SODIUM-CONCRETE
REACTION TESTS

By

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SODIUM-CONCRETE REACTION TESTS

ABSTRACT

Five small scale tests were performed in the Hanford Engineering Development Laboratory (HEDL) Large Sodium Fire Facility (LSFF) with the objective of measuring the rate of reaction between liquid sodium and concrete for a limited number of conditions. Two types of concrete were used: conventional (SiO_2) and high density (magnetite). The reaction with 4-in. diameter horizontal surfaces and 10-in. diameter vertical surfaces was studied by heating the sodium pool while it was in direct contact with the concrete surface and measuring the depth of penetration of sodium into the concrete after cooling. Magnetite concrete was penetrated at about 1-in. per hour; conventional concrete at about 0.5-in. per hour. Cracking occurred with the 10-in. vertical surface interface specimen, but not with the 4-in. horizontal interface specimens. The heat generation rate was estimated at 10,000 Btu/hr-ft² for magnetite concrete at 1200°F, with a probable error of $\pm 50\%$. The heat of reaction was estimated at 700 ± 350 Btu per lb of magnetite concrete.

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I. INTRODUCTION

Concrete is a common material of construction in liquid metal facilities and, although the probability of a large spill of sodium directly onto a concrete surface is very low, an understanding of the possible interactions resulting from such a hypothetical event is of interest for safety analysis. Because information in the literature concerning the reaction of sodium and concrete is very limited, a scoping study was performed to define the important parameters and to determine approximate reaction rates and associated energy release data.

Concrete is a complex mixture of partially bonded and hydrated chemical compounds, some of which should react with elemental sodium from a thermodynamic standpoint. Of the chief constituents of concrete, only SiO_2 , Fe_2O_3 , FeO , Fe_3O_4 , and H_2O have free energies that are less negative than the reaction products Na_2O and Na_2SiO_3 , and should therefore react with elemental sodium⁽¹⁾. Calculation of the heat of reaction is uncertain due to the complex nature of concrete, but is estimated from standard heats of reaction⁽²⁾ to be 770 Btu per lb for conventional concrete and 1050 Btu per lb for high density (magnetite sand and aggregate) concrete. These calculated values were checked by laboratory tests at Westinghouse Research Laboratory by Witkowski, Charles and Berkey using a differential thermal analysis (DTA) technique.

The results, reported in the Appendix to this report, gave values of 240 and 900 Btu/lb for conventional and magnetite concrete, respectively. Exotherms were observed at 1170°F for conventional and at 870°F for magnetite concrete, well within the range of possible accidental spill conditions. Because of the abbreviated nature of the DTA work and the probable sampling errors involved, these results are reported to be subject to errors of $\pm 100\%$ for the conventional and $\pm 30\%$ for the magnetite concretes. Nevertheless, because of the large masses of concrete available for reaction, this represents a significant potential energy source.

Very little information is available in the literature regarding the kinetics of the reaction and the associated thermal and mechanical phenomena. Broadley⁽²⁾ reported that conventional concrete with granite aggregate was

damaged to a depth of one inch when 50 lb of sodium at 1040°F was spilled onto a 2.25 ft² concrete surface and burned in air. No chemical analyses were reported. Sauvage and Fruchard⁽³⁾ reported extensive damage to a 30-ft² slab of basalt refractory concrete during fire extinguishment tests involving 400 lb of sodium burning in air. A sodium fire extinguishment test, F1, was performed at the Large Sodium Fire Facility (LSFF) at the Hanford Engineering Development Laboratory (HEDL) in which approximately 700 lb of 1100°F sodium was spilled onto a 32-ft² surface of conventional concrete (SiO₂ sand and basalt aggregate) in air⁽⁴⁾. In test F1, the 4-in. thick reinforced concrete slab reacted extensively and was severely damaged. All of the water in the slab was reacted, releasing 3x10⁻³ lb of free hydrogen per lb of concrete. Sodium silicate was identified as one of the chief reaction products, showing that sodium (or sodium oxide/hydroxide) had reacted with SiO₂ in the concrete. Temperatures in the concrete reached 1600°F, exceeding those in the sodium pool during the period of maximum reaction and showing that the reaction was occurring within the concrete mass and not just at the concrete-sodium surface. None of these tests provided a reaction rate except on a very approximate basis.

A series of five scoping tests was performed in the LSFF to determine the rate of penetration of sodium into concrete and the associated energy release rate for several test conditions. The results are reported in this document.

11. SUMMARY AND CONCLUSIONS

Five tests were performed in which 2 to 23 lb of sodium was spilled onto concrete surfaces in vessels that were heated electrically for approximately four hours. Two types of concrete were used: conventional (SiO₂) and high density (magnetite). The concrete had been cured for 30 to 60 days. Both vertical and horizontal concrete surfaces were used. Horizontal surface tests were performed with 4-inch diameter specimens; the vertical surface test with the 10-inch diameter specimen. In one test, concrete lumps of approximately 1 1/4-in. diameter were dropped into a pool of 1200°F sodium. In all tests, the rate of hydrogen evolution was monitored, the depth of sodium penetration into the concrete was measured, and the residual sodium pool, reaction product layer and concrete were analyzed chemically.

