Report on the Handling of Safety Information Concerning Flammable Gases and Ferrocyanide at the Hanford Waste Tanks

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Aerial view of the SY Tank Farm.

INTRODUCTION

On March 23, 1990, the Department of Energy's Richland Operations Office (DOE-RL) held a press conference to announce that "a new study by Westinghouse Hanford Company (WHC) scientists has raised concerns about the potential consequences of hydrogen buildup in some of the underground nuclear waste storage tanks at Hanford." The principal concern was the generation of hydrogen in a high-level radioactive waste tank in sufficient concentrations to ignite or explode, with potential consequences for worker and public health and safety.

Flammable gas is generated in certain Hanford waste tanks by chemical reactions among the organic constituents of the waste. These reactions make the waste, which is in the form of a slurry, "grow" and are well-known phenomena at Hanford in one tank in particular, tank 101-SY, which contains wastes particularly high in organic constituents. The decomposition of these constituents has led to intermittent releases of hydrogen and other gases from the tank since the late 1970's. The "new" study referred to in the DOE-RL announcement was essentially a technical summary of existing historical and operating information on Hanford tank 101-SY. This document, which had raised concerns among Savannah River* engineers when it was sent there for review in January 1990, highlighted the fact that nitrous oxide, one of the gases generated in 101-SY along with hydrogen, is a strong oxidizer that would lower the threshold concentration at which hydrogen could ignite, increasing the probability of an explosion.

The general consensus among technical reviewers of tank 101-SY is that the probability of an explosion is low. This is based primarily on the fact that combustion has not occurred during the past 13 years of operation. In addition, since March 1990 operating restrictions have been imposed to minimize the potential for ignition sources. Recognizing, however, that there are uncertainties with regard to the current composition of the waste in those tanks exhibiting slurry growth, the Department of Energy has taken the position that, notwithstanding the low risk, compensatory safety precautions are warranted until further safety analyses can be performed. These safety analyses are needed to establish what steps are required to resolve the problem of flammable gases in the Hanford waste tanks.

*The Department of Energy also reprocesses nuclear fuel and stores the resultant nuclear waste in tanks at its Savannah River site near Aiken, South Carolina. Westinghouse subsidiaries currently operate facilities at both Savannah River and Hanford.

Following the DOE-RL announcement of March 23, Governor Booth Gardner of Washington wrote a letter to Secretary Watkins expressing concern about developments at Hanford and about the manner in which information had been handled. The Director of the Office of Environmental Restoration and Waste Management (EM) formed a team of technical experts to assess whether a problem actually existed in tank 101-SY and whether similar problems might exist at DOE's Savannah River facility, the other major site in the DOE complex where large volumes of high-level waste are stored. The EM team performed a review at Hanford on April 2-3, 1990, and issued a report on April 4, 1990. The team concluded that gases trapped inside tank 101-SY could be combustible and that an explosion beneath the waste crust would be unlikely to penetrate both the internal and external steel walls of the tank, thus limiting the potential consequences of an accident.

At the same time, the Secretary directed that the respective DOE Headquarters Offices of Nuclear Safety (NS) and Environment, Safety, and Health (EH) jointly form an independent investigation team to provide an interim evaluation of the management structure for handling information about gas generation in the Hanford waste tanks. Findings of this investigation were to be factored into a broader review of Hanford's safety procedures and management structure by a Departmental environment, safety, and health "Tiger Team," which planned to begin work on May 21, 1990. The NS Director managed the conduct of the investigation and the preparation of this Report. With NS support, EH team members performed a technical assessment of conduct of operations, maintenance, design control, and event reporting. On June 6, 1990, EH forwarded their assessment to NS. (The assessment is included in Appendix C.) The leader of the Tiger Team was provided a copy of this EH assessment and was briefed on the preliminary findings of this Report.

This Report presents the results of the NS evaluation. The NS team visited Hanford from April 10 until May 18, 1990, and continued its review of documentation through June and July. The review examined two concerns that had not been identified by the team of experts formed in early April. These concerns were immediately conveyed to line management for disposition. The first concern dealt with the adequacy of steps being taken to protect workers against the possible effects of pressurization of tank 101-SY. In response, on May 14, 1990, the Manager of DOE-RL directed the contractor to take additional steps to ensure that workers were protected during future pressurizations of the tank. The second concern raised by the NS team was the possibility that hydrogen combustion might trigger secondary chemical reactions that, in combination with a hydrogen burn, might either collapse the dome of the tank or lead to prolonged radioactive releases. This issue is still under review. If it proves to be a valid concern, it could conceivably alter earlier assessments of the consequences of a potential accident and heighten the need for prompt remedial action.

Although the NS investigation focused primarily on the handling of information about the potential for hydrogen combustion, it also examined the handling of information concerning potential exothermic reactions involving ferrocyanide compounds, which were added to single-shell tanks in the 1950's. These compounds were added as part of a cesium recovery campaign. Under certain conditions, particularly in the presence of elevated waste temperatures,

ferrocyanides could react exothermically with other chemicals in a tank and cause a runaway reaction or explosion. Concerns had been raised in Congress and in the media over the possible suppression of a 1984 Hanford report on the subject. The report in question, which was not released to the State of Washington until 1989, was one factor that led the State to launch an investigation in October 1989 of the potential for explosions in Hanford's single-shell tanks. The State's investigation in turn prompted Westinghouse to develop a series of papers on tank farm safety issues, one of which ultimately surfaced the issue of flammable gas generation in the Hanford double-shell tanks, which eventually led to the March 23 announcement.

This Report actually covers more than the charge to the NS team because additional areas had to be investigated in order to understand how information was being handled. Thus, this Report deals with conduct of operations at the Hanford Tank Farm, safety analysis and documentation relevant to tank 101-SY, communication of the risks associated with the operation of that tank, and the handling of information on 101-SY and ferrocyanide by DOE and contractor management. It does not address, much less resolve, the various technical uncertainties related to the composition of the waste in tank 101-SY, nor does it establish why the waste intermittently grows and collapses, in the process releasing flammable gases. DOE and the contractor are currently coordinating their efforts to develop and implement an effective program that will safely and satisfactorily obtain the data necessary to explain what is occurring in tank 101-SY and provide a basis for remedial measures that will reduce any risk to workers or the public from potential combustion accidents.

EXECUTIVE SUMMARY

On April 4, 1990, the Secretary of Energy directed the Office of Nuclear Safety (NS) and the Office of Environment, Safety, and Health (EH) to assess the "management structure for handling information concerning gas generation in the Hanford waste tanks." Concerns had been raised about safety issues related to flammable gas generation at the Hanford Tank Farm, and DOE awareness of them, reflecting possible inadequate management attention by DOE and its operating contractors.

This Report examines those concerns. It concludes that the management actions and structure necessary to ensure an adequate level of safety at the Hanford Tank Farm have been lacking for over a decade, and it makes recommendations to remedy the problems identified. The Report concludes that DOE's operating contractors--Westinghouse Hanford Company (WHC) and its predecessors, Rockwell Hanford Operations (RHO) and Atlantic Richfield Hanford Company--its Richland Operations Office (DOE-RL), and the Headquarters Offices of Defense Programs and Environmental Restoration and Waste Management* failed to exercise appropriate safety oversight of tank farm operations to ensure that significant issues related to hydrogen flammability in tank 101-SY were promptly identified, reported, analyzed, and resolved.

Despite Department-wide Secretarial initiatives over the past one-and-a-half years to strengthen line program accountability for environment, safety, and health, deficiencies continue to be identified in safety analyses, procedures, operations, training, maintenance, and reporting. In the opinion of the NS team, these ongoing problems indicate a failure to identify root causes and develop appropriate solutions and represent a systematic failure on the part of the contractor and DOE.

