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"SODIUM-CONCRETE REACTIONS, LINER
RESPONSE, AND SODIUM FIRE EXTINGUISHMENT"

by R. K. Hilliard

Hanford Engineering Development Laboratory

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I. INTRODUCTION

The effects of a reaction between sodium and concrete may be important to the radiological consequence assessment of hypothetical accidents in LMFBR's from two standpoints. First, the water in the concrete structures surrounding the reactor may migrate during off-normal high temperature conditions to areas where it can react with sodium leaked from the reactor as a result of the accident. The resulting hydrogen poses a threat to the integrity of the containment building both by increasing the pressure due to the addition of a non-condensable gas and by the potential heat release due to a hydrogen conflagration. Secondly, if the spilled sodium contacts the concrete directly, solid components in the concrete may react exothermally to contribute to the overall heat release and sodium boil-off. Although LMFBR plants are designed to prevent escape of sodium from the primary sodium boundaries and, in addition, are designed to prevent direct contact of sodium with concrete in event of the remote possibility of a sodium spill, an evaluation of the potential consequences of a sodium-concrete reaction is necessary to complete the assessment of the accident consequences.

Steel liners are provided in reactor cavities, vaults, and equipment cells and in the head compartment area. An assessment of the extent of protection afforded the concrete by these liners is necessary, as well as an evaluation of the effect of a sodium spill on the liner itself.

Finally, in event of a release of sodium into an atmosphere which contains oxygen, a sodium-oxygen reaction would occur. An assessment of sodium fire extinguishment systems and techniques may be important in some accident evaluations.

A review of the current status of technology in each of these three areas is given in this paper. Information that has been documented previously is only briefly discussed. Because of the

author's greater familiarity with work performed at the Hanford Engineering Development Laboratory (HEDL), this is presented in greater detail. It is possible that recent work at other laboratories may have been overlooked.

II. SODIUM-CONCRETE REACTIONS

A. Background

Very little information is available in the literature regarding the reaction of sodium and concrete. Accidental spills of sodium onto concrete surfaces during normal plant or laboratory operations have been limited to small quantities, generally at relatively low temperatures, and have caused only minor damage. The largest known accidental spill in the U. S. occurred in the EBR-II secondary system and involved 80 gallons of sodium at 500°F falling onto a bare concrete floor.⁽¹⁾ Flames, reported to have reached the ceiling, presumably were due to combustion of hydrogen formed by the reaction of sodium with water in the concrete. The fire was extinguished by manual application of Met-L-X powder and the concrete floor was found to be spalled to a maximum depth of one inch.⁽¹⁾

The French performed large-scale sodium fire extinguishment tests involving the rapid spill of 400-lb quantities of sodium at 930°F onto a 13-ft² concrete surface.⁽²⁾ Although damage to the concrete was not discussed, flames were reported to reach several feet above the surface of the pools indicating that hydrogen combustion occurred. The British reported that 28-day cured conventional concrete with granite aggregate was spalled to a depth of one inch when 50 lb of sodium at 1040°F was spilled on a 2.25-ft² surface in air, but that the damage appeared to be caused by thermal stresses rather than chemical reaction.⁽³⁾ No information on hydrogen formation was reported. Nelson⁽⁴⁾ reported minor spalling of concrete with some generation of hydrogen when 3-9 lb of 1100°F sodium was spilled on 1-ft² of bare concrete in atmospheres containing 2-5% O₂. No damage was observed when 500°F

sodium was spilled on bare concrete or when 1100°F sodium was spilled on concrete lined with 1/8-inch steel. The concrete had aged 7-8 years.

Hassberger, et al⁽⁵⁾ reported the results of five small-scale tests where 2-23 lb of sodium was spilled onto bare concrete in 1-2% O₂ atmosphere and the sodium heated electrically to 1200-1500°F for 4-20 hr. Both conventional (SiO₂ sand, basalt aggregate) and high density (magnetite sand and aggregate) concrete were used. The water content of the 6-12 inch thick concrete specimens was essentially completely released, forming 0.4 to 1.0 mole H₂ per mole released H₂O. Sodium had penetrated to approximately 1-inch depths except in one case where the concrete cracked and sodium penetrated to 2.3 inches. Magnetite concrete cubes with ~ 1.25 inch dimensions reacted completely within ~ 12 minutes when dropped into 1200°F sodium, releasing approximately 800 Btu/lb concrete.

Hilliard and Yatabe⁽⁶⁾ reported that a 4-inch thick slab of conventional concrete was extensively damaged by a spill of 700 lb of 1100°F sodium directly onto a 32-ft² concrete surface. All of the water in the concrete was released and high concentrations of hydrogen (25% maximum) were observed in the cell atmosphere. The concrete had disintegrated to a considerable extent, believed due to the combined effects of thermal stress and chemical attack to form sodium silicate.

The conclusions which can be drawn from the information available in the literature are that: (1) sodium can potentially react exothermally with both the water content and some of the solid constituents of concrete, (2) appreciable quantities of hydrogen can be generated by the sodium-water reaction, (3) the hydrogen will burn in air atmospheres, producing flames to significant elevations above the sodium surface, (4) the hydrogen will accumulate in enclosures with < 5% O₂ atmosphere, and (5) a size scale effect may exist. Insufficient information is available to establish

the effects of concrete type, concrete size (surface area and thickness), reinforcing steel, concrete curing time, temperature, time at temperature, and oxygen concentration in the cell atmosphere on the kinetics of the reactions.

