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THE CONTROL OF POT CALCINER TEMPERATURES TO ENSURE CALCINATION AT 900°C

J. M. Holmes

ABSTRACT

A program will be required for controlling the wall temperature of a pot calciner during calcination in order to prevent an excessive temperature rise from internal heat generation while assuring complete calcination of the cake at 1650°F. A linear approximation to a pot wall temperature program indicates that this can be accomplished by holding the wall temperature at 1650° for 0.8 to 1.0 hrs and then cooling the wall at rates dependent upon the cake internal heat generation rate and average thermal conductivity. A similar study indicates that if it is necessary to reheat the cake for complete calcination, the wall heating time must be limited to prevent excessive temperature rise in the cake. Reheating times are also dependent upon the cake internal heat generation and thermal conductivity.

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1.0 INTRODUCTION

Pot calcination of highly radioactive wastes involves the feeding of Purex, Darex, or TBP-25 process wastes containing nitric acid and dissolved metallic nitrates or sulfates to a 8-to 12-in.-dia pot, evaporation to a solid cake and calcination of the cake at temperatures up to 900°C (1652°F). Perona (ORNL-3163) has shown that the cake deposits radially along the pot wall and has derived an expression for the temperature profile during deposition as a function of radial distance from the axis of the pot. He also presents equations for the temperature buildup in the pot upon completion of radial deposition due to the internal heat generation of the fission products in the cake. Using a constant wall temperature of 1652°F , it was shown that the entire cake would exceed the wall temperature within fifteen minutes after completion of solids deposition when the heat generation rate was 5000 Btu/hr ft^3 . The equilibrium temperature at infinite time was about 2500°F at the surface of the internal core.

The maximum cake temperature desired during calcination is in the vicinity of 1652°F in order to prevent excessive volatility of the sulfate, sodium, and fission products and excessive corrosion on the pot wall. However, in order to obtain complete calcination of the entire cake, temperatures as high as 1800°F may be permitted for short periods without excessive volatilization (1). These limitations indicate that some cooling may be necessary on the pot wall during deposition. During calcination of wastes of high fission product heat evolution, a programmed pot wall cooling rate must be used in order to completely calcine the cake throughout the pot while maintaining an absolute maximum temperature of 1800°F .

This study utilizes an analog computer to determine a linear approximation to a pot wall temperature program during calcination that will satisfy these requirements.

2.0 TEMPERATURE PROFILES DURING DEPOSITION

Recent calculations (2) have shown that deposition of the cake in a calcination pot can be accomplished without exceeding 1652°F anywhere in

(1) W. E. Clark, personal communication May 1962.

(2) S. H. Jury and J. C. Suddath, personal communication May 1962.

the cake until the radius of the vertical core decreases to a limit, r_5 , which is dependent upon the cake internal heat generation rate, thermal conductivity and the pot radius. At this time, the slope of the temperature gradient at the wall is zero (see initial temperature curve, Figs. 1 and 2) indicating that no heat is being added to or removed from the wall. If deposition is continued, it is necessary to cool the wall to a temperature dependent upon the radius of the internal cavity (r_5). The temperature profile then shows a maximum of 1652°F which moves radially inward through the cake as the internal cavity radius decreases. Under this condition, the internal heat generated in that portion of the cake between the wall and the temperature maximum must be removed by cooling the wall and the internal heat generated in the remainder of the cake is used to evaporate the liquid filling the internal cavity at 400°F . This then becomes a "self-sintering" type of calcination where the entire heating source is the internal heat generation of that portion of the cake between the temperature maximum and the core.

3.0 TEMPERATURE PROFILES DURING CALCINATION

In order to accomplish satisfactory calcination, it will be necessary to bring the entire cake up to a temperature of 1652°F during the time when the pot is connected to its vapor line. This can occur during or after completion of cake deposition. For purposes of this study, it is assumed that cake deposition is discontinued when the temperature maximum is at the wall and the temperature gradient at the wall is zero (see Figs. 1 and 2). Under this condition, the capacities of an 8-in.-dia pot for solids at two thermal conductivities is shown in Table I.

TABLE I

Capacity of 8-in. Pots if Feed is Discontinued When
Pot Wall Heating is Stopped

Pot dia = 8 in.

Heat generation rate = $4000 \frac{\text{Btu}}{\text{hr ft}^3}$

Average Cake Thermal Conductivity	r_5 = Radius Internal Cavity-ft	Pot Capacity-% of Total Capacity
0.1	.1235	86.3
0.2	.0667	96.0

Fig. 1. Initial and final temperature conditions for calciner cooling program.

