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ENGINEERING DEVELOPMENT OF NUCLEAR WASTE POT CALCINATION

M. E. Whatley C. W. Hancher
J. C. Suddath

ABSTRACT

The pot calcination process fixes the radioactivity from nuclear waste solutions by drying and calcining in pots which can be sealed for storage. Experimental data from "cold" runs have been correlated using mathematical models which will allow the prediction of plant capacity when radioactive decay heat is present. Problems in control, in the handling of concentrated waste solutions, in the specification of plant components, and in the handling and sealing of pots have been attacked experimentally in engineering facilities using simulated waste solutions.

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The selection of a method for dealing with the radioactive wastes from a nuclear power economy involves more than the development of a single process, it is the evolution of a concept. Reducing the hazard to humanity is very important, but each incremental reduction in the probability of a harmful release of radioactivity is bought at a price, and the point is reached where the probability is so small that the price could exceed the value. The criterion that we must be as safe as possible is inadequate for selection of an optimum approach. The establishment of rational criteria based on cost studies and hazard evaluation has been started but needs real data badly and has not yet born fruit. The proposals still range from the cheap but relatively unsafe perpetual storage of liquid wastes in tanks to the elaborate but prohibitively expensive idea of shooting the wastes into the sun with rockets.

Near the center of this spectrum is the pot-calcination process, which has been under development for six years at the Oak Ridge National Laboratory. This process will be tested in a "hot" pilot plant with high-level wastes at Hanford, presently scheduled to "go hot" in 1965.

A development program such as this involves many facets, some of which have already been reported. This paper is intended to concentrate on the cold-engineering development that brought the concept from early feasibility experiments to the point where the hot pilot plant can be designed with reasonable confidence. This phase of the program is the one in which almost all of the engineering problems must be worked out because the relative inflexability and the relative high cost of the installation of the radioactive pilot plant require that it be essentially a demonstration, confronted only with problems unique to hot operation and unanticipated.

1. DESCRIPTION OF THE POT-CALCINATION PROCESS

The pot-calcination process (Fig. 1) involves simply introducing the waste into an evaporator where it is concentrated as far as feasible and

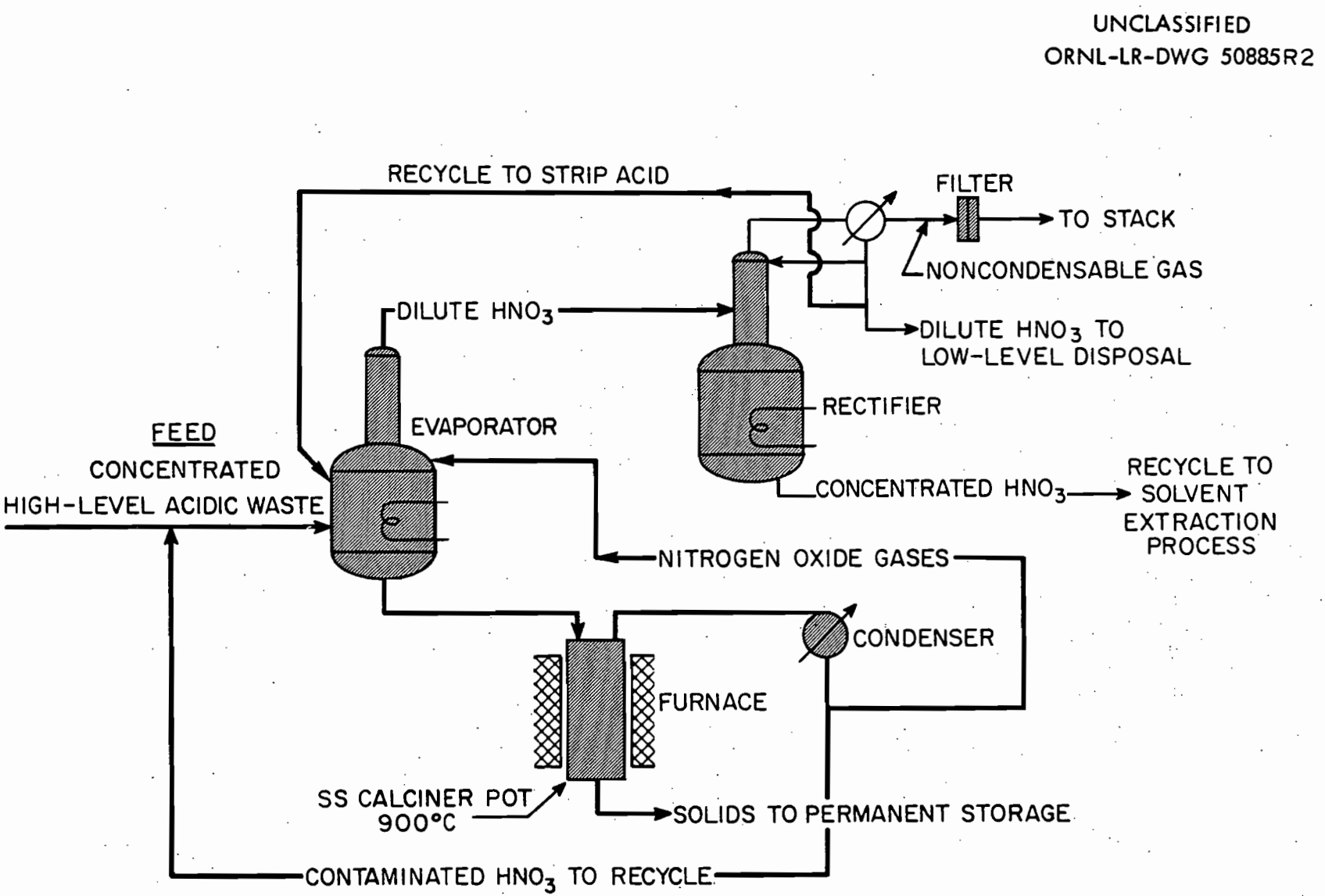


Fig. 1. Flowsheet for Converting High-Activity Wastes to Solids by Pot Calcination.

where nitric acid is steam stripped by the addition of water, and then feeding this concentrated solution into a calciner pot that operates with a constant liquid level and is heated by a furnace where the waste is denitrated, brought to a solid cake, and finally calcined in place. The pot of solids is then disconnected from the system, sealed, and the pot serves as the container for the waste during final storage at some suitable site to which it is shipped. Studies so far indicate that special salt mines may be most suitable.

An important condition placed on the evaporator is that the acidity not exceed some given value (depending on the waste type) to avoid the oxidation of ruthenium to a volatile form. It is for this reason that water is added. The evaporator is the primary decontamination step in the process, and the vapors from it, about 1.6 M in nitric acid, are sent to a distillation tower where water is separated from any entrained radioactivity and the nitric acid. The water that is not recycled for process use can be released after, perhaps, ion exchange treatment, and the nitric acid product, hopefully, will be suitable for reuse in the fuel reprocessing plant.

Since there are no process-gas requirements, the off-gas from the process is very low, one or two ft^3/liter of feed, primarily from inleakage and instrument probes.

1.1 Calciner Pot

The calciner pots used for development work were 8-in.-IPS, generally 88 in. from the bottom to the neck with the lower 78 in. in the furnace, running with a 72-in. liquid level (Fig. 2). The size of the pots in plant application should be as big as handling convenience and temperature rise due to internal heat generation will allow in order to minimize cost. The pilot plant at Hanford will use 12-in.-diam pots, which are probably as large as practical for high-level wastes from power reactors. Intermediate-level-waste pots could go to 24-in. in diameter. This limitation, incidentally, is not unique to the pot-calcination process, but is one that any scheme that reduces these wastes to solids must realize.

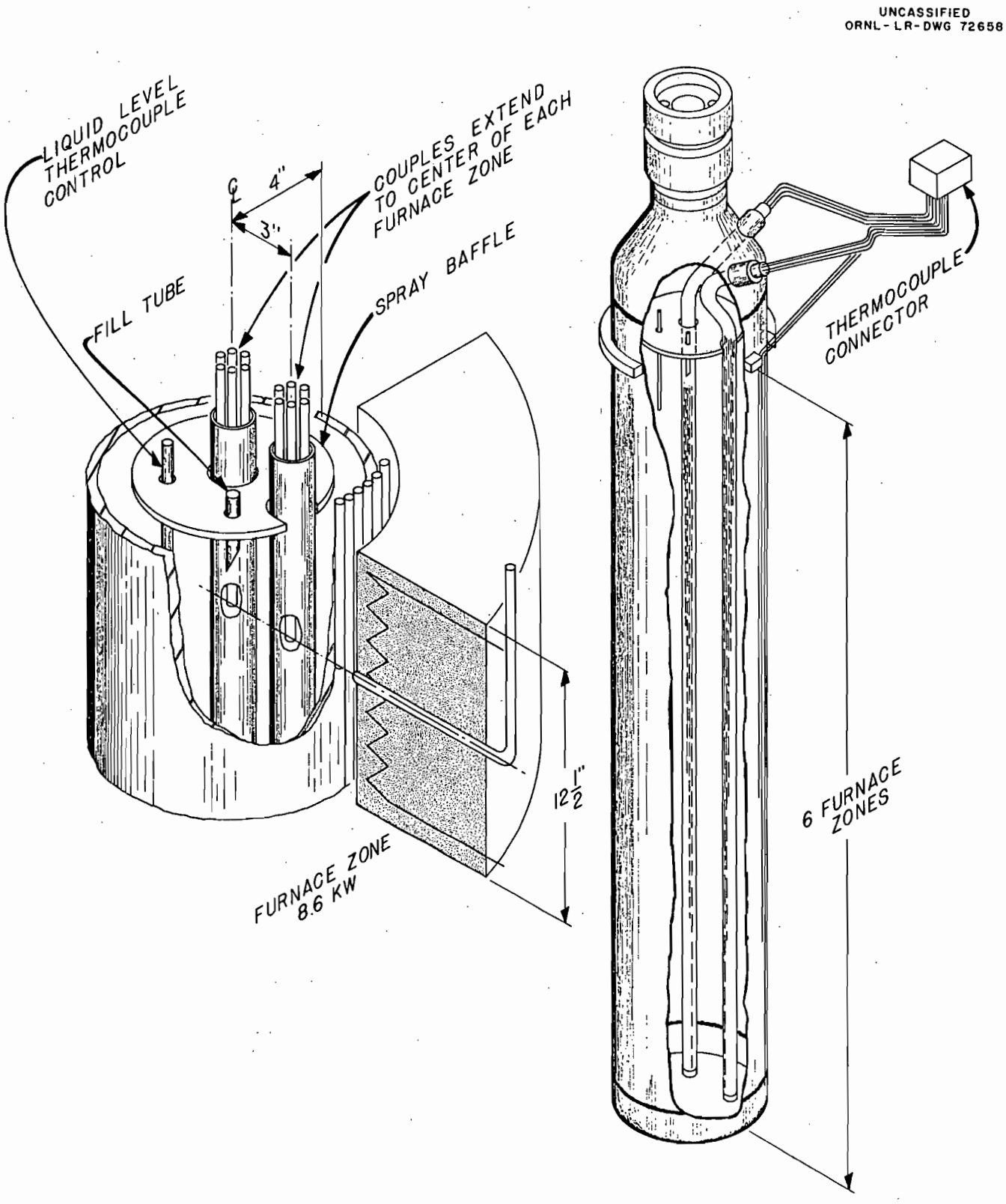


Fig. 2. Waste Calciner Thermocouple Detail.

