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LARGE-SCALE SODIUM-BASALT CONCRETE REACTION TEST LSC-1

Hanford Engineering Development Laboratory

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Large-Scale Sodium-Basalt
Concrete Reaction Test LSC-1

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R. P. Colburn

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ABSTRACT

The energy and hydrogen released from sodium-concrete reactions must be considered the analysis of beyond-design basis accidents for breeder reactors. Consequently, a large-scale sodium-basalt concrete reaction test was completed in the Large Sodium Fire Facility (LSFF) at the Hanford Engineering Development Laboratory (HEDL). 454 kg of sodium at 593°C was spilled onto 0.84 m² of basalt concrete 0.61 m deep containing two layers of reinforcing steel bar. From the data obtained, it was possible to complete a mass and energy balance for this test. The hydrogen generation and generation rate as functions of time for the duration of the test were determined. The major contribution to the chemical energy was energy associated with the formation of hydrogen (sodium-water reactions). Approximately 0.87 mole of hydrogen was produced per mole of water consumed. Two reaction sequences are postulated for sodium-concrete reactions with one adequately explaining the results for this test.

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LARGE-SCALE SODIUM-BASALT CONCRETE REACTION TEST LSC-1

I. SUMMARY AND CONCLUSIONS

The amount and rate of energy and hydrogen released from sodium-concrete reactions must be considered in breeder reactor safety analyses where it is desired to demonstrate that, even with the assumption of accidents which exceed design basis containment, integrity will be maintained in a manner which limits off-site consequences to acceptable levels. Several experimental programs have been initiated to determine energy released, rate of chemical reaction penetration into concrete, and hydrogen released from sodium-concrete reactions. Basically, the results can be separated into two areas. The first area is tests in which a chemical reaction penetration barrier appeared to be established, thus limiting the reaction penetration to a few centimeters. The energy released was dominated by sodium-water chemical reactions and the reaction products were described as of hard, rock-like consistency with high compressive strength. The second consists of sodium-concrete reaction tests with weakened concrete, such as dehydrated concrete or concrete which was substantially cracked. In these tests, the sodium reaction penetration into the concrete was very rapid and quite extensive. Again, the dominant energy contribution was from sodium-water reactions. The reaction products were described as loose, friable, of a cinder-like consistency, and having low compressive strength. From some of the larger-scale tests, very little data are available on hydrogen or energy released.

The objective of the large-scale sodium-basalt concrete reaction test (LSC-1) was to examine these reactions in a two-dimensional reaction plane with concrete restrained as nearly as possible like a cross-sectional piece of concrete in a large concrete floor. Data were to be obtained on chemical reactions, hydrogen generation, and hydrogen-nitrogen-sodium vapor ignition as the gas exited into an air atmosphere.

454 kg of sodium at 593°C was spilled onto 0.84 m² of basalt concrete 0.61 m deep containing two layers of reinforcing steel bar. After the

initial sodium quench, the sodium pool was electrically heated to 593°C. The sodium pool and concrete temperatures, gas concentrations, and sodium reservoir and test chamber pressures were continuously monitored. Audio-visual observations were made and recorded. Post-test disassembly and chemical analysis helped to determine the end state of the chemical reactions.

Major test results are:

- 1) A complete mass balance was possible from the data collected. The total amount of generated hydrogen was measured as a function of time. The remaining water in the unreacted concrete was determined post-test by chemical analysis of core samples. The mass and composition of the reaction products were determined by post-test analysis. From the concrete thermocouple data, the chemical reaction penetration rate was determined.

Approximately 3600 g-moles of hydrogen were released with 750 g-moles/h as the maximum average hydrogen release rate. 4147 g-moles of water were released, or about 81% of the total pre-test water contained in the concrete mix, sand, and aggregate. (0.87 mole of hydrogen was produced per mole of water consumed). 54% of the concrete and 15% of the sodium remained unreacted at the conclusion of the test. The sodium chemical reaction penetration rate mirrored the hydrogen release rate. The maximum reaction penetration rate occurred between 1.6 h and 3.6 h with an average reaction penetration rate of 9.1 cm/h for the two-hour period. The chemical reaction penetration rate was less than 1 cm/h for the remaining 86 hours. The minimum total reaction penetration was 20 cm, the maximum penetration was 39 cm, and the average penetration was 26 cm.

- 2) An energy balance was completed from the data. The chemistry of the reactions was sufficiently determined such that the energy associated with the formation of hydrogen and the energy associated with the formation of Na_2SiO_3 were calculated from the measured hydrogen release

rate and concrete reaction penetration data to provide a total chemical reaction energy. The calculated energies are in agreement with end point energies calculated from existing differential thermal analysis^(1,2,3) and heats of reaction. The energy losses due to heat conduction into the concrete and through the sodium reservoir walls were calculated using experimental temperature data and heat conduction theory. The electrical energy input through the sodium reservoir electrical heaters was also calculated. The difference between the total energy input and total energy lost was used to calculate the temperature of the sodium pool. The calculated and measured sodium pool temperatures are in agreement, thus suggesting that the major energy sources and losses were adequately determined.

The dominant energy source during the first 1.1 h of the test was from the electrical heaters (67%), while the dominant energy source during the remainder of the test was from the chemical energy (85% to 100%). The dominant energy loss during the entire test was heat conduction to the concrete (83% to 95%). The chemical energy generated between 1.6 h and 3.6 h (59KJ/s) was sufficient to increase the sodium pool temperature from 593°C to 775°C.

From the above two test results, the hydrogen generation and generation rate (see Figures 17 and 18), and the energy generation and generation rate (see Figures 35 and 36) as functions of time were determined for the test, along with the sodium reaction penetration (see Figure 28).

- 3) The ignition of the hydrogen-nitrogen-sodium vapor gas mixture as it exited from the sodium reservoir into the air atmosphere of the test chamber was determined. At the time of ignition, the sodium aerosol concentration was 23.23 grams of sodium per cubic meter of gas and the gas temperature was 260°C. These data are consistent and in agreement with the hydrogen ignition criteria developed by small-scale tests for hydrogen-nitrogen gas jets igniting in the presence of sodium.

The major conclusions from the test are:

- The major contribution to the chemical energy was energy associated with the formation of hydrogen from sodium-water reactions, which represented 65% to 73% of the total energy.
- A significant chemical reaction during this test was the formation of Na_2O , which would imply generation of 1 mole of hydrogen per mole of water driven from the concrete (test results were actually 0.87).
- The structural strength of the concrete had an appreciable effect on the chemical reaction penetration.

Based on these and other test results, the following reaction sequence can be postulated:

If the temperature-dependent compressive strength of concrete is greater than the compressive stress produced in the heated concrete, then significant concrete crushing would not occur, and the chemical reactions would be diffusion limited. The major reaction species would be a NaOH layer, and the major contribution to the energy would be from sodium-water reactions. In this sequence, the NaOH layer and the diffusion-limited reaction process could form a reaction product barrier. On the other hand, if the temperature-dependent compressive strength of the concrete is less than the compressive stress produced in the heated concrete, then significant concrete crushing could occur, resulting in larger surface areas of concrete for reactions and direct vent paths for steam release. The results would be a larger hydrogen generation rate and a sodium reaction with structurally weakened or crushed concrete. The major contribution to the energy would still be from sodium-water reactions, but the energy release rate and sodium reaction penetration rate would increase in proportion to the hydrogen release rate, which is related to the rate and extent of concrete crushing. The results of this test seem to apply to the second reaction sequence.

II. INTRODUCTION

A major objective of the Fast Reactor Safety Program Plan is to demonstrate that containment integrity will be maintained in a manner which limits off-site consequences to acceptable levels throughout a variety of postulated accident scenarios, including accidents beyond the design basis. With this objective as a guide, events that might conceivably lead to violation of containment integrity are identified and critically analyzed.

One progression of a core disruptive accident analyzed in safety analyses assumes that the hot core debris and sodium have penetrated through the reactor vessel and guard vessel and into the reactor cavity area. It is further assumed that hot core debris may penetrate through the cavity liner and the sodium may come in contact with insulating materials or structural concrete behind the cavity liners. The sodium may then react with concrete and water driven from the heated concrete to produce hydrogen and to liberate energy. Consequently, the results of sodium-concrete reactions must be addressed: how much and how fast can hydrogen be produced and liberated to containment, and how much energy would be produced from the reactions to add to that energy already contained in the core debris?

Several experimental programs were initiated to determine energy released, rate of reaction penetration, and hydrogen released from sodium-concrete reactions. Three series of small-scale (0.028 m^3 of concrete and 23 kg of sodium) sodium-concrete reaction tests^(3,4,5) were performed at HEDL on basalt, limestone, and magnetite concretes. The major results of these tests are summarized in Reference 6. The average sodium reaction penetration depth into the concrete after 24 hours was typically 5 cm, and the bulk of the reaction penetration occurred during the initial 8 hours, with relatively little additional reaction penetration resulting from longer sodium exposures, even up to 100 hours. Post-test analysis of the unreacted concrete generally showed that more than 80% of the moisture initially present in the concrete was released during the test. The extent of water released from the concrete resulted from heat conduction into the concrete,

rather than from sodium penetration of the concrete. A NaOH reaction product phase was produced at the concrete interface that generally formed a barrier layer of reaction products, thus limiting the reaction penetration into concrete to a few (up to 5) centimeters. Post-test examination of these limited penetration test articles showed that the reaction product was characterized as having a hard, rock-like consistency. However, in some cases, mechanical effects may prevent formation or cause disruption of the protective reaction product layer and result in rapid reaction penetration through concrete that has largely been dehydrated. The reaction products associated with deep rapid penetrations of sodium through dehydrated concrete⁽⁶⁾ were characterized as loose, friable, and of cinder-like consistency with little cohesion in contrast to the hard, rock-like consistency of the reaction products from tests with limited reaction penetrations.

To reduce the heat load to concrete, a lower cavity design may employ insulating materials between the cavity liner and structural concrete. An experimental investigation⁽⁷⁾ was completed to study sodium-concrete reactions through a faulted steel liner with various combinations of insulating materials protecting the concrete. The test articles used for the investigation were 0.028 m³ of concrete (23 kg of sodium) for the small-scale tests and 0.504 m³ of concrete (454 kg of sodium) for the large-scale tests. The major conclusions were that insulating refractory bricks tended to thermally insulate the concrete, reducing the rate of water released and hydrogen generation as well as retarding sodium migration into the structural concrete. The large-scale tests results were consistent with the small-scale test results, and the principal reaction occurred between the sodium and water released from considerable depth in the concrete.

Large-scale sodium-concrete reaction tests (normally 1.57 m³ of concrete and 20 kg to 250 kg of sodium) were also performed^(8,9,10) using a right cylindrical concrete crucible with a cylindrical cavity as the sodium reservoir. In general, the cylindrical concrete cavity badly cracked during the experiments. Chemical reaction penetrations varied from very little penetration up to 30.5 cm, with the test generally being sodium limited for

those tests in which large chemical reaction penetrations occurred. Because the concrete crucibles cracked, little hydrogen generation data are available beyond the first hour or so. In one test, the reaction products are described as a cinder-like bed of reaction products.

The small-scale sodium-concrete reaction tests supported the conclusion that a heavy, viscous reaction product may be produced that settles on horizontal surfaces and reduces the extent of sodium-concrete reactions. Both long and short-term tests were performed in which the test concrete was not substantially cracked, and neither the sodium or concrete were totally consumed. However, for dehydrated or cracked concrete in which the reaction product layer would have been prohibited or disturbed, the reaction penetration was more severe, even though the energy or hydrogen produced may not have been more severe.

The objective of LSC-1 was to examine, on a larger-scale, sodium-basalt concrete reactions in a two-dimensional reaction plane with concrete restrained as nearly as possible like a cross-sectional piece of concrete in a large concrete floor. In addition, the test was organized to provide hydrogen generation data from large-scale experiments and data regarding ignition and extinguishment of hydrogen-nitrogen-sodium vapor exiting into an air atmosphere.

III. TEST FACILITY DESCRIPTION

LSC-1 was performed at Hanford Engineering Development Laboratory (HEDL) in the Large Sodium Fire Facility (LSFF). See Figure 1. The facility is a multiroom structure with the capability to control large-scale liquid metal spills. The facility contains three test cells: a large test cell and two small test vessels. The large test cell has a sodium spill capability of 2268-kg (5000-lb) sodium at a maximum temperature of 650°C (1100°F). Small test vessels 1 and 2 have a sodium spill capability of 22.7-kg (50-lb) sodium at a maximum temperature of 871°C (1600°F). A liquid nitrogen system is included that can supply up to 5.6 m³/min (200 std ft³/min) of nitrogen to a total volume of 5943 m³ (210,000 std ft³). Building exhaust gases are swept through an exhaust tunnel to a scrubber and filter system before they exit through a 61-m (200-ft) stack.

The LSC-1 test was performed in the large test cell, 4.27 m x 4.57 m x 5.49 m (14 ft x 15 ft x 18 ft), shown in Figure 2. The cell atmosphere was exhausted through a 20.32-cm (8-in.) duct, that can exhaust gas at rates up to 7.08 m³/min (250 ft³/min). The exhaust gas was throttled by a manually controlled butterfly valve located within the exhaust ductwork. Nitrogen purging was also available from the facility nitrogen supply system.

HEDL 8011-043.34

FIGURE 1. Plan View of Large Sodium Fire Facility, 105 DR Building.

FIGURE 2. View of Large Test Cell. Neg 86466-9cn

IV. TEST ARTICLE DESCRIPTION

The test article is shown in Figures 3, 4, and 5 and consisted of a 61 cm deep by 0.836 m² square (2 ft x 9 ft²) concrete section. Basalt concrete with mix specifications as listed in Table 1 was used with two layers of No. 8 reinforcing steel bar on a 30.48-cm (12-in) grid spacing pattern. See Figure 3. A restraint mechanism (Figure 4) surrounded the central concrete section and was used to simulate periphery concrete that would be found in a large concrete floor. The test concrete was separated from the concrete used in the restraint mechanism by a 0.64-cm (0.25-in.) thick steel plate. The top section (Figure 5) was a sodium reservoir large enough to handle 454 Kg (1000 lb.) of sodium.

A. REINFORCING STEEL BAR

Reinforcing steel bar was used in the central concrete test section and restraint area. The two layers of No. 8 reinforcing steel bar in the central concrete test section (Figure 3) had 3.8 cm and 25.1 cm (1.5 in. and 9-7/8 in.) of concrete surface cover in a 30.48-cm (12-in.) grid spacing pattern. The No. 8 reinforcing steel bar in the restraint area is shown in Figure 4.

B. RESTRAINT AREA

A restraint mechanism (Figure 4) surrounded the central concrete test section. This was used to simulate the stresses and restraint that would be provided by periphery concrete surrounding a cross-sectional piece of concrete in a large concrete floor. The restraint mechanism consisted of a reinforced 38.1-cm (15-in.) square concrete beam of the same type of concrete used in the center test section and surrounded by a 20.3-cm (8-in.) I-beam.

