MASTER

**SODIUM FIRES
AND
THE RELEASE CHARACTERISTICS
OF
PARTICULATES AND FISSION PRODUCTS**

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INTRODUCTION

In the hazard analysis of sodium-cooled reactors, a significant release of energy and radioactivity is postulated to occur from a large primary-coolant sodium fire. As the previous paper has indicated, small-capsule experiments have demonstrated the essentially quantitative trapping of iodine and other, nonvolatile, fission products following the vaporization of metallic uranium in liquid sodium. There is no reason to believe that similar trapping would not result with ceramic fuels. Furthermore, there is evidence that fission products released into sodium vapor rapidly diffuse into the liquid sodium phase. Thus, if the burning sodium contains significant quantities of fission products, the radiological hazard could depend on the quantity of these contaminants which is released as a result of a fire.

Studies are under way at Atomics International, sponsored by the Division of Reactor Development of the U. S. Atomic Energy Commission, to provide information characterizing sodium fires. These studies will determine (as a function of time) the influence that initial condition variables and system design parameters have on: (1) the combustion energy release and its spatial distribution; (2) the amount of sodium released (presumably as sodium oxide); and (3) the amount of fission products released. Complementary investigation will characterize the subsequent temporal and spatial distribution of released sodium, and of any concomitant fission products, in order to assess the availability of the fire effluvia for dispersion to the environment. The results of these studies would ultimately lead to the design of engineered safeguards which could prevent, inhibit, or mitigate against any hazardous sequence of events following a major sodium fire.

About a year ago, quantitative burning experiments began to indicate the nature of sodium burning and fission product release in sodium pool burning in air. An initial oxide crust which clings to the wall, falls into the molten pool. The bulk pool temperatures stabilizes at about 1200 to 1300° F with a maximum temperature above the surface of the pool being between 1600 and 1800° F. The oxide continues to fall through the pool and builds up from the bottom until it penetrates the lowering liquid surface. As smoke production abates, a hard glassy mass forms over the

surface, apparently quenching the fire. The greatest portion of the solid residue, that beneath the white oxide crust, is 60 to 80% sodium oxide.

Small-scale (3 to 7 gm) sodium-fire experiments using sodium iodide tracers at ~300 ppm indicated a concentration of iodine in the oxide phase and a corresponding reduction in the metallic phase: Only sodium iodate and sodium iodide could be detected in the release effluvia - not free iodine. The extraction of iodine from the metallic phase was further demonstrated in an experiment in which a sodium and sodium-iodide mixture was filtered through a bed of sodium oxide. The iodine content of the original mixture was reduced from 300 ppm to zero.

Thus, we can postulate that the oxide phase in a sodium fire will contain much of the iodine originally dissolved in the sodium. If, during a sodium fire, oxide falling through the molten pool scavenges iodine (and perhaps other fission products), oxidation during the latter part of the fire will occur at the surface of sodium depleted in iodine compared to the concentration during the first part of the fire.

Since the time of the small-scale fire tests, our investigation has continued in four concurrent phases:

- (1) the analysis of energy transfer and mass transport processes based on the physical and chemical characteristics of sodium fires with contained fission products;
- (2) the development of models of large sodium fires to direct the accumulation of meaningful data which could be applied to the design and analysis of real systems;
- (3) laboratory experiments to aid in the understanding of mechanisms, to permit calibration of instruments, and to establish the feasibility of developing information on a small-model basis;
- (4) field experiments with large fires to test the influence of important variables, verify modeling, and develop scale-up procedures.

Ultimately, full-scale or very-large fires may be required to proof test the modeling laws developed. It would be impossible to report to you in detail on all of the work which has been and is being conducted, so let us just mention only a few highlights in each of these areas.

PHYSICAL AND CHEMICAL CHARACTERISTICS

The analytical model characterizing a sodium fire includes initial-condition independent variables such as geometries, temperatures, pressures, reactant concentrations, forced convection, etc. The consequences-of-concern resulting from interaction of these variables are the dissipation of the energy generated (i. e. , the possibility of pressure generation) and the distribution of reaction products (i. e. , the dispersion of radioactivity).