The pots were made of 304L stainless steel and had wall thicknesses of 100 and 340 mils. Various pot closures have been tried. The one selected for the pilot plant is a modified Grayloc connector which will simultaneously seal two feed lines and an off-gas line. Equipment to remotely connect and disconnect the pot has been developed and tested. Provision has also been made to weld a plug on the top of the pot after calcination.

1.2 Calcined Solids

During calcination the solids are brought to 900°C (1650°F). At this temperature the nitrate wastes with which we are dealing revert to refractory oxides leaving only small traces of nitrate behind. When mercury is present, it comes off. When sulfate is present, it is retained in the cake by adding calcium nitrate to the pot during the feeding period to form calcium sulfate, which stays in the cake almost quantitatively. It is intended to retain all of the fission products in the cake, but there is some entrainment and some volatilization of ruthenium, which is caught in the evaporator. The steady-state concentration of ruthenium in the evaporator is therefore slightly higher than the feed.

Waste that is primarily aluminum nitrate, like TBP-25 waste, appears to be a white porous solid when calcined, which has little strength and crumbles readily. Waste that contains "stainless steel" nitrates with sulfate, like Purex wastes, calcines to a stronger porous solid which appears less uniform.

1.3 Continuous and Batch Evaporator Alternatives

Two alternatives have been retained in the development of the pot calcination process, and they are designated as the batch flowsheet and the continuous flowsheet. In the batch flowsheet (Fig. 3) the tanks and evaporator are large enough to accommodate enough waste to fill one pot. The pot is fed from a tank of concentrated waste, while the vapors from the pot are returned to an evaporator filled with the waste for the next batch which is undergoing concentration and acid removal. The continuous flowsheet uses a smaller evaporator and returns the condensed pot vapors

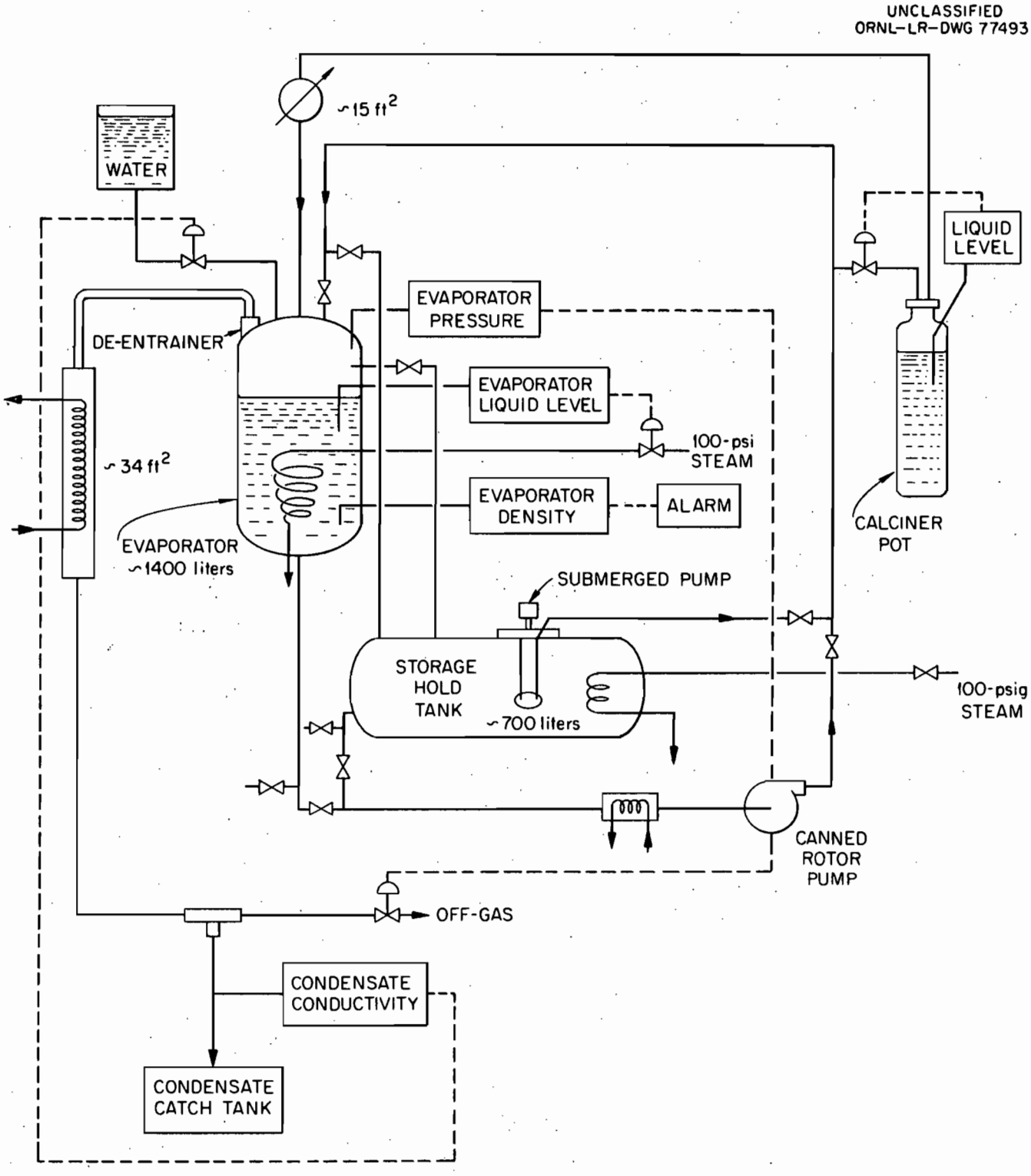


Fig. 3. Flowsheet for Unit Operations Batch Evaporation Tests for Pot Calcination.

to the evaporator from which the feed to the pot is drawn. This evaporator is fed with raw waste and continuously removes the nitrate from the system (Fig. 4). The batch flowsheet offers the advantage of simplicity in control and operation but has the disadvantage of larger equipment and larger holdup. The continuous flowsheet has the advantages of smaller holdup, smaller equipment, and more reasonable application to a plant with several pot lines fed from the single evaporator. The control of the continuous evaporator is more complex. First, you will perceive that the flowsheet is not truly continuous since pots are filled batchwise, and the evaporator is called upon to follow the transient filling of the pot. During the first part of the run the evaporator sees a high demand from the pot and receives dilute acid from it at a high rate. As the run progresses the demand falls off, but the acidity of the pot condensate increases. Finally, the demand becomes less than 10% of the initial demand, and the pot condensate becomes very strong acid at a low rate.

1.4 Process Control

During a continuous evaporator run the acidity of the evaporator vapor (presently measured by an electrical conductivity probe in the condensate) is controlled by the addition of water; the density, or solids concentration, is controlled by the boilup rate; and the liquid level is controlled by raw feed rate under the varying loads of product withdrawal and pot condensate return. This control scheme was adequate. Improved response might be achieved by the use of "look-ahead" control, but this would entail the use and the reliance upon flow measuring devices for primary control which we have sought to minimize.

Maintaining a steady liquid level in the pot was another delicate control problem. This was solved by using a temperature probe at the liquid level which exploited the high wall temperature and the cooling effect of the liquid (Fig. 5). A zero to 100% signal was obtained over a liquid-level variation of 8-in. Because this controller had to work over a flow rate range of more than a factor of 10, a logarithmic valve was used, a 200% proportional band, and a 300-minute reset time was used on the controller. Intermittent fouling of the control valve with the