TABLE 1

CONCRETE MIX SPECIFICATIONS

<u>Basalt, Concrete Mix Class C-1*</u>	<u>kg/m³</u>	<u>lb/yd³</u>
Cement	260.6	439
Pozzolan	46.3	78
Sand (#4)	840.0	1415
Aggregate (1.9 cm)	1080.4	1820
Water	152.61	257.9
WRA (Pozzolite 32)	1.5	2.5
Air Entrainment Additive	0.5	0.83
<u>Measured Water Content</u>	<u>kg</u>	<u>lb</u>
Contained in Sand	8.92	19.66
Contained in Aggregate	5.19	11.44
Used in Mix	<u>77.99</u>	<u>171.93</u>
TOTAL	92.10	203.03
<u>Measured Compressive Strengths</u>	<u>Pa</u>	<u>psi</u>
28 day	2.44×10^7	3540
670 day	2.63×10^7	3820

* Date Poured: July 11, 1978
 Surface Area: 91.54 cm x 91.54 (3 ft x 3 ft)
 Depth: 61.0 cm (2 ft)
 Volume: 0.511 m³ (18.0 ft³)

No. 8 (2.54 cm DIAM) x 86.36 cm LARGE REINFORCING BAR

FIGURE 3. Central Concrete Test Section.

HEDL 8011-043.25

(ALL REBAR NO. 8)

HEDL 8011-043.24

FIGURE 4. Sodium-Concrete Test Article.

FIGURE 5. Front View of Total Test Article Assembly.

C. SODIUM RESERVOIR

The top section of the test article (Figure 4) is the sodium reservoir sized to hold 454 kg (1000 lb) of sodium. The sodium reservoir was welded to the steel plate that separated the test concrete from the concrete in the restraint mechanism. The welds were X-ray and dye-penetrant tested to insure their integrity. The reservoir was electrically heated by immersion and side wall heaters, and was insulated with 10.2 cm (4 in.) of 128 kg/m³ (8 lb/ft³) Kaowool®. The sodium was transferred to the reservoir from the large sodium batch tank via a 7.6-cm (3-in) diameter stainless steel pipe welded to the top.

D. INSTRUMENTATION

The gas concentrations, temperatures and pressures of the test article were continuously monitored on strip chart recorders and magnetic tapes by a data acquisition system. Audio-visual observations were recorded by a video-cassette television recorder. Sodium aerosol concentrations were taken manually at predetermined times.

Gas concentrations were monitored in the test cell, sodium reservoir and facility exhaust tunnel. Temperatures were monitored in the test cell, restraint area, central concrete test section and sodium reservoir. Audio-visual surveillance of the restraint area and sodium reservoir was maintained through a window in the test cell's north wall. Diaphragm pressure transducers monitored the pressure in the test cell and sodium reservoir.

Table 2 identifies the instrumentation used to measure the gas concentrations. Approximate gas flows of 2.3×10^{-5} m³/s (3 ft³/h) were used for instrumentation.

®Manufactured by Babcock and Wilcox, Refractories Division, Augusta, GA.

TABLE 2
GAS ANALYSIS INSTRUMENTATION

<u>Instrument</u>	<u>Test Cell</u>	<u>Sodium Reservoir</u>
Beckman, Model 7C*		H ₂
Beckman, Model 71003*		O ₂
Teledyne, Model 102**	H ₂	
Teledyne, Model 326-A**	O ₂	
General Eastern, Model 1200 AP***	H ₂ O	

*Manufactured by Beckman Instrument Co, Burbank, CA.

**Manufactured by Teledyne Analytical Instruments, Hampton, VA.

***Manufactured by General Eastern Corp, Watertown, MA.

A vacuum and nitrogen purge capability was attached to the gas sample lines in case plugging occurred. Each gas sample line was fitted with a Gelman* glass prefilter to discourage plugging. The test cell sample location was in the top of the test cell directly above the vent stack from the sodium reservoir. The sodium reservoir gas sample line was located in the top corner.

Nitrogen was supplied to the sodium reservoir through a line tapped into the top wall. The line could supply a maximum of $8.19 \times 10^{-3} \text{ m}^3/\text{s}$ (17.35-ft/min) nitrogen through a rotameter and manually-regulated valve. Table 3 gives the location of all thermocouples relative to the center of the central concrete test section surface.

*Manufactured by Gelman Instrument Co, Ann Arbor, MI.

TABLE 3

THERMOCOUPLE LOCATIONS RELATIVE TO CENTER OF CONCRETE SURFACE

DAS No.	Recorder	Location	Axis (cm)		
			X	Y	Z
1	TR-F	Central Concrete Test Section	+38.1	+38.1	- 2.5
2	TR-F	Central Concrete Test Section	+38.1	+38.1	- 7.6
3	TR-F	Central Concrete Test Section	+38.1	+38.1	-15.2
4	TR-F	Central Concrete Test Section	+38.1	+38.1	-61.0
5	TR-F	Central Concrete Test Section	-15.2	+15.2	- 2.5
6	TR-F	Central Concrete Test Section	-15.2	+15.2	- 7.6
7	TR-F	Central Concrete Test Section	-15.2	+15.2	-15.2
8	TR-F	Central Concrete Test Section	+15.2	+15.2	- 2.5
9	TR-F	Central Concrete Test Section	+15.2	+15.2	- 7.6
10	TR-F	Central Concrete Test Section	+15.2	+15.2	-15.2
11	TR-F	Central Concrete Test Section	+15.2	+15.2	-61.0
12	TR-F	Central Concrete Test Section	+38.1	0	- 2.5
13	TR-F	Central Concrete Test Section	+38.1	0	- 7.6
14	TR-F	Central Concrete Test Section	+38.1	0	-15.2
15	TR-F	Central Concrete Test Section	+38.1	0	-30.5
16	TR-F	Central Concrete Test Section	+38.1	0	-61.0
17	TR-F	Central Concrete Test Section	0	0	- 2.5
18	TR-F	Central Concrete Test Section	0	0	- 7.6
19	TR-F	Central Concrete Test Section	0	0	-15.2
20	TR-F	Central Concrete Test Section	0	0	-25.4
21	TR-F	Central Concrete Test Section	0	0	-30.5
22	TR-F	Central Concrete Test Section	0	0	-45.7
23	TR-F	Central Concrete Test Section	0	0	-61.0
24	TR-F	Central Concrete Test Section	-15.2	-15.2	- 2.5
25	TR-G	Central Concrete Test Section	-15.2	-15.2	- 7.6
26	TR-G	Central Concrete Test Section	-15.2	-15.2	-15.2
27	TR-G	Central Concrete Test Section	+15.2	-15.2	- 2.5
28	TR-G	Central Concrete Test Section	+15.2	-15.2	- 7.6
29	TR-G	Central Concrete Test Section	+15.2	-15.2	-15.2
30	TR-G	Central Concrete Test Section	0	-30.5	- 2.5
31	TR-G	Central Concrete Test Section	0	-30.5	- 7.6
32	TR-G	Central Concrete Test Section	0	-30.5	-15.2
33	TR-G	Central Concrete Test Section	0	-30.5	-61.0
34	TR-G	Restraint Area	0	+50.8	- 2.5
35	TR-G	Restraint Area	0	+50.8	-15.2
36	TR-G	Restraint Area	0	-50.8	- 2.5
37	TR-G	Restraint Area	0	-50.8	- 7.6
38	TR-G	Restraint Area	0	-50.8	-15.2
39	TR-G	Restraint Area	-15.2	-50.8	- 2.5
40	TR-G	Restraint Area	-15.2	-50.8	- 7.6
41	TR-G	Restraint Area	-15.2	-50.8	-15.2
42	TR-G	Restraint Area	+50.8	+50.8	- 2.5
43	TR-G	Restraint Area	+50.8	+50.8	- 7.6
44	TR-G	Restraint Area	+50.8	+50.8	-15.2
45	TR-G	Restraint Area	+50.8	+50.8	-30.2
46	TR-G	Restraint Area	+78.7	+78.7	- 2.5
47	TR-G	Restraint Area	+78.7	+78.7	-15.2
48	TR-G	Restraint Area	+78.7	+78.7	-30.5
49	TR-J-1	Restraint Area	+50.8	-50.8	- 2.5
50	TR-J-2	Restraint Area	+50.8	-50.8	-15.2
51	TR-J-3	Restraint Area	+50.8	0	- 2.5
52	TR-J-4	Restraint Area	+50.8	0	-15.2
53	TR-J-5	Restraint Area	-78.7	0	- 2.5
54	TR-J-6	Restraint Area	-78.7	0	-15.2
55	TR-J-7	Restraint Area	-78.7	0	-30.5
56	TR-J-8	Restraint Area	-50.8	0	- 2.5
57	TR-J-9	Restraint Area	-50.8	0	- 7.6

TABLE 3 (Cont'd)

THERMOCOUPLE LOCATIONS RELATIVE TO CENTER OF CON

DAS No.	Recorder	Location	Axis (cm)		
			X	Y	Z
58	TR-J-10	Restraint Area	-50.8	0	-15.2
59	TR-J-11	Restraint Area	-50.8	0	-30.5
60	TR-J-12	Restraint Area	0	-78.7	- 2.5
61	TR-J-13	Restraint Area	0	-78.7	-30.5
62	TR-J-14	Restraint Area	-30.5	-78.7	- 2.5
63	TR-J-15	Restraint Area	-30.5	-78.7	-30.5
64	TR-J-16	Restraint Area	-61.0	-78.7	- 2.5
65	TR-J-17	Restraint Area	-61.0	-78.7	-30.5
66	TR-J-18	Central Concrete Test Section	38.1	38.1	- 1.3
67	TR-J-19	Central Concrete Test Section	-15.2	15.2	- 1.3
68	TR-J-20	Central Concrete Test Section	+15.2	15.2	- 1.3
69	TR-J-21	Central Concrete Test Section	+38.1	0	- 1.3
70	TR-J-22	Central Concrete Test Section	0	0	- 1.3
71	TR-J-23	Central Concrete Test Section	-15.2	-15.2	- 1.3
72	TR-J-24	Central Concrete Test Section	+15.2	-15.2	- 1.3
73	TR-K-1	Central Concrete Test Section	0	-30.5	- 1.3
74	TR-K-2	Vent Stack at 0 in.			
75	TR-K-3	Vent Stack at 6 in.			
76	TR-K-4	Vent Stack at 12 in.			
77	TR-K-5	Vent Stack at 17 in.			
78	TR-K-6	Vent Stack at 26 in.			
79	TR-K-7	Vent Stack at 34 in.			
80	TR-K-8	Vent Stack at 48 in.			
81	TR-K-9	Reservoir Gas Line (Pipe)			
82	TR-K-10	Reservoir Gas Line (Tube)			
83	TR-K-11	Gas Line on South Wall			
84	TR-K-12	Reservoir North, Insulation Outside			
85	TR-K-13	Test Cell Gas Line			
86	TR-K-14	Reservoir East, Insulation Outside			
87	TR-K-15	Reservoir Top, Insulation Inside			
88	TR-K-16	Reservoir Top, Insulation Outside			
90	TR-K-18	Reservoir West, Insulation Outside			
91	TR-K-19	Restraint Area, S.E. Corner			
92	TR-K-20	Restraint Area, S.W. Corner			
93	TR-K-21	Restraint Area, N.W. Corner			
94	TR-K-22	Restraint Area, N.E. Corner			
95	TR-K-23	Reservoir 12 in. From Concrete Surface, N.W. Corner			
96	TR-K-24	Test Cell Floor			
98	TR-J-3	Reservoir South, Insulation Outside			
99	TR-L-2	Test Cell 2 ft. Above Floor			
100	TR-L-3	Test Cell 10 ft. Above Floor			
104	TR-J-5	Reservoir 6 in. From Concrete Surface			
106	TR-J-7	Reservoir 12 in. From Concrete Surface			
107	TR-J-9	Reservoir Vapor Space			
108	TR-J-11	Sidewall Heater East			
109	TR-J-13	Sidewall Heater North			
110	TR-J-15	Sidewall Heater West			
111	TR-J-17	Sidewall Heater South			
120	1	Lower Test Cell H ₂ (Flowmeter) System 1			
121	3	Lower Test Cell O ₂ (Flowmeter) System 1			
122	14	Upper Test Cell H ₂ (Flowmeter) System 2			
123	13	Upper Test Cell O ₂ (Flowmeter) System 2			
124	4	(Dewpoint Meter)			
125	2	Exhaust Tunnel H ₂ (Flowmeter)			
126	5	Level Detector (Pressure Transducer)			
127	6	Reservoir (Pressure Transducer)			
128	7	Test Cell (Pressure Transducer)			
130	10	Reservoir H ₂ (Flowmeter)			
131	11	Reservoir O ₂ (Flowmeter)			

V. TEST PROCEDURES

Following installation of the test article in the large test cell, the sodium reservoir was purged with nitrogen until the atmosphere contained less than 1% oxygen. Approximately 5 minutes prior to sodium spill, the external heaters attached to the side walls of the reservoir were energized. At t_0 , the sodium valve from the batch tank was opened, and sodium spill was determined to be complete when the operator observed a decrease in argon cover gas pressure and no further decrease in the weight of the batch tank.

Following the sodium spill, the immersion heaters were energized and the controller set points were adjusted to the desired temperature of 593°C (1100°F). Gas grab and aerosol samples were taken periodically. Gas analysis and thermocouple data were monitored and recorded continuously throughout the test.

During the early phases of the test, data were acquired in relationship to ignition of hydrogen, produced from the sodium-water reaction, as it exited through the gas space of the sodium reservoir and entered the air-filled test cell. Throughout the test period, air was continuously pulled through the test cell to insure complete burning of the hydrogen and to maintain near 0% hydrogen concentration in the test cell.

At the end of the testing period, the entire assembly was allowed to cool to below 27°C (80°F). Inspection, disassembly and cleanup began immediately. The test article was moved from the large test cell to a disassembly room where the insulation was removed and the sodium reservoir was separated from the central concrete test section and restraint area.

Reaction samples were collected from the sodium reservoir and central concrete test section. Each section was photographed and reaction interface profiles were determined. Core samples were taken from the restraint concrete and central concrete test section.

A. TEST OBSERVATIONS

LSC-1 was initiated on May 12, 1980 at noon in the large test cell at LSFF. Recorded test observations are summarized below:

Time	Observations
t_0	454 kg (1000 lb) of sodium at 593°C (1100°F) were spilled onto 0.836 m ² (1 yd ²) of basalt concrete containing two layers of reinforcing steel bar with 3.8 cm and 25 cm (1.5 in. and 9.86 in.) surface cover.
$t_0 + 1 \text{ min}$	Spill completed and the sodium reservoir level detector showed the sodium pool depth at 71 cm (28 in.). The nitrogen purge to the reservoir was set at $9.44 \times 10^{-4} \text{ m}^3/\text{s}$ (2 ft ³ /min). The immersion and sidewall heaters were energized.
$t_0 + 12 \text{ min}$	The hydrogen exiting from the vent stack ignited. A steady flame of 38 cm to 46 cm (15 in. to 18 in.) was visible. Test article conditions just before and after ignition are presented in Table 4.
$t_0 + 12.6 \text{ min}$	Many small particles of reacting, molten sodium were blown out the vent stack top. The hydrogen flame was steady at 51 cm to 61 cm (20 in. to 24 in.). Visibility in the test cell was lowered to ~3.7 m (12 ft) by the sodium aerosol.
$t_0 + 1 \text{ h}$	Heaters reheated the sodium pool to 577°C (1071°F). The hydrogen flame was steady but dropped to ~51 cm (20 in.) in height. Test article conditions at $t_0 + 1 \text{ h}$ are presented in Table 5.
$t_0 + 1.5 \text{ h}$	Heaters de-energized because the sodium pool temperature reached the pre-set control point of 593°C (1100°F).
$t_0 + 1.63 \text{ h}$	Sodium reservoir nitrogen purge increased to $1.89 \times 10^{-3} \text{ m}^3/\text{s}$ (4 ft ³ /min) because the hydrogen concentration in the reservoir reached 80%. The flame was steady and increased to ~71 cm (28 in.) in height. The sodium aerosol in the test cell reduced the visual observation distance to less than 61 cm (24 in.).

