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CHEMICAL STABILITY OF SALT CAKE IN THE PRESENCE OF ORGANIC MATERIALS

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DISCLAIMER

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INTRODUCTION

The Hanford waste-solidification program utilizes an evaporation and crystallization process to reduce high-level liquid waste to a product known as salt cake. Salt cake is predominantly a water slurry of sodium nitrate ($NaNO_3$) with lesser amounts of sodium nitrite ($NaNO_2$), sodium metaaluminate ($NaAlO_2$), and sodium hydroxide (NaOH).[1] Although the salt cake presently contains 30 - 50 percent moisture, the present goal is to remove as much water as possible. In addition, trace amounts of all the fission products and transuranics are present, as well as a broad spectrum of organic materials in small but unknown amounts.

Under certain pressure and temperature conditions, almost any organic material can be exothermically oxidized by $NaNO_3$. The release of large amounts of heat along with the generation of gaseous products can result in explosive reactions. Under certain conditions organic material can become nitrated. Nitrated organics form the largest class of detonable high explosives.

The consequences of a detonation or even a deflagration within a high-level salt cake demand that the salt cake storage system be thoroughly understood and that steps be taken to insure that such reactions never occur. This report addresses itself to the problem of sodium nitrate - organic material mixtures in light of the realities of salt cake management.

SUMMARY

High-level waste stored as salt cake is principally $NaNO_3$. Some organic material is known to have been added to the waste tanks. The present state of this organic material is unknown. It has been suggested that some of this organic material may have become nitrated and transformed to a detonable state. Eight nitrate-related explosions in the nuclear separations industry have lent credence to these fears.

This report presents arguments to discount the presence of nitrated organics in the waste tanks--nitration is accomplished in concentrated nitric acid (7<u>N</u> or greater) whereas the high-level waste was neutralized prior to transfer to the tanks. Nitrated organics generated accidentally usually explode at the time of formation; it is unreasonable to expect accidentally generated explosives to survive for a sufficient time to be transported to the waste tanks. Additionally, supportive detonation tests

offer experimental evidence that salt cake and "worst-case" organic mixtures are not detonable.

Organic mixtures with salt cake are compared with black powder, a related exothermic reactant. Black-powder mixtures of widely varying composition (fuse powders for example) can and do burn explosively. Ignition temperatures of these mixes are 300-450°C. Regardless of the composition or quality of the mix, however, black-powder-type mixes cannot be ignited by radiation and are shock insensitive. Temperatures generated by radionuclide decay in the salt are by design below 175°C and therefore would be incapable of igniting any of these mixtures.

The expected effect of radiation on organics in the waste tanks is a slow dehydrogenation and depolymerization along with a slight increase in sensitivity to oxidation. These effects become noticeable (affecting a small percentage of bulk at most) only above 10^8 rads, equal to maximum expected life-time doses.

The greatest explosion hazard, if any exists, is a hydrogen-oxygen explosion resulting from radiolysis of water in the waste. Such a hazard, however, requires that the hydrogen first be generated and then trapped so that the concentration of hydrogen can rise above 4 volume percent. This is impossible in salt cake with moisture content and heat generation rates as low as those resulting from the current solidification program, even in a sealed tank. Concentrations above 4 volume percent are impossible in vented tanks containing waste much wetter and hotter than the planned salt cake product.

Final confirmation of the safety against organic related explosive reactions in the salt cake, a possibility which only could become plausible after most of the present moisture is removed from the salt cake, will be based upon analytical determinations of organic concentrations. If these concentrations are below combustion limits for such mixtures, then the mixtures can be assumed safe.

DISCUSSION

BACKGROUND

Salt Cake Origin and Composition

A common feature in all of the transuranic separations processes is the use of nitric acid. After dissolution of the fuel slug in nitric acid, solvent extraction with an organic solvent is used to effect the desired separations in all but the bismuth phosphate process. The final plutonium purification is based upon an ion exchange process using organic resins; the liquid medium is usually a strong nitric acid solution.

In the Purex process, the aqueous acidic waste from the initial fission product separation step was pre-denitrated with a sugar solution, then concentrated, and again pre-denitrated with sugar. Any excess unreacted sugar would have gone to the waste tanks. The waste was then neutralized with NaOH, forming $NaNO_3$. Flushing operations and cell drainage are other sources of large quantities of organics which can be added to the waste stream.

A variety of other organic materials have inadvertently found their way to the waste tanks: rubber gloves, rubber or plastic tubing, plastic covers or containers, cleaning cloths, and other materials primarily used in tank-farm maintenance and sampling.

Although no organic material was purposely added to the underground waste tanks, certainly some of the extraction solvents, resins, and denitration sugars must have escaped to the tanks, some as trace amounts in the normal waste stream, some accidentally, and others through immediate convenient disposal of highly contaminated material. If the waste stream contained only 0.1 weight percent organic, a one-million-gallon waste tank could contain as much as 7500 pounds of organic. Subsequent concentration of this organic could conceivably occur by phase separation, crystallization, or evaporation/condensation. This possible coexistence of $NaNO_3$ and organic materials forms the basis of this report.

Prior Experience with Nitrate-Related Exothermic Reactions in the Nuclear Processing Industry

In this section specific examples are shown of instances in which combinations of nitrates and organics have led to exothermic reactions, some resulting in explosions.

Seven occurrences have been reported in nuclear work with anion-exchange resins in which unexpected and uncontrolled exothermic reactions resulted in either explosive (in pressurizable systems) or nonexplosive (in open systems) deflagration. In each case the incident was traced to self-ignition of nitrate-form resins. In six of the seven events, concentrated HNO_3 ($>7\underline{N}$) was present; the other one occurred in a $7\underline{N}$ $LiNO_3$, $0.1\underline{N}$ HNO_3 solution. Each event was investigated and causative factors were identified. The triggering mechanisms varied from external application of heat, radioactive decay heat, heat of dilution of acid in water, heat of reaction, heat from decomposition of resin, low vessel wall heat transfer, low thermal conductivity of resin, extraneous materials acting as catalysts, resin in nitrate form, long contact time, metallic ions loaded on resins, and a pressurizable system. Only the low thermal conductivity of the resin and the nitration of the resin were common factors in all cases. These seven occurrences are listed in Table I by location and date.

The interested reader is referred to a rather detailed but concise review of these occurrences in Nuclear Safety.[2]

TABLE I

ANION-EXCHANGE - NITRATE OCCURRENCES

Location	Date	Reactants
Fontenay-Aux-Roses, France	June 26, 1962	Dowex 1-X4® (Dow Chemical Company), Pu in 10-12N HNO_3
Rocky Flats	July 14, 1963	Dowex 1-X4®, Pu in 7-8N HNO_3
Hanford (Redox)	November 6, 1963	Permutit SK® (Permitut Company), Pu in 7 N HNO_3, sodium dichromate,
Oak Ridge National Laboratory	January 1967	Dowex 1-X10®, ^{244}Cm and ^{243}Am and Ca in 8N $LiNO_3$ + 0.1N HNO_3
Kerr-McGee	May 24, 1967	IRA-400® (Rohm and Haas Company), depleted U in "concentrated" HNO_3
Brookhaven National Laboratory	July 23, 1965	Duolite A-30B® (nitrate form) (Diamond Shamrock Chemical Company), poorly mixed 12N HNO_3, unknown cations
Savannah River Laboratory	October 1, 1974	degraded-nitrated resin, 10 N HNO_3, fission product ions

"Red Oil" reactions and explosions have occurred in a number of instances in nuclear facilities. The combination of uranium, nitrate ion, tributylphosphate, and kerosene-type diluents results in a heavy organic phase that is very reactive at temperatures in the 150° C range. It is highly unlikely, however, that such combinations could exist in aged high-level wastes due to (a) low probability of formation, (b) decomposition, and (c) depletion by heat (in self-boiling wastes), evaporation, and radiolysis.

Detonation and Deflagration*

There is a rather widespread practice outside the explosives discipline to refer to all violent explosions as "detonations." Within the discipline, however, the term "detonation" is reserved for a special type of explosive reaction. Explosive reactions may be either detonations or deflagrations.[3] These two terms will be defined here and the distinction used throughout this report. It is important to make this distinction to forewarn the reader that a test which proves that a mixture does not "detonate" does not necessarily mean that it cannot explode by deflagration. Conversely, a test eliminating the possibility of deflagration does not rule out detonation.

The significant physical difference between a deflagration and a detonation is in the microscopic view of the burning process and in the propagating mechanism. In deflagration the reacted molecules move away from the explosive's deflagration front. A deflagration proceeds at subsonic velocities. The reaction zone is held close to the surface of the explosive by means of a confining pressure (which may be less than one atmosphere). Heat generated in the reaction zone vaporizes additional material which then moves away from the explosive, into the reaction zone, and reacts. The heated reaction products increase the confining pressure which promotes heat transfer by mass transport back to the explosive. Increased pressure and temperature increase the velocity of the reaction. In some materials the velocity can increase to the point of generating a supersonic (shock) wave and transform the deflagration into a detonation; in most materials, however, the transition from deflagration to detonation is not possible. Finally, in most deflagration explosions, the explosion (shock wave) arises from a physical confinement of the reaction.

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*The term deflagration is generally used to describe any exothermic reaction resulting in an explosion not classifiable as a detonation. The term "combustion" is used in this report to describe any similar process which does not result in an explosion. Since deflagrations begin and propagate as combustion reactions, we use the term combustion as the low limit hazard.

During detonation, the reacted molecules move toward the explosive, in the direction of the propagation of the detonation. A detonation, propagated by a shock wave, proceeds at supersonic velocities. The shock front "shocks" the explosive, locally increasing the pressure to many kilobars, which in turn raises the temperature to hundreds (in a solid) or thousands of degrees centigrade (in the case of a gas). If the material reacts rapidly enough at these temperatures to support the shock wave, the material is said to "detonate."

