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PILOT PLANT SHUTDOWN AND Pu-Al PROCESSING

J. C. Bresee

ABSTRACT

The large aqueous pilot plant facilities at ORNL have been cleaned and are being put in standby condition. Valuable experience was gained during the year as anion exchange was used to recover more than one kg of plutonium left in the exploded evaporator system. This experience is being applied to a new recovery program just beginning in cell 1 of Building 4507.

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PILOT PLANT SHUTDOWN AND Pu-Al PROCESSING

J. C. Bresee

(to be presented at the Chemical Technology Division Annual Information Meeting September 28 and 29, 1961)

This morning I will discuss two programs: first, the work of placing the solvent extraction pilot plants in standby and second, anion exchange recovery of plutonium during and after plant cleanup.

By way of an introduction, in the Fall of 1959, the solvent extraction complex of Buildings 3019 and 3505 (known as the Thorex Pilot Plant and the Metal Recovery Plant) had been used to process highly irradiated plutonium and were engaged in a decontamination program when an explosion occurred in cell 6 of Building 3019.

Figure 1 shows a section through the Thorex Pilot Plant and the cubicles in the double cell 6 and 7. The evaporator equipment in the upper right hand corner of cell 6 exploded and the door opposite was blown open, releasing alpha activity to the street. At last year's seminar it was reported that internal cleanout of process equipment resulted in the recovery of 1100 grams of plutonium from the ruptured evaporator. This plutonium was stored in three clean process vessels for later purification and concentration.

Before describing the final cleanup and shutdown of the aqueous pilot plants, let me first point out that details of the incident and cleanup have been very completely reported in the open literature. Eight of the most complete reports are listed in the topical bibliography in Table 1.

After the plutonium had been removed from the interior of the equipment, the difficult job of external decontamination remained. The first and most important step was to install early in October what was called a "greenhouse" (a sort of reverse glove box with the man inside the box) which projected into the cell through the cell 6 door. (See Figure 2.) The interior of the cell was thoroughly wetted down from the box, and in all later cell entries it served as an observation point. Next, three men entered the cell to load eight 55-gal drums with the debris (see Figure 3) from in front of the

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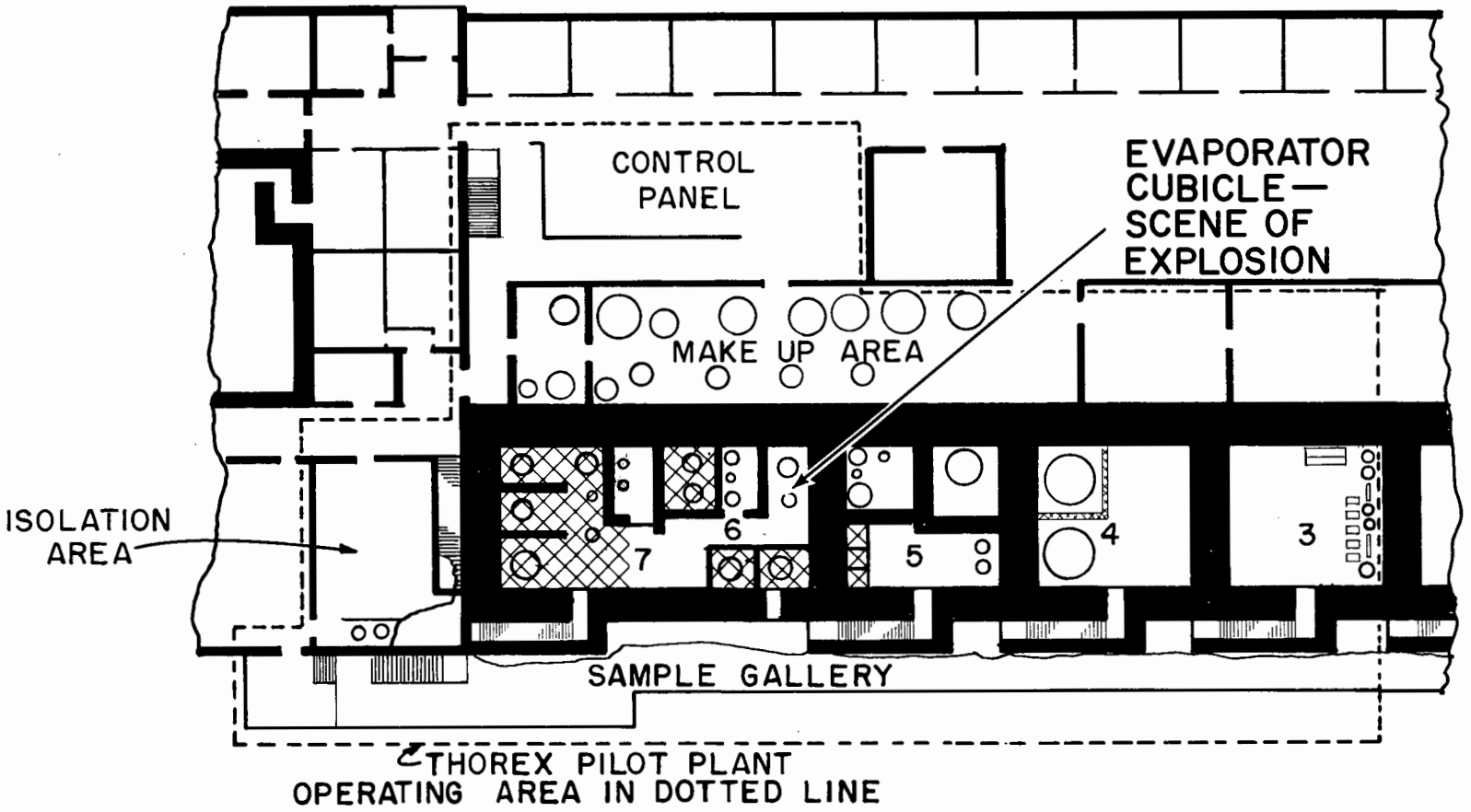

Fig. 1. PLAN OF THOREX OPERATING AREA

Table 1

REPORTS OF BUILDING 3019 INCIDENT AND CLEANUP

Topical Bibliography

1. "Plutonium Release from the Thorex Pilot Plant," Nuclear Safety, Vol. 1, No. 3, pp. 78-80, March, 1960.

