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THERMAL EFFECTS IN ANION EXCHANGE RESIN-NITRIC ACID SYSTEMS

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AUGUST, 1965

JAN 6 1969
DP Franquist 30024 MATH

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RICHLAND, WASHINGTON

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Page 1, paragraph 3, line 4: $Pu(NO_3)_2$ should be $Pu(NO_3)_4$

Page 23, paragraph 3, line 2: HNO_2 should be HNO_3

Appendix A: Heat generation rates: cal/(cm^3)(sec) may also be expressed in units of cal/(cm^3)(min) for consistency with the units used elsewhere in this report.

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Page 31, Figure 21: Radiolytic heat generation rates (curve labels) should be corrected to read megawatts per liter of bed volume,

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By

W. J. Van Slyke, G. Jansen, Jr.,
and W. H. Swift

Chemical Development Section
Chemistry Department

August, 1965

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THERMAL EFFECTS IN ANION EXCHANGE RESIN–NITRIC ACID SYSTEMS

INTRODUCTION

During the past several years a number of instances of pressurization and fires have occurred in chemical process systems for purification of plutonium nitrate, $Pu(NO_3)_4$, in nitric acid, HNO_3, solutions by anion exchange. Incidents have occurred in laboratory and plant scale equipment and in accumulations of nitrate-bearing anion exchange resins that were both unconfined and confined within process equipment.

The anion exchange process has been successfully applied for several years in the United States and Europe for recovery, purification, and concentration of plutonium. Variations of the basic process have been developed and used for similar treatment of other heavy elements, such as neptunium and thorium. However, evidence exists indicating that undesirably rapid chemical reactions can occur in the anion exchange system.

One severe incident, which has been described in detail,[1] occurred November 6, 1963 in the 233-S Building of the Redox plant of the Hanford Atomic Products Operation. A continuous counter-current anion exchange contactor used for the purification of $Pu(NO_3)_4$ in concentrated HNO_3 solution was involved. The contactor consisted of a loop of 4 in. sch 10 SS pipe approximately 26 ft tall. The reaction in the contactor ruptured process screens, blew gaskets, expanded part of the loop piping, and forcibly ejected resin from the contactor by internal pressures that may have exceeded 1500 psig. Although the reaction may have been initiated by an external heat source, most of the evidence suggested that it was triggered internally by high operating temperature and/or the introduction of a strong oxidizing chemical.

Consequently, this study was undertaken to define unsafe operating conditions, to specify appropriate safety precautions, and to clarify the causes of some of the previous incidents by characterizing the heat and gas producing chemical effects for the anion resin-nitric acid system.

SUMMARY

An analysis of the instability conditions when operating with Permutit SK® anion exchange resin in 7M HNO_3 has been made. The reaction kinetics for the system were investigated by externally heated pipe pressurization tests and by calorimeter experiments. The chemical and physical properties of the system were correlated by mathematical models for batch and flow cases to predict the conditions that permit self-accelerating chemical reactions. Uncontrolled reaction conditions are favored by:

- Increasing vessel radius
- Low vessel wall heat transfer coefficients to the surroundings
- Low thermal conductivity of the vessel contents
- High ambient and operating temperatures
- Chromium(VI) loaded on the resin

The relations between these variables for the chemical system are graphically presented. The theory, based on the concepts originally proposed by Frank-Kamenetskii,[2] is generally applicable to cylindrical shapes which generate heat with an exponential dependence on temperature. The Redox 233-S incident is discussed briefly in terms of this analysis.

STATIC SYSTEMS

Experimental

Much of the damage in addition to the contamination release during the Redox incident was caused by the effects of the accompanying fire. It was possible the fire could have started the chain of events by supplying enough heat either to pressurize the contactor directly, or to trigger a gas-producing chemical reaction in the contactor. Pressurization tests were conducted to determine how external heat might cause such an effect.

The tests used a 4-in. -diam sch 40 pipe, 4-ft long, equipped with a 4-in. rupture disk flange and heated by an 8-in. ID clam shell tube furnace (Figure 1). A flanged dummy pipe was welded to the bottom sf the capped 4-in. test section to provide a strong detachable support for a similarly flanged pipe welded to a 2-in. thick support plate. The tube furnace was also mounted on the support plate. Figure 2 shows the test equipment ready for a pressure relief test.

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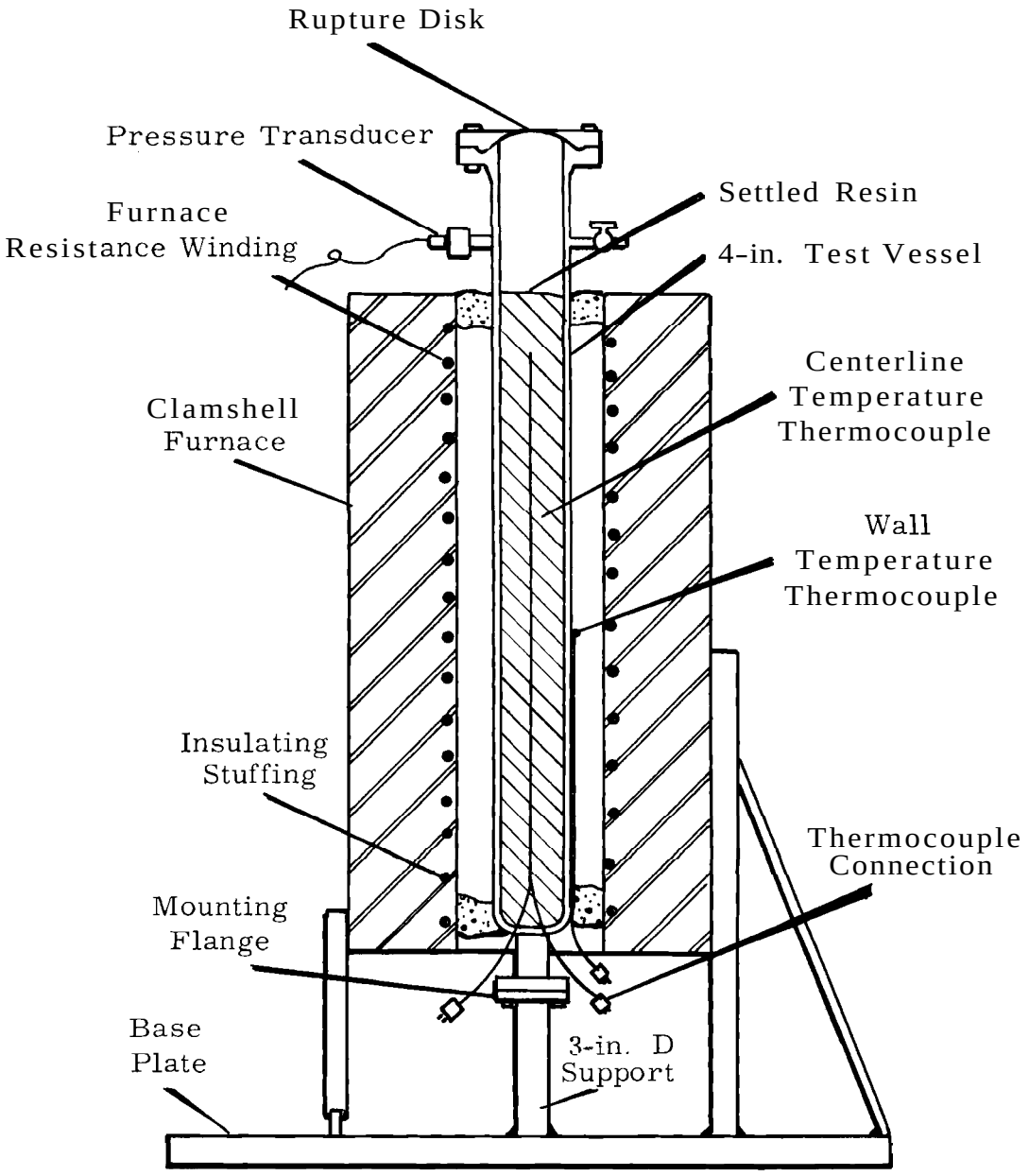


FIGURE 1

Pressure Vessel and Furnace

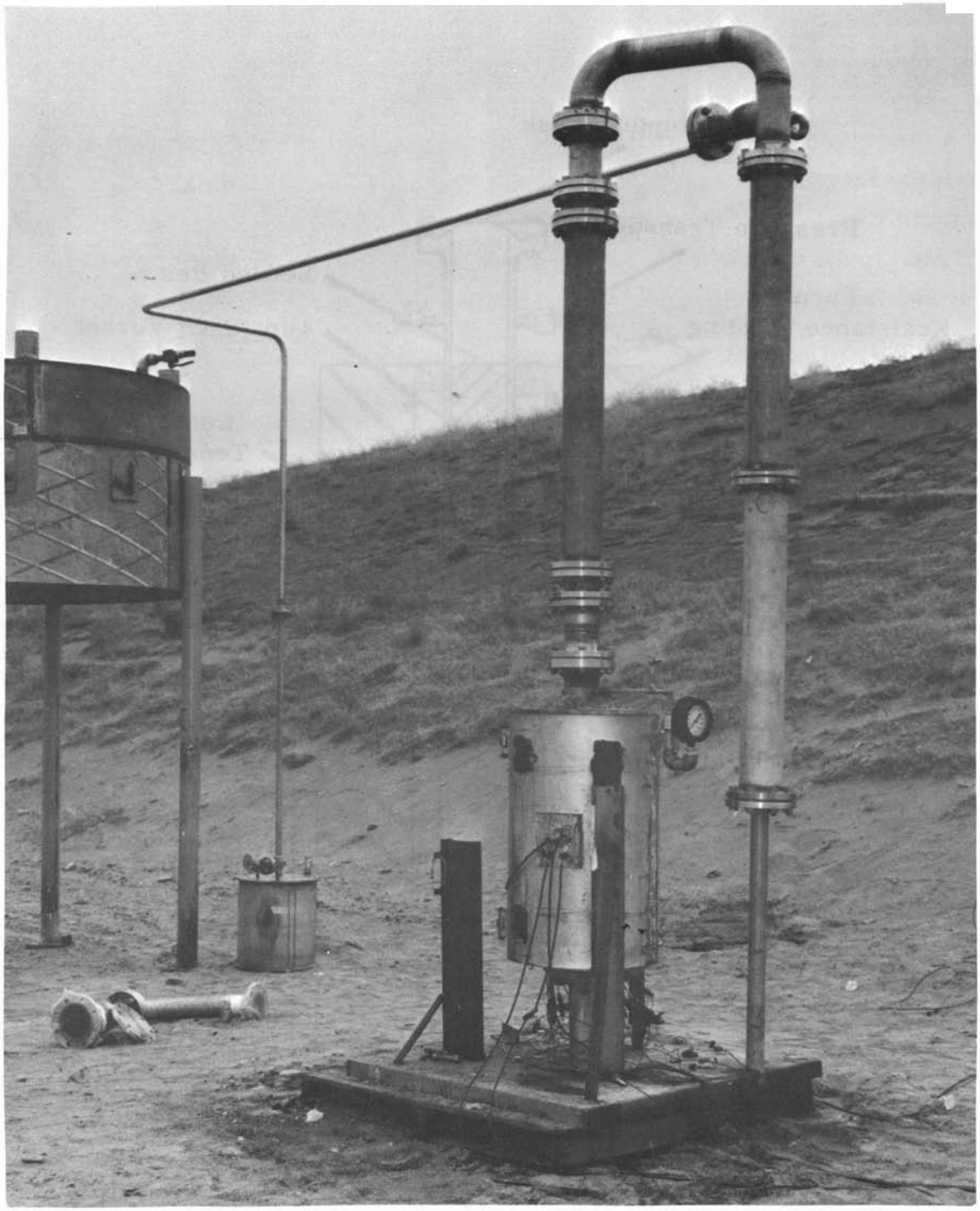


FIGURE 2
Purex Prototype Equipment for Pressurization Test 12

Test instrumentation was 200 ft away, shielded by the corner of a large bunker. The instrumentation included a 16 point temperature recorder, a temperature controller, and a pressure recorder. The instrumentation monitored and recorded four centerline and eleven wall temperature points and the internal pressure in the test vessel. One additional wall thermocouple was linked to the single point recorder-controller to supply automatic on-off control of the vessel wall temperature. Manual adjustment for heating rate and controller overshoot was provided by a 220 V variable autotransformer.

The pressurization tests were conducted with Permutit SK 20-50 mesh nitrate-form resin in equilibrium with HNO_3 solutions. The test conditions and results are summarized in Table I.

The general procedure was to fill the test vessel section with the selected resin preparation, mount the pipe on the tube furnace test stand, and seal with the rupture disk and flange. Any other piping to be included in the test (for example, the prototype contactor pressure relief Tests 12 and 13) was then assembled on the top or discharge end of the pipe test assembly. The experimental procedure was conducted from the safety of the instruments location, and the furnace and pipe assembly was not approached again until disk rupture or sufficient cooling made the assembly safe.

The first test was run with a gradually increasing wall temperature. Later tests were made with the wall temperature raised to a predetermined level and held constant. Figure 3 illustrates the thermal and pressure behavior for a typical experiment (Test 3) that resulted in a rapid pressure rise rate. The centerline temperature exceeded the wall temperature after 1.5 hr because of internal heat generated by resin decomposition. The run was terminated by a temperature excursion caused by internal heat generation at a greater rate than the removal rate through the vessel walls. The gas and steam pressure generated by the temperature rise finally burst the rupture disk. Figure 4 shows the appearance of that test (photographed by a remotely operated camera) a fraction of a second after the disk burst.

TABLE I

SUMMARY OF VESSEL PRESSURIZATION TESTS

Test	Resin Preparation	Test Conditions	Results
1	Equilibrated with 7M HNO_3 and drained.	300 psig rupture disk, rapid heating, restricted venting.	Disk ruptured, burning started due to the resin drying via the restricted vent. Burning continued for 30 to 90 min.
		Screen installed to restrain the resin.	The restraining screen was ruptured, bent, and blackened with charred resin and Pyrolysis products.
2	Equilibrated with 7M HNO_3 and drained.	300 psig rupture disk, slow external heating.	Disk ruptured at a 130 °C wall temperature. No burning.
3	Equilibrated with 7M HNO_3 and drained.	300 psig rupture disk	Stable heat generating conditions observed at vessel wall temperatures of 113 °C and lower. Higher temperatures caused runaway and disk rupture. No burning. See Figure 3.
4	Equilibrated with 7M HNO_3 and drained.	300 psig rupture disk	Same as Test 3.
5	Equilibrated with 20 g/liter sodium dichromate, 0.5M HNO_3, drained	300 psig rupture disk	Insufficient pressure to rupture the disk. Vessel cooled without incident. Slight temperature rise.
6	Not completed due to Power supply failure		
7	Equilibrated with 7M HNO_3, drained, and air dried for 15 hr.	300 psig rupture disk	Disk ruptured - resulted from a wall temperature of 125 °C
8	Equilibrated with 7M HNO_3, drained	Vented, 300 psig rupture disk	No spontaneous centerline temperature rise observed, disk ruptured only after extreme external heating to a vessel wall temperature of 205 °C.
	Equilibrated with 1.9 g/liter sodium dichromate in 7M HNO_3	300 psig rupture disk, restraining screen. Test vessel contained an excess of the solution.	Exothermic reaction observed at 143 °C, disk ruptured when the internal temperature reached 160 °C. Resin almost completely dissolved.
10	Equilibrated with 7M HNO_3 and drained.	300 psig rupture disk	Vessel wall maintained at 135 °C caused disk rupture
11	Equilibrated with 7M HNO_3, drained.	No rupture disk, restraining screen was in place.	No centerline temperature rise was observed. The restraining screen was ejected and destroyed when the vessel wall reached 170 °C. Charred resin was found.
12	Equilibrated with 7M HNO_3 and drained.	Purex prototype simulation. (See Figure 2) 160 lb rupture disk, initiated by severe external heating.	Vented controllably when the vessel wall reached 210 °C Charred resin found.
13	Equilibrated with 7M HNO_3 and drained	I-in. platinum rupture disks, 1-in. pressure release line.	Vented without incident, charred resin found.
14	Loaded with thorium from 7M HNO_3 solution. Thorium concentration on the resin was 78.3 g/liter.	300 psig rupture disk, 4 in. crossover to a catch tank with exhaust fiberglass filter.	Vented as expected, no contamination release, no charred resin produced. Peak pressure in the catch tank was 67 psig.