On a microscopic scale, the reaction zone is of the order of 10^{-2} cm in a deflagration and reaction occurs in about 10^{-4} seconds. In a detonation, the reaction zone is about 10^{-5} cm and the reaction occurs in about 10^{-10} seconds. Deflagration velocities range from 10 to 100 cm/sec; detonation velocities are of the order of 5×10^5 cm/sec.

In the standard detonation tests, an explosive is placed in contact with a 1.2-cm-thick steel plate (witness plate) and triggered at a point remote from the plate (Figure 1A). Since the molecules move in the direction of propagation in a detonation, a detonation will puncture the witness plate (or merely bulge it if of insufficient intensity). A deflagration will blow the witness plate away unharmed. See Figures 1B and 1C.

A deflagration in an unconfined explosive can terminate by blowing part of the explosive away from the reaction. This can almost never happen in the case of a detonation. A deflagrating explosive normally must be confined to produce an explosion. A detonable explosive does not have to be confined to produce an explosion.

Once the reaction is complete and the explosive expansion of the gaseous products begins to exert force on the surroundings, the distinction between deflagrations and detonations disappear. When the "rocks begin to fly" the nature of the reaction is immaterial. The distance at which the resultant pressures are essentially equivalent is about 3 times the diameter of the explosive mass.

The reader interested in the theoretical discussion of explosions is referred to a rather exhaustive treatment by Evans and Ablow.[4] For the subject of thermal explosion, see the Army Material Command Handbook.[5]

Black Powder

The similarity between black powder and any conceivable explosive mixture with salt cake demands a close look at black powder. Black powder is the oldest known propellant (explosive). Its name is derived not from its color, as is commonly assumed, but from a translation from the German "Schwarzpulver," named after Berthold Schwarz, who experimented with black powder variants in the fourteenth century. Black powder is an intimate mixture of charcoal, sulfur and potassium nitrate. Sodium nitrate can be substituted for potassium nitrate, and such a substitution results in a product commercially known as "B" blasting powder. Sodium nitrate blasting powder was used extensively in the construction of the Suez Canal.

Table II shows the composition of several varieties of black powder.[6] Nitre (generally assumed to be KNO_3) content ranges from 61-78 percent, sulfur from 2-15 percent, and the charcoal from 11-21 percent. The moisture content, about one percent, is associated with the charcoal, which normally contains 3-5 percent moisture when exposed in normal air. The function of sulfur is to lower the ignition temperature and increase the burning velocity.

TABLE II

BLACK POWDER COMPOSITION

Name of Powder:	Pebble	Large Grain	Fine Grain	Sporting	Mining	Spanish Spherical	Cocoa
Moisture (wt.%)	1.0	1.0	1.5	1.2	1.6	0.7	1.3
Nitre (wt.%)	74.7	74.5	73.9	74.7	61.9	75.6	78.9
Sulphur (wt.%)	10.1	10.1	10.0	10.4	15.1	12.4	2.0
Charcoal (wt.%)	14.2	14.3	14.6	13.7	21.4	11.3	17.8
Carbon content of charcoal (%)	85.2	86.7	78.1	78.1	83.6	76.5	---

Black powder is relatively insensitive to minor variations in composition. In fact, the black powder industry never bothered to make extensive studies on quality versus composition. No composition limits were ever determined. Ever since its invention, black powder has worked well without particular concern for composition as long as it is kept dry. In general, product quality and burning rates have been controlled mostly by mixing, grain size, and density.

Fuse powder, the only variant of black powder which is still widely commercially manufactured, is manufactured with the expressed goal of a slow, uniform burning rate. Instead of burning rates of 1000-4000 mm/sec desirable in gunpowder, fuse powder is made with burning velocities of 1-10 mm/sec. Reduced burning velocities are achieved by adding inert or difficult-to-burn materials. Additions include such things as brick dust, graphite, titanium dioxide, barium sulfate, lead sulfate, manganese trioxide, cupric oxide, zinc oxide, rosin, pitch, camphor, and urea.

The addition of moisture, above the normal 1 - 1.5 percent, to black powder first increases the pressure of the explosion by increasing the volume of product gas, then reduces the pressure by reducing the maximum temperatures attained and, at some point around 20 percent, will prevent ignition.

The ignition temperature of a KNO_3 plus charcoal mixture is about 470°C, well above the melting point of KNO_3. The addition of sulfur, a key ingredient in black powder, lowers the ignition temperature to about 300°C. The mechanism by which sulfur lowers the ignition temperature is apparently based upon the reaction

$$S + H_2 \rightarrow H_2S$$

which proceeds at 150°C. Charcoal is the source of the hydrogen. This reaction is followed by

$$KNO_3 + H_2S \rightarrow \text{Decomposition Products}$$

which proceeds at 285-290°C.[7] The ignition temperatures of $NaNO_3$ mixtures are comparable to KNO_3 ignition temperatures; however, ignition is more difficult and mixtures burn more slowly.

A KNO_3 + S mixture is very shock sensitive (will ignite if shocked), a KNO_3 + S + C mixture (normal black powder) is less sensitive to shock, and a KNO_3 + C mixture is shock insensitive. However, in no case does black powder detonate.[5] Propagation velocities are less than 400 cm/sec, well below detonation velocities.

In light of this brief discussion of black powder, salt cake with 50 percent or more $NaNO_3$ and a history of organic material additions should be assumed to burn, unless proven different, as a poor grade of fuse powder. Mixing can be assumed to be poor. Since there is no reason to expect any elemental sulfur present, the ignition temperature should be above 400°C and any combustible mixture should be shock insensitive. Furthermore, until the salt cake is dried to less than 20 percent moisture, there is no reason to expect combustion under any circumstances. Past experience with nitrates, however, suggests that the material should be considered potentially hazardous until the absence of organic material is proven.

Nitrates in Nature

The study of natural nitrate deposits sheds some light on the long-term stability of a nitrate-rich salt cake. Nitrates are formed in secretions from animals--urine, perspiration and saliva. Nitrates are also formed during decomposition of organic matter under special conditions. A small amount of ammonium nitrate is produced in the atmosphere during a lightning discharge; subsequent reaction with soil salts can result in metal nitrates. However, the relatively high solubility of all nitrates in water prevents their accumulation in all but the most arid locations. Except for very minor deposits in many of the desert areas of the world, the only significant nitrate deposits are found in India (KNO_3), southwest Africa (KNO_3 and $NaNO_3$ in nearly equal amounts), and the Atacoma Desert on the west coast of South America (predominantly $NaNO_3$). The Atacoma Desert deposits, the largest in the world, deserve attention.

The salt occurs in large flat basins on the east slope of the coastal mountains, west of the Andes. Figure 2 is a diagrammatic cross section through a nitre basin.[8] There are five not very sharply defined layers:

1. The surface layer, "chuka," consists of 2 or 3 inches of grey sand and pebbles mixed with a little sodium sulfate and gypsum. The surface layer is almost devoid of vegetation.

2. Just below the surface is a 1 to 5 foot layer of material similar to chuka, cemented together with clay, salt (NaCl) and sodium nitrate, called "costra" (a crust) by the natives.

3. Below the costra is a layer which is principally NaCl, resembling the costra and called "conjelo."

4. Below the conjelo is a massive white stratum of nitre-bearing rock, 1 to 5 feet thick, called "caliche."

5. The bottom layer, called coba, consists of clay and loam containing some sea fossils and a little salt; it lies on bedrock consisting of shale or limestone or other rock which may be outcropped.

The costra is a low-grade nitre rock with insufficient $NaNO_3$ for economic recovery. The caliche is the layer with economic value. The deposits are close to the surface and vary in composition in different places. Typical analyses of the costra and caliche are shown in Table III.

TABLE III

COMPOSITION RANGES OF SIGNIFICANT NITRATE DEPOSITS

	$NaNO_3$	KNO_3	NaCl	Na_2SO_4	$CaSO_4$	$MgCl_2$	$CaCO_3$
Caliche	35-62	0.3-26	20-42	3-7	0-64	0.4-0.7	0.1-0.15
Costra	15-24	6	22-58	3-17	8	0.4-2	0.1

Table III does not show the fact that almost all the nitrate deposits also have traces of various iodine compounds, perchlorates, chromates and other metal ions in lesser quantities.

The main nitrate deposits in Chile lie in a region 10-50 miles wide by 600 miles long. The deposits vary from several inches to several feet thick.

Although the origin of the nitrate beds is not known, it is generally agreed that the nitrogen is of organic origin, either animal or vegetable. It has been suggested, in light of the immense deposits of guano on some of the islands off the coast of Peru, that guano was the source of the nitrates. Equally likely theories attribute the nitrate beds to decaying plant life in trapped inland seas.

Of particular interest here is that, in spite of the evidence of organic origin, there is no organic matter present in the nitrate deposits. The full significance of this fact is not obvious. It could indicate several divergent points of view. (1) There is no organic material present because the organic origin theory is incorrect. (2) The nitrates were formed from organic matter in an area remote from the present deposits, then leached out and transported by water, leaving any insoluble organic residue behind. (3) At some point in time the organic material remaining after formation of nitrates was oxidized by a portion of the nitrates. If the organic residue was oxidized, it is unlikely that it was similar to a black powder deflagration, because such a reaction has Na_2CO_3 (or K_2CO_3) as one of its major products, neither of which is present in any significant quantities.