2. "Safety in Chemical Processing," Reactor Fuel Processing, Vol. 3, No. 2, pp. 6, April, 1960.

3. "Chemistry of the Intercycle Evaporator Incident of November 20, 1959," W. Davis, Jr., W. H. Baldwin, and A. B. Meservey, ORNL-2979, November 9, 1960.

4. "Decontamination Hazards," Nuclear Safety, Vol. 2, No. 2, pp. 49-51, December, 1960.

5. "Plutonium Release Incident at Oak Ridge National Laboratory," L. J. King and J. C. Bresee, ORNL CF-60-9-57, (presented at the ANS Winter Meeting, San Francisco, California, December 12-14, 1960).

6. "Plutonium Release Incident of November 20, 1959," L. J. King and W. T. McCarley, ORNL-2989, February 16, 1961.

7. "Power Reactor Fuel Processing Pilot Plant: Recovery of Plutonium During Plant Cleanout Operation, Run COAB-1 Summary," W. T. McDuffee, ORNL CF-61-5-1, March 20, 1961.

8. "Decontamination of Cells 6 and 7, Building 3019, Following Plutonium Release Incident," J. R. Parrott, ORNL-3100, August 24, 1961.

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Fig. 2. VIEW OF GREENHOUSE FROM UPPER LEVEL OF CELL 7

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Fig. 3. VIEW OF CELL 6 LOWER LEVEL PRIOR TO BLOCK AND DEBRIS REMOVAL

evaporator cubicle. The men wore two-piece air suits, and this practice continued until after essentially all plutonium was removed by steam jet cleaning (by the end of February, 1961). One man during this entry received 260 mrem in one hour, the largest single exposure during the cell cleanup operations. No one received more than 1300 mrem per quarter during the cleanup program.

Safe removal of drums of highly contaminated debris and shielding block required a special technique which is illustrated in Figure 4. Careful planning proceeded all hazardous operations and prevented injuries or the spread of contamination.

The sequence of operations for removal of the shielding block walls which were as much as 27 feet tall was: use of an elevator into which blocks were loaded to lower them to the floor, transfer to clean drums covered inside and out with plastic, covering with clean lids and removal of outer contaminated plastic as the drum is raised, recovering in the penthouse, monitoring and shipping. All block was removed from the cells by the end of December, 1960 and the remains of the evaporator were cut out and removed in January, 1961.

Before, during, and after block removal the walls and equipment were washed with a variety of reagents using a pumped spray and finally a steam jet cleaner (see Figure 5). The magnitude of the cleaning operation is more obvious when you consider that after block removal there was at least 10,000 square feet of surface remaining to be cleaned.

There were between 150 and 200 grams of plutonium on external surfaces in the cell. Only a few grams were recovered in concentration high enough to process (> 0.01 g/liter). The remainder was flushed to the ORNL high level waste storage tanks in a total of 140,000 gallons.

In addition to alpha smears and probes measured periodically throughout the cleanup program, another measure of success of the cleaning was the air activity during the program (see Figure 6). The air activity on semilog paper mirrored the work activities, with high air counts at the time of dusty operations and declining activity as the cleaning was completed.

After final smears and probes were recorded, the cells were painted with the results shown in Figure 7. Note that the air activity reaches a <u>very</u> low

