INTRA-LABORATORY CORRESPONDENCE
OAK RIDGE NATIONAL LABORATORY

August 30, 1977

TO: F. L. Culler

FROM: D. E. Ferguson

SUBJECT: Simple, Quick Processing Plant

We have looked at the problems of providing a facility capable of isolating 10 kg of plutonium and converting it to metal buttons. Actually, we estimate that it will take four to six months to start operation, with the first 10 kg of plutonium metal about one week later. We have assumed one PWR element per day throughput (about 5 kg plutonium per day).

We have assumed the following:

1. Existing small industries (winery, dairy, oil refinery) that can be pirated for instruments, tanks, fittings.
2. Sympathetic and friendly populace.
3. Adequate and ready funds.
4. Machine shop equipment (lathe, power saw, drill, welder, etc.).
5. Light construction firm (bulldozers, concrete, steel).

The construction would begin with excavation of a deep ditch, about 25 ft deep, to be lined with concrete. A 20-ft-deep well at one end receives the cask for unloading the fuel. After emplacement of the concrete, the dirt will be backfilled and the covering building completed. The dry cell will be closed with concrete slabs for shielding. Holes for periscopes are cast in the slabs.

Much of the equipment can be improvised of stainless steel 55-gal drums, but all can be easily fabricated in a small metal-working shop. It is probable that most equipment will be available from local industries, requiring, at most, minor alterations. A list of the major equipment items is attached.

OFF-GAS TREATMENT

The dissolver off-gas (~ 50 cfm maximum volume) will be passed through a caustic scrubber equipped with cooling coils to maintain the caustic near ambient temperature. The caustic will remove about 99% of the contained ^{129}I. Air will leak into the system to oxidize NO_x gas such that it can react with caustic. The effluent will contain small amounts of NO_x and water vapor. This effluent and other ventilation air (~ 500 cfm) will pass through a tunnel (~ 75 ft^2 cross section) filled with crushed limestone and then through a sand filter before being discharged to the environment.

Common carbon steel fans with good paint coating will last through a several-month campaign. Plastic pipe or concrete sewer pipe would serve adequately for air ducts.

WASTE STORAGE

The waste will be stored in four flat concrete tanks (about 2 ft deep by 1/4 acre area) containing crushed limestone, both to ensure neutralization and to "dilute" the waste for more even distribution for dissipation of the decay heat through the tank walls to the surrounding earth. This cooling, along with the decreasing heat generation rate as the fission products decay, is adequate and cooling coils are not needed. The tanks are vented, however, to the off-gas system.

Organic waste will be neutralized and stored in a similar but separate tank.

PROCESS DESCRIPTION

Dissolution, Feed Adjustment and Solvent Extraction

PWR fuel assemblies are cut under water[1] into 3 to 5-in.-long pieces of fuel rod and loaded into 55-gal-size perforated baskets, one fuel assembly per basket. The baskets are lifted from the pool into the shielded processing cell and lowered into the batch dissolver[2] tank. The dissolver charging opening cover is supported above the fuel basket in such a way that when the basket is lowered into the dissolver the cover seals into place in a water seal around the opening and the basket support rod can move up and down through a sleeve in the cover to lower the basket into the dissolvent. Dissolver instrumentation consists of a thermocouple and liquid-level and density-bubbler probes. The batch dissolver tank has previously been charged with 1300 liters of 8 *M* HNO_3 that is made up from recycled anion exchange column resin wash acid and fresh 13 *M* HNO_3. The dissolution reaction is initiated by heating the dissolver to ~ 80°C and by lowering the fuel basket slowly into the nitric acid. The reaction rate is controlled by lowering the basket at a controlled rate, thus limiting the amount of sheared fuel exposed to the dissolvent. Heating-cooling coils in the liquid and off-gas cooling-reflux coils in the vapor space also assist in temperature (reaction rate) control and minimize off-gas evolution rates. Dissolution should be essentially complete in 4 hr; 6 hr is allowed to remove > 99% of the UO_2 from the sheared fuel. At the end of the dissolution cycle, sodium nitrite solution is added to ensure that all the plutonium is present as Pu(IV). This step is optional as experience indicates that the dissolution reactions and radiation generated nitrite is usually sufficient to guarantee that all the plutonium is in the 4+ valence state. The dissolver contents are then cooled to about 30°C and the entire batch is transferred via air lift[3] to the extractor. The dissolver is refilled with a fresh batch of acid and the leached fuel cladding basket is removed from the dissolver and discarded.

The batch extractor-stripper system[4] comprises two vessels in series, each provided with a low-speed turbo-mixer contactor assembly.[5,6] The mixer drive motors are located outside the shielded cell. Fresh 30% TBP in kerosene diluent is pumped through the extractor at a rate of about 8 liters/min for 10 hr, extracting essentially all the uranium and ≥ 98% of the plutonium. (TBP is a standard industrial chemical used in plasticisers and paints.) The organic extract flows into the stripper where it is contacted with a dilute nitric acid solution containing ferrous sulfamate to reduce all the Pu(IV) to the inextractable trivalent form. The plutonium selectively accumulates in the stripper aqueous phase. Fission product decontamination is ≥ 100 for the plutonium and ≥ 98% of the plutonium is recovered by the extraction-stripping operation. The uranium-loaded solvent is discarded. The extraction-stripping operation is complete in about 10 hr. Criticality safety is achieved by limiting the plutonium concentration. (Accidental criticality in the shielded process cell in this quick and dirty plant is not a serious problem.)

