of the lanthanum, 15% of the cerium, and 75% of the praseodymium. All the other rare earths will be quantitatively extracted. Actual tests and determination of optimum conditions are needed. These can be started in the laboratory with syntehtic feeds and tested later in the Pilot Plant with irradiated plutonium feed. The use of di-2-ethylhexylphosphoric acid as an extractant will also be tested.

The rare earth removal cycle with mono-2-ethylhexylphosphoric acid for extracting rare earths from concentrated hydrochloric acid requires a great deal of investigation and development. The flowsheet conditions in Fig. 1 are based on distribution coefficients reported by Peppard, Mason, and Sironen.[12] Distribution coefficients (O/A) between 12 M HCl and 0.48 M mono-2-ethylhexylphosphoric acid are: americium, 0.079; curium, 0.11; lanthanum, 0.17; cerium, 0.30; praseodymium, 0.40; neodymium, 0.50; and promethium, 0.58. Calculations based on these data indicate that extraction of rare earths from americium and curium is

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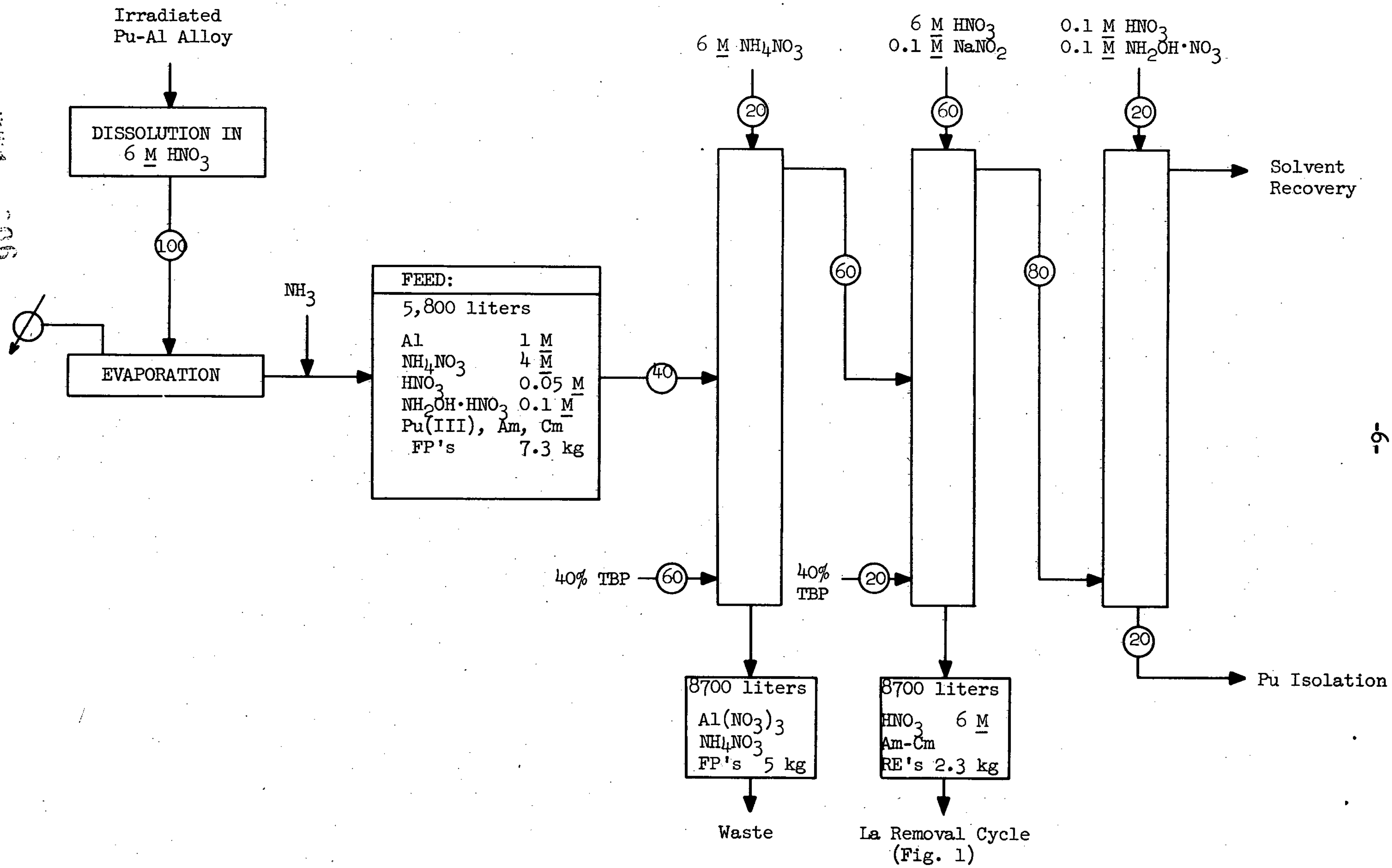

