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Hanford Tank Safety Project

Minutes of the Tank Waste Science Panel Meeting January 12-13, 1993

October 1993

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**Pacific Northwest Laboratory
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**Minutes of the Tank Waste
Science Panel Meeting
January 12-13, 1993**

Compiled by
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October 1993

Prepared for
the U.S. Department of Energy
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Preface

This document contains the minutes for the January 12-13, 1993, meeting of the Tank Waste Science Panel. The objective of this document is to provide an accurate recapitulation of the proceedings so that the diverse views of the Science Panel members can be documented. The content of this document has been reviewed by each of the Panel members to ensure its accuracy. Editorial comments are clearly marked in the text and are provided only for clarification. Because of this philosophy, this document may contain provocative statements, opinions which may run counter to facts, facts which are presented out of the context of the tank chemistry and physics, and information that may later be shown as incorrect. These meeting minutes, like the previous minutes and those which will follow, are intended to chronicle the Science Panel activities and progress toward understanding the chemical and physical mechanisms that are taking place in the waste tanks at Hanford.

Summary

The Tank Waste Science Panel met January 12-13, 1993, in Richland, Washington, to discuss flammable gas and ferrocyanide safety issues in Hanford waste tanks. The discussion of flammable gas work addressed waste level data, chemistry issues, thermal behavior in Tank 241-SY-101, efforts to model waste behavior and the effects of mixing, work with simulated waste, and results of analytical chemistry studies. The discussion of work on ferrocyanide issues addressed the results of analyses of core samples from Tank 241-C-112, a safety assessment by a subcontractor, waste aging, and analytical methods development.

The following important observations and recommendations were made by the Science Panel:

- The waste in Tank 241-SY-101 is apparently cooling more rapidly since December 1991 than previously noted. Calculations indicate that there may be about a 0.6-m-thick solid salt layer on the walls of the tank, and, if real, a change in the rate of heat loss, rather than a change in chemical heat generation, is probably responsible for the cooling.
- The rate of rise in the waste level has increased, but the rate of gas generation really has not changed; the thickness of the layer in which the gases are trapped appears to have increased.
- The Laser Raman spectroscopy work being carried out at Florida State University received critical attention by the Science Panel members. The Panel members see this tool as, at best, qualitative and, in the final analysis, could not recommend that further work be carried out.
- The organic materials in Tank 241-SY-101 must be identified and quantitated to confirm that the gas generation mechanism developed in this work is valid. This knowledge will be needed during mitigation, pretreatment, and treatment of these wastes.
- More accurate knowledge of physical property data on the waste in the tank, such as viscosity, gas content, and shear strength, is needed to improve modeling.
- The data from work with the actual waste from Tank 101-SY appear to be unreliable. In particular, the presence of significant concentrations of CH_4 indicates that something is wrong with the experiment. The Science Panel members recommended that the temperature of the experiment be lowered to that of the tank. The data presented to the Science Panel appear to be flawed and much work is needed to recover to a credible position.
- Data from the instruments on Tank 241-SY-101 seem to be unreliable. Staff at WHC must work hard to establish baseline data.

- At least two workshops were suggested - one each for the modeling efforts and simulated waste work.
- Resolution of the Ferrocyanide USQ appears to be well in hand.

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Science Panel Meeting Minutes January 12-13, 1993

Introduction

The eighth meeting of the Tank Waste Science Panel (Science Panel) was convened January 12, 1993 in Richland, Washington. A list of attendees at this meeting is provided in Appendix A. Appendix B is the agenda prepared for the meeting. It was not strictly followed.

The meeting focused on the presentation and discussion of recent information and results obtained from studies conducted to understand flammable gas released and ferrocyanide content behavior in Hanford waste tanks. The Science Panel discussed work performed at Pacific Northwest Laboratory PNL,^(a) Westinghouse Hanford Company, Florida State University, and Fauske Associates. A number of recommendations and observations were made.

The Science Panel members had been asked by the Executive Secretary to read monthly reports and other reports as part of their "homework" for this meeting. The meeting was structured not to include much review of the work that had taken place since the Panel last met in March 1992. Therefore, some of the presentations presented here may seem a bit abrupt to the reader. The reader is referred to other documents that have been issued from the Waste Tank Safety Programs at WHC (Babad 1993; McKinley et al. 1993) and PNL (Pederson and Strachan 1992; Burger et al. 1991; Strachan, Schulz, and Reynolds 1993; Reynolds et al. 1991).

Flammable Gas Program

In an attempt to provide some overview of the direction that is envisioned for the Flammable Gas Program and to give some basis upon which to evaluate the presentations of work that would follow, Mr. G. D. (Jerry) Johnson presented information on a number of tanks along with some of his views on the pertinent safety issues yet open. He discussed the number of tanks from which flammable gases are suspected of being emitted and what some of the common factors are that aroused suspicions of flammable gases (pages C.2 and C.3). When the waste levels in Tank 241-SY-101 are viewed on a relatively insensitive scale, one can come to the conclusion that the general behavior of the waste in the tank has not changed much (page C.4). Of course, it is currently felt that the behavior of the waste is changing based on recent data which were discussed in the following talks and are seen in the magnified scale of graph on page C.4 (C.5). In particular, the mean level of waste in the tank has been decreasing for the last two or three years. A large amount of data currently being obtained from the large number of monitoring devices on the tank is being added to this information data base. The monitors include H₂ monitors, a mass spectrometer, several gas chromatographs, a fourier transform infrared spectrometer (FTIR), a new thermocouple tree, two velocity-density-temperature trees (VDTT), and soon a mixing pump also fitted

(a) PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

with instrumentation. Jerry expressed the hope that there will be obvious connections between the information and the behavior of the waste in Tank 241-SY-101 and that of the waste in other tanks. The following information was presented in an attempt to highlight that connection.

Jerry discussed the waste level data obtained from several tanks other than Tank 241-SY-101 (pages C.5 to C.12). Again, the main purpose of this discussion was to highlight the need to make the connection between what is known about Tank 241-SY-101 and these tanks. The information, models, and understanding of the physics and chemistry, while not the same, should be generally applicable. There are some notable differences such as the different behavior of the waste in Tank 241-S-102, a single shell tank. The hope is that the understanding of the chemistry and physics in Tank 241-SY-101 can be brought to bear on the understanding of the observed behavior of the waste in Tank 241-S-102.

Jerry reminded the Science Panel members that more than 50 tanks are on the Watch List^(a), and that not all of them are on the list because of flammable gases. The list of safety issues to address for these tanks far exceeds the fiscal ability to address all of them. Therefore, we have to get smarter in our approach to solving these safety issues quickly. One step in this approach is to prioritize the list of tanks with safety issues. A prioritized list of the flammable gas tanks is shown on page C.13. In this list, under "remarks," is the term "stabilized." "Stabilized" means that the pumpable waste in the tank has been pumped to other tanks and what remains consists of salt cake, sludge, and capillary-held liquids.

Another category of tanks on the Watch List is the "Organic Tanks" (page C.14). Typically, these tanks contain much higher organic concentrations than the waste that exists in Tank 241-SY-101. However, some reactions that are taking place in these tanks could very well parallel the reactions that are taking place in Tank 241-SY-101. Jerry requested that the Panel members think about these connections between waste types and share their thoughts with the program participants.

Some of the chemistry issues that need to be addressed as part of the simulated waste studies were discussed by Jerry (page C.15). The chemical mechanisms work has resulted in the identification of acetate, formate, and oxalate as end product organics. It is uncertain if these exist in the tank waste as well. Although the source of N_2O and N_2 in the simulated waste work had been identified, the mechanism by which these gases are generated is not well understood. To date, the composition of the gases that are generated in the simulated waste work is different from the composition observed in the tank. Further clouding the understanding is the fact that when the waste is removed from the tank and a sample is studied under the same conditions that are used to study simulated wastes, 16% CH_4 is found in the gas whereas none is found in the gases evolved from the waste in the tank. It is uncertain to what this can be attributed. Lastly, there is the issue of how the gases are retained in the waste in Tank 241-SY-101. This is not an easily studied property in the laboratory. Yet some of these properties may be very important in the study of alternative mitigation strategies involving heating and/or dilution.

Jerry discussed some instrumentation that will be used on Tank 241-SY-101 to determine the concentrations of the various gases that are emitted during a gas release event and to establish the baseline of

(a) The term "Watch List" refers to a set of tanks for which there are unresolved safety questions and significant issues. This list has been mandated by congressional act.

these concentrations between the release events. A baseline of these concentrations is important to the understanding of the effectiveness of the mitigation test. There is a good correlation between the release of H_2 gas and the release of other gases such as N_2O . As shown in the plot reproduced on page C.16, whenever there is an increase in the H_2 as indicated using the gas chromatograph, shown as the solid line in the figure on page C.16, there is a similar response for N_2O . The FTIR method is also being used to determine the concentration of NH_3 . This method has been shown to have good detection limits with low interference from other gas species (C.17). Besides the other methods of determining H_2 , such as the mass spectrometer and the Whitaker Cells, a new gas chromatograph has been installed. A sample of the output from the new gas chromatograph is shown on page C.18. The detection limit is better than 0.5 ppm, a value that is more than adequate for the needs of the program.

During the discussion of the H_2 and N_2O analyses and preliminary results, D. M. (Denis) Strachan said that he had been looking at the data reported during December 1992. From that cursory analysis, he had concluded that there was no correlation between the H_2 and the N_2O concentrations as determined using the mass spectrometer. It was pointed out by D. A. (Dan) Reynolds that the value for the N_2O concentrations was obtained by measuring mass 30 (NO) rather than mass 44 (N_2O and CO_2). However, only about 6% of the parent N_2O yields NO in the mass spectrometer. Therefore, this number is bound to be highly variable. This confusion highlights the need to have a reliable method of determining individual gas species in a way that has little or no interference from other gaseous species.

Continuing with the chemistry issues (C.19), Jerry explained that besides the connection between the information gathered on Tank 241-SY-101 and the other flammable gas tanks, there should be valuable lessons learned for the other major Hanford programs such as the Hanford Waste Vittrification Program, Pretreatment Programs, and the Grout Program (an effort to dispose of the low-level waste in a cementitious grout). One question concerning the destruction of the organics in Tank 241-SY-101 is the residual gas generation. Will there still be gas release events that result in H_2 releases greater than the lower flammability limit, albeit at a lower frequency?

As part of the effort to uncover "unknown" chemistry issues, a meeting was held in December 1992 to which as many of the "old timers" as could be found near Richland, Washington were invited. The purpose was to determine if there were organics or other chemicals that the present staff did not know about, but may be part of the undocumented operating history of the Hanford Site. Three organics were identified as a part of this exercise (C.20).

A more detailed discussion of the modeling efforts for the mitigation test followed, but Jerry wanted to give an overview of these efforts. This overview is adequately summarized in his viewgraph on page C.21.

Thermal Behavior of the Waste in Tank 241-SY-101

Two presentations were delivered on the thermal behavior of the waste in Tank 241-SY-101. One was given by R. T. (Rudy) Allemann from Pacific Northwest Laboratory, and the other was given by G. L. (George) Fox from Westinghouse Hanford Company.

Observations by several scientists have been that the waste in the tank is cooling more rapidly since December 1991 than previously noted (D.2 and D.3). At the same time, the time between gas release events has increased (D.2 and D.4). Examination of the temperatures in the waste suggest that the depth of the nonconvecting layer of the waste has increased. Rudy suggested that there are correlations between the rate of level rise and the temperature changes, but no correlation to the size of the gas release (D.2 and D.5).

In past Tank Waste Science Panel Meetings, the appearance of the cores taken from the waste has been correlated with the depth of the isothermal or convecting layer in the waste. Traditionally, the bottom of the convecting layer and the top of the nonconvecting layer was at about 5 m (200 in.) (D.6). The current value, based on the temperature plots, is 6.4 m (250 in.). Rudy tried to understand what the effects were on the rate measurements, because it is generally believed that the nonconvecting layer is where the gas is retained. If the thickness of this layer increases, then the rate should increase correspondingly.

Part of the new instrumentation that is currently in the tank can be used to determine the density of the waste at various depths in the waste. Rudy used the density data (D.7 and D.9) to determine the effective pressure that a gas bubble would experience at that depth. The rate of level rise has increased from 2.3 mm/d (0.09 in./d) to 2.7 mm/d (0.106 in./d) (D.8). This is an apparent change in the level rise, but it must be remembered that the thickness of the layer in which the gases are trapped appeared to have increased as indicated from the temperature profile. Rudy used the approach outlined on pages D.10 and D.11 to show that the rate of gas generation really has not changed. He further calculated (D.12) the time to neutral buoyancy, the point at which the region in which the gas is stored becomes unstable with respect to release of the gas, and showed that the top part of the nonconvecting layer should release at 83 days after the last gas release event (D.13) and the bottom part of the waste should release later at 227 days.

Rudy calculated the void fraction at neutral buoyancy (D.14). This is an important part of the safety assessment, since this value yields the volume of gas that can be released during mixing. Rudy's conclusions from this portion of his presentation are shown on page D.15 and the formulae he used are listed on page D.16.

Rudy continued with a discussion of the changes in behavior observed in the waste since September 1992. These changes are manifested in the temperature profiles of the tank (pages D.17 to D.19). There is a general cooling of the waste and a development of an additional thickness of the nonconvecting layer. The development of this layer is commensurate with a significant decrease in the rate of level rise in the tank (page D.20). Only a few data were available on the concentration of H_2 in the vent gases. These are shown on page D.21 as 0.008% from November 12 to 17, 1992 and 0.06% on December 2 to 4, 1992. On December 16, 1992, a peak in the FTIR response to N_2O and NH_3 was observed coincidentally with a small drop in the surface level (so indicated on page D.21). One problem with the current set of data has to do with the fact that all of the temperature sensors are in one quadrant of the tank. All of the sensors at each level yield the same temperature (D.22). However, since the old thermocouples were removed, a good correlation cannot be made between the "old" thermal behavior and

the "new" thermal behavior. Rudy's summary of conclusions is shown on page D.23. One conclusion not shown here is that there appears to have been a major loss of sensible heat from the tank, approximately 3800 W (13 000 BTU/h).

The discussion of the thermal behavior of the waste continued with the presentation by G. L. (George) Fox from Westinghouse Hanford Company (E.1). In his presentation, George wanted to show that the waste is cooling faster than the decay rate of ^{137}Cs (E.2). He is proposing that there is a substantial amount of chemical heat from some exothermic chemical reaction. This reaction must be slowing significantly, thereby giving rise to the cooling observed in the tank. [However, this is not necessary since the waste in the tank has always cooled at a rate faster than the decay rate of ^{137}Cs because the waste was put in the tank at a temperature much higher than the current temperature.] In addition, to get the heat balance and temperature distributions observed in the tank, George assumed a significant thickness of salt precipitated on the walls of the tank. To estimate the cooling rate in the tank, George averaged the temperature from thermocouples 1 through 16 for the period July 1990 to July 1992 (E.3).

George constructed the model of the tank shown on page E.5 with the stylized thermal distribution shown. To calculate the heat losses, he needed boundary conditions that he selected at the average daily ambient temperature and the average temperature of the upper part of the tank (thermocouples 8 to 16) (E.6). The rate of cooling of the upper part of the tank should give an estimate of the heat lost from the waste in the tank. The results of this calculation are shown on page E.7. Furthermore, he calculated that to match the temperature distribution with the observed distribution, he needed to postulate a thickness of crust for the top of the waste and for the side walls of the tank. On the average, this thickness should be about 0.79 m (E.8). This result is not, however, unique. There are a multitude of crust and sidewall thicknesses that can be calculated. However, only some of these thicknesses make sense in light of what is known about the tank. The curves that show the relationship between the thicknesses are shown on page E.9. Since the temperature data from the tank suggest a 1.2-m-(4-foot-) thick crust, the implied side wall thickness would be about 0.6 m (2 feet). However, there has yet to be an accounting of the thermal resistance resulting from limitations of the vapor transport rate.

From these calculations, George concludes that there is about a 0.6-m-thick solid salt layer on the walls of the tank and there must be some chemical reaction that is or has been giving off a significant amount of heat (E.10).^(a)

Modeling of Waste Behavior and the Effect of Mixing

Two codes have been used as the mainstays for the modeling activities in support of the mixer pump to be installed in Tank 241-SY-101. Presentations were made by K. (Sathya) Sathyanarayana and M. J. (Marv) Thurgood. Sathya presented information on the capabilities and the use of GOTH and

(a) Note added by the Compilers: Results from George's later studies of the characterization of chemical heat generation that is needed to duplicate the observed tank cooling have indicated the chemical heat is probably not a major factor. George now believes that the increase in tank cooling is probably the result of increased heat loss, perhaps because of crust thinning.

TEMPEST. The GOTH code solves the conservation of mass, momentum and energy equations for multi-component, two-phase flow. The code features a flexible noding scheme that allows lumped parameter, one-, two- or three-dimensional analysis or any combination. The conservation equations are solved for three fields: gas, continuous liquid, and solid particles suspended in liquid phase. The code is used to calculate the relative velocities between these fields, including the effects of two-phase slip on pressure drop and heat transfer between solid particles and the fluid. The turbulent shear stresses and heat transport are included. Therefore, the code can be used to calculate settling of solid particles, the rise of gas bubbles, and the effects of submerged turbulent jets. The code, developed for WHC by Numerical Applications Incorporated, is ideally suited to perform the rollover type calculations with mechanistic gas release modeling to predict the gas concentrations in the tank dome air space and the removal of hydrogen through the ventilation system.

The TEMPEST code is used to solve for a single phase the three-dimensional time-dependent equations that govern the turbulent transport of momentum, energy, and mass. The single phase can be either homogeneous gases or liquids or mixtures or pseudo-fluids (slurries, etc.). The code is ideally suited for the prediction of incompressible fluid velocity and temperature fields. The code capability has been extended for constituent transport and the transport properties including the effects of non-Newtonian rheology. However, the TEMPEST code cannot be used to compute the amount of gas released during a rollover event; the release must be inferred from the resulting gas distribution within the tank mixture and a gas release criteria. Using these criteria, TEMPEST code can be used to obtain input to the FATHOMS code, an old version of GOTH, with which the concentration of gases in the dome space can be calculated (F.2).

The GOTH and TEMPEST codes have been used to estimate the quantity of gas that could be released during mixing of the tank contents. Two dimensional and 3D simulations (F.3) were performed to estimate the upper bound gas release volumes using the initial conditions that correspond to 18.9% and 24% of gas at neutral buoyancy, i.e., the amount of gas needed to make the net density of the mixture in the nonconvective layer just equal to the supernatant (convective layer) density. These calculations are needed in support of the safety assessment. If the gas release is predicted to exceed a certain volume limit set by safety analysis, then the pump may not be installed under such conditions.

The results of these calculations with GOTH code are summarized on page F.4. Two different operation modes or ramps were considered for the start and duration of pump operation. In Ramp 1, the jet velocity, as measured using velocity meters on the pump, is increased from zero to 4.6 m/s (15 ft/s) over a period of 60 s and thereafter the jet velocity is maintained constant. In Ramp 2, so called "Pump Bump," the jet velocity is increased to 4.6 m/s in 2 s, held constant for 5 s, then decreased to zero in 1 s. The results given in the table are for these simulations at 1000 and 2000 s after the starting of the pump.

The maximum allowable amount of gas that can be released to stay within the safety bounds is 371 m^3 (13,100 ft^3). With increasing amount of retained gas or the longer the duration from the time of natural release event to the time of installation of the pump, the predicted amount of releasable gas increases. The results based on the calculations performed with bounding parameters corresponding to the neutral buoyancy gas void fraction of 0.24 show that the limit will be exceeded at about 21% of retained gas, which corresponds to the tank level of 10.58 m (416.5 inches) (F.5). A comparison of gas release quantities calculated by GOTH code and TEMPEST codes is shown on page F.5. Both methods predict

increasing gas release volumes with increased initial gas content. At low initial gas fraction of the tank, the GOTH results show higher amounts of gas release than the TEMPEST estimates, but at higher initial gas fraction TEMPEST estimates are higher. The differences in results from the two codes are due to the mixture viscosity model, the gas release, and retention models as shown on pages F.6 through F.8. An envelope encompassing all of the cases, including the TEMPEST predictions, should provide an overall conservative estimate of the gas release. It should be mentioned that both codes are updated with new models for use in performing simulations of the waste behavior.

As a result of the efforts discussed by Sathya, important accomplishments and contributions have been made (F.9 and F.10) in understanding the behavior of the tank contents and in helping the design of mitigation activities through numerical modeling. Without this capability, the safety assessment would not have been on very firm ground. It is true, however, that several assumptions have had to be made to approximate the behavior of the waste. These assumptions have led to a conservative estimate of the amount of gas release and the amount of force imposed on structural components (F.11).

Marv discussed the efforts to use the GOTH code to model natural and pump-induced rollover events and validate the simulation methodology using the available tank data (G.2). The modifications, such as use of the particle field in place of the droplet field and addition of non-Newtonian fluid capability, have been made to the basic GOTH code and improved version of FATHOMS to model natural rollover events in Tank 241-SY-101 (G.3). Two events were used to estimate the parameters for the GOTH code; these were the October 1990 and December 1991 releases (G.4). These parameters were estimated based on the predicted and measured dome hydrogen concentrations, vent flow, dome pressure, and temperature inversion of the tank mixture. A significant contribution from the modeling activities using the GOTH code have been the estimation of nonconvective layer viscosities and the particle sizes which later have been confirmed through actual sample measurements (G.5). As Sathya had already discussed, the pump-induced gas releases were also calculated (G.6). A mechanistic bubble release model illustrated on page G.7 where α_g is the void fraction of the gas and α_p is the particle void fraction, was developed using the measured hydrogen concentration data for the natural burp events. The gas release model was then utilized in the prediction of gas releases as shown on pages G.8 through G.11 for the mixing pump operation.