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Fig. 2 Initial and final temperature conditions for calciner cooling program.

Figs. 1 and 2 show the initial 8-in. pot temperature profiles for 4,000 Btu/hr ft³ internal heat generation rates and conductivities of 0.2 and 0.1, respectively. From these initial profiles, the pot walls must be cooled to produce the equilibrium profiles indicated at rates which will permit each portion of the cake to reach 1652°F during the calcination but the cake should not be heated above 1800°F.

4.0 EQUATIONS

The basic equation used for the temperature distribution in a cylindrical solid with internal heat generation is

$$\frac{\partial W}{\partial t} = \alpha \left(\frac{\partial^2 W}{\partial r^2} + \frac{1}{r} \frac{\partial W}{\partial r} \right) + \frac{Q}{\rho C_p} \quad (1.0)$$

where $W = T - 300^\circ\text{F}$

α = thermal diffusivity of deposited solids

ρ = solids density

C_p = solids heat capacity

Q = heat generation of solids per unit volume

r = cylinder radius

From equation 1.0 the following finite difference equations give the temperatures in the cake as a function of time at five points located at equal increments of radius (Δr) between the wall and the interior cavity.

$$\frac{\partial W_1}{\partial t} = \frac{\alpha}{(\Delta r)^2} \left[\left(1 + \frac{\Delta r}{2r_1} \right) W_0 - 2W_1 + \left(1 - \frac{\Delta r}{2r_1} \right) W_2 \right] + \frac{Q}{\rho C_p} \quad (2.0)$$

$$\frac{\partial W_2}{\partial t} = \frac{\alpha}{(\Delta r)^2} \left[\left(1 + \frac{\Delta r}{2r_2} \right) W_1 - 2W_2 + \left(1 - \frac{\Delta r}{2r_2} \right) W_3 \right] + \frac{Q}{\rho C_p} \quad (3.0)$$

$$\frac{\partial W_3}{\partial t} = \frac{\alpha}{(\Delta r)^2} \left[\left(1 + \frac{\Delta r}{2r_3} \right) W_2 - 2W_3 + \left(1 - \frac{\Delta r}{2r_3} \right) W_4 \right] + \frac{Q}{\rho C_p} \quad (4.0)$$

$$\frac{\partial W_4}{\partial t} = \frac{\alpha}{(\Delta r)^2} \left[\left(1 + \frac{\Delta r}{2r_4} \right) W_3 - 2W_4 + \left(1 - \frac{\Delta r}{2r_4} \right) W_5 \right] + \frac{Q}{\rho C_p} \quad (5.0)$$

$$\frac{\partial W_5}{\partial t} = \frac{2\alpha}{\left(\frac{r_4^2 - r_5^2}{2} - r_5^2 \ln \frac{r_4}{r_5} \right)} \left[W_4 - W_5 \right] \quad (6.0)$$

The wall temperature is designated as W_0 while the temperature at the surface of the internal cavity is taken as W_5 . Values of the various radii are shown on Figs. 1 and 2.

The analog computer diagram for equations 2.0 to 6.0 is shown in Fig. 3. A model TR-10 Electronics Associates analog computer was used. For convenience, the coefficient of W_0 in equation 2.0 and the coefficients of W_3 , W_4 , and W_5 in equations 3.0, 4.0, and 5.0 were factored out to reduce the number of potentiometers needed.

Linear approximations to temperature programs for the pot wall were established by starting the computer at the temperature conditions given in Figs. 1 and 2 at the completion of solids deposition. The wall temperature was then varied linearly with time according to the following equation

$$W_0 = -\int C \, dt + W_0 \text{ Initial} \quad (7.0)$$

When the equilibrium wall temperature indicated on Figs. 1 and 2 was reached, the wall temperature was held constant by switching off the input of C to the W_0 integrator. The other temperature points in the cake were monitored by repeating the program for the variation of W_0 with time while recording the output of the appropriate amplifiers.

5.0 RESULTS OF COOLING PROGRAM STUDY

5.1 Program for $Q = 4000 \text{ Btu/hr ft}^3$ and $K = 0.2 \text{ Btu/hr ft}^\circ\text{F}$

Figure 4 shows the results obtained using a constant wall temperature of 1652°F for 0.4 hr and a 2.2 hr cooling period to lower the wall to equilibrium temperature. Although the inner temperatures (W_4 and W_5) reached the desired $1650\text{-}1800^\circ\text{F}$ calcination temperature range, the temperatures near the wall (W_1 and W_2) barely reached 1600°F . Figure 5 indicates that increasing the wall soaking time to 1.0 hr and cooling for 2.2 hr brought all temperatures up to 1650°F . Interior temperature W_5 rose to 1820°F which was slightly above the desired range. Decreasing the soaking time to 0.8 hr and the cooling time to 1.1 hr reduced the interior temperatures to a maximum of 1740°F and dropped those near (Fig. 6) the wall slightly below 1650°F . Therefore, a soaking time range of 0.8-1.0 hr and a cooling time range of 1-2 hr are recommended to give the proper calcination conditions.