The absence of organic material may be only an artifact of the creation of nitrates. It does, however, indicate that organic material and nitrates do not coexist for geologic times. This implies that salt cake (in the waste tanks), in the presence of organic material, is inherently unstable. Alternatively, the existence of nitrate deposits is concrete evidence that organic-free nitrates are stable for geologic times, if they remain dry.

DETONATION RISK

Nitrated Organics

Most detonable high explosives belong to a class of compounds known as nitrated organics. They include such compounds as nitroglycerin; trinitrotoluene (TNT); 1,3,5, cyclohexanetrione; N-methyl-N-2-, -4,5,-tetranitroaniline (Tetryl); pentaerythritol (PETN); hexahydro,-1,3,5 trinitro-s triazine (RDX); octahydro-1,3,5,7-tetranitro-s tetrazine (HMX); etc. There is an important similarity in the preparation of all of these explosive nitrated organics--the nitration step occurs in a concentrated nitric acid (about 7N) solution with extreme control on the temperature.

Explosive nitrated organics, when made unexpectedly or by accident, usually explode. This is true in the nuclear industry experience, as Table I illustrates.

During the generation of high-level liquid waste, processes were conducted in concentrated nitric acid, but the wastes were neutralized and made basic prior to pumping to the storage tanks. Therefore conditions in the tanks made subsequent nitration an impossible step. The accidental generation of detonable organics is not a creditable event.

Past experience in the explosives industry, however, indicates that reliance on theory alone is hazardous. It is the unexpected explosions which are the most dangerous. For this reason a number of mixtures of simulated salt cake and organic material, similar to those known to have found their way into the waste tanks, were subjected to detonation tests.

Tests with Simulated Salt Cake

A total of 20 different mixtures were concocted and subjected to detonation tests.[9] The compositions were chosen, not on the basis of the critical detonation instability, but because it was reasonable to expect that just such a mixture might exist within the salt cake in some undetermined quantity. In all but four tests, the oxidizer was a simulated salt composed of (approximately):

$NaAlO_3$	-	21 wt %
$NaNO_3$	-	33 wt %
$NaNO_2$	-	14 wt %
NaOH	-	18 wt %
Na_2CO_3	-	14 wt %

In the other four compositions, pure $NaNO_3$ was the oxidizer. A complete description of these mixtures is given in Appendix A.

Samples 1-16 were tested using the standard Naval Ordnance Laboratory gap test.* Tests 1-15 were made at zero gap thickness. Sample 16 was tested with a 0.6 cm-thick plastic gap. No evidence of detonation was observed in any of the tests on samples 1-16.

In samples 17-20, the linear dimensions of the standard NOL gap test were scaled up by a factor of 3 so that the samples were 15.2 cm in diameter by 38 cm long. The samples were pressed at 4000 psi (2.8 kg/mm^2) into steel tubes 15.2 cm ID with 1.27-cm-thick walls. Again no evidence of a detonation was observed. There was some evidence that a driven reaction occurred which released energy but did not propagate.

Samples 1-16 most closely approximate mixtures which might be expected within the salt cake. Samples 17-20 are the highest energy-per-gram mixtures one would expect. All are safe against detonation. These results do not prove, however, that no conceivable mixture exists which could detonate.

DEFLAGRATION RISK

Freedom from detonation does not insure safety. Slow combustion, similar to a peat-bog fire or a spontaneously ignited coal pile fire, would be a serious event were it to occur in a million-gallon tank full of dry salt cake. A rapid deflagration in a confined system can result in an explosion as devastating as a detonation. If the reaction is slow enough to allow the reaction products to escape with no pressure buildup the reaction is termed combustion.

Considerable insight can be gained by computing the adiabatic "flame" temperature of the reaction. The theoretical flame temperature is the temperature of the products if the heat of reaction were all used to heat the products.

If the maximum theoretical flame temperature is below the ignition temperature then the mixture will be absolutely safe. Therefore, a flame temperature versus composition curve can be used to identify combustion limits.

Explosive force is a function of the volume of the reaction products. This volume is a function of both the molar volume and the temperature of the products. Therefore the calculated flame temperature is also a measure of the potential violence of the deflagration.

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*Standard NOL gap tests: explosive shock sensitivity tests standardized by the Naval Ordnance Laboratory, Silver Springs, Maryland, depicted in Figure 1.

Theoretical flame temperatures, because they are based upon assumption of zero heat loss and ideal gas laws, tend to be about 10 percent higher than measured flame temperatures. When molecular dissociation is ignored, as it generally must be because of lack of applicable data, the computed temperatures are much higher.

Flame Temperature Estimates

Let us consider the reaction of $NaNO_3$ with elemental carbon. The stoichiometric equation is:

$$4\ NaNO_3 + 5C \rightarrow 2Na_2CO_3 + 3CO_2 + 2N_2 + 375.8\ \text{kcal} \qquad (1)$$

The maximum theoretical flame temperature, T_C, is obtained by assuming an adiabatic process:

$$T_C = 300 + \Delta T = 300 + \frac{\Delta E}{\Sigma n_i\ c_p(i)} \qquad (2)$$

where ΔE, the heat of reaction, is the difference between the sum of the heats of formation of the reactants and the sum of the heats of formation of the products, n_i is the number of moles of the ith product and $c_p(i)$ is the specific heat at constant pressure of the ith product. The specific heat at constant pressure is used to correspond more closely to an unconfined combustion process, and as such results in lower temperatures than for processes occurring at constant volume. The detailed assumptions and physical parameters used in the computations are shown and discussed in Appendix B.

In the fuel-rich region, the reaction will be similar to:

$$2\ NaNO_3 + 5C \rightarrow Na_2CO_3 + 3CO + N_2 + C \qquad (3)$$

with the formation of carbon monoxide and presence of free carbon.

In the fuel-lean region, the reaction will proceed with the formation of nitrogen oxides, e.g.:

$$2\ NaNO_3 + 2C \rightarrow 3\ Na_2CO_3 + 2CO_2 + 2NO_2 + NO + 1\ 1/2\ N_2 \qquad (4)$$

Experimentally, sodium carbonate is always formed and remains behind as a white residue. Some Na_2O is also formed, which would reduce the maximum temperature, but it has been ignored in the computations.

Although the energy released from the $NaNO_3$ + C reaction (940 cal/gm) is 84 percent that of TNT, the volume increase (280 ml/gm) is considerably less than that of TNT (986 ml/gm) so that any resulting explosion is less violent.

If water is present the temperature is reduced by the heating of water vapor and the latent heat of vaporization (10.5 kcal/mole).

The flame temperatures were computed and are plotted in Figure 3 as a function of $NaNO_3$ concentration. For non-zero moisture content curves, the percentage of $NaNO_3$ is based on the dry mixture.

The peak temperature, 3600°K, occurs at a stoichiometric ratio of 85/15 ($NaNO_3$/C) and is far above any experimentally observed reaction temperature.

Actual temperatures are limited to about 2500°K by the dissociation of Na_2CO_3; the equilibration of CO, CO_2, and C; the formation of nitrogen oxides; the formation of radicals; and ionization. This physical barrier to very high temperatures is shown by the dashed line at 2500°K*.

The practical result of the temperature limiting mechanism is that mixtures from 75 percent to almost 90 percent $NaNO_3$ can be expected to react at about the same velocity, because temperature controls velocity through the Arrhenius relationship.

A line is drawn at 1100°K. This line is the approximate low temperature limit of most hydrocarbon flames, below which they will not propagate. This same limit is not necessarily applicable to the $NaNO_3$ + C reaction, but agrees with our laboratory observation. This line predicts combustion limits, in terms of percent carbon, of 7-57 percent in a dry mixture.

The presence of water has a very pronounced effect as shown by curves 2 through 6 in Figure 3. In addition to reducing the temperature of the reaction, water narrows the combustion limits. Of equal importance, however, is the fact that a stoichiometric mixture with water (10 percent for example) will still burn with the same maximum temperature, but with more explosive force because of the increase in volume from the water vapor.

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*There is no penalty for being off by several hundred degrees in the upper temperature limit, either in this discussion or in practice.

If instead of a pure C + $NaNO_3$ mixture, one has C + $NaNO_3$ + inert, which more closely resembles actual salt cake mixtures, flame temperatures will be correspondingly reduced because of the heat absorbed by the inert material. Also such a mixture must be more nearly stoichiometric in order to support combustion.

The computations described above were repeated for the hydrocarbon decane, chosen as a reasonable substitute for normal paraffin hydrocarbon, a widely used solvent in the plutonium separation process. The results are shown in Figure 4. The peak temperature is less than for carbon and the temperatures in the fuel-rich region fall off more rapidly. The behavior in the fuel-rich region is typical of most combustion processes because the heat capacity of hydrocarbon fuels is much higher than for inorganic compounds.

Ignition

Ignition temperature is normally defined to be the minimum temperature at which a reactive material will react rapidly enough to generate more heat than is lost to the surroundings. A reaction, once ignited, will continue until either most of the reactive material is gone, or until the reaction is quenched by external effort. Ignition temperature is dependent upon heat loss, so even though ignition temperatures are specified for most materials, actual ignition temperatures are not fixed values except for specific configurations, external conditions and materials.

In principle, if a reaction is governed by the Arrhenius law, a large mass of explosive material, large enough to effectively have zero heat loss, will have no low bound ignition temperature. However, at low temperatures it may take a very long time for the reaction to proceed rapidly enough to be noticeable. Table IV makes the preceding discussion more explicit. An experimentally determined "ignition" temperature for the example in Table IV would be around 325°C.

In Figure 3 a band covering the range from 660 to 760°K is shown. This is the temperature range reported in the literature for ignition temperatures of dry KNO_3 + C mixtures[6,7,10,11] and dry $NaNO_3$ plus bitumen mixtures.[12,13,14] Recall that the ignition temperature of black powder, KNO_3 + C + S, ranges from 265 to 360°C but depends upon sulfur to lower the ignition temperature. Considering ignition temperatures, it is obvious that dry mixtures with less than 25 percent $NaNO_3$ or less than 6 percent C could not undergo combustion under any circumstances.