Because of the modeling efforts, a better understanding of the physical properties of the waste was achieved. Estimates of the gas releases under natural and mitigation conditions were made. However, one must recognize the assumptions that have gone into the development of this model. There is a paucity of data from the actual waste that is required to develop the model to the extent needed to do a good job (G.12).

Marv also made the comment that there is much energy stored in the compressed gas in the tank. The gas that is trapped in the nonconvective layer is generally agreed to be about 0.2 MPa (2 atm) pressure. The main effect of the injection of fluid through the mixer pump is to trigger a release. Once a small portion of the gas is moved and caused to expand, the expanding gas triggers neighboring areas to begin to rise. This is the general phenomenon that happens in a gas release event. The rising gas causes stirring of the solids. It is envisioned that an intermittent use of the pump is all that is needed to keep the solids in suspension.

As part of the support activities to the Safety Assessment for placing the mixer pump in Tank 241-SY-101, R. T. (Rudy) Allemann and coworkers have been performing calculations of the amount of gas to be released under various scenarios. These calculations are important because, as will become evident later, if too much gas is predicted to be released then a real safety concern exists and plans to place the pump in the tank may need to be changed.

Rudy first described the calculations that have been done to support the prediction of the amount of gas to be released during pump operation. This began with a discussion of the situation in the waste just before a gas release when the gas-solid combination is near neutral buoyancy in the liquid portion of the waste (H.3). When the pump is started, the liquid jet, formed by injecting liquid from the convecting layer of the waste into the nonconvecting layer, causes bubbles to rise toward the surface and the ensuing circulation pattern. The interface between the waste that is neutrally buoyant and the less buoyant material initially rises because the bubbles are rising; then the interface collapses as the gases are released.

With the existing models of the gas release from the tank, Rudy and coworkers, both at PNL (TEMPEST) and WHC (GOTH), have calculated the gas releases expected during pump operation as a function of the time since the gas release event that opened a "window." The results from three TEMPEST calculations and one GOTH calculation are shown on H.4. Basically, the difference between the GOTH and TEMPEST results is due to the different viscosity behavior that is used in the code. In Figures H.5 through H.7, the effects of the various phases of pump operation are depicted. The phases of pump operation are shown in Figure H.5. The plans for pump operation call for intermittent pumping of the waste rather than continuous pumping. In Figures H.6 and H.7, the effect of pumping is shown as contour plots as an indication of where the bubbles rise relative to the jet of the pump.

The effects on the H_2 concentration at various parts of the tank dome and exhaust system were calculated using the FATHOMS code. The areas of concern and the calculation grid are shown in Figure H.8. For various phases of pump operation, the concentration at the various positions was calculated and the results are shown in Figures H.9 through H.11. The supporting information was calculated using the TEMPEST code (H.12 through H.20).

Because it was not possible to use either GOTH or TEMPEST to model the behavior of a plastic material as the liquid from the jet penetrates the material, the HULL code was used. The results from this calculation are shown on pages H.21 through H.28. In general, the results suggest that much less of the waste is involved in the pump-caused gas releases, because much less of the waste is disturbed when the jet penetrates the waste (H.29 through H.32). In the case that the material is plastic, some pressure can be exerted on the plastic material during pump operation without causing flow. If the pump is turned off, then there would be a head of liquid exerting a residual stress on the plastic material. The magnitude of the liquid head was calculated by L. E. (Larry) Efferding (H.33). The effect of various liquid heads on the flow of the material is shown on pages H.34 through H.36 for 0.3 m, 0.6 m, and 1.2 m, respectively.

Although there are several uncertainties, the pump test will allow Rudy and coworkers to narrow the possibilities. Some change in the concentrations of gases in the dome space should be detectable. Based on the behavior of the waste and the resulting gas releases, some resolution of the physical properties of the waste should be possible (H.37). As part of the pump insertion, some sluice water might be added to facilitate the insertion. The use of sluice water could produce some unwanted side effects.

Extent of the Simulated Waste Work

A summary of the progress in the chemical understanding of the waste in Tank 241-SY-101 from the studies with simulated wastes was reported by L. R. (Larry) Pederson (Appendix I). Larry and S. A. (Sam) Bryan have been performing studies in three main areas: Physical Properties, Organic Destruction, and Gas Generation. At the last meeting, a presentation was made concerning the settling rates of the solids in simulated waste (SY1-SIM-92A) (Schulz and Strachan 1992). In that presentation, the settling rates were fit to a first order kinetic equation. The rates were found to increase with increasing dilution and temperature (I.3). Meanwhile, Larry has looked into the sedimentation of solids in slurries of ceramics (I.4). From these studies, it has been determined that the sedimentation of ceramic materials follows the equation shown on I.4. The behavior of the solid is illustrated in the plots, which illustrate the behavior of particles as a function of particle diameter, temperature, and solid volume fraction. Larry then reviewed the results that had been presented at the last meeting (I.5 through I.9). Settling rates were less sensitive to temperature and less scattered with increasing dilution with 2 M NaOH when organics were present than without organics (I.8 and I.9).

One important physical parameter to the modelers of the Tank 241-SY-101 waste is the thermoconductivity (not reported here) and the heat capacity. A method for measuring the heat capacity of waste is being developed. For this method, a Seebeck Envelope Calorimeter is being used (I.10). In this method, a sample and the calorimeter are heated to the same temperature as measured using the two thermocouples shown in the schematic (TC1 and TC2 on I.10). A sharp jump in the oven temperature is used to heat the sample to a new temperature. The time needed to establish the new sample temperature is used to calculate the heat capacity of the sample. Heat capacities of the sample container and calorimeter need to be measured without a sample. This method has been used in the hot cells at Oak Ridge National Laboratory and so appears readily adaptable to the heat capacity measurement of samples from the waste tanks.

As a possible mitigation/remediation strategy, the organic materials in the wastes contained in the flammable gas tanks could be destroyed. Organic materials appear to be responsible in part for the flammable gas generation in these wastes. One method of destroying the organic materials is to heat the waste to some high temperature below the critical point of water (I.11). In his tests, Larry has heated Tank 241-SY-101 waste simulants to temperatures between 200°C and 350°C. Batch reactions have been reported earlier (Schulz and Strachan 1992), so Larry concentrated on the continuous flow reactor experiments in his presentation. In these experiments, some of the same reactions occurred as were observed in the batch reactions. In the continuous flow reactor, the simulated waste was at temperature for about 5 min. The 1-L reactor has three heating zones. With increasing temperature, the EDTA rapidly degraded as witnessed by the decrease in total organic carbon (TOC) with increasing temperature (I.12). Above 300°C, the reaction was fast enough that the TOC and the amount of oxalate were the same. By 350°C, the reactions had gone to completion such that all of the TOC had been converted to carbonate (presumably). It was difficult to obtain a material balance because of the design of the apparatus.

As has been seen in other studies carried out in the Flammable Gas Project, nitrite appears to be the reactive nitrogen-bearing species in solution (I.13). Although the data are somewhat scattered, there is a general downward trend in the nitrite concentrations with reaction at higher temperatures. Also consistent with the other studies is the hydroxide ion consumption (I.14). These data seem to indicate that as the

TOC is converted to CO_3^{2-} , hydroxide ion is consumed. Larry also recalled the previously reported data from the batch experiments from which it was determined that NH_3 is generated in the reaction in stoichiometric amounts to the organic nitrogen (I.15). Although this might indicate that the source of NH_3 is the organic nitrogen, the results from the work at Georgia Institute of Technology suggest that most of the NH_3 comes from the NO_3^- (Schulz and Strachan 1992). The relationship between NO_2^- and NH_3 is shown in the Pourbaix diagram shown on I.16. At high pH and low oxygen fugacity, there is a connection between the two species. This diagram is only indicative, however, of the reactions since it is valid only for 25°C.

As indicated earlier, the design of the apparatus did not allow quantitative recovery of the gases. However, samples of the gases were analyzed and reported I.17. With increasing temperature or extent of reaction, the amount of H_2 increased and the amounts of N_2 and N_2O decreased. Not much CH_4 or O_2 was found in the off gases, although O_2 was present at the start of the reaction.

To demonstrate the effectiveness of the destruction of organic compounds on the thermal generation of gases, experiments were performed with the simulated waste solutions that had been treated at various temperatures (I.18). The gas generation experiments were carried out at 90°C. For each experiment, extra OH^- was added before the solution was heated to temperature in a batch reactor. The quantity of gas generated at 90°C after 28 days of reaction are shown to have decreased by at least a factor of 10 over the amount of gas generated from the untreated solutions.

Thermogravimetric studies were performed (I.19 through I.22) to demonstrate that $\text{C}_2\text{O}_4^{2-}$ was consumed by reaction with nitrite, but NO_2^- was not oxidized to NO_3^- in significant amounts.

Larry reviewed some results that had been presented at previous meetings concerning the generation of gases and the effect of trace components in the solution, the concentration of OH^- , and the presence of a radiation field (I.23). These data are portrayed on pages I.24 through I.30.

In the future (I.31 and I.32), experiments will be performed that more accurately represent what is in the waste. To some extent, these studies depend on the results that will come from the analysis of the actual waste. Work done at the University of Georgia by Dr. Bruce King suggests that the presence of noble metals, such as Pd, Rh, and Ru, enhance the generation of H_2 during the reaction between formate and sludges containing trace (<0.2%) quantities of these metals. The presence of these metals in these solutions, either in solution or as a precipitate, could also affect the generation of gases from the solutions of concern in this program. One critical need for the models that are being used is the constitutive relationship for the bubble/solid interactions in the waste and the effect on the rheological properties of the solutions. Investigation of these physical and physical chemical properties of the solutions will be part of the future efforts.

The studies being carried out at Westinghouse Hanford Company were reported by J. C. (Jim) Person (J.1). Recalling that the studies have been carried out using simulated waste materials in an effort to develop an apparatus that would be used to study actual waste samples from Tank 241-SY-101, Jim summarized the conditions under which the studies were performed (J.2) and the design and operation of the apparatus that was used in these experiments (J.3). Jim highlighted the results obtained to date from these experiments, suggesting that even with the samples taken from the tank, the gas composition is

different (J.4). These data are summarized in the figures on pages J.5 through J.8. In these plots, the upper scale of the bottom axis lists the type of reaction vessel used and "Gl" stands for a glass reaction vessel; "SS" for stainless steel; "T" for Teflon. The second scale is for the atmosphere used. The bottom most scale is for the waste type; "HEDTA" indicates that the waste (SY1-SIM-91A) contained HEDTA; "101-SY" indicates the results from the experiments with the actual waste from the tank. The last two points on the plot are for samples taken from Tank 241-SY-101 during Window E while the other points are from samples taken during Window C. It is most interesting that the analyses of the gases from the tank show no CH_4 , but the gases generated from the waste samples at 120°C contain up to 17% CH_4 . In addition, the use of coupons of steel similar to that from which the tank was constructed led to slightly higher gas generation rates and a slight increase in the ratio of N_2O to H_2 . The latter was changed in the opposite direction from the change when steel was used. [These differences may be the result of the lack of reproducibility when using the experimental method.]

Jim reviewed the process for converting the pressure data to the rate of gas generation (J.9). The rates are compared by normalizing the rate to the number of carbon atoms in the organic molecule of the material being tested. The plots shown on pages J.10 and J.11 summarize the data with simulated wastes, but also show the poor reproducibility that is obtained using the apparatus shown on page J.3. The rate found for the sample from the tank is about $0.3 \text{ mmol}/(\text{d}\cdot\text{mol C})$, which is about a factor of two lower than the rate observed with simulated waste containing HEDTA (J.12). Jim summarized the results of his experiment on pages J.13 through J.15.

Methods Development for Organic Analysis

Development of the analytical methods for the determination of organic compounds in waste solutions has been under study at PNL with particular emphasis on the organic materials in the waste in Tank 241-SY-101. These studies have been carried out by J. A. (Jim) Campbell. The use of derivatization techniques to separate the chelators and chelator fragments had been the main emphasis and continues to be a useful technique for some organic compounds in the waste (K.3). However, some of the organic material cannot be analyzed using this technique. In particular, the BF_3 /methanol esterification technique has been shown by Jim not to be effective for the organics in the waste that are qualitatively known, e.g., symmetrical ethylenediaminediacetate (s-EDDA) and some of the intermediates that Ashby and coworkers (see earlier Science Panel meeting minutes) have determined. These intermediates were sent to Jim for use as standards in his analytical methods. The use of other esterification techniques does offer the possibility of better recoveries, however. For instance, HCl /butanol esterification seems to work much better without some of the drawbacks that exist with the BF_3 /methanol technique. Because of the known problems with esterification and because independent techniques will be needed for confirmation, other techniques are being developed to determine the concentrations of organics such as formate, acetate, and oxalate. Until now, only about 12% of the total organic carbon has been quantitated (K.4). Results from studies at Georgia Institute of Technology indicated that oxalate could possibly account for a large portion of the remaining total organic carbon. To analyze for this organic, Jim developed the liquid chromatography (LC) method.

In the LC method (K.5), the sample is dissolved in H_2O and filtered. It should be noted that only 85% of the organic carbon is recovered during this step. At this step, most of the samples that Jim has to analyze are solid because the temperature is much lower than temperatures in the tank. Jim has found

that, by passing the sample through a cation exchange resin, the radioactivity of the samples is reduced to the point where the sample can be removed from the hot cell and handled in a hood.

Several chromatograms were shown by Jim (K.6 through K.13). The first chromatogram (K.6) is of the control sample that came from D. (Dani) Meisel at Argonne National Laboratory. The control sample is SY1-SIM-91B as made without any heating or irradiation. The peak at 11.41 minutes retention time is believed to be oxalate. The chromatogram shown on page K.7 is from the same sample as on page K.6, but irradiated. To confirm that the peak at 11.33 minutes retention is due to oxalate, Jim spiked the sample with oxalate. The resulting chromatogram is shown on page K.8. The peak has about the right retention time, although somewhat shorter. The chromatogram from a sample that had been irradiated and then heated to 60°C is shown on page K.9; the same sample containing an oxalate spike is shown on page K.10. The first peak at 11.2 to 11.5 minute retention time appears to be due to oxalate, based on the effects of the spike addition. These results are summarized in the set of chromatograms shown on page K.11. Jim also showed the chromatogram for the sample of the convecting layer from Tank 241-SY-101 (K.12) and the sample spiked with oxalate (K.13). The peak at 12.37 minutes in the chromatogram on page K.13 is oxalate. Conditions between the experiments that led to the chromatograms shown on pages K.12 and K.13 are different. The oxalate peak shown for the actual waste on page K.12 represents an oxalate concentration of about 6% of the total organic carbon in the sample.

During one of the interactions with Dr. Charles Liotta at the Georgia Institute of Technology, the possibility that oxalate could be formed during sample preparation was discussed (K.14). Jim used nuclear magnetic resonance (NMR) and simulated waste samples to confirm that oxalate was not being produced during the sample preparation steps. However, to use NMR very efficiently, labeled compounds would be needed. Jim obtained oxalate data using ion pair chromatography for the initial results on oxalate (K.14). Although it appears that the organic carbon passes through the column, more experiments are needed. It had been hoped that determination of the light-weight organics would yield a better material balance. However, Jim reported that one of the samples from the convecting layer (core composite 2, bulk sample) contained oxalate at only about 6% of the total organic carbon (10 to 20% of the remaining total organic carbon from the previous results).

Another area of concern to Jim is the approximate 85% organic recovery from the water leach at about 30°C (hot cell temperature) that is done on the radioactive samples. Jim will be investigating the use of water at higher temperatures to recover the organic carbon. He will be trying several temperatures to determine at what temperature quantitative recovery of the organic carbon is obtained from the water leach. It should be noted here that the amount of organic material that has been reported in the past is 20% of the organic carbon that is in the water leach. Therefore, the total amount of carbon recovered has been about 17% (20% of the 85%). The revelation that 6% of the organic carbon is oxalate means the actual amount is 5%.

Work that remains to be done in the near future (K.15) includes the search for other light-weight organics in the waste samples, surfactants, and the continuation of methods development. The search for possible surfactants is being spurred by speculation that the gas behavior in Tank 241-SY-101 might be due to their presence. An LC method is being developed for the detection of surfactants as a general class of organics.

Ferrocyanide Waste Tanks

Presentations concerning the various aspects of the chemistry, properties, and analytical results from the ferrocyanide studies are reported below. For convenience and to present the material in a more logical sequence, these presentations are discussed in a slightly different order than indicated in the Agenda.

Core Sample Analysis - The results from the chemical and physical analyses of the core materials from Tank 241-C-112 were discussed by B. C. (Brett) Simpson. The results discussed by Brett came from the laboratories at PNL and WHC. Brett, along with others, was responsible for the interpretation of these results to form the cohesive story described below.

Brett first described the history, or what is known of the history, of this single shell tank (L.3). Of key importance to Brett's discussion is the fact that the tank received ferrocyanide wastes from 1956 to 1958, subsequent to which other more alkaline wastes were placed in the tank. Because the tank received ferrocyanide wastes from the "in-farm" process, it is suspected of containing one of the highest ferrocyanide concentrations of all the ferrocyanide tanks. Three cores have been taken from this tank as indicated on page L.4. Note that all of the available risers through which to collect core samples are located on the periphery of the tank (L.4). Of the three cores, only two yielded sufficient sample; only limited analyses were obtained from the material in Core 35 (L.5).

The general and physical characteristics of the samples from the Tank 241-C-112 core materials are shown on pages L.6 through L.8. A summary of the results on key analytes is shown on page L.9. The cores were retrieved in segments that are 0.48 m (19 in.) in length. These segments were then divided into four quarter segments for analysis. Each segment is numbered starting at the surface of the waste, and each quarter segment is alphabetized from the top of the segment. Since the surface of the waste is calculated from the bottom of the tank, the first segment may be only partially filled. Thus, Core 34 contained enough material for an analysis of quarter segment 1D. Whereas in Core 36, sufficient material was recovered to allow a complete analysis of all quarter segments of segment 2 (L.9). Of particular note is the low heats of reaction obtained for all of these samples (L.9). The data shown on page L.9 are displayed in bar charts shown on pages L.10 through L.13 and L.15 through L.18. On page L.14, Brett summarizes the comparisons of the core samples with the simulant material that was made using the flow sheets from the 1950s. Other than the energetics and the total carbon (a measure of the cyanide in the absence of a reliable method for cyanide or ferro/ferricyanide), the comparisons are quite good.

Brett noted that the ^{137}Cs concentrations correlated with the Ni concentrations. From other work reported below, it is known that sodium nickel ferrocyanide decomposes to soluble ferrocyanide and $\text{Ni}(\text{OH})_2$. Therefore, it would be expected that if there was any ferrocyanide present or decomposed, the Ni concentration would be a good marker for where the ferrocyanide was or had been. Brett concluded his presentation by summarizing the core analyses in terms of what the results mean to the Tank Safety Program (L.19 and L.20).

The Science Panel members complimented Brett for the lucid presentation and recognized that he was reporting the efforts of a number of other contributors. The Science Panel members were very happy to finally see results of the energetics from actual ferrocyanide tank wastes. This information will make a major contribution to resolving the safety issues associated with the ferrocyanide wastes.

Safety Assessment - An "Assessment of the Ferrocyanide Issue" was presented by H. (Hans) Fauske of Fauske Associates, a subcontractor to Westinghouse Hanford Company. Hans has been working with ferrocyanide materials in an effort to determine the energetics of the decomposition of ferrocyanide materials. The compositions of the materials with which Hans has been working are shown on page M.3. As can be seen from this table, the waste that was placed in the C-Farm tanks should contain the highest concentration of ferrocyanide in the ferrocyanide tanks. High concentrations in the C-Farm result from the precipitation of sodium nickel ferrocyanide $[\text{Na}_2\text{NiFe}(\text{CN})_6]$ from a waste already depleted of iron.

Hans has developed a special calorimeter for studies of this nature, a so-called RSST Calorimeter (M.9). In this calorimeter, a small sample is heated at a constant rate until such a temperature is reached that the heat of reaction for some exothermic reaction heats the sample. The rate of heating and the heat of reaction are measured. Two examples of the results from this calorimeter are shown on pages M.5 and M.7. The first example was obtained using a sample of the simulated "U-Plant-2" material and is illustrative of a low reaction heating rate. In the second example, a sample of "In-Farm-1" material was used as an example of a very vigorous reaction.

With these results, Hans set down a logic by which passive safety of continued storage of ferrocyanide wastes could be demonstrated (M.5). The argument centers around the fact that there is sufficient water present in these wastes to ensure a reaction could not get started because the latent heat of vaporization would quench any exothermic reaction either in the bulk of the waste or in a hot spot. Some of the equations and assumptions for this argument are shown on page M.10. Using these equations, Hans showed that in order to attain 130°C the hypothetical hot spot would have to be on the order of 0.5 m in diameter or even smaller. At this diameter, the calculations indicate that the heat generated would be just enough to raise the solution temperature to the boiling point, here assumed to be 130°C . These calculations were conservative and thus indicate that the concept of a hot spot in these wastes is highly unlikely or, in Hans' words, "preposterous."

Hans and his coworkers have also performed propagation experiments in which a tube was packed with ferrocyanide material and thermocouples were placed at various distances along the tube but imbedded in the ferrocyanide material. An igniter mixture was placed at the top of the tube of ferrocyanide. When ignited, the ferrocyanide would burn and the reaction would, depending on the material being studied, propagate down the tube. As the burn front passed the thermocouples, the temperature would rise. Using the distance and the time of arrival of the burn front, the burn velocity could be calculated. An example of the output from this experiment is shown on page M.13. A summary of the burn propagation experiments is shown on page M.15. From this information, it can be determined that a material containing more than about 12% moisture will not sustain a propagating burn, that is the material will self extinguish.