Anion Exchange Plutonium Purification System

Additional fission product decontamination and separation from uranium and ionic impurities are achieved by the anion exchange system. The plutonium stripper product from the solvent extraction system is batch-transferred to either of two feed preparation-feed tank vessels. The Pu(III) solution is heated to about 50°C and sodium nitrite and nitric acid are added to oxidize Pu(III) to Pu(IV) and oxidize any unused ferrous sulfamate. A small amount of nitrogen oxides are evolved by the oxidation. The feed solution is adjusted to 7 M HNO_3 for loading on the anion exchange resin.[7] The solution is filtered and fed to load the anion exchange resin at a rate of 50 mg of plutonium per min per cm^2 bed area by an air lift. Two resin columns are required. The resin is 6 in. in diameter and 6 ft tall. The ion exchange beds are geometrically safe. A standard readily available anion exchange resin, such as Permutit SK (20 to 50 mesh) or Dowex 1 X-4, is used. It should be noted that a two-cycle process using anion exchange resins could be used instead of the solvent extraction--anion exchange combination described herein. Although not noted on the flowsheet, a low concentration of HF, about 0.01 M, would be added to the anion exchange resin feed to promote fission product decontamination. The feed is filtered through a sand bed filter before entering the resin beds. Filter cleanup is done by backflushing with nitric acid as needed. The anion exchange system is operated at 50 to 60°C for all operations to promote rapid sorption-desorption kinetics. About 3.25 hr are required to load about 1.67 kg of plutonium onto the resin at a conservatively estimated average loading of 50 g of plutonium per liter of resin. Loading losses are ≤ 5%. After loading, the resin is washed with 30 volumes of fresh 7 *M* HNO_3 containing 0.01 *M* HF to remove fission products, uranium, and ionic impurities from the resin. This washing waste is collected, butted to 8 *M* HNO_3 and recycled to the dissolver for dissolvent, recovering any plutonium losses. The small amount of fluoride is tolerable, corrosion-wise, for the limited useful life of the dissolver and is beneficial for fission product decontamination in the first extraction cycle. The plutonium is eluted from the resin using 0.6 *M* HNO_3 at a rate of about 1 ml m^{-1} cm^{-2} bed area. Essentially all the plutonium is eluted from the resin at an average concentration of 50 g of plutonium per liter. The spent resin is discarded each time, although it could be reconditioned with 7 *M* HNO_3 and reused for several cycles, as limited by radiation and chemical damage effects. About 14 hr are required to load, wash, elute, and replace the resin; 2.5 complete column cycles are required each day for 4.2 kg of plutonium. Fission product decontamination for the anion exchange operation is $\geq 10^4$, giving an overall DF of $\geq 10^6$ for the system. The plutonium product is suitable for shadow-shielded glove box operations. Plutonium recovery by anion exchange is ≥ 95%, giving an overall system recovery of ~ 93%.

PuF_3 Production

The production of PuF_3 follows a well-known, routinely used production procedure.[8] Precipitation, PuF_3 preparation, and reduction to metal is done in shadow-shielded equipment in glove boxes. The anion exchange plutonium product is collected in 1.67-kg-plutonium batches (~ 33.4 liters), reduced to Pu(III) with ascorbic acid (vitamin C), and butted to $4\ M\ HNO_3$ with fresh nitric acid and cooled to room temperature. This solution is fed at a rate of 12.5 liters/hr to a two-stage, stirred precipitation vessel made of polyethylene or some other aqueous HNO_3-HF-resistant plastic. In the first stage precipitator, $4\ M$ HF is added to maintain an HNO_3/HF ratio of ≥ 6. Residence time in the precipitator is ≥ 5 min (about 2.5 liters stage volume). The slurry overflows to the second stage, where additional HF is added (HNO_3/HF ratio ≤ 3) and additional crystal growth occurs to yield a readily filterable precipitate of PuF_3. The slurry overflows to plastic batch filters (laboratory type Buchner filters) collecting about 1 kg of PuF_3 on each filter. The precipitate is washed with dilute HF to remove traces of HNO_3 and is air-dried to about 2% moisture by drawing dry air through the cakes for 3 hr. Filtrate losses of plutonium are generally low (0.05 to 0.1%) and the filtrate is discarded to waste storage. The precipitation operation requires about 10 hr/day to process ~ 4.2 kg of plutonium, leaving adequate time for feed adjustment and precipitator cleanup operations. The air-dried PuF_3 is loaded onto shallow trays and oven-dried at 600°C for ≤ 1.5 hr in an argon or helium atmosphere to produce anhydrous PuF_3. One oven to accommodate about four small trays of PuF_3 (1 kg of plutonium per tray) is required.

Plutonium Metal Production

The production of plutonium metal follows a well-known, routinely used production procedure.[9] Anhydrous PuF_3 (1-kg-plutonium batches) is dry blended in a laboratory-size V shell blender with finely divided calcium metal and iodine booster. The calcium reduces the PuF_3 to metal and the iodine "booster" reacts with calcium metal to provide flux for the slag and additional heat to produce a solid metal button. The charge is tamped in a magnesia or calcium fluoride crucible placed in a carbon steel reduction "bomb." The bomb is capable of withstanding internal pressures ≤ 400 psi. The space between the crucible and the bomb walls is packed with refractory granules. After filling, the bomb is capped, and evacuated and backfilled with argon to remove air. The bomb is placed in an induction or resistance furnace and heated to about 300°C throughout the charge and then rapidly heated to 600°C to initiate the booster reaction and reduce the charge to plutonium metal. The reaction takes only a few seconds; much more time is consumed in heating the bomb to the initiation temperature and by cooling it to near room temperature after removal from the furnace. The bomb is opened and the crucible is removed and broken up to remove the plutonium metal regulus. The crucible, slag, and bomb are discarded. The yield of plutonium metal is generally $\geq 97\%$ and generally is $\geq 99.8\%$ pure. The plutonium "button" is cleaned by washing (pickling) in concentrated nitric acid and is ready for remelting and casting into nuclear explosive parts.

