Technical Memorandum No. 20

Sodium-Air Accident Study
for a Sodium Cooled Reactor

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Summary

The design requirements of a containment building for a sodium cooled reactor have been investigated from the point of view of a hypothetical sodium-air reaction. In particular, this study was directed toward the containment building of the Enrico Fermi Atomic Power Plant. The hypothetical accident assumes a major leak in the sodium system with a concurrent or earlier failure of the ventilation and cooling system, which allows air to enter the areas around the sodium system which are normally maintained in an atmosphere inert insofar as sodium burning is concerned. The resulting sodium pool, equivalent in burning surface to the fraction of the cross sectional area of the containment building, which is flooded, burns at a rate depending upon oxygen concentration and gas temperature in the containment building. A series of experiments were carried out to determine this burning rate and its mechanism. The resulting gas temperature and pressure due to the sodium-air incident were determined by solving a system of equations based on time dependent heat balances on the containment building and its contents. The assumed incident gives a maximum gas pressure of about 26 psig and a corresponding gas temperature of 1115 degrees F. This pressure is well below the design pressure of 32 psig for the containment vessel. In addition to the study of the sodium-air reaction in the assumed incident, the theoretical maximum pressure and temperature for the constant volume adiabatic sodium-air reaction is also discussed.

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Introduction

The potential hazard of a sodium fire and the problem of decay heat on a permanent loss of coolant to the reactor core is a problem common to all sodium cooled reactors. The study of the design criteria for a containment vessel for a fast breeder reactor was undertaken by Atomic Power Development Associates, Inc., as a part of its overall study on sodium cooled reactors. In particular, this study is directed toward the containment vessel for the Enrico Fermi Reactor. The effect of decay heat on the reactor vessel temperature which would result from a loss of coolant accident has been discussed elsewhere (1) and will not be given in this study.

The temperature and pressure specifications to which the Enrico Fermi Atomic Power Plant containment vessel was built are based primarily on the consequences of a hypothesized sodium-air incident. Due to construction schedules, the design pressure of the containment vessel had to be established long before there were any detailed studies on the magnitude of the accident that might result from a sodium-air incident. However, in some preliminary contract research work done for APDA (2) there were indications that the maximum pressure due to a sodium-air incident might be as high as 40 psig. Consideration of the correlation between the experimental work and what could occur in practice led to the conclusion that it appeared extremely likely that a building designed for 32 psig with a metal containment vessel temperature of 650 degrees F would be suitable, since a number of different design steps were apparent which could positively reduce an incident to this level. A simple heat balance on the total amount of heat that can be liberated from a sodium-air reaction will show that the specified metal design temperature of 650 degrees F is indeed conservative. The problem of determining what, if any, plant design steps were required to assure the adequacy of the building thus resolved itself into defining a sodium-air incident and determining in some detail the resulting temperatures and pressures.

In the design of the Dounreay Fast Reactor containment sphere, the British assumed (3) a hypothetical accident in which the rate of burning sodium is dependent upon the reactor decay heat, the reactor having shut down as a consequence of some accident. They assumed that the reactor decay heat vaporizes the sodium, which, in turn, burns without any feedback of the heat of combustion to produce further vaporization. Using this approach, the design pressure of their containment sphere was set at 17 psig.

In the experimental work by Hines, et al., (2), liquid sodium at 850 degrees F was atomized with a spray nozzle, under a nitrogen pressure of 360 psig, into a 500 liter cylindrical metal container. The maximum pressure attained was about 38 psig, and this pressure resulted only when a good dispersion resulted from the spray nozzle. About twenty seconds were required to atomize a stoichiometric amount of sodium into the reaction vessel. This measured pressure agreed with the theoretical analysis of the problem in which an attempt was made to account for the heat transfer, both radioactive and convective, from the hot burning sodium particles, particle size of the dispersion, and burning rate of the atomized sodium. The authors point out that from some preliminary work it was impossible to get any appreciable pressure rise unless the sodium was dispersed to a degree approximating that of a spray nozzle.

In some recent work (4) Argonne National Laboratory carried out a series of experiments in which sodium was explosively ejected into a large cylindrical container. The container was 3 feet in diameter and approximately 10 feet high. The sodium was ejected into the vessel by the ignition of a mixture of hydrogen and oxygen; the ratio of sodium to air in the container was varied by the amount of sodium ejected into the vessel. Using a molar ratio of 3.14 for Na/O_2 , a peak pressure of 6.4 atmospheres (79 psig) was measured. In another experiment, a molar ratio of 4.2 gave a peak pressure of 6.1 atmospheres. Actually this latter experiment should have given a higher peak pressure; however, with the larger amount of sodium it is probable that the sodium was not dispersed to the same degree. The report concludes that in the actual reactor installation it would be impossible to get dispersions approaching the experiment and hence the maximum peak pressures that could be developed would not approach the experimental values.

