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POT CALCINATION OF SIMULATED RADIOACTIVE WASTE WITH CONTINUOUS EVAPORATION*

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ABSTRACT

Process equipment and a control system have been developed for an evaporation-calciner process for reduction of radioactive waste solutions to solids. A 25-liter evaporator close-coupled to an 8-in. dia x 90-in.-long calciner was operated and controlled successfully. The liquid filling rates for Purex waste and TBP-25 wastes were 20 to 30 liters/hr. The evaporator overhead decontamination factor was about 10^3.

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INTRODUCTION

The over-all pot calcination process has been described before (1-3). In this process high-radioactivity-level liquid wastes from nuclear fuel processing plants would be reduced to thermally stable solids by evaporation and pot calcination to ~900°C. The calciner pot itself would serve as the ultimate waste storage container, to be disposed of by storage in a dry, protected location, such as a salt mine. The cost of this method of permanent disposal of radioactive wastes compared to the present method of tank storage as liquids is still not certain (4,5), but it should result in a large reduction in hazard.

A number of tests were made in an 8-in.-dia by 90-in.-high calcination pot, close-coupled to an evaporator, to determine the operability of the pot calcination system and the nature of the product. Simulated Purex and TBP-25 wastes containing nonradioactive ruthenium were investigated.

A batch process was also tested with these wastes, and the data and flowsheets developed will be used for design of a pilot plant to be built at the Idaho Chemical Processing site.

FLOWSHEET

In the pot calcination process, radioactive waste is evaporated as much as possible without precipitation of solids, and is then pumped to a calcination vessel in which it is thermally decomposed to metal oxides and sulfates at temperatures up to 900°C (Fig. 1). After calcination is complete, the vessel is disconnected from the system, sealed, and transported to a permanent storage site. The calcination off-gas is recycled to the evaporator, and the evaporator off-gas, containing all the nitric acid in the original waste, is passed through a de-entraining section containing, e.g., Yorkmesh or impingement plates, to remove entrained fission products. The nitric acid thus decontaminated is concentrated by distillation, and the concentrated acid is recycled to the fuel processing plant. A second evaporation may be necessary to obtain sufficient decontamination for re-use. The distillate, very-low-concentration nitric acid which has been highly decontaminated, is discharged to the environment or recycled as makeup water. The volume of off-gas discharged is small, being only that from instrument bubblers and system leakage. The system can be made essentially continuous with one evaporator feeding a number of calcining pots operating in sequence.

The heat generated in the calcined solids by radioactive decay must be removed at a rate sufficient to keep the temperature of the solids below the calcination temperature. Otherwise, residual nitrate or sulfate may be decomposed during transportation and storage, causing a dangerous internal pressure, and corrosion of the vessel may be accelerated. The pots will be 6-24 in. dia and 8-15 ft high, the diameter being limited by the ability to lose decay heat (6) under storage conditions and the length by the size and weight of shipping cask permitted on public carriers.

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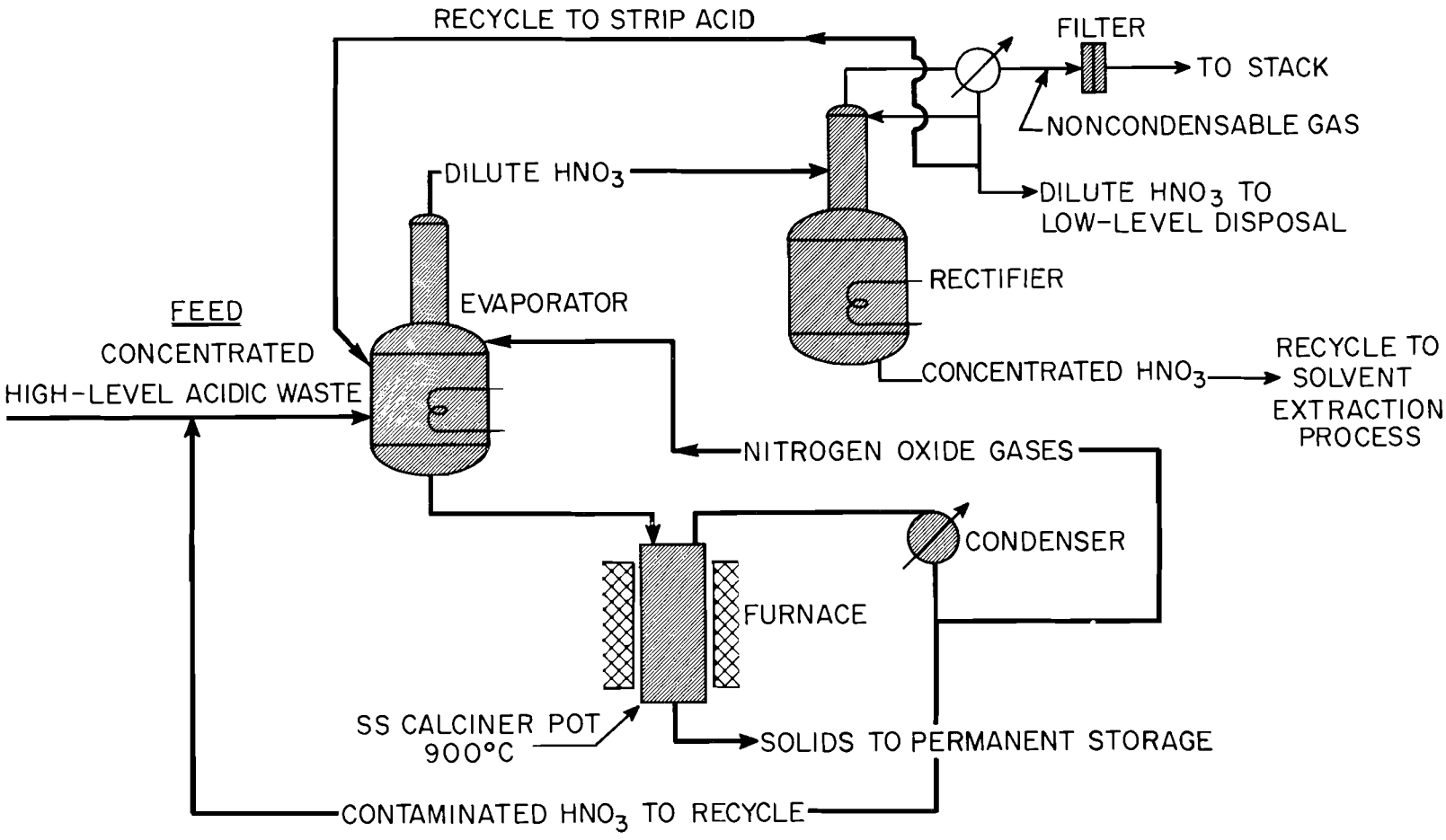

Flowsheet for converting high activity wastes to solids by pot calcination.