Some important properties of sodium (Table I) provide an insight to the nature of the reactions which take place. Examination of the energy heat-capacity relationship show that, if the reaction were to occur solely in the liquid phase, the heat of combustion would result in a calculated liquid-temperature rise of more than 10,000°F. If this energy were expended solely in vaporization, the sodium would vaporize at more than twice the measured reaction rate and, due to the good heat transfer properties of sodium, there would be large increases in bulk temperature. If the reaction were to occur solely in the gas phase, there would be a temperature rise of 7000°F under adiabatic conditions.

Since the maximum temperatures measured in the liquid phase are below 1300°F and in the gas phase do not exceed approximately 1800°F, it is apparent that there is a large amount of thermal energy which must be transported within the system. Since, after an initial period, the reaction rate is almost constant, the hypothesis is that mass transport takes away the heat in the vapor phase and that vaporization takes away the heat in the liquid. The resulting hypothesis is that the reaction takes place primarily in the vapor phase with no more than one-third of the reaction taking place at the liquid surface. The reaction rate is thus a function of the vaporization rate of sodium controlled by the rate of transport (including diffusion) of oxygen into the reaction zone.

TABLE I
THERMAL PROPERTIES OF SODIUM

PARAMETER	METRIC UNITS	ENGINEERING UNITS
Melting Point	98°C	208°F
Boiling Point	880°C	1620°F
Specific Heat	0.3 cal/gm-°C	0.3 Btu/lb-°F
Heat of Vaporization	1100 cal/gm	2000 Btu/lb
Heat of Combustion		
Na ₂ O as Product	2280 cal/gm	4100 Btu/lb
Na ₂ O ₂ as Product	2700 cal/gm	4850 Btu/lb

Figure 1. Comparison of Burning Rates of Sodium, Liquid Hydrogen, and Six Hydrocarbons

Figure 2. Sodium-Coolant Accident Diagram

When heat transfer in large pools of liquid burning in quiescent air is predominantly radiative from the flame to the liquid surface, Burgess, Grumer, and Wolfard have suggested (Figure 1), that the burning rate is proportional to the ratio of the heat of combustion to the heat of vaporization. A test of this, comparing the burning rates of sodium with liquid hydrogen and six hydrocarbons, shows good agreement. Note that the burning rate and the energy release rate for sodium are much lower than are those for hydrogen and hydrocarbons.

MODELING OF SODIUM FIRES

As a result of a large amount of research, experience, and hazard analysis of water reactors, there is a tendency to equate the maximum credible accident (and subsequent mechanisms of radioactivity dispersion) of water-cooled reactors to sodium-cooled reactors. They are not, as consideration of the sodium-coolant accident diagram (Figure 2) shows. The sodium-cooled reactor has a maximum outlet temperature 400 to 600°F below the boiling point of sodium. Due to the low vapor pressure of sodium at these temperatures, the reactor operates at essentially atmospheric pressure. Consequently, following a loss of primary system integrity, there is no immediate release of large quantities of stored energy; on the other hand, sodium can burn. If the reactor cavity and equipment vaults were filled with inert gas, there would be no oxidation and only the latent heat in the sodium would require accommodation. If the cells were filled with air, the reaction would be limited by the amount of oxygen present and the question would become one of reaction rate in a depleting oxygen environment.

It is apparent that flow, and thus mass transport of radioactivity, from the cells to the containment space (or between cells for pressure relief) is dependent on both the pressure differential and the geometry of the opening. The pressure differential is a function of the energy available and its transfer between components of the system, walls or surfaces, air, sodium, and sodium oxide. The openings have dimensions of both area and length. The area can range from about almost zero (in a closed cell) to an opening much larger than the area of the sodium (i.e., unlimited air access). The length can range from essentially zero (i.e., an opening in a wall) to very long (i.e., piping between cells).

