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HAZARDS RESEARCH
CORPORATION
Fire and Explosion Hazards Evaluation

DENVILLE, NEW JERSEY 07834

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EXPLOSION HAZARD POTENTIAL OF SIMULATED SALT CAKES

HRC Report 3808-1

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Atlantic Richfield Hanford Company
Richland, Washington

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Submitted by:

Robert C. Putnam, Ph. D.
Senior Scientist

Approved by:

Chester Grelecki, Ph. D.
Chief Scientist

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This report summarizes the results of a series of experiments performed by Hazards Research Corporation, Denville, New Jersey, for Atlantic Richfield Hanford Company of Richland Washington, under Special Agreemant No. SA-613. Contact with Atlantic Richfield Hanford Company was maintained through Mr. G. A. Beitel.

The purpose of this program was to evaluate the explosive hazard potential of simulated salt cakes.

A. MATERIALS

Complexant and Dowex 21K Resin were supplied by ARHCO.

The following materials were supplied by the Contractor (HRC):

Sodium Hydroxide Baker's Analyzed, Reagent

Sodium Aluminate Fisher Scientific, Purified

Sodium Nitrite Baker's Analyzed, Reagent

Sodium Nitrate Bakers Analyzed, Reagent

Directions for preparation of Dry Salt Cake, Drained Salt Cake, and Undrained Salt Cake, and a Testing Schedule (Appendix A and B) were supplied by ARHCO.

Following the completion of the schedule, additional work was authorized as follows:

1. Thermal stability scans of the three salt cakes with kerosene in a closed system.
2. Autoignition study of the three salt cakes with resin in an open container.

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3. Effect of heating the three salt cakes with kerosene in an open container.

4. Effect of igniting kerosene in the presence of the three salt cakes without external heating in an open container.

B. DESCRIPTION OF EXPERIMENTS

1. Thermal Stability Procedure

The thermal stability study was performed in a heavy-walled stainless steel reactor capable of withstanding high pressure. The vessel was equipped with a burst disc, thermocouple and pressure transducer. The temperature and pressure were continuously recorded during the course of the experiment. The sample was heated so that the temperature rose at 1°C per minute to a maximum of 250°C. After the scanning run, a fresh sample was incubated at a constant temperature which would allow incubation without decomposition for 24 hrs. (See Appendix B).

2. Open Cup Runs

The sample was put in an open stainless steel container placed on a heating unit. A thermocouple was embedded in the mixture and the temperature was continuously recorded. The stainless steel cup was a small cylinder having a flat bottom. Its volume was 230 ml. Its height was 75 mm and inside diameter 65 mm.

C. RESULTS OF EXPERIMENTS

C-1. Thermal Stability of Salt Cake with Resin or Complexant

The thermal stability experiments performed according to the requirements of the operating schedule (App. B) are shown on the following page. Maximum pressure is shown. None of the runs resulted in an exotherm.

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TABLE I

A. Resin in Drained Salt Cake

Run	% Resin	Sple. Wt. (g)	Test	Psig (Max.)	Exotherm
1	5	20	S	45	neg.
2	5	40	SX	55	neg.
3	5	80	SX	75	neg.
4	5	160	SX	100	neg.
5	5	160	I_1	100	neg.
10	10	160	S	90	neg.
11	10	160	I_1	140	neg.

TABLE II

B. Complexant in Drained Salt Cake

Run	%Complexant	Sple. Wt. (g)	Test	Psig(Max.)	Exotherm
13	12.5	20	S	90	neg.
14	12.5	40	SX	90	neg.
15	12.5	80	SX	135	neg.
16	12.5	160	SX	160	neg.
17	12.5	160	I_1	240	neg.
22	25	160	S	170	neg.
23	25	160	I_1	400	neg.

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TABLE III

C. Complexant in Undrained Salt Cake

Run	%Complexant	Sple. Wt. (g)	Test	Psig(Max.)	Exotherm
25	20	20	S	160	neg.
26	20	40	SX	175	neg.
27	20	80	SX	215	neg.
28	20	160	SX	250	neg.
29	20	160	I_1	300	neg.
34	30	160	S	310	neg.
35	30	160	I_1	340	neg.

The data from Tables I-III indicated that the maximum amount of each mixture run could be heated for 24 hours at 250°C, with no indication of an exotherm.

C-2. Thermal Stability of Kerosene with Salt Cakes

Each salt cake (80 g.) was run in the closed bomb with 14% (stoichiometric amount) kerosene (11.2 g.) to scan the mixture for thermal stability. The data are shown in Table IV. No exotherm occurred with the samples up to 250°C.

TABLE IV

Thermal Stability of Kerosene and Salt Cakes

Run	Material	Kerosene	Psig (Max.)	Exotherm
40	Dry Cake (80g.)	11.2 g.	50	neg.
41	Drained Cake (80g.)	11.2 g.	60	neg.
42	Undrained Cake (80g.)	11.2 g.	80	neg.