TABLE IV

TYPICAL BEHAVIOR OF A SOLID HIGH EXPLOSIVE COMPOUND FOLLOWING AN ARRHENIUS REACTION LAW*

Temperature, °C	Characteristic Lifetime, k_r^{-1}
20	1 million years
110	1 year
200	1 hour
260	1 minute
325	1 second
375	1 tenth second
435	1 hundredth second
500	1 thousandth second
825	1 millionth second

*k_r = Z exp [-E/RT] where Z = frequency factor, E = activation energy, R = gas constant, T = absolute temperature. The table is computed for Z = 10^{13} sec^{-1} and E = 35 kcal/g mole.

Explosion Scenario

The foregoing discussion will now be applied to the salt cake waste in order to construct a scenario which could lead to a deflagration.

First, it has just been shown that there is almost no possibility of ignition and subsequent explosive reaction between the $NaNO_3$ and any organic material in dry salt cake unless the percentage of organic material is greater than 6 percent. Also, no combustion can occur unless the carbon content is less than 60 percent (nitrate-bitumen experiments have confirmed this fuel-rich limit).[7,8]

Second, the following examples are offered to prove that even though "large" quantities of organic material were added to the waste stream, there was never enough to provide a uniform mixture even approaching 6 weight percent organic material.

1. The organic waste from the Redox nuclear fuel preparation plant--TBP (tributyl phosphate), NPH (normal paraffin hydrocarbon), and hexone--was stored separately from the waste salt solution. The total amount presently stored is about 100,000 kg. It is unreasonable to expect that more than 10 percent, or 100,000 kg, escaped to the nitrate-waste tanks. If all of this were deposited in a single million-gallon tank it would only constitute 0.3 percent organic content. Whatever organic entered the waste stream was actually distributed among some 20 million-gallon tanks. Even the present evaporation-concentration program could only bring the maximum concentration to about 0.9 percent. Furthermore, even this would require an ideal process, an unreasonable assumption.

2. For 10 years the resin from the ion exchange columns in the Purex plant was dumped into the waste tanks. The total amount, however, was small compared to the volume of high-level liquid waste. If it had been dumped once each month (an upper limit estimate by operations personnel) about 10,000 kg would have been added to the waste tanks. When finally dried, the Purex waste will weigh about 10,000,000 kg. The average resin concentration would therefore only be 0.1 percent.

3. Unplanned losses of resin have occasionally occurred. A break in the screen at the bottom of a cesium ion exchange column caused 250 cubic feet of Duolite ARC-359® to be lost to one of the million-gallon tanks. Again, a uniform mixture would be less than 0.2 percent resin.

One must therefore, in order to envision any explosive hazard at all, assume non-uniform mixing. Consider the following two extreme cases:

1. Accidental Stoichiometric Mixture: Random amounts of nitrates and organic materials are added to the tanks for many years. Later, after B Plant separation and evaporator treatment, a small region is uniformly mixed in a nearly stoichiometric ratio. This would require mixing by unknown and uncontrolled means and then remaining in the state long enough to be triggered to an explosion. This is totally unreasonable.

   Any dilution process probably continues to concentrations less than one percent. Any concentrating process probably continues to concentrations greater than combustion limits, e.g. a floating oil film.

2. Rapid Mixing of an Organic Rich Region with $NaNO_3$: Assume that a localized mass of nearly pure organic exists, surrounded by nearly pure $NaNO_3$. As

long as this condition remains there can be no spontaneous deflagration. The organic and the $NaNO_3$ both remain inert, separated by a thin boundary layer which if reacted would result in an inert region of Na_2CO_3 separating the two zones. A deflagration would only be possible if some mechanism caused the two zones to combine in a manner that produced rapid and complete mixing in a nearly stoichiometric mixture. It is postulated that this could occur by the mechanism illustrated in Figure 5. The following sequential steps could lead to a large-scale deflagration.

a. Initiate a pool of molten $NaNO_3$ in region A. Possible mechanisms to generate such a pool of molten $NaNO_3$ might include: a thermite bomb dropped by a terrorist or as an act of war; an operational procedure such as a shaped charge used to pierce a salt well; concentration of radioactive decay heat from the sludge layer; a meteor; or a plane crash followed by fire.

b. The molten zone expands sufficiently to allow zone B to mix, rapidly and turbulently. Either the initial heat source is great enough to cause considerable growth of zone A or the composition of zone C immediately surrounding zone A contains enough fuel to cause the molten pool to expand.

c. Explosion.

The actual obstacles to the above scenario are formidable. The heat source would have to land near, but not within the fuel rich zone B. The heat source could not dilute the surrounding $NaNO_3$ too much because then the mixture could approach the oxidant-lean limit. The temperature of the molten pool would have to be sufficiently greater than 400°C so as to remain above 400°C after mixing with zone B to permit ignition. However, if the temperature is too much above 400°C, the contact of zones A and B will cause an initial reaction of sufficient speed to prevent mixing due to the Leidenfrost effect (the behavior which causes a water droplet to bounce on a metal surface hotter than 100°C).

In summary, the miscellaneous materials that exist in salt storage tanks must be assumed to exist in a very poorly mixed state. It should be anticipated that regions exist within a salt cake with widely varying mixtures. Differentiation could be the result of density differences of immiscible phases, separation by slow precipitation, and clumping by virtue of batch-by-batch additions with mixing left to chance. If mixing were perfectly uniform the organic content would be necessarily less than one percent and the mixture would be stable against exothermic reactions under any conditions. Alternatively, if differentiation were complete, existing organics would be found in fuel-rich regions in which ignition and combustion are impossible.

EXPLOSION HAZARD

The actual risk of any potential explosion can only be judged in relation to the damage that could result. Since an explosive reaction can do much greater damage than a slow combustion reaction, this section will be restricted to discussion of hypothetical explosions.

The nature of explosives and explosions is such that the most generally applicable law is Murphy's "If anything can go wrong, it will." In addition, good advice in conjunction with the use of theoretical safety predictions for any potential explosive is an excerpt from P.A. Langwell: "They (results of computations) should be used with margins of safety dictated by engineering judgments that are strongly influenced by the magnitude of the cost of being wrong." [15]

In the field of explosions, hazard potential and blast damage are normally referenced to TNT. The heat of the reaction is computed, as described in Appendix A, and compared to the calculated specific heat of reaction for TNT (1102.3 cal/gm). Anticipated blast damage is then obtained from TNT blast effects tables for an equivalent amount of TNT.

The calculated TNT equivalency is also used to predict susceptibility to detonation. If a material has a TNT equivalency greater than 0.60, it will probably be detonable; between 0.33 and 0.60 the material may detonate with great difficulty; and below 0.33 it will not detonate. Kinetic factors may, however, preclude detonation.

Damage caused by an explosion results from both the overpressures of the associated (reflected) shock wave and the subsequent negative (relaxation) pressure. Table V shows typical structural and physiological damage as a function of pressures.

TABLE V

THRESHOLD PRESSURES FOR DAMAGE

Structural Failures	Peak Overpressure (psi)
Glass Windows	0.5 - 1
Corrugated Panelling - Wood Siding	1 - 2
Cinder Block Walls	2 - 3
Wooden Telephone Pole	5
Waste Tank Domes	10
Reinforced Concrete - 6"	500-1000
Physiological Damage	
Knock Personnel Down	1
Eardrum Rupture	5
Lung Damage	15
Threshold for Fatalities	35
50% Fatalities	50

A one kg charge of TNT detonated in an unconfined area produces shock waves and overpressures with magnitude shown in Table VI.

TABLE VI

OVERPRESSURES IN AIR FROM A 1 KG TNT DETONATION

Distance From Center (meters)	Peak Reflected Pressure (psi)	Peak Negative Pressure (psi)
0.001	2,000,000	-
0.054	82,000	-
0.2	21,000	15.0
1.0	925	10.0
5.0	9.4	1.0
10.0	3.5	0.5
100.0	0.2	0.06

The peak reflected pressure is twice the peak static pressure and assumes the presence of a target from which the shock wave can reflect. The main difference between a detonation and a deflagration occurs in the near zone (within several diameters of the explosive charge) in which the peak reflected pressures go from 10^4-10^6 psi. At distances beyond one meter there is essentially no difference.

For charges other than one kg in size, the scaling law is used, which states that a given pressure will occur at a distance from the main explosion that is proportional to the cube root of the energy yield, or:

$$D = D_O (W/W_O)^{1/3}$$

If W_O is one kg of TNT, D_O is a distance chosen from Table VI, and W is the weight of TNT (or the equivalent) of a test charge, then D is the distance from the test charge at which the pressure will equal the pressure corresponding to D_O in Table VI.

The specific heats of reaction of several $NaNO_3$ - organic mixtures are shown in Table VII.

TABLE VII

SPECIFIC ENERGY OF $NaNO_3$ - ORGANIC REACTIONS

Organic	% $NaNO_3$	Specific Energy (cal/gm)	TNT Equivalent
Carbon	85	940	0.85
Carbon	81	756	0.69
Carbon	74	550	0.50
Carbon	59	435	0.39
Carbon	41	307	0.28
Carbon	90	173	0.16
$C_{10}H_{22}$	88	1000	0.91
$C_{10}H_{22}$	92	333	0.30
$C_{10}H_{22}$	70	399	0.36
Styrene*	86	960	0.87

*Structural matrix of most ion exchange resins of interest; the 86 percent $NaNO_3$ mixture is nearly stoichiometric.