From these studies, Hans suggests that the safe approach is to make sure that the material in the tanks does not become dry. Tank farm controls may be needed for those wastes in which it can be demonstrated that a hot spot could result in elevated temperatures; still, occurrence of a hot spot is an unlikely event (M.21).

Waste Aging - Part of the question that concerns scientists at Hanford is how much ferrocyanide exists after many years of tank storage over which time other waste types entered the tank and were pumped to other tanks. This question of "aging" was addressed by M. A. (Mike) Lilga and coworkers at PNL. The outline of the scouting studies they are performing are shown on page N.2. The pH experiments used high pH solutions representative of the solutions that entered the tanks after the ferrocyanide campaigns were completed. Solutions with pH values from 12 to 14 cause rapid dissolution of the ferrocyanide (N.3 and N.4). At pH 12, there is insufficient OH^- to complete the reaction. A slight excess of OH^- is present at pH 13 and the reaction slows in response to the decreasing OH^- concentration. At pH 14, there is excess OH^- and the reaction goes to completion in a matter of minutes. The reaction that is taking place appears to be that shown on page N.5. Evidence for this reaction is from the infrared analysis of the water soluble and insoluble reaction products (N.6 and N.7) and from the x-ray diffraction analysis of the solids (N.8). Additional evidence was also obtained using the energy dispersive spectra from the scanning electron microscope (N.9). Although sodium nickel ferrocyanide becomes soluble at pH 14, there is little further break down of the ferrocyanide complex to form free cyanide (N.10).

Reactions of this nature are also affected by the total ionic strength of the solution into which the solids are dissolving. This effect was checked, in part, using a constant Na^+ concentration in which the Na^+ concentration was held at 1 M using Na_2SO_4 (N.11). There was a noticeable effect at pH values of 12 and 13 (N.12). Other anions were also used (N.13 and N.14). The effects seen between equal Na^+ concentrations with different anions are probably due to pH buffer effects.

The effect of using a simulated waste solution was also checked (N.15). It was observed that the simulated waste solution resulted in more rapid dissolution of the ferrocyanide; this is probably due to the pH buffering effect of the PO_4^{3-} (N.16). This result is supported by the results shown on page N.17, where it can be seen that the final pH value for the simulated waste solution is unchanged. Also shown in this table are some of the results from the stirred/unstirred and gamma irradiation experiments described in the following pages. The results described above were obtained from solutions that were stirred constantly. To partly determine the effect of stirring, the solids were allowed to settle. After 24 h, a sample of the solution was removed after briefly mixing to ensure a homogeneous solution phase. When the new solution was added, some stirring had to be done to get the solids mixed with the new solution, but this was held to a minimum. The effect was to slow the reaction, but it was still quite rapid. The result is that if mildly alkaline solutions came in contact with the ferrocyanide it would dissolve to the extent that there was sufficient OH^- .

Results from the gamma irradiation experiments are tabulated on page N.18. There was no net effect of gamma irradiation on solubility. There is a documented light sensitivity for $\text{Na}_4\text{Fe}(\text{CN})_6$, which dissociates in light to free cyanide. This effect is shown in the table columns headed "Dark" and "Exposed." Little or no significant decomposition of the CN^- was evident from the gas analyses (N.19). The elevated H_2 was attributed to the radiolysis of the water. The experimental setup was not appropriate for the detection of NH_3 .

The infrared absorbance frequencies for the cyanide species in these experiments are listed on page N.20. These results corroborate the results discussed above.

Cyanide Methods Development - Cyanide species-specific analytical methods are being developed at Pacific Northwest Laboratory by S. A. (Sam) Bryan and K. H. (Karl) Pool. Sam presented the analytical methods development work for direct determination of cyanides in solid samples and indirect methods using dissolved and solution samples. These methods are being developed because there is a need to determine the presence of these species for the safety assessments. Since the ability to collect a statistically representative number of samples from the single-shell tanks does not exist, a variety of data and data sources will be needed to close the safety issue for the ferrocyanide tanks. Therefore, as part of this quiver of data, a quick and easy method for the determination of cyanide species is needed (O.2). For the former goal, Sam investigated the applicability of various instrumental methods including those listed on page O.3. Although all three methods have been investigated, only three appear to be worthy of further development; namely Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy, and X-ray diffraction. The important advantage of FTIR is that the characteristic frequencies of the dissolved and solid species should be distinctly different as should the frequencies for the cyanides attached to iron in different oxidation states (ferri- and ferrocyanides), as illustrated on page O.4. This is indeed the case as can be seen from the spectra for potassium ferricyanide $[K_3Fe(CN)_6]$, potassium ferrocyanide $[K_4Fe(CN)_6]$, and sodium nickel ferrocyanide $[Na_2NiFe(CN)_6]$ (O.5). Each of these compounds has a distinct absorbance in the infrared and the absorbance is separated from other possible interferences (O.6). Good linearity is found (O.7 and O.8) and the sensitivity is more than adequate for the safety needs, which has been set at 2% in the Safety Analysis.

Sam has also measured the Raman spectra of solid, simulated ferrocyanide materials containing various concentrations of $Na_2NiFe(CN)_6$ (O.9). The method is, again, sufficiently sensitive (O.9) and the response is linear over the range of interest (O.10). Additional data concerning the application of Raman spectroscopy to the qualitative and, perhaps, the quantitative determination of ferrocyanides in simulated and actual wastes are also discussed later in this document (see page 17 of this report).

Sam indicated that his plans are to determine the extent to which other compounds, such as $NaNO_3$, $NaNO_2$, $NaAlO_2$, Na_2CrO_4 , $BiPO_4$, etc. interfere with detection and quantitation of ferrocyanide species. Also, as quickly as possible, Sam plans to employ the Raman and FTIR methods to the quantitative determination of cyanide species in solid, simulated ferrocyanide wastes.

Sam also covered the X-ray diffraction technique that he has investigated. Part of the problem with this technique is that there are no reference diffraction patterns for the $Na_2NiFe(CN)_6$, but there was a pattern for the similar material $K_2NiFe(CN)_6$ (O.11). Good linearity and sensitivity are found for this method (O.12), but the method suffers because it requires the use of a shielded diffractometer and it is time consuming.

Sam reported on the progress by Karl Pool on the development of indirect methods of determining the amount of cyanide species in ferrocyanide wastes. Two methods are being developed for dissolving the ferrocyanide (O.13). One method involves the use of EDTA and ethylenediamine to dissolve the entire sample. In this method the cyanide species is not altered, but the other elements in the sample, such as the Ni, Fe, and Al, are complexed and taken into solution. Both ferri- and ferrocyanides are soluble and enter solution where their concentrations can be determined. In the other method, advantage is taken of the rapid kinetics reported by Mike Lilga for the conversion of $Na_2NiFe(CN)_6$ to $Ni(OH)_2$ and soluble $Fe(CN)_6^{4-}$. Two methods for detecting these soluble species are being developed: ion

chromatography and solution infrared (O.13). Results are illustrated on pages O.14 through O.19. A summary of the FTIR and ion chromatography are shown on page O.20. Good agreement is observed between the two methods and with the results from total carbon and nitrogen analyses.

Sam then covered his and Karl's test plan and future work (O.21 through O.24). A schematic of the "hot cell" version of the FTIR is shown on page O.23.

Laser Raman Studies - In an activity not related to the Waste Tank Safety Program, F. R. (Fred) Reich has been working with scientists at Florida State University to develop a technique to analyze ferrocyanides in core material without having to dissolve or otherwise handle the material. Fred gave some overview, introductory, and logic material before talking about the system that is being developed (P.1 through P.7). Two needs exist that make remote sensing of ferrocyanides a reasonable technique to develop: hot cell operation and in situ waste analyses (P.8). A schematic of the device for hot cell use is shown on page P.9. Part of the system that needed development is the probe tip, since the response to the analyte is dependent on the geometry, type of solid, and other parameters. More details on this effort are shown on pages P.13 and P.14 (the test matrices are shown on pages P.10 through P.12).

Fred then discussed the spectra from reference materials that are shown in the tables on pages P.16 and P.17. The spectra for these materials are shown on pages P.18 through P.21. Although these materials are reference material, there is evidence from other work that these are not pure and may be either solid solutions or a mixture of materials. Therefore, spectra such as the one shown on page P.18 for sodium ferrocyanide [$\text{Na}_4\text{Fe}(\text{CN})_6$] have extra peaks that are not readily explained. Similarly, splitting of other peaks is also evident (P.18 for sodium ferricyanide [$\text{Na}_3\text{Fe}(\text{CN})_6$]). Work has also been performed using surrogate materials (P.23). This work, however, is very preliminary and the spectra were obtained before any baseline data had been collected on the reference material. These spectra were used only to show that clean spectra could be obtained. The assignment of the peaks and the wave numbers shown should be viewed in this context only. These spectra are shown on pages P.24 for NaNO_3 and Na_2SO_4 in three surrogate materials and for "ferrocyanides" on page P.25. Work is continuing with these materials to better characterize the spectra from the surrogate materials. Fred summarized the ferrocyanide and nitrate Raman results on page P.26.

Fred also discussed the work that has been done to determine the interference between pH and NaNO_3 (P.27 through P.31). The conclusion from this investigation (P.31) is that over the range of pH from 7 to 14, no change in the Raman lines for NaNO_3 was observed and ionic strength effects are small but significant.

Limits of detection for ferrocyanide and NaNO_3 were also measured for the Raman technique (P.32 through P.38). The limits of detection are well within the range of those needed for the safety analysis, which has a lower bound for ferrocyanide of less than 2%. The limit of detection is $4 \cdot 10^{-4}$ M for ferrocyanide (P.37).

One potential problem with the Raman technique is the presence of fluorescence that tends to interfere with the detection of the analyte. The main fluorescent compounds are uranyl ion, lanthanum ion, and neodymium ion. The scientists at Florida State University found negligible interference from these ions (P.39 through P.41).

Proposed work for the remainder of this year was also discussed by Fred (P.42).

Remaining Work - What remains to be done to close the ferrocyanide unreviewed safety question (USQ) was covered by the Westinghouse Hanford Company Program Manager, R. J. (Bob) Cash. Bob's remarks were divided into three parts:

- Part A: Review of Waste Tank Safety Logic
- Part B: Resolution of the USQ - What we need to know about the ferrocyanide safety issues.
- Part C: Schedule for Resolution of the USQ.

At a previous Tank Waste Science Panel meeting, Bob had presented and discussed diagrams which illustrate the logic being followed to resolve the ferrocyanide USQ. His discussion elicited no comments from the Science Panel members, but his viewgraph's completely and succinctly summarize what is currently known about the ferrocyanide USQ (Q.9 through Q.14). Review of the content of this material shows that the statements made follow closely from the results of the aging studies and the work carried out by Hans Fauske discussed above. Since all members of the Science Panel were in general accord with the findings as stated by Bob, there was little discussion of them.

Bob's final remarks, which elicited considerable attention from the Science Panel members, were directed toward a schedule for the resolution of the ferrocyanide USQ. This schedule, advanced by Bob, calls for

- submitting the USQ Resolution Plan to the Department of Energy by January 22, 1993
- taking and analyzing core samples from Tanks 109-C, 108-C, 111-C, 104-BY, and, perhaps 107-C
- requesting removal of the ferrocyanide USQ by mid to late FY 1994.

Tank Vapor Issues

This meeting marked the first occasion for the Science Panel to hear and discuss presentations on any of the eight organic waste tanks currently with USQs. One of these tanks, Tank 241-C-103 (referred to as 103-C) is known to contain a layer of organic solution floating on a large volume of aqueous alkaline waste solution. Tank 103-C as discussed subsequently, and its safety issues are currently of paramount concern. The other seven organic waste tanks on the USQ lists are thought to contain sufficient amounts of water-soluble organic materials to be of potential concern with respect to a dangerous thermal reaction. A report, by Reynolds, Schulz, and Strachan (1993) has been prepared to provide complete historical background and other information on the organic waste tanks to members of the Science Panel. One of the safety issues associated with the organic waste on Tank 103-C is the vapors that could be escaping the tank and possibly resulting in worker exposures to potentially toxic and/or noxious materials.

J. W. (Jerry) Osborne (WHC) presented information in two areas: the organic liquid and vapor in Tank 103-C and the need for an integrated computer model for the tank farm. As indicated earlier, Tank 103-C is far and away of the most concern from a safety standpoint; Tank 103-C is the only one of the eight organic waste tanks known to contain a separate organic phase. The major constituents are known to be tri-butyl phosphate diluted with normal paraffin hydrocarbons.

Jerry stated that the current intense interest in the composition and properties of the organic wastes in Tank 103-C stems from the 18 separate worker health incidents involving this tank which have occurred in the period 1967-1992. These incidents are thought to have resulted in two partial disabilities and several headaches and transient throat irritations, all of which have occurred in workers who were working near Tank 103-C. Several workers have also reported a noticeable fishy odor at certain times in the vicinity of Tank 103-C.

To prevent any further worker exposure to noxious vapors from Tank 103-C, administrative controls have been placed on access to the tank and environs. These controls include:

- All workers must be supplied with fresh air.
- Work restrictions equivalent to those for flammable gas tanks are enforced.

To resolve the Tank 103-C "vapors" issue, a program has been instituted whose key elements are

- Develop and implement dome gas sampling.
- Implement training communications.
- Design and install positive engineering controls for release of volatile organic materials.

A primary purpose of the tank dome sampling program is to characterize the dome space well enough to bound industrial safety risks, quantify concentrations of volatile materials, and identify toxic components. Currently, the dome sampling program is involved in testing gas sampling equipment and methodology, selecting and validating analytical methods to apply to determination of various components in the gas samples, and in actual collection, concentration, and analysis of tank vapors.

Jerry also presented some preliminary, but highly interesting, gas chromatographic/mass spectrometric (GS/MS) data obtained on vapor samples collected by two different sampling processes after the vapors had first passed through a HEPA filter. In one case, vapors were passed through multisorbent sampling tubes containing Chromosorb 106. These tubes are used at the Oak Ridge National Laboratory. Evacuated stainless steel containers of a type devised by Sandia National Laboratory personnel were also used to collect vapors exiting the HEPA filter.

Results from the GC/MS analyses of organic molecules in both types of sample collection devices showed the presence (0.3 to 1.7 ppm) of various aliphatic nitriles (cyanosubstituted alkanes), e.g., acetonitrile, propanenitrile, etc. Acetonitrile and butanenitrile are highly toxic substances; for example, the Threshold Lethal Value for acetonitrile is 40 ppm. Interestingly, aliphatic nitriles were also stated to be present in vapor samples taken by means of cryogenic techniques from Tank 103-C in the late 1980s. The source of these aliphatic nitriles in Tank 103-C vapors needs to be identified, but it is possible for organonitriles to be the result of a reaction of acetone with materials in the HEPA filter or the gasket

material. The source of acetone in the Tank 103-C dome space is not readily apparent, but Dan Reynolds indicated that acetone is always found in evaporator condensate.

Jerry also stated that efforts are continuing to develop equipment and procedures for direct sampling of the gas in the dome space of Tank 103-C. He also stated that samples of the vapors in Tank 104-BY, also an organic waste tank, were sampled both in December 1992 and in January 1993. In both cases, gas samples were taken after the vapors had exited a HEPA filter on the tank.

In response to several questions from Science Panel members concerning remediation of Tank 103-C by removal of the offending layer of solvent, Jerry indicated present thinking is that it will be 5 to 6 years before all systems are in place to permit safe removal of the organic solvent.

The last portion of Jerry's presentation centered on the question of the need for and utility of an Integrated Computer Model of the C-Farm and, perhaps, other farms as well. This computer model would be used to determine when conditions were right for vapors to exit the tank in sufficient quantity that unprotected workers could experience health effects. The ability to predict these potential events would enable workers to work in the farm without fresh air equipment except when it was predicted such equipment would be needed.

Jerry discussed the model in general terms, suggesting the types of data that might be needed on the source term (R.2 and R.3). In combination with the source-term data, meteorological data (R.4), local site data (R.5), and receptor (worker) (R.6) data are also needed. From these data a mathematical model of the farm and the various interactions and pathways would be developed. Individually and collectively, the members of the Tank Waste Science Panel felt this was a long-term project and did not see any merit to development of such a comprehensive model, especially based on past experience with attempts at meteorological modeling.

Recommendations By The Tank Waste Science Panel Members

In closed session, the Tank Waste Science Panel members discussed the presentations of the meeting. A brief overview of these recommendations were documented in a letter from Denis Strachan and Wally Schulz (S.1). The recommendations in that letter were not complete and, therefore, the comments and recommendations shown below differ from those in the letter.

Recommendations and Comments to the Flammable Gas Program

- The overview given by Jerry Johnson was very good. It showed that, as Program Manager, Jerry has a good handle on the direction the overall program should be taking to solve the issues associated with Tank 241-SY-101.
- The Science Panel members were strong in their assertion that the organics in Tank 101-SY waste be identified. The analytical methods developed to obtain these data will prove to be very useful for other wastes and other parts of the Tank Waste Safety Programs at Westinghouse Hanford Company. In addition, it is important to know that the conclusions of work carried out using simulated wastes

are correct and that the gas generation mechanism developed in this work is applicable to the real wastes. An incorrect understanding of the mechanism could have implications to mitigation, remediation, pretreatment, and disposal of the waste from Tank 241-SY-101 and other wastes in which flammable gases are generated.

- There was concern among the Science Panel members that Jim Campbell is being requested to search for possible new organic chemicals in the waste from Tank 241-SY-101 when he has not fully completed the search for the organics suspected of being present in the waste. A search for other organics should be undertaken only after the search for the organics identified in the simulated waste work has been exhausted. The results of this search will shed light on the validity of the mechanism developed to date in this program.
- Data from the instruments on the Tank 101-SY seem to be unreliable; results from the standards suggest that the instruments are either not operating or are not functioning properly. It is recommended that staff at Westinghouse Hanford Company be assigned to each of the instruments in an effort to gain reliable and meaningful data on the gas composition of the gases coming from the tank. In particular, reliable data are needed for the baseline information so much needed for the operation of the mixer pump. As much data as possible should be extracted from the operation of the mixer pump.
- From the work that George Fox presented, it is clear that heat transfer data are needed. Thermocouples on the side of the tank would be useful in this regard and should not be difficult to install.
- More than two codes are not needed to support the modeling activities for the Flammable Gas Program. Two codes are needed, however, as validation of the calculations performed in support of the mixer pump activities. Two codes may be particularly useful if problems can be performed more quickly with one code than with the other. It is recommended that the GOTH and TEMPEST - T codes continue to be used.
- The key weak point in the models used to date is the absence of accurate knowledge of the waste properties. Every effort ought to be made to obtain physical property data on the waste in the tank, such as viscosity, gas content, and shear strength. These data, while difficult to obtain, are critical to our understanding of this and other wastes in the tanks at Hanford.
- There was some concern among the Science Panel members about the future direction of the modeling efforts. It was suggested that an intensive workshop be held on the subject of modeling to better focus the modeling efforts.
- Some of the Science Panel members expressed concern that the shortcomings of the existing models may give rise to a false sense of understanding about the behavior of the waste and this could have serious implications for mitigation and, later, treatment.
- The simulated waste work still seems to be lacking some direction. This, combined with the lack of apparent reliable results from the work with the actual waste from Tank 101-SY, suggests to the members of the Science Panel that a workshop should be held in an effort to help provide direction.

- The work being carried out at Westinghouse Hanford Company on the generation of gases from actual Tank 101-SY samples needs to be redirected. The work has been in a state of disrepair now for at least two Science Panel meetings. In June 1991, Science Panel members suggested changes to the experimental apparatus. At this meeting, the first indications that changes would be made were discussed. From the Science Panel members' perspective, changes have been too long in coming. The data presented to the Science Panel to date are, in the opinion of the Science Panel members, flawed and much work is needed to recover to a credible position.
- The work with the actual waste from Tank 101-SY needs to be redone. The data do not appear to be reliable. In particular, the presence of significant concentrations of CH_4 indicate that something is wrong with the experiment. The Science Panel members recommend that the temperature of the experiment be lowered to that of the tank to see if the CH_4 decreases.
- It is clear that dramatic changes result from the irradiation of the simulated wastes. Thus, more work is needed in identifying the changes in the organic chemical mix and any possible ramifications to the chemical mechanism developed at the Georgia Institute of Technology.
- The analytical development work done by Sam Bryan, Karl Pool, and Jim Campbell seems to be on track. However, it is recommended that a group of outside consultants, experts in analytical chemistry and organic analytical chemistry, meet with Jim Campbell to validate his approach to the analysis of the organics in Tank 101-SY. The Science Panel members are confident that the approach is correct, but it would be worthwhile to make sure there are no other methods that could be useful or better in the analysis.
- The Science Panel members were critical of the Raman work being developed at Florida State University. The members believe that the use of this technique to determine the amount of ferrocyanide in the waste is, at best, a qualitative tool with which the presence or absence of ferrocyanide could be determined. This method could not be used for the quantitation of ferrocyanide because of the problems associated with sample inhomogeneity. Thus, the method might be useful in determining the location of significant quantities of ferrocyanide in a core of material taken from the tank after which the section of core could be analyzed using methods such as those being developed by Sam and Karl. In the final analysis, the Science Panel members could not recommend that this work continue to be pursued.
- High compliments were made for the work presented by Brett Simpson. It was clear to the Science Panel members that Brett had been given the time and the freedom to analyze the data and to correlate the information together with other information to make a cohesive story. The Science Panel members encourage more of this activity.
- Progress in the aging studies for ferrocyanide wastes has been slow. In part, the lack of progress is due to funding problems. Hopefully, these have been sorted out and more rapid progress will be made by the next meeting. The Science Panel members are concerned with the need and justification for simulated waste work. This subject could also be discussed at a workshop.