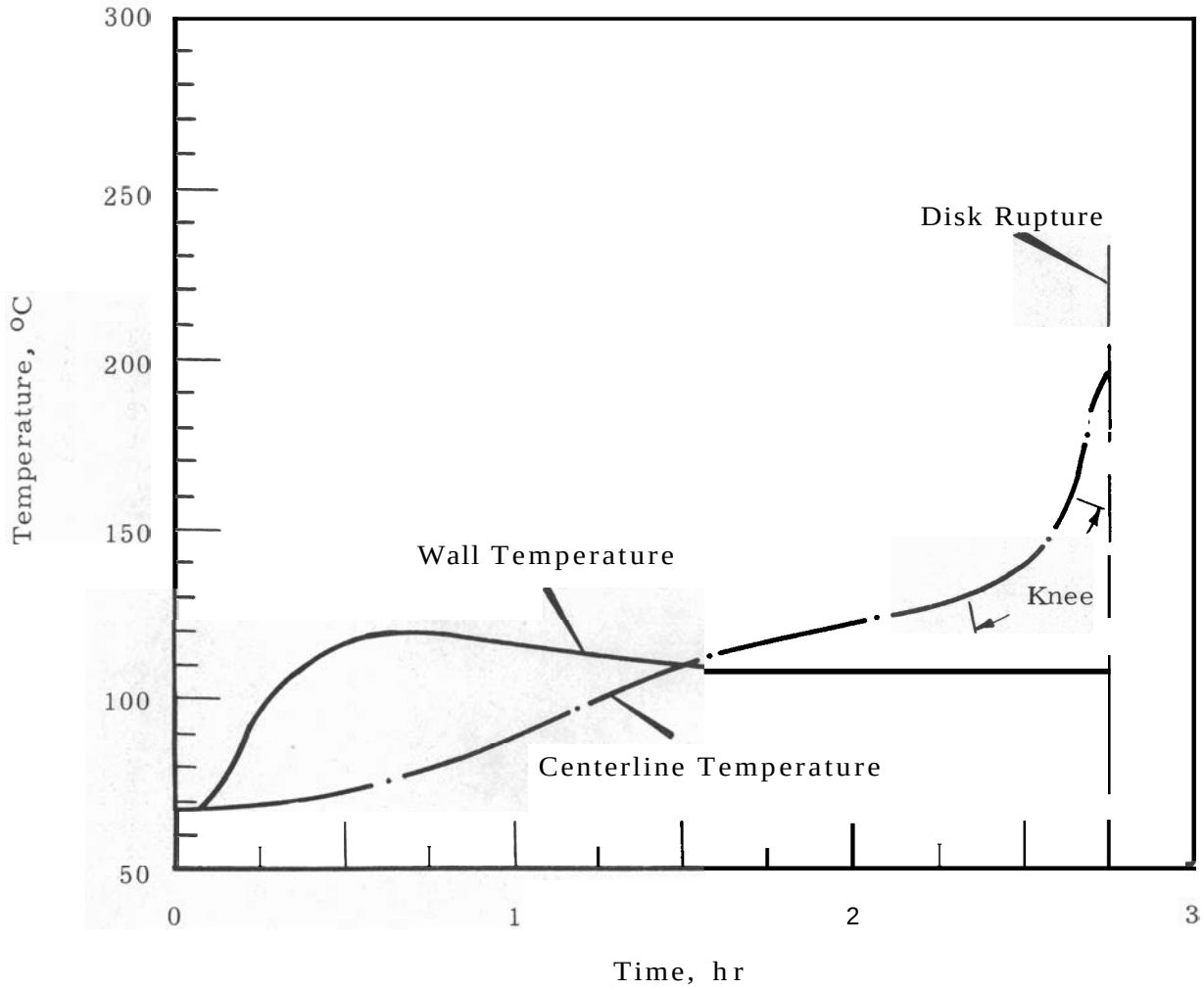


FIGURE 3

Temperature Behavior in Test 3

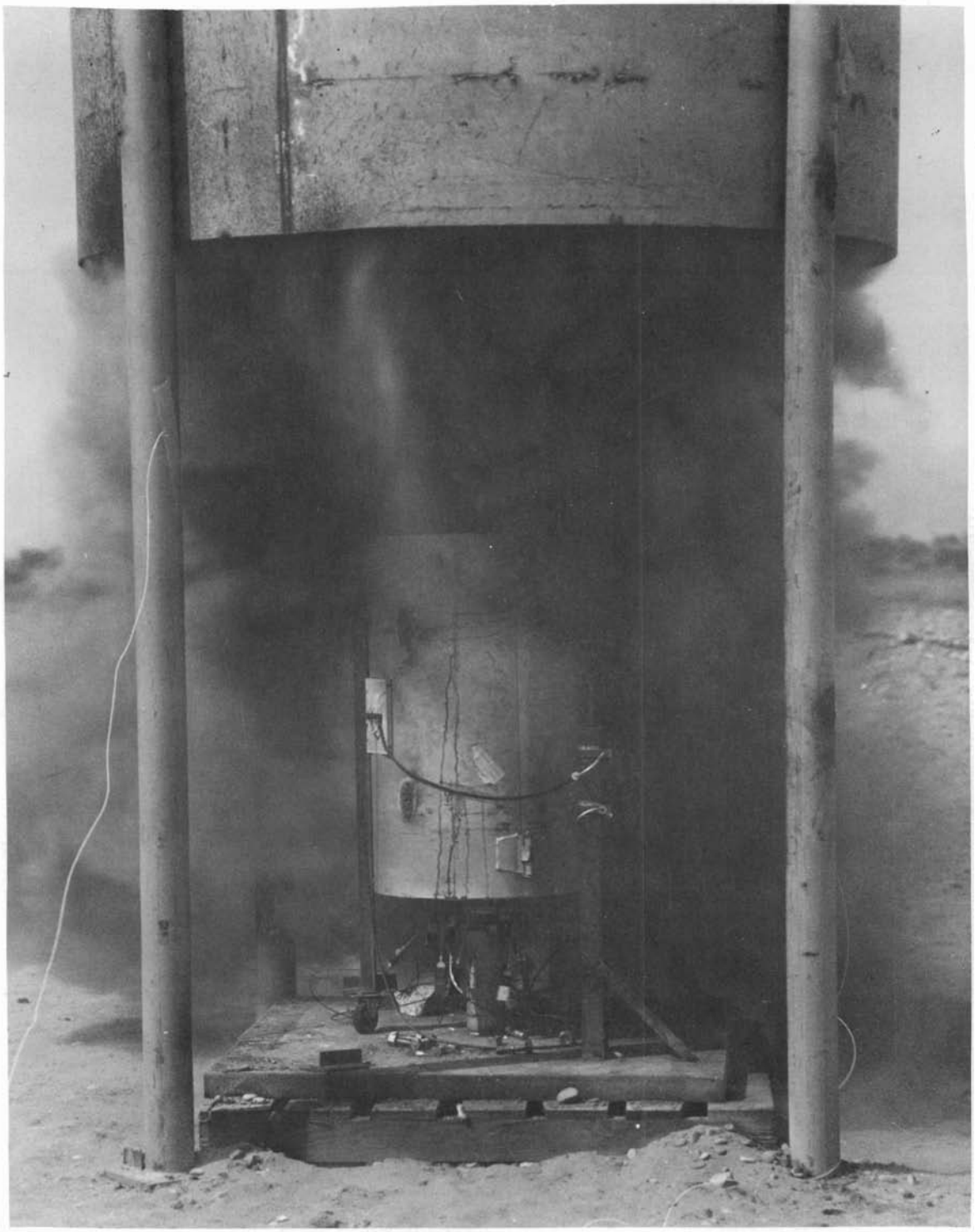


FIGURE 4

Test System Immediately After Disk Rupture in Pressurization Test 3

Figure 5 shows an internally located hold down screen used in Test 9, compared to a new piece of the same screen. Note that the screen assembly has been severely darkened although the maximum temperature before disk rupture was only 160 °C. The oxide color was formed by contact with HNO_3 and dichromate solution for less than 6 hr at temperatures below 160 °C. Similar darkening of stainless steel has been observed in a pilot contactor operating with dichromate-containing feeds at temperatures below 60 °C. The darkened stainless steel sections in the 233-S contactor after the incident were caused by dichromate at the 87 °C operating temperature and not by much higher temperatures assumed previously.[1] The resin of Test 9 was almost completely dissolved by the HNO_3 and $Na_2Cr_2O_7$ solution present. A syrupy blue liquid was ejected when the rupture disk failed.

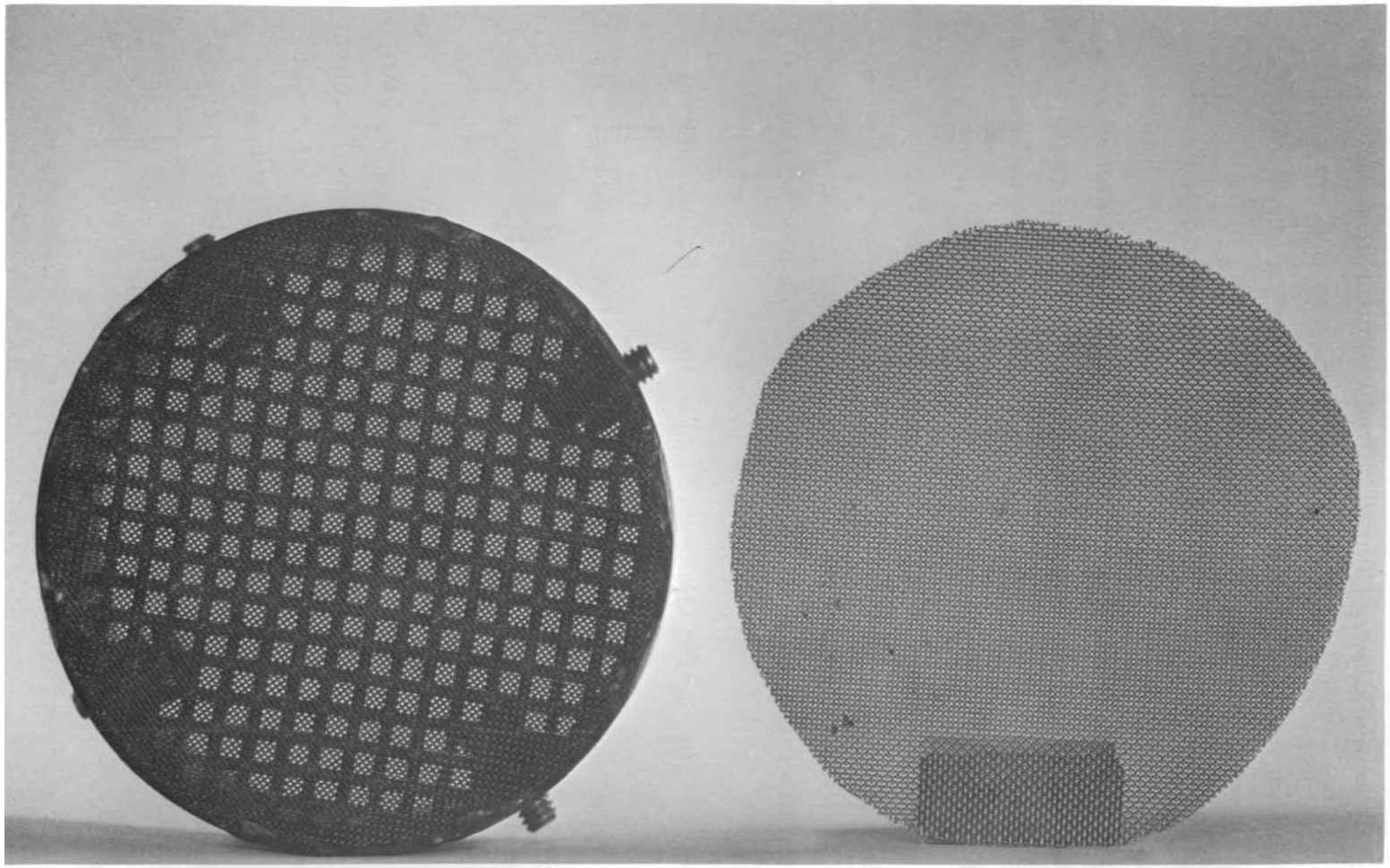
Figure 6 shows the same hold down screen after Test 11, in which the screen was forcibly ejected from the test vessel. The damage to the assembly occurred when it hit the protective canopy. The expelling force on the screen assembly was calculated to have been as high as 3500 lb based on the 300 psig rupture disk rating.

Observations made during the tests lead to the following general conclusions:

- The reaction of the anion exchange resin in 7M HNO_3 shows a strong exponential temperature dependency.
- A vessel wall temperature of 120 °C is sufficient to trigger a rapid exothermic reaction in a 4-in.-diam resin-filled pipe. However, a 100 °C vessel wall temperature will not cause a chemical excursion. Thorium loaded resin exhibits a temperature rate of rise curve that duplicates the unloaded resin curve within the experimental accuracy.
- Rapid pressure release abruptly lowers the temperature of moist resin to the atmospheric boiling temperature of the solution and effectively quenches the exothermic reaction. This "safe" pressure release point can be as high as 200 psig.

Theoretical Analysis

A theoretical analysis of a cylindrical vessel has been made. An expression describing the dependence of the critical wall temperature on the



Hold-Down Screen After 6 hr in Dichromate – HNO_3 Below 160 °C

Unexposed Screen Material

FIGURE 5

Discoloration of Stainless Steel in Dichromate – 7M HNO_3

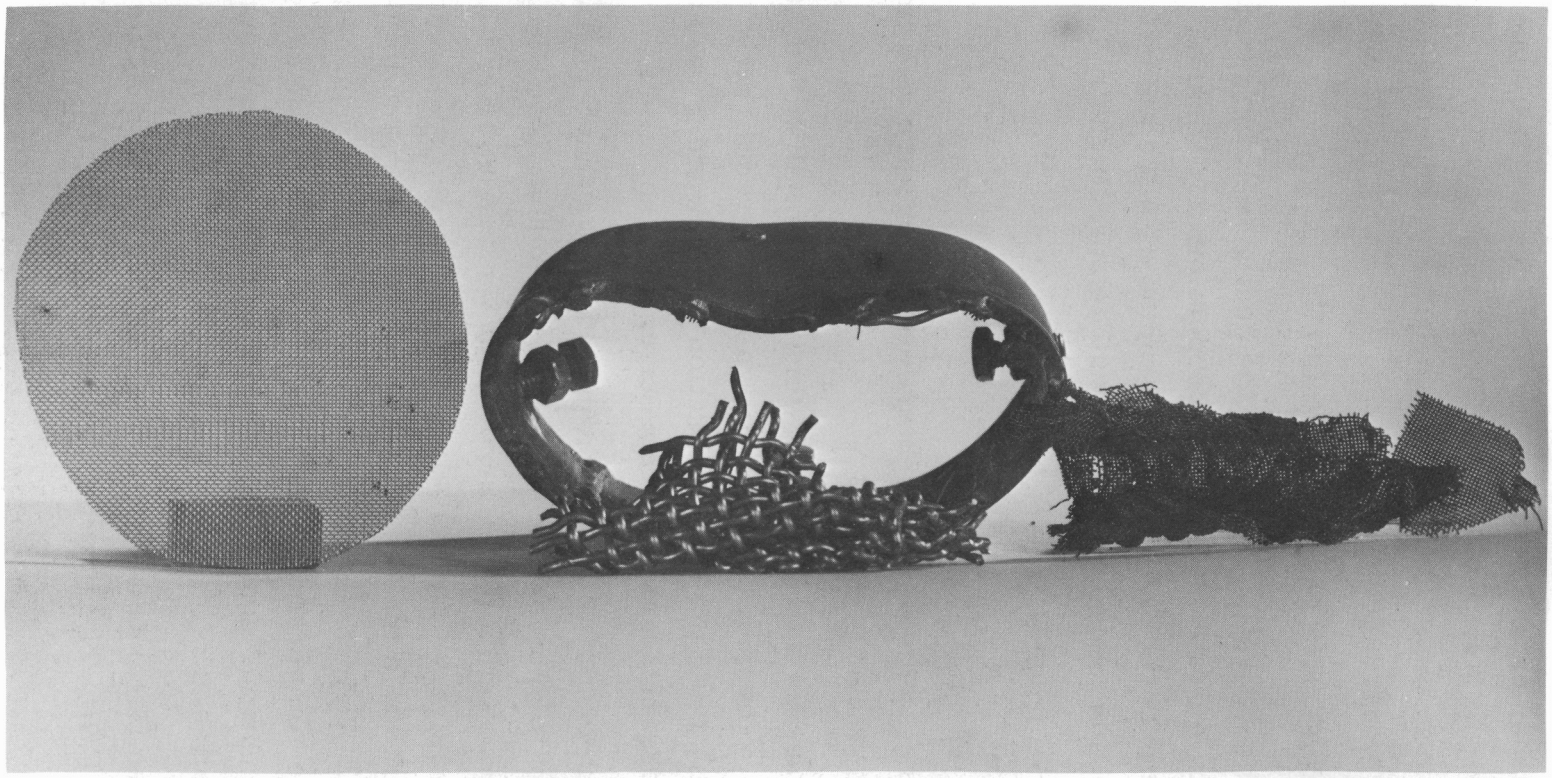


FIGURE 6
Damaged Hold-Down Screen After Test 11 Disk Rupture

container dimensions and reaction kinetics, for a static, packed heat-generating bed, is given in Appendix A. It was initially assumed that the heat generation in the resin could be adequately described by the zero order Arrhenius rate expression:

$$Q = Q_1 \exp(-\Delta E/RT) \text{ cal}/(\text{cm}^3)(\text{min}) \qquad (1)$$

where AE is the activation energy of the heat generating reaction and Q_1 is an experimentally determined proportionality constant. The derived expression defines the critical vessel radius as a function of the thermal conductivity of the resin bed (k), the wall temperature (T_w) and the reaction kinetics.

$$a^2 = 2 \frac{k}{Q} \cdot \frac{R}{\Delta E} T_w^2 \exp(\Delta E/RT_w) \qquad (2)$$

A related expression gives the centerline temperature as a function of subcritical wall temperatures.

The unknown data constants were found for these equations in several ways. Thermal conductivity was measured directly.[3] The activation energy and the heat generation factor were calculated from the vessel pressurization test recorder charts, as follows:

A graph of $\log_e (dT/d\theta)$ versus $1/T$ shows that a portion of the curve is linear for points corresponding to the knee (see Figure 3) of the vessel centerline temperature record. It was assumed and later verified by computer analysis that this portion of the curve represented an adiabatic condition in the resin zone immediately around the sensing thermocouple. Therefore, if neglibible reactant is consumed during this time, the time-temperature record is a true exponential curve and the zero order Arrhenius equation assumed in the critical temperature theory derivation applies.

The semilogarithmic plot of the data is a straight line and the slope is equal to $-AE/R$. The intercept is $(\log_e Q_1 - \log_e C_{Bulk})$,

$$Q = \frac{AT}{\Delta\theta} \qquad C_{Bulk} = Q_1 \exp(-AE/RT) \qquad (3)$$

$$\log_e \frac{\Delta T}{\Delta \theta} = -\frac{\Delta E}{R}\left(\frac{1}{T}\right) + \log_e Q_1 - \log_e C_{Bulk} \tag{4}$$

Several recorder charts were analyzed in this way and the activation energy and heat generation factor were calculated from them.

Estimating the critical radius with finite heat transfer coefficients is more complicated than Equation (2) and must be done by trial and error.[5] (Also see Appendix A). Consequently, a computer program (PROFIT) was written to calculate the critical ambient temperature as a function of vessel radius. Figure 7 presents the boundary of unsafe conditions for static beds of this resin as a function of bed radius, ambient temperature, and contactor wall heat transfer coefficient.

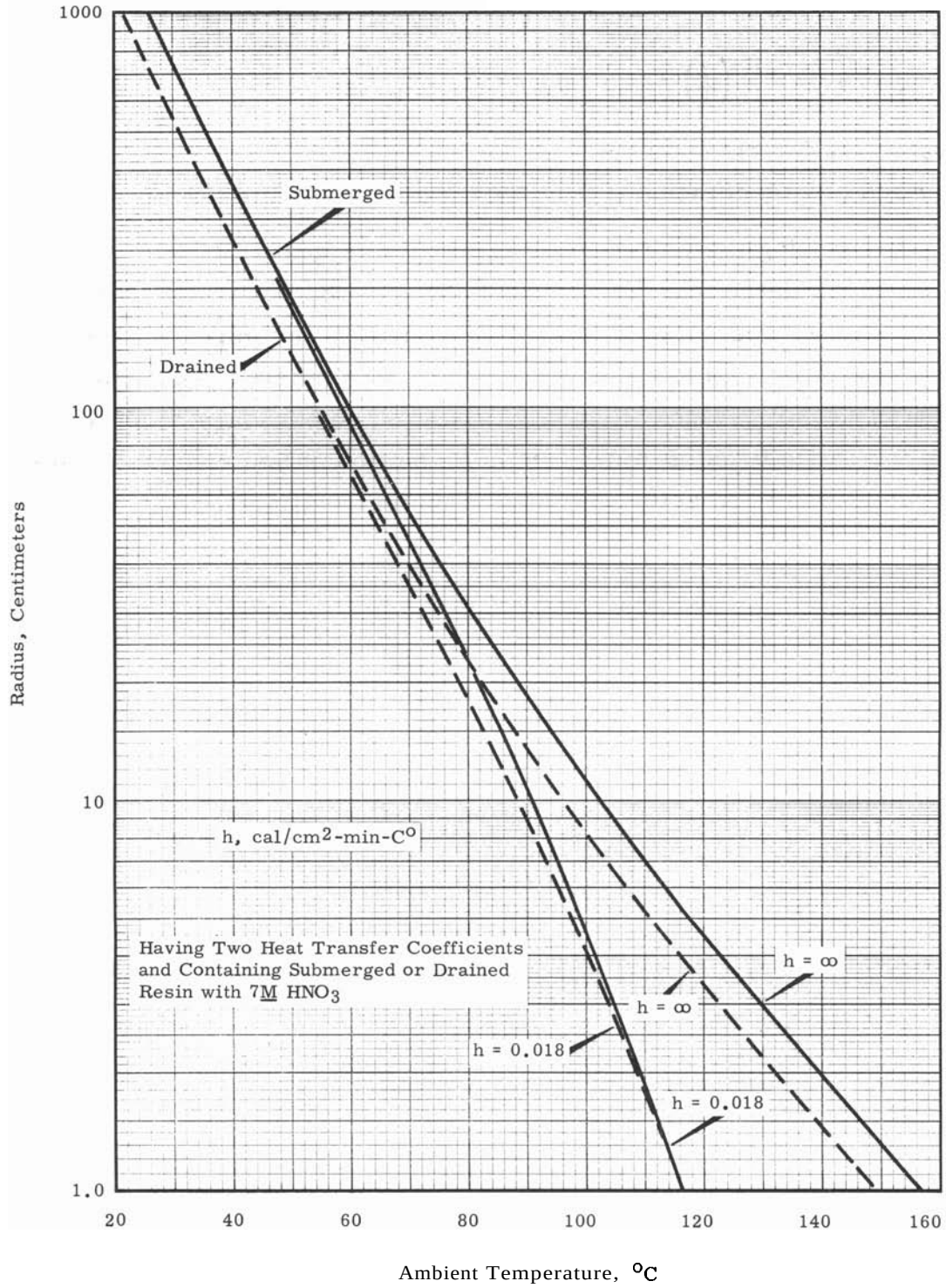


FIGURE 7

Critical Radius as a Function of Ambient Temperature for Two Wall Heat Transfer Coefficients Vessels Containing Submerged or Drained Resin with 7M HNO_3

The transient case must also be solved by machine calculation if it is desired to account for reactant consumed. A FORTRAN II computer program supplied by G. S. Nichols of Savannah River Laboratories (') (see Appendix B) was used to predict the time-temperature behavior of cylindrical and spherical resin beds of nitrate-form Permutit SK resin. The program verified the calculated values of the experimental data by duplicating the behavior observed in the pipe test up to temperatures just prior to disk rupture. At these temperatures, fast production of gases caused convective heat transfer inside the pipe, a behavior not considered in formulating the computer program. Since these actual effects increased the effective heat transfer rates in the pipe, the computer predicted slightly faster temperature rise rates and shorter time to initiation than were actually observed just before disk rupture.