In the Enrico Fermi Reactor, all of the radioactive sodium components are located in an inert atmosphere in the bottom portion of the containment vessel underneath a five-foot concrete operating floor, see Figure 1. The operating floor serves as a biological shield for any operating personnel that may be in the containment building. The access ports to any of the sodium containing components, i.e., intermediate heat exchangers, pumps, etc., are closed with steel-lined heavy concrete plugs. It is difficult to conceive of any accident where a stoichiometric amount of liquid sodium, approximately 1500 gallons, could be dispersed in an atomized spray into the containment vessel above the reactor operating floor, especially in a short period of time. If any of the sodium pipes or sodium containing equipment beneath the floor were to leak, the sodium would harmlessly collect in a pool in the bottom of the containment vessel, since the inert atmosphere in this region would prevent burning. Because of the multiple containment philosophy in the design of the reactor system, it is difficult to postulate a mechanism by which a major leak would develop. However, for this study it is assumed that a major leak does occur and at the same time the seals between the upper and lower compartments fail and air from the area above the reactor operating floor enters the area underneath the operating floor, causing the sodium to burn. The sodium burning area is taken as the area of the reactor operating floor. To carry out the calculations for an accident of this type, basic data on the burning rate of liquid sodium are needed. Once combustion begins, the burning rate is governed principally by two factors, the oxygen concentration in the atmosphere, which continually decreases because of the burning, and, the resulting temperature of the gas temperature. An experiment was carried out to determine this burning rate and from the results of the experiment it was possible to establish the burning mechanism of a sodium pool.

With the sodium burning rate established, it is then a simple matter to set up time dependent heat balances on the reactor building and to calculate the maximum gas temperature and pressure resulting from the hypothesized sodium-air accident.

In addition, it is also of interest to calculate the maximum temperature and pressure that could result from a sodium-air reaction in a constant volume reaction, i.e., a calculation of the experiment performed by Argonne.

In summary it can be said that the containment building is adequate in respect to the sodium-air accident. The experimental sodium-pool burning tests indicate that

FIG. 1-ELEVATION OF REACTOR PLANT

the burning rate is almost independent of the sodium temperature in the temperature range considered and that the sodium-air reaction is controlled by a diffusional mechanism rather than by the velocity of the chemical reaction. From this it is concluded that the burning rate is proportional to the product of the oxygen concentration and the square root of the absolute gas temperature. Using this burning mechanism, the calculated maximum gas pressure that can result from the sodium-air accident is about 26 psig.

In studies of this type, it is always of interest to calculate the maximum extreme conditions that can result from a sodium-air reaction. The maximum conditions will be obtained by assuming a constant volume adiabatic equilibrium reaction. Equilibrium calculations show that the maximum theoretical gas pressure that can result from a sodium-air reaction is 9.75 atmospheres (129 psig) and a maximum gas temperature of 3554 degrees F.

Determination of the Burning Rate Mechanism

The British (3) estimated a burning rate of one pound per second per 1000 square feet of exposed sodium surface for a pool of sodium initially at 500 degrees C. This rate corresponds to roughly 4 (lbs)/(hr)(sq ft). In order to check this value and at the same time gain some insight into the burning mechanism, APDA initiated a series of experiments in which a pool of sodium was allowed to burn in an insulated heated square pan. The pan was approximately 30 inches square and 3 inches deep, the amount of sodium initially charged was 50 pounds. In the first experiment the pan was fitted with a hood so that a metered quantity of forced air could be fed to the sodium pool. In the second experiment the pan was placed in the open atmosphere. In both cases, the pan was preheated before the hot sodium was poured into it. The pan was instrumented with a number of thermocouples in order to measure the temperatures as the burning continued. The burning rate was then determined by measuring the total time required for complete combustion; results of the burning tests are summarized in Table I.

TABLE I - Summary of Burning Tests

<u>Type of Test</u>	<u>Initial Temperature, deg F</u>		<u>Burning Rate^a</u>	<u>Air Rate</u>
	<u>Pan</u>	<u>Sodium</u>		
Hood	930	675	4.9	220% ^b
Open	800	850	6.3	Natural ^c

- a. Average burning rate, pounds per hour per square foot of burning surface.
- b. Percent excess based on a burning rate of 4 (lbs)/(hr)(sq ft).
- c. A wind velocity of approximately 9 miles per hour.