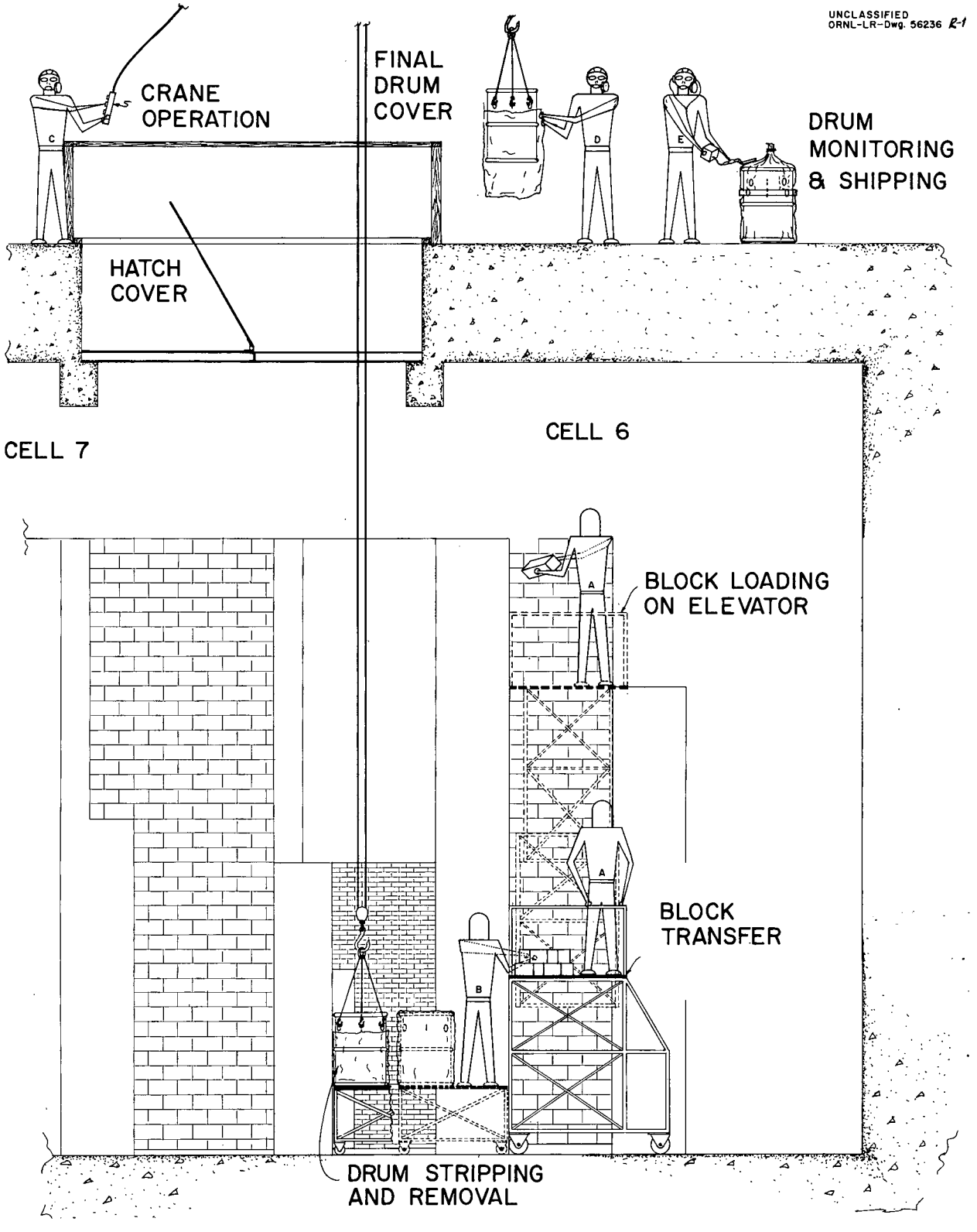

Fig. 4. SHIELDING BLOCK REMOVAL FROM CELL

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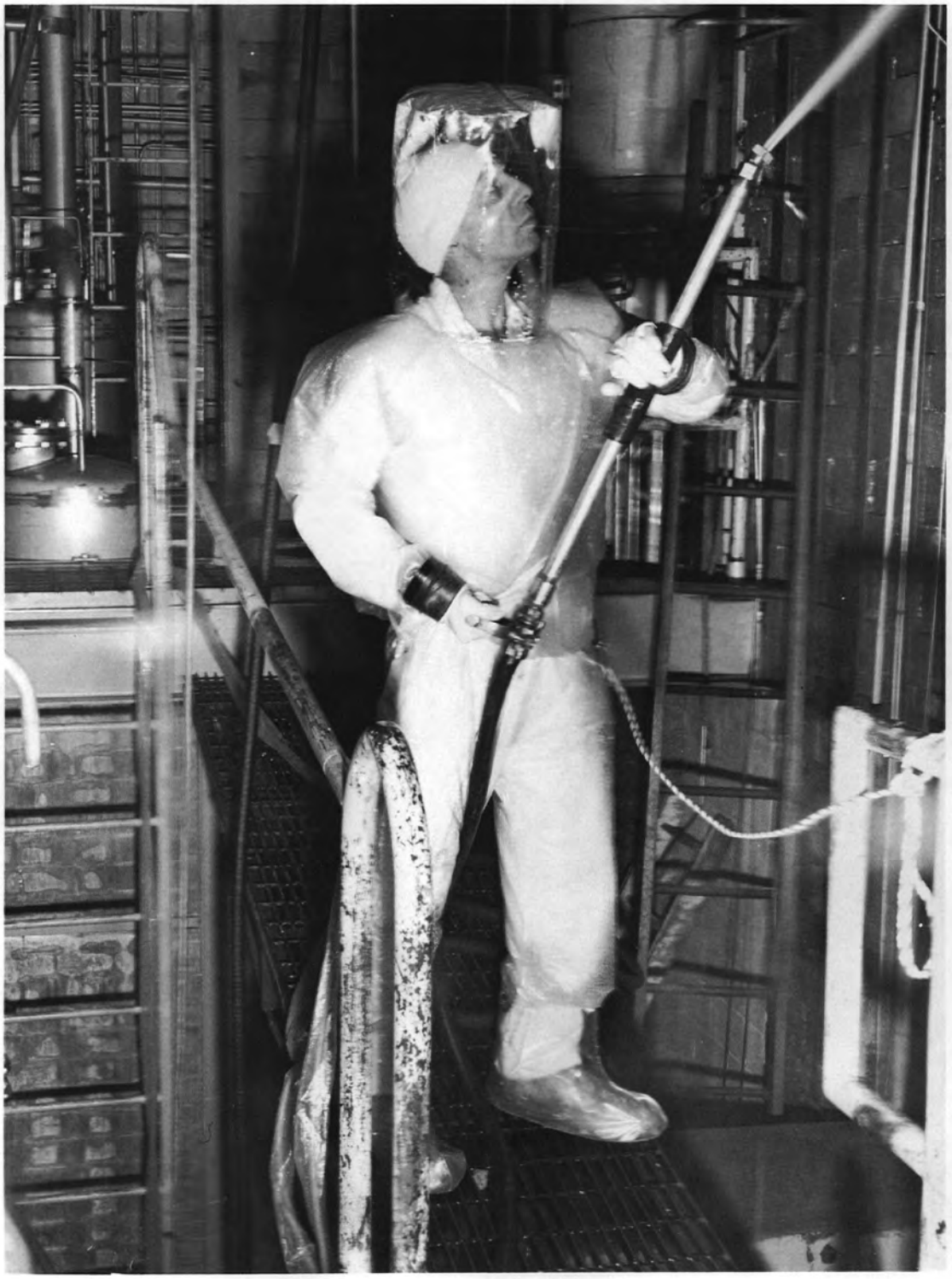

Fig. 5. CELL 6 DECONTAMINATION WITH SELLERS STEAM JET
(photographed from cell 6 greenhouse)