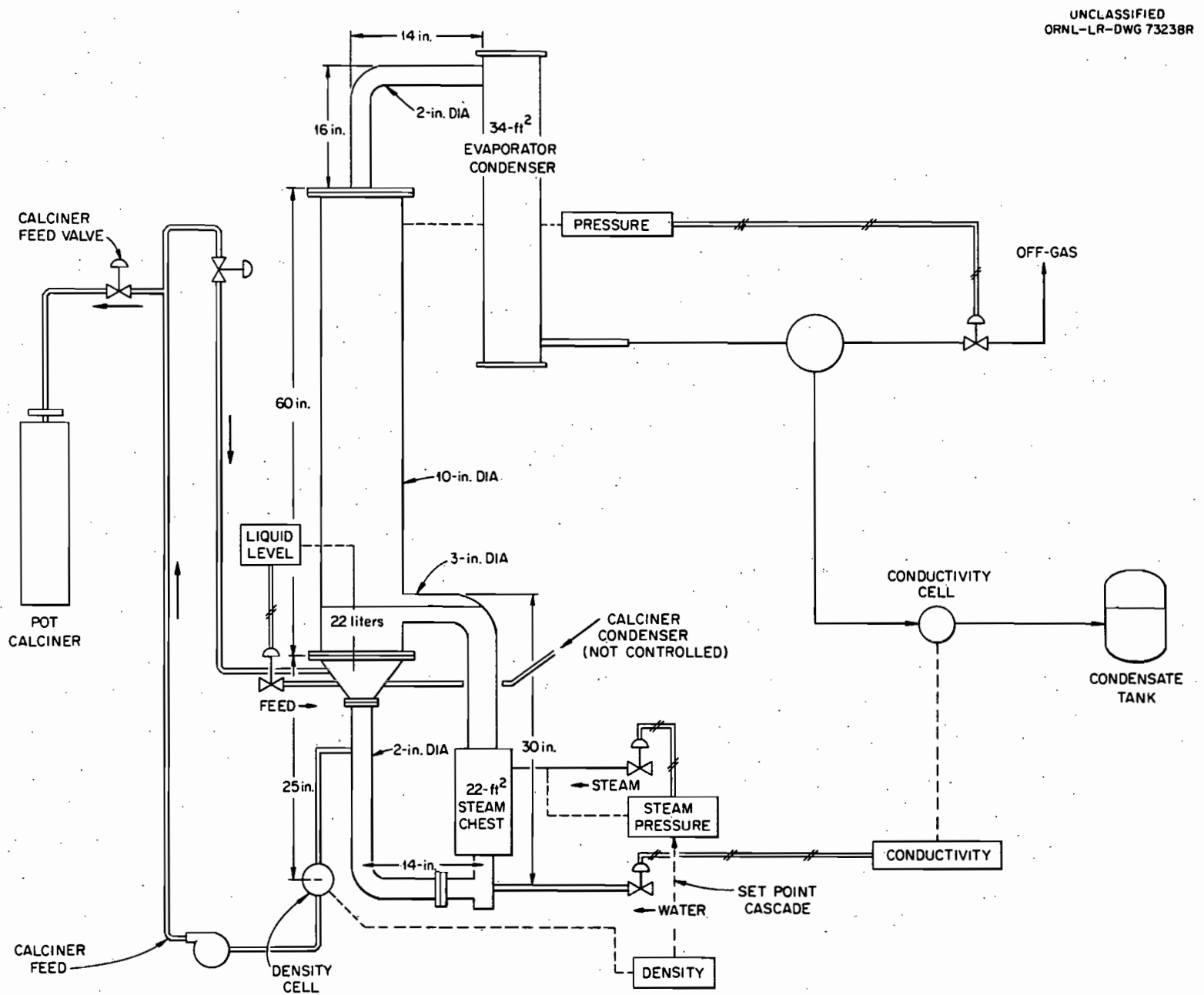


Fig. 4. Continuous Evaporator Control System.

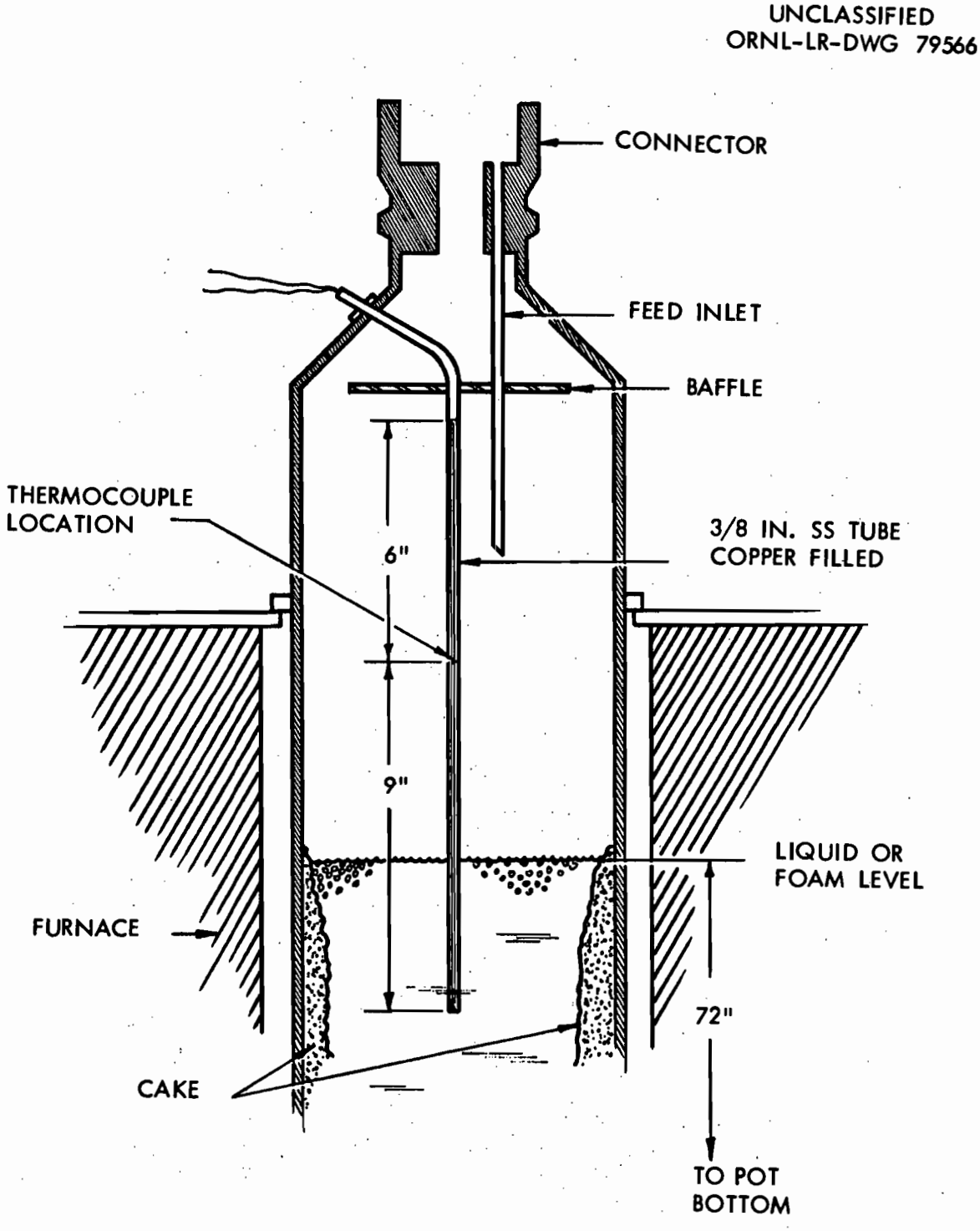


Fig. 5. Calciner Liquid Level Sensing System.

concentrated solution caused some fluctuation in control, but it was entirely eliminated by using an electromagnetic flowmeter in the calciner feed line and cascading the control. Now the signal from the calciner sets the feed rate which is measured and met by another controller that operates the feed valve in a short response time loop. The pot behaves as though it always has foam at the liquid level. Sudden changes in the feed rate can cause the buildup or the collapse of foam to give a momentary signal change in the wrong direction, resulting in an upset. This was nicely avoided by using warm feed to the pot and using a large proportional band on the controller.

2. PERFORMANCE OF THE SYSTEM DURING A TYPICAL RUN

In order to convey some qualitative feel for the performance of the continuous pot-calcination system, we can review briefly the recorder charts from a typical run. Such a run is Test 66, which used TBP-25 waste and which had as a specific objective the testing of a mercury trap of cyclone design which was placed in the pot off-gas line. This particular device did not work well, collecting only about 20% of the mercury. The temperatures in the pot off-gas line and in the trap were too low, allowing the accumulation of a partial plug of mercury oxide. Nonetheless the performance of the system components were typical and suitable for our purposes. Figure 6 is a replotting of the evaporator pressure. This serves to show that through almost all the run the pressure was maintained quite constant. The range is from -5 to +5 psig for full scale, and the setpoint was -1 psig. At about 15:30 there was a small upset, which resulted in a slight pressure transient.

Figure 7 is the record of the electrical conductivity of the evaporator condensate, which is a measure of the acidity of the condensate and reflects the nitrate ion concentration in the evaporator. Also shown are the setpoint and the limits of the acceptable range for this variable. Ten per cent of the scale at the setpoint (2.25 $\underline{M}$ H^+ during the middle of the run) corresponds to a 0.27 $\underline{M}$ change in acidity. For this run the initial feed rate to the evaporator was 55 liters/hr at hour 10:00. It dropped characteristically to 23 liters/hr at 18:00, and down to 3 liters/hr at hour 05:00 of the

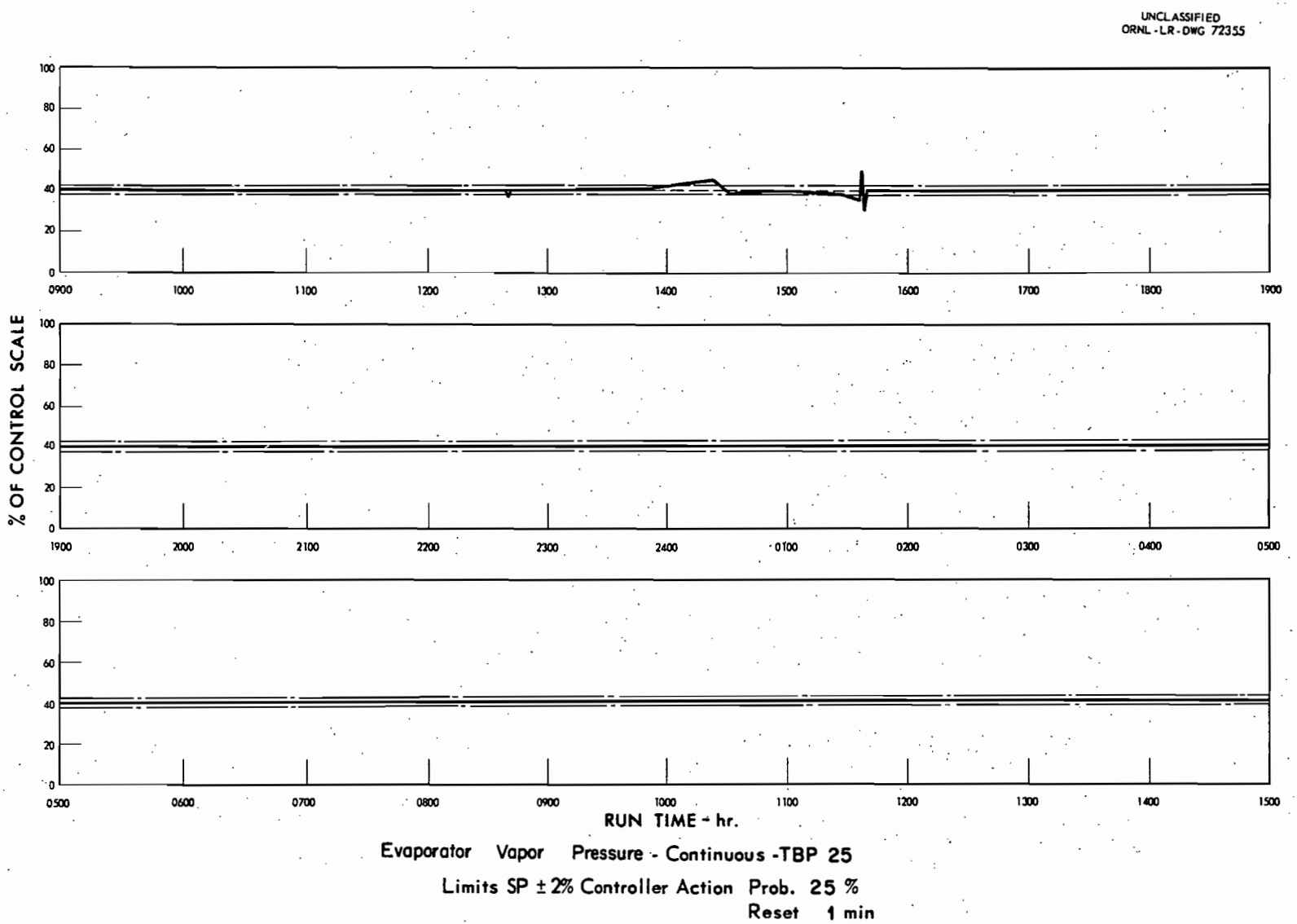


Fig. 6. Record of Pressure in the Evaporator, Test 66.