In the hood test the temperature of the burning sodium immediately reached the pan temperature and then the temperature slowly increased to about 1300 deg F in about 18 minutes. At this point the temperature leveled off and the sodium, at all times, appeared to burn at a steady rate for the remainder of the burning test, a period of about 80 minutes. During this period of 80 minutes, the sodium temperature remained almost constant and increased only about 50 degrees F. In the open pan test the sodium temperatures followed essentially the same pattern; that is, the sodium temperature remained almost constant and the sodium burned at an even rate, once the temperature leveled off and remained constant. In the open pan test the burning sodium appeared to froth slowly and boil over on the edge of the sodium pan container, thus increasing its effective area. Also in this test, a visual examination of the burning pan at the end of the burning revealed a black residual glossy mass, probably a mixture of various oxides of sodium with some unburned sodium. The value of the burning rate in this test could probably be revised somewhat downward if an estimate could be made of the actual amount of sodium burned.

In the accident calculation on sodium burning in the containment building, the initial burning rate of a large spillage of sodium is required and not the average burning rate as determined by the above experiments. Initially, as the sodium starts to burn and before it has attained its equilibrium temperature, the burning rate would probably be somewhat lower than the values given in Table I. Therefore, for the sodium-air accident study a burning rate of 5 (lbs)/(hr)(sq ft) will be used. It is worthwhile to note that the estimate made by the British (3) is in excellent agreement.

As determined from visual observation of the burning tests it would appear that the burning rate is not markedly affected by the temperature of the burning sodium. This would mean that the burning rate is primarily controlled by a diffusional process rather than by the velocity of the chemical reaction. In the cases where a reaction is primarily controlled by the velocity of the chemical reaction, a small change in temperature, of say 10 degrees C, will usually double the rate of reaction. If the burning rate of sodium were controlled by the velocity of the chemical reaction then the sodium-air reaction would tend to be autocatalytic. There is no indication of this in the results of the sodium burning test. Since the burning rate is not dependent on the velocity of the chemical reaction, the activation energy for the sodium-air reaction is zero. This is not particularly unique to the sodium-air reaction since exactly the same process occurs for the reaction of sodium vapor and chlorine (5). Since the activation energy for the reaction of sodium with oxygen is zero, then the burning rate, or rate of reaction, is dependent upon the number of collisions of sodium and oxygen. If this is a homogeneous reaction, sodium and oxygen reacting in the gaseous phase, then the burning rate would be proportional to the product of the moles of sodium and oxygen, $(n_{Na})(n_{O_2})$, times the relative velocity between the sodium and oxygen molecules. Since the relative velocity is proportional to the square root of the absolute temperature, the burning rate would be given by

$$B = k n_{O_2} n_{Na} \sqrt{T} \quad (1)$$

where k is a proportionality constant. If the reaction between sodium and oxygen takes place on the surface of the sodium, then the burning rate is independent of the number of sodium molecules and the burning rate is given by

$$B = k n_{O_2} \sqrt{T} \quad (2)$$

Since the sodium concentration, n_{Na} , is proportional to the vapor pressure of sodium, then the burning rate as determined by equation (1) would be a sensitive function of temperature since the vapor pressure is a sensitive function of temperature. The burning rate is relatively independent of the temperature, therefore, it may be concluded that the burning rate takes place on the surface of the sodium and hence can be represented by equation (2).

Sodium-Air Accident Calculation

Assuming the hypothesized sodium-air accident as described in the Introduction, the time-temperature profiles of the containment building atmosphere and building shell can now be calculated using the initial sodium burning rate of 5 (lbs)/(hr) (sq ft) and the burning mechanism as expressed in equation (2). As the sodium burns, the atmosphere in the building becomes heated, and at the same time the oxygen in the atmosphere is being consumed. The hot gases, oxygen and nitrogen, give up their heat to the metal containment shell and to the extraneous metal in the building, i.e., crane girder, structural supports, etc. The metal containment shell transfers heat to the outside atmosphere, whereas the extraneous metal does not. The containment vessel consists of a 1.03-inch thick cylindrical shell 66 feet high and 72 feet in diameter. It is capped at the top with a 0.52-inch hemispherical head and capped on the bottom with a 1.03-inch thick ellipsoidal head. The overall height of the building is 120 feet.

Basing the burning rate on the simple collision model equation (2) gives

$$\frac{B(\tau)}{B(0)} = \frac{m_{O_2}}{m_{O_2}^0} \left[\frac{T_g}{T_g(0)} \right]^{1/2} \quad (3)$$

where $B(\tau)$ is the burning rate corresponding to the oxygen concentration of n_{O_2} moles and temperature T_g and $B(0)$ is the initial burning rate. The oxygen concentration is given by

$$m_{O_2} = m_{O_2}^0 - b \int_0^\tau B(\tau') d\tau' \quad (4)$$

where b is a conversion factor relating the total amount of sodium burned to the amount of oxygen consumed. Substituting equation (4) into (3) and differentiating the resulting expression to eliminate the integral gives

$$\frac{dx}{d\tau} = \frac{x}{2T_g} \frac{dT_g}{d\tau} - \alpha x \sqrt{T_g} \quad (5)$$

where

$$x = B(\tau)/B(0)$$

$$\alpha = b B(0)/m_{O_2}^0 \sqrt{T_g(0)}$$

Equation (5) gives the necessary differential expression for burning rate as a function of the gas temperature. To arrive at the heat input of the burning sodium, the burning rate is multiplied by the heat of combustion of liquid sodium going to Na_2O . The heat of combustion is about 3900 Btu per pound of sodium burned (6).