Fig. 2. Alternative transplutonic element recovery flowsheet. Basis: 10 kg of plutonium as 6% plutonium-aluminum alloy irradiated to >99% burnup of Pu-239. Numbers in circles indicate relative flow volumes.

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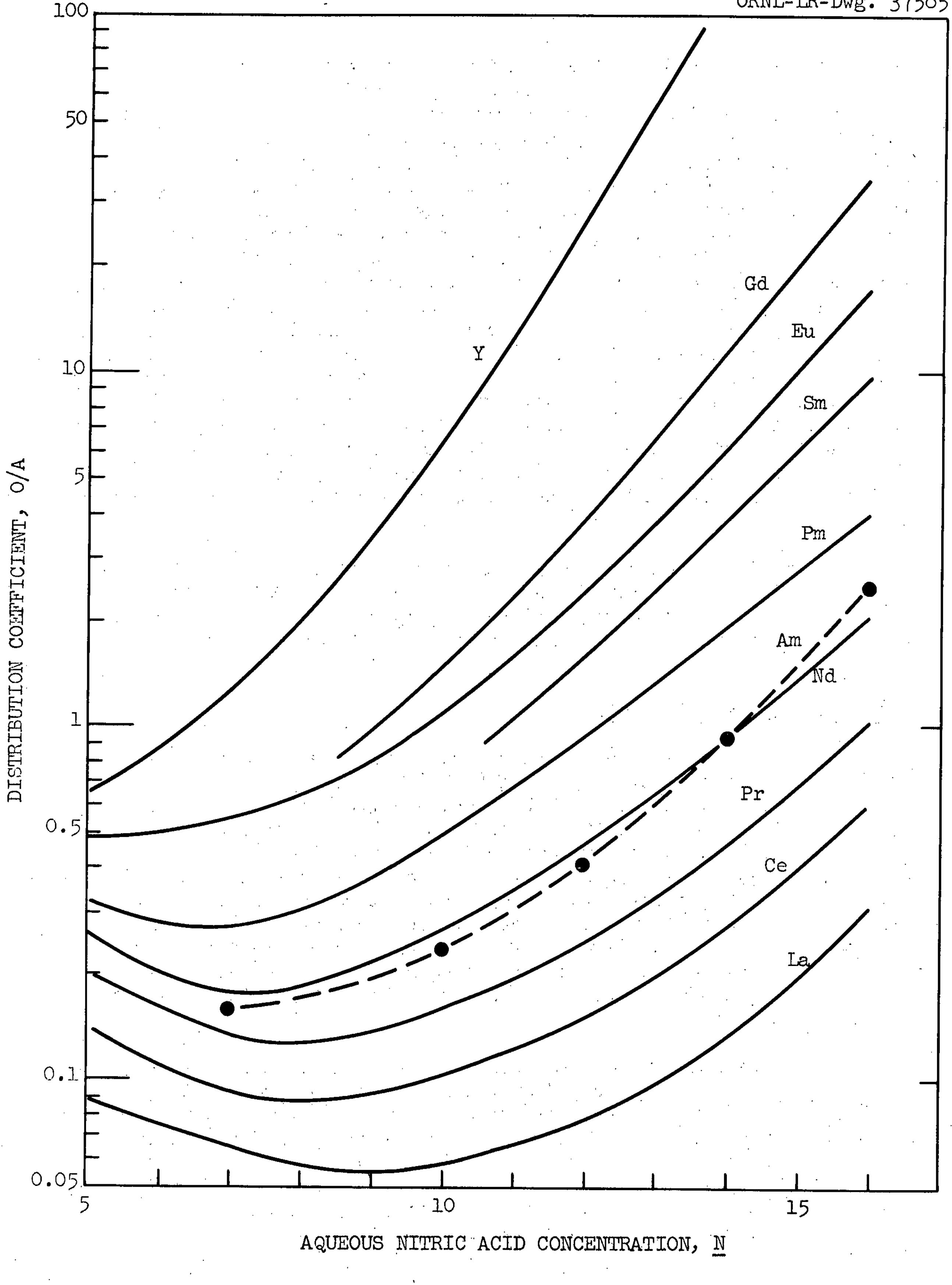