B. Solid Reactants

1. Stoichiometry

The important reactions which can occur between sodium and various constituents of concrete are listed in Table I. The heats of reaction shown in Table I were calculated from standard heats of formation.^(7,8) Other minor constituents in concrete; e.g., SO_3 ; may also react, but from a consideration of free energies, the remaining components should not react with sodium. The reactions in Table I can be divided into two groups according to the mobility of the concrete reactant. The first three reactions concern the reaction with water or hydrogen, which are mobile and thus can occur outside the concrete boundary. The remaining reactions concern solid reactants and thus must take place within the concrete matrix, with sodium being the mobile reactant. Some of the reaction products may be liquid under some conditions. The reactions producing sodium silicate are merely representative of a wide number of reactions producing $\text{Na}_2\text{O} \cdot (\text{SiO}_2)$.

2. Differential Thermal Analysis Results

Samples of conventional (SiO_2 , Basalt) concrete and high density (magnetite) type M-225 were analyzed by Westinghouse Research Laboratory ⁽⁹⁾, using a differential thermal analysis (DTA) technique. Figure 1 gives the results and includes those of samples of Portland cement, SiO_2 sand, and standards of Fe_3O_4 and NiO . The endotherms at $\sim 100^\circ\text{C}$ are due to the latent heat of fusion of the sodium. The exotherm for standard concrete occurred at 634°C (1170°F); for magnetite concrete it occurred at 464°C (870°F).

TABLE I

SODIUM-CONCRETE REACTION EQUATIONS

				$-\Delta_{H^{298}}$ <u>Btu/lb Na</u>
(1)	$2 \text{ Na}_{(1)} + \text{H}_2\text{O}_{(g)}$	$\rightarrow$	$\text{Na}_2\text{O}_{(c)} + \text{H}_2(g)$	1680
(2)	$\text{Na}_{(1)} + \text{H}_2\text{O}_{(g)}$	$\rightarrow$	$\text{NaOH}_{(c)} + 1/2 \text{ H}_2(g)$	3530
(3)	$\text{Na}_{(1)} + 1/2 \text{ H}_2(g)$	$\rightarrow$	$\text{NaH}_{(c)}$	1100
(4)	$4 \text{ Na}_{(1)} + 3 \text{ SiO}_{2(c)}$	$\rightarrow$	$2 \text{ Na}_2\text{SiO}_{3(c)} + 3 \text{ Si}_{(c)}$	2220
(5)	$6 \text{ Na}_{(1)} + \text{Fe}_2\text{O}_{3(c)}$	$\rightarrow$	$3 \text{ Na}_2\text{O}_{(c)} + 2 \text{ Fe}_{(c)}$	1350
(6)	$2 \text{ Na}_{(1)} + \text{FeO}_{(c)}$	$\rightarrow$	$\text{Na}_2\text{O}_{(c)} + \text{Fe}_{(c)}$	1420
(7)	$\text{Na}_2\text{O}_{(c)} + \text{SiO}_{2(c)}$	$\rightarrow$	$\text{Na}_2 \text{ SiO}_{3(c)}$	2630

FIGURE 1. Differential Thermal Analysis (DTA) Curves Obtained for 200 mg. Samples in Excess Sodium (1000 mg). Nickel Sample Container with Argon Cover Gas

While the authors consider these results to be only semi-quantitative, they provide a rough estimate of both the heats of reaction and the temperature at which the reaction becomes significant.

3. Heats of Reaction

The heats of reaction were calculated from the DTA data in Figure I, using calibration data provided by known weights of Fe_3O_4 and NiO . The heats of reaction are listed in Table II, along with those calculated from standard thermochemical properties and assumed compositions of the concrete and other reactants. The data from test S7 reported by Hassberger, et al⁽⁵⁾ also permits an estimate of the heat of reaction. In this test, lumps of magnetite concrete were dropped into an isothermal sodium pool at 1200°F. The temperature response is shown in Figure 2. The 45°F temperature difference existing in the sodium pool prior to concrete dump was due to the electrical heating system. Immediately after dropping the 2 lb of concrete into the sodium, the upper portion of the pool decreased momentarily by 35°F, then rose for an overall gain of 150°F during the next 12 minutes. The lower pool immediately increased by 165°F. The electrical heating power was maintained constant during the entire period, and the pool temperature eventually returned to the pre-test conditions.

The calculated heat of reaction, 700 ± 350 Btu/lb concrete, agrees fairly closely with the values calculated from the DTA data and from the heats of formation. The heat generation rate was $10,000 \pm 5000$ Btu/hr-ft², based on a 12-minute reaction time and the initial surface area of the concrete lumps.

4. Penetration Into Concrete

The HEDL small-scale tests⁽⁵⁾ showed that the rate of penetration of sodium into the concrete was highly time

TABLE II

HEATS OF REACTION

	<u>Calculated*</u>	<u>Westinghouse Research Lab</u>	<u>HEDL TME 74-36</u>
Magnetite Concrete	1050	900 $\pm$ 270	700 $\pm$ 350
Conventional Concrete	770	240 $\pm$ 240	-
Sand	1130	820 $\pm$ 820	-
Portland Cement	98	50 $\pm$ 50	-

*Calculated from Standard Thermochemical Properties. Expressed as Btu per lb concrete.