References

1. J. T. Long, Engineering for Nuclear Fuel Reprocessing, Gordon and Beach Science Publishers, Inc., 1967, pp. 394-95.
2. Ibid, pp. 276-82 and 294.
3. Ibid, pp. 436-43.
4. Ibid, pp. 225-28.
5. T. J. Colven, "Critically Safe Equipment for Aqueous Processing," Second U.N. Conference on Peaceful Uses of Atomic Energy, P/518, 1958.
6. Long (ref. 1), pp. 228-29.
7. Ryan, Wheelwright, "Anion Exchange Processing of Plutonium," Second U.N. Conference on Peaceful Uses of Atomic Energy, P/1915, 1958.
8. Plutonium Handbook, Vol. II, Gordon and Beach, Science Publishers, Inc., 1967, pp. 557-58.
9. Ibid, pp. 564-66.

EQUIPMENT LIST

1. Shear - Metal cutting saw, abrasive disk. One required.
2. Dissolver - 4-ft-diam x 8.5-ft-high, type 304 stainless steel, 0.12-in. wall with condenser coil (~ 100 ft^2) in upper portion. Lower portion water jacketed.

   Note: Suitable tank likely available from light industry.
3. Solvent extraction contactor - 3.2-ft-diam x 8-ft-tall; type 304 stainless steel tank equipped with turbomix unit (see Item 4).

   Wall thickness, 0.12 in.

   Note: 55-gal drums could be used.
4. Plutonium stripper contactor - 2.2-ft-diam x 5.5-ft-tall; 0.12 wall, type 304 stainless steel tank equipped with turbomix unit similar to one described in Paper 518, Second U.N. Conf., Vol. 17, pp. 555-63.
5. Anion exchange feed tank - 3-ft-diam x 6-ft-tall; 0.12 wall, type 304 stainless steel tank with coils for heating and cooling. Air sparger for mixing.
6. Anion exchange columns - Two required. 6-in.-ID x 7-ft-high. Glass pipe with type 304 stainless steel end pieces.
7. Plutonium product storage and PuF_3 precipitation feed tanks. Six required. 6-in.-diam x 12-ft-long. Use 6-in. pipe or manufacture from 0.12-wall type 304 stainless steel.

8. Dissolver feed tank - 0.12-in.-wall type 304 stainless steel tank, 3-ft-diam x 8-ft-high.
9. Off-gas scrubber - 2-ft-diam x 10-ft-long packed with raschig rings made from 1/2-in. stainless steel tubing. Fabricate from 0.12-wall type 304 stainless steel or three 55-gal stainless steel drums. Provide cooling coils and liquid recirculation system using air lift.
10. PuF_3 precipitation equipment - 20-ft-long hood or glove box equipped with two stirred PVC precipitation pots, Buchner funnels, drying furnace (electric resistance type, 600°C), vacuum source.
11. Metal preparation hood - 20-ft-long hood - solids blender (lab scale). 6-in.-diam x 18-in.-long steel reduction vessel. MgO crucible to fit into above vessel (one vessel and crucible per kg Pu). Vacuum pump, argon supply.
12. Metal reduction furnace - Electric resistance furnace with 6-in.-diam x 18-in.-long cavity. 600°C maximum temperature capability.

Table 1. Typical Physical Characteristics of Unirradiated LWR Fuel Assemblies

	BWR[3]	PWR[4]
Overall assembly length, m	4.470	4.059
Cross section, cm	13.9 x 13.9	21.4 x 21.4
Fuel element length, m	4.064	3.851
Active fuel height, m	3.759	3.658
Fuel element OD, cm	1.252	0.950
Fuel element array	8 x 8	17 x 17
Fuel rods per assembly	63	264
Assembly total weight, kg	275.7	657.9
Uranium/assembly, kg	183.3	461.4
UO_2/assembly, kg	208.0	523.4
Zircaloy/assembly, kg	56.9[a]	108.4[b]
Hardware/assembly, kg	9.77[c]	26.1[d]
Total structural metal/assembly, kg	67.7	134.5

[a] Includes Zircaloy fuel-element spacers.

[b] Includes Zircaloy control-rod guide thimbles.

[c] Includes SS tie-plates and Inconel springs.

[d] Includes SS nozzles and Inconel-718 grids.

Table 2. Typical Nuclear Characteristics of LWR Fuels

Parameter	BWR	PWR
Uranium per assembly, kg		
Initial	183.3	461.4
Discharge	176.3	440.7
Enrichment, wt % ^{235}U		
Initial	2.75	3.20
Discharge	0.69	0.84
Plutonium per assembly at discharge, kg	1.57	4.32
Average power, MW/assembly	4.75	17.3
Average specific power, kw/kg initial uranium	25.9	37.5
Average discharge burnup, MWd/metric ton initial uranium	27,500	33,000
Irradiation duration, full-power days	1062	880