Time	Observations
$t_0 + 2 \text{ h}$	<p>The microphone mounted on the restraint area of the test article began recording small popping and bubbling sounds. Table 6 presents the test article conditions at this time.</p> <p>Concrete temperatures at the same depth were higher in the center compared to the sides.</p>
$t_0 + 2.26 \text{ h}$	<p>A large pop was recorded by the microphone. The nitrogen purge to the sodium reservoir was increased to $2.83 \times 10^{-3} \text{ m}^3/\text{s}$ ($6 \text{ ft}^3/\text{min}$) because the hydrogen level increased to 70% in the reservoir.</p>
$t_0 + 2.58 \text{ h}$	<p>Vigorous bubbling sounds emerging from the test article were recorded by the microphone. Small popping noises were still recorded.</p>
$t_0 + 2.82 \text{ h}$	<p>A pressure pulse occurred. The emergency pressure relief vent on the test cell opened. A sodium spray was recorded in the test cell by the visual monitor. The source of the sodium spray appeared to be metallic sodium pushed out of the vent stack due to a disturbance in the sodium pool. The sodium spray in the test cell resulted in a sodium spray fire, which created a pressure pulse that opened the pressure relief vent of the test cell and the double doors to the test room. The reinforcing steel bar at 0.76 m (3 in.) began to heat up at $t_0 + 1.70 \text{ h}$, 66 minutes before the pressure pulse. Table 7 presents the test article conditions before and after the pressure pulse.</p> <p>The hydrogen in the reservoir changed 22.6% in the 8 minutes following the pressure-pulse. A nitrogen and argon purge to the test cell was initiated and the auxiliary fan started to exhaust gas from the test cell. The sodium level was recorded at 67 cm (26.5 in.) and the nitrogen purge to the reservoir was raised to $4.72 \times 10^{-3} \text{ m}^3/\text{s}$ ($10 \text{ ft}^3/\text{min}$). Visual observations of the test article were no longer possible because of the sodium aerosol, but the luminescence of a yellow flame characteristic of hydrogen burning in sodium was visible.</p>
$t_0 + 3.5 \text{ h}$	<p>The argon purge to the test cell was turned off.</p>

Time	Observations
$t_0 + 4.0$ h	The generation of hydrogen slowed down. The test article conditions are presented in Table 8.
$t_0 + 7.0$ h	The nitrogen purge and auxiliary fan to the test cell were turned off. The nitrogen purge to the reservoir was lowered to 9.44×10^{-4} m ³ /s (2 ft ³ /min). The sodium pool temperature was 709°C (1308°F) and the hydrogen was 45% in the sodium reservoir. The flame from the vent stack was visible.
$t_0 + 28.6$ h	<p>A pressure pulse was recorded in the reservoir and test cell. Far less aerosol was expelled from the test cell this time. The hydrogen flame was steady but the height could not be detected because of invisibility in the test cell. The test article conditions before and after the second pressure pulse are presented in Table 9.</p> <p>The percentage of hydrogen in the reservoir jumped from 30% to 38%, 4 minutes after the second pressure pulse and remained at the higher level for 6 minutes. The pressure in the sodium reservoir began to rise steadily 9 minutes after the second pressure pulse, and rose to 1.15×10^5 Pa (2 psig) at $t_0 + 36.2$ h. It was determined that the main vent started to plug and could not relieve the gas introduced into the sodium reservoir. The vent stack temperature began to decrease about the same time the pressure in the reservoir began to increase.</p>
$t_0 + 36.2$ h	The relief vent on the reservoir was opened.
$t_0 + 38.0$ h	The nitrogen purge to the reservoir was turned up to 8.32×10^{-3} m ³ /s (17.63 ft ³ /min) and the hydrogen was lowered to 3% in the reservoir.
$t_0 + 63$ h	The sodium pool temperature was 230°C (446°F). The purge was 8.32×10^{-3} m ³ /s (17.63 ft ³ /min) and the reservoir hydrogen was below 1%.
$t_0 + 180$ h	The sodium pool temperature was below 30°C and the reservoir hydrogen was ~0.5%. The test article was disconnected and rolled into another room for disassembly.

TABLE 4
TEST ARTICLE CONDITIONS AT HYDROGEN IGNITION

	Ignition	
	Before	After
Reservoir H ₂ (%)	21.53	24.07
Reservoir O ₂ (%)	0.257	0.261
Reservoir Pressure (Pa)	1.01×10^5	1.01×10^5
Reservoir Vapor Temperature (°C)	287	292
Reservoir Purge Rate (m ³ /s)	9.44×10^{-4}	9.44×10^{-4}
Test Cell H ₂ (%)	0.247	0.195
Test Cell O ₂ (%)	19.75	19.77
Test Cell Pressure (Pa)	1.01×10^5	1.01×10^5
Test Cell Temperature (°C)	29.86	30.31
Vent Stack Aerosol Concentration (gNa/m ³)	23.23	

TABLE 5
TEST ARTICLE CONDITIONS AT T₀ + 1 HOUR

Reservoir H ₂ (%)	44.50
Reservoir O ₂ (%)	0.0542
Reservoir Pressure (Pa)	1.01×10^5
Reservoir Vapor Temperature (°C)	498.6
Reservoir Purge Rate (m ³ /s)	9.44×10^{-4}
Test Cell H ₂ (%)	0.175
Test Cell O ₂ (%)	19.95
Test Cell Pressure (Pa)	1.01×10^5
Test Cell Temperature (°C)	39.4

TABLE 6
TEST ARTICLE CONDITIONS AT $T_0 + 2$ HOURS

Reservoir H_2 (%)	67.8
Reservoir O_2 (%)	0.28
Sodium Pool Temperature ($^{\circ}C$)	667.8
Reservoir Pressure (Pa)	1.01×10^5
Reservoir Vapor Temperature ($^{\circ}C$)	615.8
Reservoir Purge Rate (m^3/s)	1.89×10^{-3}
Test Cell H_2 (%)	0.0
Test Cell O_2 (%)	18.92
Test Cell Pressure (Pa)	1.01×10^5

TABLE 7
TEST ARTICLE CONDITIONS BEFORE AND AFTER THE PRESSURE-PULSE

	<u>Before</u>	<u>After</u>
Reservoir H_2 (%)	43.91	66.52
Reservoir O_2 (%)	0.281	0.283
Sodium Pool Temperature ($^{\circ}C$)	741.8	741.3
Reservoir Pressure (Pa)	1.01×10^5	1.01×10^5
Reservoir Vapor Temperature ($^{\circ}C$)	702.9	728.5
Reservoir Purge Rate (m^3/s)	2.83×10^{-3}	2.83×10^{-3}
Test Cell H_2 (%)	0.0	0.105
Test Cell O_2 (%)	18.23	18.03
Test Cell Pressure (Pa)	1.01×10^5	1.01×10^5
Test Cell Temperature ($^{\circ}C$)	77.1	95.8

TABLE 8

TEST ARTICLE CONDITIONS AT $T_0 + 4$ HOURS

Reservoir H_2 (%)	19.18
Reservoir O_2 (%)	0.284
Sodium Pool Temperature ($^{\circ}C$)	775.2
Reservoir Pressure (Pa)	1.01×10^5
Reservoir Vapor Temperature ($^{\circ}C$)	729.9
Reservoir Purge Rate (m^3/s)	6.23×10^{-3}
Test Cell H_2 (%)	0.036
Test Cell O_2 (%)	14.05
Test Cell Pressure (Pa)	1.01×10^5
Test Cell Temperature ($^{\circ}C$)	87.8

TABLE 9

TEST ARTICLE CONDITIONS BEFORE AND AFTER
THE SECOND PRESSURE-PULSE

	Before	After
Reservoir H_2 (%)	30.14	32.00
Reservoir O_2 (%)	0.265	0.229
Sodium Pool Temperature ($^{\circ}C$)	531.6	526.6
Reservoir Pressure (Pa)	1.01×10^5	1.01×10^5
Reservoir Vapor Temperature ($^{\circ}C$)	415.9	405.1
Reservoir Purge Rate (m^3/s)	9.44×10^{-4}	9.44×10^{-4}
Test Cell H_2 (%)	0.122	0.084
Test Cell O_2 (%)	20.32	20.22
Test Cell Pressure (Pa)	1.01×10^5	1.01×10^5
Test Cell Temperature ($^{\circ}C$)	39.1	40.4

B. TEST ARTICLE DISSASSEMBLY

The integrity of the sodium reservoir was maintained during the entire test. Two small holes at the welds between the reservoir and central concrete test section liner were formed during the test. However, it was estimated that less than 0.5 kg of sodium leaked from these holes. All sodium reservoir walls bulged slightly outward to about 0.32 cm (0.12 in). The vent stack plugged by what appeared to be sodium-oxide about 36 h into the test. At that time, the emergency relief vent was opened.

Table 10 lists the pre- and post-test mass of the concrete and reaction products. The mass of remaining concrete after the test was calculated by multiplying the pre-test concrete density by the post-test concrete volume.

TABLE 10
MASS BALANCE

Pre-Test

Concrete Mass (kg) (including water)	1213.8
Sodium Mass (kg)	<u>453.6</u>
TOTAL	1667.4

Post-Test

Remaining Concrete Volume (m^3)	0.2911
Remaining Concrete Mass (kg)	658.2
Reaction Product Mass (kg)	939.9
Water Released Mass (kg) (Table 14)	<u>74.6</u>
TOTAL	1672.7

Figure 6 shows one of sixteen or so small hairline cracks formed in the restraint area concrete during the test . The cracks were 12 cm to 20 cm (5 in. to 8 in.) long and somewhat evenly spaced. Figure 7 shows a thermocouple wire placed in a small gap that formed between the restraint area concrete and central test section liner. The gap was 0.32 cm (0.12 in.) wide and about 13 cm (5 in.) deep. Small amounts of restraint area concrete did react with sodium metal that leaked through the sodium reservoir.

Inside the sodium reservoir, the reaction products extended 60 cm (24 in.) into the reservoir volume. Figure 8 shows the reaction products observed as the reservoir was first disassembled from the concrete test section. More reaction products were lodged further up into the reservoir and are not visible in Figure 8. A discernible separate sodium pool did not exist but the reaction products were saturated with sodium metal. The top layer of rebar was pushed up into the reservoir, along with the reaction products. The rebar that had detached from the concrete and side wall steel plates during the test was deformed and is shown in Figure 9.

Two major types of reaction products were found:

Black Reaction Product -- The majority of the reaction products were a homogeneous black material of a cinder-like consistency with low compressive strength. Figure 10 shows an example of this reaction product. The chemical analysis of this product is presented in Table 11. The black reaction product was saturated with sodium metal and was the only type of reaction product located in the reservoir. Gas pockets approximately $2.0 \text{ cm}^3 \pm 0.8 \text{ cm}^3$ ($0.125 \text{ in}^3 \pm 0.05 \text{ in}^3$) in volume permeated this type of reaction product.

Brown Reaction Product -- The second type of reaction product was brownish in color. This reaction product was found in far less quantity than the first product and was located only at the reaction interface. Figure 11 shows the brown reaction product at a rebar concrete reaction product interface. The chemical analysis of this reaction product is

FIGURE 6. Hairline Crack in Restraint Area Concrete. Neg 8006130-7cn

FIGURE 7. Gap Between Restraint Area and Central Concrete Test Section Liner. Neg 8006130-25cn

FIGURE 8. Black Reaction Product Observed in Sodium Reservoir. Neg 8006275-103cn

FIGURE 9. Detached Rebar. Neg 8008355-11cn

FIGURE 10. Black Reaction Product. Neg 8006275-113cn

TABLE 11
CHEMICAL ANALYSIS OF REACTION PRODUCT
(wt%)

Sample	Observations	Total Na	Soluble Na ₂ SiO ₃	Insoluble SiO ₂	Al ₂ O ₃	CaO*
<u>Homogeneous Black Reaction Product</u>						
1	Low compressive strength Gas pockets Sodium metal saturated reaction product located at top of reservoir	38	32	45	6.5	25
2	Middle of reservoir	30	23	32	5.2	15
3	Old concrete surface	31	25	18	2.6	9.8
4	10 cm (4 in.) below old concrete surface	37	31	25	4.1	20
5	15 cm (6 in.) below old concrete surface	46	34	24	3.4	14
ALL	Average $\bar{X}$	36.4	29.0	28.8	4.4	16.8
	Standard Deviations	6.4	4.7	10.3	1.5	5.9
<u>Brown Reaction Product</u>						
6	High compressive strength No gas pockets No sodium metal visible Located in corners of concrete test section	38	29	29	6.0	18
7	Corner of concrete test section Light brown tinge	44	22	17	2.7	8.5
8	Corner of concrete test section Dark gray tinge	38	22	14	2.2	12
9	Reaction interface	43	25	15	7.3	13
10	Reaction interface	31	24	45	4.4	19
11	Reaction interface and surrounding the rebar	33	22	22	3.6	19
ALL	<u>In Corners and Reaction Interface</u>					
	Average $\bar{X}$	37.8	24.0	23.7	4.4	14.9
	Standard Deviations	5.2	2.8	11.8	2.0	4.4
12	<u>Concrete Just Below Reaction Interface</u>	0.67% moisture				

*Analyzed simply as total Ca, combining any CaO and CaCO₃, then calculated as CaO.

FIGURE 11. Brown Reaction Product at Reaction Interface. Neg 8006275-19cn

presented in Table 11. No sodium metal was found in this layer and the sodium in the chemical analysis is attributed to sodium silicate and sodium hydroxide. The compressive strength of this reaction product was slightly less than the concrete. Pieces of aggregate were discernible in the brown reaction product and no gas pockets were observed. Table 12 summarizes the properties of the two different reaction products.

TABLE 12
PHYSICAL PROPERTIES OF REACTION PRODUCTS

Properties	Reaction Products	
Consistency	Cinder, friable, and broken-up	Hard and solid layer
Mass	892 kg (95% of total reaction product)	47 kg (5% of total reaction product)
Color	Black	Brown
Presence of Sodium Metal	Yes	No
Compressive Strength	~5% of concrete	~90% of concrete
Gas Pockets	Yes	No
Discernible Aggregate	No	Yes
Location	Above reaction interface layer	Interface layer

The lower layer of the rebar was partially distorted and the final sodium reaction interface was located at the depth of the lower layer of rebar. See Figure 12. Figure 13 shows one of the voids observed under the rebar at the reaction product concrete rebar interface. Voids were also observed at one end of three of the rebars. Small cracks in the concrete were discovered

FIGURE 12. Final Reaction Interface Profile. Neg 8006491-1cn.