FIGURE 2. SODIUM POOL TEMPERATURE TRANSIENTS CAUSED BY DROPPING CONCRETE INTO SODIUM POOL

HEDL 7506-127.19

dependent as long as the concrete did not crack. Figure 3 shows the test article from test S8 after exposure to 23 lb of sodium at 1220°F for ~20 hr. The concrete surface was horizontal in this test. The reaction products, with a density of 2-3 g/cm³, formed a compact layer on the surface and extended into the concrete to a maximum depth of 1.3 inch. The concrete below this reaction product remained hard and strong, as determined by the difficulty in breaking with a chisel.

Two tests (S9 and S10) were performed in which intentionally defected liners separated the sodium from vertical magnetite concrete surfaces. Figure 4 is a schematic sketch of the test configuration. Defects were made in the liner both below and above the level of the sodium pool. Test S9 was performed with 1380°F sodium for 19 hr; S10 was with 1620°F for 2.8 hr. The concrete did not crack in either test.

The measured penetration distances into concrete for all the tests where concrete was exposed directly to sodium are listed in Table III. The approximate time that the sodium was maintained above the reaction exotherm temperature (as determined by the DTA data) are also tabulated. The penetration rates shown in Table III were calculated by dividing the penetration distance by the reaction time, and are subject to probable errors of ± 100%.

The data of Table III are shown in Figure 5 as a plot of penetration distance versus time. The two tests where concrete cracked (F1 and S4) gave results lying considerably above the other tests. Test S9, the defected liner test with no gap between liner and concrete, gave results lower than the others. The remaining tests can be correlated by a straight line having the following empirical equation:

$$y = 0.6 t^{0.25} \quad (1)$$

Figure 3. Penetration of Magnetite Concrete
by Sodium - Test S8.

FIGURE 4. TEST ARTICLE FOR DEFECTED LINER TEST S10

TABLE III

SODIUM PENETRATION INTO CONCRETE

<u>Test</u>	<u>Penetration Inches</u>	<u>Time NA Above Reaction Exotherm⁽¹⁾ HR</u>	<u>Approx. Rate FT/HR</u>	<u>Remarks</u>
S1	0.8	5	0.01	Conventional Concrete
S2	1.0	7	0.01	Magnetite Concrete
S4	2.3	7	0.03	Magnetite Concrete
S7	0.4	0.2	0.17	Lumps Dropped in Pool
S8	1.3	20	0.005	Magnetite Concrete
S9	0.7	28	0.002	Defected Liner
S10	1.3	15	0.007	Defected Liner
F1	4.0	2.5	0.13 ⁽²⁾	Large-Scale Test, Conventional Concrete

(1) 1170°F for conventional concrete,
870°F for magnetite concrete

(2) 0.9 FT/HR calculated from thermo-
couple exotherms

FIGURE 5. CONCRETE PENETRATION TIME DEPENDENCE

where y = penetration distance, inches

t = time concrete exposed to sodium at
temperatures above the exotherm, hr

Equation (1) is based on too few tests to have a high confidence level, but it does indicate that the reaction of sodium with solid components in concrete is very time dependent. The reaction rate, obtained by differentiating Equation (1), is plotted in Figure 6. This figure shows that the rate of chemical reaction decreases rapidly with time if the concrete or reaction product barrier is not cracked to expose fresh surface.

5. Composition of Reaction Products

The nominal composition of the conventional concrete used in these tests is shown in Table IV. The composition of the reaction product shown in Table IV were determined by analyzing for metallic elements and assuming the oxide form. The Na_2SiO_3 was determined by leaching the soluble Si compounds from the reaction product mixture with water. Table IV shows that most of the SiO_2 was reacted, but very little of the iron oxides. This may be explained by the fact that most of the iron oxides are present in the aggregate, which did not react significantly due to its low surface to volume ratio. The reaction product consisted chiefly of sodium oxide and sodium silicate, with some unreacted concrete components interspersed.

Table V give similar data for magnetite concrete. The magnetite (Fe_3O_4) sand was probably completely reduced to FeO and perhaps partially to metallic iron. The magnetite aggregate may also have reacted extensively. Much less sodium silicate was present in the reaction product because of the small amount of SiO_2 in the concrete.

CONCRETE-SODIUM REACTION RATE

Figure 6.

HEDL 7506-127.1a

TABLE IV

COMPOSITION OF CONVENTIONAL
CONCRETE (1) AND REACTION PRODUCTS

	<u>Weight, %</u>	
	<u>Fresh Concrete</u>	<u>Sodium Reaction Product</u>
SiO ₂	54.5	3.2
CaO	15.2	4.2
Al ₂ O ₃	10.5	
FeO, Fe ₂ O ₃	6.6	9.7
MgO	3.2	0.8
Na ₂ O, K ₂ O	3.4	60.0
SO ₃	0.3	
H ₂ O	6.0	0
Na ₂ SiO ₃	0	17.4
Other	<u>0.3</u>	<u>4.7</u>
	100.0	100.0

(1) Type C1-P

TABLE V

COMPOSITION OF MAGNETITE
CONCRETE ⁽¹⁾ AND REACTION PRODUCTS

	<u>Weight, %</u>	
	<u>Fresh Concrete</u>	<u>Sodium Reaction Product</u>
SiO ₂	2.4	1.7
FeO, Fe ₂ O ₃ , Fe ₃ O ₄	85.6	41.7
CaO	6.6	2.8
Al ₂ O ₃	0.38	0.5
MgO	0.10	0.7
Na ₂ O	0.04	48.1
SO ₃	0.21	
H ₂ O	4.45	0
Na ₂ SiO ₃	0	2.0
Other	<u>0.11</u>	<u>2.5</u>
	100.00	100.0