- No recommendation could be made by the Science Panel members for a comprehensive computer model for the emanation of toxic vapors from tanks. While this might be a useful weapon in the arsenal for preventing worker exposure to toxic vapors in the case when nothing could be done to correct the problem, it seems that if toxic vapors can be demonstrated to be coming from one or more tanks remediation of the problem is the better course to take.

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Appendix A

Attendance at the Tank Waste Science Panel Meeting

Appendix A**Attendance at the Tank Waste Science Panel Meeting**

Name	Organization
Rudy Allemann	Pacific Northwest Laboratory
Harry Babad	Westinghouse Hanford Company
Roger Bean	Pacific Northwest Laboratory
Ned Bibler	Westinghouse Savannah River Company
George Borsheim	Westinghouse Hanford Company
Sam Bryan	Pacific Northwest Laboratory
Lee Burger	Pacific Northwest Laboratory
Jim Campbell	Pacific Northwest Laboratory
Bob Cash	Westinghouse Hanford Company
Hans Fauske	Fauske Associates
George Fox	Westinghouse Hanford Company
Dave Jepson	Westinghouse Hanford Company
Jerry Johnson	Westinghouse Hanford Company
Mike Lilga	Pacific Northwest Laboratory
Norton McDuffie	Westinghouse Hanford Company
George Mellinger	Pacific Northwest Laboratory
Jerry Osborne	Westinghouse Hanford Company
Larry Pederson	Pacific Northwest Laboratory
Dave Pepson	Department of Energy, Headquarters
Jim Person	Westinghouse Hanford Company
Fred Reich	Westinghouse Hanford Company
Dan Reynolds	Westinghouse Hanford Company
Gary Rosenwald	Department of Energy, Richland Operations
Glen Russell	Iowa State University
K. Sathyanarayana	Westinghouse Hanford Company
Gary Schiefelbein	Pacific Northwest Laboratory
Wally Schulz	Consultant
Darryl Siemer	Westinghouse Idaho Nuclear Company
Brett Simpson	Westinghouse Hanford Company
Leon Stock	Argonne National Laboratory
Denis Strachan	Pacific Northwest Laboratory
Bill Thomson	Washington State University
M. Thurgood	Numerical Applications, Inc.
Dave Turner	Westinghouse Hanford Company
Graham Wallis	Dartmouth College

Appendix B

Agenda for the Tank Waste Science Panel Meeting

**AGENDA FOR THE
TANK WASTE SCIENCE PANEL MEETING
JANUARY 12-14, 1993
RICHLAND, WA**

TUESDAY, JANUARY 12

8:00 Badge-in at the main Receptionist and travel to ISB-1 White Bluffs Room

8:30 Welcoming Remarks Denis Strachan

Flammable Gas Safety Program

9:00 Common Link to Other Tanks Jerry Johnson

10:00 Break

10:15 Temperature Behavior of Tank 241-SY-101
Rudy Allemann
Tom Burke
George Fox

12:00 Lunch

12:30 Tank Modeling Results
Rudy Allemann
Tom Burke

1:45 Extent of the Simulated Waste Studies
Larry Pederson
Sam Bryan
Jim Person

3:15 Results from the Analytical Chemistry
Studies
Jim Campbell
Sam Bryan
FSU Representative
(FR Reich)

WEDNESDAY, JANUARY 13

Ferrocyanide Program

8:00 Aging of Ferrocyanide Wastes
Mike Lilga
Randy Scheele
Lee Burger

9:00 Results from the Studies at Fauske &
Associates, Inc. Hans Fauske

10:30 Break

10:45 Results from C-112 & C-109 Ferrocyanide
Tank Core Samples

Brett Simpson

11:30 What Remains to Close the Unresolved
Unreviewed Safety Question?

Bob Cash

12:00 Lunch

Toxic Vapor Program

12:30 Introduction of the Toxic Vapor Issues

Jerry Osborne

1:00 The need for an Integrated Computer Model
of the Tank Farm?

Jerry Osborne

2:00 Mitigation/Remediation Methods

Jerry Osborne

3:00 Break

THURSDAY, JANUARY 14

8:00 Open Discussion

Topics for discussion include:

What remains to be done in the simulant waste studies? Is the focus correct? How far do we need to go with the kinetic mechanism and why? What should be done at WHC with the samples of the actual waste? What is the cause of the changes in gas composition between in-tank and ex-tank?

What is needed in tank modeling? Why two or three codes? Is one code sufficient? At what point is one code sufficient for the job? Is the underlying physics correct?

What is needed to close the ferrocyanide USQ? Is there something that is missing that is critically needed?

How shall we document our discussions and transmit our recommendations to WHC in manner that is of maximum use to them?

When shall we hold our next meeting?

10:00 Executive Session

12:00 Close

Appendix C

Flammable Gas Program Overview

FLAMMABLE GAS PROGRAM OVERVIEW

Presented to:

WASTE TANK SCIENCE PANEL

January 12, 1993

Jerry Johnson

Westinghouse Hanford Co.

TOPICS

- POSSIBLE LINKS TO OTHER SAFETY ISSUES
- CHEMISTRY ISSUES
- MODELING ISSUES

POTENTIAL LINKS TO OTHER SAFETY ISSUES

(Miscellaneous Thoughts)

- 24 TANKS HAVE BEEN DECLARED TO HAVE THE POTENTIAL FOR THE GENERATION AND RELEASE OF FLAMMABLE GASES
 - 6 Double Shell Tanks
 - 18 Single Shell Tanks
- EXAMPLES OF SURFACE LEVEL DATA
 - Unabated slurry growth
- COMMON FACTORS FOR FLAMMABLE GAS TANKS
 - Slurry Growth
 - Surface Fluctuations
 - Double Shell Slurry Feed and/or Complexant Concentrate
 - Full or Nearly Full Tank
 - Presumed High Solids Content

Rank 101-SY - Surface Level Readings

FOR INFORMATION ONLY

Surface Level Readings
AUTOMATIC FIC
101-SY

Date range of data: 01/05/81 - 08/31/92

Surface Level Readings
AUTOMATIC FIC
103-SY

Date range of data: 05/81 - 12/30/95

Surface Level Readings
AUTOMATIC FIC
103-AN

Date range of data: 01/02/84 - 03/12/92

Surface Level Readings AUTOMATIC FIC 104-AN

Date range of data: 107/85 - 09/10/92

Tank 102-S - Surface Level Readings

Tank 106-SX - Surface Level Readings

FOR INFORMATION ONLY

Tank 110-T - Surface Level Readings

Square - Automatic FC Diamond - Manual FC Plus - Intrusion FC

Tank 105-U - Surface Level Readings

Flammable Gas Watch List Tanks

Original Rank	Tank No.	Waste Volume, Kgal	Waste Type	Volume of Salt Cake, Kgal	Pumpable Liquid, Kgal	Chemistry ?	Date of Last Picture	Remarks
1	101-SY	1111	CC+DSSF	560	252	Yes	(TV)	
2	103-SX	652	NCPLX	536	211	Yes	12-17-87	
3	105-SX	683	DSSF	610	238	Yes	6-15-88	
4	103-AN	952	DSS	0	15		10-29-87	
5	103-SY	747	CC	4	170	Some	10-01-85	
6	104-SX	614	DSSF	478	195	Yes	09-08-88	
7	104-AN	1064	DSSF	0	803		08-19-88	
8	102-SX	543	DSSF	426	177	Yes	01-07-88	
9	101-A	953	DSSF	950	390	Yes	08-21-85	
10	101-AX	748	DSSF	745	298	Yes	08-18-87	
11	105-AN	1128	DSSF	0	1128		01-26-88	
12	112-S	637	NCPLX	631	112	Yes	03-24-87	
13	101-SX	456	DC	343	124	Yes	03-10-89	
14	111-S	596	NCPLX	447	134	Yes	08-10-89	
15	106-SX	538	DSSF	465	233	Yes	06-01-89	
16	102-S	549	NCPLX	545	208	Yes	03-18-88	
17	110-T	379	NCPLX	0	36	Yes	07-12-84	
18	103-U	468	CC	423	166	Yes	09-13-88	
19	103-AX	112	NCPLX	110	3	Yes	08-13-87	Stabilized 8/87
20	109-SX	250	NCPLX	0	0	No	05-21-86	Stabilized 5/81
21	109-U	463	NCPLX	396	160	Yes	07-07-88	
22	105-U	418	NCPLX	349	157	Yes	07-07-88	
23	108-U	468	NCPLX	415	174	Yes	09-12-84	
	101-AW	1126	DSSF	0	1042	Yes	03-17-88	

CC: Complexant Concentrate Waste
 DC: Dilute Complexant Waste
 DSS: Double-Shell Slurry
 DSSF: Double-Shell Slurry Feed
 NCPLX: Non-Complexed Waste

POTENTIAL LINKS TO OTHER SAFETY ISSUES

(continued)

- "ORGANIC" TANKS
- THERE ARE 7 TANKS THAT HAVE BEEN DECLARED TO HAVE A POTENTIAL RUNAWAY ORGANIC-NITRATE/NITRITE REACTION
 - Need > 10 wt% (dry) sodium acetate equivalent
- ORGANIC TANKS: 103-B, 103-C, 102-S, 106-SX, 118-TX, 106-U AND 107-U
 - 102-S AND 107-U HAVE DSSF, THE OTHERS ARE NCPLX
 - 102-S AND 106-SX ARE ALSO FLAMMABLE GAS TANKS
 - 118-TX IS ALSO A FERROCYANIDE TANK
 - 103-C IS ALSO A NOXIOUS VAPOR TANK
 - "NCPLX" STANDS FOR NON-COMPLEXANT WASTES
- THERE ARE OTHERS DSTs THAT ARE NOT ON ANY WATCHLIST. BUT HAVE DSSF OR CC TYPE WASTE
 - MOST DSTs RECEIVED WASTE THAT COULD HAVE BEEN IN VARIOUS SSTs
- BOTTOM LINE: WE FEEL THAT THERE MAY BE SOME COMMON LINKS ON THE CHEMISTRY FOR THE SAFETY ISSUES. YOUR THOUGHTS ON THIS WOULD BE HELPFULL TO OUR PROGRAM PLANS

CHEMISTRY ISSUES

- IDENTIFY MAJOR ORGANIC CONSTITUENTS IN 101-SY
 - Are the end products formate, acetate and oxalate ?
- DEFINE PATHWAY FOR FORMATION OF NITROUS OXIDE AND NITROGEN
- CONDUCT TESTS WITH SYNTHETIC WASTE THAT MATCHES 101-SY IN ALL ASPECTS EXCEPT FOR RADIONUCLIDES
 - Need to try and match gas composition of 101-SY
 - Need to account for any catalytic effects
 - May need to pre-irradiate the organics in order to get the correct species
- NEED TO UNDERSTAND MECHANISMS FOR GAS RETENTION AND RELEASE
- RESOLVE PRODUCTION OF METHANE IN 101-SY GAS GENERATION TESTS
- DETERMINE EFFECTS OF HEATING AND DILUTION ON GAS PRODUCTION AND PHYSICAL PROPERTIES
- NEED ACCURATE DETERMINATION OF BACKGROUND AND "BURP" GAS COMPOSITION FOR 101-SY
 - Will use MOS sensor, chemical sensors, mass spectrometer, GC, FTIR for on-line measurements

Comparison of Nitrous Oxide and Hydrogen with FTIR and GC

Example of Infrared Spectrum Shows Unique Signature of Species

- This is the first spectrum obtained from 10SY
- Show that there are no other infrared active species besides ammonia and nitrous oxide
- bottom figure shows blow up of ammonia region
- level of nitrous oxide is approximately 25 ppm
- level of ammonia is approximately 35 ppm

Chromatogram of 50 ppm calibration gas and hydrogen in air demonstrate sensitivity of reduction gas detector to hydrogen

CHEMSITRY ISSUES

(continued)

- COMPATIBILITY OF WASTES: MIXING AND DILUTION FOR MITIGATION AND REMEDIATION
- LINK OF ISSUES TO PRETREATMENT, GROUT AND HWVP
- ONE CONCERN: IF SUBCRITICAL OXIDATION IS USED TO DESTROY THE ORGANICS (i.e., TO OXALATE) TO STOP PRODUCTION OF HYDROGEN, DO WE STILL PRODUCE NITROUS OXIDE, NITROGEN AND ENOUGH HYDROGEN FROM RADIOLYSIS OF WATER SUCH THAT THERE STILL IS A GAS GENERATION AND RELEASE PROBLEM ?

ADDITIONAL CHEMISTRY INFORMATION

- A SPECIAL MEETING WAS HELD IN DECEMBER TO OBTAIN INPUT FROM VARIOUS PEOPLE WHO HAD WORKED AT TANK FARMS IN THE PAST. FROM THOSE WHO HAD BEEN INVOLVED WITH THE "CHEMISTRY", THEY IDENTIFIED ORGANIC COMPOUNDS THAT WERE USED IN THE PROCESSING THAT WE HAD NOT CONSIDERED FOR OUR LABORATORY EVALUATIONS.
- THREE COMPOUNDS TO BE CONSIDERED:
 1. SUCROSE
 2. DIETHYLENE TRIAMINE PENTAACETIC ACID (DTPA)
 3. DI-2-EHTYL HEXAPHOSPHORIC ACID

MODELING ISSUES

- THERMAL BEHAVIOR OF WASTE
 - APPEAR TO HAVE COOLING OF WASTE GREATER THAN THAT DUE TO DECAY OF CESIUM-137.
 - THIS WILL TEND TO INCREASE THE VISCOSITY AND YIELD STRENGTH OF THE WASTE, WHICH IN TURN MAY LEAD TO MORE RETENTION OF GAS. IT MAY ALSO RESULT IN LONGER TIMES BETWEEN GAS RELEASE EVENTS.
 - POSSIBLE EFFECT ON GENERATION RATE
 - WOULD COOLING OF NON-WATCH LIST TANKS RESULT IN THE CREATION OF A TANK LIKE 101-SY ?
 - WHAT IS THE CONTRIBUTION TO THE HEAT LOAD FROM CHEMICAL REACTIONS ?
- PHYSICS OF GAS RETENTION AND RELEASE
 - THERE ARE 3 CODES USED TO MODEL THE BEHAVIOR OF THE WASTE AND EFFECTS OF THE MIXING PUMP
 - NONE OF THE CODES MODEL THE ACTUAL MECHANISMS FOR GAS RETENTION AND RELEASE. THEY ALL ASSUME THAT GAS WILL BE RELEASED WHEN A CERTAIN CONDITION EXISTS, E.G., WHEN THE NON-CONVECTIVE LAYER REACHES A CERTAIN VOID FRACTION OR DENSITY RELATIVE TO THE CONVECTIVE LAYER.
 - QUESTION: IF GASES ARE CHEMICALLY TRAPPED, WILL MIXING PRODUCE A GAS RELEASE ?

Appendix D

Temperature Behavior of Tank 241-SY-101

TEMPERATURE BEHAVIOR OF TANK 241-SY-101

PRESENTATION TO:

TANK WASTE SCIENCE PANEL

JANUARY 12-14, 1993

RICHLAND, WASHINGTON

BY: R.T. ALLEMANN, PNL

TANK TEMPERATURE PROFILE OBSERVATIONS

- 1. SINCE DECEMBER 1991, TANK IS COOLING MORE RAPIDLY**
- 2. SINCE SEPTEMBER 1992, NON CONVECTIVE LAYER IS DEEPER**
- 3. TIME BETWEEN GRE'S HAS INCREASED**
- 4. LEVEL AND/OR LEVEL RATE REDUCTIONS SHOW CORRELATION TO TEMPERATURE CHANGES INDEPENDENT OF GAS RELEASE**

101-SY TEMPERATURE BEHAVIOR

Peak Temperature Prior to Tank 101-SY Gas Release Event

FROM G.D. JOHNSON (TAP MEETING 4/29/92)

Tank 241-SY-101 Temperature Profile MIT (Riser 178)

+ 09/11/92 * 11/19/92 x 1/5/93
 □ 1/6/93 * 1/7/93 ▣ 1/8/93

TABLE 1. Temperature Effect History of 241-SY-101

DATE	$T_{\max}/^{\circ}\text{F}$	$T_{\text{nop}}/^{\circ}\text{F}$ cl.	$T_{\text{ave}}/^{\circ}\text{F}$	(rel. reaction rate) $^{-1}$	Time from last burp / days	Size of Burp/ inches
10/24/90	137	122	132	1	81	11.1
2/11/91	138	120	132	1	110	5
5/16/91	135	118	129.3	1.20	89	7.2
8/27/91	134	119	129	1.23	103	6
12/4/91	133	114	126.7	1.45	99	13
4/20/92	124	111.5	119.8	2.37	138	7.2
9/3/92	124.5	115	121.3	2.12	137	14.3
1/8/92	126	107	119.6	2.4	129	

Table 1. Historical Level of Top of N.C. Layer in Tank 241-SY-101

Date	Level of bottom of Constant Temperature Layer / in.
8/5/90	190
10/24/90	204
2/16/91	195
5/16/91	185
8/27/91	180
12/4/91	195
5/20/92	180
9/3/92	210

1/17/93 (Current value)	250

Tank 241-SY-101 Temperature Profile MIT (Riser 17B)

Tank 241-SY-101 Surface Level FIC, Radar Gauge, and Manual Tape

— Radar Gauge + FIC * Manual Tape

ESTIMATED LAYER CONDITIONS
(NOV 10, 1992)

	<u>ΔH</u>	<u>sp.g.</u>	<u>$(1 - \alpha)$</u>	<u>ΔP</u> (ATM)	<u>P</u> (ATM)	<u>P</u> (ATM)
CRUST	4'	1.3	-	.153	1.15	1.07
LIQUID	9'	1.5	0	.398	1.55	1.35
NEW N.Conv.	4.1	1.6	.8	.202	1.75	1.65
OLD N.Conv.	<u>16.7</u>	1.7	.85	.813	2.6	2.17
	33.8 (406")					

BASAL RETENTION RATE

GAS RETAINED IN 16.7' OF N.C. LAYER AT AVE. PRESS. OF 2.17 atm GAVE THE GROWTH RATE OF 0.08"/DAY AT $\alpha=0.15$ ($1-\alpha=0.85$)

$$\dot{H} A = \dot{v} H_{N.C.} A (1-\alpha) \frac{P_0}{P}$$

H = RATE OF LEVEL RISE

A = TANK AREA

$\dot{v}$ = VOL. FRACTION GAS RETENTION RATE AT P_0

P = PRESSURE

α = VOID FRACTION

$$\dot{v} = \frac{H}{H_{N.C.}} \frac{P}{P_0} \frac{1}{1-\alpha} = \frac{.08}{16.7} \frac{2.17}{.85} = 0.0123''/ft \text{ waste @ } 1 \text{ atm}$$

LEVEL GROWTH FOR ENTIRE TANK

$$\dot{H} = \int (1-\alpha) \dot{v} \frac{P_O}{P} d H_{N.C.}$$

or

$$\dot{H} = \sum_{layers} (1-\alpha) \dot{v} \frac{P_O}{P} \Delta H_{N.C.}$$

EXPECTED RATE IS:

$$\dot{H} = \frac{.0123 \times .85 \times 16.7}{2.17} + \frac{.0123 \times .8 \times 4.13}{1.65}$$

$$\begin{aligned} &= .08 & + & .031 \\ &= 0.11 & \text{vs measured } & 0.1056 \end{aligned}$$

TIME TO REACH NEUTRAL BUOYANCY

$$\frac{d\alpha}{dt} = \frac{\dot{v}}{12} (1-\alpha) \frac{Po}{P}$$

$$\frac{d\alpha}{1-\alpha} = \frac{\dot{v}}{12} \frac{Po}{P} dt$$

D.12

Solving

$$\frac{1-\alpha}{1-\alpha_1} = e^{\frac{-\dot{v}}{12} \cdot \frac{Po}{P} t}$$

$$t = - \left(\log \frac{1-\alpha}{1-\alpha_1} \right) \left(\frac{12}{\dot{v}} \frac{P}{Po} \right)$$

TIME TO REACH NEUTRAL BUOYANCY

$$t = - \ln \frac{1-\alpha}{1-\alpha_1} \frac{12}{\dot{v}} \frac{P}{P_0}$$

To 4' layer $\alpha_1 = .8$

$$t = -\ln \frac{.76}{.8} \frac{12 \times 1.65}{.0123} = 83 \text{ days}$$

Bottom 16.7' layer $\alpha_1 = .85$

$$t = -\ln \frac{.76}{.85} \frac{12 \times 2.17}{.0123} = 227 \text{ days}$$

VOID FRACTION AT NEUTRAL BUOYANCY

$$\alpha = 1 - \frac{1}{1 + \epsilon \left(\frac{P_g}{P_l} - 1 \right)}$$

$$\alpha = 1 - \frac{1}{1 + .7 \left(\frac{2.2}{1.5} - 1 \right)} = .24$$

$$1 - \alpha = .75$$

CONCLUSIONS

- DEEPER N.C. LAYER ACCOUNTS FOR INCREASED LEVEL RATE
- UPPER LAYER SHOULD OVERTURN SOONER THAN BOTTOM LAYER

FORMULAS

$$\Delta P = \rho \ g \Delta H = \frac{Sp.g. \ \Delta H}{33.9}$$

$$1 - \alpha = \frac{P_{N.C.}}{P_{mix}}$$

$$P_{mix} = (1 - \epsilon_s) P_o + \epsilon_s P_s$$

With $\epsilon = .7$ and $P_s = 2.2$, then $P_{mix} = 1.98$

$$P_{N.C.} = (1 - \alpha) P_{mix}$$

$$\rho = sp.g.$$

Where:

ΔP = change in pressure

ρ = density (or specific gravity)

g = gravitational acceleration

ΔH = thickness of layer

α = void fraction

ϵ_s = volume fraction solids (in gasless mixture)