Principal Findings

- (1) Contractor personnel were aware for nearly 13 years that slurry growth in tank 101-SY was due to flammable gas generation but did not elevate the issue to proper levels of their management or to DOE and did not resolve the problem of potential combustion in the tank.

Westinghouse and DOE-RL announced in March 1990 that tank 101-SY represented a "new" safety concern and that the significance of an

*On November 1, 1989, the Office of Environmental Restoration and Waste Management assumed line management responsibility for the Hanford Tank Farm from the Office of Defense Programs.

oxidizer--nitrous oxide--below the waste crust was not previously recognized. However, contractor documents indicate that the significance of oxidants in 101-SY was known as early as the late 1970's. Moreover, laboratory studies conducted by Rockwell Hanford Operations between 1978 and 1983 established a basis for assessing which gases were thought to be responsible for the observed slurry growth phenomenon and the potential concentrations for each gas identified. Laboratory estimates of gas concentrations under the crust were upwards of 50 percent for hydrogen and in excess of 20 percent for nitrous oxide. Concerns over tank 101-SY gas releases and pressurization events were expressed in reports by RHO (and WHC) safety personnel, but no effective action was taken. As recently as October 1988, the safety significance of 101-SY was outlined by a WHC engineer who had been asked by senior tank farm management to conduct a review of the problem tank. The engineer's October 1988 memo cited the potential for hydrogen to burn or explode during pressurization of tank 101-SY, as well as potential hazards to workers from unfiltered releases of radionuclides and toxic gases that could be emitted through tank leakage points. He also made suggestions for resolving these problems. There is no indication that this memo or its contents was provided to higher levels of WHC management. Although the 1988 memorandum was referenced in documents provided to DOE-RL's staff, the substance of the memo was not conveyed to DOE-RL until March 1990, and a copy of the memo itself was apparently not made available to DOE-RL until after the issue was made public.

- (2) **Upon being informed of the problem in tank 101-SY, DOE-RL management failed to take appropriate and required action to assure protection of public health and safety.**

On March 6, 1990, WHC first informed DOE-RL management of the flammable gas problem in 101-SY and the potential for an explosion below the crust. During the briefing, a DOE-RL manager asked a question relating to whether the potential consequences of an explosion in 101-SY were encompassed by previous analyses of the tank. When the contractor erroneously assured them that they were, the DOE-RL managers present uncritically accepted this response and failed to explore the matter further or take any action.

Over the years, DOE-RL had received information that should have alerted management sooner to the safety implications of flammable gas generation in 101-SY. Prior to 1986, DOE-RL had routinely received contractor status reports about laboratory studies on slurry growth. DOE-RL personnel also routinely received Event Fact Sheets documenting gas pressurizations in 101-SY. In 1984, RHO engineers conducted a formal briefing at DOE-RL on the slurry growth problem and on the potential for unfiltered releases during pressurizations. From the late 1970's through the mid-1980's, DOE-RL monitors routinely attended contractor program status meetings at which hydrogen and slurry growth issues were periodically discussed.

- (3) **The DOE waste management line programs at Hanford and DOE Headquarters have not adequately overseen contractor safety performance at the Hanford Tank Farm.**

The DOE Headquarters program offices responsible for waste management activities at the Hanford Tank Farm were not involved in management of the safety concerns surrounding tank 101-SY until after the issue became public. For its part, DOE-RL did not keep abreast of events and issues at the tank farms.

Lack of adequate staff and limited technical capability are partial explanations for the DOE deficiencies referred to above. In recent years, DOE-RL has relied on a support contractor to ease some of the staff burden. However, management of this contractor by DOE-RL has also been inadequate. The support contractor was asked to review Westinghouse responses to DOE-RL surveillances, and the NS team found that the contractor had closed out open WHC items without DOE-RL's knowledge or approval. Contractor responses to DOE-RL surveillance findings are required to be provided within 30 days, yet WHC delayed providing responses to surveillance reports by as much as 7 months, apparently without any DOE-RL intervention.

- (4) **Release of information by DOE-RL and its contractors to outside agencies and the public regarding problems at the Hanford Tank Farm has not been timely or appropriately complete. In the opinion of the NS team, evidence suggests that the release of information on the tank farms may have been driven less by the desire for prompt and full disclosure than by concern over disclosure by outside entities.**

In mid-October 1989, the State of Washington announced that it would conduct an investigation of safety issues associated with the Hanford single-shell tanks, including "the effects of organic decomposition with a potential for generating gas pockets." In anticipation of this investigation, WHC decided to write a technical "white paper" on each issue that might conceivably be investigated by the State. From October to December, WHC staff engineers wrote draft papers on a variety of subjects, including the potential for flammable gases in the double-shell tanks. The paper on this subject focused heavily on tank 101-SY and the slurry growth phenomenon. The penultimate draft of that paper was reviewed in December by the WHC Manager of Waste Management Engineering. In a handwritten comment made in the margin of the paper, he questioned whether the company was "ready" to clear for release to the public many of the documents referenced in the report, including the 1988 memorandum mentioned above and a variety of other background documents detailing the long history of concern about hydrogen generation in 101-SY. WHC removed these references prior to issuing the final draft.

WHC failed to mention the issue of flammable vapors in 101-SY in meetings that were held with the State of Washington, the DOE Advisory Committee on Nuclear Facility Safety, and DOE-RL engineers between

February 6, when Savannah River engineers first voiced their concerns about 101-SY, and March 6, 1990, when DOE-RL management was informed. Consultants to the Defense Nuclear Facilities Safety Board (DNFSB) were briefed on the matter on March 20-21, after they had requested that the topic be covered. An earlier draft agenda for the March 20-21 meeting between WHC and DOE-RL made no mention of the hydrogen issue, and the DNFSB consultants came away from the meeting with the impression that an attempt had been made to keep the matter from being discussed.

DOE-RL's handling of a 1984 report on ferrocyanide hazards was similar. DOE-RL did not clear the report so that it could be referenced or released publicly, on the basis that it required further work. At the time, DOE-RL's Chief Counsel advised DOE-RL management that it needed to ensure that DOE-RL was not "suppressing the report," but was merely redirecting the effort. Nevertheless, the ferrocyanide issue was not addressed again until 1988. Pressure to revive the issue stemmed from publicity surrounding DOE-RL's treatment of the potential for ferrocyanide explosions in a 1987 Environmental Impact Statement and subsequent inquiries by a private citizen. The latter raised questions about the potential for a ferrocyanide explosion, which prompted intervention by the State of Washington and by a U.S. Senate committee. The 1984 report on ferrocyanide was released by DOE-RL after the State formally requested it. Following release of the report, DOE-RL staff provided information to the press indicating that the report had not been released in 1985 because it had failed peer review and was contradicted by another report. DOE-RL later retracted these explanations but, in doing so, did not provide a valid reason for previously declining to clear the report.

- (5) DOE and its operating contractors have failed to provide and maintain a complete and coherent hierarchy of safety analyses, safety requirements, and operating limits at the Hanford Tank Farm that would allow safety operating margins to be demonstrated.

The original Safety Analysis Report (SAR) for the Hanford double-shell tanks was issued in 1977. It did not address requirements for in-tank waste sampling and analysis nor specify the spare tankage requirements that might be needed in the event of a leak, even though leakage in the single-shell tanks was a primary reason for building the double-shell tanks. The 1977 SAR also included no requirements for hydrogen monitoring, even though hydrogen generation was a well-known phenomenon in single-shell tanks.

The 1977 SAR was not revised until 1986. The revised SAR failed to consider most of the laboratory results on slurry growth and little of the extensive operating history of gas releases and pressurizations in 101-SY. The treatment of hydrogen flammability in the 1986 SAR and the Operational Safety Requirements (OSR's) accompanying it illustrate the point: although Table 9-3 in the 1986 SAR demonstrates that complexant degradation reactions produce gases under the salt crust of a potential explosive mixture which contains quantities of H_2 and N_2O , no bounding

analysis was performed of the consequences of a rapid burn of these gases.