(1) Type M-225

6. HEDL Large-Scale Test F1 Results

Test F1 was performed chiefly for fire extinguishment information, but it produced valuable information concerning the reaction of sodium with concrete. In test F1 approximately 700 lb of 1100°F sodium was spilled onto a 4-inch thick reinforced slab of conventional concrete. After being quenched to 900°F by the cold steel walls of the catch pan, the sodium pool temperature slowly increased due to the exothermic reactions with the oxygen in the cell air and probably by reaction with water released from the concrete directly into the sodium which formed a 5-inch deep layer covering the entire concrete surface.

Figure 7 shows a plot of the concrete temperature at various depths below the surface. The temperature of the sodium pool is also plotted. The concrete temperature gradually increased in a manner consistent with conductive heat transfer. However, when the sodium pool temperature reached 1130°F, the thermocouple at 1 inch below the surface increased very rapidly to ~ 1500°F, approximately 400°F above the sodium temperature. This indicated that an exothermic reaction occurred at the 1-inch depth which generated heat considerably faster than it was lost by heat transfer to cooler regions. At 9 minutes later, the temperature 2.5 inches below the surface exhibited a similar excursion, followed 7 minutes later to a somewhat lesser extent by the thermocouple located 4 inches below the surface.

Taking the time period between the temperature excursions as an indication of the reaction front, a penetration rate of approximately one foot per hour was calculated. It is noteworthy that the sodium-concrete reaction occurred after the oxygen concentration in the cell atmosphere had decreased below 5%.

FIGURE 7. CONCRETE TEMPERATURE EXCURSIONS IN TEST F1

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Post-test examinations of the concrete revealed that the concrete was almost completely disintegrated and sodium had penetrated to the full 4-inch depth. The basalt aggregate remained largely unreacted.

Since test F1 used a relatively thin slab of concrete, the possibility exists that the concrete was broken by mechanical stresses induced by warping of the steel pan. However, the uniform times of the thermocouple excursions indicate a progressive attack rather than an instantaneous cleavage of the full 4-inch-thick slab. Localized stresses caused by the non-typical geometry may have caused small-scale spalling events to occur on a broad front. It is possible that the added rigidity of a thicker mass of concrete would prevent such spallation.

C. Water Release From Concrete

1. Water Released by Heating Concrete Without Sodium

Water is present in concrete in two forms: untrapped free water and chemically bound water.⁽¹⁰⁾ Other terms are used to express these two types of water. Free water is synonymous with capillary, adsorbed and evaporable water. Bound water is synonymous with water of hydration, gel water, and combined water. The bound water content increases with curing time, though very slowly after the initial 30 days. The free water is reversibly adsorbed in the capillaries and pores, and thus is dependent on the moisture concentration in the atmosphere at the concrete-gas interface. The total water content varies with concrete type, age and atmosphere conditions, ranging from 7 to 11 lb/ft³.⁽¹⁰⁾ Approximately half of the total water is in each form.

Figure 8 illustrates how the free water can be released from concrete by being exposed to a dry gaseous atmosphere. The data in Figure 8 were obtained by breaking 1-lb specimens into particles ranging from dust to 3/4-inch diameter, passing dry nitrogen sweep gas over the sample while maintaining isothermal conditions, and collecting and weighing the released water as a function of time. The water loss at room

FIGURE 8. MOISTURE LOSS FROM CONCRETE EXPOSED TO DRY NITROGEN

temperature amounted to 3.7% of the specimen weight after 8 days, approximately 58% of the total water content. The decreasing rate of release indicates that the release rate is controlled by mass transfer. A massive concrete structure would lose its water much more slowly, though at high temperatures the rate may be appreciable.

The effect of temperature is shown in Figure 9. The broken line is taken from Hilsdorf⁽¹⁰⁾ while the experimental points were obtained from Figure 8. Higher temperatures increase the decomposition of the hydrated compounds in the cement. At 1500°F all of the water is released.

A realistic estimate of the release rate of water from concrete during an accident would require knowledge of diffusion coefficients within the concrete, atmospheric humidity concentration at the exposed surface, and temperature as a function of distance and time. An adequate model has not been developed for this purpose. Use of data such as that shown in Figure 9, combined with temperature estimates provided by existing computer codes such as SOFIRE II⁽¹¹⁾ and CACECO⁽¹²⁾, will probably overestimate the release of water.