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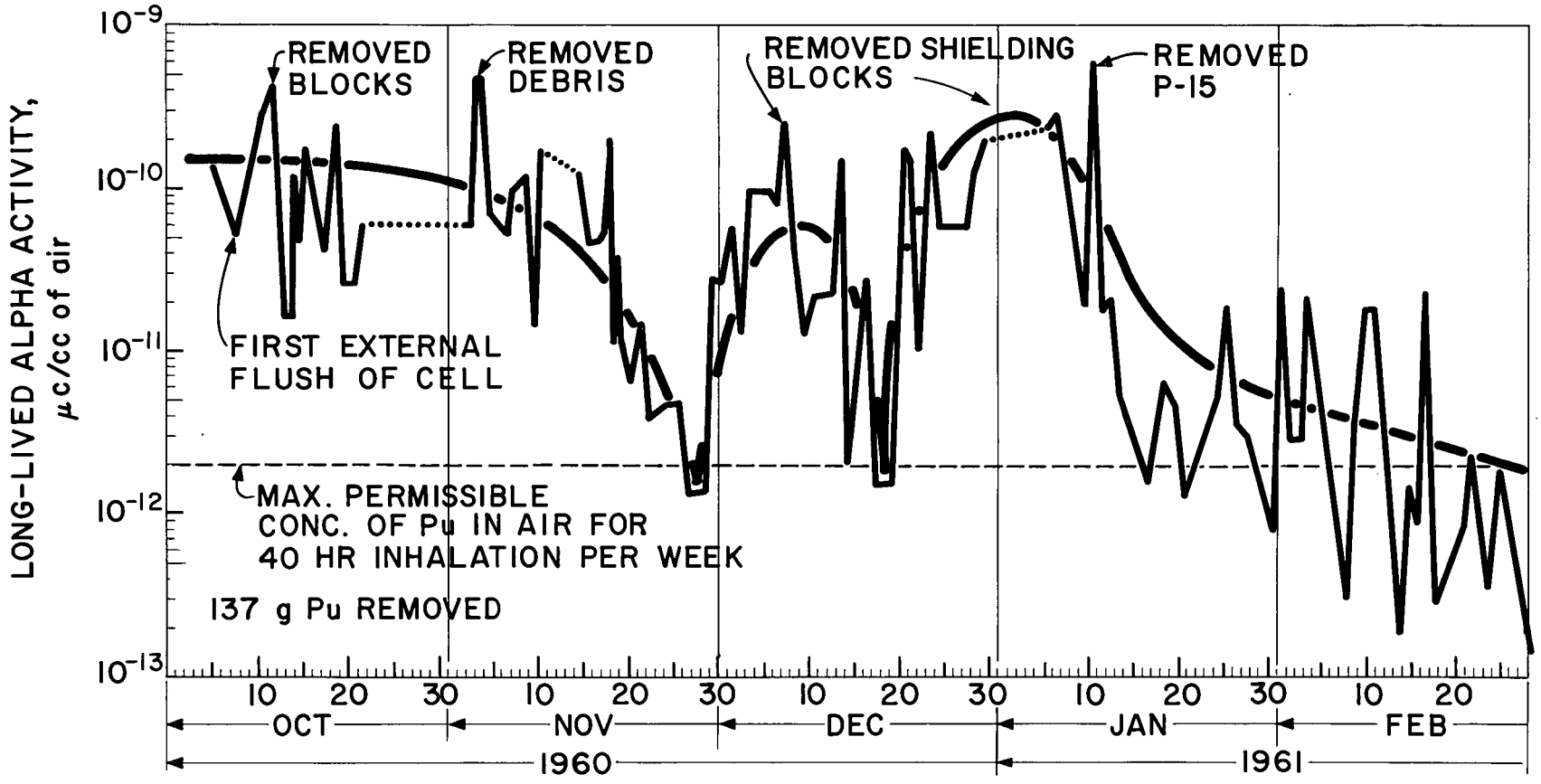

Fig. 6. LONG-LIVED ALPHA ACTIVITY DURING DECONTAMINATION OF CELLS 6 & 7

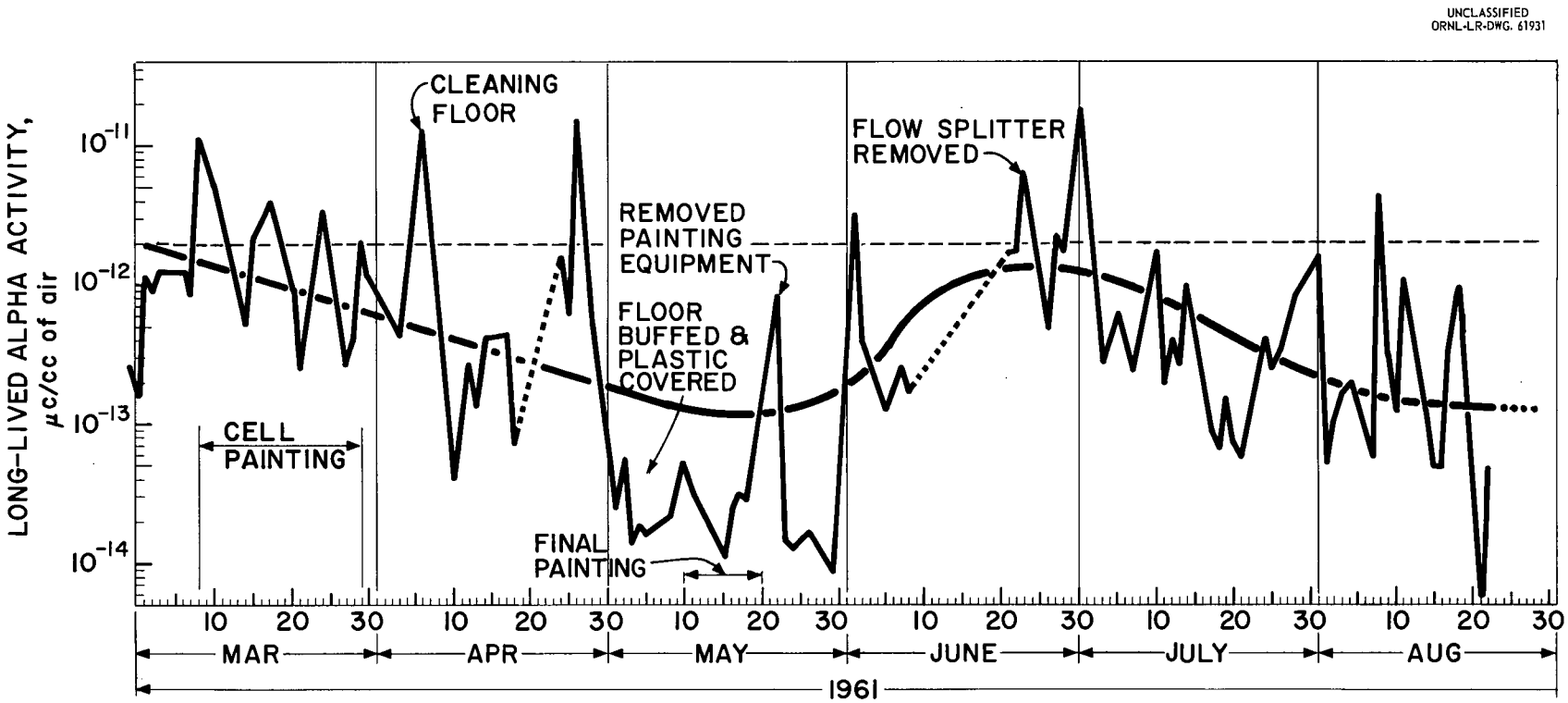

Fig. 7. LONG-LIVED ALPHA ACTIVITY DURING SHUTDOWN OF CELLS 6 & 7

value at the end of May (10^{-14} μc/cc is about one disintegration every hour per cubic meter of air). The increase in activity in June is probably from block removal in another cell which resulted in contaminated air being drawn back through the hot drain lines. Values in July and August show averages which are safe for indefinite shutdown (below the masking limit of 2×10^{-12} μc α/cc).

