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Exothermic Potential of Sodium Nitrate Salt Cake

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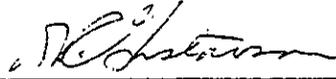
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EXOTHERMIC POTENTIAL OF SODIUM
NITRATE SALT CAKE

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June 1977

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EXOTHERMIC POTENTIAL OF SODIUM NITRATE SALT CAKE

I. INTRODUCTION

High-Level radioactive liquid waste is being reduced to a liquid slurry by an evaporation and crystallization process and stored in the existing single-shell tanks. Continuous pumping of the waste storage tank will reduce the present 30-50 percent moisture to the minimum possible. The reduced waste is a relatively immobile salt cake consisting predominantly of sodium nitrate (NaNO_3) with lesser amounts of sodium nitrite (NaNO_2), sodium metaaluminate (NaAlO_2), and sodium hydroxide (NaOH). Trace amounts of fission products, transuranics, and a broad spectrum of organic materials in small but unknown amounts are also present.

A program was initiated in 1973 to determine whether or not conditions exist which could lead to an exothermic reaction in the salt cake. This report summarizes the results of the latest series of tests conducted to determine the effects of mass and pressure.

II. SUMMARY

Hanford salt cake, as stored, cannot support combustion, and does not ignite when covered with a burning volatile hydrocarbon.

III. BACKGROUND

Under the current waste management program at Hanford, the high-level liquid waste is being reduced to a solid through evaporation and crystallization. The resulting solid, known as "salt cake" contains as much as 95 wt% sodium nitrate. During the course of waste generation some organic materials (paraffins, resins, sugars, a variety of solvents and miscellaneous objects) have been added to the waste tanks in small (less than 1 wt%) but unknown quantities. During subsequent processing (removal of cesium and strontium), large quantities (up to 7 wt%)

of organic complexant have been added.

Sodium nitrate is a solid oxidant which, theoretically, can oxidize any organic material and many metals. The energy available per gram of a stoichiometric sodium nitrate - organic mixture (80-90 wt% NaNO_3), is nearly equivalent to that of TNT. Therefore, a properly mixed sodium nitrate-organic composition can be expected to offer a hazard similar to an equal amount of TNT if kinetic factors will allow a sufficiently rapid reaction.

Sodium nitrate by itself is extremely stable. It begins to decompose endothermically at 750°C at a visibly rapid rate. This is to be contrasted with most detonable high explosives which rapidly decompose exothermically at temperatures below 250°C .

The ease with which sodium nitrate based blasting powders can be made, and because of their relative insensitivity to both composition and mixing, lends credence to the possibility of an accidental formation of an explosive mixture within the stored salt cake. All sodium nitrate based explosives have historically used charcoal (or coal) as the reductant. On the other hand, except for the ion exchange resins, most of the organic materials which have been added to the waste are relatively volatile.

IV. EXPERIMENTAL

A. Previously Reported Tests

A variety of organic materials were mixed with both simulated salt cake and pure sodium nitrate and subjected to a standard NOL gap test. No definite evidence of detonation was observed.⁽¹⁾

Additional detonation tests using a stoichiometric mixture of sodium nitrate and ion exchange resin were conducted using 200 pound (100 kg) quantities, with and without a hydrogen atmosphere.⁽²⁾ Again, no evidence of detonation was observed.

These negative detonation tests are consistent with other tests using simulated salt cake and asphalt, and the general textbook knowledge of sodium nitrate systems. ⁽³⁾

Sodium nitrate based explosives certainly explode, but the mechanism is deflagration, rapid self-supported combustion, not detonation. A series of tests was therefore designed to study the combustion behavior of simulated salt cake-organic mixtures. Small (1-2 gm) unconfined samples were ignited by a high temperature source. Organic materials with a high boiling point (or low vapor pressure) all appear to react vigorously and explosively if the organic concentration is between 10 and 30 wt%. High vapor pressure materials (hydrocarbon fuels, for example) vaporized and burned above the solid salt cake, but would not react with the sodium nitrate. ⁽⁴⁾ All ignition temperatures were observed to be 400°C or above.

The above tests are conclusive insofar as they describe the behavior of salt cake with respect to deflagration of small unconfined samples. The remaining question involves extrapolation to large samples (hundreds of cubic meters). Large masses of reactive materials tend to have a greater explosion potential because the intermediate, high reactive and metastable molecular fragments which result from spontaneous chemical decomposition can accumulate until capable of supporting a chain reaction. This mechanism prompted the pressurized tests discussed below.