Tank 241-SY-101 Temperature Profile MIT (Riser 17B)

Tank 241-SY-101 Temperature Profile MIT (Riser 178)

+ 09/11/92 * 11/20/92 x 11/22/92
 □ 11/23/92 * 11/24/92 ▣ 11/25/92

Tank 241-SY-101 Temperature Profile MIT (Riser 17B)

Tank 241-SY-101 Surface Level FIC, Radar Gauge, and Manual Tape

— Radar Gauge + FIC Gauge * Manual Tape

Tank 241-SY-101 Surface Level **.FIC, Radar Gauge, and Manual Tape**

Tank 241-SY-101 Temperature Profiles **December 23, 1992**

Old T/C at 20' Radius

—+— VDTT 1B —*— VDTT 14A —X— MIT 17B

at 20' 30' 30' Radius in tank

SUMMARY

- . TEMPERATURES INDICATE THAT THE TANK IS NOT IN STEADY CONDITION
- . ALTHOUGH STATISTICAL EVALUATIONS ARE BEING USED,
THE BASIS IS CHANGING
- . THE DECREASING TEMPERATURES MAY BE THE
CAUSE OF THE BEHAVIORAL CHANGES
- . SOME ANALYSES ARE DIRECTED TOWARD THE REASON FOR THE
TEMPERATURE REDUCTION

Appendix E

Temperature Behavior of Tank 241-SY-101

Temperature Behavior of Tank 241-SY-101

Tank Waste Science Panel Meeting

January 12-14, 1993

George L. Fox

Capsule

- Tank cooling faster than expected
- Chemical heat generation proposed
- Crust likely on tank sidewall

Tank 101-SY Average Temperature (TC #1 Thru #16)

Potential Explanations

- **Heat loss resistance changing**
- **Chemical heat generation which changes**

Tank 101-SY Temperatures (Tank Average and Air Space)

Heat Loss Analysis (convective region)

Heat Gained

Heat Convected

Heat Generated

$$\rho C_p \frac{dT}{dt} = - \frac{\bar{h}A}{V} (T - T_\infty) + \frac{Q'''}{V}$$

$$\bar{h}A = \frac{Q''' - V\rho C_p \frac{dT}{dt}}{T - T_\infty} = 1006 \frac{\text{Btu}}{\text{hr } ^\circ\text{F}}$$

(530 w/k)

Tank Conductance

$$\bar{h} = \frac{\bar{h}A}{A} = 0.12 \frac{\text{Btu}}{\text{ft}^2 \text{ hr } ^\circ\text{F}}$$
$$\left(0.68 \frac{\text{W}}{\text{m}^2 \text{ K}} \right)$$

Crust Thickness

(average top and sidewall)

$$\bar{x} \approx \frac{k_{\text{crust}}}{\bar{h}} = 2.6 \text{ ft}$$
$$(0.79 \text{ m})$$

Crust Parametrics

39301010.9 FH

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Centimeter

Inches

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Appendix F

Application of GOTH to Tank 101-SY Mitigation Modeling

**Application of GOTH to Tank 101-SY
Mitigation Modeling**

**K. Sathyanarayana
Waste Characterization Analysis, WHC**

**M. J. Thurgood and B. C. Fryer
Numerical Applications, Inc.**

**Presented by K. Sathyanarayana at
Tank Waste Science Panel Meeting
January 12, 1993**

Objectives

Estimate Gas Release due to the Operation of the Mitigation System Mixing Pump

- **Quantity of Gas Release**
- **Dome Hydrogen Concentration**

Pump Induced Gas Release

- **24% Neutral Buoyancy Condition**
- **18.9% Neutral Buoyancy Condition**
- **2-D and 3-D Simulations**
- **Estimate Upper Bound on Volume of Gas Released and Dome Hydrogen Concentration**

Summary of Best Estimate Gas Releases 1,000 Seconds Simulation

Case	Initial gas void fraction	Hydrogen concentration %	Vent flow, ft ³	Estimated gas release ft ³
1. Dec 91. Rollover Event	0.189	7.4	7553	11292
2. Oct 90. Rollover Event	0.189-0.17	6.2	8559	12730
3. Pump-Ramp 1, Extended Phase A Condition at 15 FPS	0.185	5.2	8257	12401
4. Pump-Ramp 1, Extended Phase A Condition at 15 FPS	0.134	2.8 3.1	5237 8257	7841 12363 @ 2000 s
5. Pump-Ramp 9, Pump Bump Condition	0.185	5.3	7955	11948
6. Pump-Ramp 9, Pump Bump Condition	0.134	2.0 3.2	2418 4935	3620 7339 @ 2000 s

Pump Induced Rollover

Comparison of GOTH and TEMPEST Models

- **GOTH Provides More Fundamental Model**
 - True Three-Phase
 - Gas Retention/Release via Viscosity and Bubble Size Changes
 - Gas Release from the Waste to the Dome Through Pool/Dome Interface
 - Dome H_2 Concentration
- **TEMPEST Analyses**
 - Faster Running
 - In-House Capability
 - Gas Release Considered as it Crosses the Initial Boundary into the Convective Layer
 - Dome H_2 Concentration using FATHOMS
- **Both Codes Give Similar Results Under Specific Conditions**

Bubble Rise Model

TEMPEST Bubble Rise Velocity:

1) Viscous regime:

$$V = \frac{D^2 g (\rho_c - \rho_g)}{12 \mu}$$

2) Inertial regime:

$$V = \frac{\sqrt{gD}}{2}$$

where

V = Bubble rise velocity

D = Bubble Diameter

ρ_c = Density of continuous phase (solid liquid mixture)

ρ_g = Gas density

μ = Viscosity of continuous phase

Viscosity Models

TEMPEST:

$$\left(\frac{\mu_m}{\mu_c} \right) = (1 - \alpha) K_p^C + \alpha K_g$$

GOTH:

$$\left(\frac{\mu_m}{\mu_c} \right) = (1 - C)^{-2.5 f_{mp}}$$

Where:

μ_m = mixture viscosity

μ_c = continuous phase viscosity

α = gas void fraction

$$K_p = \frac{\mu_{\max}}{\mu_c}$$

$\mu_{\max}$ = cutoff mixture viscosity, 2.5×10^6 cps

$$C = \frac{f_p}{f_{mp}}$$

f_p = local particle fraction

f_{mp} = maximum packing particle fraction

$$K_g = \frac{\mu_g}{\mu_c}$$

μ_g = gas phase viscosity

Comparison of TEMPEST and GOTH Viscosity Correlations

Accomplishments

II. Mitigation Simulations

- **Demonstrated the Importance of the Influence of Gas During Pump Operation**
 - **Potential for Rapid Mixing of Tank Contents**
 - **Potential for Significant Gas Release**
- **Identified the Importance of**
 - **Initial Gas Distribution**
 - **Initial Gas Content**
- **Predicted**
 - **Bounding Gas Release as a Function of Initial Gas Content**
 - **Hydrogen Concentration in Tank Dome during Pump Operation**

Applicability of Results

- **Used for Guidance in Establishing Pump Test Plan**
- **Used to Evaluate Safety of Pump Operation**
- **Being Used for Structural Design of Tank Internal Components**
- **Used to Gain a Better Understanding of Tank Behavior.**

Summary

- **GOTH Provides a State-of-the-Art Transient Three Phase, Three-Dimension Computer Code for Simulation of Rollover and Mitigation in Tank 101-SY (and Others?)**
- **GOTH was able to "Predict" Key Properties of the Core Samples**
- **Some Key Modeling Assumptions Remain Unverified:**
 - **Mixture Viscosity Correlation**
 - **Applicability of Simple Two Bubble Size Model Under Various Conditions**
- **Combination of GOTH and TEMPEST Provide Suitable Numerical Modeling Capability for Hydrogen Mitigation Program**

Appendix G

GOTH Simulation of Tank 101-SY

GOTH Simulation of Tank 101-SY

by

K. Sathyanarayana

M. J. Thurgood

B. C. Fryer

**Presented by M. J. Thurgood at
Tank Waste Science Panel Meeting
January 12, 1993**

GOALS

- Simulate Tank Gas Release Event**
- Validate Simulation Methodology Using Available Tank Data**
- Evaluate the Effect of the Initial Operation of the Mixing Pump on Tank Behavior and Gas release**

MODELING APPROACH

- Use FATHOMS as the basis (Two-fluid, Two-component capability).**
- Add non-Newtonian fluid capability.**
- Add a particle field.**
- Model Viscosity as a function of particle concentration.**
- Perform simulations of Tank 101-SY.**

UNMITIGATED GAS RELEASE EVENTS

- October 1990 release
- December 1991 release
- Others.
- Predict dome hydrogen concentration, vent flow, dome pressure and temperature inversion.

ACCOMPLISHMENTS

I. Roll over and gas release simulations.

- Temperature Inversion Predicted
- High viscosity of non-convective material predicted:
 - Predicted: $2.5-12 \times 10^6$ Cp
 - Later measured: 3.1×10^6 to 6.7×10^6 Cp
- Small particle size predicted:
 - Predicted 25 microns.
 - Later measured: 5 micron sm small group.
100 micron sm large group
- Dome hydrogen concentration and vent flow matched.

PUMP INDUCED GAS RELEASE

- 24% Neutral Buoyancy Condition
- 18.9% Neutral Buoyancy Condition
- 15 ft/s jet velocity
- 2-D and 3-D Simulations
- Estimate upper bound on volume of gas released and dome hydrogen concentration.

BUBBLE MODEL

$\alpha_g < 0.10$ and $\alpha_p > 0.15$ then $d_b = d_p$

otherwise

$d_b = 0.25$ in

Hydrogen Concentration Benchmark to December 4, 1991, Natural Rollover Event

dec9122
Tue Dec 1 09:07:41 1992
GOTH Version 3.4 - April 1991

Vent Flow Benchmark to December 4, 1991, Natural Rollover Event

dec9122
Tue Dec 1 09:07:58 1992
GOTH Version 3.4 - April 1991

Hydrogen Concentration Versus Time for Pump Induced Rollover Event
 Uniform $\alpha_0 = 0.185$, Ramp 1.

cv185pl
 Fri Oct 2 15:31:11 1992
 GOTH Version 3.4 - April 1991

Integrated Vent Flow Versus Time for Pump Induced Rollover Event
 Uniform $\alpha_0 = 0.185$, Ramp 1

cv185pt
 Fri Oct 2 15:39:41 1992
 GOTH Version 3.4 - April 1991

CONCLUSIONS

- A basic understanding of the gas release event phenomena, including the effects of viscosity and particle concentration on viscosity, has been achieved.
- The importance of gas content on tank behavior during mitigation pump operation has been identified and factored into pump test planning and safety analysis. Significant gas release is calculated to occur even at low pump flows and even when the pump is operated for short periods of time.
- Best estimates of the upper bound on the quantity of gas released due to initial pump operation have been provided. The volume of gas released due to pump operation is not expected to be significantly different from the volume of gas released from an unmitigated gas release event.
- Results must be tempered by the limited amount of tank data available.

Appendix H

Tank Modeling Results

TANK MODELING RESULTS

**PRESENTED TO
TANK WASTE SCIENCE PANEL**

JANUARY 12 - 14, 1993

BY: R.T. ALLEMANN

TANK MODELING RESULTS (OUTLINE)

- **MODELING FOR SAFETY - GAS RELEASE AMOUNTS**

FOR TEST ANTICIPATION - HYDROGEN CONCENTRATIONS AT SENSORS

- **GAS RELEASE FROM (TEMPEST)**
 PHASE A TESTS
 STEPPED PUMP-SPEED CASE (PHASE B)
 EXTENDED TRANSIENT (PHASE B)
- **HYDROGEN CONCENTRATIONS (FATHOMS)**
 PHASE A TESTS
 PHASE B (IN PROGRESS)
 HULL VELOCITY JET
- **GAS RELEASE IN ELASTIC MATERIAL (HULL)**
 VELOCITY JET
 CONSTANT PRESSURE JET

T. MICHENER
J. FADEFF
K. SATHYANARAYANA

S. WOOD

K. JOHNSON

Conceptual Illustrations of Tank 241-SY-101 Pump-induced Circulation Patterns

(a) Initial Gas Content Near Neutral Buoyancy

(b) Initial Gas Content $\leq 13\%$

CALCULATED GAS RELEASE ON PUMP START, TEMPEST AND GOTH PREDICTIONS, 101-SY

TEMPEST CALCULATED GAS RELEASE WITH PUMP TESTS

CONCENTRATION CONTOURS AT TOP OF SLUDGE WITH PUMP TEST - 2 MINUTES (TEMPEST)

Plot at time = 2.000 minutes
 TITLE: TANK SY-101 PUMP ON TEST - [ol ramp to 25 fps in 60 seconds
 TITLE: TANK SY-101 PUMP ON TEST - [ol ramp to 25 fps in 60 seconds

17:45:42

TEMPEST/T2.7 • 02AUG92 14AUG92 9/29/92

r-x plane at K = 24

J = 2 to 27

I = 1 to 15

plane min = 0.000*10³
 plane max = 1.423*10³
 array min = 1.332*10³
 array max = 1.510*10³

— 9 —	1.359*10 ³
— 8 —	1.208*10 ³
— 7 —	1.057*10 ³
— 6 —	9.063*10 ²
— 5 —	7.552*10 ²
— 4 —	6.042*10 ²
— 3 —	4.531*10 ²
— 2 —	3.021*10 ²
— 1 —	1.510*10 ²

Attachment 2
 Page 6 of 9

CONCENTRATION CONTOURS AT TOP OF SLUDGE WITH PUMP TEST - 3.5 MINUTES (TEMPEST)

Plot at time = 3.500 minutes
TITLE: TANK SY-101 PUMP ON TEST - jet ramp to 25 fps in 60 seconds
TITLE: TANK SY-101 PUMP ON TEST - jet ramp to 25 fps in 60 seconds

r-x plane at K = 24
J = 2 to 27
I = 1 to 15

plane min = 0.000*10³
plane max = 1.815*10³
array min = 2.406*10³
array max = 1.851*10³

17:45:42

9/29/92

14Aug92

02Aug92

TEMPEST/T2.7

9	1.666*10 ³
8	1.481*10 ³
7	1.296*10 ³
6	1.111*10 ³
5	0.256*10 ³
4	7.404*10 ²
3	5.553*10 ²
2	3.702*10 ²
1	1.851*10 ²

FIGURE 1. FATHOMS Model of Tank 101-SY

- 1 PUMP 12A
- 2 RISER 173
- 3 RISER 16A
- 4 EXHAUST 7A
- 5 INLET 73

Each FATHOMS Cell
is 5 ft. X 2 ft. High

Tank 101-SY Mitigation Hydrogen Release
FATHOMS Results Using Tempest ramp 1

— riser 17B — pump — exhaust — riser 16a

Tank 101-SY Mitigation Hydrogen Release
FATHOMS Results Tempest ramps 2, 3, 7, 8

— riser 17B — pump — exhaust — riser 16A

Tank 101-SY Mitigation Hydrogen Release
FATHOMS Results using Tempest Ramp 9

— riser 17B — pump — exhaust — riser 16A

RELEASE RATES INPUT TO FATHOMS

Table 1 - Ramp 1

Time, T_{s-c} / sec	Gas release rate / ft^3/sec
0-20	0
20-100	0.7
100-250	0.7-20
250-300	20-17.5
300-340	17.5-6
340-460	6-1
460-600	1-0.5
>600	0

Table 2 - Ramp 9

Time, T_{s-c} / sec	Gas release rate / ft^3/sec
0-20	0
20-150	0.7
150-230	0.7-13.8
230-340	13.8-7.6
340-460	7.6-1
460-600	1-0.3
>600	0

Table 3 - Ramps 2,3,7,8

Time, T_{s-c} / sec	Gas release rate / ft^3/sec
0-20	0
20-110	0.7
110-210	0.7-10.5
210-350	10.5-8.5
350-460	8.5-1.5
460-600	1.5-0.5
>600	0

**GAS RELEASE PREDICTIONS, STEPPED PUMP SPEED
(TEMPEST, Fadeff and Sathyanarayana)**

Nozzle Velocity (ft/s)	Pump Speed (rpm)
15	325
24	440
33	540
41	640
48	740
54	840

TEMPEST SIMULATION OF TANK 101-SY

STEPPED PUMP SPEED

GAS RELEASE PREDICTIONS, STEPPED PUMP SPEED
(TEMPEST, Fadeff and Sathyanarayana)
TEMPEST SIMULATION OF TANK 101-SY
JET VELOCITY = 15-24-33-41-48-54 ft/sec

**GAS RELEASE PREDICTIONS, PHASE B EXTENDED TRANSIENT
(TEMPEST, Fadeff and Sathyanarayana)**

Initial gas void fraction	Calculation Case No.	Initial extrapolated total gas release (ft ³)	Calculated total gas release (ft ³)
.134	1	4160	4080
.1565	3	12140	10430
.189	2	15460	15020

TEMPEST SIMULATION OF TANK 101-SY

JET VELOCITY = 60 ft/sec

H.24

H.25

HULL CALCULATION

K. Johnson, PNL

CALCULATED GAS RELEASED FROM NON-CONVECTIVE LAYER
WITH ELASTIC-YIELD BEHAVIOR, TWO 2.6 IN JETS,
TANK 101-SY

HULL GAS RATE ESTIMATE COMPARED TO TEMPEST

Tank 101-SY Mitigation Hydrogen Release FATHOMS Results From HULL Predictions

S. Wood, WHC

Tank 101-SY Mitigation Hydrogen Release FATHOMS Results From HULL Predictions

S. Wood, WHC

ESTIMATED PERFORMANCE OF MIXING PUMP IN 241-SY-101 SLURRY by L. E. Efferding, WHC

CONCLUSIONS

- **HYDROGEN LEVELS OF RELEASE
FROM AN ACTIVE JET WILL BE DETECTABLE**
- **A STAGNATED JET COULD OCCUR AT LOW PUMP RPM,
AND PRODUCE LESS GAS RELEASE.
SLUICE-IN WATER MAY HAVE AN EFFECT**
- **GAS-RELEASE TEST DATA SHOULD HELP DETERMINE
SOME IN-SITU PROPERTIES**

Appendix I

Simulated Tank 241-SY-101 Waste Studies

Simulated Tank 241-SY-101 Waste Studies

Sam Bryan and Larry Pederson
Pacific Northwest Laboratory
Richland, Washington 99352

Tank Waste Science Panel Meeting
Richland, Washington
January 12-14, 1993

Recent Progress

Physical Properties

Organic Destruction

Gas Generation Studies

Solids Settling Rates

Summary:

- settling rates increase steadily with increased dilution of simulated wastes
- settling rates increase with increased temperature
- settling rates diminished by presence of organics
- dependence of waste simulant preparation on settling rates being examined
- identical procedures being used to characterize actual tank waste samples

Sedimentation Velocities in Simulated Wastes

$$\text{velocity} = \frac{(\rho_s - \rho_l) g d_p^2}{18 \eta} (1 - \phi_s)^{4.5}$$

Settling Rate at 60°C for Simulated Waste at Various Dilutions

$$y = a * e^{(-k t)} + b$$

$$\frac{dy}{dt} = -a * k * e^{(-k t)}$$

Settling Velocities Increased with Increased Dilution;
Lowered by the Presence of Organic Complexants
(0.2 M HEDTA + EDTA)

Settling Rates of Solids Increase with Increased Dilution and Temperature

$$\text{solids volume} = a \exp(-kt) + b$$

k = settling rate constant

a, b = constants specific to experiment

Wt% Centrifuged Solids of Synthetic Waste is Affected by Dilution and Temperature

Wt% Centrifuged Solids of Synthetic
Waste is Affected by Dilution,
Temperature, and Organics

Heat Capacity Determination Using the Seebeck Envelope Calorimeter

- calorimeter senses thermal gradient
- area under curve divided by temperature jump yields heat capacity
- simple operation, can be used in hot cell

Organic Destruction

Batch (200-250°C)

Continuous Flow (200-350°C)

Summary:

- Ammonia formed from both organic and inorganic sources
- Nitrite, hydroxide ions consumed
- Oxalate, carbonate produced
- Capacity to produce flammable gases much reduced
- Much reduced solids solubility above 300°C
- Follow-on tests to be conducted under other funding

Total Organic Carbon Lowered by Hydrothermal Oxidation in a Continuous Flow Reactor

Nitrate and Nitrite Ion Concentrations vs.
Temperature for Simulated Tank 101-SY Wastes
in a Continuous Flow Reactor

Hydroxide Ion Consumption versus Temperature
for Simulated Tank 101-SY Wastes
Treated in a Continuous Flow Reactor

ammonia yield for synthetic wastes
heated to 243°C for 1 hour

Regions of Stability of Nitrogen Compounds (Pourbaix Diagram)

1.	$\text{NH}_4^+/\text{NH}_4\text{OH}$	pH=9.27
2.	$\text{HNO}_2/\text{NO}_2^-$	pH=3.35
3.	$\text{HNO}_3/\text{NO}_3^-$	pH=0.00
4.	$\text{NH}_4^+/\text{HNO}_2$	$E_0 = 0.864 - 0.0689 \text{ pH}$
5.	$\text{NH}_4^+/\text{NO}_2^-$	$E_0 = 0.897 - 0.0788 \text{ pH}$
6.	$\text{NH}_4\text{OH}/\text{NO}_2^-$	$E_0 = 0.806 - 0.0689 \text{ pH}$
7.	$\text{HNO}_2/\text{HNO}_3$	$E_0 = 0.934 - 0.0591 \text{ pH}$
8.	$\text{HNO}_2/\text{NO}_3^-$	$E_0 = 0.934 - 0.0886 \text{ pH}$
9.	$\text{NO}_2^-/\text{NO}_3^-$	$E_0 = 0.835 - 0.0591 \text{ pH}$
a.	$\text{H}_2/2\text{H}^+$	$E_0 = 0.000 - 0.0591 \text{ pH}$
b.	$2\text{H}_2\text{O}/\text{O}_2$	$E_0 = 1.228 - 0.0591 \text{ pH}$