Parameter	2Y	5Y	10Y	30Y	100Y	1000Y	10^4Y	10^5Y
Thermal power, watts/assembly								
Structural materials	1.00E+01[a]	4.86E+00	1.98E+00	2.06E-01	7.44E-02	1.88E-02	1.59E-02	5.08E-03
Actinides								
Spent fuel	1.06E+02	9.14E+01	9.57E+01	1.02E+02	8.89E+01	2.56E+01	6.37E+00	4.89E-01
Less (U + Pu)[b]	5.30E+01	3.15E+01	2.67E+01	1.49E+01	4.74E+00	1.12E+00	2.26E-01	2.80E-02
Fission products	2.47E+03	8.65E+02	4.54E+02	2.39E+02	4.44E+01	9.10E-03	8.68E-03	5.73E-03
Total								
Spent fuel	2.59E+03	9.61E+02	5.52E+02	3.41E+02	1.33E+02	2.56E+01	6.39E+00	5.00E-01
Spent fuel less (U + Pu)[b]	2.53E+03	9.01E+02	4.83E+02	2.54E+02	4.92E+01	1.15E+00	2.51E-01	3.88E-02
Activity, curies/assembly								
Structural materials	4.08E+03	1.72E+03	6.82E+02	2.44E+02	1.41E+02	2.72E+00	2.20E+00	8.66E-01
Actinides								
Spent fuel	5.66E+04	4.91E+04	3.95E+04	1.72E+04	3.21E+03	7.98E+02	2.08E+02	1.83E+01
Less (U + Pu)[b]	1.77E+03	1.15E+03	9.66E+02	5.15E+02	1.54E+02	4.04E+01	9.98E+00	1.18E+00
Fission products	6.11E+05	2.27E+05	1.47E+05	8.45E+04	1.62E+04	1.05E+01	9.94E+00	7.77E+00
Total								
Spent fuel	6.72E+05	2.78E+05	1.87E+05	1.02E+05	1.96E+04	8.11E+02	2.20E+02	2.69E+01
Spent fuel less (U + Pu)[b]	6.17E+05	2.30E+05	1.49E+05	8.53E+04	1.65E+04	5.36E+01	2.21E+01	9.82E+00
Ingestion toxicity,[c] m^3 water/assembly								
Structural materials	2.46E+08	2.85E+07	1.29E+07	8.30E+06	4.87E+06	2.17E+05	1.53E+05	1.03E+04
Actinides								
Spent fuel	7.66E+08	7.48E+08	7.53E+08	7.43E+08	6.29E+08	1.80E+08	4.33E+07	2.27E+07
Less (U + Pu)[b]	1.82E+08	1.44E+08	1.25E+08	7.56E+07	3.21E+07	8.10E+06	1.58E+06	7.36E+05
Fission products	1.44E+11	1.14E+11	9.73E+10	5.91E+10	1.05E+10	4.40E+04	3.86E+04	3.00E+04
Total								
Spent fuel	1.45E+11	1.15E+11	9.81E+10	5.99E+10	1.11E+10	1.80E+08	4.35E+07	2.27E+07
Spent fuel less (U + Pu)[b]	1.44E+11	1.14E+11	9.74E+10	5.92E+10	1.05E+10	8.36E+06	1.77E+06	7.76E+05

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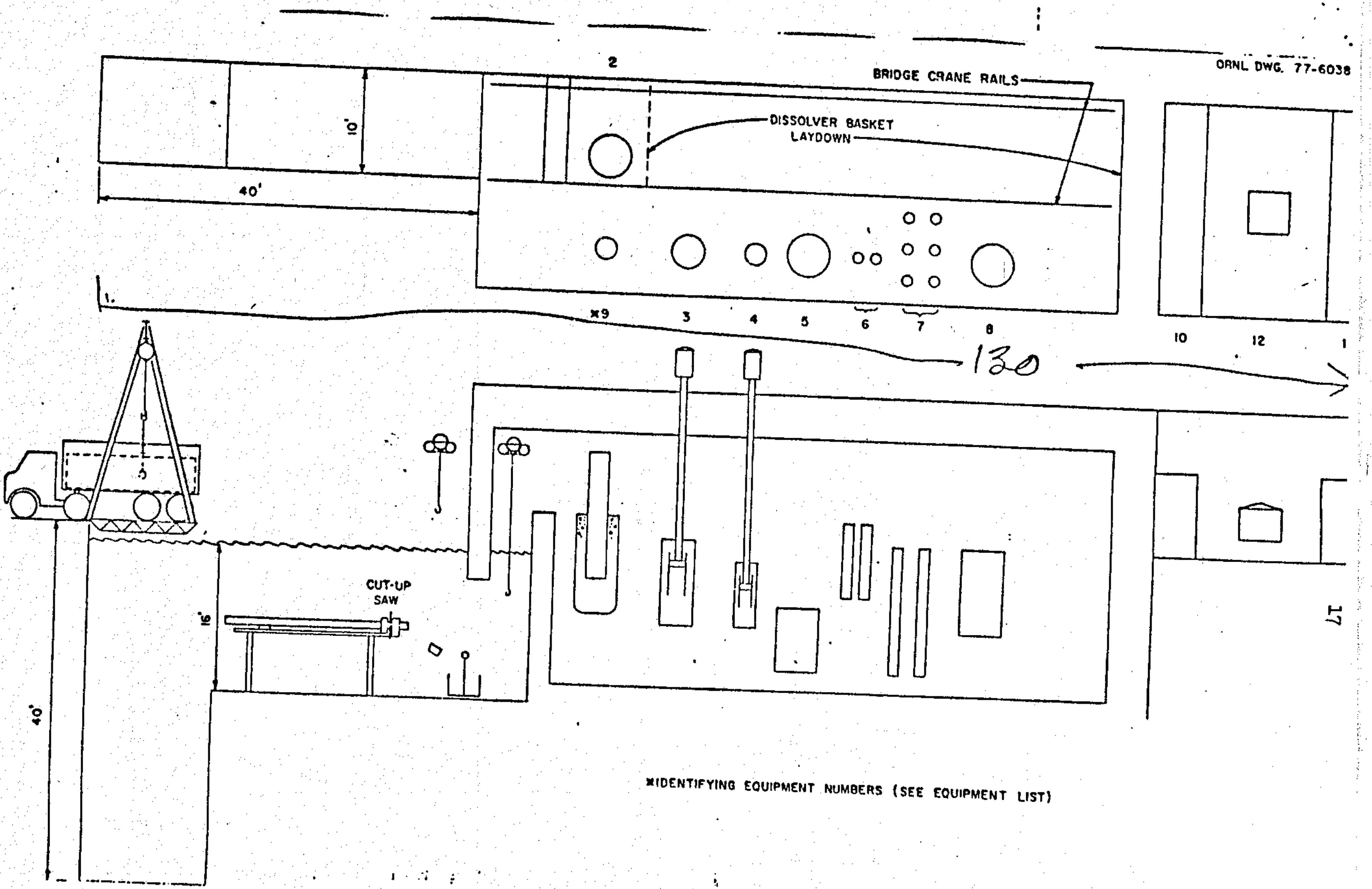
[a] Read 1.0 × 10^1