B. Recent Test Results

A series of tests was designed to resolve the reactivity of simulated salt cake (95% NaNO₃) with ion exchange resin, an HEDTA based complexant, and kerosene when heated in a heavy walled stainless steel reactor capable of withstanding the maximum pressure that could result from the decomposition reaction. The selection of the resin, complex, and kerosene was based upon the following:

- (1) prior studies found that the exchange resin, which has been added to the waste tanks can be made to react explosively with salt cake,

- (2) the total quantity of HEDTA based complexant added to the waste tanks exceeds that of any other organic material; the concentrations used closely approximate the concentrations actually observed in the waste storage tanks,
- (3) kerosene is a convenient analog of many readily available hydrocarbon fuels and solvents.

The sample sizes ranged from 20 to 160 gm and the composition from 1 to 14 wt% reactive organic material. The temperature cycle was 10°C per minute up to 250°C, a temperature limitation imposed by the heat exchange media (oil), and then a fresh sample was held at 250°C (or 10°C less than minimum temperature at which a reaction occurred) for 24 hours. Both temperature and pressure were monitored. Several additional tests using either ion exchange resin or kerosene were conducted in unpressurized containers in which the maximum temperature was 450°C and several samples were subjected to gas flames. The purpose of these unpressurized tests was to provide a tie with known combustible mixtures. Details of the tests and results are presented in Appendix A.

All pressurized tests were negative. This again is consistent with prior observations that sodium nitrate mixtures are stable at temperatures below 250°C.

The resin mixture was also heated in an open container and ignition consistently occurred at 450°C. When kerosene was heated in an open container, the kerosene evaporated before 400°C and there was no reaction. Kerosene was also added to salt cake and heated near an open flame; at the flash point of kerosene, the vapors ignited and burned, the salt cake temperature remained below 175°C and did not participate in the reaction other than to serve as a wick.

A fiberboard and paper container was filled with 17kg of NaNO_3 and 3kg of kerosene and placed above a wood fire. The kerosene vaporized and

burned leaving the nitrate prills. A larger container filled with 112 kg of NaNO_3 and 18 kg of kerosene was placed over a similar but larger wood fire. In the ensuing conflagration, the kerosene vaporized and burned; the overall fire was so intense that the NaNO_3 melted and continued to support combustion in excess of what was expected. This test was not repeated because of the testing program limitations. The nature of the reaction which occurred after the NaNO_3 had melted is not well understood. Most probably, as the molten NaNO_3 flowed across the fire bed it picked up and oxidized unburned charcoal. This would give the appearance of "combustion of the molten sodium nitrate". Another possibility is that some sodium nitrate prills from the central region of the original container were still much cooler than the molten NaNO_3 and still retained some kerosene which subsequently burned as it passed through the molten pool surrounding it.

V. DISCUSSION

One of the most widely used methods for determining the stability or instability of materials against exothermic reactions is the open cup DTA (differential thermal analysis) test. Very briefly, in DTA, a small (less than 1 gm) sample is placed in an open thimble and slowly heated. Simultaneously, and in the same environment an inert control sample is also heated. The temperature of the test sample T_t and of the control sample T_c are monitored. The differential temperature $\Delta T = T_t - T_c$ is plotted against T_c . A rapid and well defined positive (negative) rate of increase in ΔT at some control temperature T_{ci} is identified as an exotherm (endotherm) at T_{ci} . The identification of an observed differential temperature variation as an exotherm is often strongly dependent upon the qualitative judgement of the observer.

Most of the well known high explosives (PETN, REDX, TNT, TETRYL, etc.) exhibit extremely well defined exotherms between 150-200°C. Charcoal-sodium nitrate mixture (blasting powders) have exotherms between 380-450°C

as do sodium nitrate bitumen mixtures. Anion exchange resins (Dowex 21k and XE-270) mixed with simulated sodium nitrate salt waste also show strong exotherms around 400°C. A cation exchange resin ARC-359, which was retrieved from an actual waste tank, when mixed with a sodium nitrate salt solution showed a strong exotherm at 275°C, the salt solution by itself shows no exotherm below 500°C (the maximum temperature tested).