The temperature profiles of Figure 8 show how the critical ambient temperature depends on the vessel wall heat transfer coefficient. The curves are for a 4-in.-diam vessel with settled resin in stagnant 7M HNO_3. Each curve is also a subcritical temperature profile of the vessel with a higher heat transfer coefficient. With a heat transfer coefficient of 0.02 cal/(cm^2)(^{o}C)(min), which is typical of uninsulated vessels, the critical ambient temperature is 99.5 ^{o}C with a wall temperature of 108 ^{o}C and a centerline temperature of 110 ^{o}C. If the heat transfer coefficient is made very high, the critical ambient temperature increases to 116.5 ^{o}C with a wall temperature of 116.5 ^{o}C and a centerline temperature of 131 ^{o}C.

Figure 9 shows the computer-calculated time to initiation versus vessel surface wall temperature for two types of 4-in.-diam packed beds, starting from 60 ^{o}C initial bed temperature. The vertical asymptotes for these curves correspond to the critical temperatures for a 4-in.-diam bed predicted in Figure 7. The interaction of resin bed thermal conductivity and wall heat transfer coefficient is relatively complex. Figure 10 illustrates the radial temperature profiles calculated for several elapsed times after applying a 130 ^{o}C wall temperature to the 60 ^{o}C bed. This situation might be caused by an external fire. The initial slow temperature buildup which gradually accelerates to a very rapid rate near the bed centerline is quite evident,

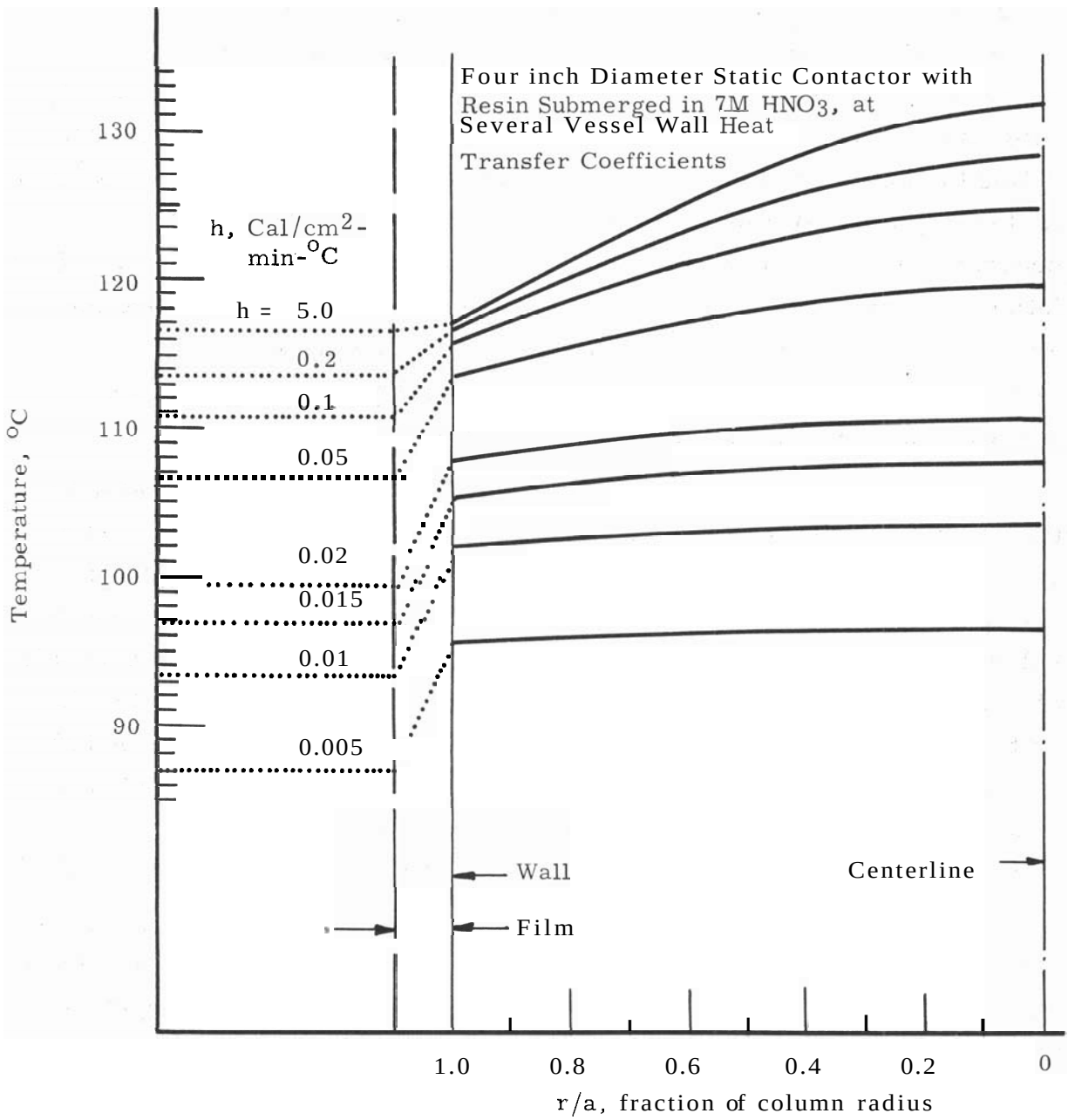


FIGURE 8

Critical Temperature Profiles

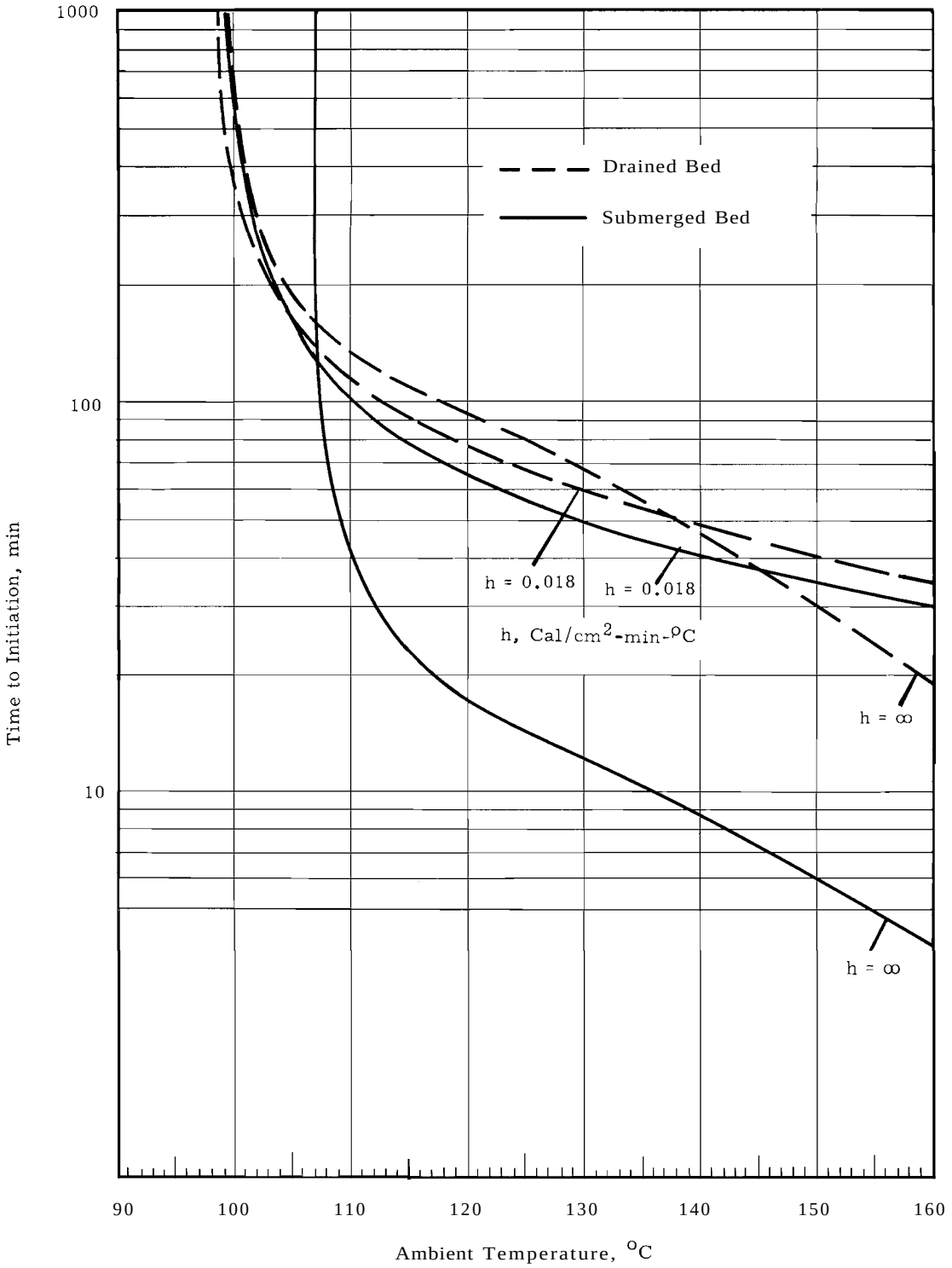


FIGURE 9

Time to Initiation Versus Ambient Temperature for 4-in.-diam Packed Beds of Permutit SK in 7M HNO_3

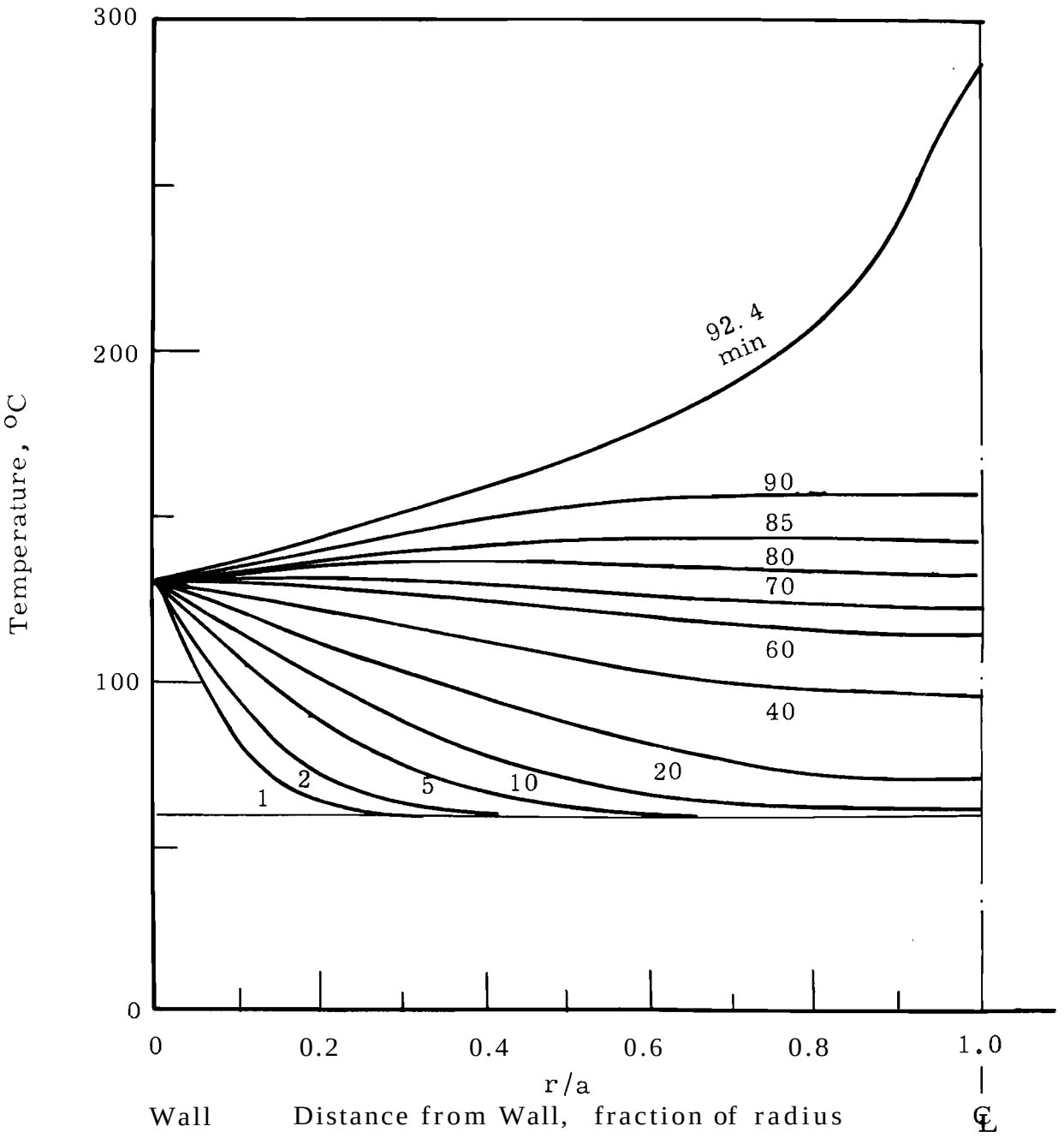


FIGURE 10

Radial Temperature Profiles at Several Elapsed Times for a 4-in.-diam Drained Resin Bed in Response to a Step Wall Temperature Change from 60 to 130 °C

DYNAMIC SYSTEMS

Simulated Contactor Tests

This series of experiments was conducted to learn how a packed bed with liquid flow could produce temperatures of 120 to 130 °C, leading to still higher temperatures and self pressurization.

Although heat effects known to accompany ion exchange processes are usually small,[7] it has been predicted that the peak temperature of a moving temperature front can increase indefinitely.[8] The subject has also been discussed[9, 10, 11] in more detail for burning carbon in solid catalyst bed regeneration. An improper choice of flowrate and gas stream oxygen concentration can cause high bed temperatures within relatively short bed lengths.

Experiments were done in a 6 ft long by 4-in.-diam Pyrex glass contactor equipped with inlet, outlet, and five equally spaced centerline thermocouples. Several experiments were performed to explore the possibility of any heating effect in the resin filled contactor. Figure 11 illustrates the centerline temperature profiles generated by the first of the experiments.

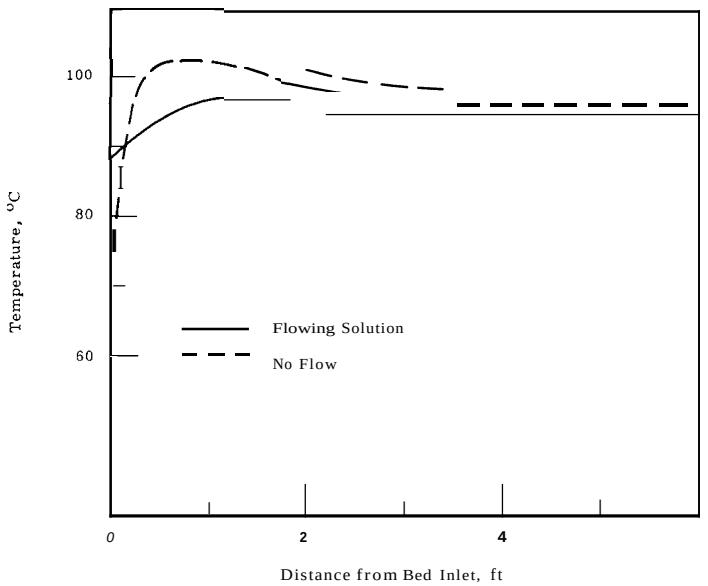


FIGURE 11

Temperature-Length Profiles for Flow Experiment 1

The inlet liquid was 7M nitric acid containing 1.7 g/liter of sodium dichromate at 0.91 liter/min and 55 °C. The curves of Figure 11 represent the temperature-length relationship at 29 min after flow started, and after the flow had been stopped for 5 min. The chromium-loaded bed was then drained, cooled, vented, and remained undisturbed overnight. The reddish-brown of the chromium-loaded stagnant bed was almost entirely changed to the intense blue color of Cr^{+3} within the next 24 hr in a frontal reaction which moved from the bottom outlet end of the test section upwards in a continually lengthening blue zone. The higher heat generation rate at the thermocouple located one foot down the bed, where chromium loading was relatively high, was evident 5 min after stopping flow.

The second and third experiments were similar to the first except that in the third, the dichromate feed was continued longer. The upper 6 to 10 in. of resin bed became so degraded and softened that the pressure drop across the column increased, and throughput dropped drastically, ending the test. Washing the resin revealed that the degraded zone was colorless and translucent in contrast to the normal opaque brown appearance of the resin. The beads had swelled to several times their normal size. Large quantities of gas were evolved in all three of these tests, both NO_2 and sometimes a clear gas alone.

Although some self heating and excessive gassing were observed in these tests, the effects were relatively mild. The fourth experiment, however, demonstrated a possibility of bridging the gap between the 87 °C Redox contactor XAF inlet temperature and the higher temperatures needed to cause a self-sustaining exothermic reaction. The instrumented 6 ft resin bed was partially loaded with chromium from a 1.8 grams-chromium(VI) per liter, room temperature 7M HNO_3 solution at 0.87 liter/min and 22 °C. After 160 liters of the solution passed through the bed, the feed was changed to 7M HNO_3 at 1.1 liter/min and 80 °C. Figure 12 illustrates the magnitude of the heating effect soon after hot acid flow started. It is evident that critical temperatures (for the unloaded resin, about 150 °C and higher) could have been reached if only a few more feet of Cr(VI) loaded resin bed had been present.