2. Water Released From Concrete During Sodium Spill Tests

Table VI compiles the HEDL data on water release from concrete during sodium spill tests. The scatter in the results when expressed on a unit area basis is not surprising, considering the wide range of experimental conditions. The prefix S signifies small-scale test with either 4-in. or 10-in. diameter concrete specimens. In the S-series tests the sodium pool was heated electrically. Tests S9 and S10 had defected liners; in the others the sodium was spilled directly on the concrete. The F-series tests were large-scale fire extinguishment tests. In F1 the sodium spilled directly onto the concrete surface. In tests F4 and F5 a free floating steel catch

FIGURE 9. WATER LOSS FROM CONCRETE AS A FUNCTION OF TEMPERATURE

HEDL 7506-127.24

TABLE VI

WATER RELEASE FROM CONCRETE
DURING SODIUM SPILL TESTS

<u>Test</u>	<u>CONCRETE</u>		<u>Fraction Of Water In Concrete Released</u>	<u>LB H₂O/Ft²</u>
	<u>Surface Ft²</u>	<u>Thickness In.</u>		
S1	0.087	12	0.77	7.6
S2	0.087	12	0.79	8.0
S4	0.55	.6	0.79	4.2
S7	0.67	1.5	1.00	0.13
S8	0.087	12	0.82	8.2
S9	0.55	6	0.96	5.1
S10	0.55	6	0.95	5.0
F1	32	4	0.97	2.9
F4	28	12	0.04	0.65
F5	158	12	0.07	0.63

pan rested on the concrete floor, with 0.25 and 1-inch air gaps on the sides, respectively. No electrical heat was used in the F-series tests, the water was released due to increased temperatures in the concrete by heat conducted through the steel pan. The fires in both test F4 and F5 were extinguished within a few minutes by oxygen starvation. Presumably, if the fire had been permitted to continue the additional heat of reaction would have caused more water to be released. The quantity of sodium spilled would also affect the amount of water released. The value of 0.65 lb H₂O/ft² measured in the tests with catch pans is probably somewhat low for a massive spill of sodium forming a pool several feet in depth but is probably representative of spills forming pools less than 6 inches deep.

D. Hydrogen Formation

The fraction of the water released from concrete which reacts with sodium to form hydrogen depends on the specific design involved. At least three arrangements are possible which would result in vastly different H₂ formation. First, the water can be released directly into the sodium pool, with essentially 100% conversion to H₂. Any hydride formed would probably decompose at the high temperatures involved in accident cases. If the oxygen concentration in the atmosphere above the pool exceeds 5%, the H₂ will burn back to water and be released into the atmosphere where it may react with sodium oxide to form hydroxide. If the oxygen concentration is < 5%, the H₂ will be released to the gas space where it accumulates unless the enclosure is purged or hydrogen recombiners are provided. Test F1 was performed under these conditions, and Figure 10 shows the resulting concentrations of hydrogen and oxygen in the enclosure atmosphere. The cell was purged slowly, beginning 54 minutes after the spill, and the hydrogen burned spontaneously at the point it entered the normal air atmosphere outside the cell. It is hypothesized that hot aerosol

FIGURE 10. HYDROGEN FORMATION DURING A DIRECT SODIUM SPILL ONTO CONCRETE--TEST F1

particles provided the ignition source. Test S9 was performed in a manner where the water was released partially into the atmosphere above the pool and partially below the sodium surface. Figure 11 shows the concentrations of hydrogen and water in the test enclosure. In this test, the water was released from the concrete through defects in a liner both below and above the sodium level. Approximately 70% of the released water was converted to H_2 , the balance was swept from the chamber by the convective flow established by the formation of steam.

The second configuration for water release is that of a catch pan or a defective liner with the defect located above the level of the sodium pool. In this case, water released from concrete would enter the atmosphere above the pool and be available for reaction at the pool surface. The fraction of the released H_2O which reaches sodium to react depends on the existing conditions. Test F5 used a steel catch pan, and in this test, only 10 lb of water reacted to form H_2 out of the 100 lb of water released. The balance of the released water was either swept from the cell by the slow nitrogen purge or condensed on cell surfaces. The sodium pool became insulated from reactants in the cell atmosphere during test F5 by the formation of a shallow layer of sodium hydroxide on the surface. Figure 12 shows that the concentration of H_2 was much lower than in the case where the sodium was spilled directly onto concrete.

The third configuration for water release is the case of a properly designed cell liner which vents the released water vapor to regions outside the affected cell. In this case, no H_2 would be formed unless sodium escaped from the cell to the point where the water was released.

Table VII is a compilation of the HEDL data on conversion of released water to hydrogen. In tests where the sodium was spilled on top of concrete in an inert atmosphere (S1, S2, S8, F1) the conversion approached a mole per mole ratio. This shows that Equation (1) in Table I is the chief reaction. In tests

FIGURE 11. HYDROGEN AND MOISTURE CONCENTRATIONS IN ATMOSPHERE FOR A TEST WITH DEFECTED LINER

FIGURE 12. HYDROGEN FORMATION IN A TEST WITH CATCH PAN RESTING ON CONCRETE

TABLE VII

HYDROGEN TO WATER RATIO

<u>Test</u>	<u>H₂ Formed lb-mole</u>	<u>H₂O Released lb-mole</u>	<u>Mole Ratio H₂/H₂O</u>
S1	0.036	0.037	0.97
S2	0.027	0.038	0.71
S8	0.036	0.040	0.90
S4	0.051	0.128	0.40
S7	0.0018	0.0047	0.38
S9	0.113	0.156	0.72
S10	0.125	0.154	0.81
F1	>2.2	4.3	>0.5
F4	>0.01	1.0	<0.01 ⁽¹⁾
F5	0.52	5.6	0.09

(1) Cover over sodium prevented entry
of released water to sodium surface.

where the water was released at least partially above the sodium, a lesser fraction was converted to H_2 , but the water that did react is believed to have reacted according to Equation (1) in Table I. Of special interest in Table VII is the low conversion in test F4. In this test, the sodium was spilled onto a perforated plate covering a sump. Water released from the concrete which surrounded the steel-lined sump could not enter the sump because a nitrogen purge prevented entry.