The further assumption is made that the burning rate of sodium, at constant temperature, is proportional to the amount of oxygen present in the building, and that the burning continues until the building atmosphere is depleted to 5 percent oxygen by volume. This latter assumption is justified by the experimental work carried out at KAPL by Nelson and Nelson (7). In the KAPL experiment, preheated sodium was allowed to flow into a vessel containing a controlled atmosphere, i.e., the percent of oxygen being varied. Visual results indicated that the burning was proportional to the percent of oxygen. At oxygen concentrations of 5 percent and below, no sodium burning was observed.

Now consider the schematic drawing of the containment vessel as shown in Figure 1 as an aid in defining the temperatures and heat transfer coefficients involved. The following nomenclature will be used:

- T_g = gas temperature in building, degrees R.
- T_m = bulk temperature of metal containment shell, degrees R.
- T_m^i = bulk temperature of extraneous metal in the building, degrees R.
- T_a = outside ambient atmosphere temperature, degrees R.
- U_i = overall heat transfer coefficient based on the temperature differences $(T_g - T_m)$ and $(T_g - T_m^i)$, (Btu)/(hr)(sq ft)(deg F).
- U_o = overall heat transfer coefficient based on the temperature difference $(T_m - T_a)$.
- $B(0)$ = initial heat input because of the initial burning rate of sodium, (Btu)/(hr).
- A = heat transfer area of the building shell, (sq ft).
- A_i = surface area of the extraneous metal within the building shell, (sq ft).
- n_g = total moles of gas in the building at time τ , (lb moles).
- c_g = specific heat at constant volume of the containment building atmosphere, (Btu)/(lb mole)(deg F).
- $T_g(0)$ = initial temperature of the containment building atmosphere, degrees R.
- c_m = specific heat of the metal, (Btu)/(lb)(deg F).
- w_m = weight of the metal shell, lbs.
- w_m^i = weight of the extraneous metal in the shell, lbs.

In order to set up the differential equations, heat balances are made on the containment building atmosphere, metal containment shell, and the extraneous metal within the building shell. For the containment building atmosphere, a heat balance gives the following

$$B(\tau) - U_i A (T_g - T_m) - U_i A_i (T_g - T_m') = \frac{d}{d\tau} \{m_g c_g (T_g - T_g(0))\} \quad (6)$$

The total number of gas moles is given by

$$n_g = n_i + n_{O_2} \quad (7)$$

where n_{O_2} is given by equation (4) and n_i is the moles of inert nitrogen plus the moles of oxygen that is assumed not to react. Substituting equation (7) into (6) and using equations (3) and (4) treating c_g as a constant gives

$$\left(1 + \frac{x n}{\sqrt{T_g}}\right) \frac{dT_g}{d\tau} = x (\delta T_g - \gamma + \beta) - (\epsilon + \zeta) T_g + \epsilon T_m + \zeta T_m' \quad (8)$$

where

$$\alpha = \sqrt{T_g(0)} m_{O_2}^0 / m_i$$

$$\delta = b B(0) / m_i$$

$$\beta = B(0) / c_g m_i$$

$$\epsilon = U_i A / c_g m_i$$

$$\gamma = b B(0) T_g(0) / m_i$$

$$\zeta = U_i A_i / c_g m_i$$

Similarly a heat balance on the metal containment shell gives

$$U_i A (T_g - T_m) - U_o A (T_m - T_a) = w_m c_m (dT_m / d\tau) \quad (9)$$

Upon rearrangement equation (9) becomes:

$$dT_m / d\tau = \eta T_g - (\eta + \lambda) T_m + \lambda T_a \quad (10)$$

where $\eta = U_i A / w_m c_m$ and $\lambda = U_o A / w_m c_m$.

Finally, a heat balance on the extraneous metal in the containment vessel gives

$$U_i A_i (T_g - T_m') = w_m' c_m' (dT_m' / d\tau) \quad (11)$$

or

$$dT_m' / d\tau = \mu (T_g - T_m') \quad (12)$$

where $\mu = U_i A_i / w_m' c_m'$. Therefore the sodium accident model is now represented by equations (5), (8), (10), and (12).