FIGURE 13. Void at Rebar, Concrete and Reaction Product Interface. Neg 8006275-20cn.

near the rebar just under the reaction interface. Figure 14 shows one particular crack in the southwest corner. The crack was 10.2 cm (4 in.) long and 0.32 cm (0.12 in.) wide. Figure 15 shows some rubbleized concrete surrounding one of the lower rebars.

The sodium reaction interface at disassembly indicated that the deepest reaction penetration [38.7 cm (15.25 in.)] was 8 cm (3 in.) from the center of the test section. See Figure 16. The reaction did not penetrate the concrete as readily near the sides and was recorded as $22.8 \text{ cm} \pm 7.6 \text{ cm}$ ($9 \text{ in.} \pm 3 \text{ in.}$). The minimum reaction penetration occurred near the walls. The average final reaction penetration was calculated as 26.14 cm (10.29 in.) by measuring the volume of the void created by the removal of reaction products.

FIGURE 14. Crack at Reaction Interface. Neg 8006275-22cn

FIGURE 15. Rubbleized Concrete at Reaction Interface. 8006491-19cn

FIGURE 16. Maximum Penetration Depth. Neg 8006491-40cn

VI. TEST RESULTS

A. HYDROGEN IGNITION

After initial sodium spill into the sodium reservoir, the hot sodium began to heat the concrete, driving off water. The released water migrated to the hot concrete surface, where it reacted with sodium to form hydrogen. The hydrogen bubbled through the sodium to the top of the reservoir, which was inerted with nitrogen.

The hydrogen-nitrogen gas, laden with sodium vapor, exited through the vent stack into the air-filled test cell. This was observed as small white puffs soon after the initial sodium spill. At 12 min after sodium spill, the gas mixture ignited in the test cell air atmosphere. Conditions associated with hydrogen ignition are listed in Table 13 and include sodium aerosol concentration in the reservoir vent stack, hydrogen concentration and jet gas temperature.

The hydrogen-nitrogen-sodium vapor mixture ignited and burned at a sodium aerosol concentration of $23.23 \pm 4.72 \text{ g Na/m}^3$ and a gas temperature of $260^\circ\text{C} \pm 30^\circ\text{C}$. These data are consistent with an ignition-criteria developed for hydrogen ignition in the presence of sodium from small-scale tests⁽¹¹⁾ and with large-scale hydrogen ignition data.⁽¹²⁾

The hydrogen exiting from the vent stack continued to burn in the test cell air atmosphere throughout the remainder of the test, as noted by visual observations. The flame height increased as the hydrogen generation rate increased and then decreased when the hydrogen generation decreased. The microphone mounted on the concrete restraint area recorded bubbling sounds that correlated with the hydrogen gas moving through the hot sodium to the top of the sodium reservoir.

TABLE 13
HYDROGEN IGNITION DATA

Vent Stack

Temperatures	(°C):	269	280	249	243
	(°F):	517	537	481	469
Hydrogen Concentration (%)					21

Nitrogen Flow

Sodium Reservoir (m ³ /s)	0.056
(ft ³ /min)	2

<u>Test Cell Oxygen Concentration (%)</u>	19.8/19.6
---	-----------

Aerosol

Sample Gas Flow Rate (m ³ /s)	0.014
(ft ³ /min)	0.5
Sample Time (min)	3

Collected in Sample Nose (g Na)	
0.328	

Collected on Sample Filter (g Na)	0.648
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Total Na Collected (g Na)	0.976
---------------------------	-------

Calculated

Aerosol Concentration (g Na/m ³)	23.23 ± 4.72
--	--------------

Hydrogen Jet Temperatures (°C)	260 ± 30
--------------------------------	----------

B. HYDROGEN GENERATION

The flow rate of nitrogen gas into the sodium reservoir was continuously monitored as was the hydrogen concentration of the gas exiting the vent stack. The hydrogen generation rate was determined from the relationship

$$\text{Hydrogen Flow Rate} = \frac{\% \text{ H}_2}{100 - \% \text{ H}_2} \times \text{Nitrogen Flow Rate.}$$

The hydrogen generation rate converted to g-moles/h is shown in Figure 17 as a function of time for 40 hours. Beyond 40 hours, the hydrogen concentration in the sodium reservoir was drastically reduced by increasing the nitrogen flow rate to the reservoir. Also shown in Figure 17 is the hydrogen generation in g-moles as a function of time obtained by integrating the hydrogen generation rate.

The hydrogen generation and generation rate of Figure 17 are shown on an expanded time scale for 8 hours in Figure 18 to highlight some interesting details. First, an initial broad peak in the hydrogen generation rate occurred at about 1 hour with a peak rate of 160 g-moles/h. The broad hydrogen generation peak can be correlated with concrete temperature profiles during the first hour when the concrete was heated by conduction from hot sodium and chemical energy at the reaction surface. The heated concrete liberated water that was driven to the hot interface, where it reacted with sodium to form hydrogen. Thus, during the first one hour and 15 minutes, the hydrogen generation rate was basically as would be expected from water released from concrete heated by thermal conduction.

The broad peak in the hydrogen generation rate is followed by a much larger peak with substructure between 1.5 hours and 2.8 hours. The substructure is real, suggesting periodic quick releases of hydrogen gas as the sodium-concrete reaction was occurring. Water released from concrete heated by normal heat conduction is more uniform in its release rate⁽¹³⁾ and, hence, so

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FIGURE 17. Hydrogen Generation and Generation Rate.

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FIGURE 18. Hydrogen Generation and Generation Rate for the first 8 Hours.

would the hydrogen generation from the sodium-water reaction that would follow. Consequently, the observed hydrogen generation rate between 1.5 hours and 2.8 hours appears to be larger and more sporadic than would be anticipated if the hydrogen were a result of sodium-water reaction with the water released from concrete by normal pressure-driven flow due to heat conduction through the concrete. The correlation between the hydrogen release rate and break up of the concrete surface will be discussed in Section X.

Increased hydrogen generation was observed starting at 2.8 hours and extending to 3.7 hours. The initiation of this hydrogen increase coincides exactly with the pressure pulse observed in the test cell at 2.89 hours. The pressure pulse was of short duration, such that the pressure transducers in the test cell did not monitor a pressure change. However, the corresponding increase in test cell temperature was observed as a temperature spike (Figure 19) at exactly 2.8 hours.

The cause of the pressure pulse in the test cell was due to sodium being rapidly expelled out of the vent stack from the sodium reservoir, creating a sodium spray fire in the test cell. The rapid heat transfer from the reacting sodium droplets to the surrounding atmosphere created a quick pressure increase, which would be predicted from the sodium SPRAY code.⁽¹⁴⁾ In response to the pressure pulse in the test cell, the pressure relief dampers opened, expelling sodium aerosol and hot gases into the test cell. The pressure pulse in the room was relieved by the opening of two double doors leading to the rest of the facility, momentarily expelling some sodium aerosol into the facility work areas.

The cause of the disturbance in the sodium reservoir that expelled sodium out the vent stack remains to be determined. One thing is certain, this pressure pulse was not related to a hydrogen deflagration. The atmosphere in the sodium reservoir was inerted with nitrogen with an oxygen concentration of less than 0.3%. The hydrogen-nitrogen gas mixture exiting the

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FIGURE 19. Test Cell Temperature.

vent stack into the test cell was burning before and after the pressure pulse occurred, as observed by an on-line TV monitor and other visual observations. Also, continuous measurements of the hydrogen concentration in the test cell showed that the hydrogen concentration never exceeded 0.2%.

It is expected that the disturbance in the sodium reservoir was related to cracking of the concrete, which would more easily release additional water to react with sodium to form hydrogen. This would account for the additional hydrogen released between 2.8 hours and 3.7 hours.

C. WATER RELEASE

From the measured hydrogen generation (Figure 17) the water released from the concrete can be calculated from two reactions:

Figure 20 shows the calculated water release from the measured hydrogen release as a function of time using the above two reactions.

The initial water content of the concrete was 92.1 kg or 5117 g-mole consisting of mix water and water contained in aggregate and sand (Table 14). A waterless core drill was made through the unreacted concrete following the test. The water content of the unreacted concrete of the core drill volume was analytically determined. An estimate was made of the total volume of unreacted concrete. From the water content of the core-drill volume, the post-test water content of the unreacted concrete was determined and is summarized in Table 14.

The calculated total water release during the test is shown in Figure 20 as a single data point at 200 hours and represents the conclusion of the test. The data point is nearest the water calculated by assuming the formation of sodium oxide by Reaction (2) in which one mole of hydrogen is formed for each mole of water released.

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FIGURE 20. Water Release Calculated from Hydrogen Release.

TABLE 14
WATER BALANCE

<u>Core Sample Data</u>		<u>Estimated Water Content</u>		
<u>Depth (cm)</u>	<u>H₂O (wt%)</u>	<u>Depth (cm)</u>	<u>H₂O (wt%)</u>	<u>Mass H₂O (kg)</u>
-38.7	1.7	26.1 to 30.5	1.7	1.39
-42.6	1.7	30.5 to 35.6	1.7	1.62
-54.0	4.0	35.6 to 40.6	1.7	1.62
		40.6 to 45.7	1.7	1.62
		45.7 to 50.8	2.7	2.59
		50.8 to 55.9	3.8	3.69
		55.9 to 61.0	5.0	4.92
				<u>17.45</u>
Initial Water (Table 1)		92.10 kg (5116.7 g-mol)		
Final Water		17.45 kg (969.4 g-mol)		
Released Water		74.65 kg (4147.3 g-mol)		
Percent of Released Water		81%		

D. TEMPERATURE PROFILES

The temperature time history of the concrete test article was monitored by 73 thermocouples (listed in Table 3) at various spatial locations throughout the concrete. Representative temperature profiles are presented which illustrate trends observed throughout the test concrete.

The sodium pool temperature as a function of time throughout the entire test is shown in Figure 21, along with the concrete temperatures at various depths at the centerline of the test article. The same data are shown on an expanded time scale for 8 hours in Figure 22. The sodium pool temperature quenched from the initial spill temperature of 593°C to about 460°C due to the large heat sink of the concrete. The sodium pool temperature gradually increased from 460°C to 590°C in about 1 hour, principally due to electrical energy added to the sodium from the internal and external heaters. From 1.1 hours to 1.6 hours after sodium spill, the electrical heaters maintained the sodium pool temperature at 590°C . At 1.6 hours, the sodium pool temperature began to increase due to chemical energy from the reactions. The sodium pool reached a maximum temperature of 775°C at 4 hours, and gradually decreased thereafter to about 75°C in 100 hours.

For convenience later, the sodium pool temperature profile will be discussed in six time periods: 1) from 0 h to 1.1 h which includes the initial sodium spill at 593°C and quench to 460°C , followed by a gradual temperature increase to 590°C ; 2) from 1.1 h to 1.6 h when the electrical heaters controlled the sodium temperature at 590°C ; 3) from 1.6 h to 2.4 h when the sodium pool temperature increased nearly linearly from 590°C to 730°C without the addition of any electrical energy; 4) from 2.4 h to 2.8 h when the sodium pool temperature remained nearly constant at 730°C ; 5) from 2.8 h to 4.4 h when the sodium pool temperature again gradually increased from 730°C to 775°C in 0.8 hour and then decreased to 750°C by 4.4 hours; and 6) from 4.4 h to 100 h when the sodium pool temperature cooled from 750°C to 75°C .

The concrete temperatures increased during the first 1.6 hours, primarily due to heat conduction from hot sodium and chemical energy at the reaction interface. Starting at 1.6 hours, the thermocouples at 1.27 cm to 30.5 cm each exhibited, in succession but at longer times, a rapid temperature increase, indicating a local chemical reaction zone. This chemical reaction zone was fairly uniform over the 0.09-m^2 ($30.5\text{-cm} \times 30.5\text{-cm}$) surface area

FIGURE 21. Sodium Pool and Center Concrete Temperatures.

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FIGURE 22. Sodium Pool and Center Concrete Temperatures for the First 8 Hours.

at the center of the test concrete, as can be seen in Figure 23, where the concrete temperatures at a depth of 1.27 cm are plotted as functions of time. Each thermocouple in this central area of concrete (8 total) indicated a rapid temperature increase between 1.6 h and 1.8 h, with the concrete temperature at this depth exceeding the sodium pool temperature, thus indicating exothermic chemical reactions. At this same time (1.6 h), the sodium pool temperature began to increase without requiring electrical energy from the reservoir heaters. This is also the time when the hydrogen generation rate showed a very rapid increase (See Figure 18).

The concrete temperatures in this central area are shown as functions of time at various depths (2.54 cm, 7.62 cm, 15.24 cm, 25.4 cm and 30.5 cm) in Figures 24, 25, 26, and 27, respectively. Each figure shows a rapid temperature increase for each thermocouple in the central area (8 total) at nearly the same time, except for the deeper thermocouples at the extreme edges, where the reaction front took longer to reach. The times when each thermocouple in the central area indicated a sharp temperature increase are listed in Table 15 for each depth with an average time and a standard deviation.

Because each thermocouple in the central area responded in a similar manner, the heat provided in the central area as noted by sharp temperature increases, can be attributed to additional chemical reactions. Thus, the sharp temperature increases can be assumed to indicate the chemical reaction penetration into the concrete. The average time the reaction penetrated to a given depth can then be determined from Table 15 and is plotted in Figure 28 as the reaction penetration (cm) versus time. A smooth curve was drawn through the data points and then differentiated to provide a penetration rate as a function of time. See Figure 28. The minimum and maximum reaction penetrations, as observed by post-test disassembly, are shown as straight lines with an average reaction penetration calculated by measuring the volume of the void in the test concrete after the reaction product was removed. The maximum penetration rate occurred between 1.6 h and 3.6 h, with an average

FIGURE 23. Sodium Pool and Concrete Temperatures at 1.27-cm Depth.

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FIGURE 24. Sodium Pool and Concrete Temperatures at 2.54-cm Depth.

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FIGURE 25. Sodium Pool and Concrete Temperatures at 7.62-cm Depth.

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FIGURE 26. Sodium Pool and Concrete Temperatures at 15.24-cm Depth.

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FIGURE 27. Sodium Pool and Concrete Temperatures at 25.4-cm and 30.5-cm. Depths.

TABLE 15
TIME/TEMPERATURE/DEPTH PROFILES

<u>Horizontal</u> <u>X (cm)</u>	<u>Vertical</u> <u>Y (cm)</u>	<u>1.27 cm</u> <u>(hr)</u>	<u>2.54 cm</u> <u>(hr)</u>	<u>7.62 cm</u> <u>(hr)</u>	<u>15.24 cm</u> <u>(hr)</u>	<u>25.4 cm</u> <u>(hr)</u>	<u>30.5 cm</u> <u>(hr)</u>
0	0	1.62	1.65	1.92	2.82	16.0	36.0
-15.24	-15.24	1.65	1.70	2.10	3.10	N.A.	N.A.
-15.24	15.24	1.65	1.68	2.70	12.0*	N.A.	N.A.
0	-30.5	1.62	1.70	2.10	2.80	N.A.	N.A.
15.24	15.24	1.65	1.90	2.80	3.10	N.A.	N.A.
15.24	-15.24	1.65	1.68	2.20	3.20	N.A.	N.A.
38.1	38.1	1.80	2.30	2.90	28.0*	N.A.	N.A.
38.1	0	1.70	1.80	2.45	3.10	N.A.	30.0
Average Time		1.67 $\pm$ 0.06	1.80 $\pm$ 0.22	2.40 $\pm$ 0.37	3.02 $\pm$.17	16	33 $\pm$ 4

* Deleted from Average Time Calculation

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FIGURE 28. Sodium Reaction Penetration and Penetration Rate.

penetration rate of 9.1 cm/h. Beyond 5 hours, the penetration rate dropped to less than 1 cm/h. The rapid penetration occurred concurrent with the rapid hydrogen release. The hydrogen generation and generation rate, and sodium reaction penetration and penetration rate are plotted as functions of time in Figure 29.