Potentiometer	Function
1	W_0 Initial
2	K in Equation 7.0
3	W_1 Initial
4	$\frac{a}{(\Delta r)^2} \left[1 + \frac{\Delta r}{2r_1} \right]$
5	W_2 Initial
6	$\frac{a}{(\Delta r)^2} \left[1 - \frac{\Delta r}{2r_2} \right]$
7	W_3 Initial
8	$\frac{a}{(\Delta r)^2} \left[1 - \frac{\Delta r}{2r_3} \right]$
9	W_4 Initial
10	$\frac{a}{(\Delta r)^2} \left[1 - \frac{\Delta r}{2r_4} \right]$
11	W_5 Initial
12	$2a \left[\frac{r_4^2 - r_5^2}{2} - r_5^2 \ln r_4/r_5 \right]$
13	$2 / 1 + \Delta r/2r_1$
14	$1 - \Delta r/2r_1 / 1 + \Delta r/2r_1$
15	$1 + \Delta r/2r_2 / 1 - \Delta r/2r_2$
16	$2 / 1 - \Delta r/2r_2$
17	$1 + \Delta r/2r_3 / 1 - \Delta r/2r_3$
18	$2 / 1 - \Delta r/2r_3$
19	$1 + \Delta r/2r_4 / 1 - \Delta r/2r_4$
20	$2 / 1 - \Delta r/2r_4$
21	$Q/\rho c_p$

Fig. 3. Analog computer diagram for pot cooling program.

Fig. 4. Calcination cooling program.

Fig. 5. Calcination cooling program.

Fig. 6. Calcination cooling program.

5.2 Program for $Q = 4000 \text{ Btu/hr ft}^3$ and $K = 0.1 \text{ Btu/hr ft } ^\circ\text{F}$

By changing the appropriate radii, plus initial and final temperature conditions as shown on Fig. 2, a temperature program for a K of 0.1 was obtained for the same internal heat generation rate of 4000 Btu/hr ft^3 . Fig. 7 shows the effects of a 0.8 hr soak period and a 1.6 hr cooling period. Temperatures near the pot wall were slightly under 1650°F while the maximum for the interior was about 1740°F . Increasing the cooling period to 2.5 hr brought all temperatures into a $1640\text{--}1810^\circ\text{F}$ range which is sufficiently close to the desired range (Fig. 8). Therefore, it is recommended that a soaking time of 0.8 hr and a cooling time range of 1.6-2.5 hr be used for a cake having a thermal conductivity of 0.1 $\text{Btu/hr ft } ^\circ\text{F}$ and a $Q = 4000 \text{ Btu/hr ft}^3$.

5.3 Maximum Cooling Rates

The maximum cooling rates required during the wall cooling period can be estimated from the temperature difference across the cake at the pot wall. At thermal equilibrium the product of this temperature difference, the thermal conductivity and the area should equal the cake internal generation rate. However, since the first temperature in the cake (W_1) is determined at a finite distance from the wall (Δr), the slope of the temperature curve between W_0 and W_1 is slightly less than the slope at the wall, so the cooling rate calculated using this method is slightly less than the internal heat generation rate. Therefore, the ratio of the maximum value of $W_1 - W_0$ and the value of $W_1 - W_0$ at equilibrium times the internal heat generation rate was used to estimate the maximum cooling rate required. Results are shown in Table II.

TABLE II

Maximum Cooling Rates Required During Programmed Cooling Period

Q Btu/hr ft^3	K $\text{Btu/hr ft}^2 ^\circ\text{F}$	Pot Wall Cooling Time - hrs	Estimated Maximum Cooling Rate - Btu/hr ft^3
4000	0.1	2.5	5450
4000	0.1	1.6	6130
4000	0.1	1.1	6300
4000	0.2	3.6	5500
4000	0.2	2.2	5750
4000	0.2	1.1	6400

Fig. 7. Calcination cooling program.

Fig. 8. Calcination cooling program.