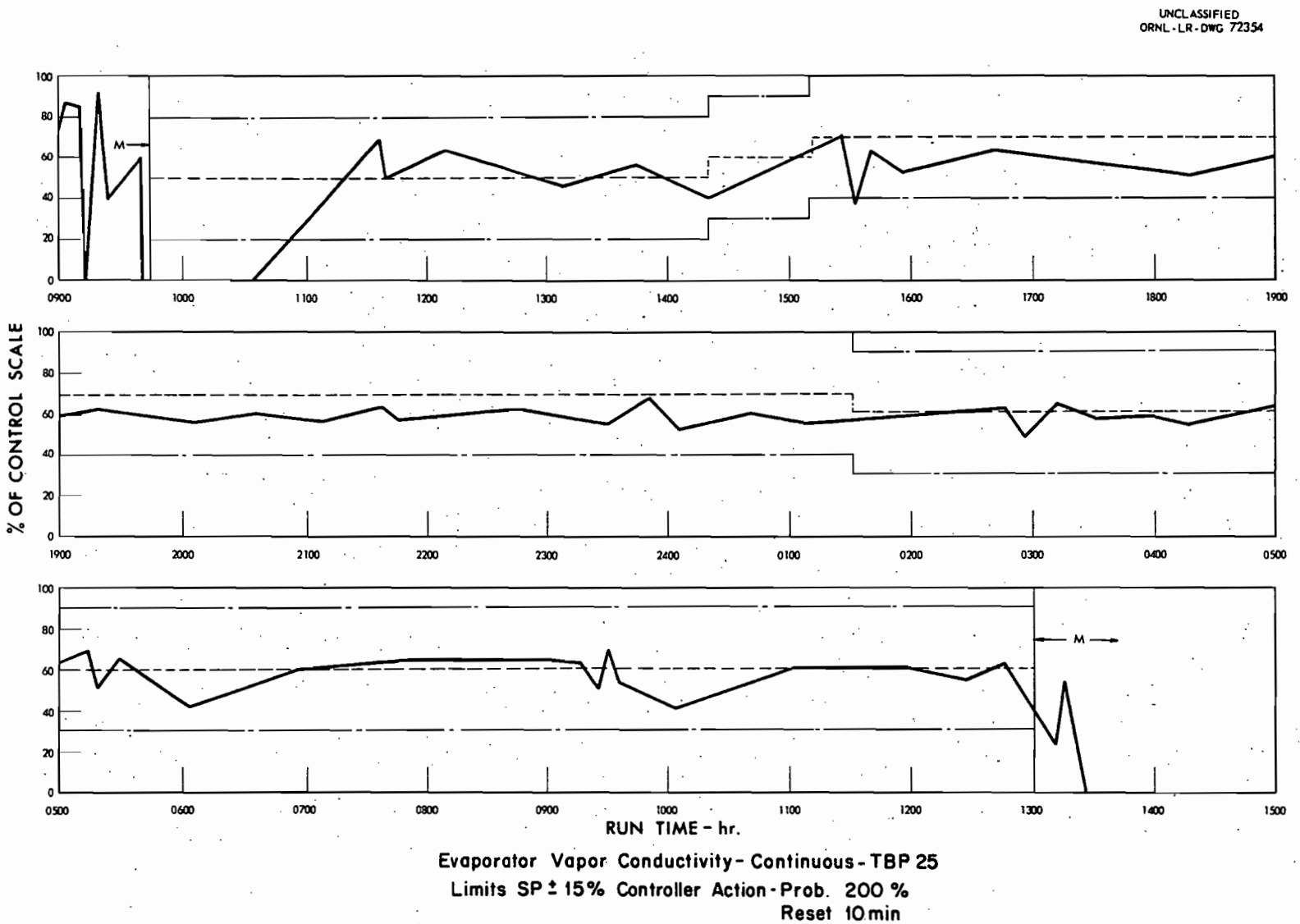


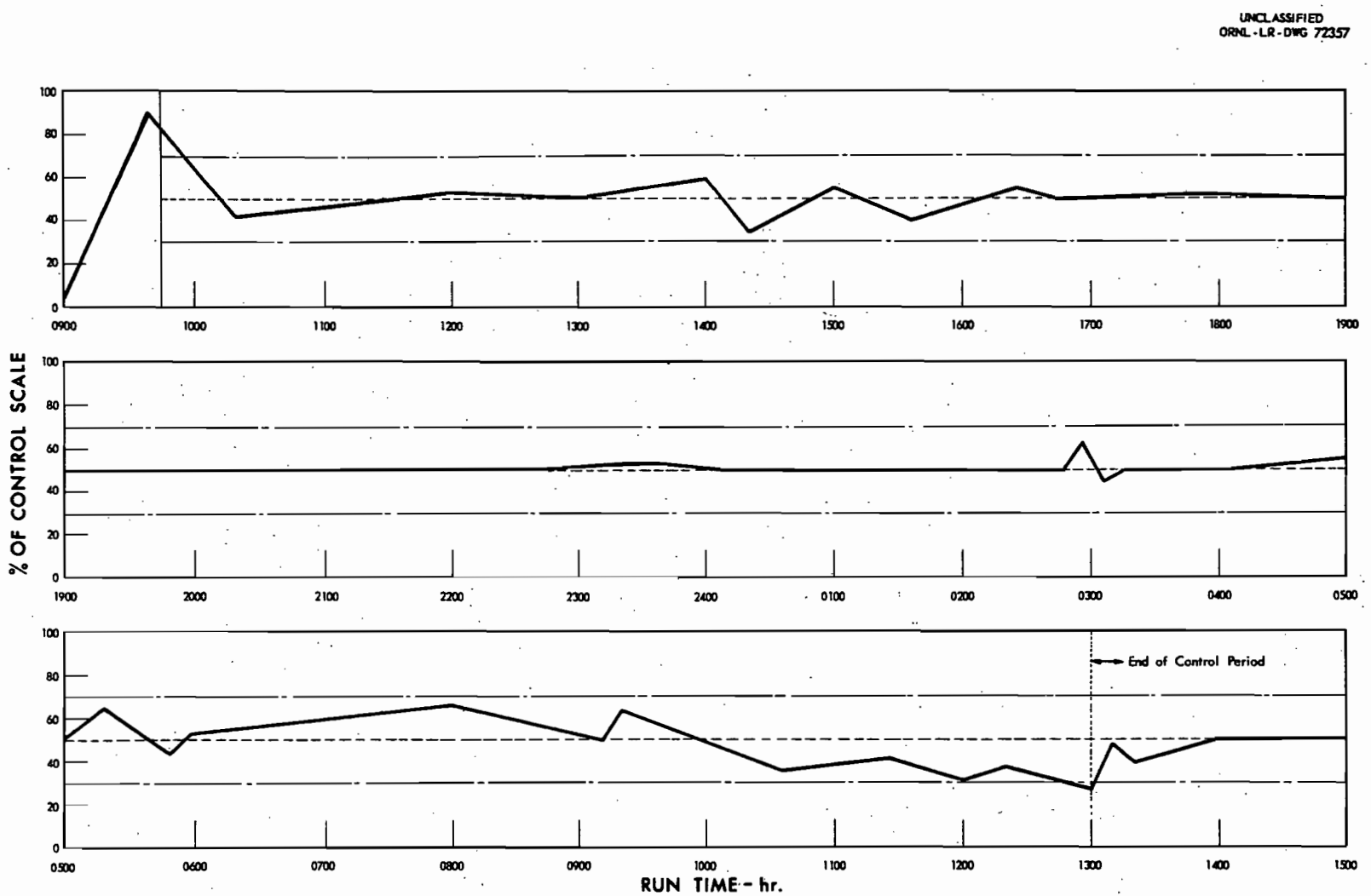
Fig. 7. Record of Electrical Condictivity of Evaporator Condensate, Test 66.

second day. The water rate, which the condensate conductivity controlled, started slowly at 25 liters/hr at hour 12:00, and demanded a maximum of 300 liters/hr at hour 15:00, from which it decreased to about 25 liters/hr at 22:00 to remain low throughout the remainder of the run. During these drastic changes in rates, the acidity did not get out of the acceptable range but once, and that coincided with the pressure upset seen previously.

Figure 8 shows the history of the liquid level in the evaporator. The control setpoint corresponds to about 20 liters and zero to 100% of scale is the range from 10 to 30 liters holdup. This is not a critical variable and is easily controlled.

Figure 9 shows the history of the density of the solution in the evaporator. Here zero to 100% represents the density range from 1 to 2 g/ml. The setpoint is 1.35 g/ml, and the allowable spread is within 1.30 to 1.40 g/ml which corresponds to a spread from 58 to 70 g of aluminum per liter. Solution instability, meaning the point at which solids would form if the solution were allowed to cool, was expected at a reading of 45%, or a density of 1.45 g/ml.