Fig. 3. Distribution coefficients[13] of lanthanide nitrates. Aqueous phase: HNO_3; organic phase: 100% TBP.

feasible. The curves in Fig. 4 indicate americium and curium losses as a function of the number of scrub stages, and the curves in Fig. 5 indicate the fractions of various rare earths that will remain with the americium and curium. If 18 scrub stages are used, the curium loss will be 1% and the americium loss $<0.01\%$. With 9 extraction stages, 6.5% of the cerium and 0.8% of the praseodymium fed to this cycle will remain with the americium and curium. Since only 15% of the total fission product cerium and 75% of the fission product praseodymium was assumed to enter this cycle, only 1% of the cerium and 0.6% of the praseodymium will remain with the product. This cycle gives very little separation from lanthanum, so that about 0.2% of the original fission product lanthanum will remain within the americium-curium. Less than 0.1% of all other rare earths will remain with the americium and curium. At present equipment and facilities are not available for this cycle using concentrated hydrochloric acid. During process development, emphasis will be placed on the use of minimum volumes. If the scale of operation can be kept small, a mixer-settler unit can be installed in the proposed Transuranic Facility. The use of lithium chloride as a salting agency may be helpful since higher distribution coefficients and larger separation factors can be obtained.

Information on chloride anion exchange is available;[3,10] however, considerable investigation in the laboratory is planned in order to set optimum conditions, to design and test equipment to be used in α-γ-n shielded cells and to familiarize personnel with the techniques.

3.0 Equipment and Facilities

Much of the development work can be carried out in glove boxes now available in the Isolation Building (3508). However, boxes with only light gamma shielding are available, and handling of solutions with high alpha and high gamma activity is not feasible in the present facilities. A limited amount of this work may be done in the High-Level Facility (Building 4507) by using specially designed glove boxes in the cells. All the processing steps through the lanthanum removal cycle (Fig. 1) can be carried out in the Power Reactor Fuel Reprocessing Pilot Plant. The major modifications required for this processing are installation of a corrosion resistant evaporator for feed adjustment and design and fabrication of equipment for removing and transporting the americium-curium concentrate.

Facilities are not now available for carrying out the rare earth removal cycle with concentrated hydrochloric acid or for handling the decagram quantities of americium and curium produced by irradiating 10 kg of Pu-239. The Cm-242 isotope makes handling difficult because of its high specific activity (7.4×10^{12} d/m/mg) and its high-energy alpha (6.1 Mev), which produces neutrons by γ-n reaction. Work with Cf-252 in present facilities is out of the question because of its high spontaneous fission rate (4.8×10^{10} fissions/m/mg).