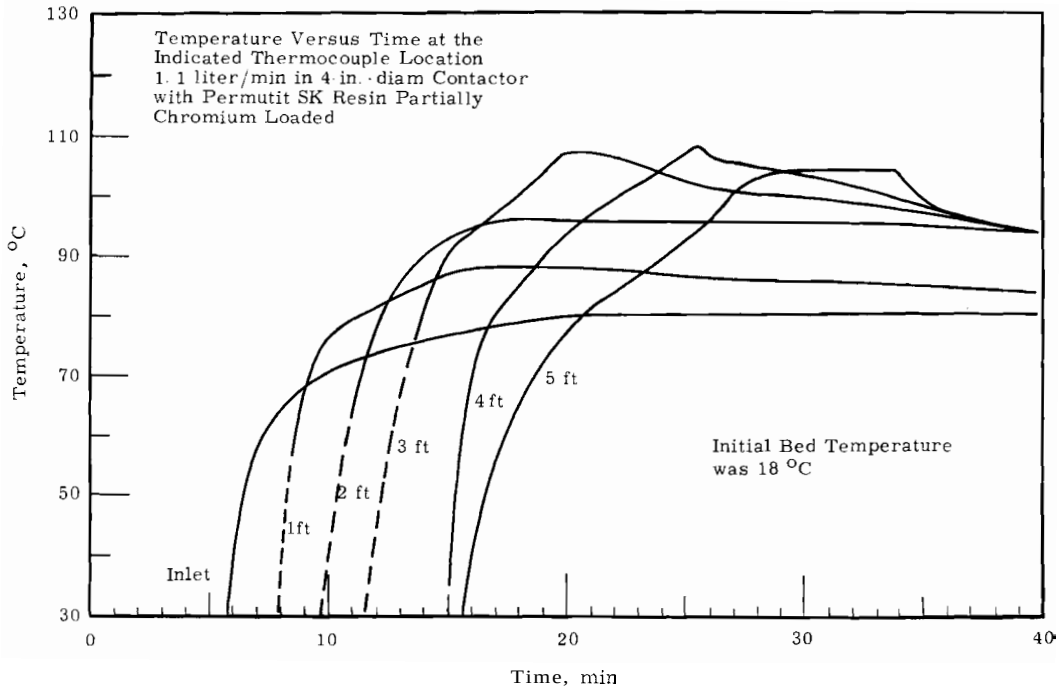


FIGURE 12

Temperature Behavior in Flow Experiment 4

These experiments demonstrated how dichromate ion in nitric acid solution could be hazardous, but gave no means for predicting the heating effects. A quantitative estimate for reaction constants of the resin-nitric acid-dichromate reaction was provided by a subsequent series of calorimeter measurements.

The fifth experiment was conducted to investigate the heat effect resulting from conversion of chloride to nitrate form resin with 0.75M acid. The temperature peaking effect was the result of the rather small nitration heat effect being intensified by the flow rate and heat capacities combination of the resin and liquid. (Figure 13). The effect demonstrated in this experiment might cause an unexpected incident during a routine anion exchange contactor operation.

Calorimeter Measurements

The stirred calorimeter in Figure 14 was used to make the tests. The measurements are referred to the settled volume of nitrate form resin in equilibrium with 7M HNO_3.

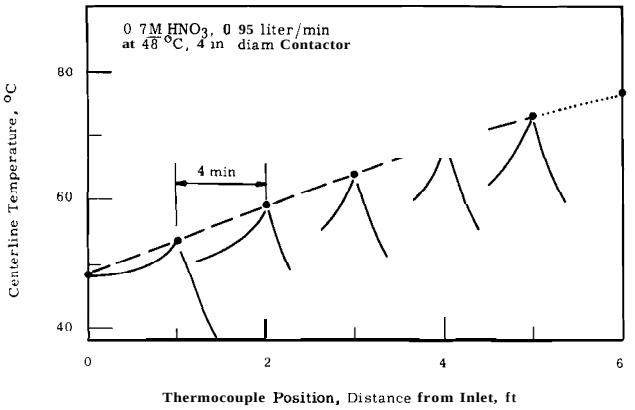


FIGURE 13

Peak Temperature Versus Bed Length During Nitration of Chloride Form Permutit SK Resin, 0.7M HNO_3, 0.95 liter/min, 48 °C, 4-in.-diam Contactor.

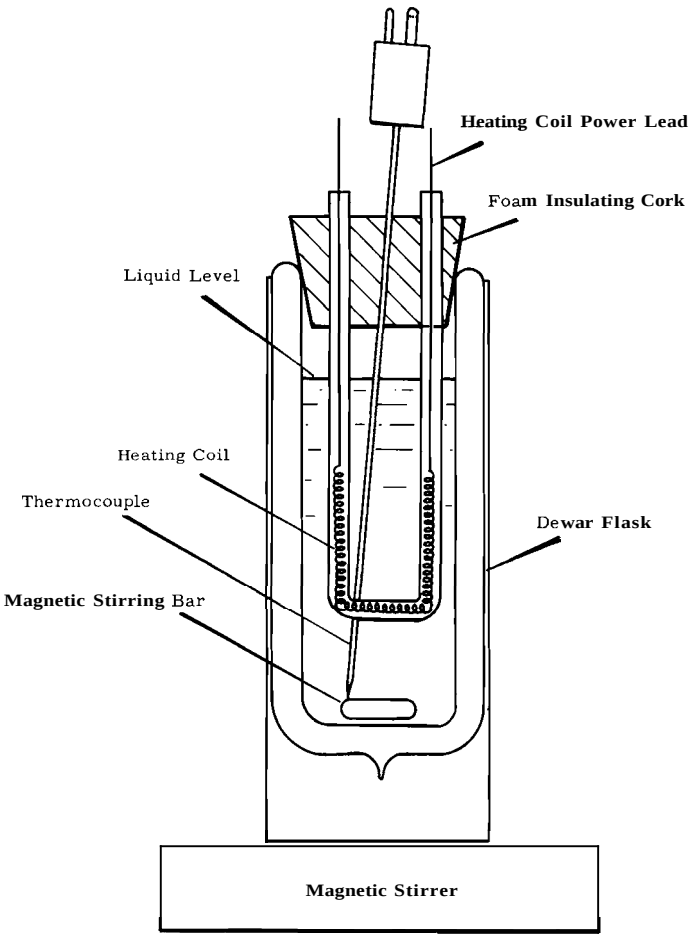


FIGURE 14

Stirred Calorimeter

A measured volume of resin was treated with 7M HNO_3, 1M $Na_2Cr_2O_7$, for predetermined time periods to achieve the desired range of resin loadings. Premature reaction of the resin and dichromate ion was prevented by loading at 0 °C.

The calorimeter heat loss was measured over the experimental temperature range before adding the loaded resin and was assumed to obey the same temperature relationship during the rest of the experiment.

After calorimeter calibration, the loaded resin was rapidly drained and washed several times with room temperature 7M HNO_2, drained well, and added to the calorimeter. The heat generation in the calorimeter was observed for 20 to 40 min, and then the total calorimeter heat capacity was measured by adding heat energy for a measured time at a known rate via the heating coil. Power to the precisely known resistance of the heating coil was supplied from a stable dc power supply. The resulting temperature change was recorded and corrected, for heat loss and continued heat generation by the resin, to give total heat capacity in calories per Kelvin degree. HNO_3

The heat generation rate, in gram-calories per cubic centimeters per minute, for the resin was calculated from the calorimeter total heat capacity and the initial rate of temperature increase when the resin was added to the hot acid in the calorimeter.

$$Q = \frac{\Delta T}{\Delta \theta} \cdot C_t \cdot \frac{1}{V_R} \quad \text{cal/(cm}^3\text{)(min)} \qquad (5)$$

where C_t is the total heat capacity, and V_R is the initial resin volume. The amount of chromium initially loaded on the resin was determined by combining the chromium in the supernatant acid solution in the calorimeter and the chromium eluted from the resin after the experiment. The combined solution was concentrated and the chromium reduced completely to Cr(III) by sugar. This solution was compared spectrophotometrically to a standard Cr(III) solution to give the concentration of the unknown chromium solution, and the initial Cr(VI) concentration of the resin tested in the calorimeter.

The graph of the data for these experiments with Permutit SK is presented in Figure 15, $\log_e \frac{Q}{[Cr]}$ versus 1/T. The slope and intercept of this curve give values of the Arrhenius equation constants for the resin-dichromate-acid reaction:

$$Q_2 = [Cr(VI)] \times (3.05 \times 10^9)\ cal/(cm^3)(min)$$

$$\Delta E/R = 6.2 \times 10^3\ (^oK)^{-1}$$

The Cr(VI) concentration is in grams per cubic centimeter of resin. The total heat available from the reaction was estimated from the calorimeter data and measured $Cr^{(VI)}$ concentrations to be:

$$\Delta H \sim 400\ [Cr^{(VI)}]\ cal/cm^3 \text{ of resin.}$$

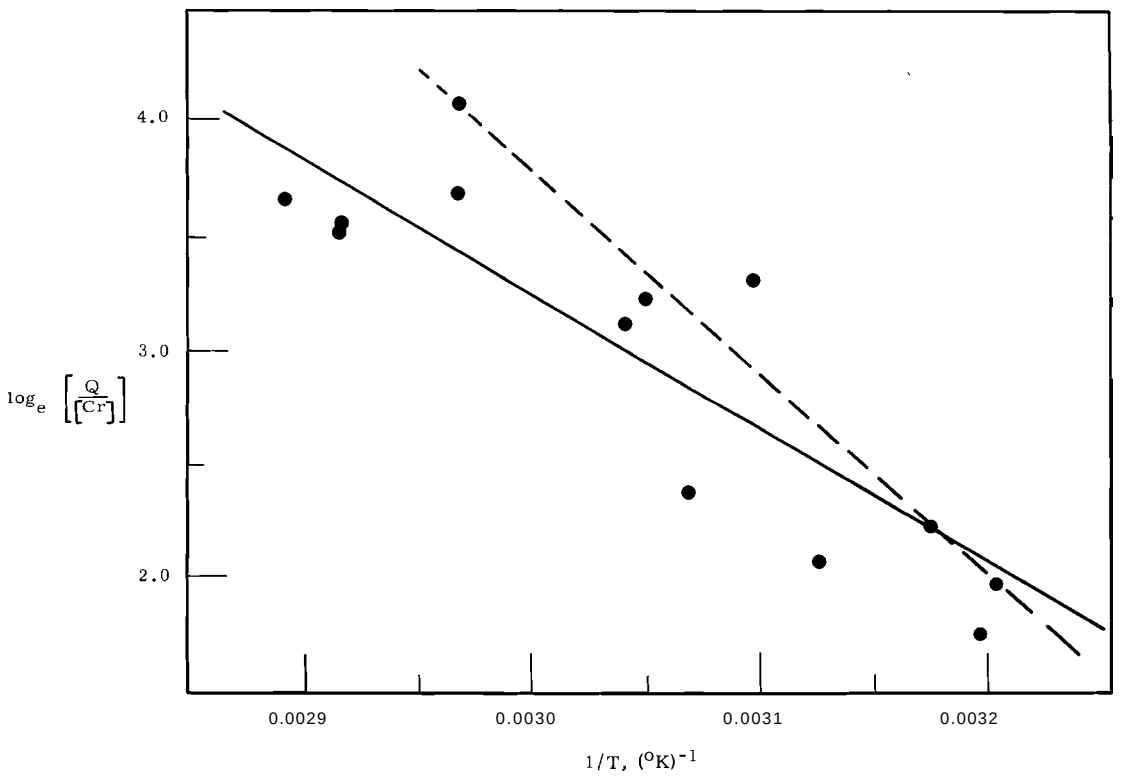


FIGURE 15

Calorimeter Data, $\log_e [Q/(Cr)]$ Versus 1/T

The calorimeter precision has been estimated to be ± 10% for the magnitude of resin heat generation rates. The calorimeter data actually shows a precision of about ± 30%, and the discrepancy between this

precision and that calculated for the calorimeter is caused by test-to-test variation in the chemical composition of the loaded resin. An activation energy and heat generation factor were also calculated for the upper limit of the data (the dotted line in Figure 15). These conservatively higher values of $Q_2 = [Cr(VI)](9.77 \times 10^{12})$ and $\Delta E/R = 8.721 \times 10^3$ were used in all the calculations presented. The comparison between the heat generation rate for dichromate loaded and unloaded Permutit SK resin is illustrated in Figure 16. At 100 °C, the heat generation rate for resin loaded with 0.1 gram Cr(VI) per cubic centimeter of settled resin is 2700 times the rate for unloaded resin.

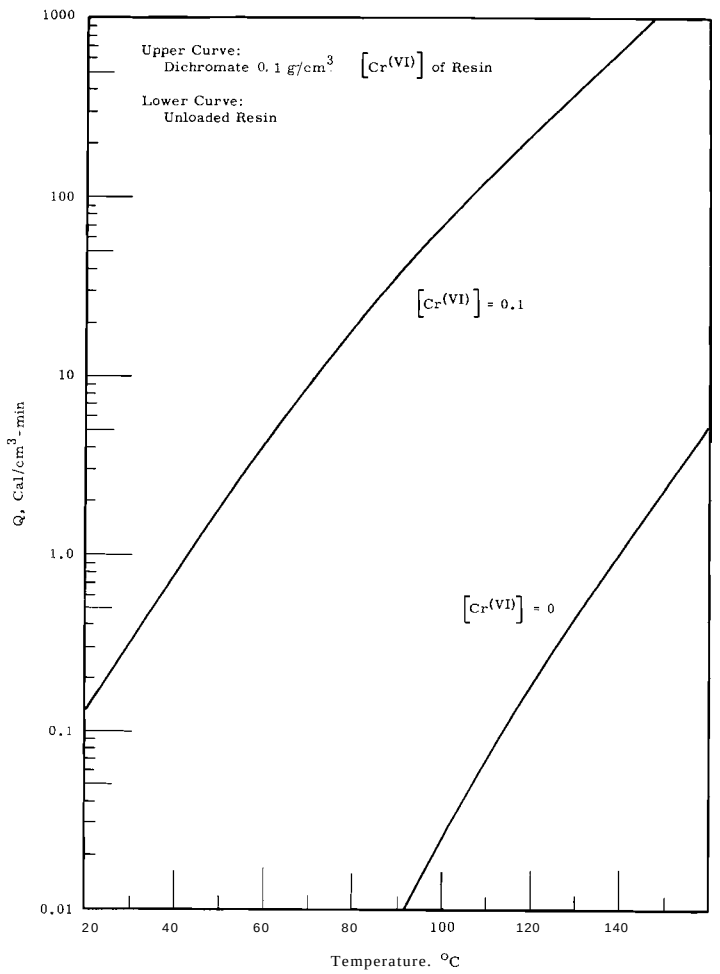


FIGURE 16

Heat Generation Rates in 7M HNO_3 and Dichromate as a Function of Temperature

Theoretical Correlations

The reaction kinetics for the resin-acid-dichromate system have been characterized, and the exact relation for time, temperature, dimensions, flowrate, and physical properties for the contents of an operating anion exchange contactor can also be calculated. Two different computer programs were written to predict the behavior of operating contactors with the assumption that temperatures are uniform across the column cross section.

HOTBED (see Appendix B)[12] performs a complete heat and mass balance over an entire contactor section repetitively in time, to duplicate its time-temperature-space behavior. The program accounts for the reactants available in three first order Arrhenius-type reactions, calculating the effect of chemical heating, contactor wall heat transfer, radioactive heating, and liquid heat transfer.

A second program, G-J BED, integrates a derived expression (see Appendix A) for the liquid holdup time in a contactor with countercurrent liquid and solid flow and steady state temperatures

$$\theta = \frac{X}{L} = \left(C_L - \frac{R' C_R}{L}\right) \int_{T_1}^{T_2} \frac{dT}{Q_{NET}} \qquad (6)$$

For a given liquid flowrate L (cm^3/sec), and inlet liquid temperature T_1, the bed length X which gives a liquid outlet temperature T_2 can be determined as a function of the specific heats C_R and C_L of the resin, the liquid resin to liquid flow ratio R'/L, and Q_{NET} the net heat gain of the flowing streams per unit volume per unit time proceeding along the column from the liquid inlet. Internal heat generation by chemical reactions and radiolytic heating and heat losses to the surroundings may be included in Q_{NET}, and the case of a stationary packed bed with liquid flowing through it may be analyzed by setting the ratio of the solid to liquid flowrate to zero.

Temperature T_2 is found by the program at the point of rapid reaction by testing for convergence to zero of the term inside the integral of Equation (6).

Since the G-J BED Program assumes zero order reaction kinetics (no reactant consumed), its results will always predict a shorter time to contactor pressurization although agreement between the two computations is usually excellent. In some borderline cases, however, G-J BED will predict an instability which cannot actually occur because of insufficient reactant availability. Figure 17 presents the dependence of critical holdup time upon inlet temperature for a resin bed in contact with 7M HNO_3. Figure 18 shows how the temperature peak develops in time and distance for a typical case calculated by the HOTBED Program.