There is no effective process or policy at the Hanford Tank Farm to govern the preparation and update of SAR's or the operating limits that are supposed to derive from them. Procedures such as core drilling, attempts at crust breaking, and air and water lancing were performed in tank 101-SY without appropriate safety evaluations. Such activities clearly presented potential safety hazards (e.g., by introducing ignition sources) that should have received proper prior analysis. The OSR's recently proposed by WHC embodied many of the deficiencies that characterized earlier versions (e.g., they were generic in scope; they did not acknowledge the existence of a solid crust or slurry growth in many tanks; and they did not adequately reflect existing knowledge of the operating history and conditions of the tank farms).

- (6) **Westinghouse has failed to comply with DOE requirements for reporting unusual events. DOE-RL has not assured contractor accountability for those requirements.**

DOE Order 5000.3, "Unusual Occurrence Reporting System," was issued by DOE Headquarters in 1984 and included illustrative examples of events subject to reporting, including "failure of effluent monitors," "releases of toxic material," and "unplanned or unexpected changes in process conditions [important] to safety, whether abrupt or long term." Contrary to DOE Order 5000.3, no formal Unusual Occurrence Report (UOR) regarding tank 101-SY was submitted to DOE until April 4, 1990, after the problem became public. On April 19, tank 101-SY experienced another gas pressurization event, but Westinghouse did not issue another UOR, maintaining that the April 4 UOR was "still open" and could be used to report the April 19 event.

DOE Notice N5480.4 was issued in June 1988. It directed contractors to notify DOE promptly of any nonroutine events with potential safety significance. The notice was issued in light of continued failure by some contractors and operations offices to report safety incidents and issues promptly to DOE Headquarters. WHC's failure over the last two-and-a-half years to notify DOE promptly of numerous incidents regarding 101-SY represents contractor nonconformance with an important Departmental requirement and DOE-RL's lack of proper oversight. (Rockwell was similarly out of compliance over a longer period of time.)

Recommendations

- (1) **DOE's Office of Environmental Restoration and Waste Management (EM) should develop and implement a plan to strengthen the technical capabilities of its staff in the areas of facility operations and chemical engineering.**

- (2) DOE-RL should be required to submit for EM approval a plan to clarify the responsibilities and improve the technical capabilities of its Waste Management Division. This plan should establish qualifications criteria and performance-based training requirements and should address staff assignments, responsibilities, and authorities, particularly with respect to facility oversight.
- (3) DOE should expedite revision of the Safety Analysis Report for the double-shell tanks at Hanford, incorporating a comprehensive set of Operational Safety Requirements.
- (4) DOE should develop a site-wide system at Hanford and other DOE sites to track and disposition safety issues "from cradle to grave."
- (5) DOE-RL should assign a full-time DOE representative to the tank farms to "walk the spaces" and closely monitor engineering and operations activities.
- (6) DOE should specify requirements for external peer review of technical research performed by and for its contractors.
- (7) DOE-RL should require that the contractor provide additional maintenance support to the tank farms.
- (8) DOE should require that the contractor expeditiously develop a plan to "redline" design drawings and establish configuration control over the tank farms.
- (9) The contractor should strengthen the authority of the Tank Farm Manager, so that he/she has operational control over support functions currently matrixed to the tank farms.

Contents of tank 101-SY showing one of the large risers. The splattering along the tank wall is evidence of past pressurizations of the tank. (False color photograph)

I. SLURRY GROWTH AND FLAMMABLE GAS RELEASES AT HANFORD: A HISTORICAL OVERVIEW

The Hanford site, located in south central Washington State, was originally acquired by the Federal Government in 1943 for the construction and operation of facilities to produce plutonium for the Manhattan Project. The site encompasses approximately 560 square miles within the Columbia River Basin. For over 30 years, Hanford facilities were dedicated primarily to plutonium production for national defense purposes and to management of the resulting wastes. In recent years, waste management has become the central focus of activity at the site, although a diverse set of other programs, including research and development for advanced reactors and renewable energy technologies, are being pursued there.

The processing of spent reactor fuels for plutonium production leads simultaneously to the production of radioactive waste. At Hanford, the bulk of these wastes is stored underground at the Hanford Tank Farm, awaiting additional treatment and processing prior to final geological disposal. Because many of these wastes will remain radioactive for thousands of years, they must be handled, contained, and disposed of safely and in a manner that guarantees protection of the environment, workers, and the public.

The Hanford Tank Farm is divided into the 200 East and 200 West Area tank farms. Wastes are stored underground at the tank farms in carbon-steel tanks ranging in capacity from 55,000 to over 1 million gallons. A total of 149 single-shell tanks (SST's) were constructed between 1944 and 1964. None of the SST's continue to receive wastes. Leaks were discovered in some of the SST's in the early 1970's, and to date 66 SST's have been confirmed as "leakers." Since leakage of the tanks was first discovered, DOE has had an ongoing program to stabilize and isolate the wastes. The stabilization program calls for removing and concentrating the liquid radioactive waste and transferring it to newer double-shell tanks (DST's). The waste is first concentrated in order to limit the number of double-shell tanks that must be constructed. Twenty-eight DST's have been built since 1968, and all are in active service. Storage of wastes in DST's is only intended to be an interim arrangement. The wastes in these tanks will eventually be pretreated and separated into high-level and low-level radioactive waste fractions. The low-level fraction will be grouted and disposed of at Hanford in near-surface vaults. The high-level fraction will be vitrified for geological disposal in a yet-to-be-determined location.

The volume of liquid radioactive waste in SST's is reduced by a process involving evaporation and crystallization. The result is a viscous mixture known as "double-shell slurry" (DSS), a term that refers to its storage in double-shell tanks. DSS consists primarily of radioactive constituents,

various waste products (NaOH , NaAlO_2 , NaNO_2 , NaNO_3 , and $\text{Fe}[\text{III}]$) from the PUREX plutonium recovery process, combined with organic complexants, such as EDTA, HEDTA,* and hydroxyacetate (citric acid). (The PUREX plant is located adjacent to the 200 East Area tank farms.) These organic constituents were used to remove ^{90}Sr , ^{137}Cs , and other fission products from the waste prior to storage in the tanks.

Fluctuations in the level of waste stored in single-shell and double-shell tanks were first recorded in the mid-1970's. A 1981 survey of monitoring data for the SST's in the West Area tank farms, covering an 18-month period between 1976 and 1978, found 10 tanks that exhibited such fluctuations. The tanks identified included four each in the SX and 241-U Tank Farms and two in the 241-S Tank Farm. The growth rate of the waste in these tanks ranged from 0.5 to 3 inches per month (i.e., about 40-300 gals/day). Of these tanks, five continue to show signs of slurry growth, two show a decline, and the level of the remainder is either stable or unknown. Other SST's have shown similar growth, including 103-SX, 101-AX, 101-A, and 110-T.

Double-shell slurry was first produced in April 1977. The first run produced 274,000 gallons of slurry, which was deposited in a newly constructed 1-million-gallon double-shell tank, tank 101-SY. The initial height of the waste in the tank was 101 inches. Over the next 6 months, this first batch of DSS exhibited a steady and unexplained growth in volume of about 2,800 gallons per month, a growth rate of 1 percent per month. In November 1977, 380,000 gallons (140 inches) of complexed concentrate (material high in organics) was added to tank 101-SY. Again, a steady growth in the liquid waste level was observed. In June and again in August 1978, 131,000 gallons and 60,000 gallons, respectively, of complexed concentrate were added to the tank. A second DSS run in November 1980 deposited 230,000 gallons of DSS into the tank. Thus, a total of five separate additions was made to the tank between 1977 and 1980, which brought the fill height of the tank to 408 inches--21 inches (over 50,000 gallons) of which were attributable to slurry growth.