One interesting side line to the simultaneous measurements of transferable surface contamination and air activity was the attempt to obtain resuspension factors -- ratios of air to surface activity. These varied from high 10^{-9} to low 10^{-7} μc/cc per μc/cm^2 compared with a literature value of 4×10^{-8}. Using the literature value, average smear values of 11,000 d/min/100 sq cm should by resuspension produce air mpc for plutonium. The average smear activity in cells 6 and 7 before painting was 19,000 d/min/100 sq cm and the present values are orders of magnitude lower.

Also in December, the 1100 grams of plutonium from the evaporator cleanout was moved by underground pipe line to the Metal Recovery Plant where equipment had been installed for anion exchange recovery and concentration of the plutonium. The plutonium solution contained nitric acid and HF, aluminum and boron cations, as well as radiochemical impurities such as zirconium - niobium. In addition to recovery, we were interested in obtaining data on the effectiveness of one cycle plutonium decontamination by anion exchange under conditions similar to those planned for recovery of plutonium from irradiated plutonium aluminum alloy this Fall in Building 4507. A comparison of the two programs is shown in Figure 8.

In the cleanout program, plutonium was concentrated by evaporation to 0.1 g/liter and by ion exchange to 16 g/liter average. The aluminum, boron, and fluoride contents were reduced essentially to zero and the fission product activity to plutonium background.

In the design of the present plutonium-aluminum processing program, similar chemical compositions are expected in the feed, but the fission product content differs enormously. Two cycles of anion exchange will be used to obtain an over-all d.f. of at least 10^6. In spite of the very high concentration of fission products, the heat content in the feed is relatively low due to long cooling of the fuel.

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Fig. 8. ANION EXCHANGE PROCESSING OF PLUTONIUM FEED AND PRODUCT COMPOSITION

COMPONENT	BLDG. 3019 CLEANOUT PROGRAM		Pu-Al PROCESSING PROGRAM	
	FEED	PRODUCT	FEED*	PRODUCT*
Pu, g/liter	0.11	15.9	0.26	~20
FISSION PRODUCTS, g/liter	$<10^{-4}$	$<10^{-7}$	0.71	$<10^{-6}$
HNO_3, *M*	7.2	1.8	7.2	2
Al^{3+}, *M*	0.3	5×10^{-4}	0.8	10^{-4}
F^-, *M*	0.04	–	0.03	–
GROSS γ, counts min^{-1} ml^{-1}	2×10^6	4×10^4	$\sim 3 \times 10^{10}$	$\sim 10^5$
curies/ml	$\sim 10^{-5}$	$\sim 10^{-7}$	0.13	$\sim 10^{-6}$
HEAT, w/liter	–	–	0.53	–

*PREDICTED

The plutonium recovery during the cleanout program was excellent (approximately 100% recovery) and the only difficulty during the anion exchange process was valence adjustment. After the recovery program the Metal Recovery Plant was cleaned and placed in standby condition. Future plutonium processing will be done in better contained facilities such as the manipulator cells in Building 4507.

The flowsheet for processing the plutonium-aluminum alloy is shown in the Figures 9 and 10. In Figure 9 the head end or feed preparation is shown. One rod is charged per run and is dissolved in 43 liters of 7 molar nitric acid. Plutonium is reduced to +3 by ferrous sulfamate and oxidized to +4 by nitrite. The feed is clarified by filtration with a sand filter and continuously adjusted with 13 M HNO_3 to the proper acidity for anion exchange.

The adjusted feed is preheated to 60°C and fed to the first ion exchange column where it is contacted with four percent cross linked Permutit SK strongly basic resin (see Figure 10). The waste and wash is accumulated for possible future recovery of gram quantities of americium and curium. The bed is loaded with plutonium from seven rods and eluted with dilute nitric acid. The product is again adjusted to 7 M HNO_3 and loaded on a second identical resin column. After washing, final elution results in approximately 20 grams per liter plutonium in 2 molar nitric acid.

I have three photographs of the facilities in cell 1, Building 4507, which will be used for the plutonium recovery program.

Figure 11 is a view of the floor in cell one. The dissolver, feed adjustment tank, and process vessels as well as the ion exchange columns are below the floor level which is now covered with six inches of lead. Figure 12 is a view of the west wall of the cell, showing the sampler in the background and the jacketed feed lines to the ion exchange columns. One interesting feature of the design is the installation of the monitoring tubes which can be used to measure the radiation intensity near the resin column and hopefully locate the band of plutonium.

Figure 13 is a view of the east wall of the cell. It shows the slug chute, the condenser, the off-gas scrubber, and the sand filter. The hot operation of this facility will begin the middle of October.