III. LINER RESPONSE TO SODIUM SPILL

A. Intact Liners and Catch Pans

No large-scale testing of cell liners by sodium spills has been performed. However, many tests have been performed at various laboratories where hot sodium was spilled into steel catch pans varying from 1/16 to 1/4 inch in thickness. No reports have been made on any failure of the catch pan due to thermal shock or corrosion. Liners which are fixed in position by welding to embedments in the concrete should be evaluated for ability to withstand any potential thermal stress.

Tests at HEDL have spilled up to 2350 lb of sodium at 1100°F (test F5) rapidly into free floating catch pans. In all tests, the cold pans quickly assumed an equilibrium temperature with the sodium and the resulting temperature one minute after the spill was within a few degrees of that calculated by assuming sensible heat transfer and neglecting heats of reaction during the spill period.

B. Defected Liners

Two small-scale test (S9 and S10) were performed at HEDL where a defected liner separated the vertical concrete surface from the sodium pool. Figure 4 is a schematic view of the test article and Figure 13 shows a view of the liner before the sodium chamber was welded closed. Four defects were provided; two

Figure 13. Pre-test View of Defected Liner
from Sodium Side .

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below and two above the level which the sodium pool would form. The holes were 0.28-in. diameter, the slits were 1-inch by 1/16-inch. The concrete was magnetite (M-225) aged approximately 200 days. In test S9 the liner contacted the concrete and the liner was 304 SS. In test S10 the liner was carbon steel and a 1/4-inch gas-filled gap was between the liner and the concrete surface. The sodium pool in S9 was heated to 1380°F for 19 hr; in S10 it was heated to the sodium boiling point (1620°F) for 3 hr.

The results for penetration of concrete by sodium was presented in Table III; for water release in Table VI; and for hydrogen formation in Table VII. In summary, the defected liner gave some protection to the concrete as shown by less penetration (Figure 5) and the fact that the concrete did not crack as it had in test S4, performed with similar geometry but at lower temperature and without a liner. Water release and H₂ formation proceeded as if there were no liner, however.

The liners themselves were severely corroded in localized regions near the defect points. Figure 14 gives a view of the liner from test S10 after cleaning. The bottom hole and slit were plugged by reaction product. Apparently, most of the water was released from the concrete through the top defects into the sodium vapor space. Both the carbon steel and the SS 304 liners were severely corroded. For the worst case (S10) the 0.28-inch diameter hole was enlarged to a 1.75-inch by 1.55-inch ellipse, and the slit from 1/16-inch by 1-inch to an ell shape with 0.95-inch by 1.62-inch dimensions. The liner weight decreased by 0.62 lb, mostly due to the enlargement of the defects, but also due to some grooves, pits and planar attack. An additional 1.3 lb of iron (1.9 lb total) was found in the reaction product layer that formed in the bottom of the sodium pool. The crystalline, reddish brown material is shown in Figure 15. It was analyzed and found to consist of a mixture of Na₂O and FeO, in approximately a 2 to 1 ratio,

S-10

Figure 14. Post-test View of Defected Liner
Showing Corrosion Effect - Test S10 .

S-10

Figure 15.

REACTION PRODUCT AT BOTTOM OF SODIUM POOL

which had a melting point of approximately 600°F. Concrete components (CaO , SiO_2 , etc.) were present in minor quantities, so most of the material resulted from corrosion of the liner and the walls of the sodium chamber.

IV. SODIUM FIRE EXTINGUISHMENT

A. Background

Sodium fire technology has been studied extensively during the past two decades, with most of the work done by Atomics International (AI) and reported in progress and topical reports too numerous to reference. However, sodium fire extinguishment technology has been less fully documented. The review by Gracie and Droher⁽¹³⁾ presents much useful basic information. Cissel, et al⁽¹⁴⁾ have provided guidelines for fire prevention, detection, and control. The International Working Group for Fast Reactors held a specialists meeting on the subject and issued a summary report.⁽¹⁵⁾ A session on sodium fires was presented at the meeting on fast reactor safety sponsored by the American Nuclear Society in Beverley Hills, California, in April 1974.⁽¹⁶⁾

Large-scale tests of extinguishment systems and methods have been performed by the French⁽²⁾, the Germans⁽¹⁷⁾ and at HEDL.^(6,18,19) The French tests showed that fixed pipe powder extinguishment systems (NaCl base) was ineffective on a shallow pool fire. Although the French authors did not mention the possibility, it is probable that hydrogen gas, formed by reaction of the sodium with water in the concrete floor, agitated the pool and prevented the extinguishment powder from forming an oxygen-excluding crust on the pool surface. The French⁽²⁾ reported partial control in a test where the sodium temperature was quenched below its ignition point by spilling into a sump filled with steel bars. However, the entire mass of sodium was not quenched and 75% of the 400-lb spill was burned.

The Germans⁽¹⁷⁾ performed tests with up to 420 lb and showed that a perforated cover over steel catch pans greatly improved the

control of the fire. Tests 23 and 25 were similar except that 23 had a sloped cover plate with one 1-inch diameter hole per ft^2 and test 25 was an open catch pan. The covered pan test gave a lower maximum sodium pool temperature (750°F vs 1350°F), a lower reaction rate (3.5 vs 8.8 lb/m-ft^2), lower total fraction reacted (30% vs 100%), and much less aerosol escaped from the pan (0.011 vs 3.4 lb/hr m^2). The Germans did not inject inert gas into the space below the cover plate.