Fig. 1

EQUIPMENT OPERATION

In tests with simulated Purex and TBP-25 waste, operation of a close-coupled evaporator and an 8-in.-dia by 90-in.-high calciner was satisfactory. The average feed rate for TBP waste was 25-30 liters/hr and for Purex waste (Table 1) concentrated to 40 gal per ton of uranium prior to evaporation, 20-25 liters/hr. The calcination time was 8-10 hr, and the change-out time 8-10 hr. Thus, in this equipment, Purex waste from processing of 1.75-2.0 tons of uranium could be calcined in 1 day on a 2-day cycle.

Table 1. Major Constituents of Simulated Waste

	Concentration, M	
Ion	Conc. Purex (40 gal/ton)	TBP-25
H^+	5.6	0.5
NO_3^-	6.1	5.4
$SO_4^=$	1.0	0.03
Cl^-		
Fe^{3++}	0.5	0.002
Al^{3+}	0.1	1.6
Ni^{2+}	0.01	
Cr^{2+}	0.01	
Na^+	0.6	

Decontamination factors across the evaporator (Fig. 2) were about 10^3 (7); this represents an average of the best data from a number of tests. The sulfate DF was 1200, iron 700, and ruthenium 1000. This evaporator was operated with little or no de-entraining material, but in a well-designed evaporator with adequate de-entraining space and media a larger DF would be expected.

Decontamination of the calciner off-gas is less important since it is recycled to the evaporator. Approximately 1% of the sulfate, 7% of the metal ions, and 8% of the ruthenium are expected to be returned to the evaporator (Fig. 2).

The system consists of a natural circulation evaporator equipped with a 22-sq ft heat exchanger, which uses 100-psi steam as the heating medium (Fig. 3). A bottom drawoff from the evaporator connects to a pump loop, which flows past the calciner pot and returns to the evaporator. To decrease chances of plugging and to maintain a constant feed to the calciner, a 10-gpm flow is maintained in this loop. The pipe for the small side-stream of liquid drawn off through a control valve into the calciner pot is kept as short as possible, 2 ft, and the control valve is placed as near the operating loop as possible. A water purge bled into the feed stream downstream of the control valve at 1 liter/hr decreases the frequency of plugging.

The calciner vapor is condensed in a 30-sq ft downdraft heat exchanger and returned directly to the evaporator. The liquid is supercooled to recover 85-95% of the nitric oxides and decrease the gas

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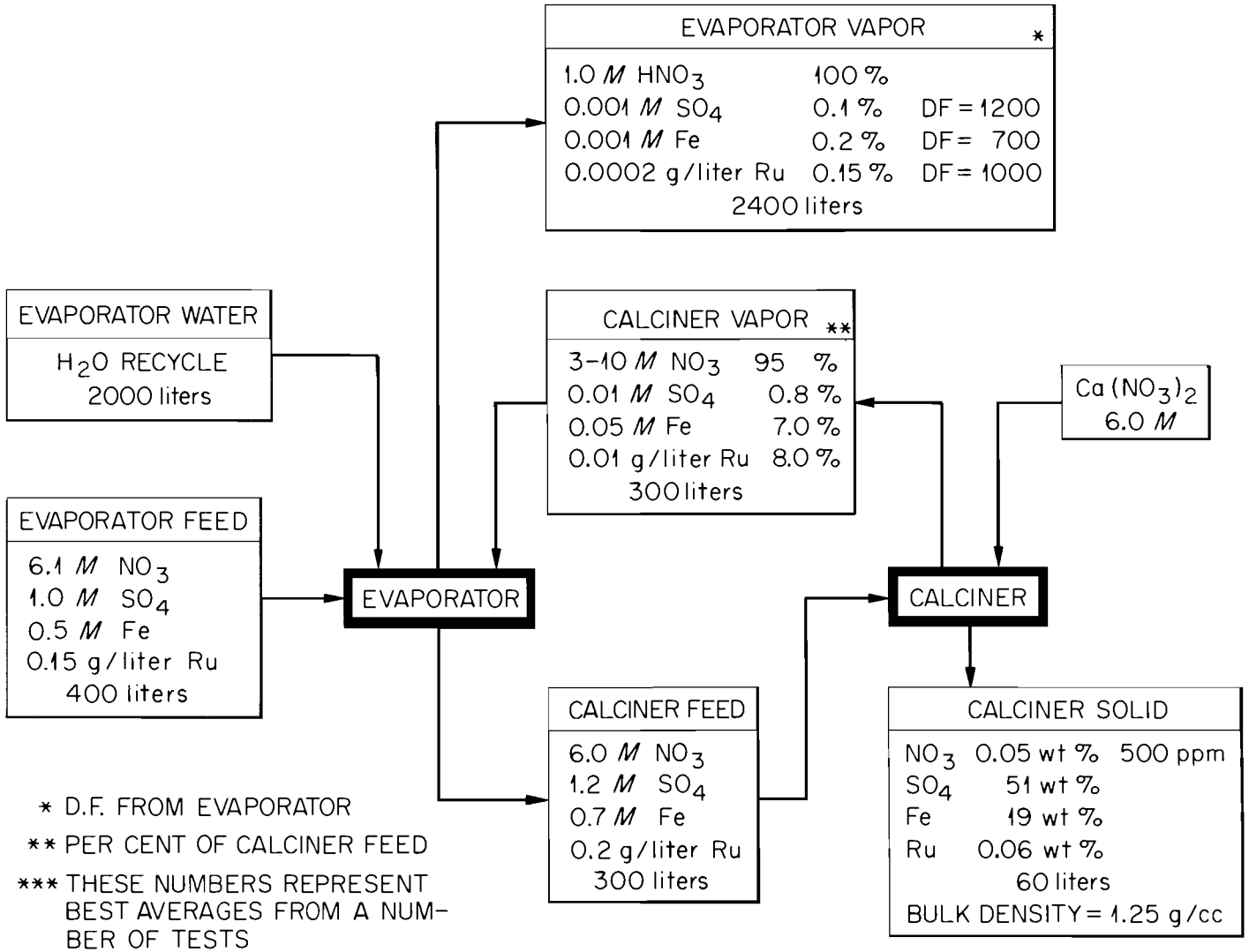