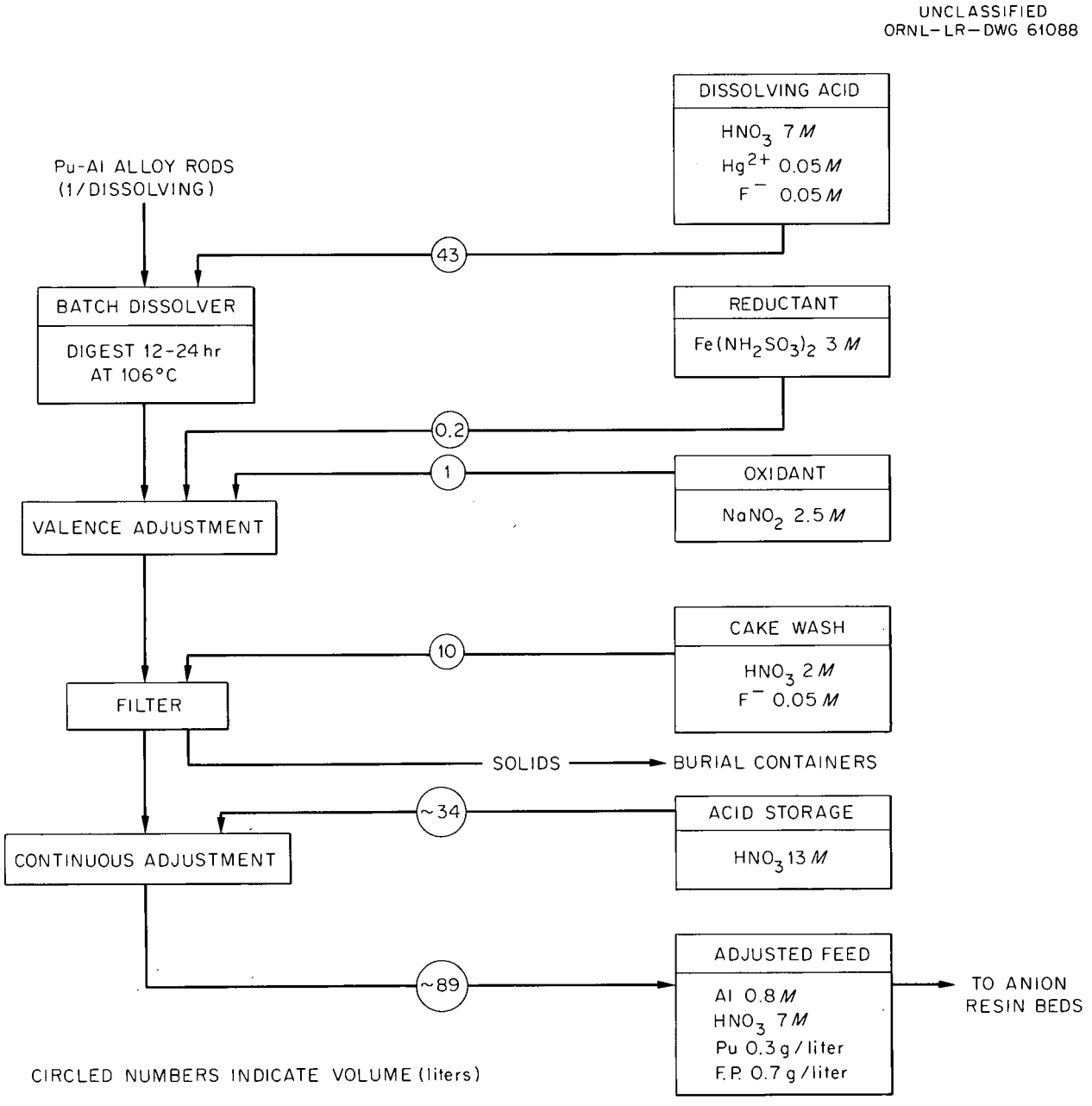

Fig. 9. PLUTONIUM-ALUMINUM ALLOY PROCESSING FEED PREPARATION

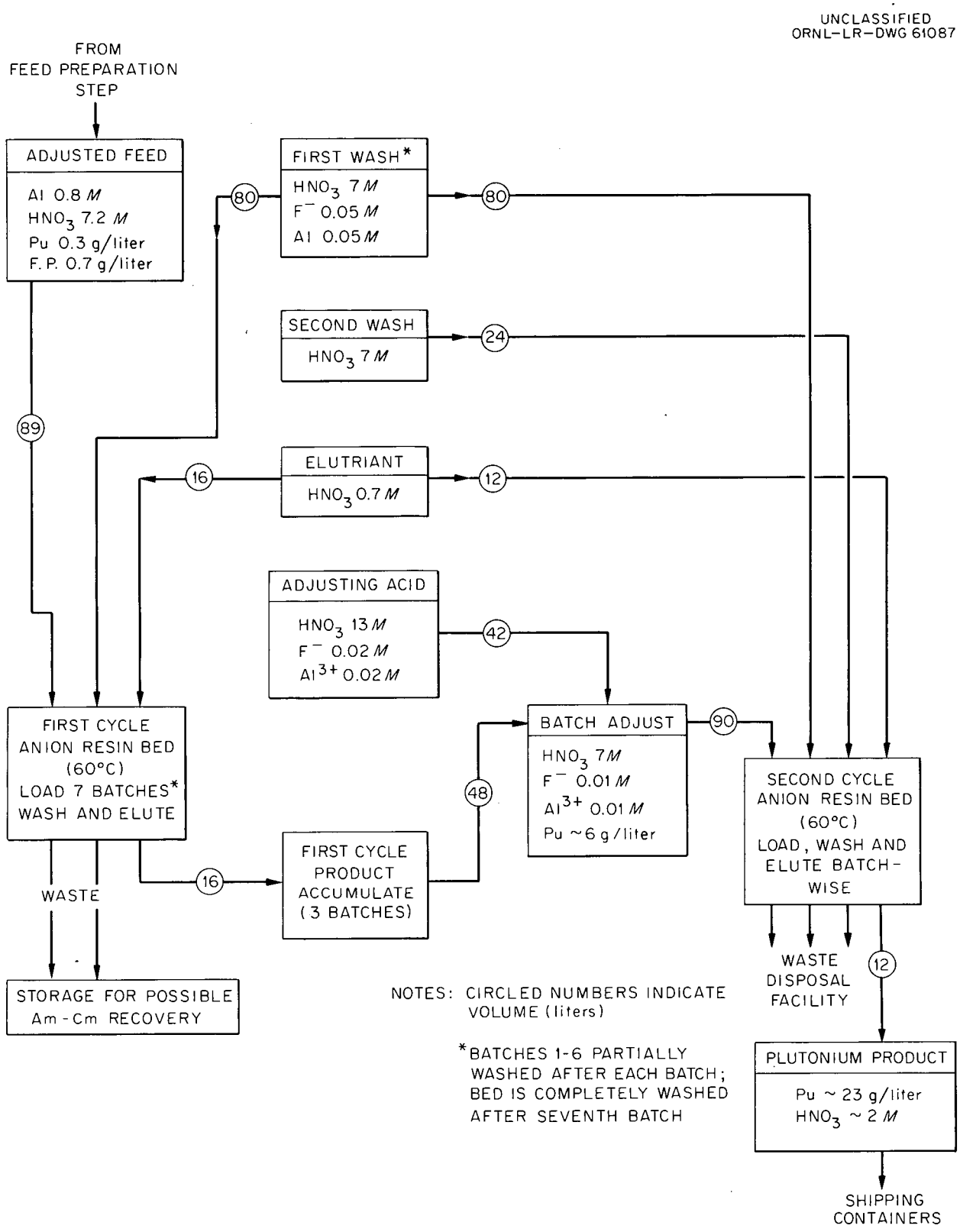