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C-3. Autoignition of Salt Cakes with Resin

The autoignition runs of the three salt cakes premixed with resin and heated in a stainless cup showed no initial change in appearance. As the temperature rose the cakes containing water dried out. The resin granules gradually turned completely black. The cake gradually melted but no decomposition or reaction was evident. Suddenly, at exactly 450°C, the melt ignited. The combustion resulted in a smoky flame 12-15 inches high, which continued until the resin was consumed.

TABLE V

Autoignition of Salt Cakes with Resin

Run	Material	Resin	Autoignition T. (°C)
43	Dry Cake (80g.)	8 g.	450
44	Drained Cake (80g.)	8 g.	450
45	Undrained Cake (80g.)	8 g.	450

C-4. Attempted Autoignition of Salt Cakes with Kerosene

Kerosene was poured over the salt cake in the test cup. No mixing was performed. The mixture was then heated and observed. The kerosene slowly fumed off without ignition at 250-300°C. The temperature was raised to a maximum of 450°C without ignition.

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TABLE VI

Attempted Autoignition of Salt Cakes with Kerosene

Run	Material	Kerosene	Max. T(°C)	Result
46	Dry Cake (80g.)	11.2g.	450	neg.
47	Drained Cake (80g.)	11.2g.	450	neg.
48	Undrained Cake (80g.)	11.2g.	450	neg.

C-5. Kerosene Ignited with Salt Cake

Kerosene was poured over the salt cake in the test cup. No mixing was performed. The kerosene was ignited with splints until it continued to burn of its own accord. No external heating was applied. The kerosene appeared to burn slightly more vigorously than it does alone. It melted the adjacent salt cake and this aided the combustion. The temperature of the mixture reached a maximum of 175°C in each case. The combustion continued until the kerosene was consumed.

TABLE VII

Kerosene Ignited With Salt Cake

Run	Material	Kerosene	Max. T (°C)
49	Dry Cake (80g.)	11.2 g.	175
50	Drained Cake (80g.)	11.2 g.	175
51	Undrained Cake (80g.)	11.2 g.	175

D. SUMMARY

The following summarizes the data obtained in the thermal stability runs.

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C-1. Thermal Stability of Salt Cake with Resin or Complexant

A. Resin in Drained Salt Cake

Samples up to 160 g. scanned to 250°C showed no exotherm with 5 and 10% resin.

Samples of 160g. held for 24 hours at 250°C showed no exotherm with 5 and 10% resin.

B. Complexant in Drained Salt Cake

Samples up to 160 g. scanned to 250°C showed no exotherm with 12.5 and 25% Complexant.

Samples of 160 g. held for 24 hours at 250°C showed no exotherm with 12.5 and 25% Complexant.

C. Complexant in Undrained Salt Cake

Samples up to 160 g. scanned to 250°C showed no exotherm with 20 and 30% Complexant.

Samples of 160 g. held for 24 hours at 250°C showed no exotherm with 20 and 30% Complexant.

C-2. Thermal Stability of Kerosene with Salt Cakes

The Salt Cakes (80g.) each run with 14% kerosene scanned to (482F) 250°C showed no exotherm in the bomb.

C-3. Autoignition of Salt Cakes with Resin

All three salt cakes (80g.) with 10% resin gave an autoignition temperature of 250°C in the open cup.

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(842F) Correct = 450°C (see C-3 on p 5)

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C-4. Attempted Autoignition of Salt Cakes with Kerosene

No autoignition of the salt cakes occurred on heating with kerosene to 450°C in the open cup.

C-5. Kerosene Ignited with Salt Cake

The Salt Cakes at room temperature with kerosene ignited by a splint burned until the kerosene was exhausted yielding a maximum temperature of 175°C. for the mixture in each case.

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ESTIMATED COMPOSITION OF SALT CAKES CONTAINING ORGANIC COMPLEXANTS

Basis: 1 liter of cake

Component	Undrained[1] (Fully Saturated) Grams	Drained[2] (Residual Saturated) Grams
$NaNO_3$	1,250	1,150
$NaNO_2$	100	40
$NaAlO_2$	100	40
NaOH	60	24
Complexant		
Carbon	150	60
Hydrogen	20	8
Oxygen	140	56
Nitrogen	70	28
Sodium	100	40
Water	250	100
Total Weight	2,240	1,546

(1) Assumes 50 volume percent solids, 50 volume percent liquor containing 2.5M complexant

(2) Assume 50 volume percent solids, 30 volume percent air, 20 volume percent liquor containing 2.5M complexant

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APPENDIX A

I. The Contractor shall supply all materials, except those supplied by ARHCO as listed below, and prepare the simulated salt cakes in accordance with the following recipes:

1. Dry Salt Cake

Recipie: Dissolve 220 gm. NaOH in 500 ml H_2O

Add 164 gm. $NaAlO_2$

Add 138 gm. $NaNO_2$

Add 170 gm. $NaNO_3$

Add H_2O to increase volume to 1 liter

Heat to 90-100°C with constant stirring and add $NaNO_3$ until solution is saturated

Cool to 50°C and stir for 24 hours

Cool to 25°C and decant supernatant liquid

The remaining solid is salt cake

Oven dry at 150°C for 2 hours

2. Drained Salt Cake
Dry Salt Cake plus $5 \pm 1\%$ H_2O

3. Undrained Salt Cake
Dry Salt Cake plus $10 \pm 1\%$ H_2O

II. ARHCO shall supply the Contractor with the following materials:

(1) 1 Liter Complexant

(2) 500 grams Dowex 21 K Resin

III. Contractor shall prepare the resin in the following manner:

Resin

Dowex 21-K, boiled for 8 hours in 4N $NaNO_3$; drain and dry at 120°C for 2 hours.