For each set of X, Y coordinates in Table 15 where $X = Y$, a reaction penetration curve was determined similar to Figure 28. The penetration data points as functions of time were curve-fit to an experimental function from which penetration depths were determined at specific times. The penetration depths for each X, Y coordinate at these specified times were then plotted in one direction resulting in isotime penetration curves shown in Figure 30. Also shown in Figure 30 is one representation of the final reaction penetration interface in one direction. The isotime penetration curves map out the reaction penetration in one direction as a function of time. A smooth line was drawn through each time step up to 2.9 hours. Beyond this time step, the smooth line was not drawn because of the closeness of the data points.

The concrete temperatures near the bottom of the test article (61 cm) are shown as function of time in Figure 31.

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FIGURE 29. Comparison of Reaction Penetration and Hydrogen Generation.

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FIGURE 30. Depth of Penetration Determined By Curve Fit.

FIGURE 31. Sodium Pool and Concrete Temperatures at 60.96-cm Depth.

VII. CHEMISTRY

The reactions of sodium with basalt concrete may proceed along a wide range of potential paths. An initial set of reactions involves the direct combination of sodium with water in concrete. Concrete contains moisture in both cement and aggregate phases, with the bulk of the moisture in the cement phase.

Two of the principal concerns associated with sodium-concrete reactions are hydrogen generation and chemical energy release. A knowledge of the actual chemical states of the different species and heats of solution for dissolved species would be required for accurate calculations of energy released in this test. However, the energies can be calculated approximately from enthalpies of formation of the various reactants and products using the JANAF Tables.⁽¹⁵⁾ These were calculated for 1100 K and listed with the reactions.

When liberated water reacts with sodium, the initial reaction generates NaOH and H₂ according to the reaction:

Other hydrogen generating reactions include:

Reaction (2) may be considered the sum of Reactions (1) and (3). Studies of the Na, NaOH, Na₂O and NaH phase system suggest Reaction (1) should have been the predominant reaction under the conditions prevailing during this test; however, the relatively large amount of released H₂ (3600 mol) compared to the amount of reacted H₂O (4147 mol) indicates that Reaction (2) made a significant contribution.

Basalt concrete consists of a complex mixture of chemical species in addition to a large amount of water. The basalt aggregate is predominantly a mixture of mineral silicates. Besides the water, SiO_2 , Al_2O_3 , and Fe_2O_3 are all potentially reactive with sodium or NaOH. Of these, SiO_2 is by far the most prevalent chemical species and is believed to be the dominant reacting species with respect to energy release. Much of the SiO_2 may be combined in species such as $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_3$, $\text{CaO} \cdot \text{SiO}_2$, and $\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$. The quantity of free SiO_2 initially present in the test concrete was not determined. However, in calculating the chemical energy releases listed below, we have assumed the "free SiO_2 " as the initial reactant material. To the extent some of the SiO_2 which reacted may have been bound initially into complex silicates, the calculated energy releases associated with the reaction would have been too large, making the calculation conservative with respect to safety analysis.

For basalt concrete additional water may be generated by the reaction:

The water generated by Reaction (4) may react with additional sodium by Reaction (1). This sequence of reactions can be expressed:

generating one mole of hydrogen from one mole of water. This provides the maximum energy released per mole of sodium reacted.

Likewise, the analogous reaction

added to Reaction (2) gives Reaction (5).

Sodium may also react directly with SiO_2 by the reaction:

Due to the high temperatures that prevailed during this test, it is presumed that the hydrogen generated by these reactions would be released as H_2 (g). A measure of the H_2 release rate may then be used to calculate the chemical energy release associated with the reaction of water with sodium, if the relative extents of Reactions (1) and (2) can be determined. Likewise, the chemical energy associated with the formation of Na_2SiO_3 may be calculated from a measure of the amount of Na_2SiO_3 formed and assuming either Reaction (5) or (6) was predominant in its formation. The total chemical energy released is approximately equal to the sum of the energies associated with these hydrogen and silicate forming reactions.

The corresponding rates of chemical energy release by these reactions can be inferred from the rate of H_2 released (see Figure 17) and rate of sodium penetration, respectively.

If one assumes Na_2SiO_3 was formed entirely by Reaction (5), the energy associated with this reaction may be calculated as:

$$E_s(t) = M_s(t) \Delta H^0$$

where:

$E_S(t)$ = The energy release (K cal),

$M_S(t)$ = Mass of Na_2SiO_3 formed (mol),

$\Delta H^0(5)$ = Enthalpy of Reaction (5) per mole of Na_2SiO_3
(96 K cal).

The quantity of M_S is related to the mass of concrete reacted by the expression:

$$M_S(t) = \frac{M_C(t) Z}{(1-X)(122 \text{ g/mol})}$$

where:

$M_C(t)$ = Mass of concrete reacted (g).

X = Mass fraction of sodium in the reaction product phase*

Z = Mass fraction of Na_2SiO_3 in the reaction product phase

For this test, the average value for $X = 0.371$ and $Z = 0.265$ were assumed constant. The mass of concrete reacted as a function of time, $M_C(t)$, was determined from Figure 30 and is shown in Figure 32. The formation of M_S moles of Na_2SiO_3 also results in the production of M_S moles of H_2 and consumption of the M_S moles of H_2O . If these quantities of H_2 and H_2O are subtracted from the total H_2 released ($M_{HT}(t)$) and total H_2O reacted ($M_{WT}(t)$), the net amount of these reaction species not involved in the silicate forming reaction is obtained. From the ratio of these net amounts, a calculation of the relative extents of Reactions (1) and (2) can be made:

$$R = 2 - \frac{M_W}{M_H}$$

*Neglects the amount of sodium initially present in concrete.

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FIGURE 32. Mass and Rate of Reacted Concrete.

where:

R = Fraction of H_2 produced by formation of Na_2O from Reaction (2)

$1-R$ = Fraction of H_2 produced by formation of $NaOH$ from Reaction (1)

$M_H(t)$ = Net moles of H_2 = $M_{HT}(t) - M_{HT}(t)$ where $M_{HT}(t)$ is obtained from Figure 17.

$M_W(t)$ = Net moles of water = $M_{WT}(t) - M_S(t)$.

The only direct measure of M_{WT} was obtained at the end of the test when a determination of the moisture remaining in the concrete was subtracted from the initial water content to give the total water consumed. This, together with the total H_2 released and measured mass of Na_2SiO_3 in the reaction product phases at the end of the test, permits an average value for R to be calculated. If this value for R is assumed constant over the entire test, then a continuous measure of the energy as a function of time may be calculated from the continuous measure of $M_S(t)$ and $M_{HT}(t)$. The final values for this test were:

$$\left. \begin{array}{l} M_{HT}(t = 200 \text{ h}) = 3600 \text{ mole } H_2 \\ M_S(t = 200 \text{ h}) = 2035 \text{ mole } Na_2SiO_3 \\ M_{WT}(t = 200 \text{ h}) = 4147 \text{ mole } H_2O \end{array} \right\} R = 0.67$$

The energy release associated with H_2 generation (but not associated with Na_2SiO_3 formation) is found by the expression:

$$E_H(t) = M_H(t)(74 - 35R)$$

where:

$E_H(t)$ = Energy release associated with net H_2 generation
(K cal)

The total energy release, E_t , is equal to the sum of the energy releases associated with Na_2SiO_3 formation by Reaction (5), E_s , plus the energy associated with the additional sodium-water reaction not involved in the silicate forming reaction, E_H . These energy releases are shown in Figure 33 and the corresponding energy release rates are shown in Figure 34.

If one assumes a different scenario where the Na_2SiO_3 is created by Reaction (6), the energy associated with this reaction is:

$$E_s(t) = M_s(t) H(6)$$

$$H(6) = \text{Enthalpy for Reaction (6) per mole } \text{Na}_2\text{SiO}_3 \text{ (48 K cal)}.$$

In this case, since no water or H_2 is directly involved in the Na_2SiO_3 formation, the energy associated with the sodium-water reaction is:

$$E_H(t) = M_{HT}(t)(74 - 35R')$$

where:

$$R' = 2 - \frac{M_{WT}(t = 200)}{M_{HT}(t = 200)} = \text{Fraction of } \text{H}_2 \text{ produced by Reaction (2)}$$

The total energy release is given by:

$$E_T(t) = E_s(t) + E_H(t).$$

Assuming the value for $R = 0.86$, the total energy $E_T(t)$, the energy released from Reaction 6, $E_s(t)$, and the energy released from the hydrogen reaction $E_H(t)$ are shown as functions of time in Figure 35. Corresponding energy release rates are shown in Figure 36.

FIGURE 33. Energy Release with Silicate Formation via Reaction (5).

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Comparison of the total energy released for these two assumed chemical reaction scenarios shows that the energy released from the first Reaction (5) dominant is slightly larger (9% total) than the energy released from the second Reaction (6) dominant .

It should be noted that in the chemical reaction scenario where Reaction (6) is dominant, the energy associated with the formation of hydrogen can be explicitly separated from the energy associated with the formation of Na_2SiO_3 . However, in the chemical reaction scenario where Reaction (5) is dominant, the energy associated with the formation of hydrogen cannot be explicitly separated from the energy associated with the formation of Na_2SiO_3 . It should be noted that the energy associated with Reaction (5) is mainly (77%) due to the sodium-water reaction which is an integral part of the reaction sequence which also generates Na_2SiO_3 . Therefore, it is seen that by either reaction scenario, the dominant energy contribution results from the sodium-water reaction which generates hydrogen.

The total mass of reacted concrete determined from Table 10 (Section V) was 555.6 kg. Since the concrete initially contained 7.6 wt% of water (Table 1, Section IV), the reacted concrete originally contained 42.2 kg of water that was driven off. This left 513.4 kg of dehydrated concrete to react with sodium. The heat of reaction for dehydrated basalt concrete was determined by laboratory differential thermal analysis (DTA).^(1,2,3) An average value of the heat of reaction observed for all exotherms is 195 ± 57 cal/g or 0.817 ± 0.249 MJ/kg. Thus, from the DTA data, 513.4 kg of reacted concrete would have produced a total of 419 ± 123 MJ of energy. If the reacted concrete at 40 h is taken from Figure 32 (395 kg) and corrected for water content (7.6%), then at 40 h, 365 kg of dehydrated concrete would have reacted with sodium to produce 298 ± 87 MJ of energy.

The energy release calculated as a function of time, assuming Reaction (6) was the dominant Na_2SiO_3 forming mechanism, is shown in Figure 35. The energy calculated for the reaction of 513 kg of dehydrated basalt concrete using the data from DTA measurements is also shown in Figure 35. It agrees with E_s .

FIGURE 34. Energy Release Rate with Silicate Formation via Reaction (5).

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FIGURE 35. Energy Release with Silicate Formation via Reaction (6).

FIGURE 36. Energy Release Rate with Silicate Formation via Reaction (6).

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As a further check on the end point energies, there were 3600 g-moles of hydrogen liberated after 40 h of the test (see Figure 17). From Reaction (2), the energy of formation is 39 K cal/g-mole of hydrogen produced. Thus, the 3600 g-moles of hydrogen would produce 588 MJ of energy. This data point and the end point total energy are plotted on Figure 35.

$$E_{HT} = 588 \text{ MJ}$$

$$E_{Con} = 298 \text{ MJ}$$

$$E_T = E_{HT} + E_{Con} = 886 \text{ MJ}$$

Note how well the end point energies agree with the calculated energies, assuming Reaction 6 is dominant.

Three major chemical reactants (Na, SiO₂ and H₂O) are involved in these chemical reactions. The total quantity of water contained in the concrete was 92.1 kg (5128 moles), the quantity of sodium poured was 454 kg (19,739 moles), and a large excess of SiO₂ was present in the concrete. A substantial (though undetermined) fraction of the SiO₂ was combined in silicate minerals and was perhaps not available for reaction with sodium. As shown in Figure 17, the total H₂ release amounted to about 3600 g-moles with approximately 1/3 of this amount released during the first 3 hours. 74.6 kg of the water reacted. The measured total mass of the reaction product phase was 937 kg. Two general types of reaction products were found: a black porous material and a hard brownish material. While these products had very different physical appearances, there was no significant difference in the average chemical composition of the two phases with respect to the major constituents (Table 11, Section V). The analysis for soluble Na₂SiO₃ was determined by measuring the amount of silicon in the reaction product dissolved in H₂O. This was reported as wt% Na₂SiO₃. The unweighted mathematical averages of the sample compositions are shown in Table 11, Section V. Of the average fraction for total sodium (37.1%), 10.0% would be due to the 26.5% of Na₂SiO₃ and the remaining 27.1% due to other sodium species such as Na metal and NaOH. If the soluble silica species were actually present as orthosilicate (Na₄SiO₄) rather than the

assumed Na_2SiO_3 , then a correspondingly larger weight fraction for the soluble silicates and a smaller fraction for the remaining non-silicate sodium species should be indicated, but this would not significantly change the energy release calculations. The chemical analysis did not distinguish between the relative amounts of Na_2O , NaOH or Na species present.

The average total sodium (37.1%), if applied to the total mass of reaction product phase (937 kg), would imply 348 kg of sodium present in this phase, leaving 106 kg of sodium from the original charge unaccounted for. This discrepancy may be due to composition variations and uncertainty in the exact total mass of reaction product phase. The average of 26.5 wt% Na_2SiO_3 found in the reaction product phase would imply 94 kg of sodium present as this species versus 254 kg present as other sodium species.

The low water content of the remaining concrete, compared with the initial water content, indicates release of 81% of the original test water from the concrete. Complete reaction of this water with the sodium would be expected. This water (74.6 kg or 4147 moles) could react with 96.0 kg (4147 moles) of Na by Reaction (1) to produce 2070 moles of H_2 . Furthermore, if the 248 kg (2035 moles) of Na_2SiO_3 found in the reaction product phase were produced by Reaction (4), it would have generated 2035 moles of H_2O , which would have produced more H_2 by reaction with the excess sodium. This would result in a total generation of 3052 moles of H_2 . This may be compared with the measured 3600 moles of H_2 released. Some of this difference may be due to some H_2 production by Reaction (2). The production of 3052 moles of H_2 by Reaction (1) would only consume 6104 moles (140 kg) of sodium leaving 314 kg of unreacted sodium from the original 454 kg charge (or 208 kg of unreacted sodium out of 348 kg of sodium species, if calculated on the basis of 37.1% Na in the 937 kg of reaction product phase). While no massive separate sodium metallic phase was observed during test disassembly, there was a substantial amount of reactive material dispersed throughout the reaction product phase, which occasionally burst into flames during disassembly. This material also reacted violently with water. Continuous oxidation of this material during disassembly and sampling did

not allow an accurate determination of the amount of this material, but clearly unreacted sodium was present at the end of the test (see Appendix A).