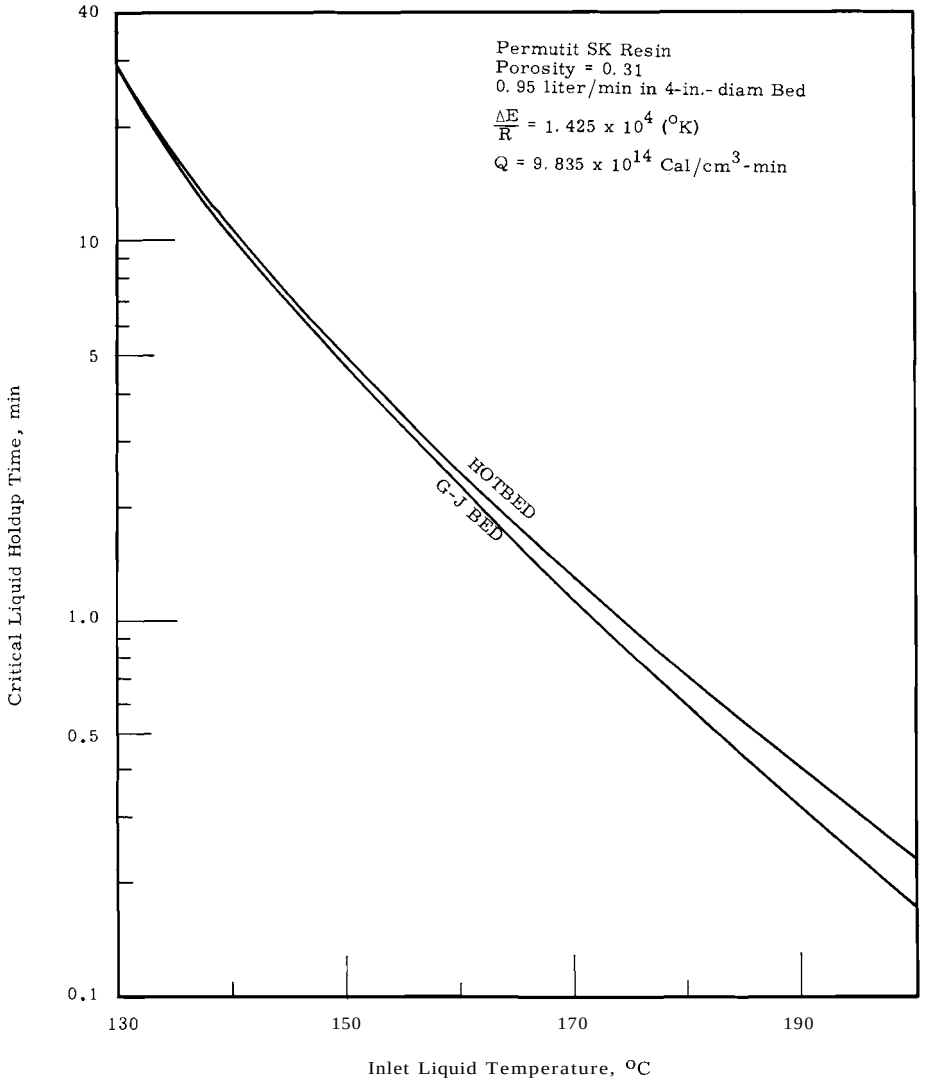


FIGURE 17

Holdup Time for Resin Instability in 7M HNO_3. Comparison of Two Computer Programs

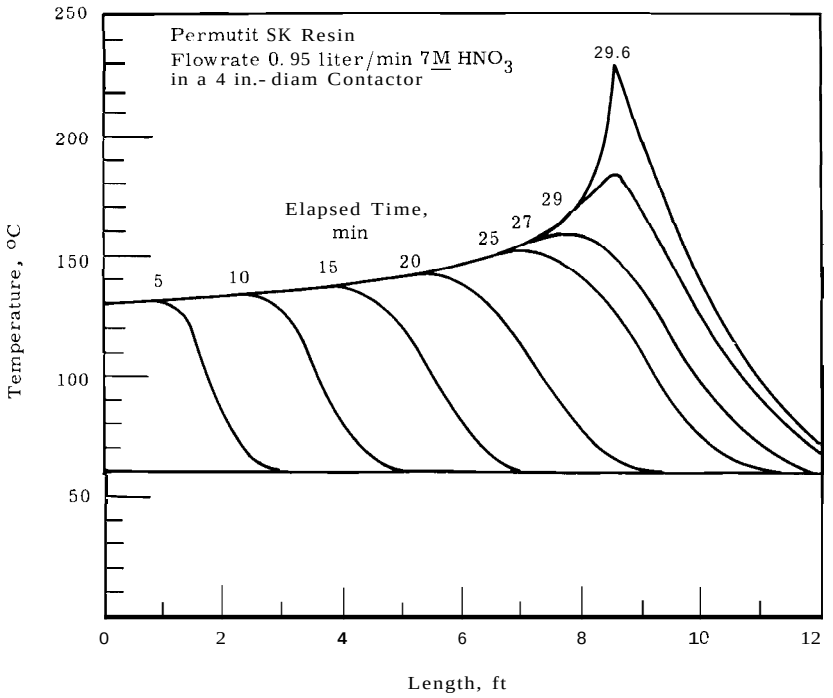


FIGURE 18

Calculated Temperature Length Profiles at Several Elapsed Times in a Flow System

For a bed initially at 60 °C with an inlet liquid flowrate of 0.95 liter/min at 130 °C inlet temperature, the critical conditions for a self-accelerating reaction occur at a bed length of 8.5 ft about 30 min after the liquid has been introduced. Figure 19 gives the G-J BED computer-calculated critical holdup times as a function of inlet temperature for unloaded resin in a 4-in.-diam contactor. The influence of heat losses to the surroundings by convection in increasing the critical holdup time is most strongly felt at low temperatures with low internal heat generation rates. In addition, the G-J BED program may be used to derive similar curves for other contactor diameters and conditions. For example, Figure 20 illustrates the relation between critical holdup time and liquid inlet temperature with curves of constant Cr(VI) loading for an experimentally determined value of $h = 0.018$ cal/cm^2-°C-min.

The effect of several hypothetical levels of radiolytic heating are shown by Figure 21 for a 4-in. contactor with no Cr(VI) content and the same heat transfer coefficient used in Figure 20.

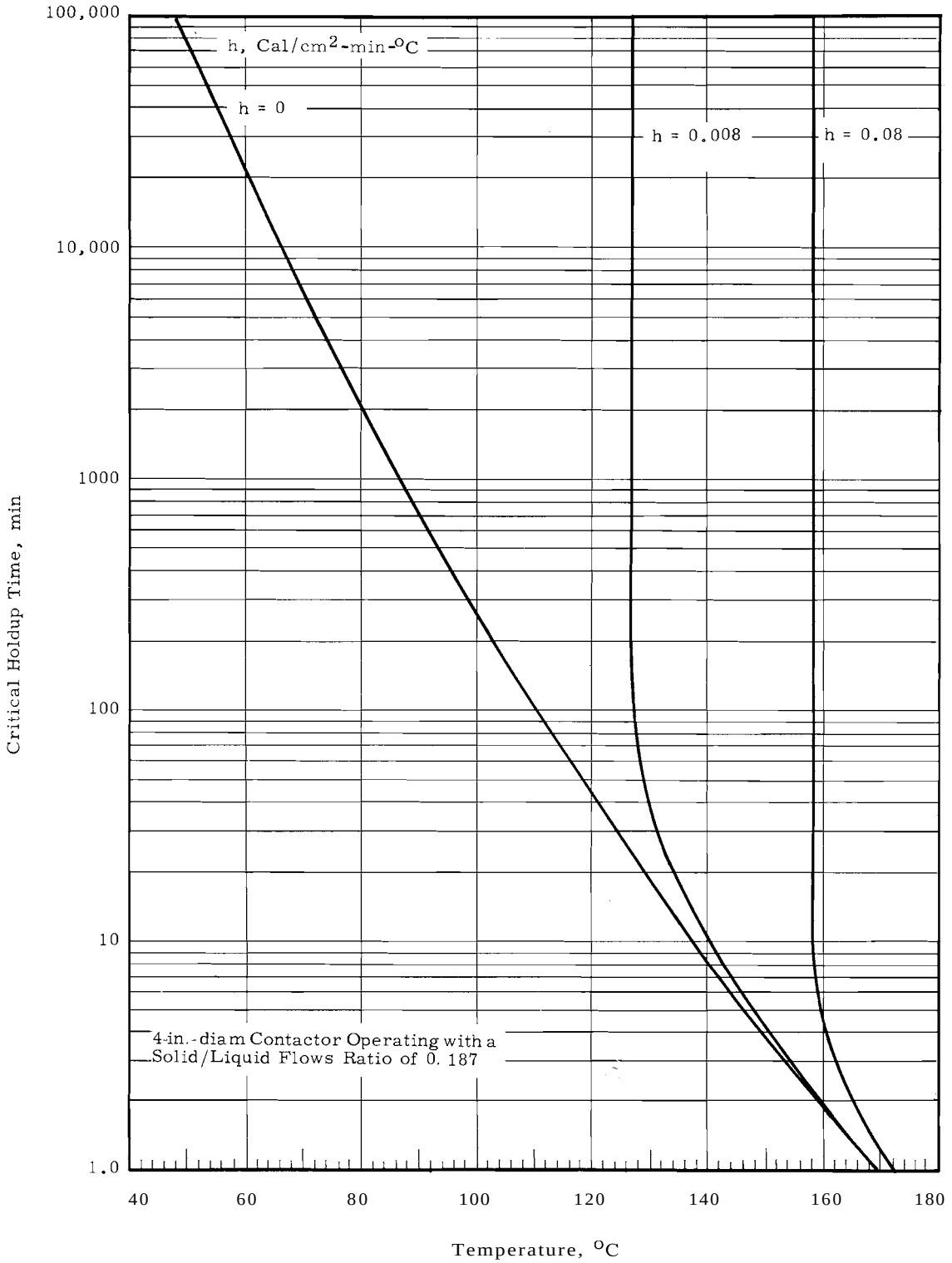


FIGURE 19

Critical Holdup Time as a Function of Inlet Temperature and Contactor Wall Heat Transfer Coefficient

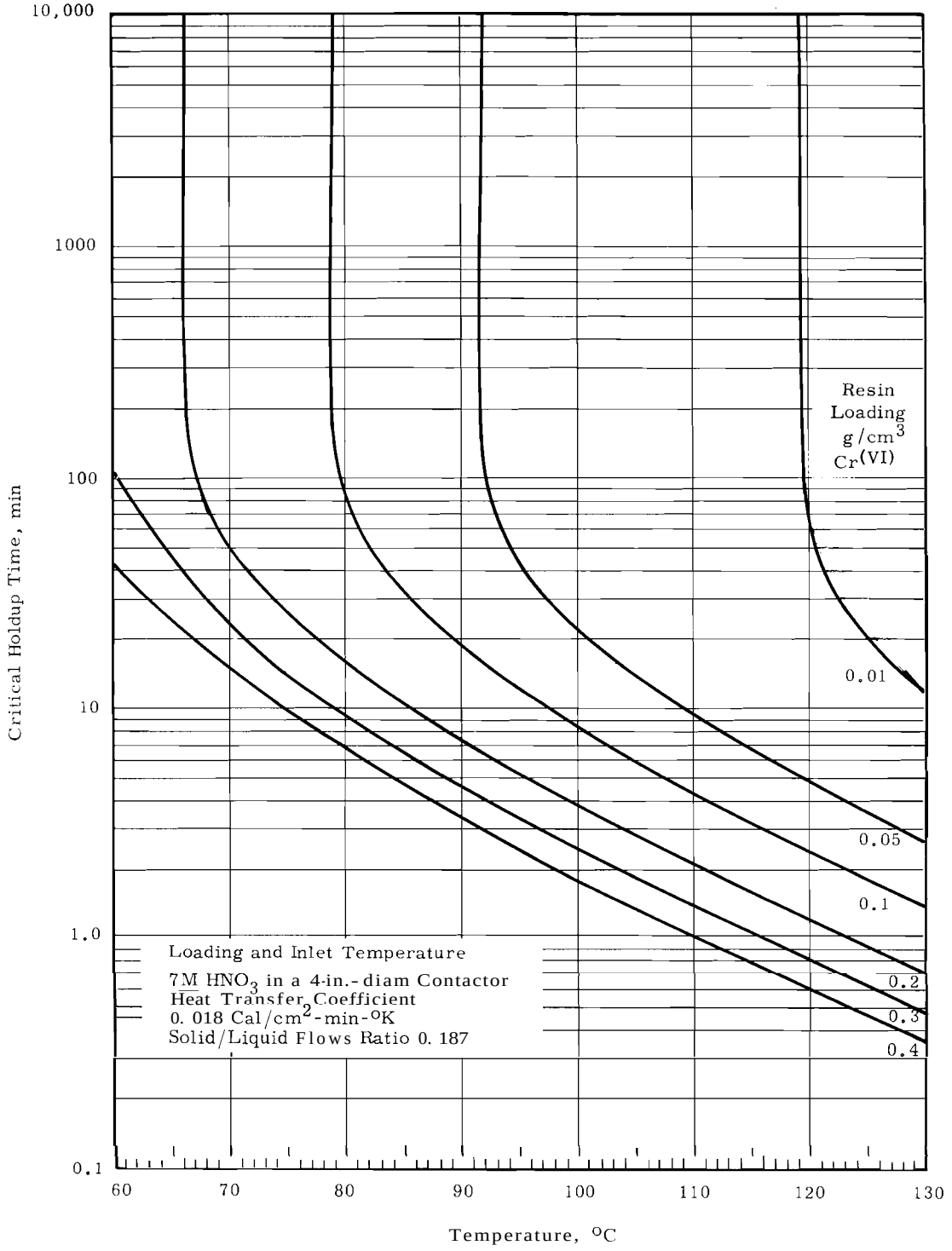


FIGURE 20

Critical Holdup Time as a Function of Resin Chromium (VI) Loading and Inlet Temperature

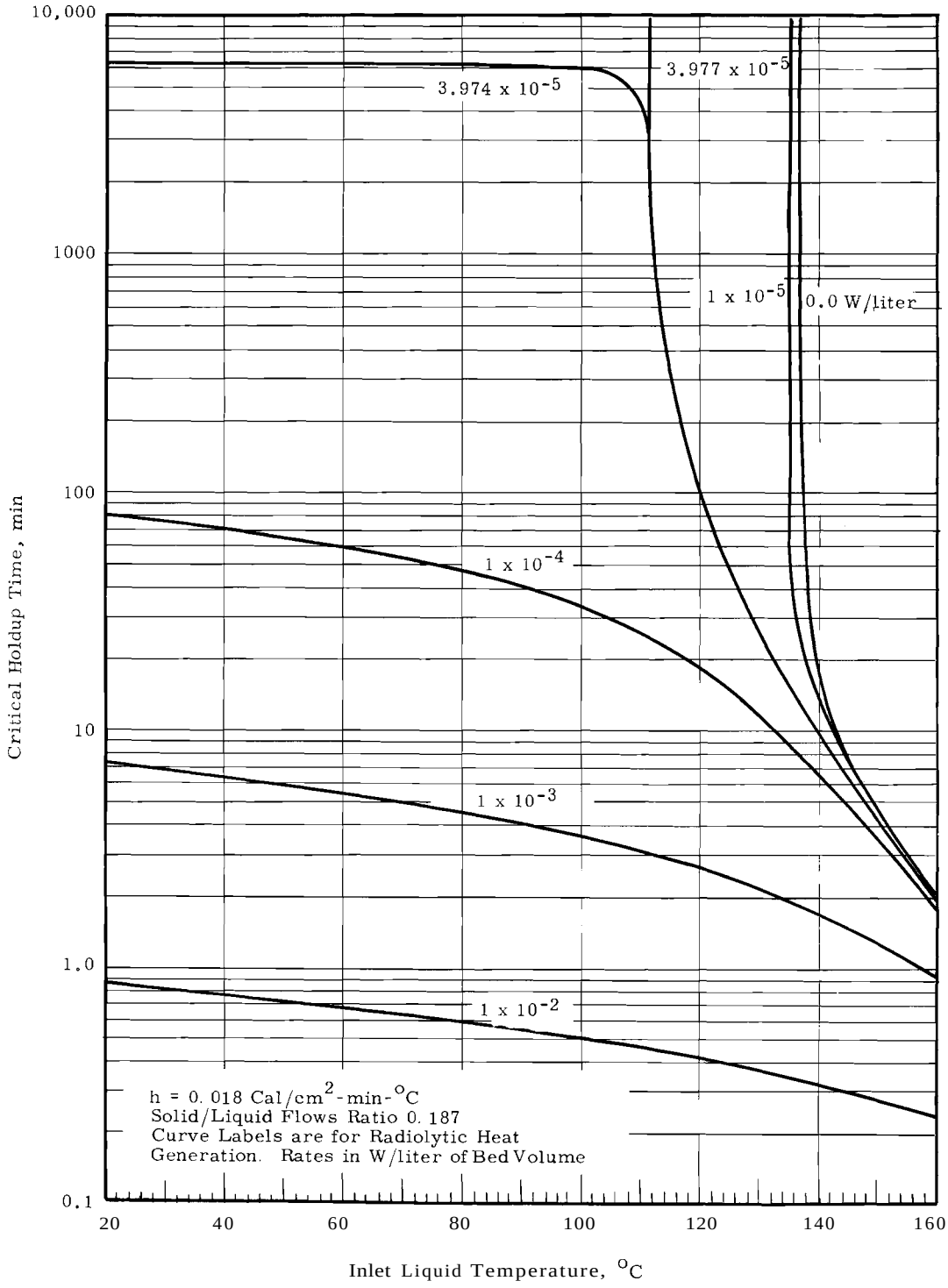


FIGURE 21

Effect of Radiolytic Heating
on Contactor Operating Stability

DISCUSSION AND RECOMMENDATIONS

Discussion of the Hanford Incident

The high internal pressures created in the 233-S L-18 contactor[1] were undoubtedly caused by a runaway exothermic gas producing reaction. The reaction must have been forced into an unstable state by either an external heat source or an abnormal exothermic chemical reaction in the resin bed.

If the incident was triggered by an external heat source, Figure 9 (solid curves) may be used to estimate the duration range of heating times at an assumed ambient temperature required to have caused the pressurization. The event could have been produced by an ambient temperature of 110 ^{o}C for 40 to 100 min or by an ambient temperature of 130 ^{o}C for only 12 to 50 min. These temperaturescould easily have been reached by a small fire within an enclosed hood.

Most of the evidence suggested that the contactor pressurization preceded the fire, and that an internal reaction caused the pressurization. This reasoning is supported by the presence of dichromate ion in the contactor feed. Conversely, it is improbable that an accidental fire would occur simultaneously with the accidental introduction of a strong oxidizing chemical like dichromate ion.

Figure **20** shows that average dichromate loadings, as chromium, on the resin would have to reach at least 0.05 g/cm^3 at inlet temperatures in excess of 92 ^{o}C to cause a runaway reaction. However, at a chromium concentration of 0.**3** g/cm^3. initiation would occur at 23 min liquid holdup time with a 70 ^{o}C inlet temperature. Holdup times prior to the incident in the L-18 contactor scrub section were about 22 min, and about 11 min in the feed (extraction) section. That chromium concentration would cause pressurization at about 5.2 rnin with the recorded 87 ^{o}C feed inlet temperature. Resin analyses following the Redox incident indicated spot chromium concentration reached at least **0.33** g/cm^3.

The presence of plutonium on the resin may have further lowered the critical operating temperature. This factor (not studied here) has been investigated by Fullam[22] with dried resin.

Safety Precautions

The mathematical analyses and supporting machine computational aids developed here allow rapid, accurate evaluation of the thermal hazards associated with first or zero order exponentially temperature dependent reactions in ion exchange systems. The analysis may be applied to storage containers containing resin, idle beds under static conditions, packed beds with flowing liquid, and operating countercurrent contactors. The data required for the analysis can be obtained by relatively easy and straightforward experiments.

High contactor wall heat transfer coefficients are desirable, as Figure 19 emphasizes, but each case should be analyzed separately since under some conditions, the resistance to heat transfer inside the resin is enough to produce dangerously high temperatures. A water-jacketed contactor (high wall heat transfer rate) may be helpful in some applications where large diameters and moderately elevated temperatures are necessary. A well-designed water jacket will also guarantee closer process temperature control than is realized in present contactors. At the other extreme, perfectly insulated, stagnant contactors are inherently unsafe, pressurizing eventually at some finite storage time if the reactant is not used up.

Strong oxidizing agents or oxidation catalysts should be avoided in organic ion exchange resin applications. Dichromate ion, in particular, even at low temperatures, rapidly degrades organic resins with the evolution of heat. Although the heat generation rate in strong HNO_3 alone is much less than for dichromate at comparable temperatures, the storage of resin in strong HNO_3 should be avoided wherever possible. The storage of the resin in water or dilute HNO_3 is preferred. Conversion of nitrate-form resins to safe forms (such as the chloride-form) before storage would lessen the hazards if high temperatures should occur because of external heating. Storage containers and idle contactors should have their contents vented and the resin covered with solution.

The runaway reaction in moist resin can be instantly quenched by venting the container or contactor at relatively low pressures (200 psig or less). Evaporation provides the cooling and quenching effect if the resin is moist. Pressure relief valves set at lower pressures (e.g., 50 psig) would safely replace the rupture disk used in the tests reported here.

Dry nitrate-form resin is inflammable and potentially explosive, and reaction quenching of dry resin cannot be achieved by pressure relief.

Gas accumulations in operating contactor resin beds have little effect on operating safety. Large discrete gas pockets are short lived in operating contactors, and small bubble accumulations in processing resin beds do not significantly change the safe operating limits. Even large discrete gas pockets could not affect the thermal conductivity of the bed enough to cause a self-accelerating reaction unless the contactor was already operating dangerously near the critical conditions. Figure 7 shows that the critical ambient temperature (heat transfer coefficient, h = 0.018) for a stagnant 4-in.-diam (5.08 cm radius) vessel containing the resin is lowered less than 2 C^{o} by draining the interstitial acid from the resin. The difference in critical ambient temperatures caused by changing the external heat transfer coefficient from infinity to a typical value, 0.018, is 13 to 18 C^{o}, however. Gas accumulations should be avoided, not because of thermal effects, but because they can produce channeling of the process streams through the packed bed with resultant lowered operating efficiency and product purity.