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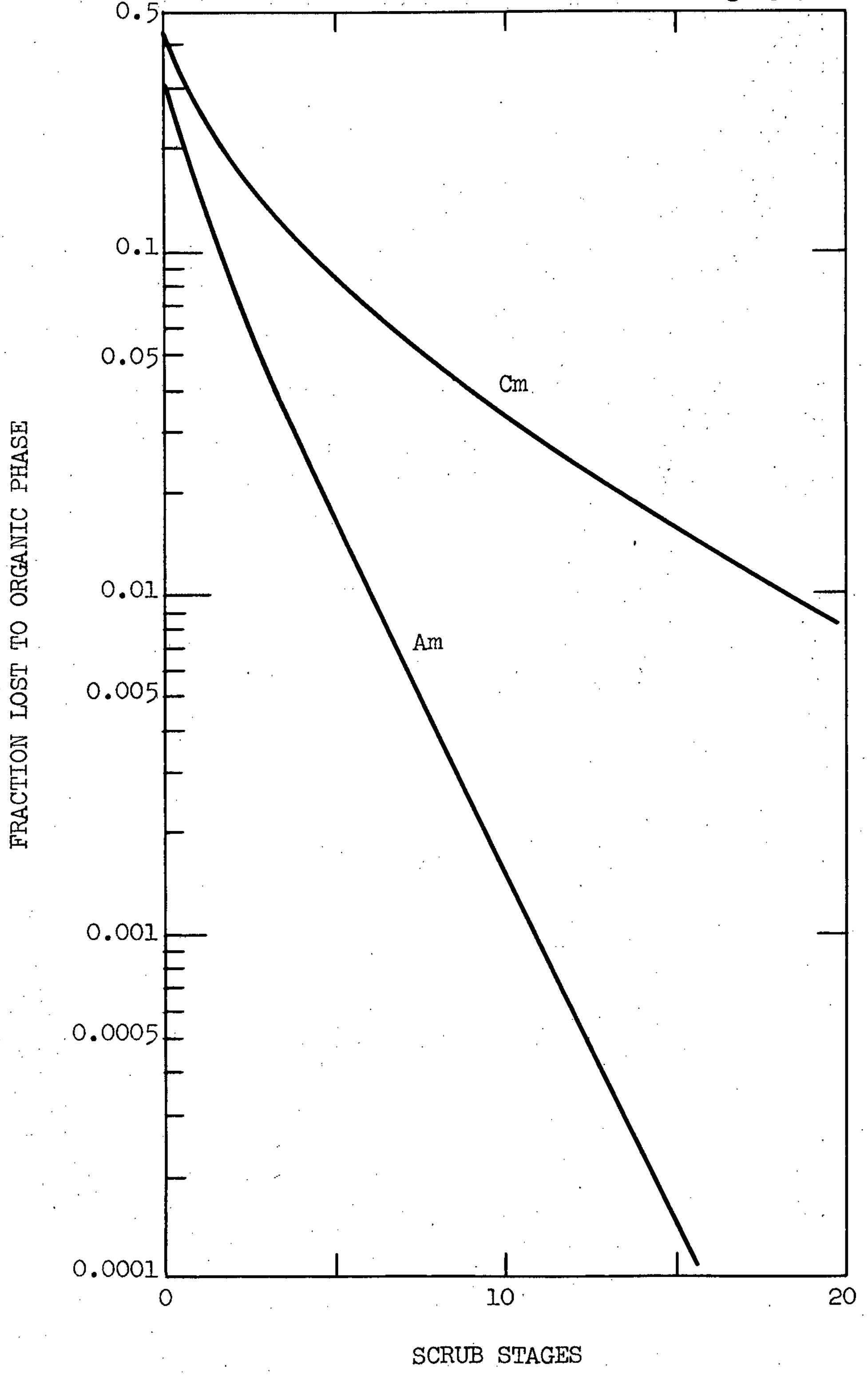

Fig. 4. Americium and curium loss in mono-2-ethylhexylphosphoric acid-HCl extraction. Feed, 12 M HCl; scrub, 12 M HCl; mono-2-ethylhexylphosphoric acid extractant, 0.48 M; feed/scrub/solvent vol ratio = 1/1/4; more than 10 extraction stages.