Another available mechanism for oxidation of sodium is the direct reaction of Na with SiO_2 by Reaction(6). Extensive reaction of this type was observed in a test⁽⁶⁾ with dehydrated basalt concrete, and might be expected any time metallic sodium contacts SiO_2 in dehydrated basalt concrete.

If 248 kg of Na_2SiO_3 were produced by this mechanism, it would imply that much of the hydrogen released could not be accounted for directly by Reaction (1), but would have had to result from Reaction (2). Under this scenario, the formation of 248 kg of Na_2SiO_3 and generation of 3600 moles of H_2 by Reactions (6) and (1) + (2) respectively, could account for oxidation of 260 kg of sodium, still leaving a substantial amount of unreacted sodium. The physical appearance of the black reaction products bore a resemblance to the loose, friable reaction products observed after tests with dehydrated basalt concrete, in which substantial reaction of Na directly with SiO_2 occurred. The brownish layer of reaction products, which extended about 5 cm above the interface with the unreacted concrete, had a close physical resemblance to the reaction product layers observed during previous tests with sodium and hydrated basalt concrete in which only limited sodium penetration (~7 cm) occurred.

VIII. STRESS EVALUATION

Hot sodium poured onto a concrete slab at ambient temperature will produce large temperature gradients and significant thermal stresses. These thermal stresses can be large enough to introduce tensile cracking and compressive crushing in the relatively brittle concrete. This section of the report summarizes efforts to quantify these stresses for the LSC-1 test and to evaluate their effects on sodium reaction penetration.

A. METHOD OF ANALYSIS

Due to the complexity of the problem, a detailed computer model was judged to be the best analytical approach. Of the computer programs available at HEDL, ANSYS⁽¹⁶⁾ appeared to be the best choice. Other programs, such as MARC⁽¹⁷⁾, ADINA⁽¹⁸⁾ and SAFECRACK⁽¹⁹⁾ are geared more towards reinforced concrete analysis, are not currently available at HEDL, and time constraints did not permit pursuing these alternative program options.

The analysis approach using ANSYS involved the following steps:

- A two-dimensional finite element of the LSC-1 geometry was developed.
- A two-dimensional thermal transient analysis was performed by applying a temperature history to the top surface boundary.
- A corresponding history of elastic stresses was obtained using the computed temperatures.
- Crack patterns were established by selecting the point in time where tensile stresses were maximum. For elements with tensile stresses above the tensile strength, cracks were introduced by reducing the elastic modulus to near zero in the direction of the maximum principal stress. This step was iteratively repeated until no tensile stresses exceeded the tensile strength. Rebar was accounted for by appropriately adjusting the elastic modulus in the direction of the bar. In areas where compressive crushing was predicted, the elements were removed from the model.

The above procedure was used to predict crack patterns in another sodium-concrete test⁽²⁰⁾ where the predicted crack patterns compared reasonably well with observed patterns.

B. ANALYTICAL MODEL

Stress analysis of an earlier HEDL Test (LSC-2) was performed prior to the LSC-1 test. The two tests were very similar, the main difference being that LSC-1 used a basalt aggregate concrete, while LSC-2 used a limestone aggregate. In reviewing the applicable material properties for the two concrete types, differences were found to be small, probably well within the statistical variation of the properties. Also, the applied thermal history was similar. Therefore, it did not appear feasible to rerun the analysis for the LSC-1 test. The LSC-2 thermal stress predictions are assumed to reasonably predict the LSC-1 values.

A full three-dimensional analysis of the LSC-1/LSC-2 geometry would have been very costly. A two-dimensional finite element approximation is shown in Figure 37. Note that axisymmetry is assumed about the geometry centerline. The axisymmetry assumption gives the constraining beam an artificial "hoop" strength, which tends to overly restrain radial expansion of the test section. The expected result is an overprediction on maximum thermal stress. This was verified in part by using the same grid for a "plane strain" analysis, which gave somewhat lower maximum stresses. Thus, the two-dimensional axisymmetric model was used as a conservative prediction of maximum thermal stress.

The temperature-dependent concrete material properties used in the analysis are shown in Table 16. The nonlinear stress-strain behavior of the concrete was not considered. The outside boundaries were assumed to be perfectly insulated for the thermal analysis. For the stress analysis, no external constraints were imposed.

**ASSUMED
AXIS OF SYMMETRY**

CONCRETE TEST SECTION

**STEEL
BEAM**

STEEL LINER

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FIGURE 37. Two-Dimensional Finite Element Model.

TABLE 16

BASALT CONCRETE MATERIAL PROPERTIES USED IN THERMAL AND STRESS ANALYSIS

Temperature (°C)	Temperature (°F)	Thermal Conductivity (Btu/in.-min-°F)	Specific Heat (Btu/lb-°F)	Density (lb/in ³)	Elastic* Modulus (10 ⁶ lb/in ²)	Expansion** Coefficient (10 ⁻⁶ in./in.-°F)	Poissons* Ratio
0	32	0.00147	0.2327	0.084	1.901	5.20	0.15
100	212	0.00152	0.3024	0.084	1.508	4.72	0.15
200	392	0.00138	0.3308	0.084	1.165	4.89	0.15
300	572	0.00120	0.3214	0.084	0.903	5.46	0.15
400	752	0.00106	0.3110	0.084	0.715	6.22	0.15
500	932	0.00100	0.3372	0.084	0.557	7.07	0.15
600	1112	0.00097	0.3474	0.084	0.400	7.93	0.15

* Ref. 21

** Ref. 22

C. LOADING

The thermal stresses in the LSC-1 concrete resulted from pouring 593°C (1100°F) sodium directly on to the top surface of the concrete. The sodium reservoir temperature history used in the stress analysis is shown in Figure 38 for both the LSC-1 and LSC-2 tests. Also shown is the temperature history at 1.27 cm (1/2 in.) below the initial concrete surface for the LSC-2 test. This 1.27-cm (1/2-in.) depth temperature curve was applied directly to the top surface of the model.

D. CONCRETE STRENGTH CONSIDERATIONS

As noted in Table 1, the LSC-1 28-day room temperature compressive strength was 2.44×10^7 Pa (3540 psi). The tensile strength of concrete is generally found to be about 10% of the compressive strength. In bending, the elastically calculated bending strength ("rupture modulus") averages about 15% of the compressive strength. (See page 178 of Reference 23.) Since the elastically calculated thermal stresses for LSC-1 are similar in pattern to beam bending stresses, the 15% value was assumed in predicting the LSC-1 crack pattern.

Concrete strength degrades significantly with temperature. A literature survey (summarized in Reference 24) indicated wide variations in reported temperature effects on concrete strength. This is illustrated in Figure 39, which was reproduced from Reference 24. For this study, it was assumed that the temperature effect on strength applied to both tensile and compressive strength. Crack patterns were predicted using a strength reduction midway between the lower and upper bound curves. For example, at 593°C (1100°F) the average reduction is 43%, giving a compressive strength of $0.43(3820) = 1643$ psi.

FIGURE 38. LSC-1 and LSC-2 Temperature Histories.

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FIGURE 39. Effect of Temperature Exposure on the Compressive Strength of Concrete - Hot Testing.(24)

E. ANALYSIS RESULTS

Temperature distributions for each point in time were saved on tape. The tape was then used for stress analysis input and for post-processing plots. Temperature contours for one point in time are shown in Figure 40. Hoop stress contours for the same point in time are shown in Figure 41. This time was selected because tensile stresses were at a maximum. The corresponding tensile crack pattern is shown in Figure 42.

The predicted maximum compressive stress history is shown in Figure 43. As indicated in Figure 41, the maximum stress location is in the top center of the test section. Note that the peak compressive stress occurs much earlier in time than the peak tensile stress.

Figure 44 shows the compressive stress at the center of each grid at 2.5 h for the top two layers of the central concrete test section. The compressive strength of concrete at this temperature is about 1.13×10^7 Pa (1643 psi). Therefore, for any grid where the compressive stress value is above 1643 psi, compressive crushing should occur. The compressive stress at the center of each grid at 3.5 h is shown in Figure 45.

F. DISCUSSION OF RESULTS

It is emphasized that the results given in the previous section are an approximation to the actual LSC-1 stress response. Probably the largest uncertainties are associated with the sodium-concrete surface. Potentially important, but difficult to quantitize, are such factors as: 1) high local surface temperatures and corresponding thermal stress due to chemical reactions; 2) strength degradation due to chemical reactions and higher temperatures; and 3) chemical erosion of the surface.

Some correlation between post-test examination and predicted stress patterns was seen, e.g. radial cracks predicted in the concrete restraining beam were indeed observed following the test. Predicted permanent deformation of the steel liner near the top was also found in the post-examination.

FIGURE 40. Temperature Contours for Time = 13 Hours.

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FIGURE 41. Elastic Hoop Stress Contours for Time = 13 Hours.

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FIGURE 42. Tensile Cracking and Compressive Spalling Predictions.

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FIGURE 43. Maximum Compressive Stress History.

As noted in Figure 43, elastic compressive stresses well above the compressive strength were predicted at the sodium-concrete interface. Due to the stress/strain nonlinearity of concrete, the elastic stresses prematurely predict compressive crushing. However, as previously discussed, the chemical reactions at the surface probably more than compensate for this conservatism. Compressive crushing due to high thermal stresses looks very probable. The "dished" crushing pattern corresponds to the shape of the observed penetration.

One test observation of interest was the two occurrences of popping sounds and pressure pulses that appeared to coincide with the penetration level reaching the reinforcing bar levels. One possible explanation is that the extra strength and constraint of the rebar temporarily halted the penetration. This permitted a greater buildup of thermal stresses and strain energy. When the ultimate strength of the reinforced section was reached, a sudden increase in depth of crushing occurred. This crushed material produced a larger surface area that reacted with sodium and resulted in a pressure increase.

The question of rebar buckling was raised as a potential cause of the popping sounds and pressure pulses. If essentially all of the rebar were exposed prior to buckling, calculations indicated that the concrete would crush at the end of the rebar prior to achieving a buckling load. If half of the rebar were still embedded in concrete, higher axial loads could be achieved in the bar, due to the bond strength of the embedments. However, the shorter length raises the bar buckling load and yielding of the rebar would occur prior to buckling. Thus, rebar buckling was not likely.

G. SODIUM PENETRATION MECHANISM - STRESS CONTRIBUTIONS

There is some evidence that the depth of sodium penetration in a concrete slab is highly dependent upon the developed thermal stress. It appears that a combination of high thermal stress and low concrete strength can result in large penetration depths. Weaker concrete would tend to produce more crushing. The crushing, in turn, would produce more surface area to react with sodium, which would result in higher surface temperatures and thermal stress, etc.

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FIGURE 44. Two-Dimensional Finite Element Model, Compressive Stresses at 2.5 Hours.

ASSUMED
AXIS OF SYMMETRY

HEDL 8011-043.37

FIGURE 45. Two-Dimensional Finite Element Model, Compressive Stress at 3.5 Hours.

IX. ENERGY BALANCE

To obtain a better understanding of energy sources, losses, and chemical kinetics, an energy balance of the sodium pool from 0.1 h to 2.4 h was calculated. Figure 46 is a schematic diagram that lists the energy sources and losses affecting the temperature of the sodium pool. The major energy sources to the sodium pool were energy from chemical reactions, Q_{CHEM} , electrical energy applied to the sidewall, Q_{SW} , and immersion heaters Q_{IM} . The major energy losses were heat losses to the concrete, Q_{CON} , sodium reservoir walls, Q_{RW} , and enthalpy of sodium vaporization, Q_{SV} .

Figure 22 (Section VI) shows the sodium pool temperature for the first 8 hours as a function of time. Three distinct time periods were considered in the calculations. Time Period 1 is from 0.1 h to 1.1 hours. During this time period, the sodium pool temperature increased from 480°C to 593°C. The electrical heaters were energized, applying heat to the sodium pool, and the hydrogen generation rate was about 150 g-moles/h. Time Period 2 was from 1.1 h to 1.6 hours. During this time period, the electrical heaters fluctuated on and off, maintaining the sodium pool at 593°C, and the hydrogen generation rate was about 150 g-moles/h. Time Period 3 was from 1.6 h to 2.4 hours. During this time period, the heaters were de-energized, and the hydrogen generation rate had increased to an average of 650 g-moles/h. Dramatic chemical reaction penetration was also recorded during this time period. The sodium pool temperature increased from 593°C to about 720°C. The major results of the energy balance calculations are presented in Table 17 and Figures 47 and 48.

To evaluate just how accurate the calculations for each energy source and loss might be, a sodium pool temperature was calculated from the sum of the energy sources and losses using the following equation:

$$(M C_p \Delta T)_{\text{sodium pool}} = \sum(\text{Energy Sources}) - \sum(\text{Energy losses}).$$

TABLE 17
ENERGY BALANCE

Energy	Time					
	0.1 h to 1.1 h	1.1 h to 1.6 h	1.6 h to 2.4 h			
	(J/s)	(%)	(J/s)	(%)	(J/s)	(%)
Sources:						
Electrical Heaters	19,710	67	1,971	15	0	0
Chemical Reactions*	9,722	33	11,111	85	59,028	100
TOTAL	29,432	100	13,082	100	59,028	100
Losses:						
Concrete	~12,000	56	~6,500	83	~33,000	95
Reservoir Walls	~2,000	13	1,100	15	1,600	4
Sodium Vaporization	182	1	182	2	182	1
TOTAL	~14,000	100	~7,800	100	~34,800	100

* See Figure 35

The calculated sodium pool temperature was compared with the experimental sodium pool temperature with the results shown in Figure 49. The major conclusion of the comparison is that the major energy sources and losses were estimated fairly well, as evidenced by the close approximation between calculated and measured sodium pool temperature.

The next three parts of this section discuss in greater detail the energy sources and losses and the sodium pool temperature calculation. More detailed energy calculations and input data are presented in Appendix B.

A. ENERGY SOURCES

The major energy sources were the heat from chemical reactions, Q_{CHEM} , and the energy applied as heat input from the electrical heaters, Q_{SW} , and Q_{IM} . The energy from chemical reactions, Q_{CHEM} , as a function of time was determined and is presented in Section VII. Two different chemical reaction scenarios [Reactions (5) and (6)] generated about the same amount of energy as functions of time. The data seem to indicate that Reaction (6) was more

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FIGURE 46. Energy Flow Diagram.

FIGURE 47. Energy Sources.

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FIGURE 48. Energy Losses.

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FIGURE 49. Experimental and Calculated Sodium Pool Temperatures.

dominant for this test. However, in the present calculation, it would not matter which reaction was used. Therefore, the chemical energy input to the sodium pool was assumed to be that calculated from Reaction (6). Figure 47 shows the chemical energy generation rate as a function of time. During Time Period 1 (0.1 h to 1.1 h), the rate of chemical energy released was about 9,722 J/s or 33% of the total energy input. The majority of the chemical energy was from the sodium-water reaction. The energy from the formation of Na_2SiO_3 was small because chemical penetration was not appreciable. During Time Period 2 (1.1 h to 1.5 h), the energy release rate from the chemical reactions remained about constant. At Time Period 3 (1.6 h), the hydrogen generation rate increased rapidly and the corresponding energy release from the sodium-water reaction also increased. Sodium reaction penetration greatly increased during Time Period 3; therefore, the energy from the silicate reaction also showed a large increase. The energy from the sodium-water reaction was still the dominant energy source. During Time Period 3, the chemical energy generation rate from chemical reactions was about 59,028 J/s. This is about 5.5 times more chemical energy than in Time Periods 1 and 2.