Fig. 10. PLUTONIUM-ALUMINUM ALLOY PROCESSING ANION EXCHANGE

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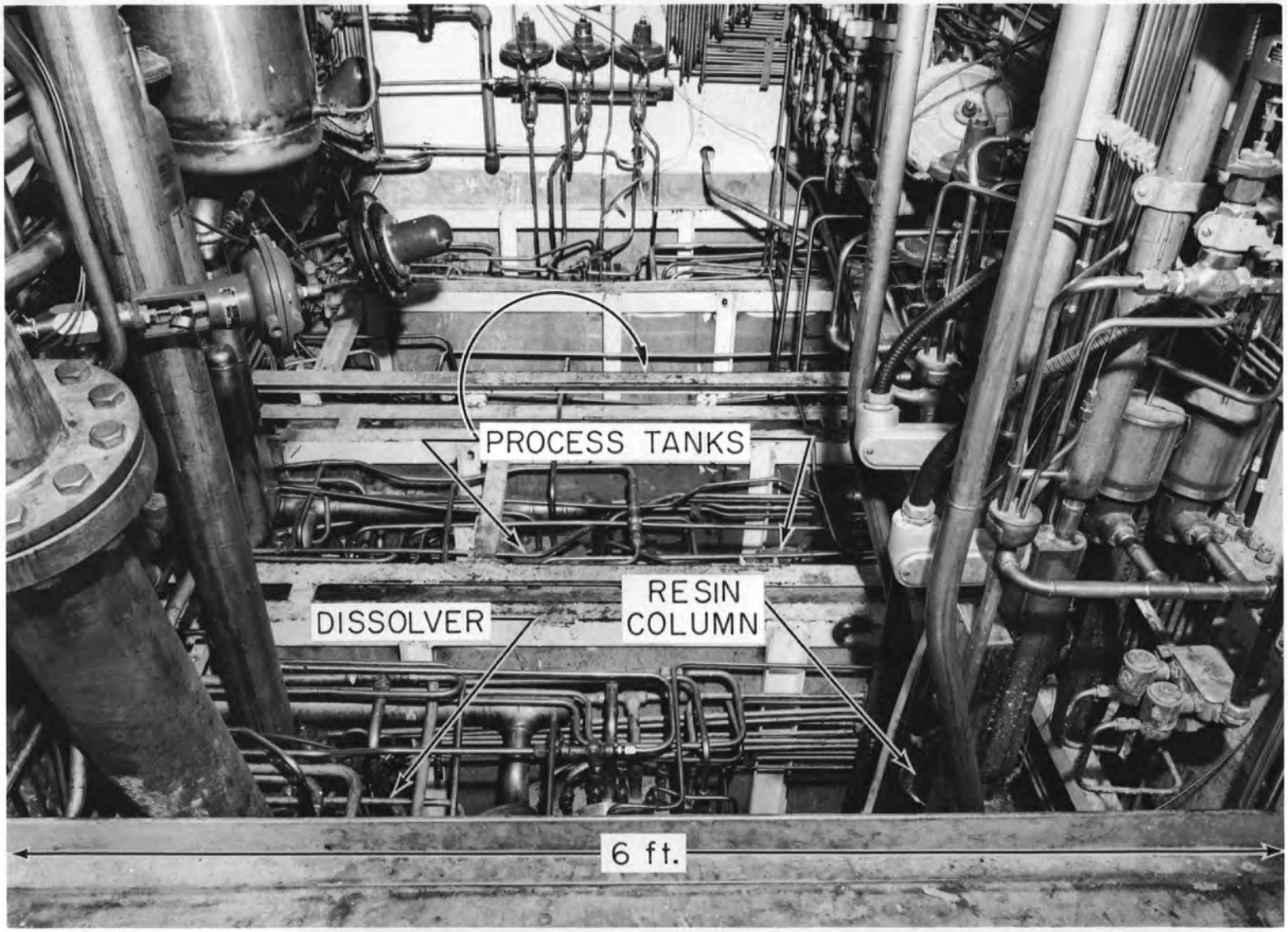