For the film heat transfer coefficient, h_i , on the inside of the building a value of 2 (Btu)/(hr)(sq ft)(degrees F) was assumed. This value presupposes that during the burning of the sodium large convection currents will be established which should tend to increase the normal value of the film heat transfer coefficient

considerably. Also during the initial period in which the gas is being heated, large temperature differences will exist between the gas and the metal. With these considerations in mind, the value of 2 for the film coefficient appears to be reasonable. In order to arrive at a value for the overall heat transfer coefficient, U_i , based on a temperature difference between the gas temperature, T_g , and the bulk metal temperature, T_m (or T_m^i), the metal resistance must be included. This will give a negligible correction to U_i , therefore a value of 2 (Btu)/(hr)(sq ft)(deg F) will be used for the overall coefficient. Similarly for the overall heat transfer coefficient, U_o , based on the temperature difference ($T_m - T_a$) the same numerical value will be used.

A breakdown of the various areas found in the containment building and their associated weights are given in Table II. It should be pointed out that only the

TABLE II - Heat Transfer Areas
and their Associated Weights

<u>Component</u>	<u>Area, sq ft</u>	<u>Weight, lbs</u>
Containment Shell ^a	15,640	503,600
Misc. Attachments ^a to Shell	8,311	161,400
Machinery Dome	1,060	27,000
Crane and Crane Girder	6,379	223,200

a. This includes only the portion of the containment vessel above the operating floor.

material above the reactor operating floor is taken into account as heat absorbing material. Assuming the sodium-air incident to take place underneath the reactor operating floor, this will tend to make the calculations somewhat conservative. In Table II only the area above the reactor operating floor is used in considering the heat transfer area for the heat loss to the outside atmosphere. It should be noted that the area A is equal to 15,640 square feet and that the extraneous area adds to 15,750 square feet, about equal to the area of the building shell. The metal weights for w_m and w_m^i are 503,600 and 411,600 pounds respectively. The use of extraneous heat absorbing surfaces in containment vessel design in order to minimize a pressure rise is not particularly unique to this calculation (8).

The initial burning rate of sodium is established at 5 (lbs)/(hr)(sq ft); however, this value applies to a normal atmosphere; i.e., 21 volume percent oxygen. In the assumed accident the normal atmosphere above the operating floor and the atmosphere below the operating floor, an inert atmosphere of nitrogen containing at most 5 volume percent oxygen, mix, giving a somewhat oxygen-depleted atmosphere.

For simplicity it is assumed that this mixing takes place before the accident begins. This resulting depleted atmosphere will lower the initial burning rate in accordance with equation (3). The total gas volume for the accident consists of 233,000 cu ft of normal air above the operating floor at 70 degrees F and 100,000 cu ft of 5 percent oxygen containing nitrogen at about 140 degrees F below the operating floor. Mixing these two gas volumes gives a resulting atmosphere containing 16.6 percent oxygen by volume at 89 degrees F. Applying the oxygen concentration correction to the initial burning rate gives $(5)(16.6 - 5)/(21 - 5)$ or 3.63 (lbs)/(hr)(sq ft) for the initial burning rate in the depleted atmosphere. The initial heat input, $B(0)$ is given by

$$\begin{aligned} B(0) &= (3.63)(3800)(3900) \\ &= 5.38 \times 10^7 \text{ (Btu)/(hr)} \end{aligned}$$

where the 3900 refers to the heat of combustion per pound of liquid sodium (5) and the 3800 is the area of the burning sodium. The constant b in equation (4) can be evaluated thusly:

$$\begin{aligned} b &= (3900 \times 23 \times 4)^{-1} \\ &= 2.787 \times 10^{-6} \text{ (moles oxygen)/(Btu)} \end{aligned}$$

for the reaction of sodium and oxygen going to Na_2O . Initially the gas temperature was taken as 89 degrees F and all metal temperatures were taken at 70 degrees F. The ambient outside temperature T_a was taken to be 70 degrees F. It should be noted that in the differential equations all temperatures are absolute, degrees Rankine. The equations and constants used are summarized in Table III. Because of the form of the equations a computer was used for their solution rather than attempting an analytical solution. The solution of the system of equations is given in Figure 2.