The results of the tests support the following observations and conclusions:

- 1) The 4-in. diameter concrete specimens with horizontal interfaces did not crack, whereas the 10-in. diameter magnetite concrete specimen with a vertical interface cracked entirely into two pieces in a plane parallel to the concrete-sodium interface. It is not known whether this is a size effect or was caused by two-dimensional temperature gradients established in the concrete because half of the surface was exposed to liquid sodium and half to vapors. A vigorous chemical reaction occurred at the time the crack developed.
- 2) For the three specimens that did not crack, the chemical reaction progressed on a fairly uniform front parallel to the original concrete surface. The depth of penetration was 0.5 in. for the conventional concrete and approximately 1-in. for the magnetite concrete specimens. The major portion of the reaction is believed to have occurred rapidly, with very little additional reaction after the first hour.
- 3) After cooldown, reaction products were found mixed throughout the residual sodium pool region, with a much lower concentration in the upper region of the pool. The bottom of the sodium pool contained mostly reaction products with very little metallic sodium. It is postulated that stirring of the pool by convection currents during heating entrained some reaction product particles, but that most of the reaction products, being more dense than sodium, either remained at the concrete surface during the reaction or settled to the concrete surface during cooling.
- 4) The reaction product appeared to be a loosely bound mixture of sodium monoxide, sodium silicate, and ferrous oxide, with smaller amounts of CaO , Al_2O_3 , MgO and other concrete constituents. This mixture was compacted to a fairly dense (specific gravity 2.0) layer near the original interface.

- 5) Magnetite concrete may have reacted more extensively than conventional concrete, as evidenced by greater penetration for similar heating times. However, this conclusion is not certain because a higher temperature was used for the magnetite test.
- 6) The initial heat generation rate due to the reaction of sodium with magnetite (M-225) concrete was estimated at 10,000 Btu/hr-ft², with a probable error of $\pm 50\%$, this includes the effect of all chemical reactants, including the water content of the concrete.
- 7) The heat of reaction of sodium and magnetite concrete was estimated at 700 ± 350 Btu per lb of concrete. This compares with 900 ± 300 Btu/lb obtained by the DTA analysis.
- 8) The heat of reaction of sodium and conventional concrete was not measured in the small scale reaction tests, but DTA analysis gave 240 Btu per lb concrete, with a probable error of $\pm 100\%$.
- 9) One test (**S7**) gave evidence that the stoichiometric mass ratio of magnetite concrete to sodium is approximately unity.
- 10) These tests are inconclusive as to the reaction mechanism or rate law that applies. The rate was shown to be greatly time-dependent for uniform penetration of undisturbed concrete surfaces. However, cracking, spalling or other mechanical disruption of the concrete causes rapid reaction on the newly created surface. The possibility exists for propagation through large thicknesses of concrete by the latter mechanism.
- 11) The importance of temperature on the reaction rate was not determined by these few scoping tests. The reaction was shown to proceed rapidly at 1040°F.
- 12) The effect of steel reinforcement was not studied. It is not known whether unequal expansion coefficients at high temperatures would cause breakup or whether reinforcing bars would add sufficient strength to prevent breakup. A large scale test would be required to answer this important question.

- 13) Approximately 80% of the total water content was driven from each concrete test specimen. Water at one foot depths in the concrete was reduced to ~40% of its original concentration.
- 14) Hydrogen was detected in the vent gas in a nearly equimolar ratio with the water lost from the concrete. This indicates that Na_2O and H_2 are the products of the sodium-water reaction.

III. EXPERIMENTAL CONDITIONS

In four of the tests, the general procedure was to spill hot sodium onto a concrete surface within specially prepared reaction vessels. In one test, the concrete was dropped into a pool of hot sodium.

A. TEST ARTICLES

Each test article was constructed in two separate sections. The concrete specimens were individually poured into their respective steel liners (with the exception of test S7 which used broken concrete chunks). The sodium reservoir sections were separately formed and joined to the concrete sections with a weld at the mating flanges.

1. Reaction Vessels

Four types of reaction vessels were used for the tests. The first two tests (S1 and S2) were performed with 4-in. diameter test vessels as shown in Figure 1. The vessels were instrumented with thermocouples in the sodium region and embedded in the concrete at the locations shown. Tubular electric heaters were attached to the exterior of the sodium reservoir immediately above the concrete level.

Test S4 was performed with the 10-in. diameter vessel shown in Figure 2. This test was done with the sodium-concrete interface in a vertical plane. As in the other tests, thermocouples were placed in both the concrete and sodium. Sodium pool areas of the vessel were heated as noted on the figure.

Because there was no definitive concrete-sodium interface, test S7 required a vessel which was capable of being disassembled while still containing a large mass of sodium. The vessel shown in Figure 3 is basically a 4-in. diameter pipe split longitudinally into two halves and flanged. The halves were seal welded to form the final reaction vessel. Thermocouple locations and heated areas are shown on the figure.

FIGURE 1. Reaction Vessel for Tests S-1, S-2

HEDL 7407-25.2

FIGURE 2. Reaction Vessel for Test S-4

FIGURE 3. Reaction Vessel for Test S-7

HEDL 7407-25.8

Test S8 was performed for an extended period (24 hours) with an ensured excess of sodium. The vessel shown in Figure 1 was modified as shown on Figure 4 to have a capacity of approximately 25 pounds of sodium and yet maintain a geometry similar to that of S1 and S2 at the concrete surface. The 10-in. diameter sodium reservoir enabled the larger amount of sodium to be contained in a vessel of reasonable size. Instrumentation and heating was located as shown in Figure 4.