From Table VII it is seen that stoichiometric mixtures of most organic materials with $NaNO_3$ can react with 85-90 percent of the energy released from an equal weight of TNT. If kinetic factors permit, such mixtures could be detonable. Note that a 5 percent increase in $NaNO_3$ over stoichiometric reduces the available energy by over a factor of 3. This implies close tolerances allowed on the composition of reactive mixtures. Departures from stoichiometry will rapidly quench any reaction.

Since 10 psi overpressure could collapse a tank dome and because the top of a salt cake is 3-5 meters from the dome, use of Table VI predicts that a one kg charge of TNT could conceivably fail a tank dome, if detonated at the surface of the salt cake.[16] If detonated within the salt cake, the salt cake would muffle the blast such that tens of kg's of TNT would be required to fail a dome. To estimate the amount of reacting material to cause a 10 psi overpressure from a relatively slow deflagration, not resulting in a shock wave, compare the volume increase (280 ml/gm) with the gas space ($50,000\ ft^3 = 1.4\times10^6$ liters) above the salt cake stored in a million-gallon tank.

Ignoring the influences of temperature, the addition of 10^6 liters of gas with little or no gas escaping would result in an overpressure of 10 psi. This requires the reaction of a minimum of 3570 kg of material. Since stoichiometric mixtures are about 12 percent organic, this requires a minimum of 428 kg of organic to fail a tank dome. Even though the reaction is assumed to be slow, it would have to be rapid enough to prevent venting. Any quantity of organic less than 428 kg which reacted would be vented to the atmosphere, causing its own special problem but no blast damage.

In summary, any reactive mixture less than one kg is essentially harmless, even if it can detonate. Reactive mixtures in amounts between one kg and 3500 kg are hazardous only if they can detonate, or deflagrate in such a manner so as to produce shock waves (confinement is required). Any reactive mixture greater than 3500 kg is potentially capable of failing a tank.

EFFECTS OF RADIATION ON SALT CAKE STABILITY

This section will very briefly discuss the role that radiation could play in increasing the chemical instability of salt cake with organic additions. Unlike the prior sections which generally argue against any formation of explosive material, the following two subsections assume that such explosives do exist and search for means to trigger an explosive reaction. In the last two subsections the possibilities for radiolytic transformation of nonexplosive material to explosive material are discussed.

Effects of Radiation on Explosives

Deflagrations can be initiated by very small localized "hot spots" with characteristic dimensions of 10^{-5} - 10^{-3} cm.[17] When fission products and alpha particles are absorbed in a material they create hot spots whose size depends upon their total energy and on the physics of the energy dissipation. Therefore, many observers have sought to initiate explosions with radiation. The motivation behind such research has been military concern for performance of rocket propellents and conventional explosives when passing through an intense radiation field caused by a nuclear blast. The high radiation fields present in the high-level waste tanks prompt consideration of the effects of radiation on explosives.

A rather extensive bibliography of recent work on the effects of radiation on explosives shows no prior studies on black-powder-type explosives.[18]

Nitrogen iodide, lead azide, and cadmium azide, all extremely unstable explosives, have been subjected to fission product irradiation.[19] The explosives were held at both room temperature and 390°C while subjected to 10^5 to 10^8 fissions per cm^3 per hour. Only nitrogen iodide exploded. The explosion of nitrogen iodide was traced, however, to the removal of ammonia from the surface of the crystal by the fission product bombardment, at which time the nitrogen iodide exploded. The initiation of explosion was not directly caused by the interaction of the fission products with the nitrogen iodide.

Irradiation by 7.4 x 10^6 R of 0.41 MEV ^{198}Au γ-rays (10^5 R/hr) of a wide variety of high explosives, principally nitrated organics, resulted in no explosions and only marginal changes.[20] The principal effect was radiolytic decomposition. Between 0.001 and 0.1 percent of the explosives were transformed to gaseous products--nitroglycerine being the most reactive. Other effects included marginal increase in impact sensitivity with accompanying decrease in detonation strength for lead azide, decrease in impact sensitivity and simultaneous decrease in detonation strength for mercury fulminate and diazodinitrophenol. No significant changes in explosive behavior were observed in TNT, tetryl, lead styphnate, PETN, and nitroglycerine.

The high explosives RDX, HMX, PETN, and nitroglycerine neither detonated nor showed changes in subsequent alpha-bombardment ignition tests (^{252}Cf, 7.36 MEV).[21] Exposures were 200-2000 fission fragments.

These tests rather adequately demonstrate that radiation cannot initiate a chemical explosion.

Heat Generation

The most direct effect of radiation in high-level salt cake is to increase the temperature. Guidelines have been established to limit the maximum amount of heat generating capacity such that the concrete tank walls never exceed 300°F (166°C). With a maximum wall temperature of 300°F at the midpoint of the tank bottom (the hottest point on the tank liner in a uniformly mixed tank), the maximum temperature within the salt cake can be only 10-20°F higher.[22] Thus the maximum design temperature is less than 175°C. These temperatures are all well below the ignition temperature of black powder (325-350°C).

Nevertheless, it will be the abnormal situation and not the "designed-for' condition which will, if ever, lead to trouble. The most plausible mechanism to spontaneously trigger any exothermic reaction in a salt cake will be thermal heat generation from a sludge layer abnormally high in ^{90}Sr. Should such a sludge layer become detached from the main salt cake by a "cracking-upon-drying" mechanism it could conceivably, because of loss of heat conductivity, increase its temperature greatly above the design maximum. Because this is the most probable high heat source, any future sampling program to determine the presence of organcs should place particular emphasis on the sludge layer - salt cake interfaces.

Radiolytic Generation of Hydrogen

The single greatest effect of radiation on the chemical stability of the waste tank components is the radiolytic decomposition of water and consequent generation of hydrogen. This particular problem has been recognized since the earliest days of high-level waste storage. As a result the tanks were ventilated to prevent the accummulation of hydrogen. Fortunately, hydrogen is light and physically difficult to accummulate. The waste has been through the high heat stage, during which hydrogen generation is greatest, with no known explosions and as such is intuitively if not absolutely safe.

When radiation is absorbed in a media which can form stable gaseous compounds, gas will be produced at a rate given by:

$$N_i = G_i \, D/N$$

where N_i is the number of moles of the ith species of radiolytically generated gas, and G_i is an empirical constant equal to the number of molecules of gas i produced per 100 eV of absorbed dose. D is the absorbed dose in 100eV and N is Avogadro's number.

Values for G_{H_2} for salt cake range from 0.1 to 0.8 as H_2O content varies from about 5-90 percent. For the range of H_2O content of interest (10-30 percent by volume), $G_{H_2} = 0.2$ is adequate. Because radiolytic decomposition of $NaNO_3$ (to $NaO_2 + 1/2\ O_2$) is possible, G_{O_2} is almost always higher than G_{H_2} and is approximately equal to 0.5. Therefore, there will always be excess oxygen to support combustion if enough H_2 is present.

Because of the high specific energy of hydrogen-oxygen combustion, (maximum of 3210 cal/gm) any combustible mixture is explosive and any mixture between 4 and 75 vol % H_2 is combustible. Table VIII presents the expected flame temperature, specific energy, TNT equivalency and resulting pressure of several $H_2 + O_2 + N_2$ mixtures. Note that even a deflagration of the 4 percent H_2 mixture in a closed volume results in an overpressure of 20 psi, twice that required to fail a tank dome.

TABLE VIII

TANK PRESSURIZATION RESULTING FROM H_2 EXPLOSION*

Hydrogen Volume Percent	Temperature	Specific Energy (cal/gm)	TNT Equivalency	Final Pressure at Constant Volume (Atm)
4	740	85	0.078	2.4
10	1350	226	0.205	4.3
16	1800	382	0.347	5.5
30	3140	834	0.757	8.9
66	9000	3210	2.913	20

*Based upon a million-gallon tank filled with 800,000 gallons of salt cake.

A calculation was made for the maximum H_2 buildup in a one-million-gallon tank filled (75 percent of capacity) with salt cake following successful evaporation-crystallization, assuming about 10 percent moisture content and that the tank was sealed so that no H_2 could escape. The maximum H_2 content would never exceed 2 vol %. A more pessimistic computation, which assumes 30 percent water and a radionuclide content of about one Ci/gal (0.26 Ci/ℓ) predicts a hydrogen evolution rate of 171 ℓ/day (in a one-million-gallon tank 75 percent full), a rate which would allow the 4 percent explosion mixture to be reached in 328 days. However, since all tanks are vented, the natural atmospheric pressure changes cause the tanks to breath. This breathing provides a continual exchange of air between the tank dead space and the atmosphere, limiting the maximum H_2 accumulation. Under these conditions, an equilibrium concentration of approximately 0.9 percent would be reached in about 300 days.

We therefore conclude that no explosion hazard exists in stored salt cake for moisture content below about 20 percent and radionuclide concentration below 1.8×10^{-3} watt/ℓ (∿ one Ci/gal). At the upper limit of these values, some limited ventilation (natural convection is sufficient) is necessary to prevent explosive accumulation of hydrogen.

Degradation of Organics

There is no reason to expect that explosive combinations, especially nitrated organics, have been added to the waste tanks. However, a variety of organic material has been added. Is it possible to radiolytically transform nonexplosive organic material, things such as plastic bags, tygon tubing, teflon, rubber gloves, into an explosive mixture?