* D.F. FROM EVAPORATOR

** PER CENT OF CALCINER FEED

*** THESE NUMBERS REPRESENT BEST AVERAGES FROM A NUMBER OF TESTS

Purex Material Distribution Flowsheet ***

Fig. 2

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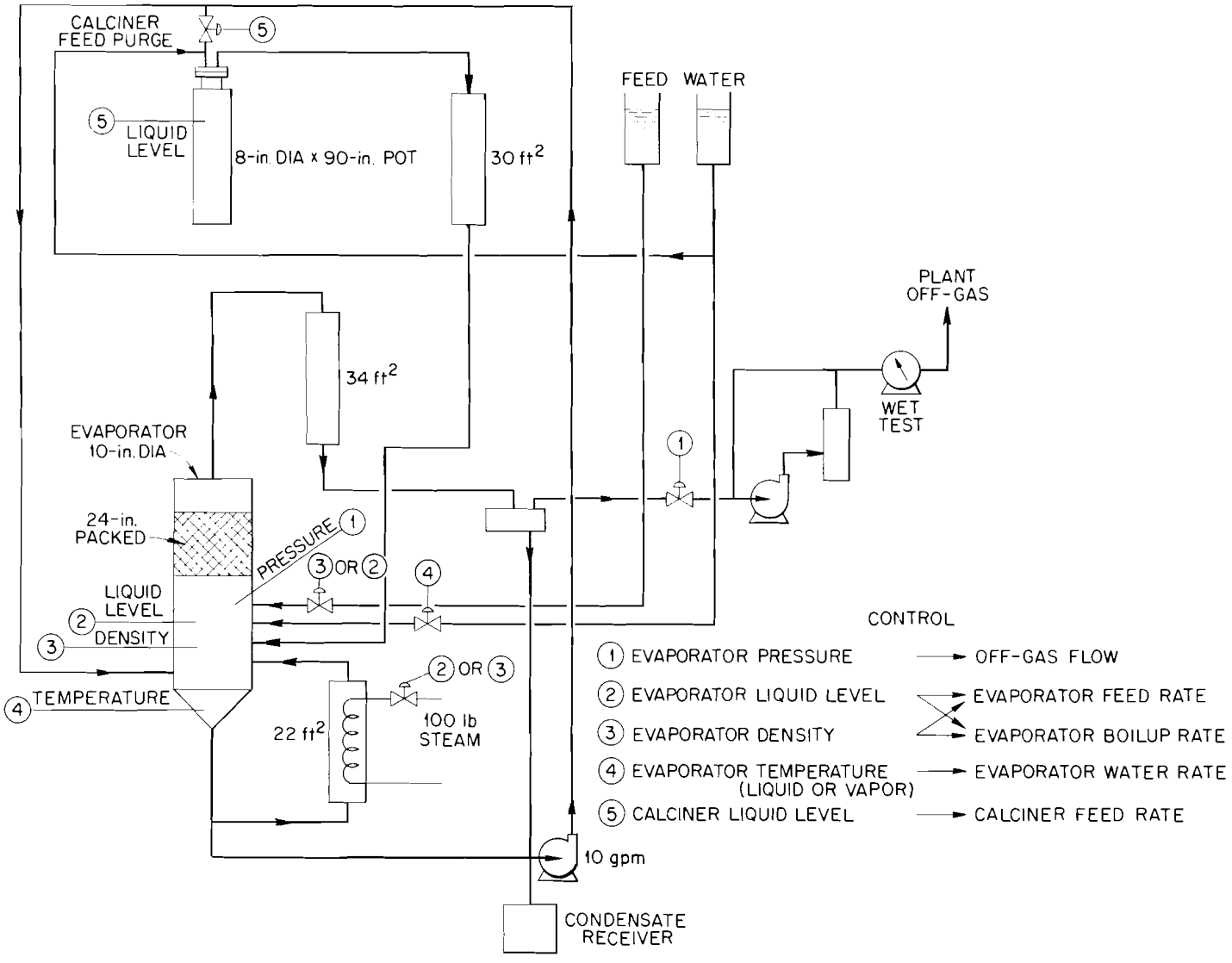


Calciner-Evaporator Control Flowsheet.

Fig. 3

volume for better decontamination. Recycled water and feed are added to the evaporator through their individual control valves from head tanks. The evaporator vapor passes through a de-entraining section and then to a 34-sq ft heat exchanger which operates downdraft. The condensable fraction of the vapor goes to a condensate receiver, where it is measured and discharged through a pressure seal. The noncondensable vapor goes to the off-gas system, where it is filtered and the volume is measured in a wet test meter.

The off-gas from a typical 30-hr Purex waste run was 1100 cu ft, or 36 cu ft/hr, of which 32 cu ft/hr was instrument purge and inleakage gas. The system operated under 1 psi vacuum. The 4 cu ft/hr of noncondensable gas averaged 3 cu ft of oxygen per hour. Excess oxygen is always present in the off-gas from decomposition of nitrate to NO_2 and O_2 (2) and at times was as high as 34 vol %. This small amount of off-gas can be easily decontaminated and discharged to the environment.

The evaporator had 4-6 liters/min boilup rate and operated normally with 25-30 liters holdup. The calciner pot had a nominal 1 liter/min water boilup rate at the full 54 kw heat input. As the solids are radially deposited on the walls of the vessel, the heat input to the pot is decreased. The external wall of the calciner is held at a maximum of 900°C by the furnace, which was divided into six sections, each about 13 in. high. The furnace temperature could go to 1050°C before there was danger of burnout.