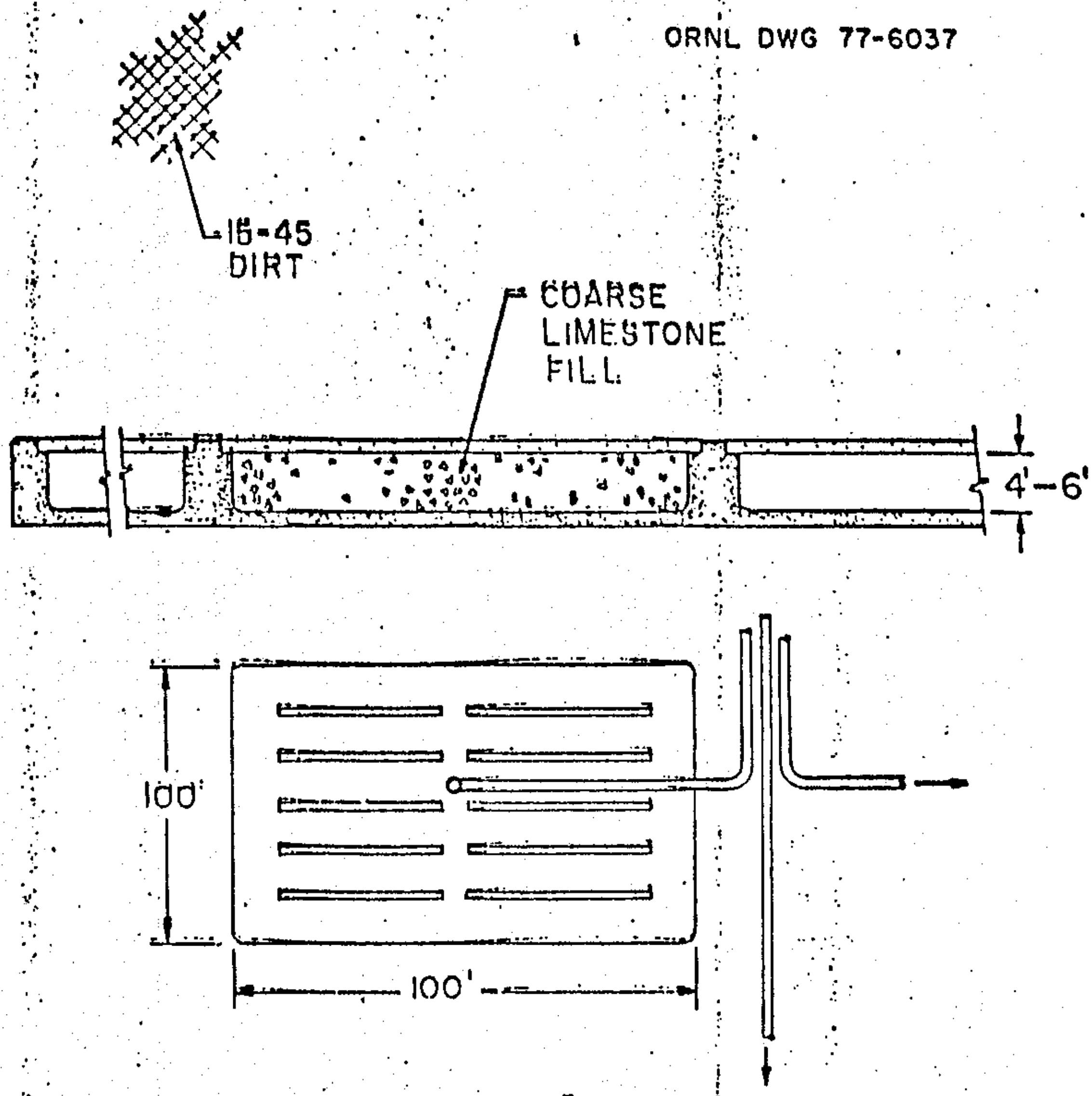
[b] 99.5% removal of uranium and plutonium assumed.

[c] Sum of the amount of waste required to dilute each isotope to the point that it is acceptable



*IDENTIFYING EQUIPMENT NUMBERS (SEE EQUIPMENT LIST)