Offgas Products from Continuous Flow Reactor Test

Gas Generation from Heat-Treated and Untreated Simulated Wastes (SY1-SIM-91A; 0.15 M HEDTA)

Date: Dec 31, 1992 08: 17am
Scanning Rate: 5.0 C/min
Sample Wt: 8.183 mg Path: a: \
File: TH1011 RLS

Perkin-Elmer TGA7

Date: Dec 22, 1992 2: 59pm
Scanning Rate: 5.0 C/min
Sample Wt: 10.306 mg Path: a: \
File: TH1010 RLS

Perkin-Elmer TGA7

Date: Jan 04, 1993 07:57am
Scanning Rate: 5.0 C/min
Sample Wt: 4.789 mg Path: a:\
File: TH1012 ALS

Perkin-Elmer TGA7

Date: Dec 30, 1992 08:27am
Scanning Rate: 5.0 C/min
Sample Wt: 6.053 mg Path: a:\
File: TH1009 RLS

Perkin-Elmer TGA7

Gas Generation Studies

Summary:

- gas product stoichiometry and formation rates significantly affected by minor waste simulant constituents
 - chloride ions
 - transition metals
- gas product stoichiometry and formation rates also affected by hydroxide ion concentrations
- radiolytic/thermal formation of nitrous oxide increased steadily with increased dilution with 2M NaOH; small effect of dilution on thermal generation of gases

Stoichiometry of Gaseous Products Affected by Minor Waste Constituents

Moles of N_2O Produced as a Function of
Time and Chloride Concentration

Moles of H_2 Produced as a Function of
Time and Chloride Concentration

Moles of Gases Produced as a
Function of Chloride Concentration

Gas Production in Simulated Waste is Affected by Dilution with 2M NaOH

Gas Production from Simulated Wastes Containing Oxalate and Formate

Gas Production from Simulated Wastes Containing Oxalate and Formate

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Future Directions

Integrated Gas Generation Studies

- more realistic organic components in simulant, including formate, oxalate, and acetate
- role of transition metals, noble metals, hydroxide ion concentrations on gas generation kinetics, stoichiometry
- heating and dilution effects
- radiolytic and thermal

Future Directions

Physical Properties

- refinement of solids settling rate measurements, comparison to actual waste behavior
- heat capacity, thermal conductivity hardware and methods to be transferred to hot cell group

Gas Retention

- comprehensive review of literature on stable foams, antifoaming agents
- influence of gas bubble content on rheological properties of slurry; start with well-characterized, monosized oxide slurries; vary identity and concentration of organics

Appendix J

Westinghouse Hanford 101-SY Waste Studies

WESTINGHOUSE HANFORD 101-SY WASTE STUDIES

by

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Westinghouse Hanford Company
Richland, Washington**

presented to

Tank Waste Science Panel Meeting

January 12, 1993

Process Chemistry Laboratory

GAS GENERATION TESTS

OBJECTIVE

**UNDERSTAND GAS GENERATION IN TANK 101-SY,
ESPECIALLY PRODUCTION OF H₂ AND N₂O**

METHOD

**MEASURE GAS PRESSURE BUILDUP, TAKE GAS
SAMPLES FOR MASS ANALYSIS**

**COMPARE SYNTHETIC SLURRIES WITH ACTUAL
SAMPLES FROM TANK 101-SY**

EXPERIMENTS AT 100°C FOR FASTER REACTIONS

Gas Generation
Test Device

GASES FORMED

H₂ AND N₂O ARE FORMED IN DIFFERENT RATIOS IN DIFFERENT MIXTURES

N₂ FORMED IN SOME MIXTURES

DETERMINE N₂ FROM Ar MEASUREMENT

NO N₂ FORMATION IN GLYCOLATE, OR IN HEDTA WITHOUT Al

- 1ST 3 POINTS ARE IN GLASS, WHICH REACTS TO REMOVE Al

GASES FORMED IN HEDTA, GLYCOLATE, 101-SY

METHANE FORMED IN HEDTA, GLYCOLATE, 101-SY

RATE MEASUREMENTS

**CONVERT PRESSURE BUILDUP RATE TO REACTION RATE BY
USING REACTION CHAMBER VOLUME AND AMOUNT OF
SAMPLE**

RATE SLOWS AS REACTION PROCEEDS

**RATE PER CARBON ATOM FASTER IN GLYCOLATE (2 C ATOMS)
THAN IN HEDTA (10 C ATOMS)**

HEDTA: MIX 90A (R11-R13), MIX 91A (R19-R24)

GLYCOLATE: RUN 17/AIR, RUNS 18-29/He

RATE ESTIMATES FOR ACTUAL 101-SY MATERIAL

PRELIMINARY RATE IN 101-SY AROUND 0.3 mmole/day/moleC

RATE IN 101-SY LOWER THAN HEDTA BY ABOUT FACTOR OF 2

**RATE CAN RESULT FROM ABOUT 8% OF CARBON IN 101-SY
PRESENT IN SPECIES WITH RATES PER CARBON AS LARGE AS
GLYCOLATE**

GAS GENERATION RESULTS

- * 28 RUNS IN SYNTHETIC SLURRIES WITH SIX ORGANIC SPECIES, 3 RUNS IN 101-SY MATERIAL**
- * RATE OF GAS GENERATION DEPENDS ON ORGANIC SPECIES**
FAST: GLYCOLATE, HEDTA
SLOW: OXALATE, CITRATE
- * PRODUCT GASES: H_2 , N_2O , N_2 (SOMETIMES), NH_3**
- * O_2 CONSUMED WHEN GASES PRODUCED**
- * PRODUCT GAS RATIOS DEPEND ON SPECIES:**

ORGANIC	N_2O/H_2	N_2 PRODUCED?
HEDTA, Al=0	28	NO
HEDTA	12-40	YES (30-50%)
GLYCOLATE	1-3	NO
101-SY	0.1,0.5,0.7-1.5	YES

GAS GENERATION RESULTS (CONTINUED)

- * TANK STEEL INCREASES GAS PRODUCTION RATE FOR HEDTA**
 - LITTLE CHANGE IN GAS COMPOSITION: SMALL INCREASE IN N₂O**
- * STAINLESS STEEL INCREASES RATE FOR GLYCOLATE**
 - SOME CHANGE IN GAS COMPOSITION: DECREASE IN N₂O**
- * AMMONIA VARIABLE (ANALYTICAL DIFFICULTY)**
 - LARGEST NH₃ ESTIMATES: 0.8, 5, 13% FOR 101-SY**
10, 11, 20% FOR HEDTA
4, 5, 6% FOR GLYCOLATE

GAS GENERATION RESULTS (CONCLUDED)

*** SOME METHANE PRODUCED IN RUNS IN 101-SY MATERIAL**

- 4 OR 5% OF PRODUCT GAS (WINDOW C)**
- 11% AFTER LONG HEATING (SLOW RATE)**
- 7.5 AND 16% FOR WINDOW E MATERIAL**
- POSSIBLY FROM RADIOCHEMICAL DECOMPOSITION OF GREASE OR RUBBER SEPTUM -- TEST IN ALL-METAL APPARATUS**
- IF CH₄ FROM WASTE, DIFFERENT ACTIVATION ENERGIES COULD CAUSE RELATIVELY LARGER CH₄ PRODUCTION AT 100°C THAN AT TANK TEMPERATURES**

Appendix K

Analytical Chemistry Studies

ANALYTICAL CHEMISTRY STUDIES

PRESENTED TO TANK WASTE SCIENCE PANEL

JAN. 12, 1993 RICHLAND, WA

DR. J.A. CAMPBELL
ADVANCED ORGANIC ANALYTICAL METHODS DEVELOPMENT
GROUP

OUTLINE

- DERIVATIZATION GC/MS REVIEW

- LC OF ORGANIC ACIDS

OXALIC ACID
ACID
BASE
MEISELS SAMPLES
TANK 101-SY SAMPLE

- LC/MS OF ORGANIC ACIDS

THERMOSPRAY
PLASMASPRAY
ELECTROSPRAY

- SUMMARY

- FUTURE EFFORTS

DERIVATIZATION GC/MS

- **UTILIZED BORON TRIFLUORIDE/METHANOL, DIAZOMETHANE, BUTANOL/HCL, SILYLATING REAGENTS, AND CHLOROETHANOL/HCL**
- **BORON TRIFLUORIDE/METHANOL DOES NOT METHYLATE ALL OF THE CHELATORS**
S-EDDA
ASHBY INTERMEDIATES
- **PAPER SUBMITTED TO ANALYTICAL CHEMISTRY**

Table 3. Concentration of Major Components (μg Carbon/g sample)*

<u>Sample #</u>	<u>NIDA</u>	<u>NTA</u>	<u>CA</u>	<u>ED3A</u>	<u>EDTA</u>	<u>HEDTA</u>
1197	750	54	10	90	120	10
1199	760	337	15	153	338	20
1215	2610	242	20	40	70	10
1214	940	165	10	20	51	10
1196	226	87	30	134	480	10
1198	Not analyzed					
1299	222	110	40	260	290	20
1306	168	65	84	210	192	10

* The concentrations are only approximate. The derivatization GC/MS method is only in the development stages and has not been validated. Numbers may be subject to change.

LC METHOD AND SAMPLE PREP

- **DISSOLVE SAMPLE IN WATER AND FILTER**
- **TAKE LEACHATE AND PUT THROUGH CATION EXCHANGE IN EITHER ACID OR BASE**
- **ANION EXCHANGE CHROMATOGRAPHY-BASE**
MOBILE PHASE CARBONATE SYSTEM
ACID-HCL AS MOBILE PHASE

Sample: 54388-35-1 Channel: Waters 494
Acquired: 05-JAN-93 11:32 Method: C:\MAX\SCOTD\AS4A
Inj Vol: 10.00
Comments: DIONEX AS4A COLUMN 75% C03 1.8 AND HC03 1.7 mM 25% H2O, 210NM

Filename: SI-5-2
Operator:

Meisel Sample SYI-SIM-916 Control, Expanded Scale

Sample: 54388-35-6 Channel: Waters 484
Acquired: 05-JAN-93 18:21 Method: C:\MAX\SCOTDAT\AS4A
Inj Vol: 10.00
Comments: DIONEX AS4A COLUMN 75% CO3 1.8 AND HCO3 1.7 mM 25% H2O, 210NM

Filename: sl-5-8
Operator:

Meisel Sample SYI-SIM-916 Irradiated

Meisel Sample SYI-SIM-916
Irradiated, spiked 0.001M Oxalic Acid

Sample: 54388-35-8
Acquired: 05-JAN-93 18:59
Inj Vol: 10.00
Channel: Waters 484
Method: C:\MAX\SCOTDATA\AS4A
Comments: DIONEX AS4A COLUMN 75% C03 1.8 AND HCO3 1.7 mH 25% H2O, 210MH
Filename: sl-5-10
Operator:

Sample: 54388-35-10 Channel: Waters 484
Acquired: 06-JAN-93 14:20 Method: C:\MAX\SCOTDAT\AS4A
Inj Vol: 10.00
Comments: DIONEX AS4A COLUMN 75% CO3 1.8 AND HCO3 1.7 mM 25% H2O, 210NM

Filename: sl-6-2
Operator:

Meisel Sample SYI-SIM-916
Irradiated and Incubated

Meisel Sample SYI-SIM-916
Irradiated and Incubated, spiked to
0.001M Oxalic Acid

Figure 5. Anion Exclusion Chromatograms of Sample 1214, Control, Irradiated/heated, and Irradiated Samples from the Study at Argonne

LIQUID CHROMATOGRAPHY OF 101-SY SAMPLE

Sample: 1214 spike Channel: Waters 484 Filename: sl-8-4
Acquired: 08-JAN-93 13:58 Method: C:\MAX\SCOTDAT\AS4A Operator:
Inj Vol: 10.00
Comments: DIONEX AS4A COLUMN 75% Carb:25% H2O, 210MM, SY101 sample from Rau

Sample 1214 from 101 SY Spiked with
0.001M Oxalic Acid by Anion Exchange

OXALATE SUMMARY

- **PRELIMINARY RESULTS INDICATE NOT FORMED DURING ACID PREPARATION BY NMR**

NEED TO USE LABELED COMPOUND TO INCREASE SENSITIVITY

- **COMPARING RESULTS OBTAINED IN ACID SOLUTION AND BASE -ANION EXCHANGE CHROMATOGRAPHY**

- **PRELIMINARY RESULTS OBTAINED USING ION PAIR CHROMATOGRAPHY**

OXALATE CONCENTRATION APPROXIMATELY 1MG/G-ACCOUNTS FOR APPROXIMATELY 10-20% OF REMAINING TOC NOT ACCOUNTED FOR BY CHELATORS

FUTURE STUDIES

- **COMPARE RESULTS FOR OXALATE IN ACID AND BASE SOLUTION**
- **ACCOUNT FOR REMAINING TOC-ACETATE, FORMATE?**
- **LC METHOD FOR SURFACTANTS**
- **CONTINUE TO DEVELOP LC/MS METHODS**
- **INCREASE TOC LEACHED**

ACKNOWLEDGMENTS

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Appendix L

Analytical Results from Ferrocyanide Tank 241-C-112

Analytical Results from
Ferrocyanide Tank 241-C-112

presented to

Tank Waste Science Panel

by

Brett C. Simpson
Westinghouse Hanford Company
January 13, 1993

Presentation Outline:

- Introduction
 - History
 - Present Tank Status
 - Riser Configuration
- C-112 Core Sample Data
 - Physical Characteristics
 - Radiological Characteristics
 - Chemical Characteristics
 - Energetics
- Comparison of Sample Data with Simulant and Historical Information

Introduction: C-112 Historical Information

- Tank C-112 originally received first cycle decontamination BiPO_4 waste which was disposed to ground in 1952, leaving a 15 Kgal heel. The tank was filled with unscavenged uranium recovery waste in 1953 and 1954.
- In 1956 tank C-112 was mostly emptied. The tank was then used for ferrocyanide waste settling from 1956 to 1958.
- After the end of scavenging in 1958, tank C-112 remained in active service until 1976. Several small transfers occurred after 1958, having relatively high concentrations of ^{90}Sr .
- C-112 has an estimated ferrocyanide inventory of 31,000 g-mol. C-112 is considered to have one of the highest ferrocyanide concentrations of all the SSTs.
- Present waste temperature in C-112: $\sim 85^\circ\text{F}$ and the estimated heat load in the tank is less than 10,000 BTU/hr.
- The most recent waste inventory measurement reports 104,000 gallons of solids and 32,000 gallons of drainable liquids (~ 38 inches of waste). The tank was administratively interim stabilized on 9/90, and is considered sound.

C-112 Core Sample Data: Riser Configuration

Tank 241-C-112 was constructed in 1943-1944;
it has a diameter of 75 feet and a nominal capacity of 500,000 gallons

C-112 Samples on Extrusion:

Core No.	Segment	Core Recovery	Total Mass	Comments
Core 34 Upper	92-001	62%	136.88 g	Liquid contained suspended solids. Solids portion was 1.25 cm (1/2 in.) long.
Core 34 Lower	92-002	75%	211.82 g	Grey/white streak at edge of solids. Solid segment recovered was 35.56 cm (14 in.) long.
Core 35 Upper	92-003	0%	N/A	No sample recovered; valve remained open.
Core 35 Lower	92-004	35%	109.05 g	Liquid contained suspended solids. Solid segment recovered was 7.6 cm (3 in.) long.
Core 36 Upper	92-005	45%	105.8 g	Medium brown color; no drainable liquid. Solid segment was 21.6 cm (8.5 in.) long.
Core 36 Lower	92-006	90%	263.7 g	Thin brown sludge at bottom of segment with the material gaining consistency and gradually changing color to grey/white moving up the core. Solid segment was 43.2 cm (17 in.) long.

C-112: Physical Characteristics Summary

Core No.	Segment	Solids Sample Mass (g)	Liquids Sample Mass (g)	Solids Sample Volume (mL)	Liquid Sample Volume (mL)	Solids Bulk Density (g/mL)	Liquids Bulk Density (g/mL)
Core 34 Upper	92-001	20.99	115.89	14	100	1.5	1.2
Core 34 Lower	92-002	175.75	36.07	110	30	1.6	1.2
Core 35 Upper	92-003	N/A	N/A	0	0	NA	None
Core 35 Lower	92-004	58.7	50.35	30	35	2.0	1.4
Core 36 Upper	92-005	105.8	0.0	85	0	1.3	None
Core 36 Lower	92-006	263.7	0.0	170	0	1.6	None

General characteristics of C-112 waste materials:

- Drainable liquids were all rust to dark brown in color and contained significant amounts of suspended solids prior to filtration. After filtering, the liquids were dark yellow.
- Solids ranged in color from grey/white to tan to dark brown.
- The solids also ranged in consistency from a thin slurry to a very thick, chunky sludge. They appeared to be saturated with liquid.
- The solids tended to slump somewhat, but held their shape relatively well (high viscosity, non-Newtonian fluids).

C-112 Radiological Characteristics:

- Gamma scans were performed as a scoping procedure on Cores 34, 35 and 36 to obtain a qualitative measurement of the activity of the waste and to identify the major contributors.
- The radiological activity of the C-112 waste material was relatively low (0.15 - 2 R/hr, measured through the drill string).
- No significant gamma emitters were found in the tank waste except ^{137}Cs . The other major source of radiological activity was found to be ^{90}Sr .
- No significant radiological activity was found in the drainable liquid in the tank or in the water digestion of the samples (i.e. the radionuclides are relatively insoluble).

C-112 Core 34 Key Analytes:

Quarter Segment	^{137}Cs (uCi/g)	^{90}Sr (uCi/g)	Wt % Total Carbon	Wt % Water	Heat of Reaction (cal/g dry waste)
1D	243	1316	1.26	45	No Measurement
2B	612	4860	0.84	52.9	-32.5
2C	795	1140	0.83	57.9	-27.6
2D	508	2510	1.05	52.3	-32.0
Composite	750	2456	No Measurement	38.1	-33.2

C-112 Core 36 Key Analytes:

Quarter Segment	^{137}Cs (uCi/g)	^{90}Sr (uCi/g)	Wt % Total Carbon	Wt % Water	Heat of Reaction (cal/g dry waste)
1C	410	400	1.12	48.5	-5.2
1D	1240	15	1.03	58.3	-10.7
2A	884	20	0.85	57.3	-7.4
2B	532	71	0.52	41.0	-4.7
2C	103	144	0.64	64.1	No exotherm
2D	35	199	0.52	55.8	No exotherm
Composite	793	508	0.70	45	-16.4

Core 34: Radionuclides as a Function of Depth

Core 36: Radionuclides as a Function of Depth

Core 34: Fuel Content, Water Content and Reactivity as a Function of Depth

Core 36: Fuel Content, Water Content, and Reactivity as a Function of Depth

C-112 Comparison of Waste Material with Simulants

Analyte	In-Farm Simulant Values	Core 34 Values	Core 36 Values
Ni (ug/g).	27,600	Quarter segment range: 22,217-28,253 Composite Value: 30,039	Quarter segment range: 924-22,958 Composite Value: 12,790
Ca (ug/g)	36,400	Quarter segment range: 21,702-28,199 Composite Value: 28,983	Quarter segment range: 2,128-28,570 Composite Value: 20,390
Wt % H ₂ O	41-50%	Quarter segment range: 45-58% Composite Value: 38%	Quarter segment range: 41-64% Composite Value: 45%
Wt % Total Carbon (wet basis)	3.38%	Quarter segment range: 0.83-1.26 Composite Value: No measurement	Quarter segment range: 0.52-1.12 Composite Value: No measurement
ΔH (cal/dry g)	-250	Quarter segment range: -27.6 to -32.5	Quarter segment range: -4.7 to -10.7
Density (g/ml)	1.51	Bulk Value: 1.5 - 1.6	Bulk Value: 1.3 - 1.6

- Agreement between synthetic sludge properties and observed waste material characteristics are within the constraints of the synthetic recipes and assumptions regarding chemical behavior in the tank.

*-----Ni concentrations are potentially biased high; Values are derived from ICP fusion performed in a Ni crucible. However, in each case the blank value was an order of magnitude (or greater) less than the measurement. The fusion values are comparable with acid digestion values, where both are available.

Nickel Concentration as a Function of Depth

Calcium Concentration as a Function of Depth

Aluminum Concentration as a Function of Depth

C-112 Core Sample Data: Indications from Core 34 Data

- Core 34 has physical and chemical properties corresponding to ferrocyanide waste. Water content, Ni, Ca concentrations, and density values are consistent with the simulant values.

C-112 Core Sample Data: Indications from Core 36 Data

- Core 36 appears to have ferrocyanide waste overlying a first cycle decontamination and/or uranium recovery waste heel. The concentration of Ni, Ca, ^{137}Cs , and U as a function of depth appears to confirm this observation. In addition, this behavior is consistent with historical information.

C-112 Core Sample Data: Core Sample Summary

- 5 ICP analytes (Al, Ca, Fe, Na, Ni, and U) account for over 90% of the cations; 2 IC analytes (NO₂ and NO₃) account for almost 80% of the anions, and water accounts for between 41 - 65% of the total mass.
- DSC results from C-112 indicate that the material is not as energetic as the corresponding waste simulant.
- No significant regional concentrations [hot spots] of radioisotopes or fuel (from a safety aspect) were detected along the vertical axis.
- The gamma activity pattern obtained from the scans and the ICP cation distribution indicate some gross layering of the waste in the tank (i.e differences in waste types).
- The regions with high Ni concentrations correlate with the ¹³⁷Cs peaks
- Compositing procedure appears to give conservative and consistent values for analytes of importance.