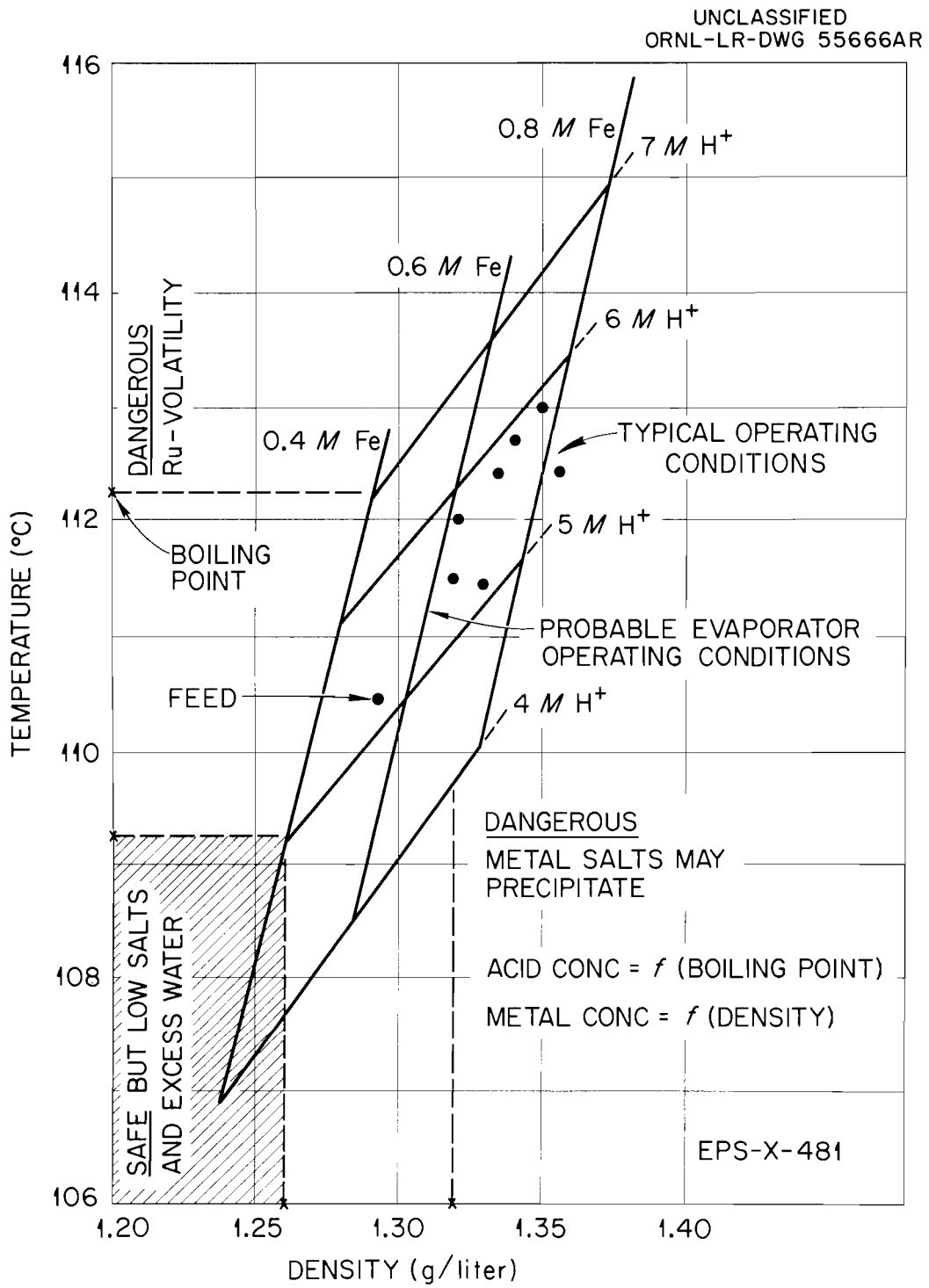
The variables that must be controlled in the process are:

1. Acidity in the evaporator. The evaporator is operated with an acidity of 6 M or less to reduce ruthenium volatility. This concentration is maintained by recycling water or weak nitric acid from the distillation column to the evaporator, the amount recycled being controlled by the temperature of the evaporating liquid or the vapor. The vapor temperature was a better indication of the nitric acid concentration of the liquid when metal ions were present in varying concentrations. The vapor temperature and liquid density are related (Fig. 4), and the preferred operating range is between 0.5 and 0.7 M iron and between 4 and 6 M hydrogen ion for Purex waste. Increasing the rate of water addition increased the vapor volume and therefore the total amount of fission products entrained in the evaporator off-gas.

2. Metal ion concentration in the evaporator. The metal ion concentration in the evaporator is kept at a maximum, limited by solution stability, by controlling the liquid density, which is done by controlling the amount of steam used to vaporize the liquid.

3. Liquid level in the evaporator. The liquid level in the evaporator is controlled by the amount of evaporator feed added to the system.

4. Pressure in the evaporator. The pressure in the evaporator is kept below atmospheric, to prevent outleakage of radioactive off-gas, by regulating the off-gas vacuum pump.



Boiling Point vs Density as Function of Acid and Metal Salts at Atmospheric Pressure for Purex Waste.

Fig. 4

5. Calciner pot liquid level. A differential pressure bubbler satisfactorily controlled the calciner liquid level until the latter part of the test when the bubbler tubes became plugged and a high-liquid-level signal cut off the feed. A differential temperature device found satisfactory consisted of a rod down the center of the calciner pot extending 9-12 in. below the liquid level (Fig. 5). When the liquid level is above the lower thermocouple but has not reached the control rod itself, the rod is heated by radiation from the walls of the pot. When liquid reaches the end of the rod, the rod begins to transfer its heat to the liquid. The temperature at the thermocouple point is a function of the height of liquid on the thermocouple rod, and, by maintaining a temperature difference of 100°C between the two thermocouples, it is possible to maintain a liquid level 4 in. lower than the thermocouple in the rod.

SOLIDS RESULTING FROM CALCINING OF WASTE

Both Purex and TBP waste are calcined with radial solids deposition (Fig. 6), leaving a liquid core down the center of the pot until near the end of the feeding period. At the end of the feeding period the resulting liquid is evaporated, leaving void space.

The bulk density of calcined Purex waste was 1.1-1.4 g/cc, while that of TBP waste was 0.4-0.8 g/cc (Table 2). The bulk density, which is calculated from the weight of solids in the calciner pot after the run and the volume of the calciner vessel to the liquid level operating point, reflects the fraction of the calciner vessel unfilled (8). This fraction varied from 0 to 20%, depending on the filling time. The test was usually terminated when the feed rate to the calcining pot dropped below 5-10 liters /hr. An economic evaluation of the procedure will be needed to determine the best cut-off time.

Table 2. Calcined Solids Characteristics

Waste	Density, g/cc	Thermal Conductivity at 600°F, Btu/hr.ft.°F	Residual NO_3,* ppm	Appearance
Purex	1.1-1.4	0.2	300	Brown, hard
TBP-25	0.4-0.8	0.1	500	White, cellular

*Best results.

The volume reduction from Purex solvent extraction raffinates to calcined solids is 240-fold (1200 to 5 gal/ton of U processed) (Fig. 7). For TBP-25 waste, in which the salt concentration is much higher, the volume reduction is 6- to 8-fold. Volume reduction is important because one of the major costs of the process is the calciner vessel.