B. HEDL Large-Scale Extinguishment Tests

1. Summary of Test Conditions

Four large-scale sodium fire extinguishment tests were performed at HEDL in support of the FFTF secondary sodium fire protection system design. Table VIII summarizes the test conditions. All tests were performed in a full-scale sheetmetal mockup of an FFTF pipeway which had a pretest leak rate of 3.5 cell volume per hour at 0.5 in H_2O pressure. A 3-ft. by 3-ft. pressure relief vent opening at 2 in. H_2O pressure was provided. Figure 16 gives a schematic diagram of the experimental arrangement used in Test F1.

2. Test F1 Results

Test F1(6) showed that large sodium spills onto a concrete surface cause extensive damage to the concrete and significant formation of hydrogen. The H_2 concentration in the cell atmosphere is shown in Figure 10 and reached a maximum of 25%. The test also showed that oxygen can re-enter a semi-leaktight enclosure to a much greater extent than can be accounted for by cooling, and this was shown to be due to convective flow of outside air induced by the chimney effect. No large pressure pulses were measured during the spill or at later times. All the sodium was reacted, at an average rate of 8 lb/hr ft^2 . Reaction with the concrete accounted for approximately half of the total, with H_2 , Na_2O ,

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Figure 16. Conceptual Diagram of Experimental Arrangement - Test F1.

TABLE VIII

TEST CONDITIONS FOR HEDL LARGE-SCALE
SODIUM FIRE EXTINGUISHMENT TESTS

	<u>F1</u>	<u>F2</u>	<u>F4</u>	<u>F5</u>
Na Mass Spilled, lb	710	770	770	2350
Na Spill Temp., °F	1080	1100	1120	1100
Spill Duration, sec	20	20	20	66
Cell Volume, ft ³	3350	3350	3300	2500
Cell Atmosphere	Air	Air	Air	Air
Burn Pan Material	Concrete 4-in thick	C. Steel Pan on Fire Brick	C. Steel Lined Con- crete sump	C. Steel Pan on Concrete
Burn Surface, ft ²	32	32	10	110
Pool Depth, in.	5	5.5	16	5.1
Extinguishing Method	Space Isolation	Space Iso- lation With N ₂ Flood	Covered Sump Plus N ₂ Flood	Space Iso- lation With N ₂ Flood
N ₂ Flood Rate, hr ⁻¹	0	1	1	1
N ₂ Flood Duration, hr	0	3.4	2.2	2.1

and Na_2SiO_3 the chief products. The cell structure was not damaged.

3. Test F2 Results

Two changes were made from the F1 conditions before performing test F2.⁽¹⁸⁾ Concrete was eliminated and a nitrogen "flooding" system was installed. The nitrogen flooding system consisted of a piping system which fed gaseous N_2 into the cell near the ceiling at a relatively low rate of approximately one cell volume per hour. The N_2 system was activated manually at 15 minutes after the sodium spill and controlled manually at the predetermined rate of 60 SCFM until the sodium pool temperature had decreased below 400°F.

The conclusions from Test F2⁽¹⁸⁾ were that the fire was effectively controlled, only 100 lb of sodium reacted (13% of spill mass) which was in agreement with SOFIRE-IIB predictions⁽¹⁶⁾, only 0.5% of the spill mass was released from the cell as aerosol particles, the oxide crust on top of the pool contained sufficient Na metal particles to cause the crust to be pyrophoric during cleanup operations, and there was no significant H_2 formation.

4. Test F4 Results

In test F4⁽¹⁹⁾, the same conditions were used as in test F2 except that instead of an open pan, a covered sump concept was used. The sodium was spilled onto a flat steel deck (22 ft²) which drained to a steel lined concrete sump through a cover plate which had two 1-inch holes per ft². Figure 17 gives a view of the spill deck and coverplate arrangement. A portion of the nitrogen flood gas flow was introduced below the coverplate at 22 SCFM, a rate which gave an exit velocity through the 1-inch diameter holes of 200 ft/min (STP).

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Figure 17. Top View of Spill Deck and Sump
Coverplate - Test F4.

The conclusions from test F4(19) were that a covered sump was very effective in controlling a large sodium spill when supplemented by a nitrogen purge introduced below the coverplate. The bulk of the sodium (97.6%) drained rapidly into the sump, and only 1.3% of the sodium which entered the sump was found to be reacted. The steel liner prevented a direct concrete-sodium reaction, but approximately 18 lb of water was released from the concrete to the cell atmosphere. No H_2 was formed because the coverplate prevented entry of the water vapor to the sodium in the sump. All of the sodium retained on the spill deck and coverplate (~ 20 lb) was completely oxidized. Smoke release from the cell was even less than in test F2, 0.03% of the spill mass.