Appendix M

Assessment of the Ferrocyanide Issue

ASSESSMENT OF THE FERROCYANIDE ISSUE

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TANK WASTE SCIENCE PANEL MEETING

**RICHLAND, WASHINGTON
JANUARY 12-14, 1993**

ASSESSMENT OF THE FERROCYANIDE ISSUE

OUTLINE

- **ADIABATIC CALORIMETRY DATA - SIMULATED FERROCYANIDE SLUDGES.**
- **PROPAGATION VELOCITY DATA - IN FARM 1 SYNTHETIC FLOW SHEET MATERIAL.**
- **PASSIVE SAFETY CONSIDERATIONS - TANK 112C.**
- **HOTSPOT CONSIDERATIONS - TANK 112C.**
- **CONCLUDING REMARKS.**

**CHEMICAL COMPOSITIONS OF
SIMULATED FERROCYANIDE SLUDGES**

<u>Chemical</u>	<u>Weight Fraction</u>			
	<u>U Plant-1</u>	<u>U Plant-2</u>	<u>In Farm-1</u>	<u>In Farm-2</u>
Ferrocyanide	0.015	0.03	0.13	0.11
Nitrate-Nitrite	0.24	0.24	0.31	0.32
Water	0.66	0.66	0.50	0.50
Others	0.085	0.07	0.06	0.07
	BY Tanks		C Tanks	

ADIABATIC CALORIMETRY TEST RESULTS

- **DRIED U PLANT MATERIALS DO NOT EXHIBIT PROPAGATING OR EXPLOSIVE REACTIONS. (NOTE THAT RUNAWAY REACTIONS CAN OCCUR AND DEPEND ON SIZE AND COOLING CHARACTERISTICS.)**
- **DRIED IN FARM MATERIALS DO EXHIBIT PROPAGATING-LIKE REACTIONS (~ 250°C).**
- **ADIABATIC VSP CALORIMETRY DATA WITH U PLANT-1 AND U PLANT-2 SAMPLES SUGGEST $\Delta H_R \approx 4 \text{ MJ KG}^{-1}$ OF FERROCYANIDE.**
- **THE DATA SUGGEST AT LEAST 13 W% OF FERROCYANIDE IN A COMPLETE DRY MIXTURE (GIVEN ADEQUATE OXIDIZER) IN ORDER TO EXHIBIT A PROPAGATING-LIKE REACTION.**

Measured self-heat rate data with a completely dried U Plant-2 Bottom sample using the adiabatic VSP calorimetry methodology. The measured adiabatic temperature rise is about 350°C. With a ferrocyanide concentration of about 0.088 for the dried sample, and using a sample specific heat of $1000 \text{ J kg}^{-1} \text{ K}^{-1}$, results in a heat of reaction of about 4 MJ per kg of ferrocyanide.

ITEM	
1	Magnetic Stirrer Bar
2	Test Cell Heater
3	Guard Heater Assembly With Aluminum Can and Lid
4	Fiberfrax Insulation
5	Magnetic Stirring Assembly
T	Thermocouple
P	Pressure Transducer

VSP apparatus

Measured self-heat rate data with a completely dried in Farm-1 Bottom (-26 wt ferrocyanide) sample using the adiabatic RSSST calorimetry methodology. The rapid temperature rise following onset of the propagating reaction at about 250°C is illustrated in the next viewgraph.

Measured temperature rise data with a completely dried In Farm-1 Bottom sample indicating self-heat rates in excess of $10^6 \text{ } ^\circ\text{C min}^{-1}$.

RSST

RSST calorimeter containment vessel with cut-away view of test cell.

**NECESSARY WATER CONTENT PREVENTING
PROPAGATING REACTIONS WITH IN FARM MATERIALS**

$$x_{H_2O} > \frac{N}{N + 1}$$

$$N = \frac{(x - x_n) \Delta H_R - C_M (T_o - T_i)}{\lambda + C_{H_2O} [T_B - T_i]}$$

x = weight fraction of FeCN (In Farm-1 Bottom, x ≈ 0.26, In Farm-2 Bottom; x ≈ 0.23).

$$x_n = 0.13$$

$$\Delta H_R = 4 \text{ MJ kg}^{-1}$$

↓

$$x_{H_2O} \approx 0.12 \text{ (In Farm-1 Bottom)}$$

$$x_{H_2O} \approx 0.08 \text{ (In Farm-2 Bottom)}$$

DEDICATED PROPAGATION TESTS

- **IN FARM-1 BOTTOM SAMPLE WITH 8 W% WATER EXHIBIT A SUSTAINING REACTION WHILE A SAMPLE WITH 15 W% WATER DID NOT PROPAGATE. AT A WEIGHT FRACTION OF WATER OF 12 W%, A PARTIAL PROPAGATION REACTION WAS NOTED.**
- **THE REACTION TEMPERATURE OF $1150 \pm 100^{\circ}\text{C}$ IS IN GOOD AGREEMENT WITH THE ESTIMATED HEAT OF REACTION FROM THE ADIABATIC CALORIMETRY TESTS WITH U PLANT MATERIALS OF ABOUT 4 MJ kg^{-1} OF FERROCYANIDE.**

25 mm diameter sample holder used in burn velocity tests.

TEMPERATURE (C)

$\times 10^3$

1.5

1.2

.9

.6

.3

0

OVERALL SPEED 5.3 CM/MIN

Temperature response and propagation velocity for Test Item #7, InFarm1-Bot., sample at 8 wt.% H₂O in 25 mm sample holder. Reaction propagation velocity ≈ 5 cm/min, initial temperature and pressure 26°C and 0 psig, respectively.

DRY COMPOSITION OF FERROCYANIDE TEST MIXTURES

REAGENT	INFARM1-BOT.	
	& VWV-IF1 Wt. %	VWV F/O (30/70) Wt. %
--Fe(CN) ₆	26.0	29.5
NaNO ₃	50.0	56.7
NaNO ₂	12.2	13.8
Na ₃ PO ₄	5.2	0.0
Na ₂ SO ₄	3.8	0.0
NIS	<u>2.8</u>	<u>0.0</u>
TOTALS	100.0	100.0
Fuel/Oxidizer*	0.418	0.418

*Fuel is --Fe(CN)₆ and oxidizer is taken as NaNO₃ + NaNO₂.

SUMMARY RESULTS OF TESTS COMPLETED TO DATE ON FEBROCTANIDE BURN PROPAGATION RATE STUDIES

ITEM	TEST ID	TEST SAMPLE	TEST PARAMETERS								MATRIX TEST#
			DIA. (mm)	DENSITY gm/cc	WATER CONTENT wt. %	PRESS. (psig)	TEMP. °C	BURN Y/N	PROPAGATION RATE	MAXIMUM TEMPERATURE °C	
1	T0709-1	InFarm1-Bot.	50	1.37	50	0	26	N	As Received	-	12
2	T0715-1	InFarm1-Bot.	25	1.20	Dry	0	26	Y	See T0727-1		
3	T0723-1	InFarm1-Bot.	25	1.53	14.6	0	26	N	Still too Wet	-	
4	T0724-1	InFarm1-Bot.	25	1.22	8.0	0	26	Y	< 16 cm/min	1000°C	
5	T0727-1	InFarm1-Bot.	25	1.23	Dry	0	26	Y	10 cm/min	1150°C	4
6	T0728-1	InFarm1-Bot.	25	1.28	12	0	26	N	Ignited but Stopped	-	
7	T0729-1	InFarm1-Bot.	25	1.13	8.0	0	26	Y	5.3 cm/min	900°C	
8	T0810-1	VWV-IF1	25	1.24	Dry	0	26	Y	7.5 cm/min	1050°C	
9	T0819-1	VWV-IF1	25	1.25	Dry	750	60	Y	2.2 cm/sec	Melts Steel	2*
10	T0820-1	VWV-IF1	25	1.23	Dry	750	60	Y	4.5 cm/sec	Repeat of 9	
11	T0821-1	VWV-IF1	25	1.23	Dry	25-50	60	Y	20 cm/min		
12	T0825-1	VWV F/O 30/70	50	1.87	18	750	60	Y	5 cm/min	900°C	9
13	T0826-1	VWV F/O 30/70	25	1.72	25	750	25	Y	**		
14	T0827-1	VWV F/O 30/70	50	1.13	Dry	0	60	Y	4 cm/min	700°C	6
15	T0828-1	VWV F/O 30/70	25	1.81	18%	750	25	N	No Burn		3
16	T0831-1	VWV F/O 30/70	50	1.14	Dry	0	60	Y	9 cm/min	950°C	

*Will be repeated with InFarm1-Bot. material.

**Burned, but results suspect due to loss of water during test set-up preparations.

Tank 112 C
(~ to Scale)

Total Heat Generation, ~ 600w
Weight Fraction Ferrocyanide < 0.13
Weight Fraction Water ~ 0.50

HF92N037.CDR

Ferrocyanide Issue and Passive Safety

Current

Hypothetical

$$t_a \gg t_c$$
$$q \ll q_{\text{crit.}}$$

Tank Integrity Assured

TANK 112C

Passive Safety

Typical requirements employed in the chemical process industry.

$$\begin{array}{l} \uparrow \rightarrow \rightarrow \rightarrow t_a \gg t_c ; t_c \approx \frac{H_{\max}^2}{\alpha} \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \\ \uparrow \end{array} \quad \begin{array}{l} \\ \\ \approx \frac{1.2^2}{1.5 \cdot 10^{-7}} \text{ (Tank 112C)} \\ \\ \approx 111 \text{ Days} \\ \downarrow \\ \downarrow \end{array}$$
$$\leftarrow \leftarrow \leftarrow \leftarrow t_s \gg t_c \leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$$

Latent Heat/Reaction Heat > 1

~ 2 (Tank 112C)

Tank 112 satisfies standard passive safety conditions.

FERROCYANIDE ISSUE

Hypothetical Bulk Runaway Scenario

Critical Heat Production

$$q_{\text{crit}} \approx \frac{k T_o^2}{H^2 \rho (E_a/R)}$$

$\sim 5.6 \cdot 10^{-3} \text{ w kg}^{-1}$ (In Farm-1 $< 10^{-4} \text{ w kg}^{-1}$)
(Decay Heat $\sim 10^{-3} \text{ w kg}^{-1}$)

Corresponding Half Life

$$t_{1/2} \approx \ln 2 \frac{\Delta H_R}{q_{\text{crit}}}$$

$\sim 2 \text{ years}$

At 400K (Boiling)

$$q \sim 2.4 \text{ w kg}^{-1}$$

Corresponding Steam Production

$$\sim 0.7 \text{ kg s}^{-1}$$

Venting Capacity (4-inch Vent Line)

$$\sim .4 \text{ psi overpressure}$$

Ferrocyanide Issue

Hypothetical Hotspot Scenario (Self-Regulating Effect)

HF931025.CDR

CONCLUDING REMARKS

- **TANK 112C SATISFIES STANDARD PASSIVE SAFETY CONDITIONS.**
 - **PASSIVE COOLING.**
 - **LATENT HEAT > REACTION HEAT.**
- **HYPOTHETICAL HOTSPOT(S) LIMITED TO ~ 130°C.**
 - **SELF-REGULATING.**
 - **LATENT HEAT > REACTION HEAT.**
- **CONSISTENT SAFETY METHODOLOGY AND CRITERIA SHOULD BE APPLIED TO EACH SET OF TANKS (E.G. BY, C. ETC.).**
- **FARM OPERATIONAL CONTROLS AND PROCEDURES TO ASSURE MINIMUM WATER LOSS.**

Appendix N

Aging of Ferrocyanides Wastes

Ferrocyanide Safety Project

"Predecisional Information"

AGING OF FERROCYANIDES WASTES

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Tank Waste Science Panel Meeting
Richland, WA
January 13, 1993

Aging Studies

- Solubilization
- Hydrolysis

Variables to be Investigated

- Time
- pH
- $[\text{Na}^+]$
- Anion Effects
- Stoichiometry
- Temperature
- Stirring/Static
- Gamma

Solubility of Vendor Material as a Function of pH

Solubility of Vendor Material as a Function of pH

IR ANALYSIS OF REACTION PRODUCTS IN THE REGION OF CN^- ABSORBANCE

Vendor-1
(max abs. 2085 cm^{-1})

0.1 M Insoluble Reaction Product
(max abs. 2085 cm^{-1})

0.1 M Soluble Reaction Products
(max abs. 2060 cm^{-1})

IR ANALYSIS OF REACTION PRODUCTS IN THE REGION OF 4000 - 3000 cm^{-1}

Ni(OH)_2

0.1 M Soluble Reaction Product

1.0 M Soluble Reaction Product

0.1 M Insoluble Reaction Product

1.0 M Insoluble Reaction Product

4000
3000
 cm^{-1}

XRD Spectra for Solids From pH 14 Vendor Dissolution

EDS Spectra of Soluble and Insoluble Solids, pH 13 Dissolution

Solubility of Vendor Material Free Cyanide and Soluble Fe, pH 14

Solubility of Vendor Material
[Na⁺] = 1 M (as sulfate)

Solubility of Vendor Material [Na⁺] Dependence, pH 13

Solubility of Vendor Material [Na⁺] Dependence, pH 14

Composition of Single-shell Tank Simulated Salts.

<u>SST Component</u>	<u>Wt.% Anhydrous Salt</u>
NaNO ₃	80.47
Na ₃ PO ₄	9.04
NaNO ₂	4.37
NaOH	3.12
Na ₂ CO ₃	1.52
Na ₂ SO ₄	1.48

Solubility of Vendor Material SST Simulant Salts, pH 13

Solubility of Vendor Material

[Na⁺] = 1 M, pH 13

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4 of 5

Starting and Final Solution pH in Dissolution Experiments

<u>Experiment</u>	<u>Starting pH</u>	<u>Final pH</u>
pH Variation		
0.01 M NaOH	12.0	11.6
0.1 M NaOH	12.9	12.4
1.0 M NaOH	14.0	13.4
1 M [Na ⁺] as SO ₄ ²⁻		
0.1 M NaOH	12.9	12.4
SST Simulant Salts		
stirred	13.0	13.0
static	13.0	12.9
Gamma Pit		
irradiated	13.0	12.9
control	13.0	12.9

Concentrations of Free Cyanide Ion and Iron in Supernate Solutions (144-h samples) Containing SST Simulant Salts.

<u>Experiment</u>	<u>[CN⁻], ppm^(a)</u>		<u>[Fe], ppm</u>	<u>% Dissolved Fe</u>
	<u>Dark</u>	<u>Exposed</u>		
SST Static	11.8	112.	1898	91%
Gamma-Irradiated	11.2	49.3	1291	62%
Gamma Control	2.97	52.6	1291	62%

(a) Dark solutions were protected from sunlight and analyzed.

Exposed solutions were placed in sunlight for 0.5 h and re-analyzed.

Final Moles of Gas Present Over the Gamma Pit
Control and Irradiated Solutions.

<u>Gas</u>	<u>Final Moles of Gas</u>		<u>Irradiated/Control</u>
	<u>Control</u>	<u>Irradiated</u>	
CO ₂	7.33 x 10 ⁻⁷	8.06 x 10 ⁻⁷	1.10
Ar ^(a)	2.83 x 10 ⁻³	2.91 x 10 ⁻³	1.03
O ₂ ^(a)	7.22 x 10 ⁻⁴	9.19 x 10 ⁻⁴	1.27
N ₂	1.11 x 10 ⁻⁴	7.42 x 10 ⁻⁵	0.67
H ₂	2.57 x 10 ⁻⁶	1.30 x 10 ⁻⁴	50.58
CO	3.67 x 10 ⁻⁶	4.03 x 10 ⁻⁶	1.10
He	BDL ^(b)	BDL	-
CH ₄	BDL	BDL	-
N ₂ O	BDL	BDL	-
NO _x	BDL	BDL	-

(a) initial moles: Ar, 2.93 x 10⁻³; O₂, 7.55 x 10⁻⁴

(b) BDL = Below Detection Limits (<0.01 vol%)

Table 3.4 Infrared Absorbances (cm^{-1}) in the Cyanide Region for Samples in the Solid State^(a)

<u>Experiment</u>	<u>Soluble Solids</u>	<u>Insoluble Solids</u>
pH 12	2025w, 2059s	2090
pH 13	2060 ^(b)	2093
pH 14	2024w, 2060s	2089
Gamma Control	2023w, 2054s ^(b)	2006m, 2025w, 2047s, 2064sh, 2094m
Gamma Irradiated	2025w, 2057s ^(b)	2008s, 2025w, 2046sh, 2055s, 2094w
Static SST Salts	2025w, 2058s ^(b)	2003w, 2054sh, 2093s
$\text{Na}_2\text{NiFe}(\text{CN})_6$ ^(c)	-	2092
$\text{K}_4\text{Fe}(\text{CN})_6$	2047 ^(b)	-
$\text{Na}_3\text{Fe}(\text{CN})_5(\text{H}_2\text{O})$	2043 ^(d)	-
$\text{K}_3\text{Fe}(\text{CN})_6$	2125 ^(d)	-

(a) w = weak, m = medium, s = strong, sh = shoulder.

(b) In solution, these materials gave a single absorbance at 2036 cm^{-1} .

(c) Vendor-prepared material.

(d) from K. Nakamoto, 1970. Infrared Spectra of Inorganic and Coordination Compounds, 2nd Edition, Wiley-Interscience, New York, p. 179.

Appendix O

Cyanide Species Analytical Methods Development

Cyanide Species Analytical Methods Development

presented to

PNL Science Panel

by

**SA Bryan and KH Pool
Pacific Northwest Laboratory
January 12, 1993**

Approach for Developing Analytical Methods for Determining Cyanide Species in Wastes

Objectives

- **Develop methods for quick determination of cyanide species with little or no sample preparation.**
- **Produce qualified analytical producers for solution methods**

Scope of Work

- **Performed literature survey on known chemistry, detection, and measurement of ferrocyanide complexes.**
- **Investigated techniques useful for direct analysis of cyanides in solids**
- **Investigated techniques useful for indirect analysis of cyanides in solution**

DIRECT METHODS DEVELOPMENT

- **Investigated**
 - **Infrared Spectroscopy (FTIR)**
 - **Raman Spectroscopy**
 - **X-ray Diffraction (XRD)**
 - **Scanning Electron Microscopy- Energy Dispersive Spectroscopy (SEM-EDS)**
 - **Mössbauer Spectroscopy**

Structures of "free" ferrocyanide and nickel ferrocyanide

The ferrocyanide anion, $[\text{Fe}(\text{CN})_6]^{4-}$.

One-eighth of the unit cell of $\text{NiFe}(\text{CN})_6^{4-}$. The alkali-metal ions and water molecules are omitted for simplicity.

**Solid $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and
Flowsheet $Na_2NiFe(CN)_6$ can be
Distinguished by IR**

IR bands in the $\nu(C\equiv N)$ region show that "free" ferri- and ferrocyanides can be differentiated from FeCN flowsheet material.

Full Scale FTIR Spectrum of Ferrocyanide In-Farm Flowsheet Material

Standard Addition Characterization of Solid U-Plant Ferrocyanide Simulant

analyzed 0.89 wt% CN⁻ [1.21 wt% as Fe(CN)₆⁻⁴] in this sample

FTIR Method using ATR Cell
 $\text{Na}_2\text{NiFe}(\text{CN})_6$ in Synthetic Waste
<1.0 Wt% Addition Follows Beer's Law

Raman Solid Spectra of Various
Concentrations of $\text{Na}_2\text{NiFe}(\text{CN})_6$
in Synthetic Waste Matrix

Raman Response is Linear with
Respect to $\text{Na}_2\text{NiFe}(\text{CN})_6$ Concentration
in Synthetic Tank Waste

X-ray Diffraction (XRD) of Synthetic Washed In-Farm Waste Indicates Presence of Sodium Nitrate and a Compound Similar to $K_2NiFe(CN)_6$.

$NaNO_3$

$K_2NiFe(CN)_6$

XRD Analysis of $\text{Na}_2\text{NiFe}(\text{CN})_6$
in Synthetic Waste Gives
Linear Response at < 1 wt%

INDIRECT METHODS DEVELOPMENT

- Dissolution method developed for dissolving pure $\text{Na}_2\text{NiFe}(\text{CN})_6$ and flowsheet material
 - EDTA and Ethylenediamine (true solution)
 - NaOH ($\text{Ni}(\text{OH})_2$ precipitation)
- Analyze dissolved solids using
 - Ion Chromatography (IC) methods for cyanide species
 - Suppressed conductivity detector
 - UV-vis detector
 - Solution Infrared

Solution FTIR Spectra of Cyanide Standards and Various Flowsheet Materials

Solution Spectra of Cyanide, Ferrocyanide and Ferricyanide in Aqueous Solution

Infrared Spectra of Cyanide (2080 cm^{-1} , 0.98 wt%), Ferrocyanide (2038 cm^{-1} , 0.51 wt%), and Ferricyanide (2118 cm^{-1} , 0.78 wt%) Ions in Aqueous Solution.