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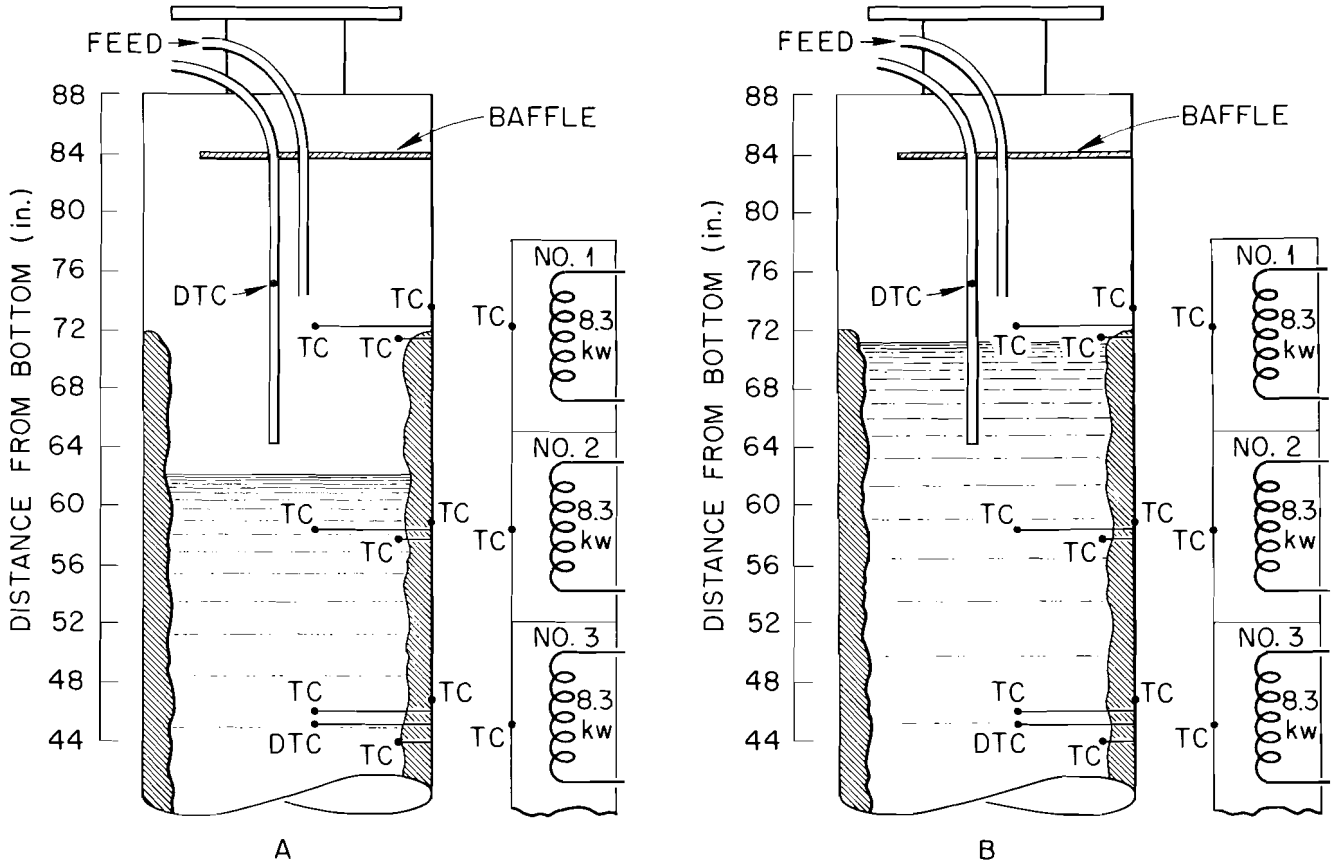


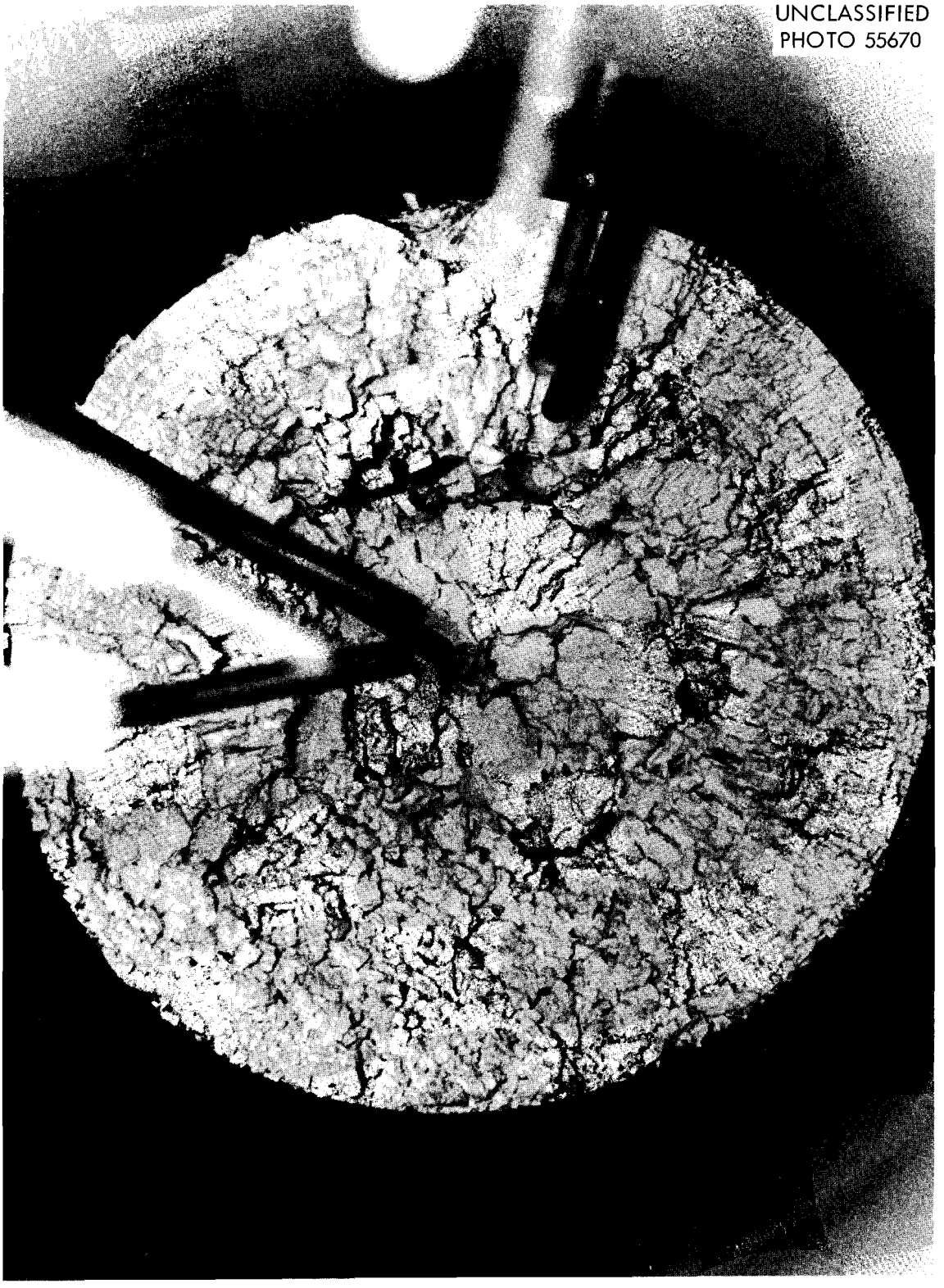
DCT $\Delta T = 600°C - 120°C = 480°C$
TOP BOTTOM

DCT $\Delta T = 220°C - 120°C = 100°C$
TOP BOTTOM

CONTROL RANGE = 50–150°C FOR 0–100% CONTROL OUTPUT

Dual Thermocouple Temperature Control System.