NOMENCLATURE

a	Vessel radius, cm
B_c	A function of a and δ_c defined in Appendix A, Equation (16) dimensionless
C	Specific heat capacity, cal/(cm^3)(°K)
C_{BULK}	Bulk heat capacity, cal/(cm^3)(°K)
C_L	Liquid heat capacity, cal/(cm^3)(°K)
C_R	Resin heat capacity, cal/(cm^3)(°K)
C_T	Total calorimeter heat capacity, cal/°K
ΔE_i	Activation energy for resin decomposition by the ith reaction, cal/gram mole
G	A function of β defined in Appendix A, Equation (8), dimensionless
h	Vessel-to-ambient heat transfer coefficient, cal/(cm^2)(min)(°K)
ΔH	Heat of reaction, cal/gram mole
k	Bulk thermal conductivity of the resin bed, cal/(cm^2)(min)(°K)/(cm)
L	Liquid flow rate, cm^3/min
Q	Volumetric heat generation rate, cal/(cm^3)(min)
Q_w	Volumetric heat generation rate at the wall temperature T_w, cal/(cm^3)(min)
Q_i	Heat generation factor in the Arrhenius equation, defined in Appendix A, Equation (1), cal/(cm^3)(min)
Q_L	Convective heat loss from a resin bed per unit volume of bed, cal/(cm^3)(min)
Q_{NET}	Net heat gain of a resin bed proceeding from the liquid inlet, defined in Appendix A, Equation (20), cal/(min)(cm^3 of resin bed)
Q_s	Volumetric heat generation rate due to radioactive decay, cal/(cm^3)(min)
r	Radial position, cm
R	Gas constant, 1.987 cal/(gram mole)(°K)
R'	Resin flow rate cm^3 of wet settled resin/min
T	Temperature, °C

T_{CL}	Centerline temperature in a cylindrical, self-heating resin bed, °C
T_1	Temperature of liquid entering a resin bed, °C
T_2	Temperature of liquid leaving a resin bed, °C
T_o	Ambient temperature, °C
T_w	Vessel wall temperature, °C
X	Ion exchange contactor bed length, cm
	= ha/k, Nusselt number, dimensionless
	$= \frac{(\Delta E)(a^2)(Q_i)\exp(-\Delta E/RT_w)}{RT_w^2 k}$
β_c	The critical value of β
	$= \frac{(\Delta E)(a^2)(Q_i)\exp(-\Delta E/RT_o)}{RT_w^2 k}$
δ_c	The critical value of 6
	First order rate constant for resin decomposition, per min
κ_o	Proportionality constant in definition of κ, per min
ρ	Resin bulk density, g/cm^3
θ	Time, min

ACKXOWLEDGMEXT

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The authors also appreciate the encouragement and information given by the Chemical Processing Department of the General Electric Company Richland, Washington.

APPENDIX A

DERIVATION OF EQUATIONS

The correlations derived in this section are based on the assumption that a series of simultaneous chemical reactions generate heat at a rate given by

$$Q = Q_1 \exp\left(-\frac{\Delta E_1}{RT}\right) + Q_2 \exp\left(-\frac{\Delta E_2}{RT}\right) + Q_3 \exp\left(-\frac{\Delta E_3}{RT}\right) \text{cal}/(\text{cm}^3)(\text{sec}) \tag{1}$$

where ΔE_i is the activation energy for a reaction, R is the gas constant, and Q_i is a proportionality constant. The heat generation rate Q for a single chemical reaction is related to the chemical reaction rate by $Q = \rho \kappa \Delta H$ where ρ is the density of the resin, ΔH is the heat of reaction, and κ is the first order rate constant for the chemical reaction. In this treatment, it is assumed that a negligible fraction of the resin reacts in generating the heat to attain critical conditions. With this assumption, the rate of heat generation is zero order regardless of the mechanism of the reactions. The form of the temperature dependence of the heat generation rate follows directly from an expression for the reaction rate constant of the form $\kappa = \kappa_o \exp\left(-\frac{\Delta E}{RT}\right)$, which is often encountered in chemical kinetics. If only one resin decomposition reaction is present, the experimental determination of Q at two temperatures will allow the fixing of Q_1 and ΔE_1 for a specific chemical system.

For a system to exhibit a runaway exothermic reaction, heat must be generated internally at a rate greater than it can be transferred away by conduction, convection, or radiation. In 1928. Semenoff[12] considered the case for which the external resistance to heat transfer is controlling and the internal temperature is uniform. In 1939, Frank-Kamenetskii[2] considered a constant wall temperature with the internal thermal conductivity

of the medium controlling the heat transfer to the wall. Semenoff's condition will be used here for flow systems, and Frank-Kamenetskii's will be applied for static systems. Thomas[5] has analyzed the static system with a constant heat transfer coefficient to the surroundings. Others have also analyzed self-accelerating reactions in which a fraction of the reactant is used up,[14-16] but numerical methods are usually necessary to solve the equations, and the results cannot be expressed in concise form.

STATIC SYSTEM

The wall temperature of a long, cylindrical column of ion exchange resin is held constant at T_W. The resin is being decomposed by a single chemical reaction which generates heat at the rate

$$Q = Q_1 \exp\left(-\frac{\Delta E_1}{RT}\right) \text{ cal/(cm}^3\text{)(sec)} \quad . \tag{2}$$

At steady state, heat is being generated throughout the cylinder and conducted toward the wall according to the equation

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} + \frac{Q}{k} = 0 \tag{3}$$

where k is the thermal conductivity of the resin bed, and the boundary conditions are

$$\text{At } r = 0, \ \frac{dT}{dr} = 0 \tag{4}$$

$$\text{At } r = a, \ T = T_{wall} \quad . \tag{5}$$

To solve the problem analytically, it is necessary to assume that the absolute value of the temperature does not vary appreciably from the wall to the centerline near critical conditions. Reviews by Thomas[17] and Parks[18] find this assumption reasonable since the variation is about 5% for most cases. This gives an expression for Q as follows:

$$Q = Q_1 \exp\left(-\frac{2\Delta E}{RT_w}\right) \exp\left(\frac{\Delta E}{RT_w^2} T\right) = Q_1 \exp\left(\frac{2\Delta E}{RT_w}\right) \exp\left(\frac{\Delta E_1}{RT_w^2} T\right) \tag{6}$$

$$Q_1 \exp\left(\frac{\Delta E_1}{R}\left(\frac{1}{T_w} - \frac{T}{T_w^2} + \frac{T_w}{T_w}\right)\right)$$

where Q_w is the heat generation rate at the wall temperature T_w. The mathematical problem has been solved for the heating of dielectrics[19] and for self-heating chemical systems[20] to give

$$T = T_w + \frac{RT_w^2}{\Delta E} \log_e \frac{8G}{\beta(1 + Gr^2/a^2)^2} \tag{7}$$

where

$$G = \frac{4 - \beta - \sqrt{8(2 - \beta)}}{\beta} \tag{8}$$

and

$$\beta = \frac{\Delta E\, Q_w\, a^2}{RT_w^2 k} = \frac{\Delta E\, Q_i\, a^2 \exp(-\Delta E/RT_w)}{RT_w^2 k} \tag{9}$$

The steady-state centerline temperature is given by

$$T_{CL} - T_w = \frac{RT_w^2}{\Delta E} \log_e \left(\frac{8G}{\beta}\right) \quad . \tag{10}$$

For conditions at which G ceases to be a real number, no steady-state solution exists and the temperature increases without limit. The threshold of this region is given by $\beta = 2$. Thus the critical conditions are given by

$$\frac{\Delta E}{RT_w} \cdot \frac{Q_1 a^2}{kT_w} \exp\left(-\frac{\Delta E}{RT_w}\right) = \beta = 2 \tag{11}$$

and the centerline temperature difference at the threshold of instability is

$$T_{CL} - T_w = \frac{RT_w^2}{\Delta E} \log_e 4 \quad . \tag{12}$$

The critical diameter (2a) may then be plotted versus operating wall temperature. Once the values of Q_1/k and ΔE are determined for the system, a single curve will suffice to predict the critical conditions.

For infinite slabs the critical value of β is 0.86, and for spheres it is 3.32.[5] Analytical solutions which allow calculation of temperature profiles for critical and subcritical conditions are available for the slab,[5,20] Although no analytical solution has been found for the sphere, a complete description of the system can be obtained with the aid of known tabulated functions.[5,21,22]

FINITE HEAT TRANSFER COEFFICIENT

For a cylinder with a finite convective heat transfer coefficient to the surroundings, Equation (5) is replaced by

$$\left(\frac{dT}{dr}\right)_{r=a} + \frac{h}{k}(T_w - T_o) = 0 \tag{13}$$

With the new boundary condition the critical value of β is less than 2 and is a complex function of the boundary conductance parameter ha/k and the other variables of the system. For convenience, an analogue of β based on the ambient temperature T_o was used by Thomas[5]

$$\delta = \frac{\Delta E\, Q_1\, a^2 \exp(-\Delta E/RT_o)}{RT_o^2 k} \tag{14}$$

the critical value of 6 is given by

$$\log_e \delta_c = \log_e \frac{8\, B_c}{(B_c + 1)^2} - \frac{4\, B_c}{\alpha(B_c + 1)} \tag{15}$$

where

$$B_c = \frac{-2k}{ha} + \sqrt{1 + 4k^2/h^2a^2} \quad . \tag{16}$$

If the diameter is given, the value of δ_c is calculated from Equations (15) and (16), and Equation (14) is solved by trial and error for To (the critical ambient temperature). The wall temperature is found from

$$T_w = T_o + \frac{RT_o^2}{\Delta E} \cdot \frac{4\, B_c}{(B_c + 1)} \frac{k}{ha} \tag{17}$$

Since Equations (7), (8), (9), and (10) are still valid, the internal temperature profiles may then be calculated for the new critical conditions. For subcritical conditions the most useful relationship between the wall and ambient temperatures is

$$T_o = T_w - \frac{2k\ RT_w^{\ 2}}{\Delta E\ ha} \cdot \frac{2G}{1 + G} \tag{18}$$

FLOW SYSTEMS

An energy balance on a differential volume element (dX) of a cylindrical countercurrent ion exchange contactor at steady state with liquid flow rate. L, and resin flow rate, R', and generation and heat losses to the surroundings by convection gives the following relationship:

$$\frac{dT}{Q_{NET}} = \frac{dX}{LC_L - R'C_R} \tag{19}$$

where C_L and C_R are the liquid and resin specific heats, respectively, and where the net heat gain of the flowing streams per unit volume of column per unit time proceeding along the column from the liquid inlet is given by

$$Q_{NET} = \sum_i \left[Q_i \exp\left(-\frac{\Delta E_i}{RT}\right)\right] - \frac{2h}{a}(T - T_o) + Q_s \quad . \tag{20}$$

The first term in Equation (20) is the heat generated by chemical reaction, the second term is the heat loss to the surroundings, and the third term is the heat generated by radioactive decay.

Integration of Equation (19) from the liquid inlet gives the liquid holdup time as a function of the liquid inlet and outlet temperatures, T_1 and T_2, respectively.

$$\theta = \frac{X}{L} = C_L\left(1 - \frac{R'C_R}{LC_L}\right)\int_{T_1}^{T_2} \frac{dT}{Q_{NET}} \tag{21}$$

The critical holdup time for spontaneous ignition is found by putting in an arbitrary value for the outlet temperature T_2 that makes $1/Q_{NET}$ negligible. If the resin flow rate R is set equal to zero, the results give the liquid holdup time in a fixed bed.

If Q_{NET}, the net heat gain per unit volume of column, is zero or negative at T_1 the column is always safe, no matter how great the holdup time is. The integral can be rigorously evaluated only by numerical methods. However, for the case with only one heat generating term, no radiolytic heating and no heat losses, a close approximation to the exact answer is given by

$$Q_{NET} = Q_1 \exp\left(-\frac{\Delta E_1}{RT}\right) = Q_1 \exp\left(-\xi_1 \frac{T_1}{T}\right) \tag{22}$$

where

$$\xi_1 = \frac{\Delta E_1}{RT_1}$$

$$\int_{T_1}^{T_2} \frac{dT}{Q_{NET}} = \frac{T_1}{\xi_1 Q_1 \exp(-\xi_1)} \tag{23}$$

For only one heat generating term and constant heat losses Q_L cal/(sec)(cm^3 of resin bed):

$$Q_{NET} = Q_1 \exp\left(-\xi_1 \frac{T_1}{T}\right) - Q_L + Q_s \tag{24}$$

and

$$\int_{T_1}^{T_2} \frac{dT}{Q_{NET}} = \frac{T_1}{\xi_1 Q_1 \exp(-\xi_1)} \frac{-\log_e\left[\dfrac{Q_L - Q_s}{Q_1 \exp(-\xi_1)}\right]}{\dfrac{Q_L - Q_s}{Q_1 \exp(-\xi_1)}} \tag{25}$$

APPENDIX B

IBM 7090 COMPUTER PROGRAMS

1. NICHOLS II

This FORTRAN II program, provided by G. Starr Nichols of the duPont Savannah River Laboratories, repeats an otherwise laborious Schmidt calculation to quickly generate time-temperature-position descriptions of cylindrical or spherical packed beds of a first order heat generating chemical. The thirty quantities of input data are entered with a 7E10.5 format on five cards, preceded by an alphanumeric card for case identification. The input data is identified in the following tabulation. A compatible system of units must be used.

Variable Name	Definition	Units
R	Geometrical radius	cm
AN	Number of increments of radius, limited to 21 in the program as listed	dimensionless
H	Height (for the finite cylinder, an untried case by us)	cm
AK	Number of increments of height, limited to 21 or less	dimensionless
DELT	Length of time increments	min
ALF	Thermal diffusivity	cm^2/min
THCON	Thermal conductivity	$(cal)(cm)/cm^2)(min)(^\circ K)$
HT	Top heat transfer coefficient	$cal/(cm^2)(min)(^\circ K)$
HB	Bottom (finite cylinder) heat transfer coefficient	$cal/(cm^2)(min)(^\circ K)$
HS	Side heat transfer coefficient	$cal/(cm^2)(min)(^\circ K)$
TSTART	Starting bed temperature	$^\circ K$
TT	Topside bath temperature	$^\circ K$
TB	Bottom side bath temperature	$^\circ K$
TS	Side bath temperature	$^\circ K$

Variable Name	Definition	Units
FPH	Steady rate volumetric heat source	$cal/(cm^3)(min)$
CH	Chemical heat energy available for the first chemical reaction	cal/cm^3
S	Arrhenius equation frequency factor, $(CH \times S = Q_1)$	min^{-1}
EACT	Activation energy for the first Arrhenius equation, $\Delta E/R$	°K
TLIM	Maximum temperature allowed, program concludes when this temperature is, reached anywhere	°K
CHLIM	Total chemical heat energy available	cal/cm^3
PRINT	Number of calculations before temperature profile printout	dimensionless
TSI	Varying bath temperature coefficient	dimensionless
GEOM	Geometric mode	dimensionless
TYMLIM	Iteration (computed) time limit	min
HT	Control number to fix the locations of infinite heat transfer coefficient	dimensionless
CH2	Chemical heat energy available for the second chemical reaction	cal/cm^3
S2	Frequency factor for the second Arrhenius equation	min^{-1}
TSTOP	Top sink temperature	°K
TSBOT	Bottom sink temperature	°K
CHGNO	Array change signal	dimensionless

The program as listed incorporates some modifications. A SAVE subroutine was added to allow the program to be discontinued at a predetermined time limit, producing a set of binary restart cards to allow continuation of the case if desired. Other minor modifications were necessary to allow the program to run on the Hanford IBM 7090 computer.