Four inches of insulation* surrounded the concrete and sodium sections of each vessel. Lids were provided to contain splash, reduce heat losses from the pool, and to limit the entry of nitrogen purge to the vessel itself. The lids were loose fitting and were not intended to seal the vessel.

Tests S1 through S7 were performed in a small test containment made from a 55-gallon drum. Figure 5 shows a schematic of tests S1 and S2 configuration within the drum. Thermocouple and heater leads extended through sealed penetrations in the drum. The nitrogen purge line and sodium dump line also were sealed penetrations. A 2-inch diameter vent line from the drum was provided with the end open to a 3350 ft³ cell. A 1/2-in. line tied into the ventline for vent gas sampling purposes. Thermocouples were located on the surface of the vessel insulation and in the atmosphere within the drum. Figure 6 shows a view of the drum installed within a cell mockup.

The test vessel used for S8 was too large to fit within the drum used in the earlier tests. For this test, a steel relay cabinet was modified to provide the necessary containment. As before, sealed penetrations were made for sodium, vent and nitrogen lines and thermocouple and heater leads.

The entire enclosure for each of the tests was placed in a controlled ventilation cell discussed in Section B.

2. Concrete

Two types of concrete were used: conventional concrete, designated type C1-p; and high density (magnetite) concrete, type M-225. The composition of each type at the time of mixing is given in Table I.

*Kaowool ceramic fiber, 1-in. thick blanket, 8 lb/ft³, k = 0.030 Btu/hr ft°F at 600°F, manufactured by Babcock and Wilcox Co.

HEDL 7407-25.7

FIGURE 4. Reaction Vessel for Test S-8

HEDL 7407-25.6

FIGURE 5. Schematic of Reaction Vessel in Drum Enclosure

(74H0434-3)

FIGURE 6. View of 55-Gallon Drum Installed in Cell Mockup

TABLE I

CONCRETE COMPOSITION AT TIME OF MIXING

	Conventional (C1- lb/ft ³)		High-Density M-225)	
				%
Portland cement	16.8	11.4	23.5	10.1
Sand (SiO ₂)	52.7	35.8		
Aggregate (basalt), 3/4 in.	65.4	44.5		
Water	9.3	6.3	11.6	5.0
Pozzolan	2.9	2.0	1.6	0.7
Aggregate (magnetite), 3/4 in.			107.6	46.2
Sand (magnetite)			88.6	38.0
TOTAL	147.1	100.0	232.9	100.0

Test S1 was performed using the conventional (C1-p) concrete. After the concrete was poured, the sample was vibrated on a shaker table and the top surface smoothed with a wood trowel. The sample was 29 days old when the test occurred.

The remaining tests (S2, S4, S7, S8) were done with the high density (M-225) magnetite concrete. The specimens were vibrated and leveled after the pour. The ages of the specimens S2, S4 and S8 were 27, 32 and 67 days respectively at the time of testing. The samples used for test S7 were broken from a separate concrete sample of type M-225 and were 74 days old at the time of the test.

B. TEST FACILITY

The tests were performed in the LSFF. ⁽⁴⁾ A plan view of the facility is shown in Figure 7. The test articles were installed within a sheetmetal cell mockup used in previous large scale proof tests. The mockup was equipped with a nitrogen flooding system with a capacity for delivering measured flow-rates up to 200 SCFM. Temperature measurement was by thermocouples recorded on multipoint stripchart recorders. Gas sampling capability was by a pump and multiple sample tubes, leading to an oxygen meter, hydrogen analyzer and hygrometer, with the O₂ and H₂ concentrations recorded on strip chart recorders.

FIGURE 7. Floor Plan of Large Sodium Fire Facility

Electrical current and voltage to the test articles were monitored by meters and the current was recorded on a strip chart recorder. The room in which the cell mockup was located was ventilated by 5000 CFM of air. The exhaust air was scrubbed, filtered and discharged to a 200-ft stack.

A small (approximately 4-lb capacity) electrically heated sodium dump tank was used for all tests except S8, which used a 55-gallon drum melt station.

C. TEST PROCEDURE

The basic test procedure included the following:

- System purge with N_2 .
- Melt and preheat sodium.
- Preheat sodium vessel reservoir.
- Dump the sodium into the vessel.
- Increase system temperature to desired level while watching for signs of chemical reaction.
- Stabilize system at desired level for required time.
- Stop electrical heating and let system cool down.
- Post-test disassembly, visual examination and photograph.
- Perform chemical analysis.

These basic procedures **were** modified for each individual test, depending upon the specific goal of the test, the results of the previous tests and behavior during the particular test. In one test (S7), the procedure was changed and chunks of concrete were dropped into a pool of sodium.

D. TEST CONDITIONS

The initial scope of the test series included three primary variables: 1) type of concrete (conventional and magnetite); 2) interface orientation (horizontal or vertical); and 3) presence or absence of a failed liner. This scope was modified as results of early tests were obtained. The absence of detectable thermal behavior attributable to chemical reaction with the bare concrete specimens in tests S1 and S2 caused the failed liner tests to be

cancelled. A new test, S7, was devised to emphasize the surface area and surface condition effects on reaction rates.

A pool of sodium was preheated in a special vessel and 15 chunks of freshly broken concrete (M-225) were dropped into the sodium. The test was run with an excess of sodium in order to see if all the concrete would be consumed. For this test, the heater power was kept constant in order to make energy release data more readily obtainable from the temperature responses.

The test conditions for all five tests are summarized in Table 11.