Figure 3. Deposition of Sodium Oxide Particles (x450)
in Settling Chamber

The extent of the reaction and the reaction rate are dependent on the accessibility of oxygen to the reaction zone. It is significant that oxygen flow to the reaction zone is countercurrent to the mass flow from the reaction zone. Thus it would appear to be possible to design a system in which the passive elements of the system (i. e., the geometrical arrangement) could be used to effectively control or at least inhibit reaction rates. The resulting reduction in mass transport could be supplemented by active elements such as heat-removal, inert-gas, or air-cleaning systems.

In this discussion, any fission products present in the sodium could be presumed to follow the sodium oxidation products. This may be true of transport; however, the release may not be proportional to the sodium due to chemical or physical reactions with other fission products, sodium, oxygen, or surfaces within the system and the scavenging action of sodium oxide. The release rate is particularly significant due to the quantitative trapping of fission-products by sodium.

LABORATORY EXPERIMENTS

Other passive elements of the system also act to reduce the availability of sodium oxide particles (and any concomitant fission products) for dispersion to the environment. Imagine a reactor cell or containment space as being a huge reaction chamber; then, particles injected into this chamber will agglomerate, fall out, deposit on surfaces, or be swept into the air-cleaning system and the remainder will be transported through the stack or openings in the containment to the environment for further dispersal. Elementary considerations of a major sodium fire postulated to occur in a typical containment space show that the decrease in mass availability occurs much more rapidly than leakage through the containment.

Smoke collected from gram-size fires in a 1-ft high settling chamber (Figure 3) indicate rapidly decreasing airborne particle sizes and concentrations. The time for the airborne concentration to decrease to one-half the original value was typically less than one hour. A Royco Particle Size Analyzer was used to determine the relative particle size

Figure 4. Airborne Sodium Oxide Particle Distribution and Size

Figure 5. Laboratory Sodium-Burning Chamber

Figure 6. Results of One Sodium-Burning Experiment

distribution (Figure 4) near the bottom of the settling chamber as a function of time. The maximum particle size measured was approximately 3 microns, and there was a significant reduction in the size of the particles remaining airborne.

In order to study particle production mechanisms, size distribution dependence, and removal phenomena, a laboratory sodium-burning chamber (Figure 5) was constructed. The main chamber is 6.5 ft high and 3.0 ft in diameter and has provisions incorporated for controlling and sampling the chamber atmosphere. The sodium is contained in a separate small container (within the main chamber) with provisions by which the sodium can be heated and the burning initiated from outside the large chamber. Plating and fallout strips can be inserted and removed through external sampling ports during experiments.

The results of an experiment (Figure 6) with 179 gms of sodium at 1000°F in the bottom of the laboratory burn chamber is typical. The initial oxygen concentration was 1.3% by volume; the initial water vapor concentration was 650 ppm by weight which corresponds to 3% relative humidity at 80°F. The final oxygen concentration was ~0.8% and the final humidity 250 ppm. About 30 to 33 gms of sodium oxide was produced. The fraction of sodium oxide released (airborne) was approximately 20%. Airborne concentrations were measured periodically 3 ft from the top of the chambers with midget impingers filled with water.

The maximum concentration of $5\mu\text{gm/cc}$ was reached at the sample position in 20 minutes and there was no further evidence of reaction. Subsequently, the mass concentration decreased 50% in 30 minutes; in 3.5 hours, the mass concentration decreased to 1%; and at 6.0 hours the concentration was 0.2%.

The initial airborne distribution was calculated with tranquil settling assumed. The data indicate a log normal distribution with a Stokes equivalent mass median diameter of 2.5 microns. This corresponds to a number median diameter of 1.1 microns (or about 5×10^5 particles per cc if all were assumed to be 1.1 microns). This is approximately the same concentration postulated to occur in a major sodium fire in a

Figure 7. Early Experiment with Large Quantity of Sodium

Figure 8. Sodium Residue from Early Experiment

Figure 9. Burning Sodium and Sodium-Oxide Fumes

Figure 10. Burnpot and Sodium Residue

typical cell under similar initial conditions. In a 30-ft high cell, the relative mass concentration would be expected to decrease at a rate about one-tenth of the experimental rate. This is 300 to 350 times faster than in a cell which leaks 1% per day. Thus, the half-time would be about 5 hours. In 24 hours, the mass concentration would decrease to 3.5% of its original maximum.