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TABLE III - Equations and Constants for the
Sodium Burning Accident Calculations

Equations:

$$\begin{aligned} dx/d\tau &= (x/2T_g) dT_g/d\tau - \alpha x \sqrt{T_g}, \quad x = B(\tau)/B(0) \\ (1 + x\eta/\sqrt{T_g}) dT_g/d\tau &= x(\delta T_g + \beta - \gamma) - (\epsilon + \xi) T_g + \epsilon T_m + \xi T_m' \\ dT_m/d\tau &= \eta T_g - (\eta + \lambda) T_m + \lambda T_a \\ dT_m'/d\tau &= \mu (T_g - T_m') \end{aligned}$$

Constants*

$$\begin{aligned} \alpha &= h B(0)/m_{O_2}^0 \sqrt{T_g(0)} = 0.0662 & \epsilon &= U_i A / c_g m_i = 8.46 \\ \eta &= \sqrt{T_g(0)} m_{O_2}^0 / m_{O_2} = 3.07 & \xi &= U_i A_i / c_g m_i = 8.53 \\ \beta &= B(0) / c_g m_i = 14600 & \eta &= U_i A / w_m c_m = 0.479 \\ \gamma &= h B(0) T_g(0) / m_i = 112 & \lambda &= U_o A / w_m c_m = 0.475 \\ \delta &= h B(0) / m_i = 0.204 & \mu &= U_i A_i / w_m' c_m = 0.586 \\ T_a &= 530 \end{aligned}$$

*Units: Btu-ft-hr-degrees R

Initial Conditions $T_m = T_m' = 530$ degrees R
 $T_g = 549$ degrees R.

The pressure as a function of time can very easily be calculated by the ideal gas law, $P = n_g RT_g / V$, where V is the volume of the containment building, 333,000 cu ft. The total number of gas moles can be calculated from equation (7) where n_{O_2} is given by equation (3). The maximum values of the temperatures and pressures are summarized in Table IV.

TABLE IV - Summary of Calculations

<u>Quantity</u>	<u>Max. Value^a</u>	<u>Time, hrs^b</u>
T_g , deg F	1115	0.183
T_m , deg F	253	1.0
T_m' , deg F	350	1.4
x	1.33	0.08
P , psig	25.8	0.175

a. Values from Figure 2.

b. Time at which maximum value occurs. 173 014

The peak gas temperature is very insensitive to the value of the overall heat transfer coefficient U_o , and therefore would be insensitive to the outside ambient temperature T_a . From some preliminary calculations on an outside insulated containment building, the effect on the peak gas temperature was found to be negligible. There was, however, a considerable effect on the peak metal temperature T_m . For the insulated calculation the maximum value of T_m was about 400 degrees F as compared to the 253 degrees F for the uninsulated case. In contrast to the above, a change in U_i will greatly effect the peak gas temperature. A change of 25 percent in the value of U_i will produce a change of about 25 percent in the peak gas temperature. If it is assumed, contrary to the KAPL experiment, that all of the oxygen is to react, then calculations show that the gas pressure of 26 psig may be increased to about 30 psig. One effect that cannot be simply factored into the equations is the blanketing of the burning sodium by the combustion products; this, of course, would tend to decrease the magnitude of the incident. However, this may be a relatively small effect since the peak gas temperature and pressure is obtained in a relatively short time.

It should, perhaps, be pointed out that a similar accident calculation was carried out where the sodium was assumed to burn on the top of the operating floor utilizing only the gas space above it. This results in a somewhat more severe accident giving a calculated gas pressure of about 40 psig and a gas temperature of 1660 deg F. A gas pressure of this magnitude above the reactor operating floor is completely unrealistic because of the mechanical design of the seals in the operating floor. In the reactor floor there are a number of openings to the reactor area underneath the floor which are normally sealed off by neoprene gas seals. During the course of the sodium air incident these gas seals would be destroyed, and hence the free volume underneath the floor would be available for additional expansion. Assuming the two gas volumes to mix, the resulting pressure is only 28 psig. This value is still conservative by the very nature of the problem. It can reasonably be assumed that this mixing will certainly occur before the maximum pressure is attained in the upper part of the containment vessel. If so, then there will be additional dilution of the reacting oxygen with the nitrogen below the operating floor and hence a lower gas temperature will result which will tend to give a lower burning rate, and hence a lower overall gas temperature, i.e., the hypothesized sodium-air reaction as considered in the introduction.

Sodium-Air Equilibrium Calculations

In the case of a sodium-air reaction in the containment building, it is a simple matter to calculate the maximum temperature and pressure possible. The maximum conditions are obtained by considering a constant volume adiabatic reaction of sodium and air, the extent of reaction being dictated by the chemical equilibrium relations. In order to approximate the initial conditions as they might exist in the plant, it is assumed that the sodium is initially at 800 degrees F and that the available air is present at 77 degrees F. In the equilibrium calculations the following equilibria were assumed to exist

where the K's represent the equilibrium constants. Because of the relatively high temperatures encountered above 1000 degrees K, it was assumed that sodium would form the monoxide rather than the peroxide. According to Brewer and Margrave (9) the gaseous Na_2O is of little importance, and hence its vaporization equilibrium was not considered. At the equilibrium temperatures and pressures encountered in the sodium-air reaction, all of the sodium is completely vaporized so that the equilibria represented by equation (13) can be omitted.