The program source listing is reproduced below.

```
      DIMENSION A(27,53),B(27,53),C(27,53),D(27,53),E(27,53),
     1F(27,53),Q(27,53),CHL(27,53),T(27,53),NTMP(27),CHL2(27,53)
      DIMENSION   RMULT(28),HMULT(28)
      DIMENSION N1(5),K1(5),XA(5),FPHA(27,53)
C      THIS PROBLEM SOLVES THE HEAT DIFFUSION EQUATION  IN CYLINDRICAL
C     GEOMETRY IN ONE OR TWO DIMENSIONS WITH AN ESSENTIALLY CONSTANT (IN
C     TIME) HEAT SOURCE FPH, AND TWO HEAT SOURCES, CH AND CH2, THAT
C     DISSIPATE THEMSELVES WITH TWO DISTINCT RATES.  THE UNKNOWN IN THE
C     PROBLEM IS THE T ARRAY* THE TEMPERATURE.   THE EXPLANATION OF THE
C     ITEMS ON THE READ IN LIST IS GIVEN IN THE OSR FORM FOR INPUT DATA.
C     THE ARRAYS A, B, C, D, E ARE COEFFICIENT OF TEMPERATURE TERMS IN
C     THE ITERATION EQUATION.  THE FPHA, CHL, AND CHL2 ARRAYS ARE THE
C     HEAT SOURCE ARRAYS  IF GEOM IS 0.0 A TWO DIMENSIONAL PROBLEM IN
C     (R,Z) SPACE IS DONE--IF 1.0 A ONE-D RADIAL-- AND IF 2.0 A ONE-D
C     SPHERICAL IS DONE.  A AND B ARRAYS FOR RADIAL DIRECTION.
C     C AND D ARRAYS FOR THE AXIAL DIRECTION
      NTT=3
      WHITE OUTPUT TAPE NTT,64
    3 NT=2
  600 READ INPUT TAPENT,68
      WRITE OUTPUT TAPE NTT,68
   77 READ INPUT TAPE NT,1,R,AN,H,AK,DELT,ALF,THCON,HT,HB,
     1HS,TSTART,TT,TB,TS,FPH,CH,S,EACT,TLIM,CHLIM,PRINT
     2  ,TS1,GEOM,TYMLIM,HTX,CH2,S2,EACT2,TSTOP,TSBOT,CHGNO
C     CHGNO IF ZERO NO CHANGES IN THE 8 ARRAYS
C     IF NON ZERO   EXPECT SOME CHANGES*
      IF(R-1.E-7)  777,777,776
  777 CALL EXIT
  776 IHTX=HTX
      IHTX=IHTX+1
      DO 59 N=1,27
      DO 59 K=1,53
      CHL(N,K)=0.0
      CHL2(N,K)=0.0
      FPHA(N,K)=0.0
      A(N,K)=0.0
      B(N,K)=0.0
      C(N,K)=0.0
      D(N,K)=0.0
      E(N,K)=0.0
   59 T(N,K)=0.0
      MG=GEOM
      MG=MG+1
    1 FORMAT(7E10.5)
      IF(MG-2)120,109,109
  109 AK=0.0
  120 IF(AN)2,103,2
    2 DELR=R/AN
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  103 CONTINUE
      IF(AK)102,104,102
  102 CONTINUE
      DELH=H/AK
  104 CONTINUE
      X=DELR*DELR
      Y=DELH*DELH
      NM=AN
      NN=NM+1
      KM=AK
      KK=KM+2
      WKITE OUTPUT TAPE NTT,4,R,AN,H,AK,DELT,ALF,THCON,HT,HB,HS,
     1TSTART,TT,TB,TS,FPH,CH,S,EACT,TLIM,CHLIM,PRINT
     2  ,TS1,GEOM,TYMLIM,HTX,CH2,S2,EACT2,TSTOP,TSBOT
    4 FORMAT(1H 5E15.5)
      DO 10 N=1,NN
      DO 10 K=2,KK
C     HMULT IS A VOLUMETRIC WEIGHT FACTOR IN THE Z DIRECTION
      HMULT(K)=1.0
      EN=N
C     THE FOLLOWING GO TO STATEMENT  PROVIDES FOR DIFFERENT VOLUMETRIC
C     FACTORS IN THE A,B,C,AND D ARRAYS FOK THE THREE DIFFERENT GEOMS
      GO TO (110,110,111),MG
  110 GM=2.0
      EN2=4.0
      EN1=0.25
      GO TO 112
  111 GM=1.0
      EN1=0.0833
      EN2=6.0
  113 EN=EN*EN
  112 CONTINUE
      IF(N-NN)11,12,11
C     EQNS FOR OUTERMOST RADIAL POINT ARE DIFFERENT THAN OTHERS
   12 A(N,K)=(2.0*DELT*HS)/(ALF*DELR)
      B(N,K)=((1.0-1.0/(GM *(EN-1.0)))*2.0*THCON*DELT)/(ALF*X)
      T(N+1,K)=TS
C     RMULT IS THE RADIAL VOLUMETRIC WEIGHT FACTOR
      RMULT(N)=EN
      GO TO 10
   11 IF(N-1)14,15,14
C     EQUATIONS FOR THE CENTRAL POINT ARE DIFFERENT THAN OTHERS
   15 A(N,K)=(EN2*THCON*DELT)/(ALF*X)
      B(N,K)=0.0
      RMULT(N)=EN1
      GO TO 10
   14 XY=(THCON*DELT)/(ALF*X)
      A(N,K)=(1.0+1.0/(GM *(EN-1.0)))*XY
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```
      B(N,K)=(1.0-1.0/(GM *(EN-1.0)))*XY
      RMULT(N)=2.0*EN
   10 CONTINUE
   68 FORMAT(55H
      KJ=KK+1
      NJ=NN+1
      GO TO (105,107,107),MG
  105 DO 20 N=1,NN
      DO 20 K=2,KK
      IF(K-KK)21,22,21
C     EQUATIONS FOR BOTTOM POINT ARE DIFFERENT THAN OTHERS
   22 C(N,K)=(2.0*HB*DELT)/(ALF*DELH)
      D(N,K)=(2.0*THCON*DELT)/(ALF*Y)
      T(N,K+1)=TB
      HMULT(K)=0.5
      GO TO 20
   21 IF(K-2)23,24,23
C     EQUATION5 FOR TOP POINT ARE DIFFERENT THAN OTHER5
   24 C(N,K)=(2.0*THCON*DELT)/(ALF*Y)
      D(N,K)=(2.0*HT*DELT)/(ALF*DELH)
      T(N,K-1)=TT
      HMULT(K)=0.5
      GO TO 20
   23 C(N,K)=(THCON*DELT)/(ALF*Y)
      D(N,K)=C(N,K)
      HMULT(K)=1.0
   20 CONTINUE
  107 CONTINUE
   63 FORMAT(1H0)
   64 FORMAT(1H1)
      IF(CHGNO)505,506,505
  505 DO 9035 ITE=1,4
C     THE FOUR READS IN THIS LOOP READ INDIVIDUAL VALUES RESPECTIVELY OF
C     A(N,K),B(N,K),C(N,K),AND D(N,K).
C
C     IF NO INDIVIDUAL CHANGE IS MADE FOR A PARTICULAR ARRAY, A BLANK
C     CARD SIGNAL5 THIS FACT.  WHEN CHANGES ARE MADE, CARD READING FOR
C     THAT ARRAY CEASES WHEN THE FIRST ZERO INDEX IS ENCOUNTERED
C
      READ INPUT TAPE NT,9031,(N1(J),K1(J),XA(J),J=1,5)
 9031 FORMAT(5(I2,I2,E10.5))
      DO 9032  J=1,5
      IF(N1( J))9033,9035,9033
 9033 IW=N1(J)
      IV=K1(J)
      GO TO (9034,9036,9037,9038),ITE
 9034 A(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9051,IW,IV,XA(J)
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      GO TO 9032
 9036 B(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9052,IW,IV,XA(J)
      GO TO YO32
 9037 C(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9053,IW,IV,XA(J)
      GO TO 9032
 9038 D(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9054,IW,IV,XA(J)
 9032 CONTINUE
 9035 CONTINUE
      NN=IW
      KK=IV
      KJ=KK+1
      NJ=NN+1
 9051 FORMAT(10H  A(N,K)   ,I3,I3,E11.5)
 9052 FORMAT(10H  B(N,K)   ,I3,I3,E11.5)
 9053 FORMAT(10H  C(N,K)   ,I3,I3,E11.5)
 9054 FORMAT(10H  D(N,K)   ,I3,I3,E11.5)
  506 DO 30 N=1,NN
      DO 30 K=2,KK
      CHL2(N,K)=CH2
      CHL(N,K)=CH
      FPHA(N,K)=FPH
      E(N,K)=A(N,K)+B(N,K)+C(N,K)+D(N,K)-1.0
      T(N,K)=TSTART
   30 CONTINUE
      IF(CHGNO)507,508,507
  507 DO 8035 ITE=1,4
C     THE FOUK READS IN THIS LOOP READ INDIVIDUAL VALUES RESPECTIVELY OF
C     FPHA(N,K),CHL(N,K),CHL2(N,K),T(N,K).
C
C     IF NO INDIVIDUAL CHANGE IS MADE FOR A PARTICULAR ARRAY, A BLANK
C     CARD SIGNALS THIS FACT. WHEN CHANGES ARE MADE, CARD READING FOR
C     THAT ARRAY CEASES WHEN THE FIRST ZERO INDEX IS ENCOUNTERED
C
      READ INPUT TAPE NT,9031,(N1(J),K1(J),XA(J),J=1,5)
      DO 8032  J=1,5
      IF(N1( J))8033,8035,8033
 8033 IW=N1(J)
      IV=K1(J)
      GO TO (8034,8036,8037,8038),ITE
 8034 FPHA(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9055,IW,IV,XA(J)
      GO TO 8032
 8036 CHL(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9056,IW,IV,XA(J)
      GO TO 8032
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 8037 CHL2(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9057,IW,IV,XA(J)
      GO TO 8032
 8038 T(IW,IV)=XA(J)
      WRITE OUTPUT TAPE NTT,9058,IW,IV,XA(J)
 8032 CONTINUE
 8035 CONTINUE
 9055 FORMAT(10H FPHA(N,K),I3,I3,E11.5)
 9056 FORMAT(10H CHL(N,K) ,I3,I3,E11.5)
 9057 FORMAT(10H CHL2(N,K),I3,I3,E11.5)
 9058 FORMAT(10H  T(N,K)  ,I3,I3,E11.5)
C     SUM THE TOTAL ENERGY CONTENT OF GH
  508 SUM1=0.0
      DO 9030 N=1,NN
      DO 9030 K=2,KK
      SUM1=SUM1+   RMULT(N)*HMULT(K)*CHL(N,K)
 9030 CONTINUE
      SUM1=SUM1*CHLIM
      TEST=0.0
      TIME=0.0
      SUM2=SUM1/CHLIM
      GO TO 60
C     PCOUNT IS THE INDEX TO TELL WHEN TO PRINT THE ARRAY OF TEMPERATURE
   79 PCOUNT=1.0
   78 TIME=TIME+DELT
      TMAX2=0.0
      TMAX=0.0
      SUM2=0.0
      DO 40 N=1,NN
      DO 40 K=2,KK
      IF(N-NN)1009101,100
C     LETS T BATH BE FUNCTION OF TIME
  101 T(N+1,K)=TS+TS1*TIME
  100 IF(K-2)500,501,500
  501 T(N,1)=TT+TSTOP*TIME
  500 IF(K-KK)502,503,502
  503 T(N,K+1)=TB+TSBOT*TIME
  502 CONTINUE
      SZ=EXPF(-EACT2/T(N,K))
      SZZ=CHL2(N,K)*S2*SZ
      Z=EXPF(-EACT/T(N,K))
      ZZ=CHL(N,K)*Z*S
      Q(N,K)=(FPHA(N,K)+ZZ+SZZ)/ALF
      CHL(N,K)=CHL(N,K)-ZZ*DELT
      CHL2(N,K)=CHL2(N,K)-SZZ*DELT
C     THIS GO TO STATEMENT PERMITS THE EFFECT OF AN INFINITE HEAT XFER
C     COEFFICIENT AT VARIOUS BOUNDARIES AS FOLLOWS--1 FOR TOP, 2 FOR
C     BOTTOM,3 FOR SIDE,  4 FOR TOP AND BOTTOM* 5 FOR TOP AND SIDE,
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C     6 FOR BOTTOM AND SIDE, AND 7 FOR TOP, BOTTOM, AND SIDE
      GOTO(201,202,203,204,210,211,212,223),IHTX
  202 IF(K-2)201,206,201
  206 F(N,2)=T(N,1)
      GOT0117
  203 IF(K-KK)201,207,201
  207 F(N,KK)=T(N,K+1)
      GOTO117
  204 IF(N-NN)201,208,201
  208 F(N,K)=T(N+1,K)
      GOT0117
  210 IF(K-2)203,220,203
  220 F(N,2)=T(N,1)
      GO TO 203
  211 IF(K-2)204,221,204
  221 F(N,2)=T(N,1)
      GO TO 204
  212 IF(K-KK)204,222,204
  222 F(N,K)=T(N,K+1)
      GO TO 204
  223 IF(K-2)224,225,224
  225 F(N,2)=T(N,1)
  224 IF(K-KK)204,226,204
  226 F(N,K)=T(N,K+1)
      GO TO 704
  201 IF(MG-2)115,116,116
C     THIS IS THE ITERATION EQUATION IN ONE DIMENSION
  116 F(N,K)=A(N,K)*T(N+1,K)+B(N,K)*T(N-1,K)-E(N,K)*T(N,K)
     1 +Q(N,K)*DELT
      GOT0117
C     THIS IS THE ITERATION EQUATION IN TWO DIMENSIONS
  115 F(N,K)=A(N,K)*T(N+1,K)+B(N,K)*T(N-1,K)+C(N,K)*T(N,K+1)
     1+D(N,K)*T(N,K-1)-E(N,K)*T(N,K)+Q(N,K)*DELT
  117 CONTINUE
      SUM2=CHL(N,K)*RMULT(N)*HMULT(K)+SUM2
      IF(N-1)300,301,300
  301 IF (F(N,K)-TMAX2)300,300,302
C     GETS TMAX IN THE CENTER OF THE CYLINDER IF TWO DIMLNSIONAL
  302 TMAX2=F(N,K)
  300 CONTINUE
      IF(F(N,K)-TMAX)40,51,51
C     GETS MAXIMUM TEMPERATURE IN SYSTEM
   51 TMAX=F(N,K)
   40 CONTINUE
      DO130N=1,NN
      DO130K=2,KK
  130 T(N,K)=F(N,K)
C     END PROBLEM IF TIME EXCEEDS INPUT DATA TIME LIMIT
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      IF(TIME-TYMLIM)200,54,54
C     IF PCOUNT EQUALS THE PRINT FREQUENCY, GO TO PRINT
  200 IF(TMAX-TLIM)53,54,54
C     END PROBLEM IF ANY TEMP IS GREATER THAN TMAX
   53 IF(SUM2-SUM1)54,56,56
   56 IF(PCOUNT-PRINT)50,52,50
   50 PCOUNT=PCOUNT+1.0
      GO TO 78
C     SINCE PRINTING INSTRUCTIONS ARE ESSENTIALLY A SUBROUTINE, TEST IS
C     SET UP BEFORE ENTERING THE PRINT INSTRUCTIONS TO KNOW WHETHER TO
C     END THE PROBLEM OR GO BACK TO DO MORE COMPUTING
   52 TEST=0.0
      GO TO 60
   54 TEST=1.0
      GO TO 60
   60 Z=(SUM2*CHLIM/SUM1)*100.0
      WRITE OUTPUT TAPENTT,61,TMAX,Z,TIME,TMAX2
   61 FORMAT(1H04E15.5)
      DO 70 K=1,KJ
      DO 71 N=1,NJ
   71 NTMP(N)=T(N,K)
C     PRINT TEMPERATURES
   7U WRITE OUTPUT TAPE NTT,62,(NTMP(J),J=1,NJ)
C  FORMAT STATEMENT CHANGE RESTRICTS DIMENSION 27 TO 21
   62 FORMAT( 1H0, 21I5)
      IF(KJ-26)72,72,73
   72 WRITE OUTPUT TAPE NTT,63
      GO TO 74
   73 WRITE OUTPUT TAPE NTT,64
   74 DO 75 K=2,KK
      DO 76 N=1,NN
      Z=(100.1*CHL(N,K))/(CH)
   76 NTMP(N)=Z
C     PRINT PER CENT OF CHL ENERGY REMAINING*  100.1 IS USED INSTEAD OF
C     100.0 FOR ROUND OFF PURPOSES
   75 WRITE OUTPUT TAPE NTT,62,(NTMP(J),J=1,NN)
      DO 32 K=2,KK
      DO 33 N=1,NN
      Z=(100.1*CHL2(N,K))/CH2
   33 NTMP(N)=Z
C     PRINT PER CENT OF CHL2 REMAINING
   32 WRITE OUTPUT TAPE NTT,62,(NTMP(J),J=1,NN)
      IF(TEST) 5333,53339600
 5333 IF (SENSESWITCH 1) 5344,79
 5344 CONTINUE
 5353 WRITE OUTPUT TAPE 395355
 5355 FORMAT(1H0,13HRESTART CARDS)
 5354 CALL SAVE(0)
 5356 GO TO 79
*     END
      DEBUG
N
   54 DUMP 1,2, $ SUM1,SUM2,TEST
 5333 DUMP 1,12$ SUM1,SUM2,TEST
 5256       DUMP 1,1$ SUM1,SUM2,TEST
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2. HOTBED

HOTBED, a FORTRAN IV routine, was programmed by R. L. Engle from finite differences equations describing the heat and mass transfer behavior of an ion exchange contactor with liquid flowing through a static bed. The program makes the calculations repeatedly, to produce a time-temperature-length analysis for the fixed bed contactor. Reactant consumption is also calculated to enable the program to accurately describe the effect of the first order chemical reaction.

Although the source program listing reproduced below is self-explanatory, the effect of the variable DELT may cause trouble. It is the time interval which the program uses to calculate the successive temperature-location arrays. DELT will cause undue inaccuracy if too large, and excessive machine time if too small. A value of 0.1 was found to be near optimum for the cases of interest.

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    IDENT CUS448  XD            W J VAN SLYKE 321 BLDG 300 AREA PHONE 3481
$JOB
$EXECUTE       IBJOB
$IBJOB
$IBFTC D1      LIST,REF
C        MAIN PROGRAM TO CALCULATE TEMPERATURES IN A PACKED CYLINDRICAL BED
C
C
C        INPUT CONSISTS OF 1 CARD OF ALPHANUMERIC INFORMATION WHICH IS
C        USED AS A CASE TITLE, FOLLOWED BY 4 CARDS CONTAINING 26 FLOATING
C        POINT VARIABLES, USING A (7E10.6) FORMAT*  THE 26 VARIABLES ARE
C      NAME       DESCRIPTION                                UNITS
C
C        CROL     C RO LIQUID PRODUCT                        CAL/DEGC. CCM
C        CROS     C RO SOLID PRODUCT                         CAL/DEGC. CCM
C        EPS      BED POROSITY
C        DELT     TIME INCREMENT                             MINUTES
C        RADIUS   RADIUS OF BED                              CM
C        U        VOLUME FLOWRATE                            CCM / MIN
C        C1,C2,C3  REACTANT AVAILABLE FOR EACH REACTION      CAL / CCM
C        CO       TOTAL REACTANT AVAILABLE                   CAL / CCM
C        S1,S2,S3  PROPORTIONALITY CONSTANTS FOR ARRHENIUS   CAL/CCM  MIN
C        E1,E2,E3  DELTA E(1,2,3) / R                        DEG K
C        H        HEAT TRANSFER COEFFICIENT                  CAL/SCM MIN DEGK
C        TA       AMBIENT TEMPERATURE                        DEG K
C        TI       INLET TEMPERATURE                          DEG K
C        TS       STARTING BED TEMPERATURE                   DEG K
C        A        TOTAL BED LENGTH                           CM
C        B        LENGTH INTERVAL OF REAOOUT                 CM
C        M        CONSTANT RATE HEATING COEFFICIENT          CAL/CCM MIN
C        THETA    TIME INCRLMENT OF READOUT                  MIN
C        TMAXT    MAXIMUM ALLOWABLE TEMPERATURE              DEG K
C        HITHET   MAXIMUM ITTERATION TIME                    MIN
C
C
C        ITERATION WILL BE STOPPED FOR THE FOLLOWING REASONS
C        1.  THE ITERATION TIME EXCEEDS THE MAXIMUM (INPUT HITHET)
C        2.  A CALCULATED TEMPERATURE EXCEEDS MAXIMUM ALLOWABLE (INPUT TMAXT)
C        3.  THE OUTLET TEMPERATURE DECREASES AFTER IT HAS ONCE
C             INCREASED*
C
C        IF THE INPUT VARIABLE HITHET IS 0, A MESSAGE IS WRITTEN TO THE
C        OPERATOR TO SET SENSE SWITCH 1 DOWN AFTER THE STOP TIME
C        SPECIFIED ON THE APPLICATION CARD.  THIS MESSAGE SHOULD ALSO
C        BE WRITTEN ON THE APPLICATION CARD UNDER COMMENTS*  THEN WHEN
C        SENSE SWITCH 1 IS SET DOWN, MEMORY IS SAVE0 ON TAPE UNIT B2 BY
C        SUBROUTINE KEPR.  THIS TAPE MAY THEN BE RELOADED BY PROGRAM
C        LOAD, AND ITERATION WILL CONTINUE WHERE IT LEFT OFF FOR THE
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C        TIME INDICATED ON THE SECONU APPLICATION CARD.  A TAPE LABEL
C        AND LOCATION SHOULD BE SUBMITTED WHEN THIS FEATURE IS USED*
C
C
      COMMON    T(3750),C1(3750), C2(3750), C3(3750), DIST(3750),
     1    TMAX(3750), BLURB(10), N, C0, B
      REAL M
    9 FORMAT (10A6)
   10 FORMAT (7E10.6)
   11 FORMAT ( 42H1 TEMPERATUKES IN A CYLINDRICAL PACKED BED, 10X,10A6/
     1  4(//1X,1P7E12.4))
   12 FORMAT (1H1,1PE11.5,22HDEG TEMP CALCULATED AT, E13.5,33H CM. FROM
     1INLET.  ELAPSED TIME IS, E13.6,  37H MIN.  EXCEEDS MAXIMUM ALLOWAB
     2LE TEMP /  6H CASE , 10A6, 17H HAS BEEN STOPPED)
   13 FORMAT (19H1 TEMPEKATURES FOR , 1PE12.5,5H MIN., 10X 10A6)
   14 FORMAT (36H1 MAXIMUM TEMPERATURE FOR THIS CASE ,10A6 /1PE14.5,
     1 10H DEG CENT ,  E17.5,  7HMINUTES ,   E17.5, 15H CM. FROM INLET /
     2 44H  OTHER TEMPERATUKES CALCULATED AT THIS TIME)
   15 FORMAT ( 39H1 SENSE SWITCH   ON AFTER ITERATION AT ,1PE12.5, 10X,
     1  10A6)
   16 FORMAT ( 59H0 PAUSE TO RESET SENSE SWITCH 1 UP BEFORE STARTING NEX
     1T JOB)
   17 FOKMAT  ( 40H0   RESET SENSE SWITCH 1 UP FOR NEXT JOB)
   18 FORMAT (57H0 PLEASE MAKE SURE SENSE SWITCH 1 IS UP, THEN PRESS STA
     1RT /   117H  THEN IF THE EXECUTION TIME SPECIFIED ON THE APPLICATI
     2ON CARD IS EXCEEDED, SET SENSE SWITCH 1 DOWN - BUT DO NOT STOP  /
     3        75H  SHORTLY AFTER SENSE SWITCH 1 IS SET DOWN, THIS PROGRA
     4M WILL BE TERMINATED)
   19 FORMAT ( 14H0 NUMBER DEL Z, I6,36H EXCEEDS MAXIMUM, THIS CASE BYPA
     1SSED)
   20 FORMAT (34H1 OUTLET TEMP DECREASING FOR CASE ,10A6)
      PI = 3.14159
   50 READ (2,9) BLURB
      READ (2,10) CROL, CROS, EPS, DELT, RADIUS, U,C1(1),C2(1), C3(1),
     1  C0, S1, S29 S3, E1, E2, E3, H, TA, TI, TS, A, B, M, THETA,  TMAXT
     2  , HITHET
C                    DELZ = DISTANCE INCREMENT IN CM. - N = NO OF INCREMENTS
      IF(HITHET) 60,60,70
   60 PRINT 18
      PAUSE
      CALL SSWTCH (1,J)
      GO TO (60,70),J
   70 DELZ = U * DELT / (PI*RADIUS*RADIUS*EPS)
      RPTTIM = THETA
      WRITE(3,11)BLURB,CROL,CROS,EPS,DELT,RADIUS,U,C1(1),C2(1),C3(1)
     1  ,C0, S1, S2, S3, E1, E2, E3, H, TA, TI, TS, A, B, M, THETA,TMAXT
     2   , HITHET
      N = A/DELZ
```

```
      IF(N-3750) 90,90,80
   80 WRITE(3,19) N
      GO TO 50
   90 DIST(1) = 0.
      OO 100 I=2,N
      DIST(I) = DIST(I-1)+ DELZ
      C1(I) =C1(1)
      C2(I) =C2(1)
      C3(I) =C3(1)
  100 T(I) = TS
      T(1) = TI
      PLRSTT = T(N)
      LARGER = 0
      CKOB = EPS * CROL + (1.-EPS)* CROS
C                    INITIALIZE
      TIME = 0.
      TEMMAX = 0.
  110 TIME = TIME + DELT
C         CALCULATE REACTANT DIMINISHING WITH TIME FOR EACH REACTION
C         AND  TEMP FOR EACH DISTANCE INCREMENT
      TPREVZ = T(1)
      HITEM= T(1)
      IHI  = 1
      DO  150 I=2,N
      X1=S1*DELT JCO * EXP(-E1/T(I))
      X2=S2*DELT /CO * EXP(-E2/T(I))
      X3=S3*DELT /CO * EXP(-E3/T(I))
      TPREV1 = T(I)
      T(I) =(EPS* TPREV2* CKOL + (1.-EPS)*CROS*T(I) +  C1(I) * X1
     1   + C2(I) * X2  + C3(I) * X3  + M* DELT +(TA-T(I)) * 2.* H *DELT
     2  / RADIUS )  /  CROB
      C1(I) = C1(I) - C1(I)*X1
      C2(I) = C2(I) - C2(I)*X2
      C3(I) = C3(I) - C3(I)*X3
C              FIND MAXIMUM TEMP FOR THIS TIME
      IF (T(I)-HITEM)150,145,145
  145 HITEM= T(I)
      IHI  = I
  150 TPREV2 = TPREV1
C              CALCULATE MAX TEMP FOR ENTIRE CASE
      IF (HITEM - TEMMAX)  165,1659160
  160 TEMMAX = HITEM
      HIDIST = DIST(IHI)
      TIMAX = TIME
      DO 161  I=1,N
  161 TMAX(I) = T(I)
  165 IF (HITEM - TMAXT)  200, 200,170
C         MAXIMUM ALLOWABLE TEMP EXCEEDED -  REPORT AND THEN STOP PROCESSING
```

```
  170 WRITE(3,12)HITEM,DIST(IHI), TIME,  BLURB
      CALL REPT   (T,TIME)
      GO TO 500
  200 TIME = TIME + DELT*0.001
      L = TIME /DELT
      FL = L
      TIME = FL * DELT
      IF (TIME  + DELT - RPTTIM) 205,205,210
C         REPORT
  205 IF (TIME- HITHET) 230,206,206
  206 IF(HITHET)230,230,210
  210 WRITE (3,13) TIME,BLURB
      RPTTIM = RPTTIM + THETA
      CALL REPT   (T,TIME)
      IF (TIME - HITHET) 230,214,214
  214 IF(HITHET) 230,230,215
  215 WRITE (3,14) BLURB* TEMMAX, TIMAX, HIDIST
      CALL REPT(TMAX,TIMAX)
      GO TO 500
  230 CALL SSWTCH ( 1  ,J)
      GO TO ( 240, 250)  ,J
C         SAVE CORE
  240 WRITE (3,15) TIME* BLURB
      CALL REPT (T,TIME)
      PRINT 17
      CALL KEPR
      PRINT 18
      PAUSE
      WRITE (3,13) TIME, BLURB
      CALL REPT (T,TIME)
      GO TO 110
  250 IF(T(N)-PLASTT)300,270,260
C        OUTLET TEMP INCREASING
  260 LARGER = 1
  270 PLASTT = T(N)
      GO TO 110
C        OUTLET TEMP NOW DECREASING    STOP PROCESSING
  300 IF(LARGER) 110,110~310
  310 WRITE(3,20)BLURB
      CALL REPT(T,TIME)
      PLASTT = T(N)
      GO TO 215
  500 CALL SSWTCH(1,J)
      GO TO (501,502),J
  501 PRINT 17
      PAUSE
  502 RFTURN
      END
```

```
$IBFTC D2       LIST,REF
C         SUBROUTIN TO WRITE TEMPERATURE ARRAY
      SUBROUTINE REPT (TEMP* TIME)
      DIMENSION TEMP(3000)
      COMMON    T(3750),C1(3750), C2(3750), C3(3750), DIST(3750),
     1    TMAX(3750), BLURB(10), N, C0, B
    1 FORMAT (18H0    CM FROM INLET* 3X13HDEGREE KELVIN,6X7HC1 / C0,
     1  9X 7HC2 / C0,  9X7HC3 / C0/)
    2 FORMAT (1X  5(1PE16.6))
    3 FORMAT  (1H1, 20X10A6)
      NLINES = 5
      WRITE (3,1)
      RPTDIS = 0
      DO LOO  I=1,N
      IF (DIST(I)-RPTDIS) 100,20,20
   20 C1R = C1(I)/C0
      C2R = C2(I)/C0
      C3R = C3(I)/C0
      WRITE(3,2) DIST(I), TEMP(I),C1R, C2R, C3R
      RPTDIS = RPTDIS + B
      NLINES = NLINES +1
      IF (NLINES - 45) 100,100,30
   30 WRITE (3,3)  BLURB
      WRITE (3,1)
      NLINES = 3
  100 CONTINUE
      RETURN
      END
```