The second large energy source was provided by electrical heaters. There were two sets of heaters provided, sidewall and immersion heaters. The sidewall heaters surrounded the walls of the sodium reservoir and the immersion heaters were immersed in the sodium pool. The electrical heaters were connected to a 3-phase circuit. The current and voltage of the circuit were monitored at specified times. The power consumed by a 3-phase system is calculated by

$$P = \bar{V} \bar{I} \sqrt{3}$$

Where:

$\bar{V}$ = Average voltage

$\bar{I}$ = Average current

Figure 47 shows the power input by the heaters as a function of time. During Time Period 1, the heaters were on continuously because the sodium pool was below the desired temperature of 593°C (1100°F). The power input of the heaters during this time period was about 19,710 J/s, which represents the majority of the energy provided to the sodium pool (about 67% of the total). In Time Period 2, the electrical heaters were oscillating on and off and controlling the sodium pool at the desired temperature of 593°C (1100°F). The energy input was 1971 J/s or 15% of the total energy input. At Time Period 3, the energy input from the chemical reactions increased rapidly, consequently the sodium pool temperature surpassed the desired controlled temperature of 593°C (1100°F), and the electrical heaters cycled off.

B. ENERGY LOSSES

Major energy losses shown in Figure 48 were the concrete, Q_{CON} , sodium reservoir walls, Q_{RSV} , and enthalpy of sodium vaporization, Q_{SV} . The heat losses to the concrete were calculated by use of the Watre Code⁽¹³⁾. Equation (1) is the finite difference equation expressing energy transport from the Watre Code. The symbols are defined in Appendix B.

$$\begin{aligned}
 & \left[T(N-1) - T(N) \right] AH(N-1,N) + \left[P(N-1) - P(N) \right] A(N-1,N) \\
 & \left[\frac{C_p(N) + C_p(N-1)}{2} \right] \left[\left[T(N) + RH(N) \left[T(N-1) - T(N) \right] AH(N-1,N) \right] \right] \quad (1) \\
 & = \left[T(N) - T(N+1) \right] AH(N,N+1) \\
 & + \left[P(N) - P(N+1) \right] A(N,N+1) C_p(N) + C_p(N+1) T(N) \\
 & + RH(N) \left[T(N) - T(N-1) \right] AH(N,N+1) + q(N) X(N) \\
 & + CPCON(N) \rho(N) \left[T'(N) - T(N) \right] \cdot X(N)
 \end{aligned}$$

The terms on the left of the equal sign express the quantity of energy flowing into the node and represent two contributions. The first contribution is the energy of conduction. The second contribution is the energy of transpiration. There are four contributions to the terms on the right: 1) energy transport due to conduction; 2) transpiration; 3) phase change; and 4) heat up of the concrete. The Watre Code⁽¹³⁾ provides as output the energy into the top node as a function of time. The top node for this calculation was the concrete surface; therefore, a heat flux to the concrete from the sodium pool was available. The thermal history of the sodium pool was provided as input to the Watre Code. Figure 50 shows the experimental and calculated temperatures as a function of time for 1.27 cm and 7.62 cm nodes. The calculated temperature profiles were in good agreement with the experimental temperature profile; therefore, the energy flux at the surface of the concrete was accepted to be reasonably accurate. The Watre Code does not account for chemical reaction penetration; therefore, at Time Period 3 (1.6 h), the calculated temperatures and the experimental temperatures deviated drastically. Because of the deviation, the calculated energy flux to the concrete after 1.6 hours was not accepted. Instead, a hand calculation was used to estimate the energy losses to the concrete after 1.6 hours. It was assumed that the energy of transpiration and phase change were small; therefore, an estimate of the energy flux during chemical reaction penetration can be made by using the expression:

$$q/A = h\Delta T \quad (2)$$

where:

- $h = K/\Delta X$
- $q = \text{Energy flow (J/s)}$
- $A = \text{Area of energy flow (m}^2\text{)}$
- $h = \text{Energy transfer coefficient (J/m}^2\text{s)}$
- $\Delta T = \text{Temperature driving force (K)}$
- $K = \text{Thermal conductivity (J/s K cm)}$
- $\Delta x = \text{Thickness of energy transport (m).}$

The temperature of the sodium interface was estimated from the upper bound of the temperature profiles of Figure 22. The position of the interface was estimated from the sodium reaction penetration. See Figure 28. Once the temperature and position of the reaction interface were known, the temperature and position of the nearest thermocouple were used to calculate ΔT and x . The values of the energy flux as a function of time are shown in Table 18.

TABLE 18
ENERGY FLUX TO CONCRETE DURING PENETRATION

Time	Interface		Node		Energy Flow (J/s)
	Depth (in.)	Temp (°C)	Depth (in.)	Temp (°C)	
1.60	0.5	600	1	260	41,300
1.80	1.6	790	3	140	27,400
2.00	2.1	790	3	185	38,900
2.25	2.95	1040	6	80	17,100
2.50	3.75	920	6	110	20,400

The energy flux data were plotted and a line was drawn through them. During the time period for which an energy balance was calculated, the energy loss to the concrete was the largest contribution. During Time Period 1, the concrete was relatively cold compared to the sodium pool, so the driving force for heat conduction (ΔT) was large. The energy loss during Time Period 1 was 12,000 J/s or about 86% of the total energy losses. In Time Period 2, the energy flux to the concrete was lower because the driving force for energy transport was reduced. Reduction in the driving force (ΔT) resulted because the temperature of the concrete at the surface was higher than at later times before penetration. At Time Period 3, reaction penetration began and the elevated temperature concrete on the surface was ablated; therefore, the driving force (ΔT) jumped to a high value again. The energy loss to the concrete was about 33,000 J/s or 95% of the total energy losses.

Energy losses to the sodium reservoir walls were less significant than that to the concrete. During Time Period 1, the energy loss through the reservoir walls was estimated by the use of Equation 3 presented in "Transport Phenomena,"⁽²⁵⁾ for a semi-infinite slab.

$$q_y = \frac{k}{\sqrt{\pi \alpha t}} (T_1 - T_0) \quad (3)$$

where:

$$\alpha = \frac{k}{\rho C_p}$$

q_y = Energy flux at time y

k = Thermal conductivity at time t

T_1 = New instantaneous temperature

T_0 = Initial temperature

ρ = Density of the material

C_p = Heat capacity of the material.

The assumption of a semi-infinite slab is considered to be valid if the thermal penetration depth μ_T is less than the thickness of the reservoir walls during the time of consideration. The thermal penetration depth is equal to the depth where the temperature changed less than 1% and is calculated by the equation:

$$\mu_t = 4 \sqrt{\alpha t} \quad (4)$$

The thermal penetration depth after one hour was 13.5 cm (5.32 in). The wall thickness was 10-cm (4-in.) thick Kaowool, therefore, the semi-infinite assumption was acceptable. During Time Period 2 and Time Period 3, the heat transport through the reservoir walls was assumed to be at steady state and Equation 3 was used to calculate the energy losses. The thermal

properties of the Kaowool were from "Kaowool Ceramic Fiber Product Catalog".⁽²⁶⁾ The driving force ΔT was calculated from the measured inside and outside insulation temperatures presented in Appendix B, see Figures B-1 and B-2.

During Time Period 1, the energy losses to the reservoir walls was about 2,000 J/s or about 13% of the total energy losses. During Time Period 2, the energy losses were about 1,100 J/s or about 15% of the total. Once chemical reaction penetration began at 1.6 hours, the energy loss through the reservoir walls went up slightly because of the higher sodium pool temperature, but not as drastically as the concrete energy losses. The energy losses during this time period were about 1,600 J/s or 4% of the total energy losses.

The energy lost from sodium vaporization was calculated from the difference between the enthalpy of sodium liquid and vapor. The concentration of sodium was assumed a constant and equal to the concentration at the time of hydrogen ignition (see Table 13, 23.23 ± 4.72 g of Na/m³). From these two quantities, an energy loss of 182 J/s was calculated. The energy loss from sodium vaporization during all time periods was about 1% of the total.

C. SODIUM POOL TEMPERATURE CALCULATION

To check the accuracy of the estimated energy sources and losses, a sodium pool temperature calculation was made and compared with the experimental sodium pool temperature. The first step in calculating a sodium pool temperature was to subtract the total energy losses, Q_L , from the total energy sources, Q_I , for a specified time period. For this analysis, a time period of 0.1 h was found adequate. The net energy gain would be equal to the amount of energy needed to heat the sodium pool by ΔT during the 0.1-h time period, as expressed by:

$$Q_I - Q_L = \Delta Q = mC_p \Delta T..$$

The calculated sodium pool initial temperature (461°C) was taken as the experimental sodium pool at 0.1 hours.

Figure 50 shows the experimental and calculated sodium pool temperatures. The largest areas of disagreement are at the points where the experimental temperature made abrupt changes, e.g., when the sodium pool temperature leveled off at 593°C (1100°F). The calculated sodium pool temperature could not respond to these abrupt changes in heat flow because the time frame of the calculation was too large. If smaller time frames were chosen for the calculations, the ability of the calculated sodium pool temperature to respond to the abrupt temperature changes would be improved.

During early time periods, the energy from the electrical heaters was the dominant energy source; however, at later times, the chemical reactions dominated the energy input. For all times, the concrete acted as the largest energy loss. Table 17 presents the energy fluxes for the different energy sources and losses. In general, the calculated temperature corresponds to the experimental temperature to confirm that possibly the major energy sources and losses have been adequately quantized.

FIGURE 50. Experimental and Watre Code(13) Concrete Temperatures.

X. DISCUSSION

Major results from this sodium-basalt concrete reaction test are summarized in Figure 51, in which the sodium pool temperature, hydrogen generation rate, and reaction penetration are plotted as functions of time for the first 8 hours. In Time Period 1 (0 h to 1.1 h), the sodium pool was heated by chemical energy from the sodium-water reaction and electrical energy. The heat from the sodium pool was transmitted into the concrete, heating the concrete and liberating water that in time reacted with sodium to produce hydrogen. Sodium penetration into the concrete was limited to the near surface (less than 1.27 cm).

In Time Period 2 (1.1 h to 1.6 h), the chemical energy and intermittent electrical energy added to the system was sufficient to maintain a constant sodium pool temperature. Heat from the sodium pool was conducted into the concrete, increasing the concrete temperatures. The amount of water liberated was stabilized such that the rate of hydrogen produced from the sodium-water reaction tended to approach a constant value. The chemical reaction penetration was still limited to the near surface. The stress analysis suggests that at about 1.5 hours, compressive crushing of the concrete would begin to be appreciable.

Time Period 3 (1.6 h to 2.4 h) was marked by rapid hydrogen release with several hydrogen release peaks that could be attributed to rapid water release caused by compressive crushing of the concrete. Concrete cracks would have provided vent paths that would rapidly release steam to react with sodium. Crushed concrete would have provided more concrete surface area for water release and chemical reactions. The chemical energy was dominated (see Section VII) by the sodium-water reaction and was sufficient to heat the sodium pool from 593⁰C to 730⁰C. This time period was marked by a large average (9.6 cm/h) sodium reaction penetration rate.

In Time Period 4 (2.4 h to 2.8 h), the hydrogen release rate decreased suggesting that the rapid water release rate of the earlier period had

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FIGURE 51. Sodium Pool Temperature, Hydrogen Generation Rate, and Reaction Penetration Rate.

subsided. The lower water release rate resulted in reduced, but sufficient chemical energy to maintain the sodium pool at a near constant temperature of 730°C . The sodium reaction penetration continued during the early part of this period at nearly the same rate.

At 2.8 hours, a disturbance occurred in the sodium pool, spraying sodium from the reservoir and producing a pressure pulse. This disturbance could have been caused by additional concrete cracking or crushing, presumably involving a large amount of concrete. The hydrogen generation rate showed a rapid increase at 2.8 h that would also be explained by concrete cracking or crushing, which would rapidly provide additional concrete surface area and vent paths for more rapid release of water to react with sodium. From 2.40 h to 3.02 h, the sodium reaction penetration increased from 7.62 cm to 15.24 cm or an average rate of 12.3 cm/hour. During this time period, the sodium reaction penetration rate was the largest, which could be consistent with considerable cracking or crushing of the concrete. The sodium pool temperature also increased by about 45°C (from 730°C to 775°C) following the pressure-pulse indicative of added chemical energy, presumably due to increased sodium-water reaction.

After about 3.5 hours, the hydrogen production rate (less than 100 g-moles/h) and sodium reaction penetration rate (1 cm/h) both rapidly decreased. The sodium pool temperature gradually decreased after 4 hours.

In essence, the major hydrogen release rate, sodium reaction penetration rate, and chemical energy release rate all occurred during the first 4 hours of the test. During this time, nearly 25% of the total water contained in the concrete was released (see Figure 20 and Table 14) and 18% of the sodium was consumed (371 kg of 454 kg of sodium remained at 4 h, see Appendix A).

For the remaining 86 hours (until the sodium pool temperature dropped below the melting point of sodium), water was released from the concrete at a slow rate as temperature increased by heat conduction, and the water continued to

react with sodium. The sodium reactions continued with a structurally weak, dehydrated concrete front. The sodium and sodium-concrete reaction products formed a liquid slurry in the sodium reservoir volume. Table 19 summarizes the amounts and average rates of hydrogen generation, energy production, and chemical reaction penetration during these two time periods. This confirms the fact that the major events really occurred during the first 4 hours of the test.

TABLE 19
COMPARISON OF ENERGY PRODUCTION, HYDROGEN GENERATION,
AND CHEMICAL REACTION PENETRATION

Item	Time		Average Rate		Change
	(0 h to 4 h)	(4 h to 90 h)	(0 h to 4 h)	(4 h to 90 h)	
Hydrogen Generation (g-mol)	0 to 1380	1380 to 3600	345	26	2200
Energy Production (MJ)	0 to 430	430 to 1000	108	7	570
Chemical Reaction Penetration (cm)	0 to 19.5	19.5 to 38.8	4.9	0.2	

Observations made from the chemistry results in Section VII are:

- Since Reaction (2) may be considered the sum of Reactions (1) and (3), one may consider that both NaOH and Na₂O are being formed by the chemical reactions, but that Reaction (2) represents an end state.
- In Figure 20, the total water released during the test agreed very well with the calculated water released from the hydrogen generation data, assuming the formation of sodium oxide by Reaction (2). From this and the final reaction products observed, it is evident that the formation of Na₂O was a significant reaction during this test, i.e., an end state rather than an intermediate state.
- Reaction (5) can be considered an end state for the formation of Na₂SiO₃ either by Reaction (1) plus Reaction (4) or by Reaction (2) plus Reaction (4'). However, Reaction (6) is the formation of Na₂SiO₃ directly from the reaction of sodium with SiO₂.