No evidence of agglomeration effects was noticed during preliminary examination of the data. Consideration of the agglomeration rate at the large mass concentration which existed, indicates that the time to reach a number median diameter of one micron would be short compared to the 20 minutes required to reach maximum concentration in the burning chamber.

LARGE FIRES

Since the "maximum" fire in a sodium-cooled reactor is postulated to involve many thousands of pounds of sodium, small fires involving grams of sodium do not provide adequate verification of modeling laws. Early burning experiments (Figure 7) with large quantities of sodium (35 to 170 pounds) and unrestricted access to air, indicated a release (as sodium oxide) of less than 40% of the sodium burned (Figure 8). An oxide crust was apparent after the fire was completed. The greatest portion of the residue, originally thought to be unburned sodium because of its silvery color, is 60 to 80% sodium oxide. In a typical pool fire, the sodium burns over the entire surface (and very near the surface) with copious fumes (Figure 9) of oxide being released. As smoke production abates near the end of the fire, an oxide crust forms and yellow peroxide formation at the surface is noted. The residue remaining in the burnpot (Figure 10) contains about two-thirds of the original sodium, approximately one-quarter of which is unburned.

However, studies of the safety requirements for economic sodium-cooled reactor systems indicated the need for more accurate values of burning and release rates and for information on the effect of reduced oxygen concentration on energy release and mass transport. Information is also needed to model enclosure effects including the natural

Figure 11. Scheme of Burn-Test Chamber and Associated Equipment

Figure 12. Photograph of Burn-Test Chamber and Associated Equipment

convection velocities of full-scale fires and the temporal and spatial distribution of energy and matter. As a result, an improved installation for determining such characteristics (Table II) of large sodium fires was designed and constructed. Emphasis was placed on good instrumentation to determine: material and energy balances; sodium burning rates; and accurate values for the release and distribution of sodium oxide and any associated fission products.

The burning chamber (Figures 11 and 12) is 5-1/2 ft in diameter, 5 ft deep, and is provided with a conical cover containing four air-inlet holes. The chamber can accommodate burn pots containing up to 3000 lbs of sodium. A 10-in. diameter pipe connects the top of the cone to a wet-scrubbing system to remove released matter from the effluent stream. A positive displacement blower is used to control flow and to eliminate pressure fluctuations. This also keeps the system at negative pressure to minimize dispersion of material to the environment. The effluent air velocity and oxygen concentration can be measured. Effluent sampling points throughout the system may be used to determine materials released and transport phenomena. A 2000-gallon supply tank supplements the water in the scrubber to ensure adequate caustic dilution. During an experiment, samples of the cleaning system liquor are taken to determine the amounts of sodium and radioactive tracers released. Chamber wall, sodium, and air temperatures are continuously recorded to aid in determining heat balances and burning rates.

In the first experiment conducted in the system, 615 lb of sodium were placed in a heavily thermocoupled 2-ft diameter by 4-1/2-ft deep burnpot, Figure 13, (4 ft depth of sodium) with one gram of NaI containing 6.5 mc of I-131. The space between the burnpot and the chamber was filled with vermiculite insulation; the conical lid was placed on the chamber; the cross-over piping was put in place; and the system was flooded with nitrogen. The heaters were energized but the heater leads failed at 350°F. The system was then purged with air and the sodium was agitated to cause ignition at this temperature. The air flow was set at 140 cfm (about 7 ft/min over the surface of the fire). Thermocouple readings (Figure 14) in the wall of the burnpot indicated the temperature distribution in the sodium. Thermocouples located near