Studying Slurry Growth (1978-1983)

From 1978 to 1980, a series of parametric studies was performed in the Rockwell Hanford Operations (RHO) laboratory using synthetic double-shell slurry. A Rockwell chemist studied slurry growth on a microscopic scale and concluded that the entrapment of gases below the surface of the slurry was responsible for the observed growth.¹ Another senior chemist reported finding 4.2-percent hydrogen in diluted gas samples of synthetic slurry and expressed concern over hydrogen flammability.² He reported subsequent results that showed hydrogen and nitrous oxide concentrations in synthetic DSS on the order of 11.8 and 20.7 percent (by volume), respectively.³ In a 1980 summary of laboratory studies of synthetic DSS, yet another Rockwell chemist concluded

*EDTA: ethylenediaminetetraacetic acid, tetrasodium salt
HEDTA: N-(2-hydroxyethyl) ethylenediaminetriacetic acid, trisodium salt

that the phenomenon was due to "gas generation caused by the oxidative degradation of the complexant HEDTA."⁴ He further concluded that several gases were being generated, principally nitrogen, nitrous oxide, and hydrogen.

Slurry growth has been observed in tank 101-SY since the first DSS run in 1977. Since the last deposit of DSS in that tank in 1980, the waste surface has been cyclically rising and abruptly falling approximately once every 2-3 months. The abrupt collapse of the waste has coincided with pressure increases that have ranged as high as 1 inch water gauge (w.g.) over and above the existing pressure of the tank atmosphere, which is normally maintained negative by forced ventilation. (Absolute measures of these pressure pulses are not known owing to the type and condition of the instrumentation that was available to measure them.) Increases and subsequent collapses in the waste level have been documented using two devices, a conductivity probe made by the Food Instrumentation Corporation (an FIC gauge) and a manually operated tape. The data indicate that a significant portion of the waste surface is involved in these evolutions. In January 1983, despite a fully operating ventilation system drawing a negative pressure on the vapor space above the waste in 101-SY, a positive pressure (above atmospheric) was measured. This "overpressurization event" followed a drop in the tank's waste level. Since that date, vapor space pressurization accompanied by eventual waste level subsidence has regularly occurred. A recent event on April 19, 1990, resulted in another pressurization to 0.1 inch w.g.

From 1981 to 1983, Rockwell scientists continued to conduct laboratory analyses to try to predict the rate of slurry growth and better understand the source of the problem. Double-shell slurry growth was an increasing concern to RHO because the whole point of producing DSS--to reduce the volume of stored waste--was being undermined by indications that the slurry was growing. Rockwell undertook a series of new experiments that focused on the rate and extent of DSS growth using actual DSS samples.⁵ (These DSS samples were not taken from tank 101-SY; they were feed material from continuous DSS runs.) The experiments confirmed that gases were formed as byproducts of the degradation of organic complexants (HEDTA, EDTA, and hydroxyacetate) in the waste. The degradation of these organic constituents, the presence of iron as a catalyst, the role of temperature, and the availability of oxygen to feed the reaction were found to be important variables controlling the rate of reaction. These studies showed that various gases were generated as the organics degraded, including hydrogen, nitrogen, nitrous oxide, and carbon dioxide, thus confirming earlier laboratory results.

Both laboratory and pilot studies of slurry growth indicated that gas bubbles adsorb into fine solids in the waste, causing the solids to float toward the surface. This process continually adds to the thickness of a solid layer of material on the surface of the waste that forms a crust referred to as "salt cake." It has been postulated that, as gas accumulates under the crust, the crust itself gradually rises within the tank, until increased gas volume and pressure lead to a breach or fissure in the crust layer. As noted above, it has been established that sudden releases of compressed gas into the tank vapor space can offset the negative draw from the tank ventilation system, occasionally causing a positive tank pressure (overpressurization). After the release of these gases, waste levels have been known to drop as much as 9

inches. The trend through 1988 was toward ever greater fluctuations in the level of the waste, thus implying that the crust was becoming more difficult to breach and that more and more gas was accumulating underneath the crust, possibly due to its increasing thickness.

During overpressurization events in tank 101-SY, the concentration of hydrogen has approached and occasionally exceeded the threshold of hydrogen flammability in dry air (4 percent of the total volume of the tank's vapor space). On one occasion, an actual measurement of the hydrogen concentration in a tank exhaust riser during a pressurization event found a transient concentration exceeding 4 percent. (The meter actually "pegged out" at 4 percent, and Rockwell engineers inexplicably recorded the measurement as 5-percent hydrogen.)⁶ Given the buoyancy of hydrogen and its tendency to mix rapidly with air, it is probable that the actual localized hydrogen gas concentration in the tank vapor space under the riser was higher still. Concentrations under the crust would have been even higher because of compression of the gas from the weight of the slurry and the overlying crust. Indeed, it is likely that the concentration of hydrogen gas in the bottom layers of DSS in 101-SY exceeded the lower detonable limit in dry air (18 percent). This likelihood is supported by laboratory experiments and calculations based on synthetic complexant wastes, which found hydrogen concentrations of 50 percent and higher.⁷ (As noted before, more recent measurements also indicate gas concentration of greater than 50 percent hydrogen.)

The availability of oxygen either in the tank vapor space or within the DSS itself would be cause for concern regarding the potential for hydrogen combustion in 101-SY. But other oxidizers may also be present in significant quantities. For example, nitrous oxide, generated as a reaction product when complexants degrade, is a strong oxidizer. In a nitrous oxide environment, the lower flammability limit for hydrogen can decrease to 3 percent of the total volume. In addition, the energy released from a hydrogen and nitrous oxide combustion is significantly greater than from combustion of hydrogen in air. The relative concentrations of gases and the extent to which they mix within the waste is not well known, although laboratory studies suggest that both hydrogen and nitrous oxide are major constituents of the DSS gases in 101-SY. The relative concentrations of gases released in the event of April 19, 1990, were measured using a mass spectrometer. After compensating for the presence of air, the results indicated that the gases measured in the tank vapor space were 57-percent hydrogen and 43-percent nitrous oxide.

For any of these gases to ignite, there must be an ignition source. Ignition sources within the tank have not been firmly established, although it is clear that core sampling, flash photography, and crude attempts to break the crust manually (all of which have been conducted during operations at 101-SY) provided potential ignition sources.

An analysis of slurry growth in 101-SY conducted on October 7, 1983, concluded that previous laboratory studies had left significant questions about the probable causes of the phenomenon unanswered. For example, it was pointed out that the maximum growth expected in the level of the waste and the potential for radionuclide emissions during pressurizations were still not clearly understood. Lancing and physically breaking the crust were suggested as

available methods to control waste level and to mitigate uncontrolled pressurizations. Lancing of the waste was first attempted on October 20, 1983.

Addressing Slurry Growth As A Problem (1984-1989)

A relatively large pressurization event occurred in July 1984. It prompted the contractor to form a task force to reassess the problems at 101-SY. The 1984 task force recommended routine lancing as a short-term measure to control waste level increases in the tank.⁸ The task force also recommended a number of long-term measures, including installation of a liquid observation well, sampling for radionuclide emissions, monitoring for vapor space hydrogen, and core sampling to characterize the physical and chemical properties of the waste. Both the temporary installation of a hydrogen monitor and limited core sampling were conducted in 1985. However, these actions were not sufficient to resolve the problem.