IV. RESULTS

A. GENERAL

The results of the present small scale tests confirm earlier reports(3,4) of an exothermic reaction between sodium and concrete. Insufficient test conditions were investigated to enable definitive information to be obtained concerning the effects of all the parameters that probably are important to the reaction rate. However, the test results provide **some** positive information that greatly extends the knowledge of the sodium concrete reaction process.

In the following sections, the test results are discussed in detail, including the temperature history, H_2 evolution rate, water release from concrete, visual observations during test article disassembly, chemical analyses of sodium pool and reaction products, and the heat of chemical reaction.

B. TEMPERATURE HISTORY

The temperature traces of each of the five tests are reproduced on Figures 8 through 12. Spatial temperature profiles generated by the three tests with the 4-in. diameter specimens are given at time $t = 150$ minutes in Figure 13.

Figure 8 summarizes the sodium pool and concrete temperatures of test S1. There is no apparent deviation from the smooth temperature increases produced by heater power input.

Test S2 response was slightly different than that of test S1. The vessel was not preheated and there was no hold at 1400°F . The resulting temperature distributions are given on Figure 9. The slight increase in slope of the pool temperature at $t = 150$ minutes corresponds to an increase in heater power at

TABLE II
SUMMARY OF TEST CONDITIONS

Test No.	S1	S2	s4	s7	S8
Date	3/5/74	3/14/74	3/19/74	3/27/74	4/23/74
Concrete:					
Type	Conv. C1-p	Hi Dens. M-225	Hi Dens. M-225	Hi Dens. M-225	Hi Dens. M-225
Age (days)	29	27	32	74	67
Mass (lb)	13.7	20.6	68.5	2.0	20.6
Surface area (in. ²)	12.5	12.5	78.5 ^(a)	97 ^(b)	12.5
Thickness (in.)	12	12	6	~1.25	12
Surface condition	Trowelled	Trowelled	Trowelled	Freshly Broken	Trowelled
Surface orientation	Horiz.	Horiz.	Vertical	Both ^(c)	Horiz.
Sodium:					
Mass (lb)	2.1	2.1	3.8	3.8	23
Pool depth (in.)	6	6	3 ^(d)	10	14
Temperature History:					
Max sodium temp (°F)	1500	1525	1365	1400	1220
Time above 1100°F (hr)	5	4.2	4.6	3.0	18.7
Pool Temp 3 min after dump (°F)	800	400	500	1300	320
Miscellaneous:					
N ₂ Purge rate (SCFM)	2	2(t<1 hr) 3(t>1 hr)	3	3	8
Average O ₂ concentration in vent (%)	1.0	1.9	1.0	0.4	0.3

(a) Half of the total surface was initially in sodium pool, half in vapor space above pool.

(b) Surface area was estimated from dimensions of chunks.

(c) Test S7 was performed by dropping chunks of concrete into preheated sodium.

(d) Three inches is dimension from concrete surface to backplate of pool vessel.

FIGURE 8. Temperatures and Heater Power During Test S-1

FIGURE 9. Temperatures and Heater Power During Test S-2

FIGURE 10. Temperatures and Heater Power During Test S-4 Figure 11.

FIGURE 11. System Temperatures During Test S-7

that time to bring the peak system temperatures up to 1500°F. As before, the concrete temperature profile produced a smooth curve at 150 minutes into the event as shown in Figure 13.

Test S4 was the first test in which thermocouple behavior indicated that an exothermic reaction had occurred. At approximately 70 minutes into the event, the temperatures in the pool and at the 1-in. concrete level showed sharp increases in temperatures (see Figure 10). It is estimated that the reaction lasted approximately 15 minutes; during this time, a large amount of hydrogen was released. The rapid response noted in the thermocouples located one inch within the concrete was not noted in the thermocouples located at greater distances into the concrete. Pool temperatures after 160 minutes are uncertain, for the pool thermocouples failed and estimates of pool temperatures were made from the temperatures indicated by the thermocouple attached to the vessel wall.

Test S7 was performed by heating a vessel filled with sodium to 1200°F and dumping 2.0 pounds of broken concrete chunks into the sodium. Heater power was carefully stabilized prior to adding the concrete chunks and kept constant for the remainder of the test. As can be seen in Figure 11, the temperatures increased at a ramp rate of approximately 33°F/min almost immediately. Since the concrete was colder than the sodium at the time of the drop, and the heater power was held constant, the temperature increase could only be due to release of energy through a chemical reaction between the concrete and the sodium. The reaction lasted for approximately 15 minutes, after which the system temperatures decayed back towards the pretest 1200°F level, eventually restabilizing at the original 1200°F temperature.

Temperature traces during the extended term (24-hr) test S8 are shown on Figure 12. The temperatures during the heatup period are very similar to those of test S2, although starting at a lower temperature. There was no indication of a sufficient chemical energy release to alter the thermocouple responses to a discernible level. The spatial temperature distributions 150 minutes into the test (Figure 13) show a marked similarity to those of test S2.

FIGURE 12. Temperatures and Heater Power During Test S-8

HEDL 7407-25.11

FIGURE 13. Spatial Temperature Distributions in Concrete at $t = 150$ minutes

C. HYDROGEN EVOLUTION AND WATER RELEASE

Throughout the entire series of tests, the vented purge gas was continuously monitored for hydrogen, oxygen, and water vapor content. The hydrogen concentration traces are reproduced on Figure 14 for each of the five tests. At various times during each test, grab samples were taken for later mass spectrometer analysis. Table III summarizes the results of those analyses and compares the hydrogen and oxygen concentrations with those given by the on-line analyzers. The agreement is good. Mass spectrometer analysis points are also shown in Figure 14.