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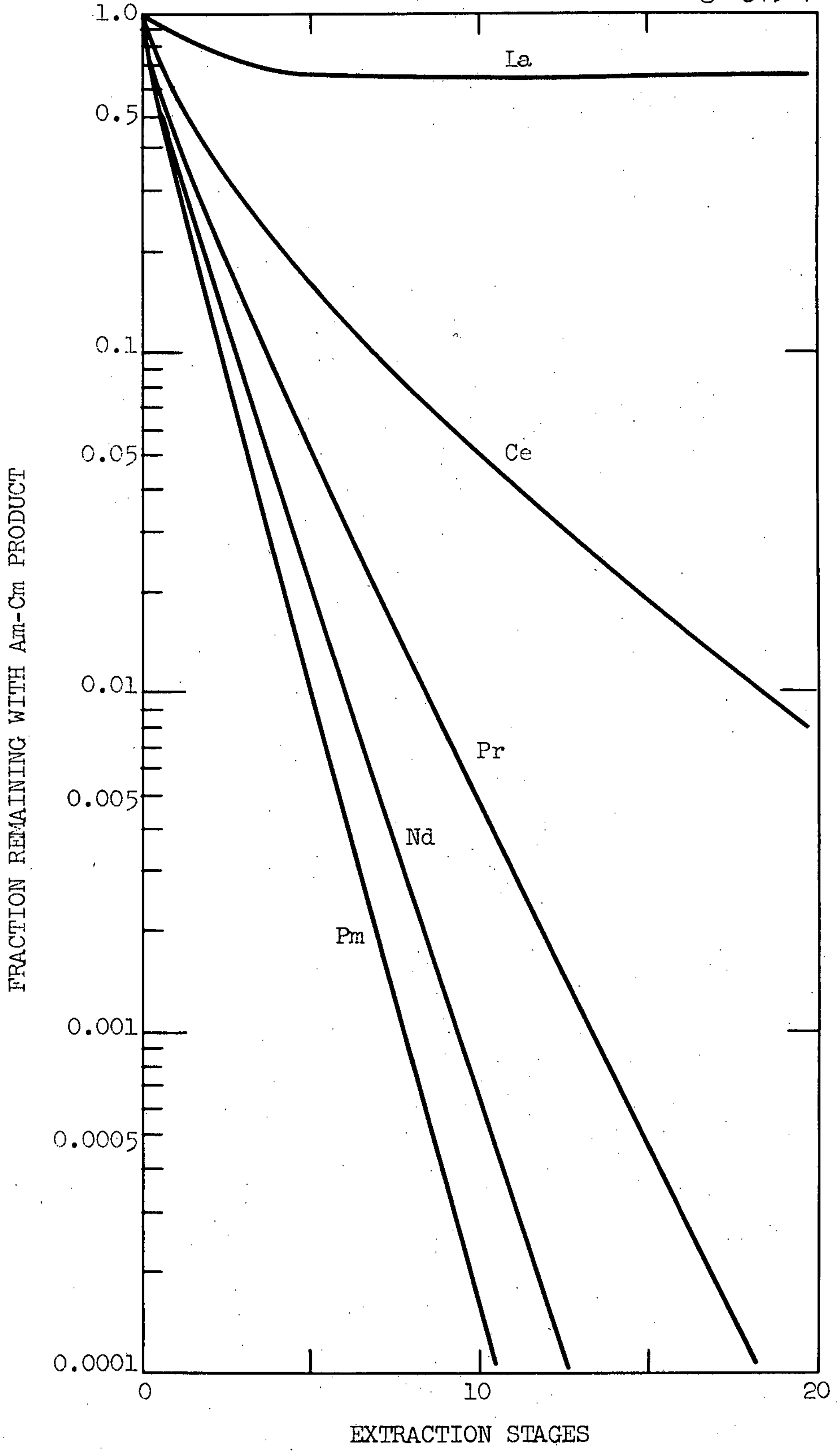

Fig. 5. Rare earths remaining in product of mono-2-ethylhexylphosphoric acid--HCl extraction. Feed, 12 M HCl; scrub, 12 M HCl; mono-2-ethylhexylphosphoric acid extractant, 0.48 M; feed/scrub/solvent vol ratio = 1/1/4; more than 10 scrub stages.

The Transuranic Facilities proposed for addition to the Isolation Building will provide laboratories for work with alpha-active materials and cells for work with alpha-, gamma-, and neutron-active materials. A floor plan of the present and proposed building is shown in Fig. 6. This building will house essentially all the laboratory scale alpha work of the Chemical Technology Division and the principal Analytical Chemistry Division laboratories for highly alpha-active samples. The building will be designated as a contamination zone, and personnel will be required to enter and leave through change rooms.

Detailed design of the Transuranic Facility will begin July 1959. Construction will start March 1960 and should be complete by March 1961.

A cell mockup will be constructed in the attic of Building 3508 during the latter part of FY-1959. This mockup will be used to test designs of the cells for the Transuranic Facility. Later it will be used for assembling and testing equipment to be used in the cells.

4.0 Irradiated Plutonium for Process Testing

Before the 10 kg of highly irradiated plutonium is processed, the processes will be tested in the Pilot Plant. Irradiated plutonium for this testing will be available from several sources. Table 2 lists the material that will be available and gives the approximate processing dates.