Fig. 11. FLOOR OF CELL 1, BLDG. 4507

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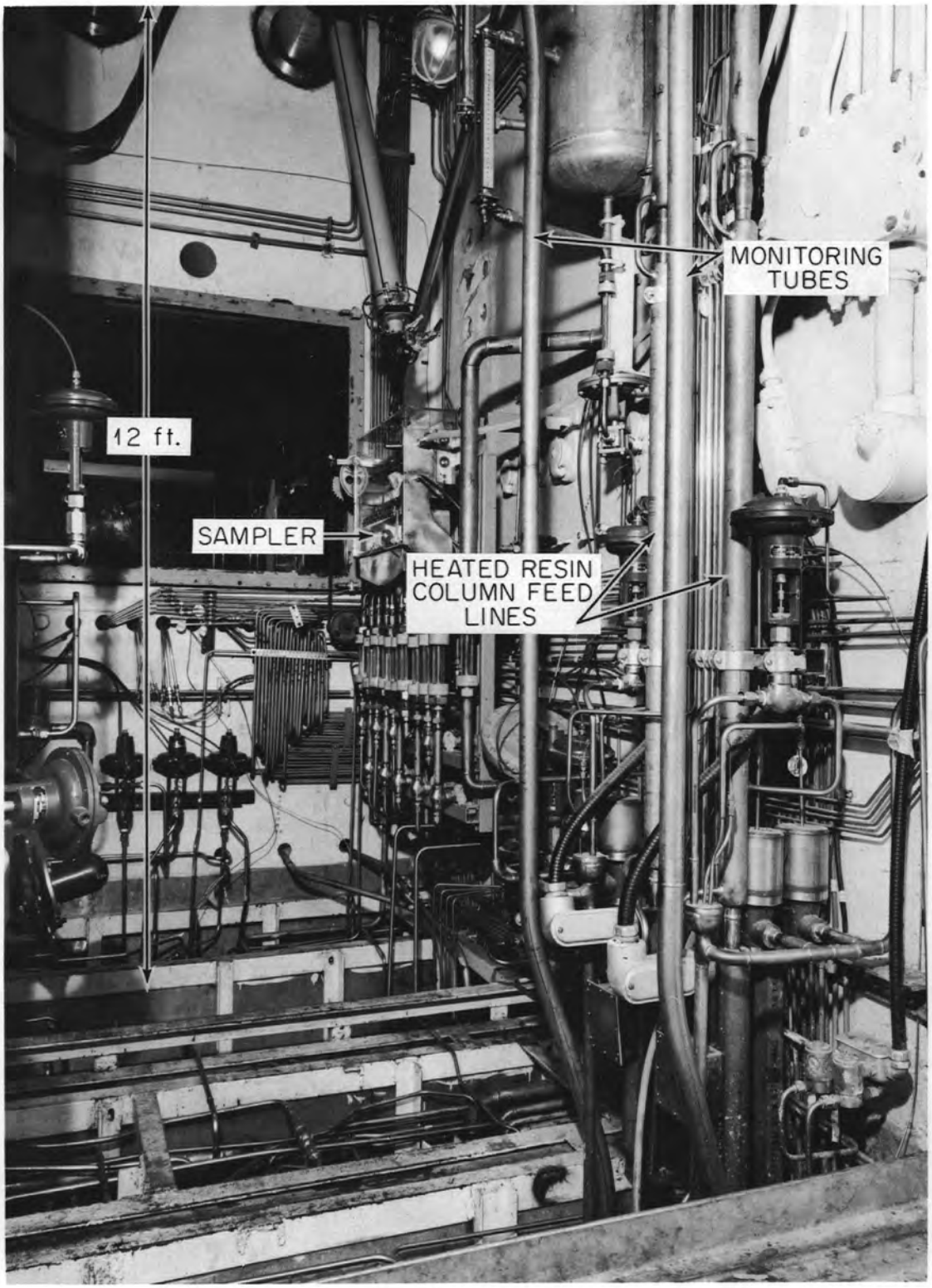

Fig. 12. WEST WALL, CELL 1, BLDG. 4507

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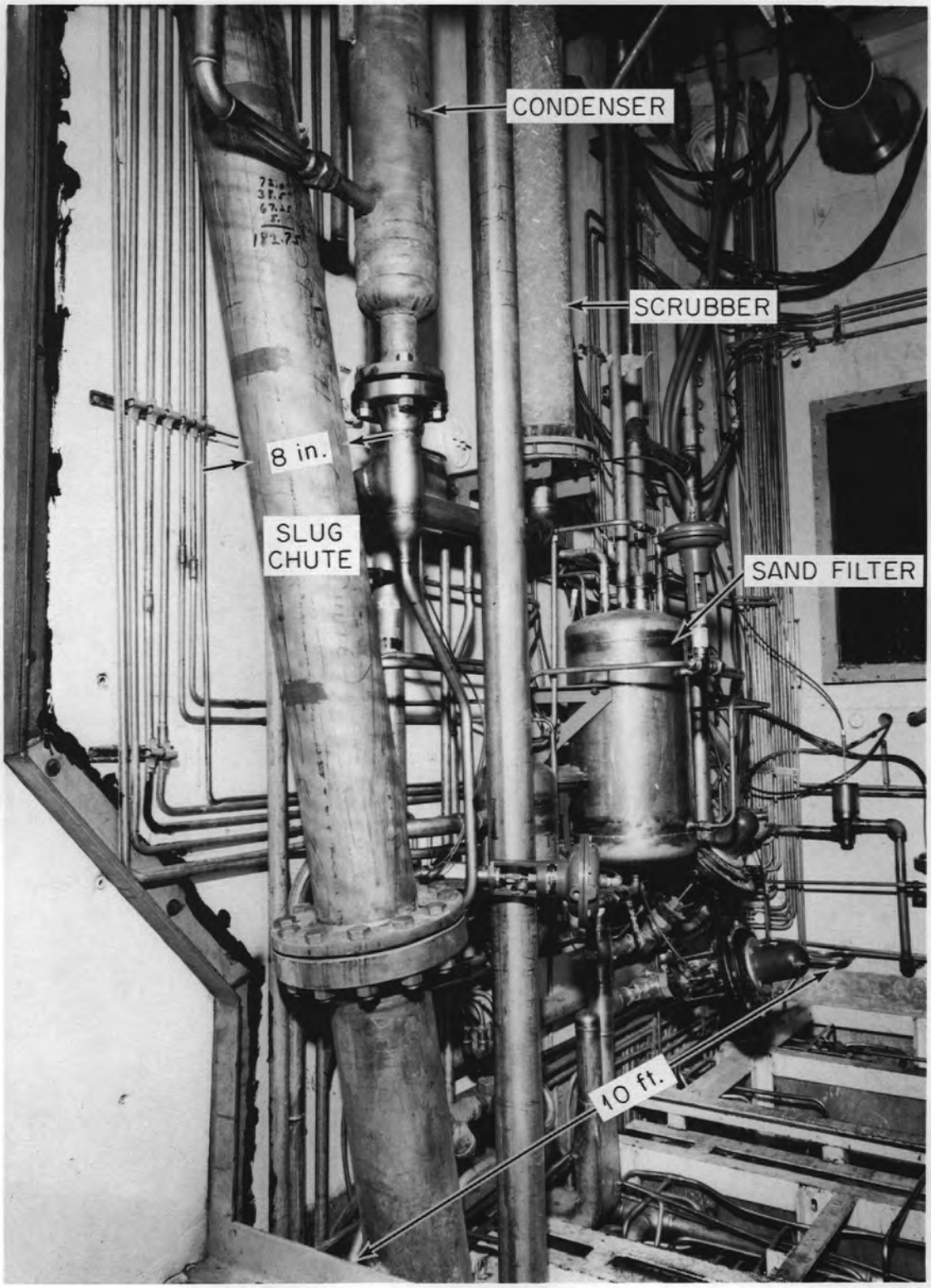

Fig. 13. EAST WALL, CELL 1, BLDG. 4507

In summary, the large aqueous pilot plant facilities at ORNL have been cleaned and are being put in standby condition. Valuable experience was gained during the year as anion exchange was used to recover more than one kg of plutonium left in the exploded evaporator system. This experience is being applied to a new recovery program just beginning in cell 1 of Building 4507.

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