High-pressure water lancing of the crust had been used to control waste growth in single-shell tanks. As noted above, lancing of the crust in tank 101-SY was first performed on October 20, 1983. It resulted in an immediate decrease in waste level as gas was released from the tank. At least 27 separate lancing operations using portable lances were conducted between October 1983 and April 1986, with each operation adding approximately 400 gallons of water to the tank. To reduce the potential for the spread of contamination during lancing operations, permanent lances were installed in 1986. Rockwell engineers eventually became concerned that the regular addition of water to 101-SY would lead to violation of operating specifications that established the maximum permissible tank level. Rockwell then began to consider air lancing as an alternative. Rockwell commenced air lancing on November 25, 1986. After the transition from Rockwell to Westinghouse Hanford Company (WHC) in mid-1987, Westinghouse continued lancing 101-SY with both air and water through 1988. In 1989, lancing operations were terminated after a review demonstrated that the tank level was repeatedly exceeding operating specification limits and that the lancing operations themselves were not only ineffective, but were apparently contributing to the problem. During the last 2 years, the level of tank 101-SY has declined from a maximum of 423 inches in 1988 to its current level, which fluctuates between roughly 410 and 416 inches.

Radionuclide venting and the potential release of toxic gases during pressurizations of tank 101-SY were raised as issues after the initial pressurizations in early 1983. DST's were designed with exhausters to maintain negative pressure within the tanks, and the exhausters have high-efficiency particulate air (HEPA) filters installed on them. This method of containment is defeated in 101-SY whenever the tank pressurizes above atmospheric pressure. Containment is lost because gases are able to escape through several unfiltered penetrations (pump pits, sampling and monitoring access ports, and other maintenance ports). Hazardous levels of radionuclides or off-gases have yet to be measured after a pressurization event, but the possibility exists.

In response to a June 1988 increase in waste level, which exceeded operating specifications, a WHC engineer was asked to conduct a review of 101-SY slurry growth. In an internal memorandum transmitted on September 7 and retransmitted on October 25, 1988,⁹ the engineer raised serious safety concerns regarding 101-SY, identifying the potential for (1) a hydrogen fire or explosion during a pressurization event, (2) radionuclide emissions during pressurizations, and (3) the release of hazardous levels of ammonia gas. He stressed the need for a permanent solution to these concerns or, short of that, concerted actions to control slurry growth. At a minimum, he stated, WHC should pump out a portion of the waste in 101-SY and attempt to seal off all tank in-leakage points. He also recommended installing additional level detectors and gas monitors, requiring workers at 101-SY to wear protective masks, increasing the tank ventilation rates, and improving air-lancing procedures. Despite early efforts to respond to some of the recommendations in his memorandum (e.g., installation of a backup portable exhaustor), little real progress toward ameliorating the situation occurred prior to March 1990.

Responding to Outside Concerns About Hydrogen (1989-1990)

In October 1989, WHC began developing a technical reevaluation of existing historical and operating information on tank farm safety issues, including tank 101-SY. This effort resulted in a series of issue papers, one of which dealt with hydrogen flammability in double-shell tanks, and was completed in December 1989. These papers were reviewed in January 1990 by the WHC Safety and Environmental Advisory Council and sent to Westinghouse engineers at the Department's Savannah River site (SRS) for their evaluation.

On February 6, 1990, the WHC Manager of Waste Management Engineering was informed by the Westinghouse Savannah River engineers that they were particularly concerned about the potential flammability of hydrogen in the presence of an oxidizer, nitrous oxide, under the crust of the waste in 101-SY--a possibility that was acknowledged in the issue paper but was discounted owing to lack of ignition sources in the tank. A followup phone call to Savannah River by the WHC engineer who had prepared the issue paper referred to above took place on February 12, but no immediate action was taken. The Manager of Waste Management Engineering was again briefed on the Savannah River concerns on February 27. Following another briefing--this one for WHC senior management--DOE-RL was informed on March 6 in a briefing attended by the DOE-RL Acting Assistant Manager for Operations and other DOE-RL staff.

On March 7, operating restrictions were imposed on 101-SY and several other tanks to control work being performed, so that the potential of an ignition source (sparks, heat, friction, etc.) could be minimized.¹⁰ These restrictions were formalized on March 20, 1990.¹¹

On March 20-21, consultants to the Defense Nuclear Facilities Safety Board were briefed on the issue of slurry growth. Following the briefing, the DOE-RL Deputy Manager immediately contacted the DOE-RL Manager, who was in Washington, D.C., at the time. On March 22, immediately upon his return from Washington, the DOE-RL Manager was briefed on the issue. The following day he held a press conference to announce the "new information" that had surfaced.

On March 30, in an effort to determine if similar safety issues existed at other DOE sites, the Headquarters Office of Environmental Restoration and Waste Management (EM) requested that all DOE waste management operations assess and report whether other unreviewed issues existed. WHC responded in writing to this request with a list of additional issues at the tank farms, including flammable alcohol in waste tank liquid observation wells (LOW's), potential releases of radioactive contamination or toxic fumes through tank in-leakage points during positive pressurization events, and overall deterioration of the material conditions of the tank farm physical plant. WHC also noted that safety analyses and operational safety requirements (OSR's) for the tank farms did not satisfy requirements for DOE facilities.

On April 2-3, a special technical review team established by the DOE Headquarters Office of EM conducted an evaluation of the potential hazards associated with gas generation in tank 101-SY. On April 4, 1990, the team reported the following: (1) large pockets of gas form beneath the crust in the tank; (2) it is not credible that a rapid burn or explosion of gases trapped below the crust could cause large scale structural damage to the dome of the tank; (3) it is credible that combustion in gases trapped below the crust could cause local failure of the side wall of the primary tank; and (4) it is not credible that a combustion event that would damage the side wall of the primary tank liner would also damage the side wall of the secondary tank.¹²

The team recommended the imposition of operating restrictions, consultation with outside experts, and the formation of an internal task force to develop solutions to technical and safety issues associated with the tanks. (All three measures had already been undertaken by the operating contractor.) The root cause for the late recognition of the safety issues concerning flammable gas generation in tank 101-SY was identified by the review team as a "lack of realization that combustible mixtures could form beneath the surface of the waste." It was noted that the "[WHC] staff investigating the slurry growth phenomena did not realize that nitrous oxide (N_2O) was an oxidant."¹³

On April 2, concurrent with the Headquarters technical team's review, DOE-RL sent a letter to WHC directing the contractor to expedite responses to outstanding tank farm safety issues, including those from a recent DOE-RL self-assessment that identified deficiencies in the tank's design.¹⁴ This letter directed that the operating restrictions established on March 20 be considered interim Operational Safety Requirements (OSR's). It also requested a response to outstanding DOE-RL surveillance findings and a root-cause analysis of the reasons for the lengthy delay in recognizing and reporting 101-SY flammable gas concerns, including an explanation of why WHC "incorrectly concluded that the potential 101-SY flammable gas source term did not represent an Unreviewed Safety Question."** On April 6, WHC provided dates when it would be able to implement these directives.¹⁵

**In general terms, an Unreviewed Safety Question is any change in operational status that either has not been previously evaluated in the Safety Analysis Report (SAR) for the facility or increases the risk of an accident that has been previously evaluated.

On April 5, DOE-RL initiated a self-appraisal of site-wide communications of off-normal conditions. This appraisal, conducted by Stone & Webster Engineering Corporation (a DOE-RL support contractor), "was motivated by concern over the timeliness of communication surrounding the ongoing assessment of hydrogen buildup in high-level nuclear waste double-shell tanks at Hanford."¹⁶ On April 23, Stone & Webster submitted a report concluding that the event-reporting process "functioned well once identification of the event takes place" but found fault in what was characterized as the recent lowering of event-reporting thresholds by DOE Headquarters. Stone & Webster concluded that the action trivialized and overburdened the DOE-RL reporting process.