ORNL DWG 77-6037



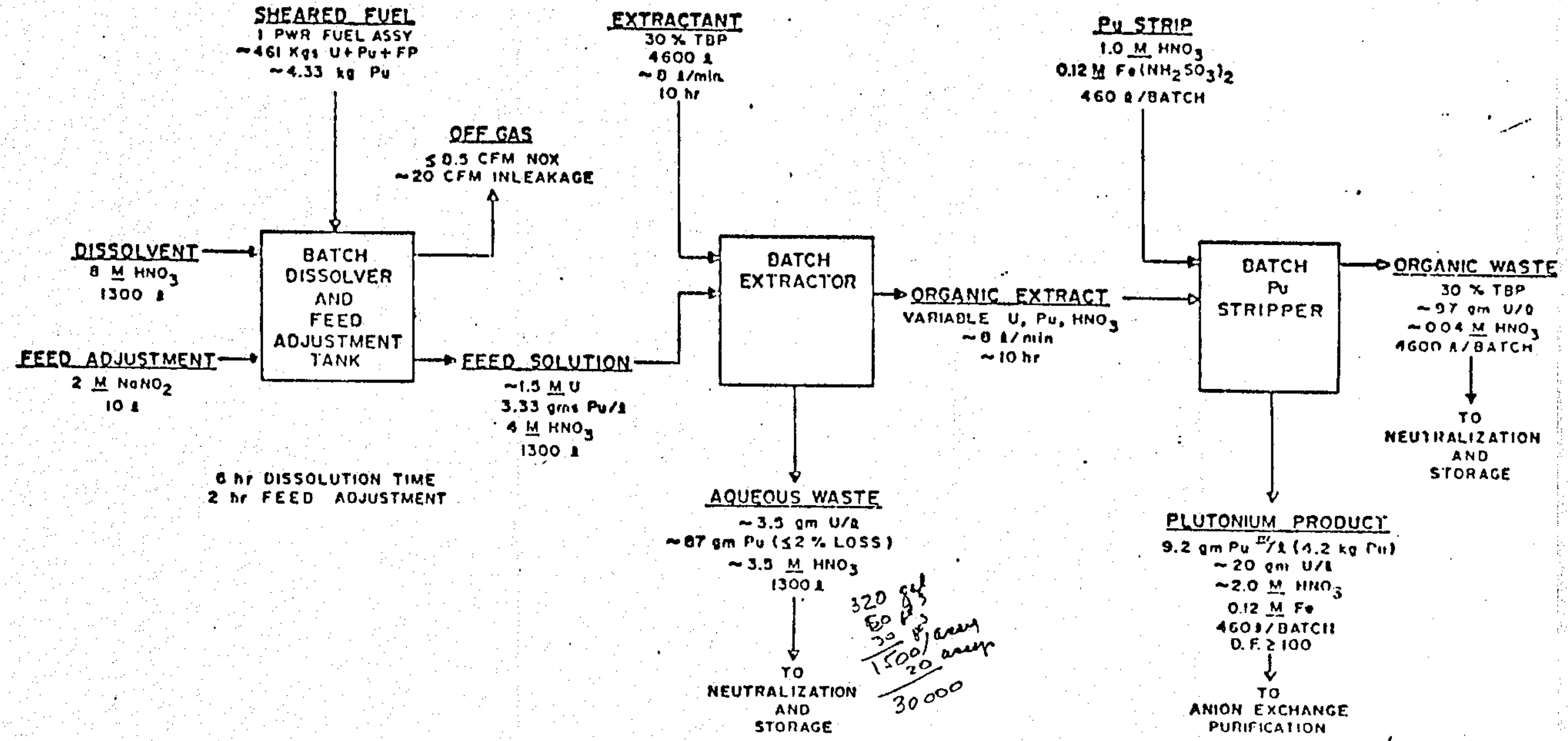
20,000 FT^3
4-REQ'D. (1 ACRE)

WASTE STORAGE

8 HR 1 ASSEMBLY/DAY	**SAW FUEL** UNDER WATER ABRASIVE CUT-OFF SAW
8 HR	**DISSOLUTION** TRANSFER SHEARED FUEL TO DISSOLVER ADD NITRIC ACID
10 HR	**EXTRACTION AND STRIPPING** TRANSFER DISSOLVER SOLUTION TO EXTRACTOR PUMP ORGANIC THROUGH EXTRACTOR AND STRIPPER
14 HR/CYCLE (2 COLUMNS)	**ION EXCHANGE** PASS STRIP SOLUTION THROUGH ION EXCHANGE WASH COLUMN ELUTE COLUMN
4 HR/BATCH 4 BATCHES/DAY	**FLUORIDE PRECIPITATION** REDUCE TO Pu^{3+} ASCORBIC ACID ADD HF FILTER (BUCHNER FUNNEL) DRY CAKE
~8 HR/BATCH 4 BATCHES/DAY	**METAL REDUCTION** ADD IODINE AND CALCIUM METAL TAMP MIXTURE IN CRUCIBLE IN STEEL REDUCTION BOMB EVACUATE AND BACKFILL - ARGON RAISE TEMPERATURE TO 600°C COOL AND REMOVE METAL