The traces given in Figure 14, when compared to the sodium pool temperatures shown in Figures 7 through 12, show that the peak hydrogen release rates correspond in time to the maximum energy release rates as represented by the strong temperature increases noted in tests S4 and S7. In general, it is also noted that the hydrogen release rate increases with increasing temperature.

The water released from the concrete test specimens was calculated by the difference in water content of pre- and post-test samples. Table IV summarizes the concrete water analyses for the post-test samples. Samples of pre-test conventional (C1p) concrete analyzed 6.3 wt% water. Pre-test samples of high density (M-225) concrete analyzed 4.25 wt% water. Table IV shows that approximately 80% of the total water content of each specimen was lost during each test.

In all of the tests except S4, the water was released from concrete that was submerged in sodium. Thus, the water either reacted with sodium within a solid matrix of reaction product near the original concrete surface or, if the release rate were sufficiently high, formed bubbles of water vapor which rose up through the sodium pool, reacting at the bubble edges. In test S4, half of the concrete was submerged in liquid sodium, but half of the vertical surface was exposed to the cover gas (N_2 , H_2) over the pool and some water could have escaped from the vessel without contacting sodium.

The sodium-water reaction can form either Na_2O or $NaOH$ as shown by Equations (1) and (2), respectively.

FIGURE 14. Hydrogen Concentration in Purge Gas

TABLE III
COMPARISON OF GAS SAMPLE ANALYSES

Test No.	Sample Time (min)	Mole %				
		N ₂ Mass Spec (a)	O ₂ Mass Spec (a)	O ₂ On-Line (b) Analyzer	H ₂ Mass Spec (a)	H ₂ On-Line (c) Analyzer
S1	63	95.6	1.03	1.2	3.26	3.1
S2	75	95.9	1.98	1.95	1.94	1.9
S4	74	86.8	2.78	2.9	10.2	14.0
S7	2	91.1	0.36	0.52	8.32	8.6
S8	65	99.4	0.01	0.45	0.6	0.5

- (a) Mass spectrometric analyses were performed on grab samples taken over a 30-sec period of time.
- (b) On-line oxygen analysis was by Beckman Model 742, read at middle of grab sample period.
- (c) On-line hydrogen analysis was by MSA Thermal Conductivity Analyzer Model T-3, Type TC, read at middle of grab sample period.

TABLE IV
WATER CONTENT OF CONCRETE

Depth Below Concrete Surface (In.)	Wt% H ₂ O Remaining After Cooldown			
	S1	S2	s4	S8
0.75	0.55			
1.0			0.46	
1.5			0.78	0.47
2.25			1.09	
3.75			0.89	
4.0			1.10	0.49
5.0	1.07	0.88		
7.0	1.56			
8.0		1.33		
9.0	2.1			0.94
11.0	2.66	1.66		
11.5				1.47
Weighted Average Entire Specimen	1.45	0.90	0.89	0.77
Pretest Water Content	6.3	4.25	4.25	4.25
Water Remaining (%)	23	21	21	18

If the reaction proceeds according to Equation (1), one mole of H_2 is formed per mole of water. If Equation (2) describes the correct reaction, only one half mole of H_2 is produced per mole of water.

Table V summarizes the water releases for the five tests and compares them with the observed H_2 evolution. The last column of Table V gives the mole ratio of free H_2 evolved to water released from the concrete. Tests S1 and S8, with a mole ratio of nearly unity, show that Equation (1) applied. Since there is no apparent reason why the same reaction was not valid for the other three tests, the low mole ratio is probably due to a deficiency of metallic sodium for tests S2 and S4 and to the very rapid release of water in test S7. It is concluded that the H_2 concentration curves in Figure 14 are reasonably proportional to the reaction rate between sodium and water in concrete for the particular conditions of these tests.

Test No.	Initial H_2O Content (lb)(a)	H_2O (b) Release (wt %)	H_2O Released (lb)	H_2O Released (lb-mole)	H_2 (c) Evolved (lb-mole)	Mole(d) Ratio H_2/H_2O
S1	0.863	77	0.665	0.037	0.036	0.97
s2	0.876	79	0.692	0.038	0.027	0.71
s4	2.91	79	2.30	0.128	0.051	0.40
s7	0.085	100 ^(e)	0.085	0.0047	0.0018	0.38
S8	0.876	82	0.718	0.040	0.036	0.90

(a) Based on chemical analysis of pre-test concrete: 6.3 wt % in conventional concrete; 4.25 wt% in magnetite M-225.

(b) Post-test chemical analysis of residual concrete.

(c) Integration of H_2 concentration in enclosure vent multiplied by vent flow rate.

(d) Ratio of observed H_2 evolved to H_2O lost from concrete.

(e) Estimated.

D. POST-TEST EXAMINATION

After the test articles had cooled to about 130°F, they were disassembled, photographed, examined visually and sampled for chemical analysis.

White powder on the cell floor and other cell internal surfaces was deposited from the aerosol formed by condensed or oxidized sodium vapor vented from the test vessel enclosure. It was chiefly fine particles of low density material, but **some** large "snowflake" particles precipitated near the drum.