- Figure 35 shows that the chemical energy calculated from the total mass of reacted concrete and the experimental heat of reaction determined by differential thermal analysis agreed very well with the chemical energy release associated with the formation of Na_2SiO_3 directly by Reaction (5). Hence, referring to Figure 35, the total chemical energy released was dominated by the energy associated with the formation of hydrogen, which represented 65% to 73% of the total energy released.
- Oxidation of sodium by direct reaction of sodium with SiO_2 , Reaction (6), was extensively observed in tests⁽⁶⁾ with dehydrated basalt concrete. In these tests, reaction penetrations were extremely rapid (15 cm/h) until the sodium supply was exhausted. Total reaction products were characterized as black with a loose, friable, cinder-like consistency, easily broken by hand.
- Reference 6 summarizes a series of sodium-concrete reaction tests in which the principal sodium species associated with the final reaction products was NaOH . The energy release was dominated by sodium-water reactions. The depth of reaction penetration was typically 5 cm, with a very low reaction penetration rate (0.6 cm/h), and the reaction products were characterized as of solid, hard rock-like consistency with a very high compressive strength.

It was concluded that the NaOH phase at the concrete interface generally formed a barrier layer of reaction products, thus limiting this reaction penetration to a few centimeters. However, mechanical effects could prevent formations or cause disruptions of the protective layer, resulting in rapid penetration of dehydrated concrete by liquid sodium.

These differences may be partially explained by a hypothesized reaction sequence:

- 1) When hot sodium is spilled onto cold concrete, the concrete surface layer receives a high thermal shock.
- 2) A high pressure zone develops just below the concrete surface in semi-confined spaces from quickly vaporizing water.
- 3) As more water is vaporized by heat transfer from the hot sodium to the concrete, the high pressure zone proceeds deeper into the concrete.

FIGURE 52. Experimental Pore Pressures of Basalt Concrete.

This effect can be seen in Figure 52, which shows the measured pore pressure in a concrete cylinder heated at one end (Water Release Demonstration Test, WRD-7) as a function of time for two different depths in the concrete. Figure 52 demonstrates that the peak pressure zone moves deeper into the concrete with increasing time.

- 4) The concrete behind the pressure zone would be partially or completely dehydrated (very porous with lower compressive strength). The sodium would then move into this porous concrete and react with dehydrated concrete. A sodium-concrete reaction product layer would begin to build up at the reaction interface.
- 5) As more heat is conducted into the concrete from both the hot sodium plus the chemical energy in the reaction zone, the concrete in front of or near the progressing pressure zone would begin to thermally expand with a compressive stress building up in the layer.
- 6) If the concrete above the layer is dehydrated, or if the temperature-dependent compressive strength of the concrete is less than the compressive stress produced, then compressive cracking would occur, resulting in a larger surface area of concrete to react with sodium and direct vent paths for steam to contact sodium. The succession of this sequence could continue indefinitely producing large reaction penetrations. A major energy source would be sodium-water reactions, and direct reactions of sodium with SiO_2 , Reaction (6), would occur, i.e., sodium reacting with dehydrated concrete.
- 7) If the temperature-dependent compressive strength of the concrete was greater than the compressive stress produced, then compressive cracking would not generally occur in large amounts. The chemical reactions would be dependent on diffusion of water vapor and sodium through the reaction layer, and would be diffusion limited. The sodium-hydroxide rich reaction layer would continue to increase in thickness until no more sodium could diffuse to contact fresh concrete, thus establishing

a reaction product barrier. The major reaction species would be NaOH, since water vapor would continue to diffuse through the reaction products, there would be little direct reaction of sodium with SiO_2 , and the major energy source would again be the sodium-water reactions. The reaction products would be principally NaOH with dehydrated concrete, which when solidified, were demonstrated by separate effects test SET-3⁽⁶⁾ to be of a hard, rock-like consistency with high compressive strength.

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A P P E N D I X A

SODIUM POOL LIFETIME

SODIUM POOL LIFETIME

At post-test disassembly (approximately 200 h after t_0), a coherent sodium pool did not exist but sodium metal was dispersed throughout the black reaction products (approximately 892.6-kg mass, see Table 12). Metallic sodium weight percent in the black reaction product was 7.4 wt% (see Table 11).

Therefore, of the original 454 kg of sodium, approximately 70 kg of sodium metal was left unreacted at the end of 200 hours. Two level sensing devices recorded a liquid sodium pool up to 16.5 hours. A float mechanism monitored the liquid level for 4.5 hours when the float handle froze in place due to sodium condensing on the handle at the exit point. The float mechanism measured the liquid level depth at 71 cm (454 kg) immediately after the sodium spill, 71 cm (454 kg) at 34 minutes, 67 cm (428 kg) at 2.92 hours, and 58 cm (371 kg) at 4.0 hours. These data are plotted as function of time in Figure A-1.

A pressure level detector located 15 cm above the concrete surface maintained a small flow of nitrogen gas to the sodium pool. Figure A-1 shows the pressure reading of the level detector as a function of time. At 16.5 hours, the pressure began to increase because of plugging. An attempt to blow back the heated pressure line proved futile; therefore, at 16.5 hours, the nitrogen flow was terminated. The pressure readings of the level detector for the first 4 hours were correlated against the liquid level readings (total sodium mass) to extrapolate the liquid sodium level (mass) up to 14 hours, with the extrapolated data also shown in Figure A-1. The data indicate that as much as 240 kg of sodium remained at 14 hours and from the sodium temperature profiles (Figure 21 and Figure A-2), it appears that a major amount of sodium existed as a coherent pool up to as long as 38 hours. Beyond 38 hours, the amount of sodium continually decreased and was mixed with the reaction products.

Figure A-1. Mechanical and Pressure Level Detectors.

FIGURE A-2. Sodium Pool Temperatures.

A P P E N D I X B

ENERGY BALANCE CALCULATION

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ENERGY BALANCE CALCULATIONS

I. ENERGY SOURCES

A. CHEMICAL REACTIONS

The energy from chemical reactions was calculated from Figure 35. Table B-1 presents the calculated energy release.

TABLE B-1
ENERGY GENERATION RATE FROM TOTAL CHEMICAL REACTIONS
USING REACTION (6)

	Time		
	<u>0.1 h to 1.1 h</u>	<u>1.1 h to 1.6 h</u>	<u>1.6 h to 2.4 h</u>
Chemical Reaction (6) (J/s)	9,722	11,111	59,028

B. SIDEWALL AND IMMERSION HEATERS

Time Period 1 (0.1 h to 1.1 h) -- Electrical circuit was monitored by a voltmeter. Readings are shown in Table B-2.

TABLE B-2
VOLTMETER READINGS FOR TIME PERIOD 1

	<u>Voltage (V)</u>				<u>Current (amp)</u>			
Phase A	190	205	190	190	50	37	37	68
Phase B	190	180	200	190	70	57	53	79
Phase C	18	185	185	190	70	78	49	71

The power consumed in a 3-phase circuit is calculated by Equation B-1.

$$P = \frac{(V_A I_A + V_B I_B + V_C I_C)}{3} \sqrt{3} \quad (B-1)$$

$$P = 19,710 \text{ J/S}$$

Time Period 2 (1.1 h to 1.5 h) -- During this time period the strip-charts show the heaters were on about 10% of the time

$$P = 1,971 \text{ J/S}$$

Time Period 3 (1.6 h to 2.4 h) -- The electrical heaters were never on during this period.

II. ENERGY LOSSES

A. CONCRETE Q_{CON}

Time Periods 1 and 2 (0.1 h to 1.6 h) -- Energy transport due to conduction, transpiration, and phase change are accounted for in the Watre Code (13) by the finite difference Equation (B-2).

$$\begin{aligned} & \left[T(N-1) - T(N) \right] AH(N-1, N) + \left[P(N-1) - P(N) \right] A(N-1, N) \\ & \left[\frac{C_p(N) + C_p(N-1)}{2} \right] \left[\left[T(N) + RH(N) \left[T(N-1) - T(N) \right] AH(N-1, N) \right] \right] \quad (B-2) \\ & = \left[T(N) - T(N+1) \right] AH(N, N+1) \\ & + \left[P(N) - P(N+1) \right] A(N, N+1) \left[C_p(N) + C_p(N+1) \right] \left[T(N) \right. \\ & \left. + RH(N) \left[T(N) - T(N-1) \right] AH(N, N+1) \right] + q(N) \cdot X(N) \\ & + C_{\text{PCON}}(N) \rho(N) \left[T'(N) - T(N) \right] \cdot X(N) \end{aligned}$$

$T(N)$ in Equation (B-2) refers to the temperature at the Nth node. Heat transfer admittance $AH(N-1, N)$ is defined by:

$$AH(N-1, N) = \frac{1}{RH(N-1) + RH(N)}$$

where:

$$RH(N) = \frac{X(N)}{2K(N)}$$

$X(N)$ = Thickness of Nth Node

$K(N)$ = Thermal conductivity of concrete in the Nth node

Other terms appearing the Equation B-2 are:

$P(N)$ = Total gas pressure in the Nth node

$C_p(N)$ = Heat capacity of vapor phase in the Nth node

$C_{PCON}(N)$ = Heat capacity of concrete in the Nth node.

$\rho(N)$ = Density of concrete

$q(N)$ = Heat generation rate per unit volume in Nth node

$$A(N,N+1) = \frac{1}{RTOT(N) + RTOT(N+1)}$$

$$RTOT(N) = \frac{X(N)}{2 K(N)} \frac{(N)}{[1-f(N)]}$$

$\nu(N)$ = Kinematic viscosity of gas phase in Nth node

$K(N)$ = Permeability of concrete in Nth node to gas flow

$f(N)$ = Fraction of pore volume filled with liquid water

Δt = Time interval for calculational step.

The left side of Equation (B-2) is equal to the energy input into the node.

The Watre Code⁽¹³⁾ calculates the energy transport into the top node (top concrete).

Time Period 3 (1.6 h to 2.4 h) - During this time period Watre⁽¹³⁾ cannot account for penetration. Therefore, assuming the energies of

transpiration and phase change are small, an estimate of the heat flux during penetration can be made using the following equation:

$$q/A = h\Delta T \quad (B-3)$$

$$h = K/\Delta X$$

The temperature of the sodium reaction interface can be made from the upper bound of the temperatures in the sodium pool and central concrete test temperatures graph. Once the temperature and position of the interface are known, the properties of the nearest node are used to calculate ΔT and ΔX . The thermal properties of concrete are presented in Table 16. The heat flux as a function of time values are shown in Table B-3.

TABLE B-3
THERMOCOUPLE READINGS AT 1.5 HOURS

Time	Interface		Node		Energy Flow (J/s)
	Depth (in.)	Temp (°C)	Depth (in.)	Temp (°C)	
1.60	0.5	600	1	260	41,300
1.80	1.6	790	3	140	27,400
2.00	2.1	790	3	185	38,900
2.25	2.95	1040	6	80	17,100
2.50	3.75	920	6	110	20,400

The energy flux at the wall of a semi-infinite slab with unsteady-state heat transport can be estimated by Equation B-5⁽²⁶⁾.

$$q_{wall} = \frac{K}{\sqrt{\pi \alpha \tau}} (T_1 - T_0) \quad (B-5)$$

where:

T_1 = New instantaneous temperature ~803K

T_0 = Initial temperature ~300K

Table B-4 presents the calculated energy flux values through the reservoir walls.

TABLE B-4
ENERGY LOSSES THROUGH THE RESERVOIR WALLS

t(s)	600	1,200	1,800	2,400	3,000	3,600
q(J/s)	3,703	2,616	2,136	1,852	1,655	1,509

Time Period 2 (1.1 h to 1.6 h) -- Energy transport was assumed to be steady-state, therefore Equation (B-3) was used. The driving force ΔT of energy transport was calculated from Figures B-1 and B-2. Table B-5 presents the thermocouple readings of the insulation and reservoir walls at 1.5 hours. It was assumed a temperature drop of 67°C (120°F) existed between the outside of the reservoir wall and the inside of the insulation.

These heat flux points were plotted and a line drawn through them.

TABLE B-5
OUTSIDE RESERVOIR WALL AND INSULATION
TEMPERATURES AT 1.5 HOURS

Das No.	Location	TC Reading
84	North, insulation outside	131.6
86	East, insulation outside	168.0
87	Top of reservoir, insulation inside	985.4
88	Top of reservoir, insulation outside	189.2
90	West, insulation outside	172.1
98	South, insulation outside	149.1
108	Side wall heater, East	1098.8
109	Side wall heater, North	1097.8
110	Side wall heater, West	1096.6
111	Side wall heater, South	1095.3

B-8

HEDL 8011-043.22

FIGURE B-1. Outside and Inside Insulation Temperatures.

FIGURE B-2. Reservoir Wall and Inside Insulation Temperatures.

B. RESERVOIR WALLS Q_{RSV}

Time Period 1 (0.1 h to 1.1 h) -- Energy flow across the insulation was calculated from the thermocouple data from the test.* The thermal penetration depth μ_T is presented in Equation (B-4).⁽²⁶⁾

$$\mu_T = 4\sqrt{\alpha t} \quad (B-4)$$

where:

$$\alpha = K/\rho C_p$$

$$K = \text{Thermal conductivity} = 0.043 \text{ J/ms K}$$

$$\bar{C}_p = \text{Heat capacity} = 1067.6 \text{ J/kg K}$$

$$\rho = \text{Density} = 128.14 \text{ kg/m}^3$$

Penetration depth after 1 hour was 13.5 cm. (5.32 in.), therefore the temperature changed less than 1% at 0.135 m (5.32 in.). Table B-6 presents the calculated energy losses.

TABLE B-6
ENERGY LOSSES THROUGH THE RESERVOIR
WALLS AT 1.5 HOURS

Location	$\Delta T(K)$	$h(J/m^2 \cdot sK)$	$q/A (J/m^2 \cdot s)$
Top	442.3	0.5678	251
North	470.1	0.5678	267
South	459.0	0.5678	261
East	450.4	0.5678	256
West	446.9	0.5678	254

$$\therefore \bar{Q}_R = 1077.7 \text{ J/s}$$

*The thermal properties of the Kaowool are in Reference 23.

C. SODIUM VAPORIZATION

Sodium aerosol concentration at hydrogen ignition was $23.23 + 4.72$ g Na/m³. Gas flow out of the reservoir averaged about 0.0018 m³/s. The enthalpy of sodium vaporization at 402°C is 4,324 J/g.⁽²⁸⁾

181.8 J/s of energy for Na vaporization.

The enthalpy of sodium vaporization was assumed constant throughout the test.

III. SODIUM POOL TEMPERATURE CALCULATION

Once all energy sources and losses were determined, the difference between these values was calculated, and an average heat flux at interim periods was determined using Equation (B-5):

$$\frac{(q_{t+1} - q_t)}{2} + q_t = q_t + 1/2 \quad (B-5)$$

where:

$$q_t = Q_t (\text{sources}) - Q_t (\text{losses})$$

Equation (B-6) was used to calculate the amount of energy liberated during this time period.

$$(q_{t+1/2})(t) = J_{t+1/2} \quad (B-6)$$

Equation (B-7) was used to calculate the change in temperature during this time period.

$$\frac{J_{t+1/2}}{mC_p} = \Delta T_{(t-1/2) - (t+1/2)} \quad (B-7)$$

Then the temperature at $t - 1/2$ was added to the ΔT to receive a value at $T_{(t+1/2)}$:

$$T_{t-1/2} + \Delta T_{(t-1/2) - (t+1/2)} = T_{t+1/2} \quad (B-8)$$

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