adds to 52 hrs.
Cutler used 100 hrs
to be conservative

ORNL DWG. 77-1425

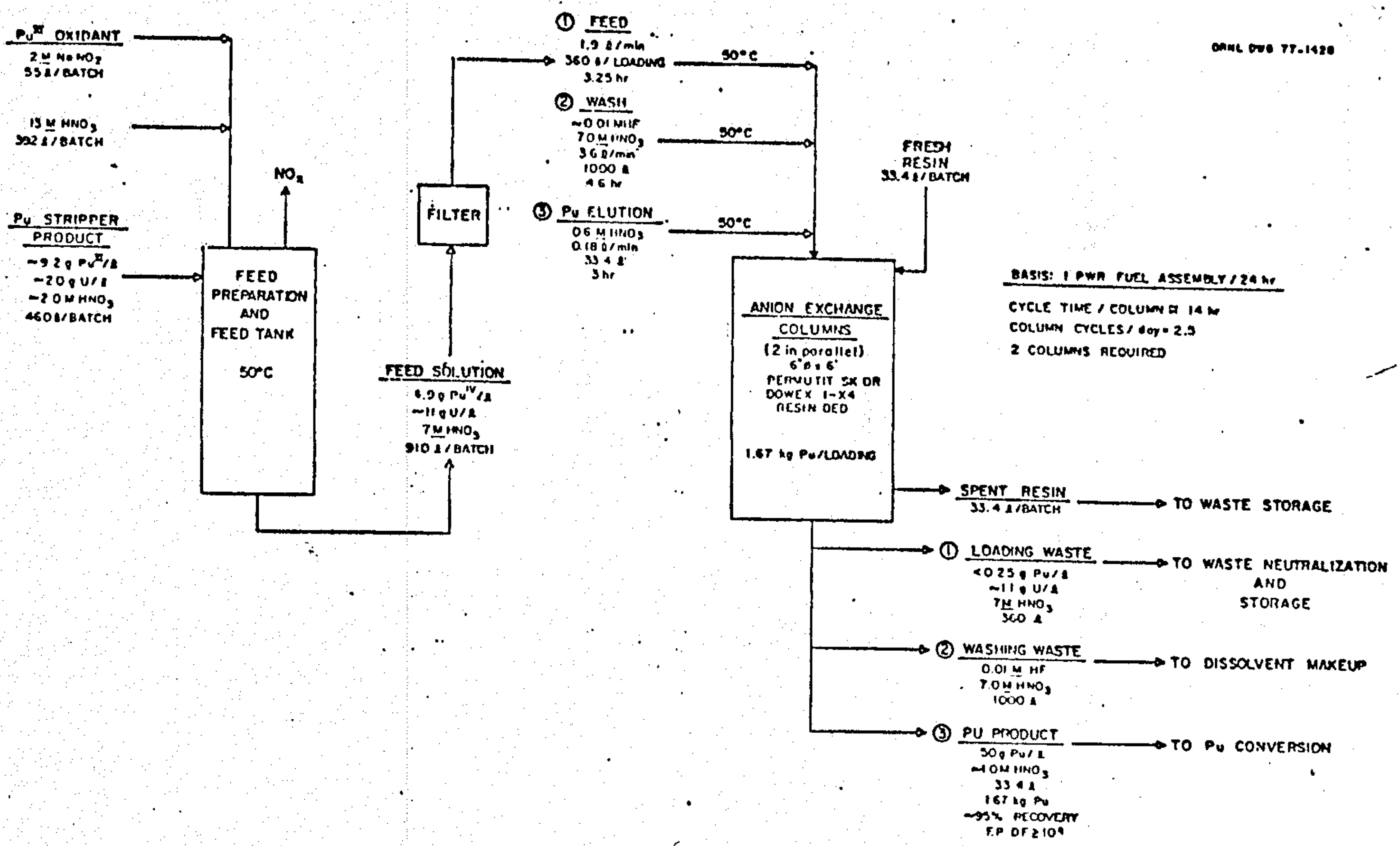


320 gal
50 ft3
30 ft3/assy
1500
20 assy
30000

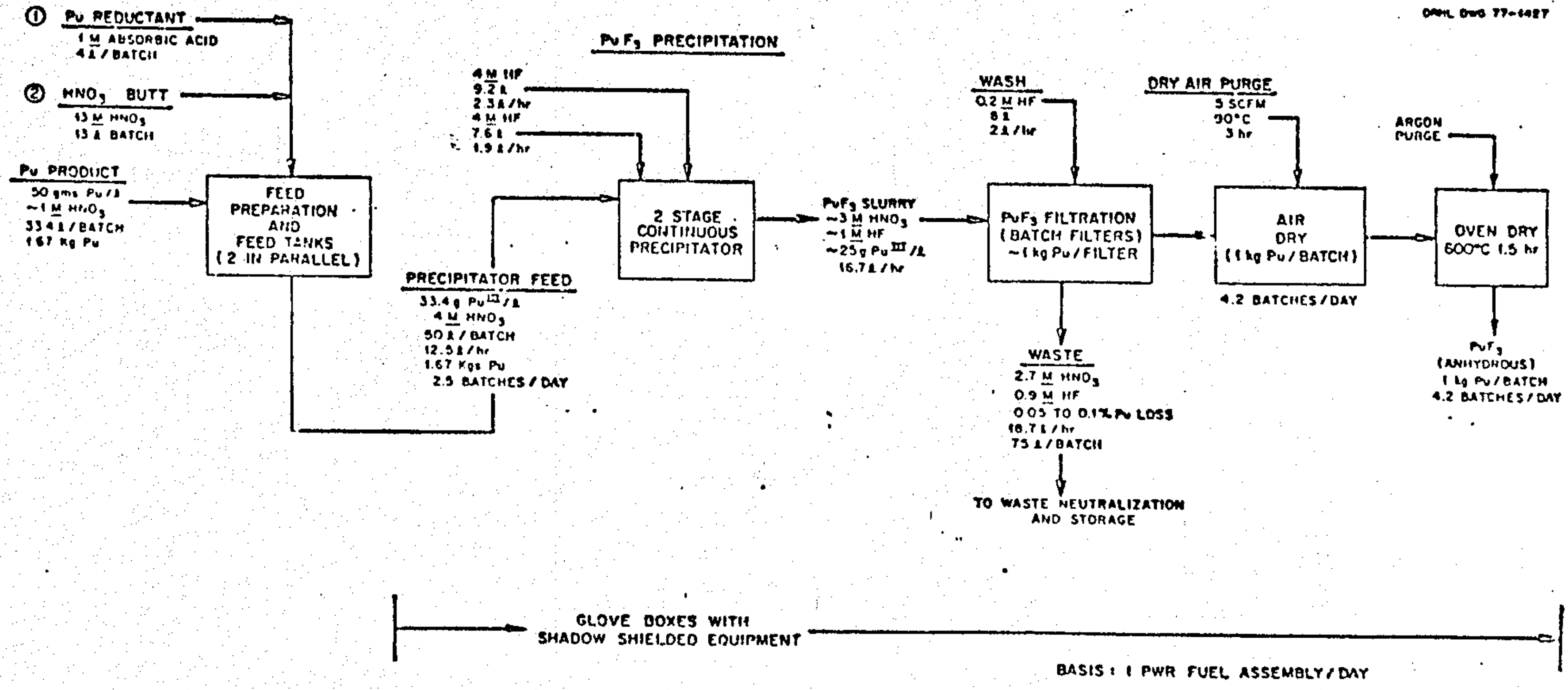
BASIS: 1 PWR FUEL ASSEMBLY/24 hr

DISSOLUTION, FEED ADJUSTMENT AND SOLVENT EXTRACTION

ORNL DWG 77-1428



ANION EXCHANGE Pu PURIFICATION SYSTEM


ORNL DWG 77-4427
① Pu REDUCTANT
1 M ABSORBIC ACID
4 ℓ / BATCH
② HNO$_3$ BUTT
13 M HNO$_3$
13 ℓ BATCH
Pu PRODUCT
50 gms Pu/ℓ
~1 M HNO$_3$
33.4 ℓ / BATCH
1.67 Kg Pu
FEED PREPARATION AND FEED TANKS (2 IN PARALLEL)
PRECIPITATOR FEED
33.4 g Pu^{III}/ℓ
4 M HNO$_3$
50 ℓ / BATCH
12.5 ℓ / hr
1.67 Kgs Pu
2.5 BATCHES / DAY
PuF$_3$ PRECIPITATION