5. Test F5 Results

Test F5 was performed in April, 1975, and the results have not yet been reported. In this test the cell used in previous tests was reduced in size by partitioning off the 3.5 ft wide ell, leaving a 10-ft by 15-ft floor area. A 12-inch thick reinforced concrete (conventional, type C1-P) was poured over the cell floor and 2-ft high concrete walls 9 inches thick were poured on top of the concrete floor. A free floating steel catch pan was installed directly on the concrete floor, with 1-inch air gaps between the pan and concrete walls. A splash shield was installed to guide any sodium sprayed on the walls across the gap and into the pan, but the air space in the gap was open to the cell atmosphere. Whereas in previous tests, the sodium was delivered to the catch pan surface to minimize splashing, in test F5 the sodium was released from the 3-inch diameter spill pipe at an elevation 6 ft above the pan. Approximately 300 gallons of 1100°F sodium was spilled at a rate of 300 GPM. The nitrogen

flood began 15 minutes after the spill and continued until the pool temperature had decreased below 400°F.

The observations and conclusions drawn from test F5 are as follows:

- Space isolation with nitrogen flooding is an effective method for controlling large sodium fires, as evidenced by the rapid cooling of the sodium pool (at freezing point 7 hr after spill), the small amount of smoke released from the cell ($< 0.1\%$ of spill mass), the lack of damage to the concrete or cell structure, and the safe concentration levels of hydrogen and oxygen (see Figure 12).
- Approximately 6% of the spill mass (133 lb) reacted. About 24 lb reacted with the water released from the concrete, the balance with O_2 in the atmosphere.
- Approximately 100 lb of water was released from the concrete interface. Approximately 0.5 lb-mole of H_2 was produced, giving 0.1 mole of H_2 per mole of released water. The balance of the water was swept from the cell by the N_2 flood (23 lb) or reacted with Na_2O to form a NaOH solution.
- The H_2 concentration was essentially zero during the initial 10-minute period, while the O_2 concentration exceeded 5%. It attained a maximum value of 3.7 mole% one hour after the spill, when the O_2 concentration was 0.5%. When the N_2 flood was terminated, both the H_2 and the O_2 concentrations increased slightly, but at no time was a combustible mixture present.
- The cell atmosphere temperature increased much more rapidly than in previous tests, due to the splashing that occurred during the spill. An average atmospheric temperature of 750°F was measured at the end

of the spill. A calculated venting rate of 10,000 ft³/min (maximum) was attained during the spill. This was vented out the 3 ft by 3 ft pressure relief vent which had been held open during the spill and closed immediately afterward. This points out that enclosures where large sodium spills can occur should be either capable of withstanding high pressure or equipped with suitable pressure release devices.

- After cooling to room temperature, the residual sodium was successfully disposed of by pouring oil over the surface and cutting into ~ 5-lb chunks with pneumatic tools. Figure 18 gives a view of the disposal operation. The oxide/hydroxide crust on the pool surface was partially liquid with NaOH solution, and was not pyrophoric as in the dry atmosphere test F2.

C. Motion Picture of FFTF Proof Tests

A 15-minute motion picture⁽²⁰⁾ summarizing the four F-series tests was made from the TV videotapes taken of each test.

V. CONCLUSIONS

The overall conclusions on the status of technology of sodium-concrete reactions, cell liner response, and sodium fire extinguishment are as follows:

- Concrete is reactive with hot sodium. The water in concrete can react either at the Na-concrete interface, or it can migrate to other areas to react far from the concrete. SiO₂ and iron oxide are the other two important components of concrete which are reactive with sodium. Sodium must migrate to the reaction site within the concrete matrix in order for these reactions to occur. The solid reaction products tend to form a

Figure 18. View Showing Disposal of Residual Sodium with Pneumatic Tools - Test #5

barrier and limit the rate of reaction unless the concrete is cracked by mechanical or thermal stresses. When cracking occurs, the reaction can propagate rapidly. Large-scale testing is required to evaluate the cracking phenomena.

- No valid model for estimating the rate of water release from concrete is presently available. A mass transfer model supported by empirical diffusion coefficient data would allow realistic predictions of water release rates that are probably much lower than those presently used.
- Significant quantities of hydrogen can be formed under hypothetical, severe LMFBR accident conditions. The potential for hydrogen formation must be evaluated on a case by case basis. Not all the water released from concrete necessarily reacts with sodium, depending upon the specific configuration involved. What water does react forms H_2 on a mole per mole basis.
- Properly designed liners and catch pans can be effective in limiting water release, hydrogen formation and concrete damage. Design of liners should consider water release and venting requirements for the design basis accident conditions. A small defect in a cell liner can potentially grow in size due to rapid corrosion by water and its reaction products if exposed to steam and sodium at high temperatures. The corrosion process may cease when the concrete becomes dehydrated and water no longer reached the liner.
- Small sodium fires can be effectively controlled by application of powder extinguishing agents, by smothering with air-excluding blankets or inert gas, or by permitting it to burn out and controlling the smoke

by suitable ventilation. Large sodium spills require considerably different technology due to the larger enthalpy, both sensible and chemical. Six different techniques for extinguishing large sodium fires have been demonstrated by workers in Germany, France, and the U. S. In decreasing order of effectiveness they are: (1) covered sump with N_2 purge gas introduced below the coverplate, (2) space isolation by partitions, doors, and ventilation dampers, supplemented by nitrogen flooding, (3) covered sump without nitrogen purge below the coverplate, (4) space isolation alone, (5) quenching in heat sink provided by steel bars stacked in a sump, and (6) fixed pipe powder extinguishment applied directly onto the sodium pool surface. Tests using the latter three methods failed to control the fire, although variations in the techniques may improve their effectiveness. The first three methods gave effective control for the conditions tested, with the covered sump with N_2 purge being superior.

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