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The resins and complexant shall be added to the simulated salt cake mixture in accordance with the testing schedule contained in Appendix B.

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APPENDIX B

Contractor shall conduct the following tests in accordance with the schedule below. The sample size key and the test key are defined below:

Sample Size Key

M = Maximum safe sample size based upon S and SX tests.

P = Sample size selected after completing first sequence of tests - maximum safe size.

Q = Sample size selected after all prior tests - maximum safe size.

Test Key

S = Screening test on 20 gm. sample. Contractor shall heat the sample, increasing the heat at a rate of approximately 1°C per minute, until a reaction occurs. When the sample reacts, the maximum pressure generated and the rate of pressure rise shall be obtained and recorded.

SX = Screening tests as defined above on 40, 80, or 160 gm samples. The larger samples shall be used to identify the optimum (maximum) sample size.

I_1 = Using a freshly prepared sample, Contractor shall incubate the sample defined in the schedule below for a period of 24 hours (or until a reaction occurs) at a temperature of 10°C below the temperature at which reaction occurred.

I_2 = A second incubation test, as defined above, performed at a temperature that will allow an incubation period of 24 hours.

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Testing Schedule for Determining Exothermic Reaction Potential of Stored Salt Cake

A. Resin in Drained Salt Cake

Test No.	Wt. % Resin	Sample Size (gm)	Test
1	5	20	S
2	5	40	SX
3	5	80	SX
4	5	160	SX
5	5	M	I_1
6	5	M	I_2
7	2.5	P	S
8	2.5	P	I_1
9	2.5	P	I_2
10	10	Q	S
11	10	Q	I_1
12	10	Q	I_2

B. Complexant in Drained Salt Cake

Test No.	Wt. % Complexant	Sample Size (gm)	Test
13	12.5	20	S
14	12.5	40	SX
15	12.5	80	SX
16	12.5	160	SX
17	12.5	M	I_1
18	12.5	M	I_2
19	6	P	S
20	6	P	I_1
21	6	P	I_2
22	25	Q	S
23	25	Q	I_1
24	25	Q	I_2

9 1 1 2 0 5 4 0 7 1 9

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C. Complexant in Undrained Salt Cake

Test No.	Wt. % Complexant	Sample Size (gm)	Test
25	20	20	S
26	20	40	SX
27	20	80	SX
28	20	160	SX
29	20	M	I_1
30	20	M	I_2
31	10	P	S
32	10	P	I_1
33	10	P	I_2
34	30	Q	S
35	30	Q	I_1
36	30	Q	I_2

Tests number 9, 12, 21, 24, and 33 are defined as checkpoint tests, and the Contractor shall follow the instructions contained in Article I of this agreement.

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EXPLOSION HAZARD POTENTIAL OF SIMULATED SALT CAKES

HRC Report 3808-1A
Addendum

- to -

Atlantic Richfield Hanford Company
Richland, Washington

July 27, 1977

Submitted by:

Robert C. Putnam, Ph. D.
Senior Scientist

Approved by:

Chester Grelecki, Ph. D.
Chief Scientist

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This addendum to HRC Report 3808-1 summarizes further experiments performed by Hazards Research Corporation, Denville, New Jersey, for Atlantic Richfield Hanford Company of Richland, Washington, under Special Agreement No. SA-613. Contact with Atlantic Richfield Hanford Company was maintained through Mr. G. A. Beitel.

A. MATERIALS

The materials used were sodium nitrate, commercial prills, and kerosene.

B. DESCRIPTION OF EXPERIMENTS

A mixture of sodium nitrate and kerosene containing 14% of the latter was prepared as a stoichiometric mixture.

A 3.5 gallon Fiberpak was filled with 44.3 pounds of the mixture.

A 23 gallon Leverpak (Continental Can M 2305-8X) was filled with 278 pounds of the mixture.

Each filled container was placed on a 2 foot high steel grating and exposed to the effect of a wood fire started with kerosene. The combustion was filmed.

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sition of the sodium nitrate continued to melt and decompose it in the self-sustained reaction.

D. CONCLUSIONS

The presence of sodium nitrate in sufficient quantity adds to and surpasses the combustion of kerosene. The melted and decomposing sodium nitrate constitutes an extreme hazard. Cartons containing sodium nitrate should be isolated from other materials especially combustibles and stored where they cannot be subjected to a fire.

*It must be noted that although the reaction as observed, appeared to be self-sustained and supported by the decomposition of sodium nitrate, in fact, sodium nitrate decomposes endothermically and requires the presence of a fuel to sustain the reaction.

G. A. Beitel - Technical Administrator.

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