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POTENTIAL FOR EXOTHERMIC CHEMICAL REACTIONS IN WASTE TANKS

PNL--7526

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DE91 001296

February 3, 1983

Received by OSTI

APR 25 1990

Background

Organic chemicals have been added to Hanford waste tanks, particularly as ferrocyanides and when processing sludges at B Plant. Recent planned or ongoing activities involving stored wastes have possibly increased the potential for reaction of these wastes with nitrate salts in the waste tanks. Risk evaluations appear to be deficient in assessing the consequences of a deflagration, and in determining the probability of either a deflagration or detonation. The present question is whether current plans and recent safety-related documentation have given proper consideration to the available information about organic compounds in waste tanks.

The principal organic additions to Hanford waste tanks¹ are 1200 tonnes of "organic carbon" and 500 tonnes of $\text{Ni}_2\text{Fe}(\text{CN})_6$. Analyses² of total organic carbon in certain waste tanks have shown up to 11 M total organic carbon (p. 50) in solution, and Tank 104-T is reported to contain 10.2 weight percent total organic carbon in "water insoluble" material (p. 51). These numbers are the maximum values for carbon concentration of which I am aware.

An early hazards evaluation³ called attention to the cyanide problem (pages 7, 12, 17-19). It stated on p. 18, "A tank sampling program could be used to determine the presence or absence of cyanide. If it were found to be present, an experimental laboratory program aimed at determining the specific chemistry of the hazard would be justified. As the first step in evaluating this possible problem, it is recommended that a sampling and analytical program be commenced to determine the presence or absence of cyanide in TK-241-BYR-101. In addition, potential input wastes to the 101 Tank should be sampled and analyzed for cyanide." I am not aware of the existence, nature, or results of such a program.

A later preliminary safety analysis⁴ noted on p. 14 a maximum permissible salt cake temperature of 250°C, and stated, "Prior to evaporation, a representative sample of the contents from each tank will be collected, dried,

and heated to temperatures of 260°C to assure that no significant exothermal reactions occur." The exothermic reaction of principal concern in this study was decomposition of ammonium nitrate. The means of assuring a "representative" sample were not discussed.

A 1980 assessment of risks⁵ states on p. 42, "Self-Explosion (Chemical)". This event represents an explosion of the mixture in the tank. The basic constituent is sodium nitrate, and there is a very small admixture of organic material. Powerful explosives can be made by mixing proper proportions of organics and sodium nitrate, but this is not possible here because there is too little organic material with respect to the sodium nitrate. There is also no way to reach the detonation temperature of 400°C (Beitel, 1977). The release estimate is that <1% of the tank contents would be expelled to air in the form of respirable particles." It also addressed (p.31) a thermal excursion without identifying the source or rate of temperature rise. The thermal excursion is identified (p. 99) as the initiating event with highest product of frequency and consequence.

Another 1980 report on technical status of environmental aspects of waste management⁶ did not refer to organics at all based on my rapid examination of a microfiche copy in the library.

Another 1980 report⁷ described a reaction observed in Tank 241-SY-101 between dissolved oxidants and organic material, reported to have occurred in April 1977.

Explosion Studies

Kenneth A. Gasper of Rockwell Hanford Operations was recently requested to supply copies of reports about organic constituents in tanks and reactions that occur when they dry. He supplied the following:

T.C. Goodale, "Test Summary, The Sensitivity of Nuclear Waste to Detonation," Stanford Research Institute, PYD 3339, August 13, 1975.

Latter, December 15, 1975, L. E. Bruns to G. L. Hanson, "Explosion and Fire Hazards Associated with Z-9 Top Sediments Removal".

G. A. Beitel, "Sodium Nitrate Combustion Limit Tests," Atlantic Richfield Hanford Company, ARH-LD-123, April 1976.

G. A. Beitel, "Final Report on Investigation of Stability of Organic Material in Salt Cake," Atlantic Richfield Hanford Company, ARH-LD-126, April 1976.

The first item⁸ describes two series of tests with sodium nitrate or simulated salt cake and various organic materials. The first series (2" dia. x 5" long) showed no detonation. The second series (6" dia. x 15" long) led the author to state, "We concluded that the ionized waves observed in the second series of tests could have been detonation waves, their low velocities being accounted for by the low energy of the detonation reaction per gram of sample."