The method of calculation is a trial and error procedure. First, an equilibrium temperature is assumed, and then the equilibrium composition is calculated as dictated by equations (14) and (15). Once the compositions are calculated, the change in enthalpy, ΔH , going from the initial to the equilibrium conditions, can be calculated. Correcting this value of ΔH by subtracting the pressure volume product, $\Delta(pV)$, gives the change in internal energy, ΔE . Since this is a constant volume reaction, the corrected temperature is attained when ΔE is equal to zero. An example of an equilibrium calculation is given in the Appendix, and may be referred to for the detailed method of calculation.

Equilibrium calculations were carried out for various values of the initial Na/O_2 molar ratio. The pertinent results are summarized in Table V and Figure 3.

TABLE V - Sodium-Air Reaction^a

Na/O_2^b	Temp deg K	Pressure, Atm	Final Gas Moles ^c	Mole, Na_2O formed ^c
2	2004	6.59	0.980	0.176
4	2170	8.16	1.12	0.288
6	2202	9.46	1.28	0.390
8	1776	9.54	1.60	0.420
10	1315	8.24	1.87	0.420

a. Adiabatic constant volume reaction with air at 77 deg F and sodium at 800 deg F. Assuming sodium forms Na_2O .

b. Initial molar ratio.

c. Based on the initial conditions of 1 gm mole of air. The moles of Na_2O formed shows the extent of the reaction.

The maximum possible pressure and temperature possible is about 9.75 atmospheres and 2230 degrees K. This corresponds to 129 psig and 3554 degrees F. It should be noted that these peaks do not occur at the same molar ratio of Na/O_2 . The temperature does not peak at the stoichiometric amount of sodium, molar ratio $\text{Na}/\text{O}_2 = 4$, because with

increasing amounts of sodium the equilibrium in equation (15) is shifted to the right. Table V shows that at Na/O_2 equal to 4, only 0.288 moles of Na_2O are formed; whereas at Na/O_2 equal to 6, 0.390 moles of Na_2O are formed; therefore, more heat of reaction is made available in this later case. This amount of heat is more than enough to account for the heat of vaporization of the excess sodium. At a molar ratio of 8, the reaction of sodium and oxygen goes to completion utilizing the total amount of oxygen available, and hence the temperature rapidly decreases because the heat of reaction is utilized vaporizing the excess sodium. The pressure curve follows essentially the same type of reasoning, except in this case it is complicated by the fact that the amount of gaseous moles increase with an increasing molar ratio of Na/O_2 .

In the calculations of the theoretical maximum temperatures and pressures by Argonne (4), they assumed other oxides of sodium, other than Na_2O as was done in the present calculation, as their end product of combustion depending upon the initial oxygen concentration. Even after accounting for this difference their calculated theoretical temperatures appear to be too high whereas the calculated pressures appear to be in the same range as calculated in this present study. If the increase in gaseous moles was not taken into account this could explain the discrepancy. In their experimental work, as mentioned earlier, using a molar ratio of 3.14 for Na/O_2 a peak pressure of 6.4 atmospheres was obtained; this is still somewhat lower than the maximum theoretical pressure. This should point out that it is indeed difficult to attain the maximum possible pressure even with elaborate experimental methods and that in any possible accident the theoretical pressures will not be approached. The maximum pressure and temperature obtainable in this case is not particularly high, since any heat loss during the reaction will reduce the resulting temperatures and pressures. Even with the atomizing techniques used by Hines, et al., (2) in dispersing the sodium, only a 38 psig pressure was developed which means that a considerable amount of heat must be lost from the reaction.

APPENDIX

Sodium-Air Equilibrium Calculation

Consider as a basis 1 mole of air initially at 77 degrees F (25 degrees C) with a stoichiometric amount of sodium at 800 degrees F (700 degrees K). Therefore the initial composition is: 0.79 moles N_2 , 0.21 moles of O_2 and 0.84 moles of Na. The volume of the reaction chamber is given by the volume occupied by the air at 25 degrees C and 1 atm. pressure, i.e.,

$$V = nRT/\pi$$
$$= (1)(0.08206)(298)/(1) = 24.45 \text{ liters}$$

Let x be defined as the moles of $Na_2(g)$ formed by equation (14) and y the moles of Na_2O formed by equation (15), then

$$\frac{2 \text{ Na}(g)}{(0.84-2x-2y)} = \frac{Na_2(g)}{x}, K_2 \quad (16)$$

$$\frac{2 \text{ Na}(g)}{(0.84-2x-2y)} + \frac{\frac{1}{2} O_2}{(0.21-0.5y)} = \frac{Na_2O(c,l)}{y}, K_3 \quad (17)$$