Fig. 5



TBP-Calcined Solids

Fig. 6

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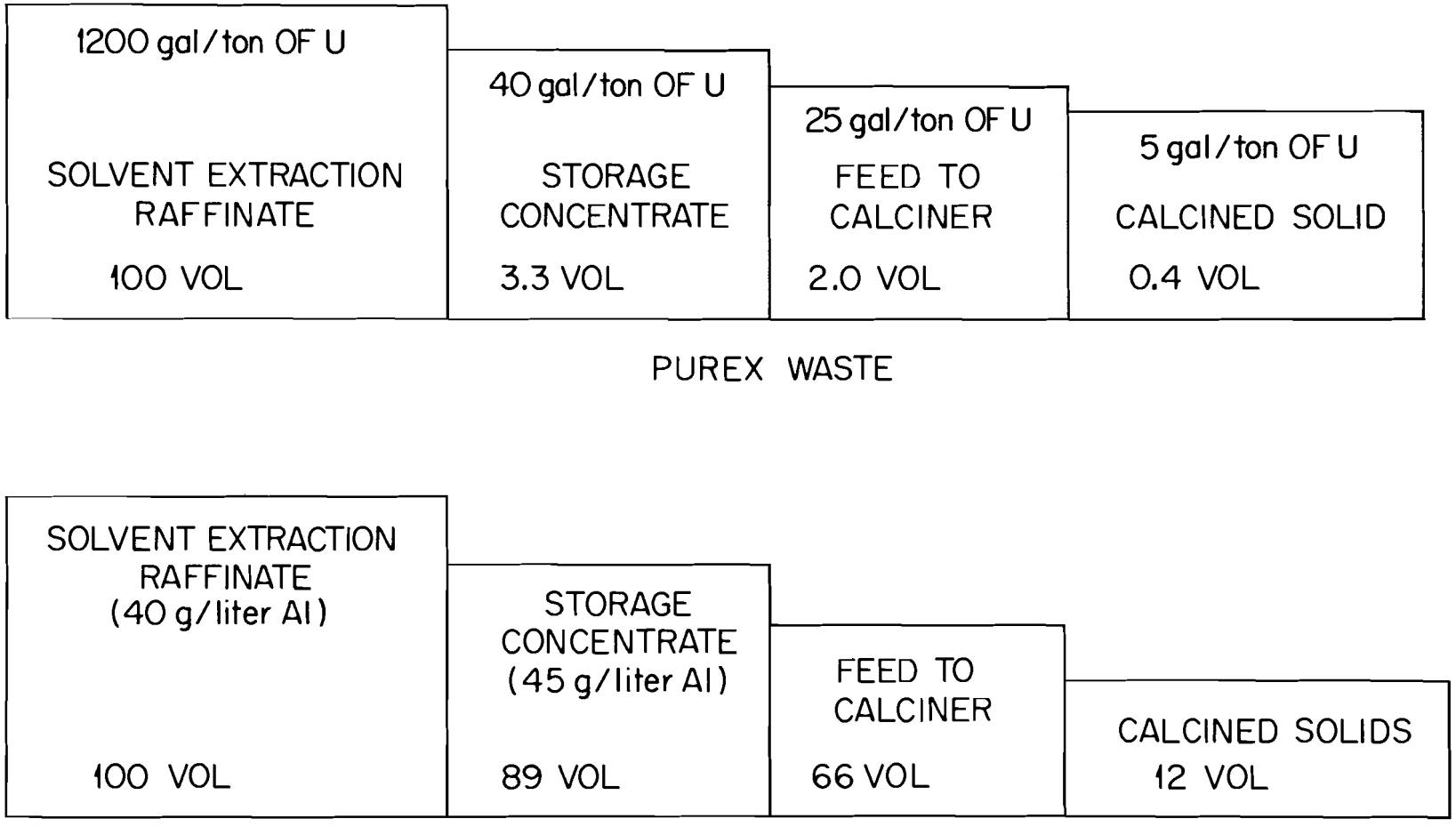


Pot Calciner Volume Reduction from Liquid to Solids

Fig. 7

The thermal conductivity of the Purex cake is approximately 0.2 Btu /hr.ft.°F and of the TBP 0.1 Btu/hr.ft.°F, both measured at 600°F (9,10).

The volatility of sulfate during the calcination of Purex waste is decreased by adding calcium to form calcium sulfate. The addition of calcium to the evaporator feed as calcium hydroxide forms a slurry which is difficult to feed. Calcium nitrate added to the calciner as a separate stream at a fixed rate, keeping an excess of calcium to sulfate in the calciner vessel, decreased sulfate volatility to about 1%.

The volatility of mercury from a TBP-25 calcination process is a problem still unsolved. About 0.5% to 3% of the mercury remained with calcined solids. This mercury value may be lower in pilot plant operation because some of the products were not calcined completely. One approach may be to install a mercury trap in the calciner off-gas line operating at a temperature low enough to condense or absorb the mercury in whatever form it may be but high enough to keep the nitric acid going through the mercury trap as a vapor. This mercury trap could be removed from the process when filled and disposed of as a separate item.