On April 9, DOE-RL requested that WHC prepare short-term and long-term action plans for both double-shell and single-shell tanks. These plans were to address the following: (1) evaluations of potential chemical reactions, (2) operational activities to relieve or eliminate safety problems during transfer and storage operations, and (3) improvements in operational management to increase the discipline of operations.¹⁷ WHC submitted a plan on April 19, outlining measures necessary to mitigate hazards associated with the Hanford waste tanks and describing actions to respond to recommendations from the Defense Nuclear Facilities Safety Board. The plan proposed tank characterization (including core sampling of the 101-SY's contents), operational and engineering remedies (including interim operational safety precautions), upgraded safety analyses (including an analysis of the combustion of a hydrogen and nitrous oxide mixture under the crust), and improvements in management practices. A 1983 "Laboratory Plan to Study Gas Generation During Slurry Growth" was revived and approved as a means to understand slurry growth better.¹⁸ WHC's Waste Tank Safety Task Team, formed in March, was given the responsibility for identifying, evaluating, and planning necessary corrective actions.¹⁹

WHC had installed a hydrogen monitor (a Teledyne Model 225 thermal conductivity analyzer) on March 20. A gas chromatograph was installed on April 12 to provide a means of measuring nitrogen, oxygen, various oxides of nitrogen, carbon monoxide, and carbon dioxide. WHC also plans to install an automated cryogenic sampler.²⁰

WHC also formed a Senior Chemists' Panel, which met on April 27, April 30, and May 1, with the "specific objective of defining chemical reaction hazards that must be considered before core drilling in tank 101-SY."²¹ The panel concluded: "The single greatest perceived risk is that of a spark during the drilling operation that would ignite the gas mixture."²² They offered an assessment of the necessary considerations and precautions that should be taken into account before core drilling in 101-SY began.

On May 14, DOE-RL formally notified the Headquarters Office of Environmental Restoration and Waste Management that the "matter of hydrogen and nitrous oxide evolution within the material in certain waste tanks and subsequent hypothetical ignition is an unreviewed safety question."²³ This letter stated: "We do not believe that this situation creates an undue risk to public health and safety. All activity in the affected tanks has been curtailed...except that necessary to maintain them in a safe condition, and to

conduct the investigations into this problem." DOE-RL made the following commitments: (1) WHC would provide a Safety Analysis Topical Report on the consequences of a hydrogen/nitrous oxide burn in tank 101-SY, subject to DOE-RL's independent review; (2) DOE-RL would conduct an operational readiness review prior to resumption of routine operations at the tank farm; and (3) prior to resumption, revised permanent OSR's would be in effect.

Current Status of Followup Actions

In May 1990, the NS team informed EM of its concern that a hydrogen burn or detonation could possibly initiate a secondary exothermic reaction involving sodium or ammonium nitrate in the crust, and that this issue deserved analysis. The waste crust in tank 101-SY is known to contain sodium nitrate, and ammonium nitrate had been observed in the solids in other Hanford tanks. The implications of the presence of ammonium, cesium, and strontium nitrates in dry crystalline form on the surface of the crust are currently viewed as potentially significant contributors to either a primary or secondary burn in the tank.²⁴ On May 24, in response to this issue and the previously existing concerns regarding hydrogen, DOE-RL announced several actions including:

- Sampling to determine the extent of chemical compositions and potential chemical reactions and options to eliminate gas buildup in the tank wastes.

- Performance of a safety analysis to determine whether a wetting system applied to the surface of the crust can be safely installed and operated until sampling and corrective actions are implemented.

- Application of a wetting system, if the analysis confirms the feasibility of this option....

- Establishment of a technical panel to review Hanford's plans to address safety issues for waste tanks.

- Implementation of operational restrictions to significantly reduce the potential risk to worker health and safety from release of radioactivity and toxic fumes through unfiltered release paths.

- Continuation of the management review being conducted by DOE's Office of Nuclear Safety and Environment, Safety and Health.²⁵

Around the same time, EM formed a Technical Advisory Panel for High-Level Waste Tank Issues. This panel was asked to:

- review and evaluate issues related to the safe, efficient operation of high-level waste tanks at DOE facilities. Activities will include but not be limited to reviewing operations to independent-ly determine hazard potential. Adequacy of

mitigation actions are to be evaluated, and recommendations will be provided where appropriate.²⁶

On May 30, DOE-RL submitted to DOE Headquarters a draft safety evaluation that WHC had written to justify installation of a wetting system for tank 101-SY. The transmittal noted:

[DOE]-RL believes that the proposed water additions, which are designed to maintain the Tank 101-SY waste crust in a wet condition, can reduce the potential for secondary exothermic chemical reactions which could be initiated by a hydrogen burn event. In particular, the potential for ammonium or sodium nitrate reactions is reduced by the present [sic] of water.²⁷

On June 13, the Director of EM received a recommendation from his staff that WHC and DOE-RL be permitted to install spray equipment in 101-SY prior to approval of the draft safety evaluation in order for there to be "water spray capability in event of an emergency." The recommendation stated that after installation EM would only allow "water addition to commence upon adequate resolution of issues."²⁸ Following objections from a DOE Headquarters office that the analysis that had been submitted to DOE Headquarters provided inadequate justification for the proposed system, the Director of EM approved a staged approach to implementation, subject to resolution of the expressed objections. WHC and DOE-RL line managers later decided to revise the evaluation and incorporate it into an ongoing safety evaluation needed to permit sampling of the tank's contents.

This episode heightened concerns within DOE Headquarters that middle and lower level line managers in both EM and DOE-RL did not sufficiently understand the level of technical detail that was necessary to support safe operation of the tank farms. In submitting the safety evaluation of the water spray, for example, WHC had provided no calculational data or bounding analysis to support the proposal to immediately install the equipment as a compensatory emergency response capability. Moreover, the DOE-EM project manager stated that the water spray system might be used to mitigate potential burning of the waste crust subsequent to a hydrogen combustion event, even though there was no technical basis for assuming that a water spray system would be effective for this purpose. (As this Report details, efforts to take action prior to having in hand a valid safety evaluation of that action are not new at the tank farms. Lancing, crust breaking, and in-tank photography were all undertaken without a proper evaluation of their potential safety implications.)

In the meantime, on June 7, WHC had transmitted to DOE-RL a revised plan for safety improvements at the tank farms. This plan, entitled "Safety Improvement Plan--Hydrogen in Waste Tanks," was prepared under the direction of the WHC Waste Tank Safety Task Team formed in late March. The plan stated:

The scope of this plan (now revision 1) includes work to evaluate the hazard of the hydrogen and nitrous oxide mixture, to identify the means to mitigate this hazard, and to implement the mitigations. The scope also includes gathering and analyzing information about the wastes and waste tanks to assure that the

hazard is fully understood, that the means of mitigation will be productive, and that the mitigation will be effectively implemented. The plan deals primarily with the 23 tanks which have the highest likelihood of trapping a significant quantity of hydrogen and nitrous oxide (the "watch list" tanks) and is focused at the outset on tank 241-SY-101.²⁹

The plan noted that various milestones were interrelated and that budgetary resources and existing environmental compliance agreements imposed constraints on remediating the problem of flammable gas generation in the Hanford waste tanks.

As this Report was going to publication in late July, considerable work was underway to evaluate the contents of tank 101-SY and to remove the threats posed by slurry growth and flammable gas generation in the Hanford waste tanks.

NOTES*

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*Unless otherwise indicated, all contractor files related to the operation of the Hanford Tank Farm are maintained by the current operating contractors in Richland, Washington. Some documents appear under initial release dates, with subsequent revisions attached. Individual page revisions have not been tracked in the endnotes, though such changes will be evident when the appropriate sources are accessed.

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II. MANAGEMENT ASSESSMENT OF FLAMMABLE GAS CONCERNS

Chapter II examines contractor and DOE management of flammable gas generation in the Hanford waste tanks. It begins with an evaluation of the safety documentation that Hanford contractors developed over the years to govern operation of the double-shell tanks. This is followed first by an evaluation of the operating contractors' role in the management of flammable gas generation and then by an assessment of DOE management's handling of the issue.