Finally Fig. 10 shows the pot calciner liquid level. The range here covers about an 8-in. interval at the top of the pot and inversely zero represents a full pot and 100%, 8 in. below this. Actually, above zero there is about 18 in. of freeboard. Generally speaking, when the pen is on the chart, the pot liquid level is in good control. In this particular test the controller was not well set at the beginning of the run and the rate to the pot was excessive. Since the controller used a 200-minute reset time for stability, for 2-1/2 hours of operation the liquid level ran high. This is far from catastrophic and no ill effects were observed during the run. Even the most abrupt changes in liquid level shown on this plot are slower than critical for a foam instability in operation. Although it is not evident on this plot, from about hour 18:00 to the end of the run the rates to the pot were continually decreasing. By 08:00 on the second day the rates were quite small and the cyclic operation observed here is characteristic. At the final "M" (for "manual control") the pot was filled and the feed rate set to zero for calcination. The performance shown on this chart, particularly in the beginning of the run, is much worse than



Evaporator Liquid Level - Continuous - TBP 25

Limits SP ±20% Controller Action Prob. 50 %

Reset 10 min

Fig. 8. Record of Liquid Level in the Evaporator, Test 66.

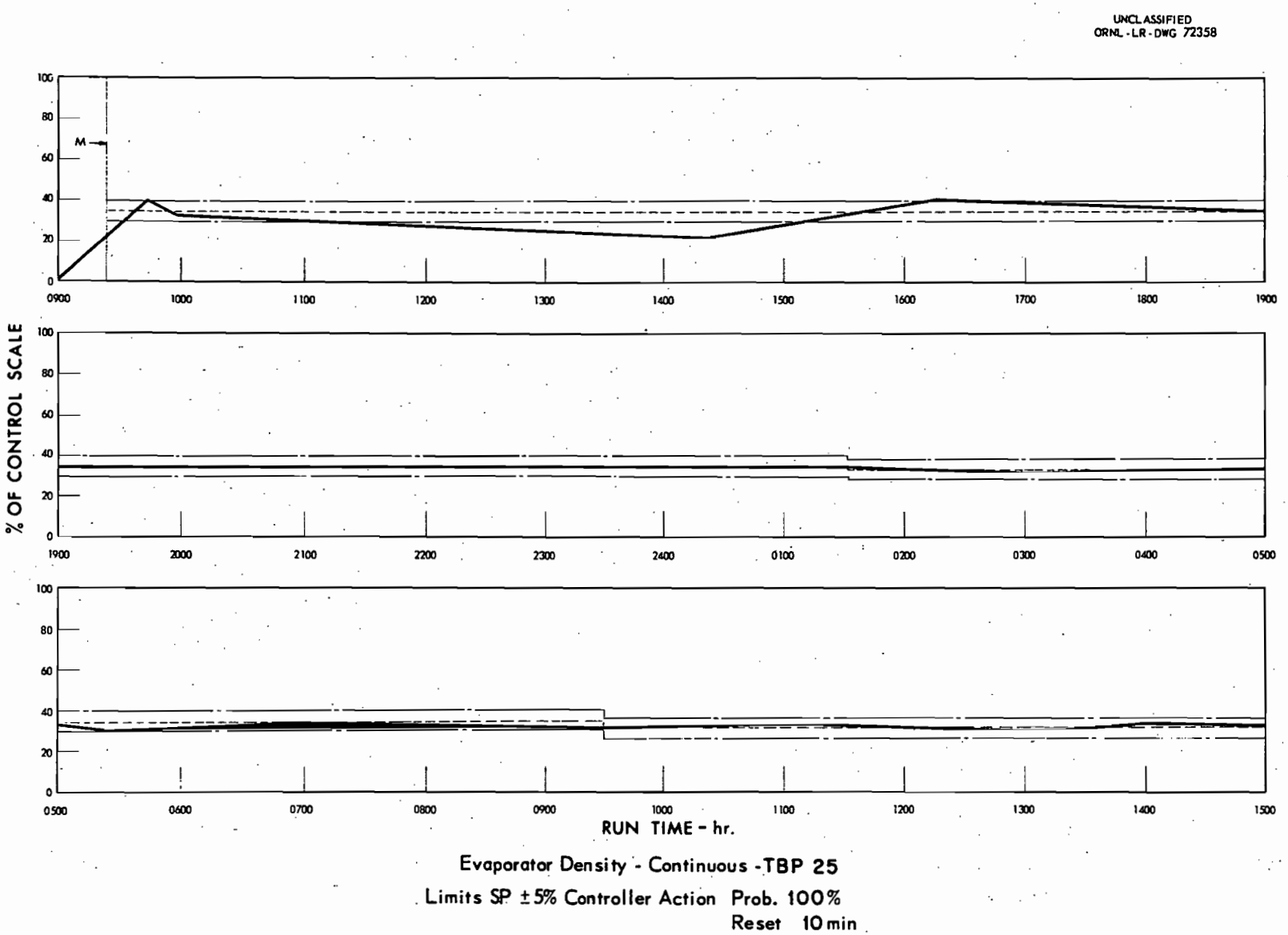


Fig. 9. Record of the Density of Evaporator Liquid, Test 66.

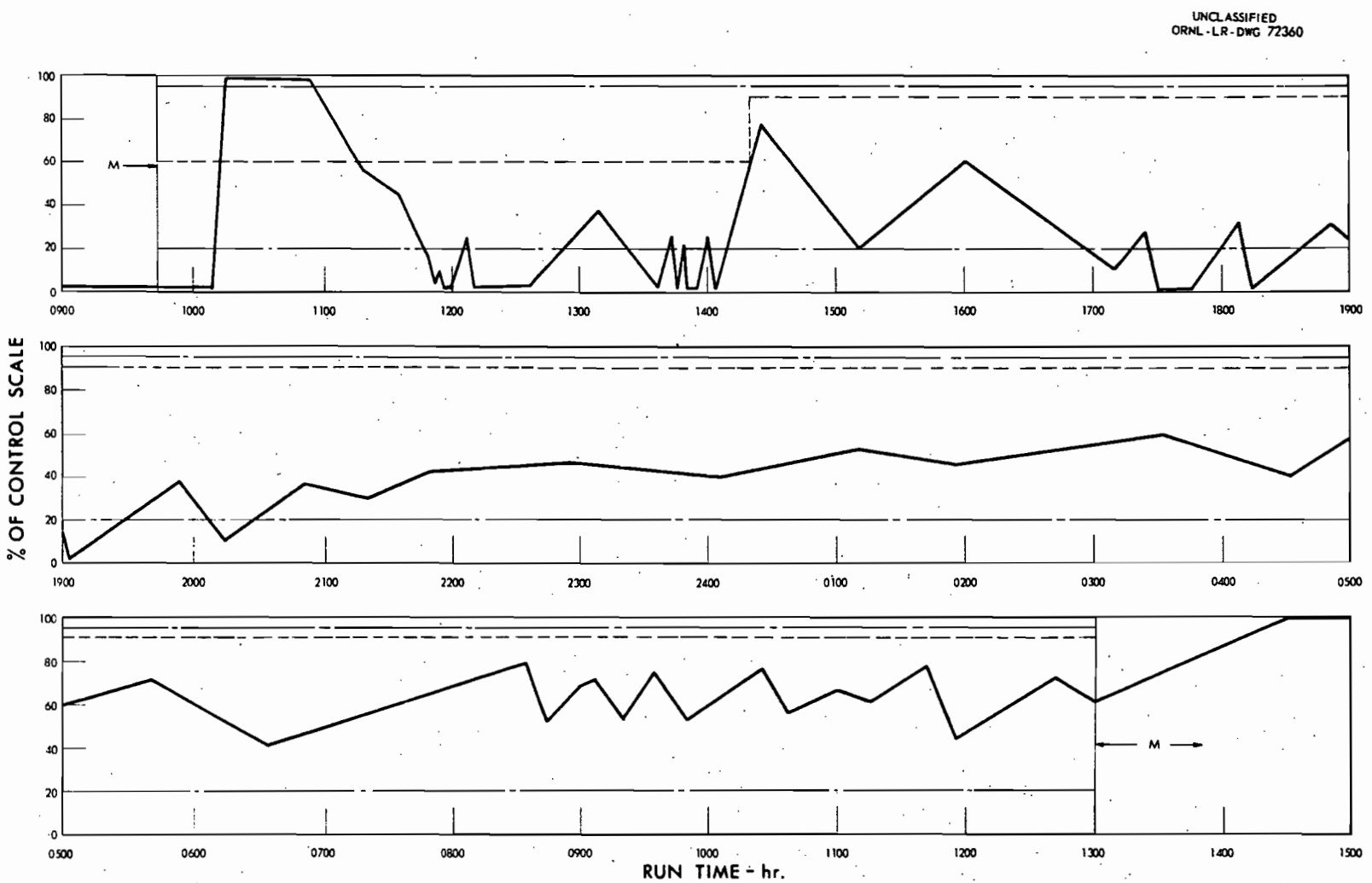


Fig. 10. Record of the Liquid Level in the Calciner Pot, Test 66.

is usually seen in the control of the pot liquid level. In each case the charts omitted most of the operation during the calcination period when the evaporator was receiving the final acid from the pot and reboiling it out of the system. In all cases this period has excellent control and gives no problem.

3. POT FILLING RATE CORRELATIONS

The recognition of the consistent occurrence of circular stratification of the calcined waste cakes suggested the mathematical treatment of the rate by a radial deposition model. Table 1 shows the equations that have been derived for various cases. Since all nonradioactive engineering work must be done in the absence of internal heat generation, only Eq. (1) was validated experimentally. For mathematical convenience it expresses time as a function of the radius to the liquid-solid interface, r_o. The parameters are: R is the pot radius; λ is the latent heat of vaporization per liter of feed; β is the ratio of feed volume to cake volume; k is the effective thermal conductivity of the cake; and T_w and T_b are the wall temperature and the boiling temperature respectively. The assumptions involved in this equation are: that the parameters are essentially constant during the run, that the cake deposits radially and uniformly and that the rate of change of position of the liquid-solid boundary is small compared with the characteristic rates for temperature transients within the cake. Since these assumptions are also required for the equations for deposition with internal heat generation, it was felt that its validation would lend credence to the equations for the internal-heat-generation case. Our studies used the group in the brackets, which we call the "F factor", plotted against time to evaluate the filling-rate coefficient which embodies all parameters.