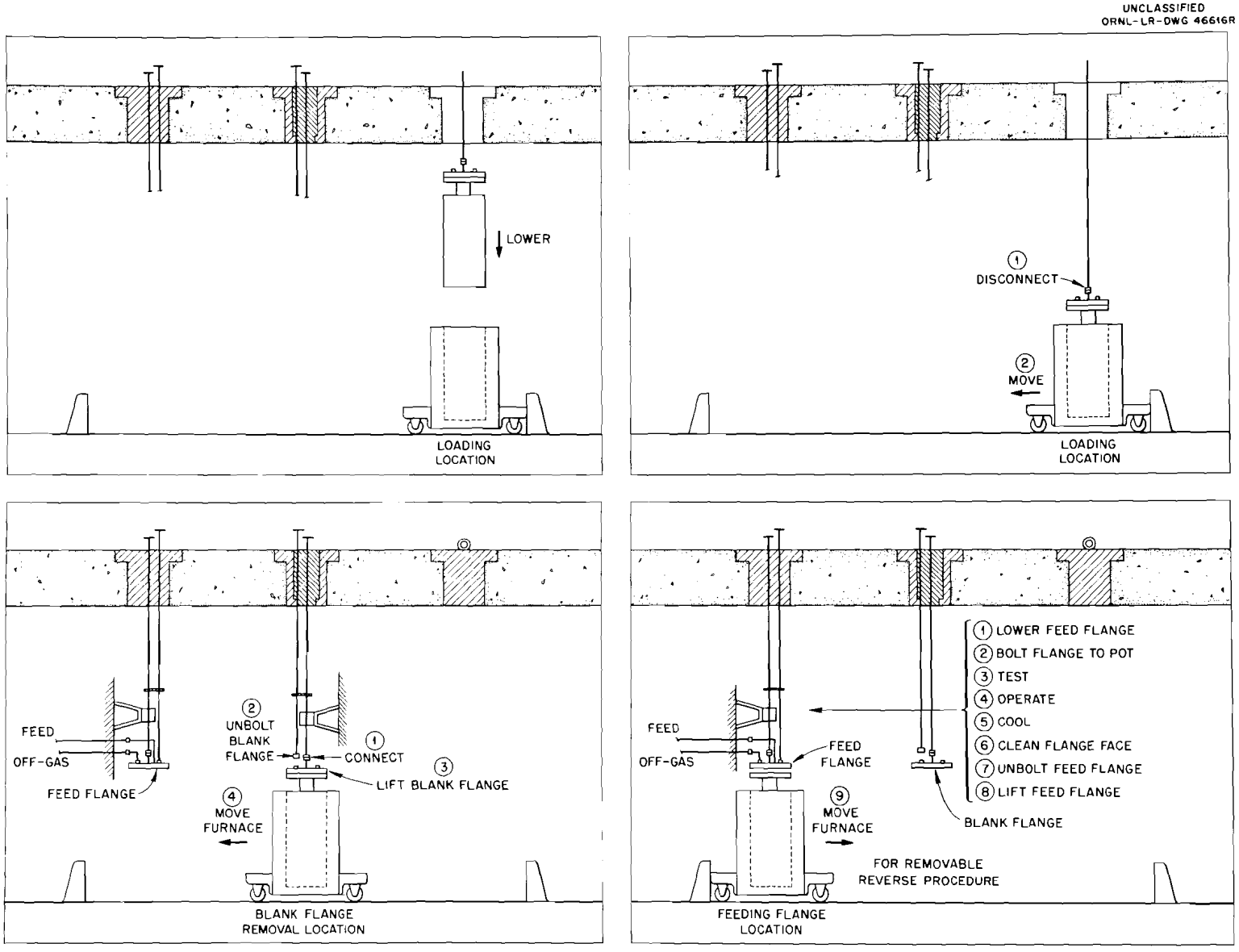
MECHANICAL HANDLING

One proposed pot handling method for a pot calcining plant is placement of the calcining vessel in the calciner furnace, which is then moved under a feed flange built with lines through which the evaporator product is fed and the off-gas is removed from the pot (Fig. 8). This feed flange provides all connections for thermocouples and sensing elements. After the calcination, the flange is disconnected from the filled calciner vessel, which is then capped and/or sealed. The vessel is moved to a different portion of the cell for surface decontamination and monitoring, and later moved to a permanent storage area. Twenty-six thermocouples were attached to the 8-in.-dia by 90-in.-high calciner pots (Fig. 9) used for the tests described, this large number being necessary for experimental purposes. These thermocouples were in six sets, each set including one attached to the exterior of the pot, one inside the pot 1 in. from the wall, one inside the pot at the center line, and one in each furnace section. In addition, there were two thermocouples for the differential liquid level control system.

Two types of flanged tops were used to connect the calciner to the feeding and off-gas system. The standard bolted flange used for development studies is not applicable to a remote disconnect system, and a Grayloc flange was tested which would be applicable (Fig. 10). In a remote disconnect system all the feed lines and liquid level lines must terminate at the top level of the pot so that the pot can be disconnected from the feed flange and moved in laterally with a minimum of flange-to-pot separation.

CONCLUSION

The pot calcination process may be the simplest and most direct approach yet studied for preparing high-activity liquid wastes for



A Proposed Procedure for Remote Connection of Waste Calciner to Feed System.

Fig. 8

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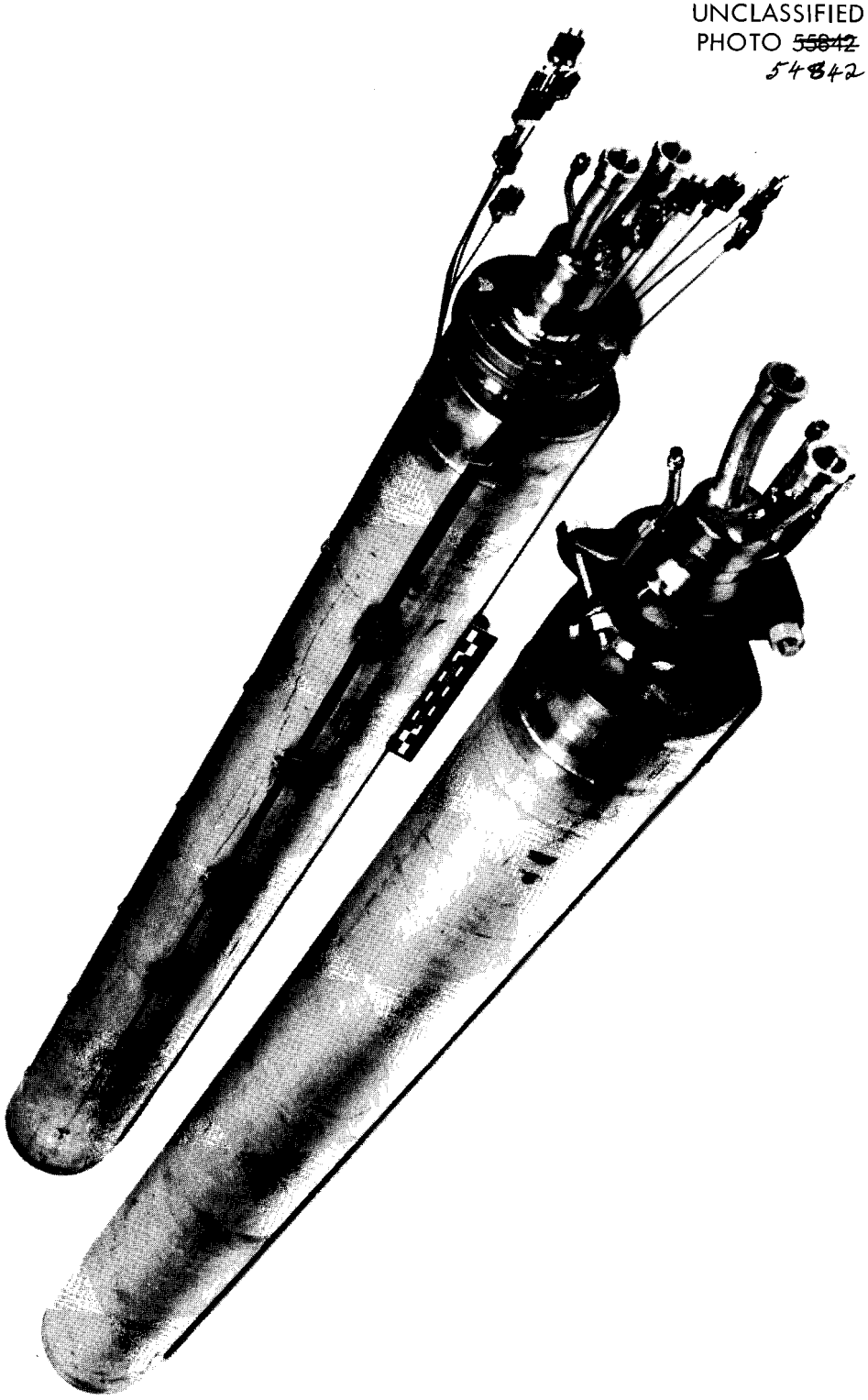