A. SAFETY ANALYSIS AND DOCUMENTATION

There are a number of safety documents that contain requirements applicable to tank farm operations. These range from functional criteria used to design the tanks to safety analyses governing specific operations. The NS team found that DOE-RL and contractor safety documentation did not conform to DOE standards and, in a number of specific instances, operations did not meet documented requirements.

Background

Functional Design Criteria (FDC) set forth the specific conditions to which the final design of a facility must conform. The design of the facility must also adhere to certain specified national codes and standards and include a sufficient margin of safety.

The Functional Design Criteria for the SY Tank Farm were issued in November 1973 in a document establishing requirements for three 1-million-gallon double-shell tanks (DST's) that DOE planned to build at the SY Tank Farm.¹

A Safety Analysis Report (SAR) for a nuclear facility is a formal document that a contractor must prepare prior to the initiation of operations. The SAR is intended to ensure that the risks associated with postulated accidents have been conservatively analyzed, that a margin of safety has been identified, and that the basis for safe operation has been defined.

The SAR must include a safety assessment of the site, a description of the facility, the design basis for the facility, and the possible accidents or hazards associated with the facility. It must also provide an analysis that adequately envelopes those accidents or hazards, and specify the required operational constraints (limits or margins of safety) that must be applied to keep the risks to an acceptable level and to mitigate the consequences of any credible accident over the lifetime of the facility.

In the judgment of the NS team, the SAR for a waste tank should also include a description of:

- o The nuclear process to be performed;
- o The instrumentation and control systems, including ventilation, filters, electrical, auxiliary, emergency, and radioactive waste handling systems;
- o The means available to detect radioactive releases;
- o The kinds and quantities of radioactive materials expected to be stored in the tank;
- o The methods to be used to limit radiation exposures of individuals below specified limits;
- o The organizational structure, responsibilities, authorities, and personnel qualifications requirements of the operating contractor;
- o The managerial and administrative controls necessary to assure safe operations;
- o The preoperational testing required;
- o The maintenance program;
- o The operational safety requirements;
- o The methods to be used to monitor, control, and evaluate hydrogen generation and corrosion;
- o The measures available to make emergency transfers of stored wastes; and
- o An emergency plan.

A Safety Analysis Report (SAR) for double-shell waste storage tank facilities was prepared in 1977.² A revision (Rev. 0) was prepared in December 1985 and submitted to DOE-RL for review and approval.³ Based on DOE-RL comments, a new SAR (Rev. 1) was issued in May 1986.⁴

Operational Safety Requirements (OSR's) are a formal set of requirements that must be followed to ensure the safe operation of a nuclear facility. The SAR provides the basis for preparing the OSR's. The requirements included in the OSR's must derive from the analyses and evaluations that are provided in the SAR.

OSR's consist of (1) safety limits, (2) limiting control settings, (3) limiting conditions for operations, (4) recovery actions, (5) surveillance requirements, (6) design features, and (7) administrative controls.

- o Safety limits are limits on operating parameters or systems that are required to protect the integrity of the physical barriers that guard against the uncontrolled release of radioactivity. If a safety limit is exceeded, the facility must be placed in a safe condition until the cause is determined and appropriate corrective action has been taken to preclude recurrence.
- o Limiting control settings are required for significant safety functions and will often automatically alarm when a predetermined setting is reached. However, the specific setting chosen either must correct the situation automatically or permit manual corrective actions to be taken before a safety limit is exceeded. Procedures must be defined to determine the cause of the condition and the basis for corrective action to preclude a recurrence.
- o Limiting conditions for operation (LCO's) are defined as the lowest equipment performance levels that will sustain safe operation of the facility. If an LCO is exceeded the facility must be placed in a safe condition or the corresponding remedial action required by the OSR's must be followed until the condition can be met. The appropriate remedial actions for each LCO must be specified in the OSR's.
- o Surveillance requirements define the test, calibration, or inspections needed to assure that the necessary quality of system and component performance is maintained, that facility operation will be within the safety limits, and that the limiting conditions for operation will be met.
- o The facility design features that must be specified in the OSR's are those such as construction materials and geometric arrangements that would have a significant effect on safety if altered or modified and that have not been covered elsewhere in the OSR's.
- o Administrative controls describe the organization and management systems, procedures, recordkeeping, review, audit, and reporting requirements necessary to ensure safe operation of the facility. Administrative controls should include:
 - Management controls for prompt updating of the SAR as new information and data become available;
 - Management systems to ensure prompt corrective action if a limit or other requirement of the SAR is violated; and
 - Prompt reporting to DOE Headquarters of all occurrences for which an LCO has been exceeded (a written followup report is also required).

The facility OSR's for the Hanford double-shell tanks are contained in Chapter 11 of the 1986 SAR. These OSR's do not provide many of the above elements. The historical practice at Hanford had been to include most operational controls for the tank farm in an Operational Specifications Document (OSD);

the 1977 SAR, for example, did not contain any OSR's. The four OSR's that were included in the 1986 SAR were previously contained in the OSD. Although the OSD is technically a lower tier document that, unlike the OSR's, does not require DOE approval, it still contains many of the operational controls, including the safety limits, that are necessary for safe operation and are supposed to be included in the OSR's.

The OSD has been used at the Hanford Tank Farms since at least 1973. The 1973 OSD stated:

Specifications define process and operating limits which have been established to meet accepted criteria in order to protect personnel, environs, and facilities from potential damage while producing the desired quality products....Section 5.0 contains the standards defining process and operating limits established as control points which, when exceeded, provide warning of approaching specification limits.⁵

Modified many times, this specifications document has been continuously used by all subsequent tank farm operating contractors. A 1977 revision of the OSD was the first to include specifications and standards for the SY Tank Farm.⁶ The 1977 OSD document stated:

Specifications are not to be violated. If an operational specification is violated, an orderly and immediate shutdown of the involved process or laboratory is required until the situation is formally investigated (occurrence report) and corrective action taken....A violation of standards limits is an indicator that specifications could be in jeopardy but does not necessarily require a process shutdown. Prompt corrective action and documentation (nonconformance report) by responsible management are required.⁷

Functional Design Criteria for the SY Tank Farm

Figure A is a schematic of tank 101-SY. As can be seen, each double-shell tank consists of three concentric structures: (1) an outer tank structure of reinforced concrete; (2) a carbon-steel secondary tank, lining the concrete structure; and (3) an inner, free-standing, primary tank completely enclosed with carbon steel, which is located within the secondary tank and separated from it by an annular space. The upper dome of the DST is not doubly contained. Both the primary and secondary tanks are contained within the reinforced-concrete structure, which supports the bottom and the wall of the secondary steel tank, as well as the primary tank and its contents.

As required by the 1973 FDC for the SY Tank Farm, the primary tank would hold radioactive wastes identified and characterized in the FDC document. The tank was to have a 50-year life expectancy and was to be able to withstand corrosion, stress corrosion cracking (caused by high concentrations of sodium hydroxide and nitrates in the radioactive waste), hydrostatic loads, internal

Figure A. Schematic Drawing of Double-Shell Tank at Hanford

pressure, thermal loads, and stresses associated with a seismic event as defined by the Safe Shutdown Earthquake specification for the site.

The primary tank was to have dome penetrations to permit tank monitoring and processing activities. Waste-monitoring facilities for the primary tank were required to monitor liquid level, sludge level, temperature, and pressure and were to include observation ports. A primary tank ventilation system would control radioactive particulate emissions to the environment. Gases and vapors vented from the tank were to be double filtered by high-efficiency particulate air (HEPA) filters, sampled, and monitored for radioactivity before they were released to the atmosphere. Measurement of the airflow and in-place testing of the HEPA filters was also to be provided. The primary tanks were required to be operated under a slight negative pressure to ensure containment of radioactive airborne materials within the tank.