Figure 13. Burnpot in the Large Sodium-Burning Test Equipment

Figure 14. Burnpot Temperature Profiles

TABLE II

SODIUM FIRE VARIABLES

ITEM	DESIGN VARIABLE	PARAMETER
Sodium Container	Geometry	Diameter Height Insulation
	Properties	Material Insulation
Sodium	Geometry Pressure Temperature Surface Condition	Weight Initial Pressure Initial Temperature Oxide Crust
Enclosure	Geometry	Size Air Flow O ₂ Content
	Leak Tightness	Pressure Air Inlet Size Air Flow O ₂ Content
	Properties	Material
Air	Temperature Pressure Humidity Flow O ₂ Concentration	Temperature Pressure Humidity Flow O ₂ Concentration

Figure 15. Conical Top of Sodium-Burning Test Equipment

Figure 16. Burnpot Section of Test Equipment

Figure 17. Temperature Profile of Burning

Figure 18. Burning Rate and Release Rate for Sodium

the top of the burnpot indicated a rapid temperature rise from 350 to well over 1000°F. Subsequently, thermocouples at lower positions indicated similarly. Since the duration of the fire was about 30 hours, the bulk sodium temperature was over 1000°F during most of the experiment. Scrubber air and sodium samples were taken during the fire. The equipment was dismantled (Figures 15 and 16), visually inspected, and oxide deposits were taken for analysis.

The temperature near the surface, measured with an optical pyrometer, was approximately 1600°F. Temperature profiles (Figure 17) taken with a thermocouple probe indicated a temperature of 1800°F in a narrow band just above the sodium surface.

The burning rates (Figure 18) (determined by the decrease in sodium depth as indicated by wall thermocouples), oxygen depletion (measured with the oxygen analyzer), and heat balance calculations are in good agreement — an average of 6.2 lb/hr-ft² between the 2nd and 17th hours. The release rate of sodium was determined from the concentration of sodium in the cleaning system. The release rate averaged less than 30% of the burning rate.

The iodine release rate was determined from the activity in the sodium samples and the scrubber samples (Table III). About 90% of the iodine accounted for remained in the residue. The 10% iodine released is in contrast to the 30% sodium released. The concentration of iodine released with sodium oxide was about one-third of the original concentration in the liquid sodium.

No iodine or sodium was detected in high volume air samples taken at the stack exhaust. However, it was possible to measure the concentration of iodine and sodium in the condensate of the hot moisture-laden air from the scrubber. If the only iodine and sodium released from the scrubber were associated with this vapor, the efficiency of the scrubbing system for iodine would be 99.99% and for sodium 99.88%.

0 TIME

STAGE 2

2 MINUTES LATER

STAGE 3

8 MINUTES LATER

30μ

(STAGE 4 OF SAMPLE NO. 1)

STAGE 4
SAMPLE 9B

30μ

Figure 19. Cascade Impactor Data on Particle Size and Distribution

TABLE III

IODINE AND SODIUM MATERIALS BALANCE

SAMPLE DESCRIPTION	I-131 (μ c)	Na (lbs)
Remaining in burnpot in solution	2800	334
Remaining in burnpot as precipitate	1039	35
Leak from burnpot in solution	76	37
Leak from burnpot as precipitate	460	0
Scrubber and bubbler solution	465	132
Scrubber and bubbler precipitate	34	0
Plated on pipes and cone	26	35
Scrubber and bubbler; escaped from burnpot during dissolution of Na ₂ O	48	4
	—	—
TOTAL	4948	577

Particle size distribution measurements (Figure 19) were made during the fire with a cascade impactor. Samples taken directly over the surface of the sodium (Sample No. 1) through an 8-ft long sample-tube had a mass median diameter of less than one micron. These samples clearly indicate the deliquescent nature of small Na_2O particles. Samples taken just upstream of the bubbler (Sample 9B), are larger than those taken just downstream from the burning sodium surface. These results tend to confirm the particle phenomenology observed in laboratory-scale fires.