Internal heat generation is both an asset and a detriment. Since this heat source is close to the liquid-solid interface where it is needed, filling times will be decreased by 10 to 20% and calcination times reduced to a matter of two or three hours. It does, however, create the problem of avoiding excessive temperatures. It is desirable to use pots of such a radius that during storage the center-line temperature will be the maximum

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RADIAL DEPOSITION FILLING RATE EQUATIONS

1. NO INTERNAL HEAT GENERATION

$$t = \frac{\lambda\beta R^2}{4k(T_w - T_b)}\left[1 + \left(\frac{r_0}{R}\right)^2 \ln\left(\frac{r_0}{R}\right)^2 - \left(\frac{r_0}{R}\right)^2\right]$$

2. WITH INTERNAL HEAT GENERATION; WALL TEMPERATURE CONSTANT

$$t = \frac{\lambda\beta}{Q} \ln \frac{T_w - T_b + \frac{QR^2}{4k}\left[1 + \left(\frac{r_0}{R}\right)^2 \ln\left(\frac{r_0}{R}\right)^2 - \left(\frac{r_0}{R}\right)^2\right]}{T_w - T_b}$$

3. WITH INTERNAL HEAT GENERATION; CONSTANT TEMPERATURE, T_m, AT $\frac{dT}{dt} = 0$

$$\frac{dr_0}{dt} = \frac{Q}{2\beta\lambda}\left[\frac{r_m^2 - r_0^2}{r_0}\right], \quad T_m - T_b - \frac{Qr_m^2}{4k}\left[1 - \left(\frac{r_0}{r_m}\right)^2 + \ln\left(\frac{r_0}{r_m}\right)^2\right] = 0$$

$$T_w = T_b - \frac{QR^2}{4k}\left[1 + \left(\frac{r_m}{R}\right)^2 \ln\left(\frac{r_0}{R}\right)^2 - \left(\frac{r_0}{R}\right)^2\right]$$

Table 1. Radial Deposition Filling Rate Equations.

allowable while the wall is near ambient temperature. Obviously, if the pots were allowed to calcine with the wall at the maximum temperature, the center-line temperature would very much exceed this. In most cases, in fact, it will be necessary to decrease the wall temperature even before the end of the filling period.

Equation (2) is the feeding-rate equation using a constant wall temperature as a boundary condition. The heat generation rate per unit volume is Q. An alternative boundary condition was imposed in case 3. When the time arrives that the heat flux at the wall goes to zero, that is, when the temperature gradient at the wall becomes zero, the wall temperature is programmed so that the maximum temperature in the cake is maintained at a constant value and the location of this maximum, r_m, moves toward the center of the pot. It was not possible to get an analytical solution for this case. The differential equation for r_o involves the location of the maximum temperature, r_m, which is given by the implicit relation of r_o and r_m involving the two known temperatures, the maximum temperature and the boiling temperature. The wall temperature, which must be programmed, is given by the last equation.

Figure 11 is a plot of F factor versus time for run R-70. The ratio (r_o/R) was actually computed from the feed, using the ratio of solids fed to the solids necessary to fill the pot. The adequacy of this correlation is basis for confidence in the radial-deposition model. The slope of this line is the filling-rate coefficient which will later be presented as a characteristic index to the overall rate for the run. Note that the reciprocal of the filling-rate coefficient is the theoretical time required to completely fill the pot. This is interesting, but not useful because of the low rates toward the end of the run in the absence of internal heat generation. Further, at half the theoretical filling time, when the F factor equals 1/2, the pot is about 81% full.

Figure 12 shows calculated temperature profiles in the cake during filling with and without internal heat generation. Note the considerably steeper temperature gradients towards the end of the run for the internal-heat-generation case, which gives rise to the higher rates. Note also that the temperature in this case gets considerably higher than the wall temperature, a condition which is presently thought intolerable.

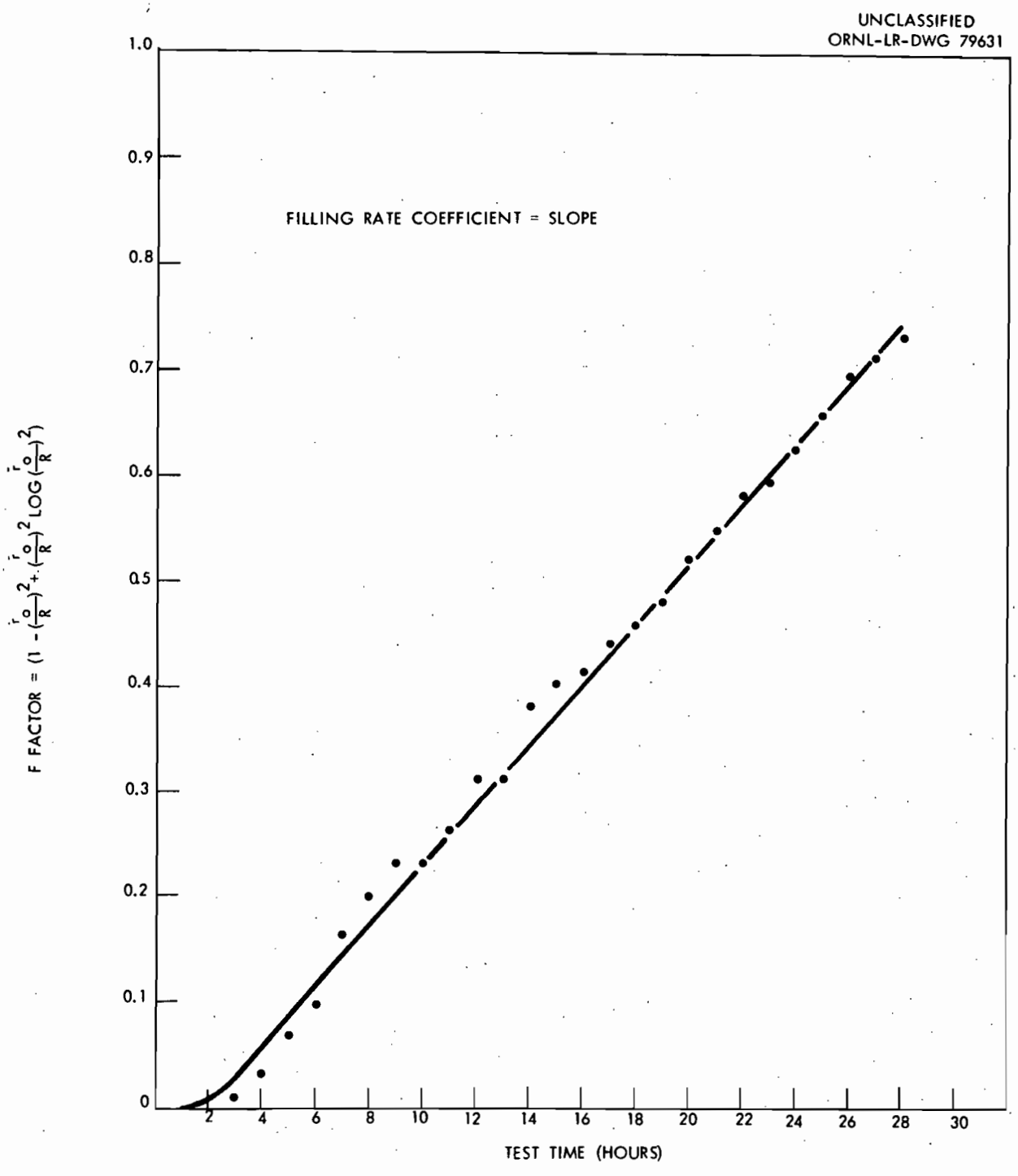

Fig. 11. F Factor Test Versus Time for Purex FTW-65 Waste Run R-70.

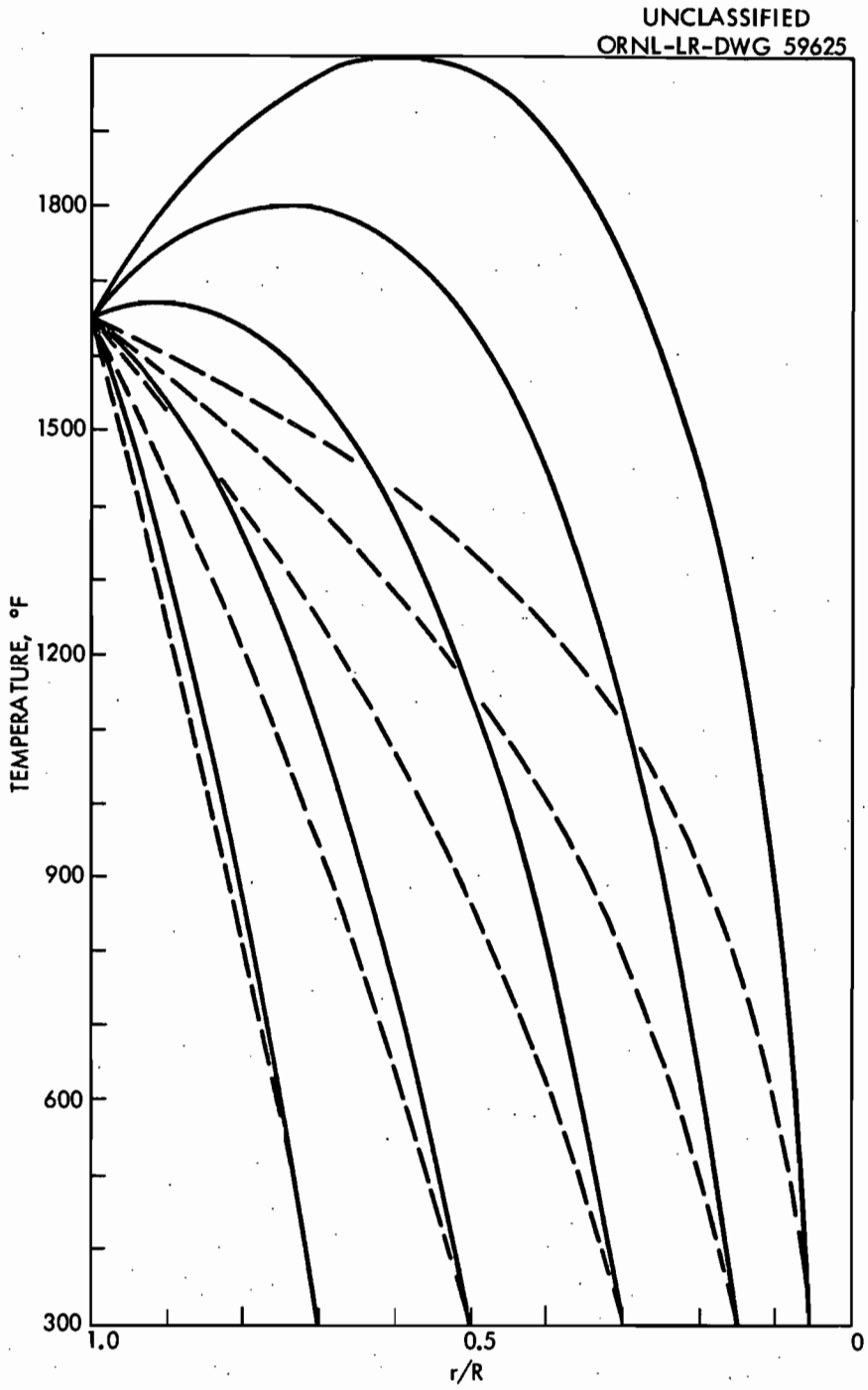

Fig. 12. Temperature Profiles in Deposited Purex Solid Waste in a 12-in.-diam Vessel. Solid line, Q = 5000 Btu/hr.ft^3; Dashed line, Q = 0.