The effects of radiation on organic polymers are widely dependent upon the type of material, environment during irradiation, and radiation dosage.[23,24,25] However, guideline dosages are rather clear cut. Under 10^5 Rads, no macroscopic effects are observed. Macroscopic effects begin at 10^6 Rads; this is the level at which some polymers are cured (cross linked) in commercial processes. Degradation of polymers begins at 10^8 Rads. Severe degradation, to the point of transforming resilient plastics into crumbly, powdery depolymerized substances, occurs above 10^{10} Rads; at these dosages plastics are dehydrogenated and their susceptibility to oxidation is greatly increased. One would therefore expect the combustion hazard of stable plastics to be increased after exposures above 10^{10} Rads.

On the other hand, the total expected cumulative dose during waste tank storage is between 10^7 and 10^8 Rads. The dose any organic material experienced prior to having been added to the tank was probably less the 10^6 Rads (incipient failure); therefore, the total dose including pre-storage exposure cannot be expected to greatly exceed 10^8 Rads. Expected results are a very slow dehydrogenation oxidation process affecting at most 1.0 percent of the organic material. Whatever organic has found its way into the tanks will therefore be essentially unaffected by radiation.

Radiolytic Decomposition of Sodium Nitrate

Sodium nitrate has approximately the same resistance to radiolytic decomposition as organic materials. Exposure to 1.4×10^8 Rads (electron beam) results in the decomposition of approximately 0.6 percent of a $NaNO_3$ sample.[26]

CONCLUSIONS

PRESENT SAFETY STATUS

There is no evidence of an explosive exothermic reaction in any of the salt-cake storage tanks. Hypothetical worst-case mixtures subjected to detonation tests have shown no tendency to detonate or even enhance the explosive blast of the initiating charge.

Existing salt cake has a moisture content of 30-50 percent. With this moisture content, a uniform mixture of even the most explosive material conceivable would be impossible. Even a stoichiometric $NaNO_3$ and charcoal mix will not react with a moisture content greater than 20 percent. Therefore, the existing salt cake is stable to exothermic reactions under all conceivable circumstances. However, the present objective is to dry the salt cake to perhaps a 5 percent moisture level, the minimum believed possible. When such levels of dryness are reached, safety can only be assured on the basis of proof that no concentration of organic exists.

REACTIONS WITH METAL POWDERS

Exothermic reactions between salt cake ($NaNO_3$) and reduced metals have been consciously deleted. These reactions, however, cannot be totally ignored. Sodium nitrate can react rapidly with any one or more of the following powdered metals, reaching temperatures up to several thousand degrees centigrade: Al, Si, Mg, Ca, Mn, Mo, Cr, Va, W, Ti, Zr, and Fe on any of the ferroalloys with these metals.[27] Simulated salt cake has been reacted with powdered FeSi and sand to produce a sodium ferrosilicate (or with powered SiAl to produce a sodium aluminosilicate) in mixtures as dilute as 35 percent simulated salt cake, 50 percent sand, and 15 percent metal.[28]

Experience provides proof that great caution is required when handling powdered metals and $NaNO_3$. While preparing scrap uranium - aluminum cermet cores for subsequent Purex recovery of ^{235}U, an unexpected violent exothermic reaction melted the cores.[29] The reaction was traced to the presence of $NaNO_3$ on the scrap. The topic of $NaNO_3$ and powdered metals is limited to this brief discussion because of the absence of any powdered metal used in plutonium separation processes, and consequent absence of any in the waste tanks.

INFORMATION GAPS

The assurance of safety against exothermic reactions requires a knowledge of (a) the concentration of organic material and (b) combustion limits. Neither of these two factors are known.

A program has been initiated which, in conjunction with the salt cake characterization program, will analyze samples for total carbon and total organic carbon.

Tests are presently under way to determine combustion limits for mixtures of sodium nitrate, carbon, and water. Although charcoal is being used for the carbon source in most tests, resin and NPH will also be used. Ignition tests will be conducted at room temperature and at elevated temperatures.[30]

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APPENDIX A

COMPOSITION OF SALT CAKE - ORGANIC MIXTURES USED IN DETONATION TESTS

The synthetic salt mixture used in each of the first 5 samples had the following composition (dry wt.%):

$NaNO_3$	31.8
$NaAlO_3$	23.8
NaOH	17.5
$NaNO_2$	13.7
Na_2CO_3	13.2

Sample 1

Salt plus 1/2 wt.% each of:

Latex rubber
Tygon
Buna N rubber
Teflon
Neoprene (charred)
Neoprene (uncharred)
PVC
Aspnaltic resin cement
Gunite Accelerator (Monoset T-1)
Total organic - 4 1/2%

Sample 2

Salt plus 1/2 wt.% each of:

TCP
2-ethylhexyl phosphoric acid
NPH
TBP
DBP
MBP
HEDTA
Hexone
EDTA
NTA
Fe_2O_3
NH_4NO_3
Nickel ferrocyanide
Total organic - 5 1/2 wt.%

Sample 3	Same as 2 except 1/4 wt. % of each compound
Sample 4	Same as 2 except not irradiated after preparation
Sample 5	Anion A580 Resin (Permutit SK)
	Boiled for 8 hours in aqueous synthetic salt solution

Samples 1-3 were irradiated to 1.4 x 10^7 Rad and then boiled for eight hours in aqueous solution. They were then dried in a vacuum oven at 80°C for one week.

Sample 4 was prepared in a similar manner except it was not irradiated. The approximate total carbon content of each sample was:

Sample	Carbon Content (wt%)
1	4
2	4
3	2
4	4
5	75

Samples 6-16 were mixed, boiled for 1 hour, and irradiated. The synthetic salt mixture used in samples 6-16 had the following composition (dry wt.%):

$NaNO_3$	33
$NaAlO_3$	21
NaOH	18
$NaNO_2$	14
Na_2CO_3	14

Sample Number	Resin (wt.%)	Density (g/cm^3)	Initial Temperature (°C)	Resin Designation	Irradiation* Exposure of Resin In HNO_3 (min)	Irradiation* Exposure of Resin In Salt (hours)
6	0.0	1.90	21	----	----	----
7	9.1	1.23	24	Duolite A61-X4	33	0.9
8	9.1	1.34	24	Duolite A61-X4	33	10.0
9	10.0	1.37	24	Duolite A61-X4	33	96.0
10	8.4	1.34	24	Permutit SK	33	0.9
11	9.1	1.35	24	Permutit SK	33	10.0
12	10.0	1.37	24	Permutit SK	33	96.0
13	20.0	1.52	21	Duolite A61-X4	----	----
14	35.0	1.52	27	Duolite A61-X4	----	----
15	50.0	1.46	27	Duolite A61-X4	----	----
16	20.0	1.52	150	Duolite A61-X4	----	----

*Irradiated to 1.4 x 10^7 Rads.

Samples 17-20 were made with pure $NaNO_3$ and were neither boiled nor irradiated.

Sample	Composition Wt% Resin
17	5
18	10
19	15
20	20

APPENDIX B

FLAME TEMPERATURE COMPUTATIONS

The method and assumptions used to compute flame temperatures shown in Figure 3 and 4 are presented in this appendix.

A number of specific mixtures were arbitrarily selected. The chemical reaction equation was written. The reaction products were identified by 1) incorporating all available sodium into Na_2CO_3, 2) assigning available oxygen to form CO, 3) using excess oxygen from Step 2 to form H_2O with all available hydrogen, 4) using remaining oxygen to form CO_2, 5) assigning any remaining oxygen to form nitrogen oxides, 6) forming N_2 (gas) from all nitrogen not bound as nitrogen oxides, 7) treating any water in the reactants as inert, 8) forming H_2 (gas) from all hydrocarbon hydrogen for which there is insufficient oxygen to form H_2O.

The heat of the reaction (ΔE_r) is then computed by using:

$$\Delta E_r = \Sigma\, H_{fi}(\text{products}) - \Sigma\, H_{fj}(\text{reactants})$$

The heats of formation used are shown in Table B-1:

TABLE B-I

HEATS OF FORMATION

Compound	H_f @ 25°C (kcal/mole)
$NaNO_3$	-111.7
Na_2CO_3	-270.3
H_2O (gas)	- 57.8
H_2O (liquid)	- 68.4
CO	- 26.4
CO_2	- 94.0
NO	+ 21.6
NO_2	+ 8.1
$C_{10}H_{22}$	- 59.7

The flame temperature, T_c (°K), is then computed from the equation:

$$T_c = 300 + \frac{\Delta E_r}{\Sigma n_i \; c_p(i)}$$

The values of n_i (number of moles of products and reactants) are fixed by the arbitrarily selected mixture, and the values of specific heats at constant pressure, $c_p(i)$, have been obtained from Tables in "The Science of High Explosives", by Melvin A. Cook, American Chemical Society Monograph Series, Reinhold Publishing Corp., New York (1958), and are shown in Table B-II.

TABLE B-II

AVERAGE IDEAL MOLAL HEAT CAPACITIES (From 300°K to T°K)
(cal/mol/K°)

T°(K)	N_2	CO_2	CO	H_2O	NO	Na_2CO_3*	C	H_2
700	7.0	10.7	7.0	8.2	7.3	27.1	3	6.9
1000	7.3	11.4	7.4	8.7	7.6		4	7.0
1200	7.5	11.8	7.5	9.2	7.7		4.5	7.1
1500	7.7	12.3	7.7	9.6	7.9		4.5	7.2
2000	7.9	12.8	8.0	10.2	8.1		4.5	7.4
2500	8.1	13.3	8.2	10.6	8.3		4.5	7.6

*Data only available for $T < 700$°K

Several additional assumptions were made:

1. Initial temperature of reactants is 25° C.
2. The reaction occurs adiabatically.
3. No $NaNO_3$ or $C_{10}H_{22}$ remains after the reaction.
4. H_2O is driven off at the maximum flame temperature.
5. No molecular dissociation occurs in the products.
6. No ions or radicals are formed.