The second item refers to the top Z-9 crib sediments, and is only of peripheral interest to waste tank concerns.

The third item by G. A. Beitel⁹ includes useful background (pages 2-4) on combustion, deflagration, and detonation. Beitel states on p. 4, "the fact that a small quantity will not support combustion does not prove that the large mass will not support combustion." Related to some experiments with simulated salt cake rather than pure NaNO_3 , he observes on p. 13, "These effects were most likely due to the presence of NaNO_2 , which is more unstable (reactive) than NaNO_3 even though it has a lower oxidizing power." One of the recommendations he makes (p. 22) is, "Additional information should be obtained on the pressure dependence of paraffin or resin combustion with NaNO_3 . One-kg samples in sealed, pressure-limited containers should be tested with a variety of compositions at pressures of one to 100 atmospheres. Again, such tests have the potential of being destructively explosive and would require the respect accorded to similar quantities of TNT."

The fourth item, also by Beitel¹⁰, refers on p. 1 to the SRI tests (item 1 above) and states, "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)." This statement seems to be at variance with the statement quoted above from the SRI report.

A detonation is an unlikely but severe event. The studies discussed above leave uncertainties about the effects with cyanides, effects of scale, and possible role of sodium nitrite. Cyanides were not a part of the study. Scale-up from 2" dia. to 6" dia. changed from no observed effect to a possible low order detonation, but no extrapolation is made to the actual size of waste tanks. Sodium nitrite is observed to be more unstable than sodium nitrate, but the potential effects are not fully analyzed.

Although there are still some uncertainties about detonation, the studies do serve to answer the concerns about salt cake containing homogeneously distributed organics at less than one weight percent. They do not answer questions at higher organic contents, such as sludges (e.g. ferrocyanide precipitates) or the concentrated organic materials which may deposit from solutions.

Exothermic Reactions

A recent article by David W. Smith¹¹ describes runaway reactions and thermal explosions, based on thermodynamic data, kinetic parameters, and physical properties. Two observations are especially pertinent: (1) "Typically for a runaway situation (e.g., a polymerization), there is an induction period with slow 'slipping away' of temperature control; then after reaching a certain temperature, the reaction apparently takes off." and (2) "a critical volume (or critical radius) exists for the product or reaction mixture for each temperature above which a thermal runaway reaction or decomposition must occur."

My concerns are that a slow, apparently controlled temperature increase may become a runaway reaction, and that the large system size (a million gallon test tube) may cause the reaction to occur at a lower temperature than would be predicted based solely on observations in much smaller systems.

The observed reaction⁷ in Tank 241-SY-101 apparently occurred when one component of the organic material (HEDTA or hydroxyethyl ethylenediamine triacetic acid sodium salt) was partially oxidized, involving only two of the ten carbon atoms. Other organic components and the balance of the HEDTA were apparently not affected. No problems resulted from this reaction of organic matter with oxidants, but the reaction is expected to be exothermic and accelerating with increasing temperature. If the rate of the reaction had

been greater by either having a shorter half time or by involving a greater fraction of the total organic carbon, then the tank temperature could have increased appreciably. The important points are that a reaction of organic complexant with oxidizing salts has been observed, that the reaction was unexpected, and that the rate or extent of reaction was not known beforehand. If corrective action (such as dilution) were necessary to control the reaction rate, it is doubtful that adequate information is available to the tank farm operators to assure prompt and correct remedial action.

Winters² identifies organic complexants actually added to wastes amounting to 2.2 kilotons of organic, and states, "These complexants represent only about 1% of the total weight of the waste inventory but may be as high as 24% of the B Plant and Purex waste." Actual measurements of total organic carbon in waste tanks are quoted by Winters as up to 11M total organic carbon in solution, and up to 10.2% by weight as insolubles. At 11M carbon, a solution would contain 500 g of carbon per gallon. The salts in the solution are largely nitrates or nitrites, which provide the oxidizing power for causing the organic carbon to explode.