Figure 13 shows the progression of the temperature profile within the cake for an ideal calcination run with internal heat generation. Early in the run the deposition rate is limited by the heat output from the furnace, and the wall temperature increases as the cake deposits. Then the wall temperature is held constant as the cake continues to build. At the point where the heat flux at the wall goes to zero, the temperature of the wall is decreased. The maximum temperature then moves away from the wall. At some predetermined degree of fullness, probably dictated by vapor velocity in the decreasing center zone, the feed is turned off and the now dry inner boundary begins to heat. The location of the maximum temperature continues to move towards the center, while the wall temperature must be further decreased. At the end of the run the wall temperature should be not much higher than the temperature intended for storage, and the center temperature should be at the maximum. Even if all the assumptions that go into the calculation of the predicted performance were valid, practical operating conditions would make such ideal operation impossible. However, by slightly relaxing the requirement on maximum temperature, there are good methods of using this prediction to program wall temperatures safely. The simplest of these, which allows only about a 200°F rise above the intended maximum, uses only a linear approximation for the wall-temperature program. It is not now clear that such restrictions on maximum temperature are necessary, and work with radioactive material may show much higher temperatures to be allowable.

4. SUMMARY OF DATA FROM POT CALCINATION RUNS

In this development program over 75 runs have been made, the most significant of which are the last 30, which were run in the last two years in the present system. The feed types investigated included TBP-25 solvent extraction waste which is mostly aluminum nitrate, Darex waste which results from the dissolution of stainless steel fuel elements and is characteristically low in sulfate concentration, conventional Purex 1WW waste, and Purex formaldehyde-treated waste which is the anticipated waste product in 1965. Analysis of these wastes are shown in Table 2.

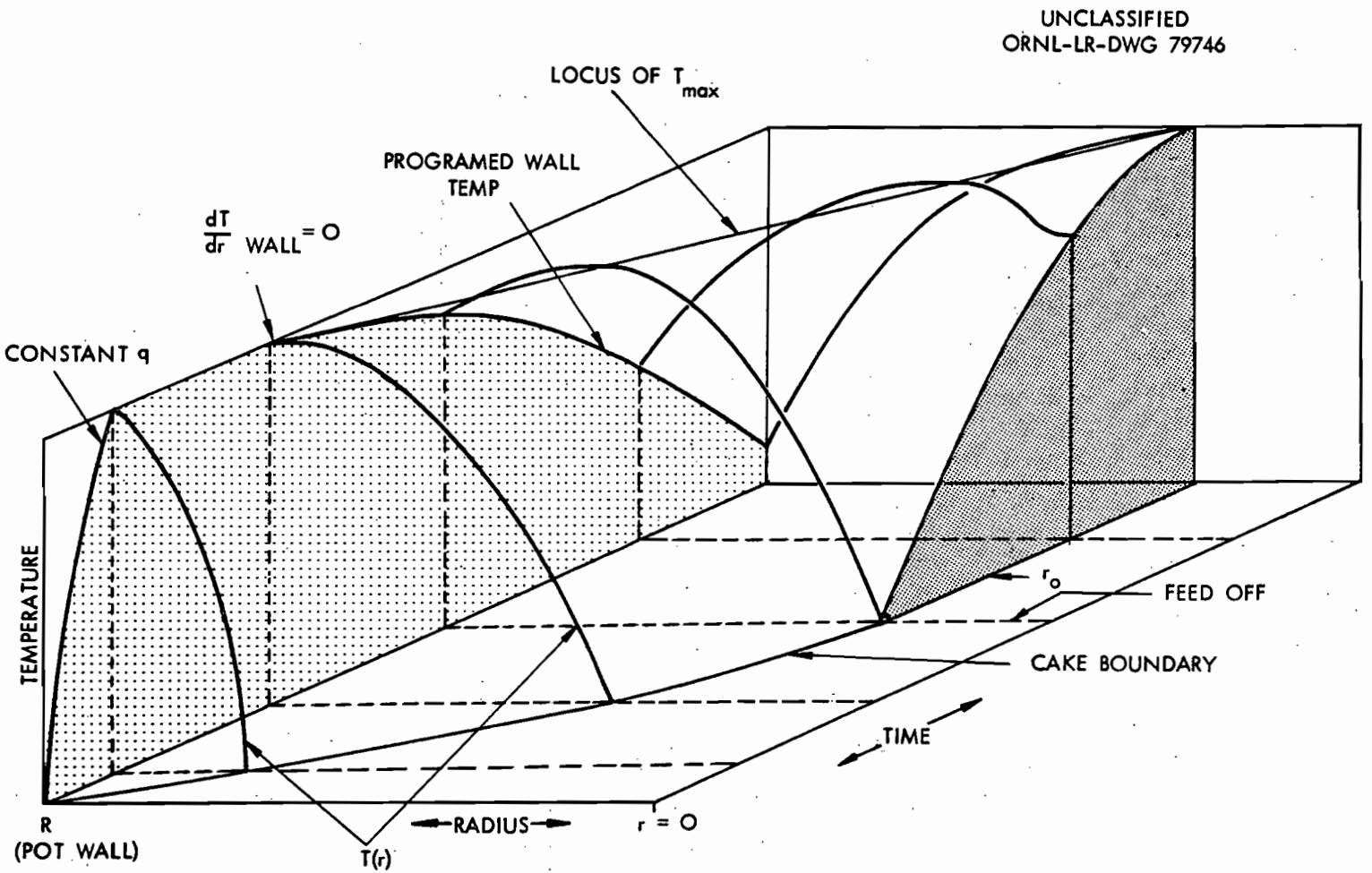

Fig. 13. Cake Temperature During an Ideal Pot Calcination Run with Internal Heat Generation.

Table 2. Major Constituents of Simulated Waste

	TBP-25	Darex	1WW-Purex	FTW-65 Purex
		(moles per liter)		
H^+	0.5	3.0	5.6	0.5
NO_3^-	5.4	6.0	6.1	1.03
SO_4^{-2}	0.03		1.0	0.15
Cl^-		300 ppm		
Fe^{+3}	0.002	0.68	0.5	0.2
Al^{+3}	1.6	0.12	0.1	0.05
Ni^{+2}		0.08	0.01	0.01
Cr^{+2}		0.16	0.01	0.02
Na^+			0.6	0.3
		Additives to Decrease SO_4^{-2} Evolution		
Ca^{+2}			0.8	0.03

Though all the runs were made in the same basic system and have common facets, each run was made for some special purpose, such as testing a new pump, or a modification of the control system, or the effect of using some additive. Runs have been made with silica added to the feed to simulate the presence of solids. The method for adding calcium nitrate to the pot has been considerably varied. In most cases these changes made a noticeable but not drastic change in the system performance. The data are presented here in tables which do not point out these changes, and much of the scatter can be attributed to them.

To some runs, a small amount of organic solvent, mono- and dibutyl phosphate, was added to the feed to determine the effect of these chemicals in plant operation. The effect of these additives was of sufficient importance to note it.

4.1 TBP-25 Waste

Table 3 shows the data from runs with TBP-25 waste using the 8-in.-diam by 72-in.-high calciner pot. The performance of the batch flowsheet runs, those marked with a B, was not significantly different from the continuous flowsheet runs. The variation in feed volume to the pot is primarily an operational variable and could have been made more consistent than appears in this paper. The water-to-feed volume ratio, which indicates the amount of water necessary to strip the nitric acid from the evaporator, should run about 2.3. Instances where it is high indicate an unnecessarily low setpoint for the acid in the evaporator overhead. The feed to the evaporator is about 23 g of aluminum per liter, so the calciner feed is only slightly concentrated over the original waste. Although one run was made at over 100 g of aluminum per liter going into the calciner, this was thought to be a dangerous operating procedure. The filling-rate coefficients were determined from plots of the F factor from the radial-deposition equations against time. The only term in this coefficient not computable through other data is the effective thermal conductivity of the cake. The term β, which is the ratio of calciner feed volume to cake volume, is proportionally related to the calciner feed aluminum concentration, these ratios are seen to be fairly uniform. The "starred" run numbers designate runs

Table 3. Summary of Pot Calcination Runs TBP-25 Waste

Run No.	Feed Volume (liters)	Water to Feed Volume Ratio	Calciner Feed Al^{+3} Concentration (g/liter)	Filling** Rate Coefficient (hr^{-1})	Calcination Time (hr)	Nitrate Remaining in Solids (wt %)	Solids Density (g/cc)
47	429	3.4	78.5	0.053	10	6.0 to 0.36	0.57
48	468	2.8	57.0	0.015	13	6.0 to 0.10	0.77
50*	346	2.4	50.5	0.005	7	4.1 to 0.08	0.52
51-B*	308	2.5	57.5	0.003	9	6.0 to 0.08	0.59
52-B*	440	2.3	57.0	0.018	10	0.18 to 0.06	0.44
54	428	2.7	44.0	0.017	11	0.85 to 0.10	0.65
55	469	3.5	57.5	0.024	4	0.56 to 0.10	0.60
59-B*	397	-	49.3	0.015	6	1.00 to 0.07	0.61
62	446	4.5	53.0	0.022	10	2.00 to 0.20	0.63
63	421	2.3	47.0	0.022	10	2.00 to 0.20	0.61
64	560	2.0	42.5	0.024	11	0.20 to 0.002	0.80
65	476	3.1	115.5	0.034	9	0.19 to 0.06	0.68
66	449	6.4	55.0	0.037	17	0.04	0.65
67	391	2.8	45.1	0.003	20	0.007	0.50
68	343	2.6	47.5	0.056	20	0.019	0.54
69-B	469	5.4	45.0	0.025	17	0.111	0.64

*Organic added.