All the DTA tests referred to above were performed in "open cup" test capsules. The open cup capsules makes it possible for all volatile compounds and reaction fractions, some of which are very reactive, to escape before having an opportunity to react. Also any moisture will evaporate before the observed exotherm occurs. These confounding factors make it difficult to relate the DTA results to an actual system.

Explosives can be held at an elevated temperature for a period of time (seconds to days depending upon the material, temperature, total mass, and confinement) with no apparent change in either mass or temperature and then suddenly without warning, explode. This behavior is more readily observed in large masses and confined samples. The accepted explanation is the potentially explosive materials undergo decomposition at all temperatures, the rate of decomposition being exponentially dependent upon temperature. The decomposition products are often more reactive than the original compound. For example TNT will decompose to reaction nitrous oxides, sodium nitrate may decompose to NO and NaNO_2 both of which are more reactive but with lower energy than sodium nitrate. If these fragments cannot escape, because of the bulk or confinement of the samples, the rate of reaction, at a constant temperature, will continually increase until it reaches the run away stage.

These observations are the motivation behind the pressurizable DTA tests described in this report. The larger mass (160 gm) and the

sealed container make the tests more severe and more closely simulate the expected behavior of a large (thousands of kg) mass and/or a deflagration once initiated. Observe that in an explosively propagating reaction any water present will be heated to the reaction temperature and thus lower the maximum temperature, whereas in an open cup DTA test the water is normally gone by the time the reaction temperature is reached.

VI. CONCLUSIONS

Within the limitations of the following assumptions, a number of conclusions can be drawn regarding the exothermic reaction potential of sodium nitrate based salt cake.

A. Assumptions

1. The salt cake consists of 95 percent NaNO_3 , with the bulk of the remainder composed of NaNO_2 , NaAlO_2 , and NaOH .
2. Possible organic substances added to the salt cake are ion exchange resins, complexant (a mixture of citric acid, ethylenediaminetetraacetate (EDTA and HEDTA), hydrocarbon liquids and traces of rubber, plastic and cotton.
3. There are no nitrated organics present and furthermore the caustic state of the salt cake precludes the conversion of any organic material to the nitrated state.
4. The salt cake is dry.

B. Conclusions

1. Sodium nitrate based salt cakes containing organic materials are stable against deflagration for temperatures below 250°C .

2. Sodium nitrate based salt cakes will ignite and react explosively with most organic materials which are still liquid or solid at temperatures above 400°C. Ignition will occur between 380 and 450°C.
3. If a volatile hydrocarbon is added to a sodium nitrate based salt cake and subsequently heated slowly and uniformly, the hydrocarbon will evaporate unreacted before ignition temperatures (~400°C) are reached.
4. If a volatile hydrocarbon is added to a sodium nitrate based salt cake and subsequently ignited, the hydrocarbon will flame above the salt cake, reacting with environmental gaseous oxygen (assuming an adequate source is available). The salt cake will act as a wick, transporting the hydrocarbon to the surface by capillary action and evaporation will cool the salt cake to below ignition temperatures.

VII. SENSITIVITY ANALYSIS

In the case of actual salt cakes, water will be present in quantities from 2 to 20 percent. The presence of water increases the difficulty of reacting the material. Sodium hydroxide and sodium aluminate may also be present in quantities in excess of 5-10 weight percent. Their presence reduces the reactivity of the salt cake. Although sodium nitrite may be present and is more reactive than sodium nitrate, it is less energetic and to the extent it is present, reduces the worst possible hazard.

Any departure of the concentration of organic material from stoichiometry reduces the reactivity. Finally, since it is known that the quantity of organic material, except for volatile solvents and complexants added to the waste stream was far less than 1 percent, the

two most probable forms for it is either in very diffuse concentration throughout or concentrated in a few locations. In neither case is an exothermic reaction likely since the most probable fate of volatile solvents is evaporation and removal during the storage, evaporation and crystallization process.

VIII. RECOMMENDED ADDITIONAL STUDIES

The unresolved test involving a large mass of sodium nitrate and a flammable hydrocarbon fuel (kerosene) should be investigated in greater detail. The current salt cake does not contain any significant amount of any flammable hydrocarbons and therefore is stable regardless of any possible reactions between flammable hydrocarbons and sodium nitrate. Nevertheless, such potential reactions are of interest because of the credible possibilities of accidentally adding hydrocarbon fuels to a waste tank as a result of a vehicular accident (truck or plane, for example).

