ARH-LD-126
Informal Report

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Approved by A. E. Repp for D. R. Gustavson

FINAL REPORT ON INVESTIGATION OF STABILITY OF ORGANIC MATERIALS IN SALT CAKE

G. A. Beitel

Hanford Waste Engineering Section
Advanced Waste Engineering Department
Research and Engineering Division

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Atlantic Richfield Hanford Company
Richland, Washington 99352

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INTRODUCTION

This document summarizes the activities of the past two years which were directed toward identifying potential hazards arising from the presence of organic materials in stored high-level waste salt cake. A series of detonation tests were carried out by Stanford Research Institute (SRI) in fiscal year 1975.[1] Document ARH-LD-119, "Chemical Stability of Salt Cake in the Presence of Organic Materials," based upon a literature survey and compilation of prior research at Hanford, attempted to predict the potential hazards of storing a nitrate-rich salt cake containing small amounts of organic material.[2] Laboratory tests conducted during the first half of FY 1976 were directed toward establishing combustion limits for organic mixtures with salt cake; the results were published in ARH-LD-123, "Sodium Nitrate Combustion Limit Tests."[3]

DISCUSSION

Stanford Research Institute conducted detonation tests on both simulated salt cake and pure sodium nitrate mixtures with a variety of organic materials in various concentrations. No evidence of detonation was seen in any of the samples, a finding in agreement with the literature which states that black powder (a nitrate plus charcoal type explosive) is shock insensitive (cannot be triggered by a shock wave). Several of the samples consisting of pure sodium nitrate and a nearly stoichiometric amount of organic material showed evidence of exothermic activity, but this was believed to be a driven instead of a self-propagating reaction.

The controlling variables for determining explosive potential are gas generation, energy release, and reaction rates. The reaction of any nearly stoichiometric mixture of sodium nitrate with an organic can generate enough gas and release enough energy to be explosive. Reaction rates are, therefore, the controlling variable. Unfortunately, reaction rates are too difficult to predict to be of any value in predicting safety.

Since one kilogram of detonating material could conceivably cause a waste tank dome to fail, primary attention has been focused on the possible existence of nitrated organics, a class of materials known for their high explosive nature. Detonable nitrated organics are only formed in concentrated nitric acid (7 N or greater). The high-level waste, on the other hand, was neutralized prior to transfer to the tanks. Nitrated organics generated acidentally 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 waste tanks. Furthermore, there is no basis to expect nonexplosive organic material, such as was added to the waste tanks, to be or have been transformed to an explosive under the stimulus of radiation.

The effects of radiation on organic polymers are widely dependent upon the type of material, environment during irradiation, and radiation dosage. However, 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 on the type of material in question become noticeable only above 10^8 Rads (affecting only one or two percent of the bulk of the material at doses above 10^8 Rads). The dose any organic material experienced prior to having been added to the tank was probably less than 10^8 Rads (incipient failure); and since cumulative doses during waste tank storage are between 10^7 and 10^8 Rads, the total dose should never greatly exceed 10^8 Rads.

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

The amount of organic material that could have been added to the waste tanks is estimated to be 0.3 to 0.9 weight percent of the total waste. This estimate is based upon the chemical process procedures used in the separations operations that initially generated the high-level liquid waste. The figures are supported by published analyses of "typical" salt cake.[4] Much of this organic material consisted of volatile solvents, hexone, normal paraffin hydrocarbon, etc., which can be expected to have been volatilized and removed during either the boiling period or the subsequent evaporator-crystallizer stage. The maximum expected, 0.9 percent, is far less than the minimum 5 percent required to support combustion and even further from any expected explosive composition, 12 to 20 weight percent.

The experimental combustion tests used sodium nitrate and simulated salt cake mixtures with ion exchange resin, charcoal, paraffin, and sugar in one-gram unconfined samples.[3] Nominally dry (∿3 weight percent moisture) mixtures of charcoal and sodium nitrate supported combustion with fractional charcoal concentrations from 6 to 66 percent. Stoichiometric (charcoal) mixtures with up to 22 weight percent moisture supported combustion.