where the quantities under the terms in the above equations represent the moles present at equilibrium. From the usual definition for the equilibrium constant for equation (16)

$$K_2 = p_{Na_2}/p_{Na}^2 \quad (18)$$

where the p's represent the partial pressures. Substituting for the partial pressures, $p_i = n_i RT/V$, equation (18) becomes

$$n_{Na_2}/n_{Na}^2 = K_2(RT/V). \quad (19)$$

Now substituting for the moles from (16) equation (19) becomes:

$$x/(0.84-2x-2y)^2 = K_2(RT/V) \quad (20)$$

The analogous equation for the reaction expressed in (17) is given by

$$(0.84-2y-2x)^2(0.21-0.5y)^{-\frac{1}{2}} = K_3(RT/V)^{5/2} \quad (21)$$

Values of K_2 are given by Benton and Inatomi (10) and K_3 can be determined from the free energy function, ΔF° , as given by Coughlin (4). Assuming an equilibrium temperature of 2180 degrees K gives

$$K_2 = 0.0036$$

and

$$RT/V = (0.08206)(2180)/(24.45)$$
$$= 7.32$$

Relating ΔF° and K_3 gives

$$\begin{aligned}\Delta F^\circ &= -RT \ln K_3 \\ \log K_3 &= -\Delta F^\circ / (2.303 RT) \\ &= -(4600) / (2.303)(1.987)(2180) \\ &= -0.4612 \\ K_3 &= 0.3458.\end{aligned}$$

Therefore equations (20) and (21) become

$$\begin{aligned}x / (0.84 - 2x - 2y)^2 &= 0.02635 \\ (0.84 - 2x - 2y)^{-2} (0.21 - 0.5y)^{-\frac{1}{2}} &= 51.45.\end{aligned}$$

Solving the above for x and y gives:

$$\begin{aligned}x &= 0.0019 \\ y &= 0.282\end{aligned}$$

The ΔH for the equilibrium composition can be calculated by considering the following individual reactions:

From Thomson and Garelis (11)

$$\begin{aligned}\Delta H_1 &= (0.84)(5601 - 3525) = 1744 \text{ cal} \\ \Delta H_2 &= (0.84)(23,741) = 19,942 \text{ cal.}\end{aligned}$$

Using a value of 4.968 (cal)/(mole)(deg) for the c_p for the monomer

$$\begin{aligned}\Delta H_3 &= (0.84)(4.968)(2180-1000) \\ &= 4924 \text{ cal.}\end{aligned}$$

From Benton and Inatomi (10)

$$\begin{aligned}\Delta H_4 &= (0.0019)(-18,315) \\ &= -35 \text{ cal}\end{aligned}$$

and from Coughlin (6)

$$\begin{aligned}\Delta H_5 &= (0.282)(-128,300) \\ &= -36,181 \text{ cal.}\end{aligned}$$

Using the heat capacities for oxygen and nitrogen as given in Perry's (12)

$$\begin{aligned}\Delta H_6 &= (0.21)(15,620) = 3280 \text{ cal} \\ \Delta H_7 &= (0.79)(14,550) = 11,495 \text{ cal.}\end{aligned}$$

Summing the above values of ΔH ,

$$\Sigma \Delta H = 5169 \text{ cal.}$$

For the total gaseous moles:

$$\begin{aligned}O_2 &: 0.21 = 0.5y \\ N_2 &: 0.79 \\ Na &: 0.84 = 2y - 2x \\ Na_2 &: \frac{x}{2} \\ n_0 &= 1.84 - 2.5y - x \\ &= 1.133.\end{aligned}$$

The total pressure is then given by

$$\begin{aligned}\pi &= n_0 RT/V = (1.133)(0.08206)(2180)/(24.45) \\ &= 8.29 \text{ atm}\end{aligned}$$

therefore

$$\begin{aligned}\Delta(\pi V) &= (8.29 - 1)(24.45)(24.2) \\ &= 4313 \text{ cal}\end{aligned}$$

and

$$\begin{aligned}\Delta E &= \Delta H - \Delta PV \\ &= 856 \text{ cal.}\end{aligned}$$

The assumed temperature of 2180 is too high; by assuming a temperature of 2165 a value of -387 cal is obtained. Summarizing these calculations gives

<u>T °K</u>	<u>ΔE</u>	<u>n_o</u>	<u>y</u>
2180	856	1.133	0.282
2165	-387	1.111	0.291

Linearly interpolating the above gives

$$T = 2170 \text{ °K}$$

$$n_o = 1.12 \text{ moles}$$

$$y = 0.288.$$

Therefore the calculated pressure is given by

$$\begin{aligned}\pi &= n_o RT/V = (1.12)(0.08206)(2170)/(24.45) \\ &= 8.16 \text{ atm.}\end{aligned}$$

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