Solution FTIR Data For $\text{Na}_2\text{NiFe}(\text{CN})_6$
Standard Curve is Linear Over
Three Orders of Magnitude $[\text{Fe}(\text{CN})_6^{-4}]$

Solution FTIR Data From $\text{Na}_2\text{NiFe}(\text{CN})_6$
Standard Solutions

Typical IC Chromatograms Flowsheet Material Contains $\text{Fe}(\text{CN})_6^{-4}$

Ion Chromatography Calibration Curve

Cyanide Species Analyses

<u>Material</u>	<u>Method</u>			
	FTIR (wt%)		Ion Chromatography (wt%)	
	<u>Fe(CN)₆⁻⁴</u>	<u>total CN⁻¹</u>	<u>Fe(CN)₆⁻⁴</u>	<u>total CN⁻¹</u>
In Farm 1 (Top)	6.3	4.7	5.3	3.9
In Farm 1 (Bottom)	8.9	6.5	8.4	6.2
In Farm 2 (Top)	5.5	4.1	5.5	4.1
In Farm 2 (Bottom)	7.5	5.5	7.6	5.6
U Plant 2 (Top)	1.4	1.0	1.3	0.97
U Plant 2 (Bottom)	2.0	1.5	2.0	1.5

Test Plan

Indirect Methods Subtask Objective

- produce qualified analytical producers for solution IC and IR methods

Planned Activities

- dissolution method optimization
 - complexants, solute/solvent ratios, temperatures, etc.
- determine interferences with solution techniques (IC and IR)
 - NO_3^- , NO_2^- , CrO_4^{2-} , BiPO_4 , OH^- , etc.
- determine extent of interconversion of iron-cyanide species
 - $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, CN^- stability and oxidation state interconversion will be assessed in the presence of oxy-anions and complexants
- quantification of cyanide species
 - simulants (In-farm, U-plant, etc.) analyzed via QC protocols including duplicates, spikes, blanks, etc.
 - data used to verify method

Test Plan (cont)

Direct Methods Subtask Objective

- Development of methods for quick determination of cyanide species with little or no sample preparation. Techniques narrowed to FTIR and Raman based on FY92 results.

Planned Activities

- interferences with solid techniques
 - determine the extent NaNO_3 , NaNO_2 , Na_2CrO_4 , BiPO_4 , etc. interfere with detection and quantification of cyanide species.
- quantification of cyanide species
 - simulants (In-farm, U-plant, etc.) analyzed via QC protocols including duplicates, spikes, blanks, etc.
 - data used to verify method

Sample Cell and Assembly for Remote Infrared Analysis

Appendix P

Laser Raman Spectroscopy Sensing

WASTE ANALYSIS
Laser Raman Spectroscopy Sensing
FSU Feasibility Study

FR Reich

Westinghouse Hanford Company

January 1993

Deployment Success – Attention To Complete Life Cycle

Technology Track to Deployment

Innovative Technology Development & Deployment

TWRS Raman Characterization Draft Five Year Plan

Figure 1

TWRS Raman Characterization Draft Five Year Plan

Figure 1

System Development And Certification

System Development:

System Certification:

Hanfords Applications:

Need:

Raman System Optimized For Hanford's Hot Cell & Waste Tank Applications Satisfying Deployment, Safety, & Regulatory Issues

- **Hot Cell**
 - **Semi-Remote Operation - Short F.O. Cables**
 - **Campaign Lengths In Hours**
 - **Moderately Hostile Environment**
 - **Waste Tank Extruded Cores**
- **In-Situ Waste Tank**
 - **Remote Operation - Long F.O. Cables**
 - **Campaign Lengths In Days & Weeks**
 - **Hostile Radiation & Chemical Environment**
 - **Cone Penetrometer/Early Deployment Arm/LODs**

FSU Feasibility Study
Raman Test Matrix

Table II

Composite U Plant Synthetic Sludge Test Matrix

<u>Chemical Name:</u>	<u>Chemical Composition:</u>	<u>Concentration (Wt%):</u>	<u>Comments:</u>
Disodium mononickel ferrocyanide	$\text{Na}_2\text{NiFe}(\text{CN})_6$	0 - 5%	
Nickel ferrocyanide	$\text{Ni}_2\text{Fe}(\text{CN})_6$	0 - 5%	
Sodium nitrate	NaNO_3	10 - 30%	
Sodium nitrite	NaNO_2	0 - 5%	
Strontium phosphate	SrHPO_4	0 - 5%	
Sodium phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0 - 5%	
Sodium sulfate	Na_2SO_4	0 - 5%	
* Sodium aluminate	NaAlO_2	0 - 10%	Reference only. Test as interference material.
* Sodium chromate	Na_2CrO_4	0 - 5%	Reference only. Test as interference material.

Interference Tests:

1. pH Sensitivity: pH range of 8 - 14 (8, 10, 12, 14). Use NaOH to adjust pH range.
2. Rare Earth Sensitivity: Sensitivity to La and Nd background of 1ppm - 1/1000 Wt. Use nitrate forms of materials.
3. Sodium chromate: Sensitivity to sodium chromate (Na_2CrO_4), 0 - 5% Wt (0, 0.5, 2, 5).
4. Aluminate: Sensitivity to aluminate over range of 0 - 10 Wt% (0, 0.5, 2, 5, 10) sodium aluminate (NaAlO_2).

Table III

Composite In-Farm Synthetic Sludge Test Matrix

<u>Chemical Name:</u>	<u>Chemical Composition:</u>	<u>Concentration (Wt%):</u>	<u>Comments:</u>
Disodium mononickel ferrocyanide	$\text{Na}_2\text{NiFe}(\text{CN})_6$	10 - 25%	
Nickel ferrocyanide	$\text{Ni}_2\text{Fe}(\text{CN})_6$	10 - 25%	
Sodium nitrate	NaNO_3	0 - 40%	
Sodium nitrite	NaNO_2	0 - 10%	
Sodium phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0 - 5%	
Nickel sulfide	NiS	0 - 5%	
Sodium sulfate	Na_2SO_4	0 - 5%	
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	0 - 10%	
* Sodium aluminate	NaAlO_2	0 - 10%	Reference only. Test as interference material.
* Sodium chromate	Na_2CrO_4	0 - 5%	Reference only. Test as interference material.

Interference Tests:

- 1.) Evaluate pH, rare earth, aluminate, and chromate interference impacts only if there is a strong U Plant material response. If no U Plant impact exists, no impact is expected with the In-Farm material.
- 2.) Phosphate Sensitivity: Phosphate over range of 0 - 30 Wt% (0, 10, 20, 30) sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$).

Components of FSU Raman system.

Jig for solid samples in preparing analytical curves.

**Base-Line Raman Spectra
Of
Pure Waste Tank Materials**

Table 1
Index of Reference Spectra for Solid Materials

Spectrum No.	Compound Name	Compound Formula
1	sodium ferrocyanide	$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$
2	potassium ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
4	sodium ferricyanide	$\text{Na}_3\text{Fe}(\text{CN})_6$
5	potassium ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$
7	nickel ferrocyanide	$\text{Ni}_2\text{Fe}(\text{CN})_6$
8	sodium nickel ferrocyanide	$\text{Na}_2\text{NiFe}(\text{CN})_6$
9	sodium cesium nickel ferrocyanide	$\text{NaCsNiFe}(\text{CN})_6$
10,24	ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$
12, 22	sodium sulfate	Na_2SO_4
13	potassium sulfate	K_2SO_4
15,23	sodium nitrate	NaNO_3
16	potassium nitrate	KNO_3
18	sodium nitrite	NaNO_2
20	sodium phosphate	$\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$

Table 2
Index of Raman Spectra for Aqueous Solutions

Spectrum No.	Species observed	Solution composition
11	NH_4^+	1 <i>M</i> $(\text{NH}_4)_2\text{SO}_4$ in 1 <i>M</i> NaNO_3
14	SO_4^{2-}	0.1 <i>M</i> Na_2SO_4 in 1 <i>M</i> NaNO_3
17	NO_3^-	1 <i>M</i> NaNO_3
3	$\text{Fe}(\text{CN})_6^{4-}$	10 <i>mM</i> $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in 1 <i>M</i> NaNO_3
6	$\text{Fe}(\text{CN})_6^{3-}$	10 <i>mM</i> $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in 1 <i>M</i> NaNO_3
19	NO_2^-	1.13 <i>M</i> NaNO_2 in H_2O
21	PO_4^{3-}	sat'd $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ in 1 <i>M</i> NaOH

1. Solid Sodium Ferrocyanide

2. Solid Potassium Ferrocyanide

3. Ferrocyanide in Solution

4. Solid Sodium Ferricyanide

5. Solid Potassium Ferricyanide

6. Ferricyanide in Solution

7. Nickel Ferrocyanide

8. Sodium Nickel Ferrocyanide

9. Sodium Cesium Nickel Ferrocyanide

10. Solid Ammonium Sulfate, Ammonium Region

11. Saturated Ammonium Sulfate in Water, Ammonium Peak.

Base-Line Raman Spectra

From

In-Farm, U-Plant 2-13, And U-Plant 2-14

Surrogates

SUMMARY TABLE
ESTIMATED COMPOSITIONS OF COMPOSITED SYNTHETIC TEST MIXTURES

<u>Sludge Component</u>	<u>Estimated Compositions of Compositated Test Mixtures</u>			
	<u>Weight Fraction</u>			
	<u>U Plant-1</u>	<u>U Plant-2</u>	<u>In-Farm-1</u>	<u>In-Farm-2</u>
Disodium Mononickel	0.018	0.037	-----	-----
Ferrocyanide				
Disodium (0.025 mole	-----	-----	0.204	0.149
fraction Cesium)				
Mononickel Ferrocyanide				
Ferric Hydroxide	0.030	0.035	-----	-----
Strontium Phosphate	0.012	-----	-----	-----
Calcium Phosphate	-----	-----	-----	0.094
Nickel Sulfide	-----	-----	0.023	-----
Sodium Nitrate	0.235	0.182	0.248	0.245
Sodium Nitrite	-----	0.049	0.068	0.066
Sodium Phosphate	0.017	0.018	0.029	0.019
Sodium Sulfate	0.021	0.022	0.021	0.019
Ammonium Sulfate	0.007	0.007	-----	-----
<u>Water</u>	<u>0.661</u>	<u>0.65*</u>	<u>0.41**</u>	<u>0.41***</u>
TOTAL	1.00	1.00	1.00	1.00

- * Estimated based upon synthetic U Plant-1 sludge measured value.
- ** Estimated based upon measured value for sludge prepared with same flowsheet except all nitrate oxidant instead of nitrate/nitrite.
- *** Estimated based upon synthetic sludge measured value for sludge prepared from In-Farm-1 flowsheet except all nitrate oxidant.

FSU Exploratory Raman Spectra (514 nm Argon Ion Laser)

FSU Exploratory Raman Spectroscopy

(514 nm Argon Ion Laser)

Raman Spectra Summary

Cyanide Containing Compounds:

- **Raman Features Near 2150 cm^{-1}**
- **Unique Line Positions From Each Compound**
- **Spectral Changes $>$ Detection Limit (0.1 cm^{-1})**

Nitrite/Nitrate & Others:

- **Raman Features Between $500 - 1500\text{ cm}^{-1}$**
- **Spectra Are Sharp Lines Except For Ammonia**

**Conclusion: Detection & Qualitative Measurement
Possible With Any Or All Compounds Tested
In Solid & Aqueous Forms**

pH and NaNO₃
Raman Spectra Interference

Table 3 Effect of pH and NaNO₃ Concentration on Position of 2135 cm⁻¹ Line of 0.1 M Fe(CN)₆³⁻					
NaNO ₃ Concentration	pH				
	8	10	12	13.5	13.9
1 M NaNO ₃	2134.64	2134.67	2134.66	2134.74	2134.97
Saturated NaNO ₃	2135.62	2135.67	2135.72	2135.70	2135.78

Table 4 Effect of pH and NaNO₃ Concentration on Positions of 2058 and 2095 cm⁻¹ Lines of 0.1 M Fe(CN)₆³⁻					
NaNO ₃ Concentration	pH				+
	7	10	12	13.5	13.9
1M NaNO ₃	2058.09 2094.50	2058.11 2094.54	2058.07 2094.52	2058.26 2094.59	2058.35 2094.71
Saturated NaNO ₃	2058.95 2094.97	2058.81 2094.97	2058.81 2094.97	2058.81 2094.97	2059.04 2094.93

Table 5 Effect of pH and NaNO₃ Concentration on Position of 1340 cm⁻¹ line of 10% NaNO₂				
Matrix	pH			
	7	10	12	14
water	1339.9	1340.1	1339.9	1339.9
1 M NaNO ₃	1340.7			
Sat'd NaNO ₃	1342.7			

pH & NaNO₃ Impact on Raman Spectra

1340 cm⁻¹ line of 10% NaNO₂

pH & NaNO₃ Impact on Raman Spectra

2135 cm⁻¹ line of 0.1M Fe(CN)₃⁻

Summary:

pH and NaNO_3 Raman Interference

- **Over pH Range of 7-14 An Insignificant Effect On Raman Lines Was Obtained ($0.2\text{-}0.3\text{ cm}^{-1}$)**
- **Ionic Concentration Changes Produce Small But Significant Raman Peak Shifts (large as -2.7 cm^{-1})**

Level Of Detection (LOD)

Level Of Detection

Need: Establish A Base-Line Feasibility/Sensitivity For Using Raman In Qualitative Analysis.

Method:

- **Measure Raman Response For 5-6 Solutions Ranging In Concentration From A Point Near Expected LOD To Approximately 50 Times This LOD**
- **Prepare Analytical Curve Of Least-Squares Fit (LSF) Of Raman Response vs Concentration.**
- **Calculate LOD: Three-Times the Standard Deviation Of The Intercept Of the LSF Line Divided By The Line Slope.**

Ferricyanide in 1 M NaNO₃

Ferrocyanide in 1 M NaNO₃

Nitrite in Water

Table 6 Limits of detection for aqueous ions	
ion	LOD, <i>M</i>
NH_4^+	0.13
SO_4^{2-}	1×10^{-3}
$\text{Fe}(\text{CN})_6^{4-}$	4×10^{-4}
$\text{Fe}(\text{CN})_6^{3-}$	3×10^{-4}
NO_2^-	1.4×10^{-2}

LOD Conclusions:

- **LOD Measurements Show:**
 - **Excellent Linearity Of Raman Response vs Concentration**
 - **LOD Limits Measured Are Well Below A 1% Accuracy Limit**
- **Raman Spectral Features Are Visible At Concentrations That Are 1/3 Or Lower Than The LOD Values**

Raman Spectroscopy

Fluorescence Interference Measurements

Raman spectrum of uranyl nitrate

Raman spectrum of lanthanum nitrate.

Raman spectrum of neodymium nitrate.

Conclusions

Fluorescence Interference Effects

- **Uranyl Nitrate Shows Strong Fluorescence Background With Argon Ion Laser**
 - **Raman Peaks Still Visible Against This Strong Fluorescence Background**
- **No Fluorescence Obtained With La & Nd Nitrites**
- **Longer Wavelength Laser Diode (800 nm Line) Will Show Less Fluorescence Than This Argon Ion Laser Line**

Raman Spectroscopy
Proposed FY-93 Work Scope

Proposed FY-93 FSU Work Scope:

- **Speciation Algorithm To Extract Qualitative & Quantitative Data From Waste Tank Surrogate Raman Spectra**
- **Continue Identification & Archival Of Raman Spectra From Waste Tank Materials**
- **Determine Feasibility Of A Raman Spectroscopy Based Method For Measuring Water Content In Salt Cake Materials.**
- **Provide Raman Technical Assistance (As Needed Basis)**

Appendix Q

What Remains to Close the Ferrocyanide Unreviewed Safety Question

**What Remains to Close the Ferrocyanide
Unreviewed Safety Question?**

presented to

Tank Waste Science Panel

by

**R. J. (Bob) Cash
Westinghouse Hanford Company
January 13, 1993**

FERROCYANIDE UNREVIEWED SAFETY QUESTION

- **The USQ:**
 - 1) Intimate mixtures of $\text{Fe}(\text{CN})_6^{-4}$ and $\text{NaNO}_2/\text{NaNO}_3$ within the waste may be able to react and propagate violently
 - 2) Resultant dose consequences of such a reaction may exceed those bounded in the 1987 EIS
- **Present SAR:** Ferrocyanide treated as a fuel and fuel/nitrate reactions were historically considered incredible; consequences were not calculated

1987 EIS considered a ferrocyanide explosion: dose consequence was 200 mrem for short term exposure

GAO report calculated a dose 10 - 100 times higher for an explosion

WASTE TANK SAFETY LOGIC OVERVIEW

LOGIC FOR WASTE TANK SAFETY ISSUE RESOLUTION IN NETWORK FORMAT (BY TANK OR GROUPS OF TANKS)

Q.4

**LOGIC FOR WASTE TANK SAFETY ISSUE RESOLUTION
IN NETWORK FORMAT
(BY TANK OR GROUPS OF TANKS)**

LOGIC FOR WASTE TANK SAFETY ISSUE RESOLUTION IN NETWORK FORMAT (BY TANK OR GROUPS OF TANKS)

1.0 EVALUATE AND DEFINE THE PROBLEM

1.1 Establish Preliminary Hypothesis

1.1.1 Develop (Select) Model

1.2 Obtain Data on Tank and Contents

LOGIC FOR WASTE TANK SAFETY ISSUE RESOLUTION IN NETWORK FORMAT (BY TANK OR GROUPS OF TANKS)

1.0 EVALUATE AND DEFINE THE PROBLEM (CONTINUED)

**LOGIC FOR WASTE TANK SAFETY ISSUE RESOLUTION
IN NETWORK FORMAT
(BY TANK OR GROUPS OF TANKS)**

1.0 EVALUATE AND DEFINE THE PROBLEM (CONTINUED)

RESOLUTION OF THE UNREVIEWED SAFETY QUESTION

What We Know About the Ferrocyanide Safety Issue

- Highest Tank Temperature $< 55^{\circ}\text{C}$
- Three Flowsheets used: U-Plant, T-Plant, and In-Farm
 - U-Plant simulant is self-extinguishing but will not propagate
 - T-Plant should be very similar to U-Plant
 - In-Farm simulant burns when dry but only at 5-10 cm/min; 12-15 wt% moisture precludes propagation
- Moisture content of C-112 waste samples was ≈ 50 wt%
 - In-Farm simulant retain 50 wt% moisture after centrifugation at 2500 g
 - U-Plant simulant retains 66 wt% moisture
- Energetics of C-112 waste $< <$ than expected
 - Degradation by radiolysis and alkaline hydrolysis has undoubtedly occurred

RESOLUTION OF THE UNREVIEWED SAFETY QUESTION

Key Safety Criteria - Show Criteria Exist for Bulk Waste

No Significant Bulk Temperature Rise is Possible

- **Passive Cooling without significant moisture loss**
- **Measured tank Temperatures are low**
- **Chemical Heat Rate is Insignificant ($\ll$ Decay Heat) at storage temperatures and still low at the boiling point**
- **Local Reactions cannot Propagate through the bulk material**
- **Moisture Loss is slow and can be controlled (limited)**

RESOLUTION OF THE USQ (Continued)

Key Safety Criteria - Bulk Waste

Any Bulk Heating Event is Benign

- **Temperature is Limited to the Boiling Point ($\approx 120\text{ }^{\circ}\text{C}$) if moisture is present**
- **Heat of Vaporization (water) $\gg$ Reaction Heat**
- **Heat Transfer of Moist Waste $>$ Reaction Heat**
- **Hot Spots of concern are Incredible**

RESOLUTION OF THE USQ (Continued)

Key Safety Criteria - Local Region (In-Farm Flowsheet)

Local Propagation Cannot Occur

- **Volumetric Heat Rate to reach Boiling Point must be > > higher than Bulk average values ($T < 120\text{ }^{\circ}\text{C}$)**
- **Chemical Heat Rate at the Boiling Point is still Low**
- **Concentration of Decay Heat to reach required levels ($T > 120\text{ }^{\circ}\text{C}$) is Unlikely**
- **Heated volumes will be cooled - Temperature is Limited to Boiling Point [up to very high heat flux]**

RESOLUTION OF THE USQ (Continued)

Key Safety Criteria - Local Region (In-Farm Flowsheet)

- **If Dryout Should Occur, dry volume is limited by heat source available**
- **Heat available in 4 C-Farm tanks is low [$< 7,500$ BTU/Hr or < 2200 watts]**
- **Decay Heat hot spots would reach a steady state temperature of < 120 °C with no net moisture loss from the tank**
- **RISK = Probability X Consequence**
 - **Probability is believed to be incredible**
 - **Do Consequence Analysis to show a propagating event would not exceed onsite and offsite guidelines**

RESOLUTION OF THE USQ (Continued)

Schedule

- **USQ Strategy Letter sent to DOE on October 28, 1992**
- **USQ Resolution Plan due to DOE on January 29, 1993**
- **Core Sample Results needed from In-Farm flowsheet tanks C-109, C-108, and C-111 to confirm waste composition and energetics - September 1993**
- **Likewise similar results needed from at least one U-Plant tank, BY-104, with backup from T-107 - December 1993**
- **Request removal of USQ in mid to late FY 1994**

Appendix R

The Need for an Integrated Computer Model of the Tank Farm

The Need for an Integrated Computer Model of the Tank Farm?

**Presented to
TANK WASTE SCIENCE PANEL**

**By
J. W. (Jerry) Osborne
Westinghouse Hanford Company
January 13, 1993**

Source Data

- **Physical and chemical characteristics (molecular weight, diffusivity, viscosity, conductivity, vapor pressure, temperature, boiling point, specific heat, latent heat, vapor liquid equilibria data).**
- **Geometry of source (dimensions of facility and release hole, position of release relative to liquid or gas in tank, height above ground)**
- **Plant operating procedures (characteristics of safety valves and plugs, control valve closing times, ventilation devices).**

Source Data (con't)

- **Time variation of release rate**
- **Underlying ground surface (topography, dike position, thermal conductivity, density, specific heat, moisture content, and porosity of ground)**
- **Fraction of gas, liquid, and aerosol**

Meteorological Data

- **On-site wind velocity (one representative site if terrain is flat, multiple sites if terrain is complex)**
- **On-site net radiation flux (default: cloudiness)**
- **Temperature, relative humidity, turbulence, stability**

Site Information

- **Local topography, including building and storage tank dimensions, dike dimensions, equipment and operating information**

Receptor Information

- **Location, sampling and averaging times, spatial averaging over line, area, or volume**
- **Air exchange rate for a building**
- **Toxicological data; location of ignition sources**

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