4 M HF
9.2 ℓ
2.3 ℓ / hr
4 M HF
7.6 ℓ
1.9 ℓ / hr
2 STAGE CONTINUOUS PRECIPITATOR
PuF$_3$ SLURRY
~3 M HNO$_3$
~1 M HF
~25 g Pu^{III}/ℓ
16.7 ℓ / hr
WASH
0.2 M HF
8 ℓ
2 ℓ / hr
PuF$_3$ FILTRATION (BATCH FILTERS) ~1 kg Pu / FILTER
WASTE
2.7 M HNO$_3$
0.9 M HF
0.05 TO 0.1% Pu LOSS
16.7 ℓ / hr
75 ℓ / BATCH
TO WASTE NEUTRALIZATION AND STORAGE
DRY AIR PURGE
5 SCFM
90°C
3 hr
AIR DRY (1 kg Pu / BATCH)
4.2 BATCHES / DAY
ARGON PURGE
OVEN DRY 600°C 1.5 hr
PuF$_3$
(ANHYDROUS)
1 kg Pu / BATCH
4.2 BATCHES / DAY
GLOVE BOXES WITH SHADOW SHIELDED EQUIPMENT
BASIS: 1 PWR FUEL ASSEMBLY / DAY

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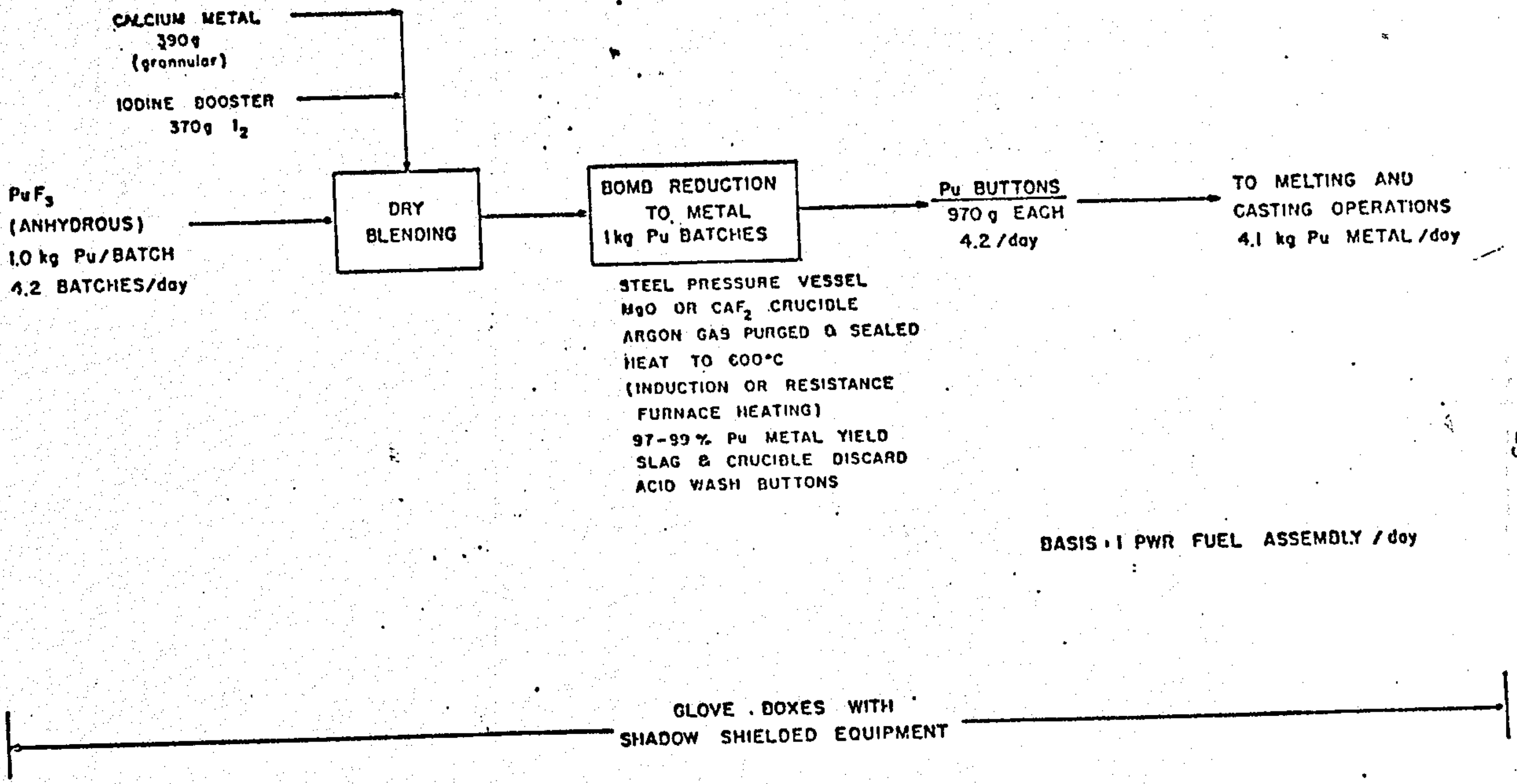

Pu METAL PRODUCTION