Beitel⁹ studied propagation of combustion through various mixtures of sodium nitrate or salt cake with charcoal, paraffin, resin and sugar. The most reactive materials were sugar and charcoal. When sugar was mixed with salt cake, it gave "violent combustion" with 25 wt% sugar, "very slow" reaction with 15 wt% sugar, and no combustion with 10 wt% sugar. Beitel's tests with sugar were apparently limited to an 8 mm dia. tube. He reports comparative tests for other materials in 8 mm and 16 mm dia. tubes, with consistently more vigorous combustion in the larger sized tubes. The minimum weight fraction of sugar required to sustain combustion in a large vessel cannot be estimated from his data. He did not study any of the complexants listed in Winters² as having been added to waste tanks.

Citric and tartaric acids are chemically similar to sugar, and might be expected to behave similarly in reactions with sodium nitrate. Winters² states that 3.3×10^6 moles (about 634 tons) of citric acid have been added to the waste, and he uses tartaric acid as a component of his synthetic feed. Thus, appreciable amounts of easily oxidized organics are likely to be present in waste tanks, along with much larger amounts of organics which are more difficult to ignite but which burn with a greater energy per gram of fuel.

Potential Consequences

Beitel¹⁰ states, "...one kilogram of detonating material could conceivably cause a waste tank dome to fail...". Thus, even one gallon of solution with 11M total organic carbon poses a potential threat to the integrity of a waste tank. Of course, a "trigger" must be available to release this energy by detonation in order for this small amount to cause a significant effect.

The quantity of organic material added per day while processing sludges at B Plant¹² is stated as 3.87 tons, based on 4,000 gallons of feed per day. If the waste were concentrated to a volume equal to the feed volume, a million gallon waste tank would correspond to 968 tons of organic material used in B Plant.

The existence of gross amounts of both organics and nitrates in waste tanks has been confirmed by analyses. Detailed studies have not been found which address the potential for releasing this energy at an undesirable rate, using either the major or the most unstable organics which are indicated to be present in the tanks. The actual composition of the organic in the waste tank is unknown; in fact, Winters² cites chemical analyses to account for only 2.2M carbon of the 7.4M which was observed in a particular tank, with the remainder being uncharacterized.

A 1964 hazards evaluation⁵ states, "More than 100 tons of cyanide (calculated as cyanide ion) were added during the waste scavenging program and distributed among various tanks." It also adds, "Mixtures of solid salts at nitrate-to- $\text{Cs}_2\text{ZnFe}(\text{CN})_6$ mole ratios in the range of about 0.4 to 0.6, exploded when heated to approximately 350° C (660° F)." It is not stated whether this is the minimum ignition temperature under credible conditions.

One intriguing data point presented by Winters² is the 10.2 wt% water insoluble total organic carbon in Tank 104-T which is stated to contain "1st Cycle Bismuth Phosphnate Sludge." This could represent ferro- and ferricyanide precipitates used for cesium removal. If so, there is a potential for a severe explosion in this tank if a suitable initiation source is ever present.

According to a recent study⁵ (as stated on pp. 82-83) the consequence of structural failure of a tank is 0.0014 potential latent fatal cancers (PLFC) and the consequence of a chemical explosion throughout a tank is 43 PLFC.

This might help to place the physical consequences in perspective. However, the consequences with regard to future funding or to public perception are not quantified.

Reaction Probabilities

Initiation of a combustion reaction requires a significant source of heat. This may be supplied conventionally or by a detonation wave. A detonation wave could be provided by an explosive compound such as nitrated organics or heavy metal azides (possible decomposition products of hydrazine). The more likely initiating event would be thermal initiation of a reaction of an easily oxidized organic (e.g., citrates or tartrates), which would provide enough heat to initiate reaction of more stable organics. The latter materials would react throughout the tank as either a deflagration or detonation depending on conditions.

A side observation is that the existence of significant quantities of organic materials in waste tanks does not provide data on the probability of exothermic reactions. It does provide data on the maximum consequences of exothermic reactions. Probability is dependent on presence of an initiating event, and changes in any parameter may alter this probability. For example, changes in moisture content may be extremely important. It would be much easier to estimate the probability of an initiating event if it were known what conditions were required for the initiating event.

The most recent report by Beitel that I have found¹³ says on page 8, "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." While this is true, the presence of sodium nitrite may be expected to increase the probability of an initiating event.

One data point exists. An unexpected exothermic reaction between organics and waste did occur, even though it had no significant impact. The next unexpected event may not be so benign. Statistics do not permit estimation of the time to next failure or the magnitude of the next failure. Is it prudent to assume this risk without further studies?

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