B - Batch evaporator runs.

$$** = \frac{4k(T_w - T_b)}{\lambda \beta R^2}$$

made with organic solvents (dibutyl phosphate and monobutyl phosphate) added to the feed. In these cases the filling-rate coefficient was significantly lower.

The nitrate remaining in the solids is quite sensitive to the calcination time. At 20 hours of calcination the residual nitrate was reduced to a very low level. In all cases the low numbers are more characteristic of the bulk of the cake, and the high numbers come from a small region in the center top part of the calciner. When fission product heat is available, there should be no problem in removing nitrate to any desired level.

The solids density as reported here is the pot volume to the controlled liquid level point divided into the weight of solids in the pot and is not corrected for the void which usually occurs in the center; therefore, higher densities usually go with the higher volume of feed. This number will run about 0.62 g/cc.

4.2 Darex Waste

Table 4 gives the data for runs using simulated Darex waste. Since the nitrate content of the feed is higher, the water-to-feed ratio is higher and will be between 3 and 4. The filling-rate coefficient divided by the calciner feed concentration, iron in this case, was reasonably consistent, varying by about a factor of two from the lowest coefficient to the highest. The residual nitrate in the calcined solids again is a function of the calcination time, and the solids density averaged about 1.3 g/cc.

4.3 Purex 1WW

Table 5 summarizes data from Purex 1WW waste runs. Again the water-to-feed ratio should be about 4 to remove the nitrate. The filling-rate coefficients are rather erratic for this series of runs, which reflects primarily the fact that these runs were made early in the campaign, when the precision of the experiments was not yet well refined.

4.4 Purex FTW-65

The data from formaldehyde-treated Purex waste is summarized in Table 6. These are our latest runs and show improved precision that goes with

Table 4. Summary of Pot Calcination Runs Darex Waste

Run No.	Feed Volume (liters)	Water to Feed Volume Ratio	Calciner Feed Fe^{+3} Concentration (g/liter)	Filling* Rate Coefficient (hr^{-1})	Calcination Time (hr)	Nitrate Remaining in Solids (wt %)	Solids Density (g/cc)
56	383	4.1	64.5	0.010	11	0.09 to 0.02	0.86
57	641	3.2	76.0	0.019	10	0.53 to 0.01	1.40
58	576	3.0	109.0	0.038	4	0.17	1.42
60-B	336	5.5	102.0	0.028	4	0.007	1.29
61-B	307	3.8	92.5	0.025	4	2.00 to 0.10	1.13

B - Batch evaporator runs.

$$* = \frac{4k(T_w - T_b)}{\lambda \beta R^2}$$

Table 5. Summary of Pot Calcination Runs Purex 1WW Waste

Run No.	Feed Volume (liters)	Water to Feed Volume Ratio	Calciner Feed Fe^{+3} Concentration (g/liter)	Filling* Rate Coefficient (hr^{-1})	Calcination Time (hr)	Nitrate Remaining in Solids (wt %)	Solids Density (g/cc)
42	495	4.4	48.5	0.021	16	2.3 to 0.02	1.50
44	409	7.8	71.0	0.0161	13	0.14 to 0.06	1.14
45-B	328	3.9	32.0	0.012	12	4.7 to 0.01	1.17
46-B	325	4.1	31.0	0.0142	10	3.7 to 0.01	1.55

B - Batch evaporator runs.

$$* = \frac{4k(T_w - T_b)}{\lambda \beta R^2}$$

Table 6. Summary of Pot Calcination Runs Purex FTW Waste

Run No.	Feed Volume (liters)	Water to Feed Volume Ratio	Calciner Feed Fe^{+3} Concentration (g/liter)	Filling** Rate Coefficient (hr^{-1})	Calcination Time (hr)	Nitrate Remaining in Solids (wt %)	Solids Density (g/cc)
70	1818	0.75	46.9	0.029	28	0.04 to 0.01	1.25
71	1843	0.57	34.6	0.028	36	0.02 to 0.01	1.30
72	1912	0.10	26.7	0.023	24	0.026 to 0.004	1.33
73*	1838	0.20	40.2	0.017	9	0.103 to 0.006	1.23
74*	1968	0.34	49.2	0.022	23	0.016 to 0.015	1.30
75*	1793	0.72	33.8	0.012	11	0.01	1.26

*Organic added.

$$** = \frac{4k(T_w - T_b)}{\lambda \beta R^2}$$

experience. The large feed volumes reflect the dilute nature of the feed. The initial iron concentration is about 12 g/liter; so, the evaporator concentrates the feed three- or fourfold. Also reflecting the dilute nature of the feed, the water-to-feed volume ratio is less than 1. The filling-rate coefficients are very uniform, showing two groups: those without organic in the feed and those with organic in the feed. The presence of organic matter cuts the filling-rate coefficient in half. The nitrate in the residual solids is reduced to an insignificant level by adequate calcination time, and the density of the solid groups nicely around 1.3 g/cc.

4.5 Ruthenium Decontamination During Simulated FTW-65 Run

Run 72 was made with a spike of 0.087 g of natural ruthenium per liter. The fate of this ruthenium is shown in Fig. 14. The top curve for the first 50 hours exactly follows the concentration factor for the evaporator, after which the ruthenium-to-iron ratio crept up to about twice the initial ratio. The ruthenium concentration in the calciner condensate increased steadily throughout the run - to a maximum when the last bit of water and nitrate were being driven from the cake. The evaporator condensate was generally 1/5000 of the evaporator concentration and shows some of the peaks that occur in the calciner condensate. The overall decontamination factor was about 3×10^3. The evaporator de-entrainer, which is a two-stage, close-clearance impingement device, gives a decontamination factor of about 10^4 for nonvolatile constituents.

5. CONCLUSIONS

The development program has included much work on mechanical closures, pump evaluation, corrosion, chemical characterization, and automatic data processing, none of which was presented here.

The pot-calcination process continues to emerge as a workable, safe, and economical method for preparing nuclear wastes from solvent extraction plants for ultimate storage as calcined oxides. Runs have been made with all significant nitrate solvent extraction wastes. All significant operational problems, amenable to study in the absence of radioactivity, have been isolated through experience in a large number of runs and workable

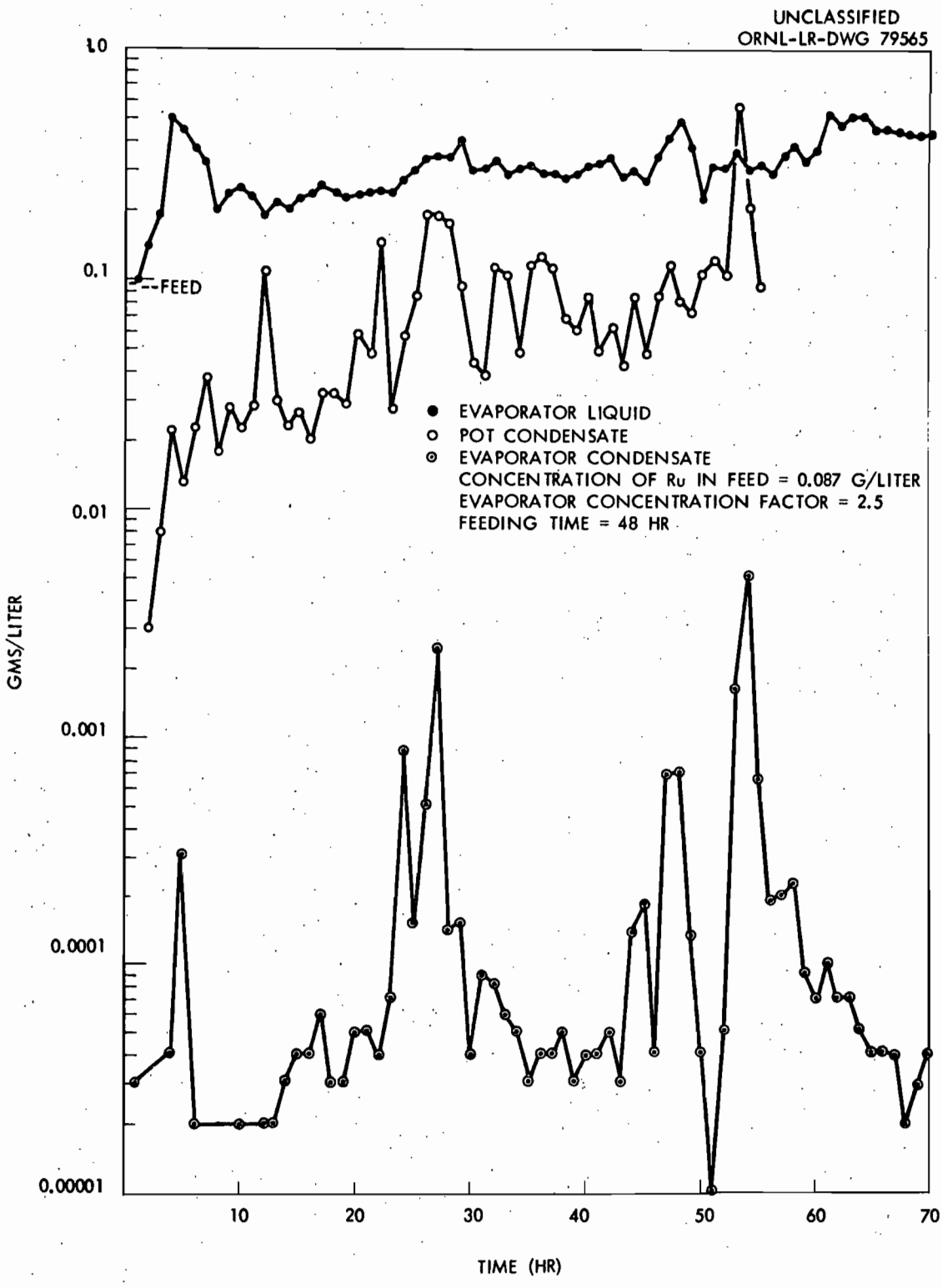

Fig. 14. Ruthenium History During R-72 (Purex FTW).

solutions provided. The probability of successful demonstration in a hot pilot plant is high.

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