Hydrocarbon fuels are readily available in significantly large quantities, and, being liquids, possess the physical ability to flow into a tank and mix with the salt cake. Furthermore, because of the known stability under 250°C, a material which is to be considered a real hazard must offer the possibility of increasing the temperature near or above 400°C. An air supported hydrocarbon fuel fire could conceivably provide the high ignition temperature.

The test involving 130kg of material as reported in this paper is unrealistic from the point of view that the igniting fire was beneath the test material. In any conceivable waste tank fire, the initial fire would be at the top of the salt cake.

Additional tests using kerosene, jet fuel, diesel oil or similar fuels and sodium nitrate or simulated sodium nitrate based salt cakes in quantities greater than 100 kg are recommended. The test should be set

up to resemble an underground tank, with ample fuel to provide an initial gas phase fire and still have 10-20 wt% fuel available for a potential solid liquid phase reaction. Various ignition sources and techniques should be incorporated into the test program.

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3. G. A. Beitel, Chemical Stability of Salt Cake in the Presence of Organic Materials, ARH-LD-119, April 1976.
4. G. A. Beitel, Sodium Nitrate Combustion Limit Tests, ARH-LD-123, April 1976.
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APPENDIX A
SUMMARY OF TEST DETAILS

A. MATERIALS

1. Dry Salt Cake

Receipe: Dissolve 220 gm. NaOH in 500 ml H₂O
 Add 164 gm NaAlO₂
 Add 138 gm. NaNO₂
 Add 170 gm. NaNO₃
 Add H₂O to increase volume to 1 liter
 Heat to 90-100°C with constant stirring and
 add NaNO₃ 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
 (Approximately 95 wt% to NaNO₃)

2. Drain Salt

Dry Salt Cake plus 5[±] 1% H₂O

3. Undrained Salt Cake

Dry Salt Cake plus 10[±] 1% H₂O

4. Complexant

Composition:

NaAlO ₂	-	0.66 M
NaOH	-	0.86 M
NaNO ₂	-	0.09 M
NaNO ₃	-	4.14 M
NaCO ₃	-	0.4 M
HEDTA	-	0.54 M
EDTA	-	0.27 M
H ₂ O	-	Remainder
Density	-	1.466 g/cm ³

Note: HEDTA = C₁₀ H₁₅ O₇ N₂ Na₃

EDTA = C₁₀ H₁₂ O₈ N₂ Na₄

APPENDIX (CONTINUED)

4. (Continued)

This complexant mixture contains approximately 5 wt% oxidizable carbon and 1 wt% oxidizable hydrogen. It closely approximates the residual liquor found in some of the stored salt cakes. The tests in which 20 to 30 wt% complexants was added to 70 to 80 wt% salt cake, contain less than 2 wt% oxidizable carbon plus hydrogen. This in turn approximates the actual storage conditions.

5. Resin

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

B. TEST RESULTS1. Resin in Drained Salt Cake

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

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

2. Complexant in Drained Salt Cake

Samples up to 160 g. scanned to 250°C showed 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.

3. Complexant in Undrained Salt Cake

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

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

APPENDIX (CONTINUED)

4. Thermal Stability of Kerosene with Salt Cakes

The salt cakes *(80 g. each) run with 14% kerosene scanned to 250°C showed no exotherm.

5. Autoignition of Salt Cakes with Resin

All three salt cakes (80 g.) with 10% resin gave an autoignition temperature of 450°C in the open cup.

6. 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.

7. 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.

8. Fiberpak Filled With 17 kg NaNO₃ and 2.8 kg Kerosene

Fiberpak was placed above a wood fire. The vaporizing kerosene burned in the flame. The sodium nitrate contributed to the fire only when it fell on the coals below.

9. Leverpak Filled With 108 kg NaNO₃ and 17.6 Kerosene

The large carton sat above the fire for six minutes with only blackening and no apparent external harm. One minute later bright spots of flame appeared near the sides of the top of the carton. At eight minutes from the start the sides of the carton gave way and a tremendous conflagration ensued with flames reaching high into the air. The contents tumbled into the fire. White smoke (indicative of a sodium nitrate supported reaction) appeared in great volume. The sodium nitrate melted and decomposed and generated much heat which could be felt 150 feet away. The kerosene had long since burned away, as judged by the absence of black smoke.

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