The reaction vessel was removed from the enclosure and weighed. The seal weld was ground off at the flange at the original concrete-sodium interface, as shown in Figure 75. The test vessel was then separated at the flange to expose the initial surface region for visual examination and sampling.

The concrete and reaction products of the 4-in. diameter test specimens were very similar in appearance. Figure 16 shows the concrete-sodium interface in test S1 after the vessel was separated at the flange. The reaction product was a dense tannish brown mass. The products of test S1 showed silver metallic strata throughout the layer. The tests S2 and S8 reaction product had bright green streaks throughout the material, due to the high iron content of the concrete in those tests. The reaction product layer penetrated to average depths of 0.5, 0.9 and 1.0 inches for tests S1, S2 and S8, respectively.

In all three tests, the concrete itself remained hard and nearly normal in appearance. There was some discoloration of the concrete due to dehydration, the degree of discoloration lessening further away from the reaction layer. Figures 17 through 19 show the concrete after partial disassembly of the reaction vessel. The penetration of the concrete by the reaction is clearly visible.

When the 10-in. diameter vertical interface specimen was opened along the length of the concrete, it was found to have cracked during the test. Figure 20 shows the crack extending completely through the specimen in a vertical plane, starting 0.75 in. from the sodium vapor interface at the top and ending 2.25 in. from the sodium-concrete interface at the bottom. A reddish-brown material filled the crevice. The sodium "pool" was a crescent shaped segment 3.75 in. deep, weighing 6.2 pounds, with an apparent density of 2.1.

(74H0438-8)

FIGURE 15. Grinding Off Seal Weld at Sodium-Concrete Interface

(74H0438-18)

FIGURE 16. Post-test View of Original Interfacial Area - Test S1

(74H0438-7)

FIGURE 17. Side View of Concrete - Test S1 (74H0438-7)

(741923-10)

FIGURE 18. Side View of Concrete - Test S2

(7428021-1)

FIGURE 19. Side View of Concrete - Test S8

(742039-3)

FIGURE 20 Side View of Concrete Showing Crack - Test S4

This material was brittle and had no metallic sodium remaining. Some white coral-like material deposited near the vent was found by chemical analysis to be NaOH crystals. The concrete surface in the sodium vapor space had an adherent layer of reaction product approximately 3/8 in. thick of various shades of brown and green.

The 4-in. diameter reaction vessel of test S7 was sectioned longitudinally, as shown in Figure 21. Much of the residue was metallic sodium. A dense, brittle material was found at the bottom of the vessel, forming a continuous layer approximately 1-in. thick. Above this layer (and actually a part of it) were several lumps of material of the same apparent composition. The residue took on a "plaster cast" image of the vessel surface, indicating that it had either been molten or a slurry. No original concrete or aggregate was discernible. The pool above the lumps appeared to be fairly pure metallic sodium. The visual observations made are summarized on Table VI.

E. CHEMICAL ANALYSES

Samples of the residual sodium pool, reaction product and concrete were analyzed for major elements, and the results are summarized in Table VII. The exact chemical form of the reaction product was not determined and is probably quite complex. However, assuming that all of the soluble silicon exists as sodium metasilicate, other reacted sodium is in the monoxide form, iron is present as FeO, and all other metallic elements exist as their stable oxides, the approximate composition shown in Table VIII was calculated. It is postulated that these materials are loosely bound together to form the compacted powder-like material found during sampling.

Some miscellaneous notes on chemical analyses are:

- The residual sodium pools contained $<0.1\% \text{Na}_2\text{O}_2$.
- The reaction products contained 0.01% soluble iron.
- The iron in one sample of reaction product in test S4 was predominantly metallic.
- Most reaction product material was non-magnetic.
- Na_2CO_3 and NaOH were found in the top of the residual sodium pool in test S4.

(742198-14)

FIGURE 21. View of Reaction Products at Bottom of Metallic Sodium Pool - Test S7

TABLE VI
SUMMARY OF VISUAL EXAMINATIONS

	TEST				
	S1	S2	s4	S7	S8
Weight Na Dumped (lb)	2.1	2.1	3.8	3.8	23
Weight Na Pool Residue (lb)	2.56	2.93	6.2	5.8	21
Volume Na Pool Residue (ft ³)	0.026	0.024	0.048	(a)	0.32
Sp Gravity Na Pool Residue	1.6	2.0	2.1	(a)	1.05
Metallic Na Evident In Pool	Mnor	Mnor	None	Major	Major
Evidence of Na Leakage Between Steel Wall and Concrete	Nb	Nb	Nb	--	Nb
Concrete Cracked	Nb	Nb	Yes	--	No
Sp Gravity of Reaction Product	(a)	2-3	--	(a)	--
Avg Penetration of Na Into Concrete (In.)	0.5	0.9	1.5(bI	(c)	1.0
Mx Penetration of Na Into Concrete (In.)	0.75	1.0	2.3(b)	(c)	1.25

(a) Not measured.

(b) Concrete cracked.

(c) Entire concrete lumps (approximately 1.5 inch) reacted.