Waste Calciner Vessels

Fig. 9

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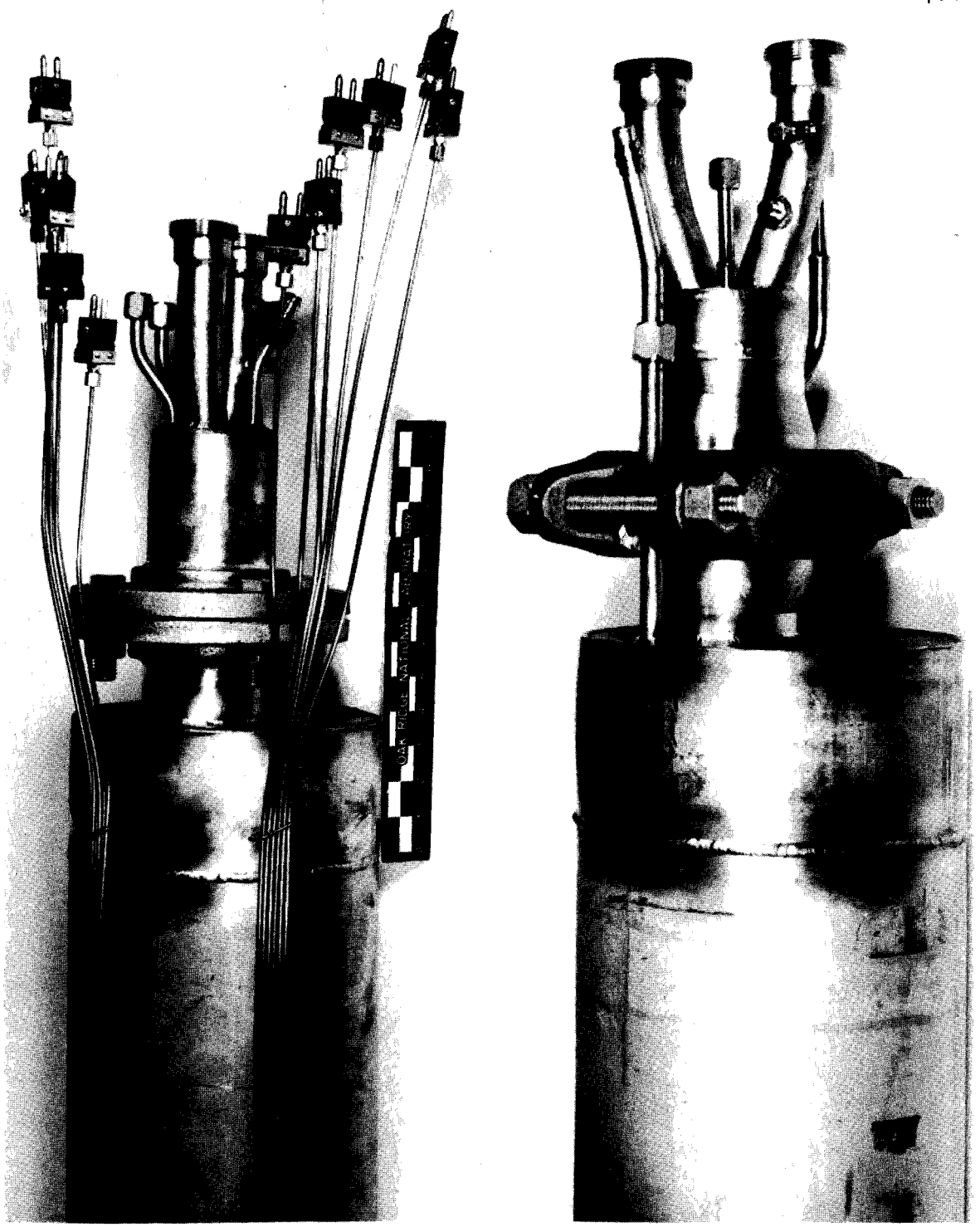

Waste Vessel Feed Flanges
Fig. 10

disposal; hopefully, it requires a small number of processing steps. It is versatile enough to handle a variety of fuel processing wastes, e.g., Purex, TBP-25, and it produces a minimum volume of off-gas to be processed for recycle or disposal to the environment. Rehandling and packaging of the calcined solids are not required since the pot serves as the permanent storage vessel. The high temperature and prolonged heating at temperatures achievable in the pot decrease nitrate in the solids to about 500 ppm under ordinary conditions, leading to greater stability during storage in sealed containers. Ingredients for improving the physical or thermal properties of the solids or for fixation of isotopes can be incorporated in the system if desired.

Potential limitations still to be resolved are capacity and mechanical operations. Although initial results indicate a satisfactory calcination rate, it has yet to be demonstrated that such factors as foaming, entrainment, or subsequent difficulties in off-gas handling are not the limiting factors rather than heat transfer. The techniques and equipment to make and break process lines to the calciner vessel, seal the vessel, remove it from the operating area, and ultimately transport it to a permanent disposal site, possibly many miles distant, must be developed and demonstrated.

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