These assumptions influence the calculated flame temperature to varying amounts, almost always in the direction of making the calculated temperature T_c, higher than the actual flame temperature T_m. Five specific variations are shown below:

1. If the initial temperature is higher than 25°C, T_c will also be higher. However, since specific heats generally increase with temperature, the change in T_m will be less than the change in initial temperature.

2. If combustion is incomplete (as is generally the case) T_m will be lower than T_c.

3. If H_2O is driven off at a lower temperature, T_m could be much higher. However, the effect is not large since most of the energy in H_2O vapor is associated with the latent heat of vaporization.

4. Any decomposition, including formation of radicals and ions, decreases the energy available for temperature increases and severely limits T_m. Also, should actual temperatures approach 2000°C, nitrogen oxides will be formed in greater abundance and further limit peak temperatures.

5. The specific heat used for Na_2CO_3 is lower than actual for all temperatures above 700°K; however, better values were not available. The use of lower values of specific heat has increased T_c.

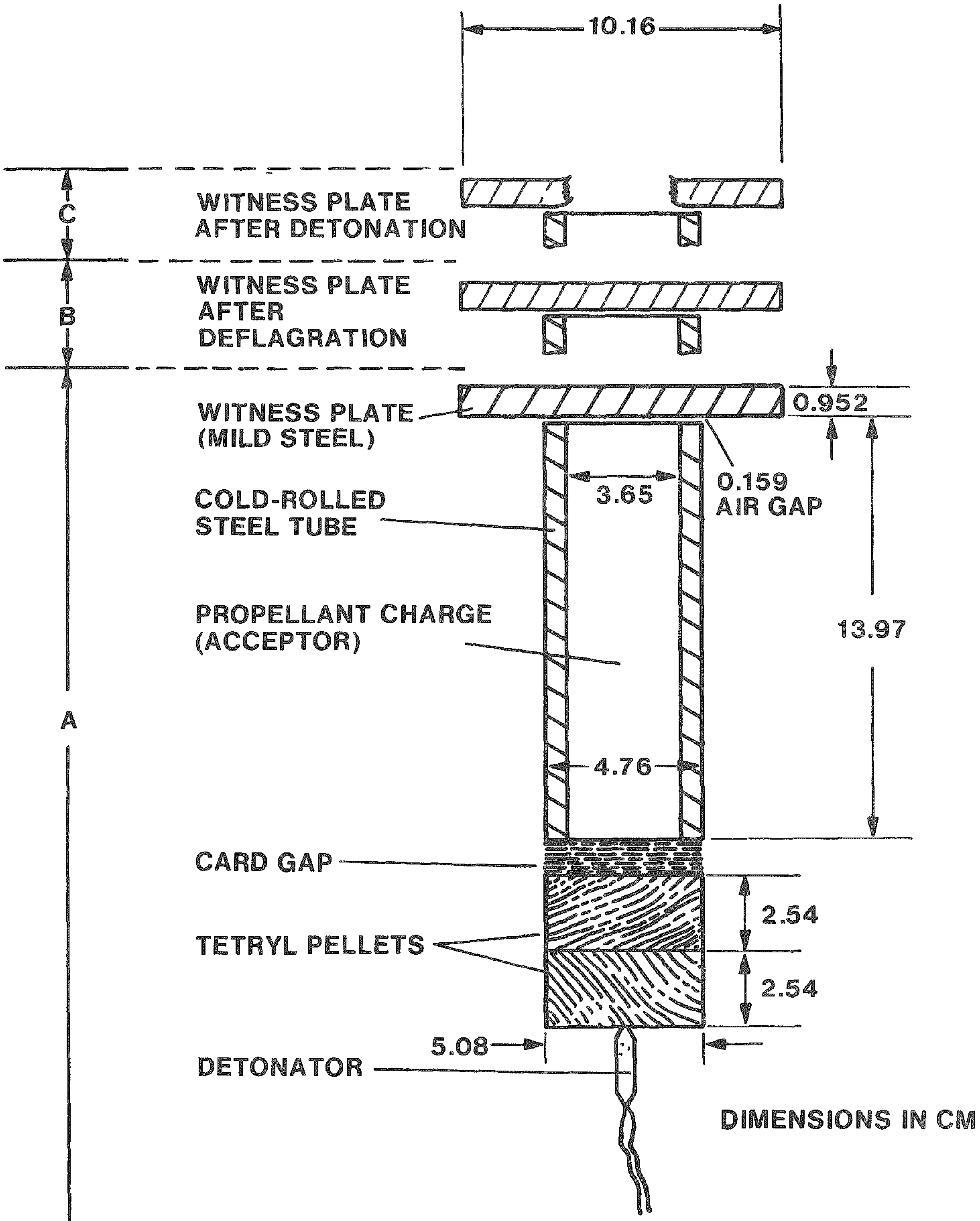

FIGURE 1

STANDARD DETONATION TEST ARRANGEMENT

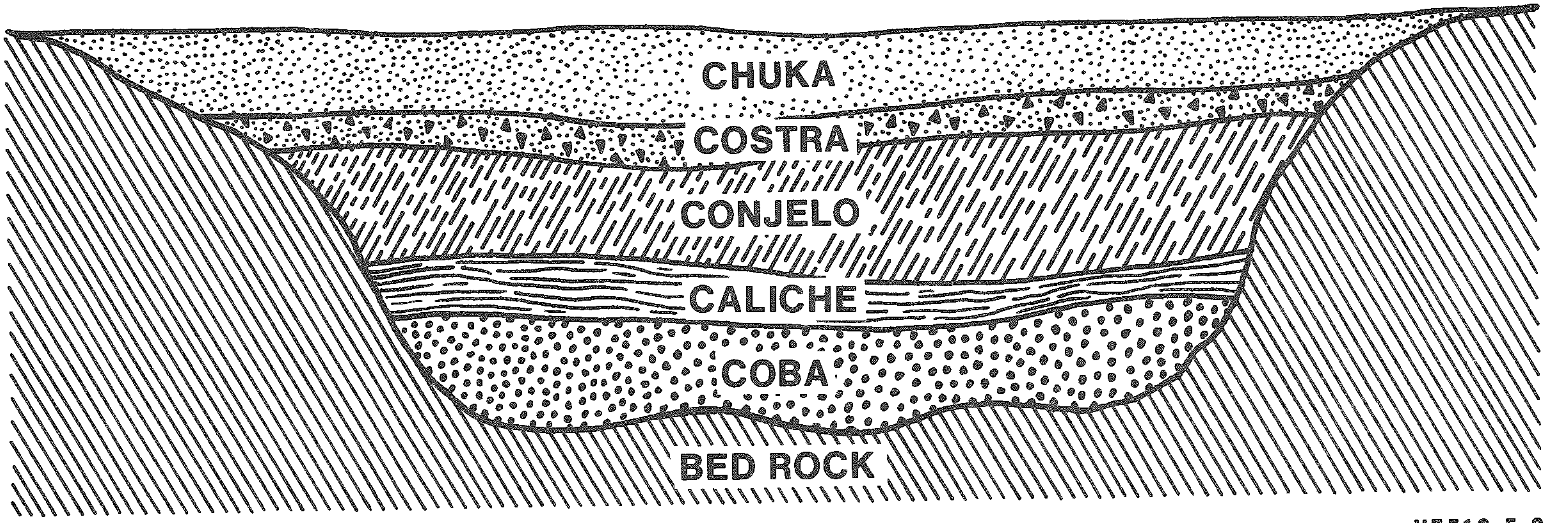

FIGURE 2

CROSS SECTION OF A NITRE BED

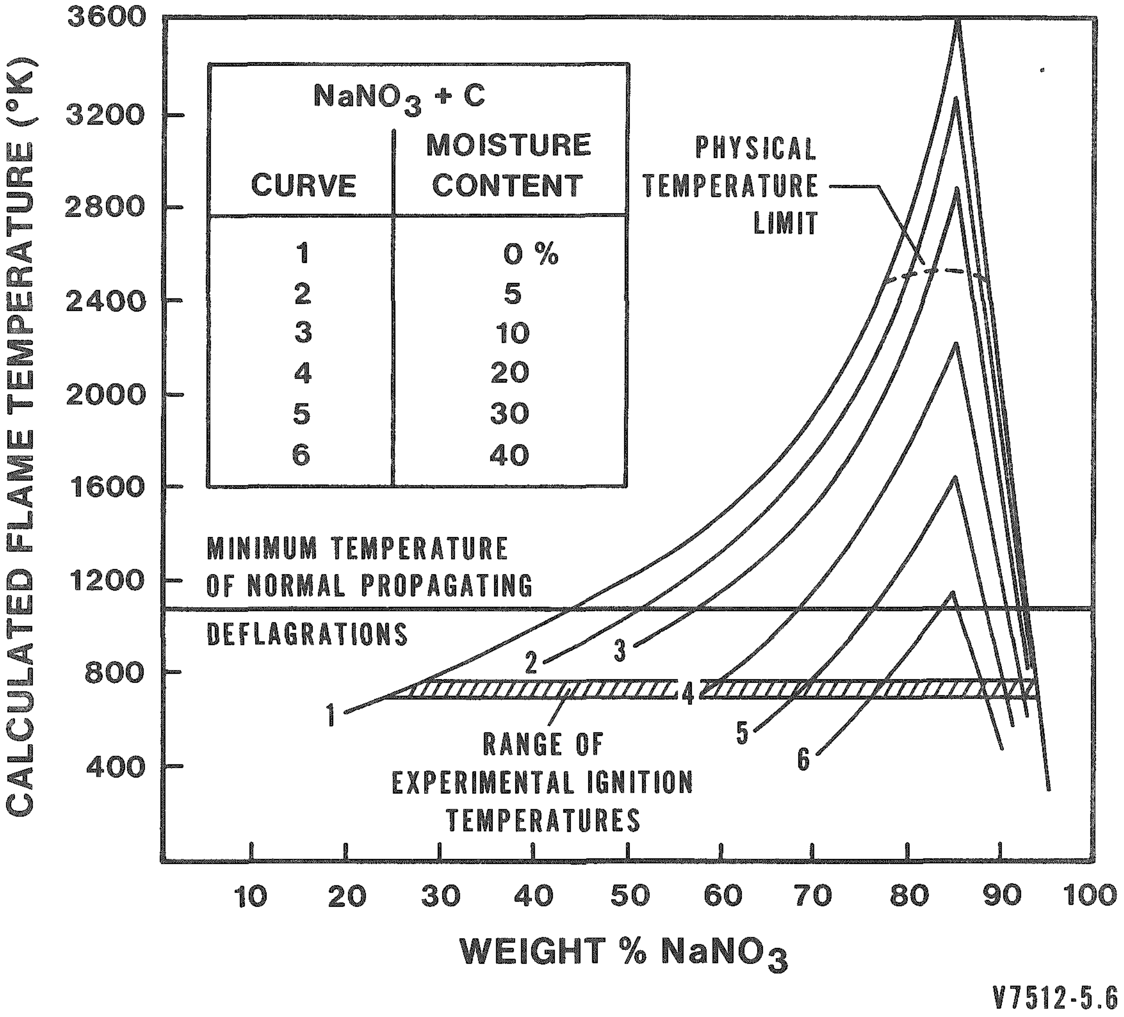

FIGURE 3

UNCONFINED DEFLAGRATION
$NaNO_3 + C$

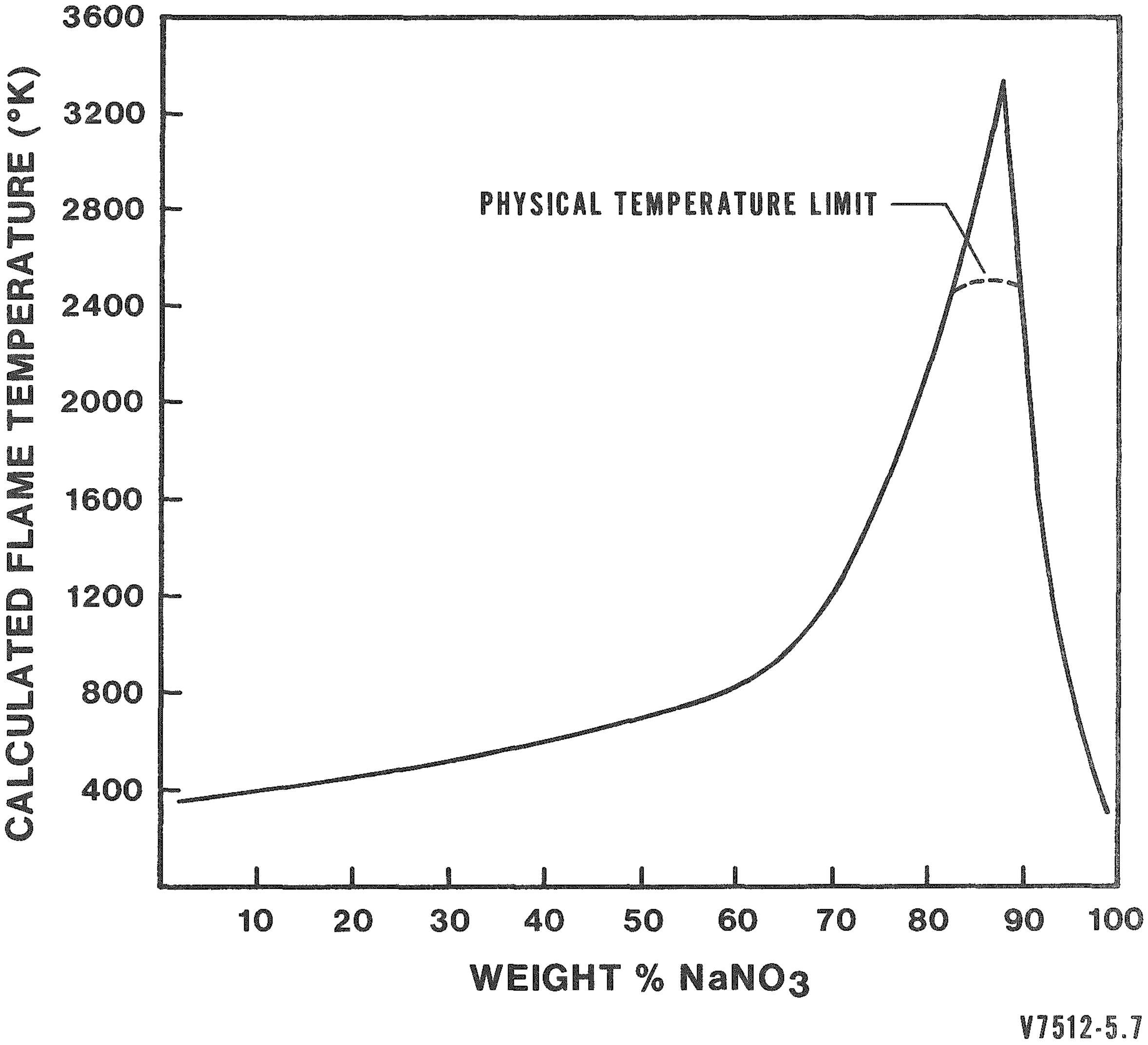

FIGURE 4

UNCONFINED DEFLAGRATION
AT ZERO MOISTURE
$NaNO_3 + C_{10}H_{22}$

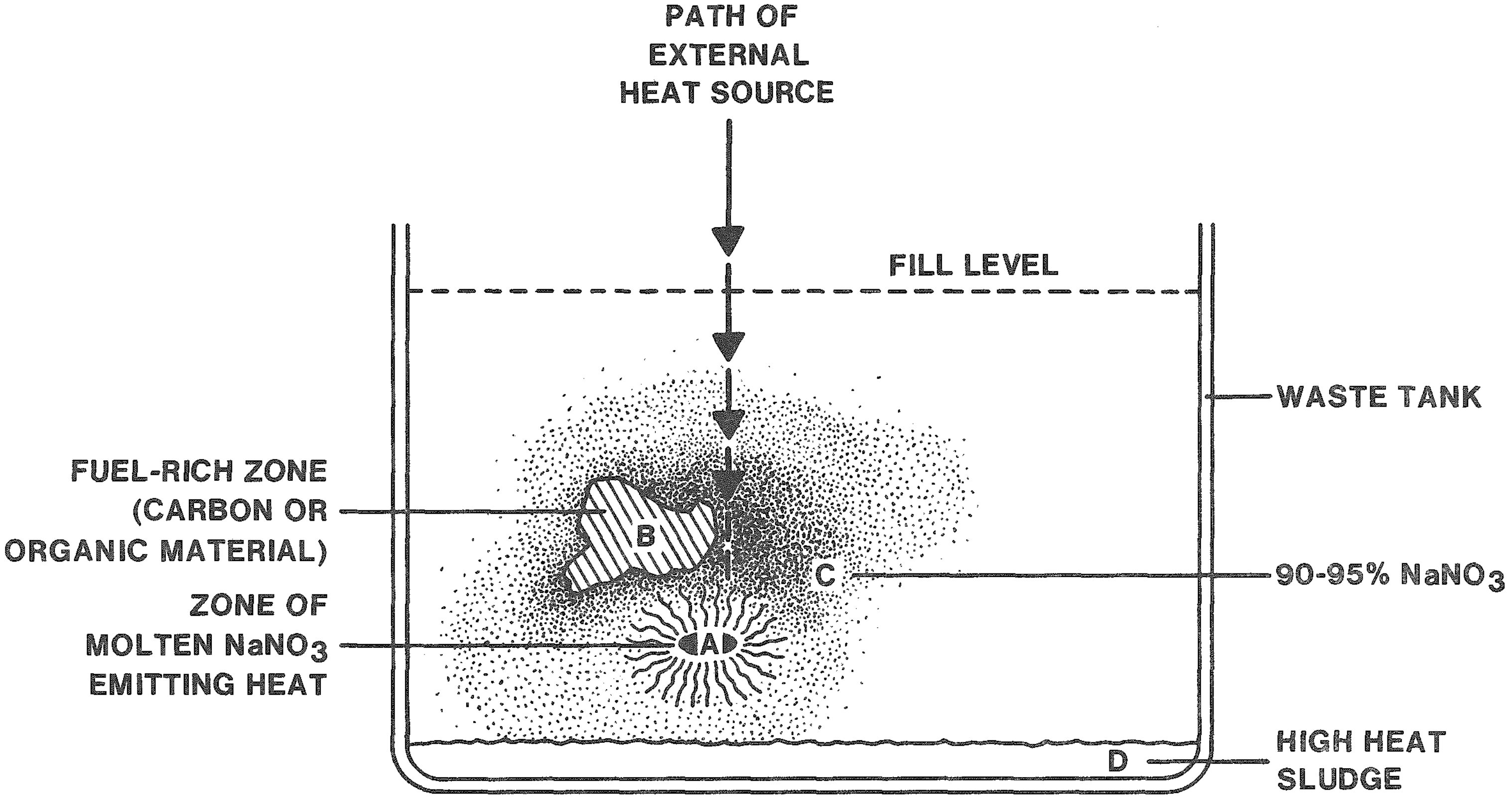

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FIGURE 5

HYPOTHETICAL MECHANISM TO IGNITE A
COMBUSTIBLE REGION WITHIN A DRY SALT CAKE

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