TABLE VII
SUMMARY OF CHEMICAL ANALYSES

	Weight Percent				
	S1	S2	s4	S7	S8
Metallic Na	6.6	2.5	0.05	34	>80
Total Na		51	30		
Fe		19	30		
Total Si		1.4	0.6		
Soluble Si (a)					
Ca		2.0	4.3		
Al		0.3	0.3		
Mg			0.8		
Cr, Mn, Ni			0.1		
Water-Soluble Material	81	66	43		
Reaction Product (b)					
Metallic Na		0.05		1.5	~20
Total Na	51	42	40	32	30
Fe	7.6	31	30	37	30
Total Si	5.5	1.7	1.5	1.2	1.0
Soluble Si (a)	4.0	0.5	1.0	0.5	
Ca	3.0	1.2	1.4	4.0	2.7
Al		0.2	0.2	0.4	
Mg	0.5		0.4		
Cr, Mn, Ni			0.1		
Water-Soluble Material	78	60	52	53	48
Total Na	0.01	0.06	0.02	--	
H ₂ O	0.7	0.5	0.8	--	0.5
Total Na	0.01	0.05	0.02	--	
H ₂ O	1.3	1.0	1.1	--	0.6

TABLE VIII

APPROXIMATE COMPOSITION OF REACTION PRODUCT

	Calculated Weight Percent			
	TEST			
	S1	S2	s4	s7
Na_2O	60.0	51.8	51.8	40.6
Na_2SiO_3	17.4	2.2	1.6	2.3
FeO	9.7	39.4	38.1	47.7
SiO_2	3.2	2.6	1.1	1.5
CaO	4.2	1.7	2.0	4.7
Al_2O_3		0.4	0.4	0.8
MgO	0.8		0.7	
Other	4.7	1.9	4.2	1.4
TOTAL	100.0	100.	100.0	100.0

F. HEAT OF REACTION

Definite exothermic reactions were noted only during tests S4 and S7. The temperature traces for these tests gave measureable changes in the temperature ramp rates in the sodium pool. Two approaches by which energy release rates may be obtained from the data appear useful:

- The ultimate temperature change applicable to the chemical energy release can be determined from the data and, using the appropriate thermal masses, heat capacities and surface areas, the energy release rate can be calculated.
- The initial temperature slope change caused by the chemical energy release can be measured and, again using the applicable heat capacities, energy release rates obtained.

There are several shortcomings to both of these approaches which increase the complexity or decrease the accuracy of the analysis:

- Both approaches suffer from a large uncertainty in defining the thermal masses actually involved in the event.
- The first approach requires that the maximum response temperatures be determined. In test S4, the trace heater power was not kept constant throughout the apparent duration of the event.
- Heat losses at higher temperatures, particularly in an unsteady state condition, become less definable.
- The quenching of the sodium pool by the concrete in test S7 makes it more difficult to define the initial temperature ramp rate.
- Uncertainties exist in defining the area of interface between the sodium and the concrete in order to express the energy release rate in terms of unit surface area.

Figure 22 details the average sodium pool temperature for test S4 at the time of the strong energy release. Shown on the figure are the extrapolated slopes of the temperature trace immediately before and immediately after the start of the reaction. Figure 23 shows the same data for test S7. By taking these slopes and defining the total heat generation rate as in Equation (3), total instantaneous heat release rates may be computed.

$$q = \sum_0^n \frac{C_{pi} M_i dT_i}{dt} \quad (3)$$

where: q = heat of reaction, Btu/min

C_p = specific heat, Btu/lb-°F

M = mass involved in thermal transient, lb

T = temperature associated with M , °F

t = time, min

i = individual species of mass involved

n = number of species of mass.

FIGURE 22. Sodium Pool Temperatures During Test S4 at Time of Reaction

HEDL 7407-25.13

FIGURE 23. Sodium Pool Temperatures During Test S7 at Time of Reaction

By assuming various limiting values for responding thermal masses and affected surface areas, a broad range of energy release rates was defined. The average of these various rates gives a best estimate of the value for the energy release rate of $10,000 \text{ Btu/hr-ft}^2 \pm 50\%$.

The reaction period in test S7 lasted 12 ± 2 minutes. If we combine these data with the $10,000 \text{ Btu/hr-ft}^2$, and assume that the entire two pounds of concrete was reacted, the heat of reaction on a mass basis can be calculated as $700 \pm 350 \text{ Btu per pound of magnetite concrete}$.

V. ACKNOWLEDGEMENTS

The tests were performed by D. L. Ballard, R. E. Menard and R. E. Sadler. The test articles were prepared with the assistance of J. D. McCormack, J. J. Mahoney and W. H. Romsos. Pittsburgh Testing Laboratory poured the concrete, with Quality Assurance provided by F. E. Schack, Bechtel. Valuable suggestions for planning and evaluating the tests were given by P. R. Shire, G. R. Armstrong, W. H. Caplinger and W. H. Yunker.

VI. REFERENCES

1. N. A. Lange, Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio, 1946, 6th edition, p. 1531.
2. D. Broadley, "Secondary Sodium Circuit Integrity and Fire Fighting Procedure for UKAEA Prototype Fast Reactor," in TID-26076, p. 133, May, 1972.
3. M. Sauvage and Fruchard, "Extinguishment of Sodium Fires," in TID-26076, p. 53, May, 1972.
4. R. K. Hilliard and J. M. Yatabe, "FFTF Secondary Sodium Fire Protection System Test Fl," HEDL-TME 73-48, dated April, 1973.

APPENDIX A

Retyped from original letter from Westinghouse Research and Development Center, Beulah Road, Pittsburgh, Pa 15235.