When combustion was attempted with paraffin or as-received resin, the paraffin and a significant fraction of the resin volatilized at temperatures well below 400° C. This evaporation rapidly cooled the test capsule. The resulting vapors could not support combustion because the sodium nitrate was left behind, still a stable solid. Only when the resin was preheated to drive off most of the volatiles could a sodium nitrate combustion process be supported. Sugar, on the other hand, is much less volatile than resin and leaves a large fraction of the original quantity as a solid carbonaceous residue when it decomposes. It reacted quite violently with the sodium nitrate. Sugar has a lower reducing power, gram for gram, than carbon and therefore cannot support combustion at as lean a mixture; hence, sugar mixtures with less than 10 percent sugar would not burn.

All these tests were conducted at atmospheric pressure. The reason that low-temperature volatilization of the fuel prevents combustion is that volatilization removes the fuel from the sphere of influence of the sodium nitrate. If these volatile fractions could be held by means of increased pressure, sodium nitrate could react explosively with paraffin oil (or any other organic). Such a pressure may or may not be attainable within the physical realities of salt cake management.

CONCLUSIONS

On the basis of this work we arrive at the following conclusions, which all contribute to confidence that salt cake is stable against exothermic reactions:

1. Organics added to the waste tanks were not nitrated at the time of addition and cannot have been subsequently transformed to detonatable nitrated organics.
2. Whatever organic has found its way into the tanks has been and will be essentially unaffected by radiation.
3. Mixtures of the types of organics which could have been added to the waste tanks with either simulated salt cake or pure sodium nitrate are not detonable.
4. The maximum amount of organic which could have been added to the waste tanks is less than 0.9 weight percent of the salt cake, a concentration far below the concentration required to support combustion.
5. The many years during which the liquid high-level waste was boiling, and the subsequent evaporation-crystallization processing, have allowed many of the more volatile organics to be distilled off, further reducing the maximum expected concentration of organics.
6. The occurrence of an explosive exothermic reaction of an organic in the waste tanks would require concentration and mixing by an unknown and uncontrolled means. The mixture would then have to remain in its concentrated state long enough to be triggered by an explosion, a totally unreasonable hypothesis.

7. Even if a combustible concentration existed, temperatures generated by radionuclide decay in the salt cake are by design below 175° C and therefore would be incapable of igniting any of these mixtures.

8. Furthermore, even if any of the major organic solvents were present in concentrations theoretically adequate to support combustion, they probably would not burn. Because of their volatility, they are more difficult to react than charcoal, the normal fuel in sodium-nitrate-base explosives, and may be impossible to ignite.

RECOMMENDATIONS

A key factor yet to be established is the concentration of organic material within the salt cake. Special efforts are being made to incorporate total organic carbon determinations into the salt cake characterization program.

Additional tests with 5 to 10 percent resin (as received), charcoal, or paraffin mixed with sodium nitrate in 50 to 100 kg lots should be conducted to determine size effects. Because of the size and potential explosive nature of these tests, they would have to be conducted using all the precautions of high explosives testing.

Additional information should be obtained on the pressure dependence of paraffin or resin combustion with sodium nitrate. One-kilogram samples in sealed, pressure-limited containers should be tested with a variety of compositions at pressures of one to 10 atmospheres. Such tests have the potential of being destructively explosive and would require the respect accorded to similar quantities of TNT.

REFERENCES

1. Purchase Order #WRN-666-93399 under Atomic Energy Commission Contract AT(45-1)-2130, 1975, T. C. Goodale, "Test Summary; the Sensitivity of Nuclear Waste to Detonation." (The methods, results, and conclusions described in this report may also be found in reference 2 below.)

2. ARH-LD-119 (unclassified), April 1976, G. A. Beitel, "Chemical Stability of Salt Cake in the Presence of Organic Materials."

3. ARH-LD-123 (unclassified), April 1976, G. A. Beitel, "Sodium Nitrate Combustion Limit Tests."

4. ARH-ST-110 C (unclassified), May 1975, M. J. Kupfer and W. J. Van Slyke, eds., "Atlantic Richfield Hanford Company Quarterly Report, Waste Management and Transportation Technology Development, January 1975 through March 1975."

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