The processing date for 10 kg Pu given as July 1962 is not definite but will be dependent upon the irradiation schedule. This is discussed in a secret supplement to this memo.[16]

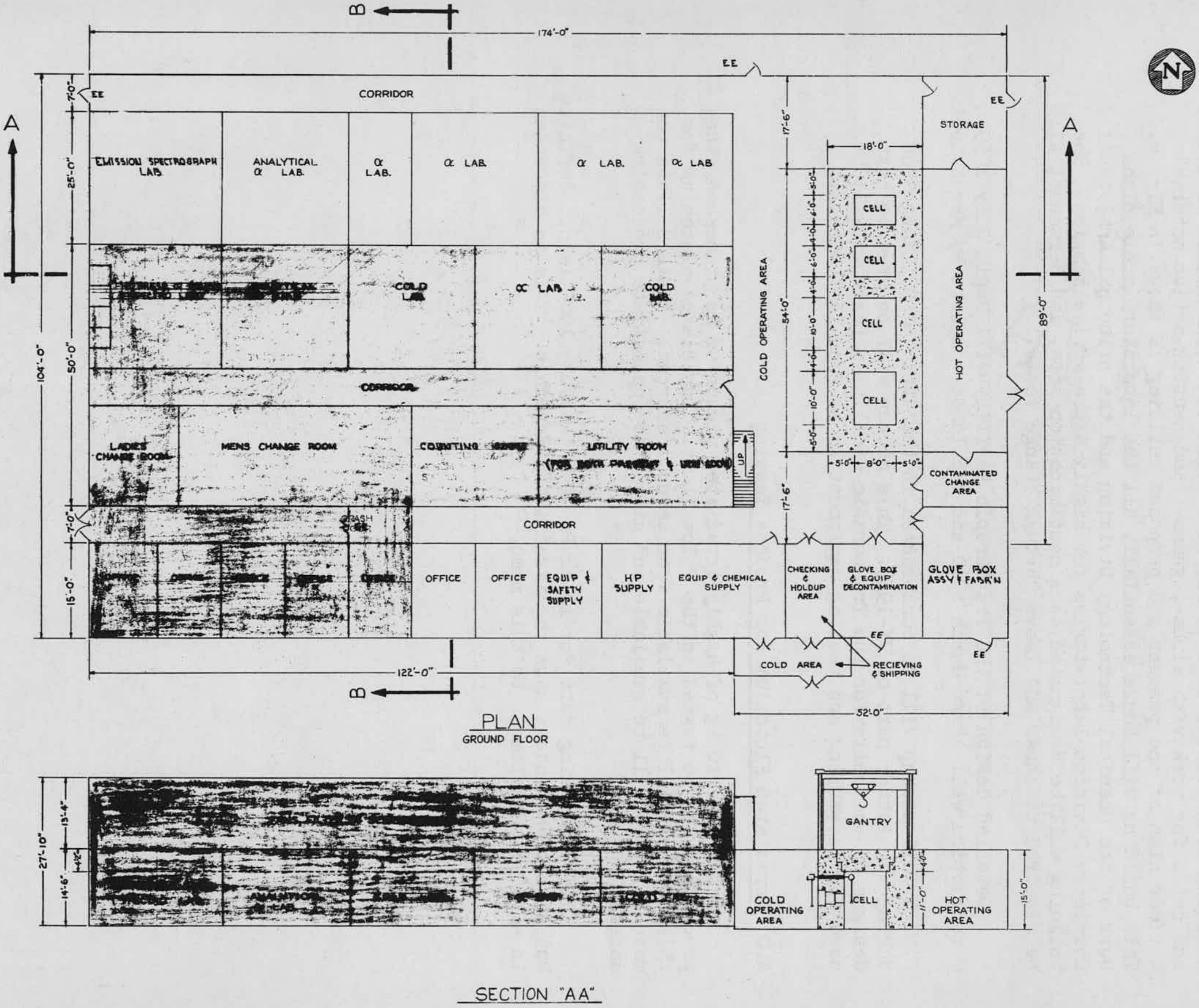

Fig. 6 Proposed Transuranic Facility

Table 2. Irradiated Plutonium Scheduled for Processing at ORNL

		Plutonium Irradiation				
Process Batch	Processing Date	Original Pu-239 Content, g	Fabrication Site	Reactor	Burnup, %	Material Allocation
1	10-59	516	ORNL	MTR	70-90	Cross-section measurement
		500	HW	MTR	70-90	
2	1-61	300	ORNL	MTR	70-90	Cross-section measurement
		or 3000	HW	MTR	70-90	
		2000	HW	SRR	70-90	
3	1-62	150	ORNL	ORR	>99	Transuranic element process development
		450	HW	ORR	>99	
4	7-62	10,000	HW	SRR	>99	Transplutonic element production

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