February 20, 1974

Dr. Wayne H. Yunker
Westinghouse Hanford Company
P.O. Box 1970
Richland, Washington 99352

Dear Wayne:

As per your letter of January 21, 1974 and our subsequent telephone conversations, we have studied the chemical reaction behavior of high density concrete (M-225) with sodium by differential thermal analysis (DTA) over the temperature range of 25 to 800°C. In addition, we have also examined your sample of standard concrete and, for comparison purposes, separate samples of sand and Portland cement (Type IA). The apparatus employed in this work was specifically designed to study the reaction of materials with sodium at elevated temperatures and is described in detail in a recent Westinghouse Research Laboratories scientific paper.¹

The results of this work are presented in Table 1, which identifies the temperature at which the exotherm occurred and the heat of evolution for each material studied. Please note that the heat of evolution values ($-\Delta H$, cal/gram) are based on the calibration of the DTA apparatus with known weights of NiO and Fe₃O₄ that were run individually with excess sodium. The results are, at best, semiquantitative and are probably accurate to within a factor of two, although, because of the calibration technique employed, the result obtained for sample M-225 is probably much better than this.

For your information, we have included in Figure 1 the DTA curves which were obtained on the samples, and in Figure 2, a plot of the cover gas pressure within the sealed DTA sample tube as a function of temperature for each individual run. (Such pressure readings are of value in detecting gaseous products of reaction, such as hydrogen.)⁵

From these results, the following conclusions may be drawn:

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- A. Concrete sample M-225 reacts at a lower temperature with sodium than standard concrete and generates considerably more heat. This is presumably due to the presence of Fe_3O_4 in the material, see Figure 1. The high reactivity shown by M-225 suggests that an alternate densifying material besides Fe_3O_4 should be considered. A likely candidate for this could be iron shot since iron metal will be much more stable with sodium over the range of conditions at which this work was carried out.²
- B. For the sodium reactions of sand, standard concrete and Portland cement, single peaks were observed and are probably due to the reaction:

Alternatively, the product may possibly be a sodium silicide. However, it has been shown that sodium silicide dissociates at elevated temperature to elemental silicon.^{3,4} For sample M-225, the single peak observed is probably due to the reaction:²

The exotherm temperature shift noted between sample M-225 and the standard Fe_3O_4 , as shown in Figure 1, may be due to particle size differences, or, alternatively, the other components of the concrete in sample M-225 may be providing some degree of protection for the Fe_3O_4 , thus leading to a higher reaction temperature.

- C. No definite evidence for hydrogen evolution, due to the reaction of sodium with water in the concrete, was noted by monitoring the sample tube pressure during the DTA runs, see Figure 2.
- D. No DTA peaks were noted that could be assigned to the reaction of sodium with water, even though the presence of $-\text{OH}$ in sample M-225 was definitely indicated by the infrared spectrum, see Figure 3. It is surprising that no reaction with bound water was unequivocally observed; further studies are indicated to clarify this point.

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We hope that this information will fulfill your near-term requirements. If you have any additional questions concerning this study, please feel free to give us a call.

Sincerely,

original signed

Robert E. Witkowski

original signed

Robert G. Charles
Chemistry of Liquid Metals

jmw

Approved: original signed
E. Berkey, Manager
Chemistry of Liquid Metals

cc: Karen L. Jones, Westinghouse Hanford Company
R. M. Lowy, Westinghouse Research Laboratories
W. T. Lindsay, Jr., Westinghouse Research Laboratories
PIC-2-file

Dr. Wayne H. Yunker
February 20, 1974
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References

1. R. G. Charles, "Differential Thermal Analysis as a Means for Studying Chemical Reactions on Liquid Sodium," Westinghouse Research Laboratories Scientific Paper 73-1B6-INDIS-P1, July 3, 1973.
2. R. G. Charles and P. H. Biggs, "Thermomagnetic Analysis and Calorimetric Studies of the Reaction of Ferric Oxide with Liquid Sodium," in "Chemical Aspects of Corrosion and Mass Transfer in Liquid Sodium," S. Jansson, Ed., The Metallurgical Society of AIME, New York (1973), p. 381.
3. H. Nowotny and E. Scheil, "A Ternary Compound in the System Aluminum-Silicon-Sodium," Z. Metallkunde ~~17~~, 76 (1947).
4. E. Hohman, "Silicides and Germanides of the Alkali Metals," Z. Anorg. Chem. ~~257~~, 113 (1948).
5. R. G. Charles, "Liquid Sodium-Oil Interactions," Westinghouse Report I.W.R. Y3M-IWR-00705, October, 1973.

TABLE 1
DIFFERENTIAL THERMAL ANALYSIS RESULTS
FOR THE REACTION OF 200 mg SAMPLES IN EXCESS SODIUM
NICKEL SAMPLE CONTAINER WITH ARGON COVER GAS

Dwg. 6226A67

Sample Identification	Exotherm °C	*Heat Evolution, $-\Delta H$ Cal/ Gram	Sample Preparation
M-225	464	+ 501	Ground in Shatter Box to Approx. 100 Mesh.
Sand	538	+ 457	As Received Washed with Distilled Water, Oven Dried.
Standard Concrete	634	+ 134	Ground in Shatter Box to Approx. 100 Mesh.
Portland Cement (Type IA)	576	+ 27	Cast Sample, 'Aged 4 Days, Ground with Mortar and Pestle.
*Based on Calibration of Apparatus with Known Weights of NiO and Fe_3O_4 with Excess Sodium

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

FIGURE 2. Sample Tube Pressure vs. Temperature During DTA Run

A-8

FIGURE 3. Infrared Spectra of Sample M-225, KBr Pellet

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