3. G-JBED

G-JBED, also written in the FORTRAN IV source program language, integrates the analytical expression derived in Appendix A, Equation (21), to compute the more important results calculated by the HOTBED program. It uses a zero order expression to describe the first order case, an approximation which ordinarily causes negligibly small error. The machine calculation rapidly and efficiently computes the time to deflagration, in terms of the inlet temperatures, flow rates, and chemical and radioactive decay heat generation rates, The use of a finite heat transfer coefficient may cause a decreasing temperature in the contractor, and the program indicates this by printing out, "This systems shows a net heat loss, always safe", Provision has been made in the input data (KTU, KTINT) for scanning a variable range of liquid inlet temperatures, and the maximum operating temperature may be found to the nearest degree Kelvin.

The source program listing follows. Any compatible system of units may be used.

```
*   IDENT CUS448  XU            W J VAN SLYKE 321 BLDG 300 AREA PHONE 3481
SJOB
$EXECUTE        IBJOB
$IBJOB
$IBFTC D1       LIST,REF,SDD
C  PROGRAM TO INTEGRATE THE JANSEN EXPRESSION FOR
C       THE CRITICAL HOLDUP TIME FOR A CYLINDRICAL HEAT GENERATING BED
C       WITH CONVFCTION HEAT TRANSFER AT THE WALL.
    1 FORMAT (1H0,47H THIS SYSTEM SHOWS A NET HEAT LOSS,  ALWAYS SAFE)
    2 FORMAT (7E10.3/7E10.3/E10.3,2I10)
    3 FORMAT(1H0,31H INTEGRATION WITHIN THE BOUNDS ,1PE12.3,70H DEGREES
     1KELVIN AND THE TEMPERATURE LIMITING THE INTEGRATION ERROR TO //E12
     2.3,14H TERMINATED AT,E12.3,56H DEGREES KELVIN.  THE VALUE OF THE C
     3OMPUTED INTEGRAL IS ,E12.3,10H MINUTES.   )
    4 FORMAT (1H0,1P5E14.6//1P5E14.6//5E14.6,2I10)
    5 FORMAT(1H0,30H THE CONTACTOR OPERATING WITH ,1PE12.3,65H CALORIES
     1PER CUBIC CENTIMETER PER MINUTE RADIOLYTIC HEATING AND ,1PE12.3//
     275H DEGREES KELVIN INLET TEMPERATURE WILL REACH A STEADY STATE TEM
     3PERATURE OF ,1PE12.3//19H DEGREES KELVIN AT ,1PE12.3,22H MINUTES H
     4OLDUP TIME.  )
      DIMENSION DATE (3), V(11)
    7 FORMAT (A3)
      READ (2,7) (DATE (I),I = 1,3)
    8 FORMAT (1H1,100X, 3A3//)
    9 CONTINUE
   13 READ(2,2)TO,TA,ERR,E1,Q1,E2,Q2,E3,Q3,Q4CR,H,A,CL,CR,FR,KTU,KTINT
C          INTERPRETATION OF THE INPUT VARIABLES
C     FORTRAN NAME  VARIABLE                        UNITS (COMPATIBLE)
C         TO        TEMPERATURE OF THE LOWER        DEGREES KELVIN
C                     INTEGRATION LIMIT
C         TA        AMBIENT TEMPERATURE             DEGREES KELVIN
C         ERR       INTEGRATION PRECISION LIMIT     DEGREES KELVIN
C         E1        (DELTA E)/R, FIRST REACTION     DEGREES KELVIN
C         Q1        HEAT GENERATION FACTOR, FIRST   CAL/(CM)3*MIN.
C         E2        (DELTA E)/R 2ND REACTION        DEGREES KELVIN
C         Q2        HEAT GEN. FACTOR, 2ND           CAL/(CM)3*MIN.
C         E3        DELTA E/R, 3RD                  DEGREFS KELVIN
C         Q3        HEAT GEN. FACTOR, 3RD           CAL/(CM)3*MIN.
C         Q4CR      CONSTANT RATE HEATING TERM      CAL/(CM)3*MIN.
C         H         HEAT TRANSFER COEFFICIENT       CAL/(CM)2*MIN*DEG K
C         A         HEAT TRANSFER AREA              (CM)2/(CM)3
C         CL        HEAT CAPACITY, LIQUID           CAL/(CM)3* DEG K
C         CR        HFAT CAPACITY, SOLID            CAL/(CM)3* DEG K
C         FR        SOLID/LIQUID FLOWS RATIO        DIMENSIONLESS
C         KTU       DO INDEX FOK THE UPPER LIMIT OF TO
C         KTINT     DO LOOP TEMPERATURE INCREMENTS FOR TO
      IF (TO .LT. 1.) GO TO 70
C    BLANK DATA CARD LETS THE PKOGKAM STOP
```

```
      DO 65 K = 1,KTU,KTINT
      WRITE (3,8) DATE
   15 WRITE(3,4)TO,TA,ERR,E1,Q1,E2,Q2,E3,Q3,Q4CR,H,A,CL,CR,FR,KTU,KTINT
      T = TO
      VALUE = 0.0
   20 IF(Q1*EXP(-E1/T)+Q2*EXP(-E2/T)+Q3*EXP(-E3/T)+Q4CR-H*A*(T-TA))21,
     1 30,30
C  HEAT BALANCE  --  NO TEMPERATURE RISE IS POSSIBLE IF NEGATIVE*
C     TEMPERATURE DECREASES WITH TIME*
   21 WRITE (3,1)
      GO TO 63
C  CALCULATE HEAT GENERATION OVER A ONE DEGREE INTERVAL IN
C        INCREMENTS OF 0.1 DEGREE.  THIS INCLUDES A HEAT LOSS
C      TERM FOR CONVECTION AT THE CYLINDRICAL WALL.
   30 DO 40 I = 1,11
       B = I
      F = (B - 1.)/ 10.
      V(I) = 1./(Q1*EXP(-E1/(T+F))+Q2*EXP(-E2/(T+F))+Q3*EXP(-E3/(T+F))
     1+Q4CR -H*A*(T+F-TA))
   40 CONTINUE
      T = T + 1.0
C   COMPUTE THE INTEGRAL OVER A ONE DEGREE INTERVAL USING
C       SIMPSONS RULE*
      VAL = CL *(1.-(FR*CR)/(   CL))*(.1/3.)*(V(1) + V(11) +
     14.*(V(2) +V(4) + V(6) + V(8) +V(10)) +2.*(V(3) +V(5) +V(7) +V(9)))
C   ADD THE INTEGRAL JUST CALCULATED TO THE TOTAL INTEGRAL
C       FROM TO TO T.
      VALUE = VALUE + VAL
      IF(Q1*EXP(-E1/T)+Q2*EXP(-E2/T)+Q3*EXP(-E3/T)+Q4CR-H*A*(T-TA)
     1.LT.0.0) GO TO 55
C   TEST TO STOP THE INTEGRATION IF THE INTEGRAL HAS CONVERGED*
   50 IF ((T - TO)*VAL/VALUE - ERR) 60,30,30
C     WRITE THE RESULTS FOR A STABLE CASE WHERE A TEMPERATURE RISE OCCURS.
C     THIS OUTPUT OVERESTIMATES THE STEADY STATE TEMPERATURE BY NOT MORE THAN
C     1 DEGREE, AND UNDERESTIMATES THE HOLDUP TIME.
   55 WRITE (3,5) Q4CR,TO,T,VALUE
      GO TO 63
C       WRITE OUT THE RESULTS IF CONVERGED,   START NEXT CASE*
   60 WRITE (3,3) TO,ERR,T,VALUE
   63 CONTINUE
       TO = TO + FLOAT (KTINT)
   65 CONTINUE
      GO TO 9
   70 STOP
      END
$DATA
```

4. PROFIT

PROFIT uses FORTRAN IV source language to calculate temperatures for a stagnant infinitely long cylindrical vessel using the method described in the Appendix A Equations (17), (7), (8), (9), and (10). The critical ambient temperature is found by trial and error, starting from an initial temperature guess, TGUESS, A poor estimate for TGUESS may increase the running time slightly, or possibly cause program instability signaled by the machine error message, "Divergent, go to next case." Other temperatures are then calculated in a straightforward manner. The following tabulation briefly explains the input variables.

Variable Name	Definition	Units
TGUESS	Initial temperature guess	°K
H	Vessel wall heat transfer coefficient	cal/(cm^2)(°K)(min)
R	Vessel radius	cm
TK	Bed thermal conductivity	(cal)(cm)/(cm^2)(min)(°K)
ER	Activity energy term, $\Delta E/R$	(°K)
Q	Arrhenius equation heat generation factor	cal/(cm^3)(min)
ERR	Maximum temperature error desired in calculating the ambient temperature	°K
K	Index to determine the number of equally spaced radial temperatures to be calculated	dimensionless integer

If K is 100, only the ambient temperature, wall temperature, and centerline temperatures are reported. K greater than 100 causes only the ambient and wall temperatures to be calculated, but K equal to 10 would produce radial temperatures at every tenth of a radius increment, and so on.

The source program listing is reproduced below.

```
*   IDENT CUS448  XD            W J VAN SLYKE 321 BLDG 300 AREA PHONE 3481
$JOB
$EXECUTE        IBJOB
$IBJOB
LIBFTC D1       LIST,REF,SDD
C PROGRAM TO CALCULATE STEADY STATE STATIC RESIN BED TEMPERATURE
C PROFILES AT THE CRITICAL AMBIENT TEMPERATURE AS A FUNCTION OF THE
C BED RADIUS, HEAT TRANSFER COEFFICIENT,AND CHEMICAL PARAMETERS*
    1 FORMAT (7E10.3/       I10)
    2 FORMAT (A3)
    3 FORMAT (1H0,50X,11H INPUT DATA  //3X,7H TGUESS,5X,2H H,12X,2H R,
     110X,3H TK,9X,3H ER,8X,2H Q,10X,4H ERR,8X,            2H K/)
    4 FORMAT (1H0,1P7E12.5,4X,I3)
    5 FORMAT(1H0,45X,24H CALCULATED TEMPERATURES//13H AMBIENT TEMP,3X,
     1 10H WALL TEMP,2X,48H TEMPERATURES EVENLY SPACED TO THE CENTER LIN
     2E   I
    6 FORMAT (1H0,(1P9E12.5//))
    8 FORMAT (1H1,100X,3A3//I
    9 FORMAT (1H0,30H DIVERGENT,  GO TO NEXT CASE         )
      DIMENSION T(101), DATE(3)
   24 READ (2,2)(DATE(I),I=1,3)
   25 READ (2,1) TGUESS,H,R,TK,ER,Q,ERR,     K
      IF (TGUESS.LT.1.) GO TO 100
      WRITE (3,8) DATE
      WRITE (3,3)
      WRITE (3,4) TGUESS,H,R,TK,ER,Q,ERR,K
   30 CONTINUE
      TPREV = TGUESS
      ALF = H*R/TK
      BC=(-4.+SQRT(16.+4.* ALF*ALF))/(2.*ALF)
      DENOM=ALOG((8.*BC/(BC+1.)**2)*(TK*  TPREV**2/(Q*ER*R*R)))-4.*BC/
     1(ALF*BC+ALF)
      TA  =-ER/DENOM
   40 CONTINUE
      DT = ABS(TA-TPREV)
      TPREV = TA
      DENOM=ALOG((8.*BC/(BC+1.)**2)*(TK*  TPREV**2/(Q*ER*R*R)))-4.*BC/
     1(ALF*BC+ALF)
      TA  =-ER/DENOM
      IF(ABS(TA-TPREV).GT.DT) GO TO 80
      IF(ABS(TA-TPREV).LT.ERR) GO TO 50
      GO TO 40
   50 CONTINUE
      DC=(8.*BC/(BC+1.)**2)*EXP(-4.*BC/(ALF*BC+ALF))
      DO 70 J=1,101,K
      Z = (100. - FLOAT(J-1))/100.
      THETAR=ALOG(8.*BC/(DC*(1.+BC*Z*Z)**2))
      T(J)=THETAR*TA**2/ER+TA

   70 CONTINUE
      WRITE (3,5)
      WRITE (3,6) TA,(T(J),J=1,101,K)
      GO TO 25
   80 WRITE (3,9)
      GO TO 25
  100 STOP
      END
$DATA
```

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