From these data the maximum cooling rate required would be about 1.6 times the internal heat generation rate of 4000 Btu/hr ft³.

6.0 POT REHEATING STUDY

The programs recommended above for cooling the pots upon completion of cake deposition assume that the cake is uniformly distributed radially along the pot wall leaving a cavity along the pot axis. However, actual engineering scale calcinations have shown this to be true for only the top portion of the deposited cake. In many runs, the bottom 1/3 of the pot is filled solidly with cake. Under these conditions, the above programs could be used for the upper portion of the cake where true radial deposition occurred but the cake in the bottom would probably require more drastic cooling rates in order to keep the center below the specified maximum of 1800°F. In addition, the final equilibrium temperature profile is much steeper. For example, a solid 8-in.-dia cake of 0.1 Btu/hr ft °F conductivity and 4000 Btu/hr ft³ heat generation rate would have an equilibrium temperature difference between the wall and center of about 1111°F. Therefore, if during deposition the bottom zone of the pot filled and went dry while liquid remained in the upper pot zones, it would be necessary to cool the pot wall to 539°F in order to keep the center temperature at 1650°F. UNOP experience has indicated that this large temperature differential tends to produce thermal stresses that crack the cake. If this occurred, liquid from the upper pot zones could run down into the lower zone where calcination was already completed. This circumstance would necessitate a reheating of the entire pot after completion of the run in order to ensure calcination of the entire cake at 1650°F.

Calculations were made to determine the optimum times for reheating a solid cake at thermal equilibrium with a 300°F wall temperature and having internal heat generation rates of 2000 and 4000 Btu/hr ft³ and K's of 0.1 and 0.2 Btu/hr ft °F. Equations 2.0 to 5.0 remained the same for the analog solution but equation 6.0 was simplified to the following since $r_5 = 0$ and $\Delta r = r_4 - r_5 = r_4$:

$$\frac{\partial W_5}{\partial t} = \frac{4\alpha}{(\Delta r)^2} (W_4 - W_5) \quad (8.0)$$

The procedure involved raising the pot wall temperature from 300°F to 1650°F at time = 0 when the cake temperatures were at thermal equilibrium. The wall temperature was held at 1650 long enough to bring the temperatures near the wall up to 1650°F and then dropped back to 300°F instantaneously in order to prevent the interior temperatures from rising above 1800°F. The locations of the temperature points were $W_5 = 0"$, $W_4 = 0.8"$, $W_3 = 1.6"$, $W_2 = 2.4"$, $W_1 = 3.2"$ and $W_0 = 4.0"$ from the pot axis.

Fig. 9 shows the results of heating a $Q = 4000$ and $K = 0.1$ cake for 1.5 hr. Although the centerline temperature reached 1740°F, the temperature W_2 was only 1520°F at its peak. Increasing the heating time to 1.87 hrs (see Fig. 10) raised W_2 to a maximum of 1610°F and increased the centerline to about 1820°F which is just slightly higher than the specified maximum of 1800°F. It would not be desirable to heat longer than this to increase W_2 to 1650 since the centerline temperatures would rise well above 1800°F. Therefore, a maximum heating time of 1.8 hrs is recommended for these cake conditions.

When the cake Q is reduced to 2000 Btu/hr ft³ with a $K = 0.1$ Btu/hr ft °F, reheating is much easier. Fig. 11 shows that a 5-hr heating time would bring all the cake temperatures above 1650°F with a maximum of 1720°F. By dividing the time scale by 2, these same data can be used for a cake with $Q = 4000$ and $K = 0.2$. In this case a heating time of 2.5 hrs would suffice to completely calcine the cake. Fig. 11 also shows the time-temperature curves for this case.

7.0 RECOMMENDED COOLING AND REHEATING PROGRAMS

A summary of the results of the linear approximation for both the pot cooling program and pot reheating are given in Table III.

TABLE III
Programs for Pot Cooling During Calcination
8-in. Diameter Pot

Q	K	Soaking Time (Wall at 1650°F)	Pot Wall Cooling Time (Wall Cooled to Equilibrium Temp.)
4000	0.1	0.8 hrs	1.6-2.5 hrs
4000	0.2	0.8-1.0 hrs	1.0-2.2 hrs

TABLE III (cont.)

Programs for Pot Reheating

Q	K	Heating Time
		(Pot Wall at 1650°F)
4000	0.1	1.8 hrs
2000	0.1	5.0 hrs
4000	0.2	2.5 hrs

Fig. 9. Pot preheating study.

Fig. 10. Pot reheating study.

Fig. 11. Pot reheating study.

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