The secondary tank was to be designed to contain and support the primary tank and its contents. Specifically, the secondary tank would collect and detect any materials that might leak from the primary tank into the annular space. The secondary tank must contain the radioactive caustic liquids that might leak as a result of failure of the primary tank and must serve as an effective backup until the waste can be safely removed to a reserve tank. The purpose of the secondary tank was to ensure that no radioactive materials escaped to the environment in the event of a primary tank failure.

Air supplied to the annulus was to be sufficient to permit moisture removal and thus prevent condensation. Upon exhaust from the annulus and prior to release to the atmosphere, the air would be monitored for detection of any radioactivity, passed through two stages of HEPA filters, and sampled. Measurement of the airflow and in-place testing of the HEPA filters would also be provided. (Table 1 summarizes the structural design criteria for DST's.)

Table 1. Functional Design Criteria Requirements⁸

Selected Design Limits:

Liquid storage capacity for each tank	1,000,000 gallons
Earth cover (backfill) for radiation	6 1/2 feet minimum
Live loading on backfill over tank domes	40 psf uniform plus 50 tons concentrated
Internal vacuum	6 inches H ₂ O
Internal pressure	60 inches H ₂ O

Waste Characteristics:

Temperature	250° F maximum
Heat generation rate per tank	50,000 BTU's per hour
pH	8 to 14
Specific gravity	1.7 maximum
Liquid viscosity	2-20 centipoise
Slurry viscosity	100-300 centipoise

Channels between the primary and secondary tank bottoms would convey any leakage from the primary tank to detection points in the annular space and would be used for air purge to remove residual moisture. The design required that the liquid eventually drain to a leak detection pit, which in turn required pumping capability, leak detection, liquid level measurement, temperature measurement, and radiation detection equipment.

The FDC for the SY tanks also required that integral wall, dome, and haunch thermocouples be installed in the reinforced-concrete tank to facilitate administrative control of thermal gradients and the resulting stress to the tank. The reinforced-concrete tank base was also to have thermocouples. Design requirements for the primary tank included installation of thermocouples, as well as requirements for liquid level and sludge level measuring devices to monitor the waste contents of the tank. The annulus between the primary and secondary tanks was to be supplied with detectors to identify leaks from the primary tank. The leak detection pits were required to have leak detectors, liquid level measuring devices, thermocouples, and radiation detectors to detect and measure any leakage from the secondary tank. Installation of radiation monitors and air samplers were also required for the ventilation systems for the primary tank and the annulus in order to detect radioactive releases to the atmosphere.

Finding II(A)1: The Functional Design Criteria for tank 101-SY developed by the contractor did not take into account the mixture of waste types subsequently stored in the tank and, consequently, did not specify design features and limits to mitigate or prevent the effects of those waste combinations.

Safety Analysis Report

The failure of a HEPA filter and/or a de-entrainer, resulting in a release of contamination to the environment, is the maximum credible DST accident analyzed in the SAR. This type of accident could occur as a result of excessive moisture in the ventilation system or vessel pressurization, either of which could rupture the exhaust HEPA filters. Filter contamination itself is limited because the filters are changed whenever the dose rate exceeds 100 millirem per hour at the point monitored. Only a fraction of the contamination available for release would be released by failure of the de-entrainer.

As defined by the SAR, limits for human exposure assume the maximum allowable radiation contamination to be equivalent to that contained in 0.06 gallons of double-shell slurry (0.1 Ci, ⁹⁰Sr, and ¹³⁷Cs). The dose commitment (summation of external radiation and inhalation doses for on-site and off-site personnel) to an individual, calculated for the first year following a filter rupture (assuming a 30-minute exposure), is illustrated by Table 2.

Table 2. Calculated 1st Year Dose Commitment to an Individual Following Filter Rupture (in rems)⁹

	<u>Total body</u>	<u>Bone</u>	<u>Lung</u>
On-site	0.2	2.4	0.14
Off-site	0.0005	0.002	0.00015

Some DST's were equipped with airlift circulators. Airlift circulators are relatively simple devices composed of two basic components: a vertical, lift-riser pipe measuring 30 inches in diameter and an air nozzle 1 foot long, located within and near the lower end of the pipe. A 6-inch pipe suspends the lift-riser from the tank dome. A 1-inch pipe extended into the 6-inch pipe supplies forced air.

The introduction of air into the circulator serves to decrease the specific gravity of the solution within the tank. As a result, a hydrostatic head at any point within the pipe will be less than that at the same elevation outside the pipe and vertical movement of the liquid in the tank will be initiated. The vertical movement provides sufficient agitation to prevent the formation of "hot spots" and tends to keep solids entrained.

The ventilation system for each tank farm consists of two completely separate systems, a primary tank ventilation system and an annulus ventilation system. The primary tank ventilation system is designed to remove vapors from the waste and to provide a tank pressure that is negative relative to atmospheric pressure. Each primary tank exhaust system for the SY Tank Farm consists of a moisture separator, heater, filter bank, and fan. This contrasts with the primary tank exhaust system for the AN, AP, and AW Tank Farms, which have two de-entrainers, two heaters, two filter banks, and two fan systems. (One of each device is always in service; the other is on standby.)

The annulus ventilation system is used to cool the primary tank, minimize moisture condensation in the annular space, and serve as a sensitive method for detecting leakage of radioactive materials from the primary tank. The SY Tank Farm has four air supply lines per tank, while the AN, AP, and AW Tank Farms have eight per tank. Adverse conditions that can occur during operation of the vent system include breach of HEPA filtration, high differential pressure across the HEPA filters, excessive dose rate from the filters, moisture buildup on the filters, high differential pressure across the de-entrainer, and failure of the exhaust fan or stack monitoring equipment. At all double-shell tank farms except SY, failure of the HEPA system results in diversion to the backup exhaust system. For the SY Tank Farm, a portable exhaust system could be connected to the tanks while the filters were being repaired.

Tank instrumentation and alarm systems are provided to monitor operating parameters for each tank. These include liquid level detectors, sludge level detectors, temperature detectors, leak detection equipment, airflow differential pressure indicators, and radiation monitoring instruments. All instrument readouts for the tank farms are available at a local instrument building and/or at a nearby continuously manned facility.

Each tank is equipped with an automatic liquid level gauge. Sludge level detectors are installed to monitor the height of the solids in the tanks. Each tank is also equipped with thermocouples for monitoring temperatures throughout the tank structure. A single probe containing 18 thermocouples is used to monitor waste temperatures at various depths in the primary tank. All thermocouple readouts are monitored at the Control Room or at the Computer Automated Surveillance System (CASS) monitors located in a nearby building.

Drain channels are embedded into an insulating concrete structure and are designed to carry any leakage from the primary tank to the annulus. The annulus also houses three leak detection facilities (in the form of conductivity probes extended into each tank annulus and installed at 120-degree intervals around the tank). There are 17 of these probes at each location, with readouts provided at the tank farm instrument building. An analysis of liquid level in the annulus is obtained by rotating each of the three probe selector switches through 17 positions. Each position coincides with a different probe elevation, and turning the selector to a probe elevation that is in contact with liquid will activate both an indicator light at the panelboard and an alarm at the control building annunciator. These selectors are checked once per shift.

Finding II(A)2: Rapid combustion of hydrogen and nitrous oxide (occurring above or below the crust and resulting in failure of the primary tank and HEPA filters) was not considered in the SAR analysis of worst-case accidents.¹⁰

- o Table 3 is an adaptation of a hazard analysis table originally published in the 1986 SAR. It includes seven accident events. The event titled "Burping and Liquid Level Increase" describes the following possible sequence: "Complexant degradation reactions produce gases and rapid increase in liquid level occurs and explosive mixture is produced." Under the corresponding column labeled "source term," nitrous oxide is listed among the gases released during the event. The "preventative features" for this accident sequence are stated to be "sampling of tank content and liquid level allows operators to take action."

The next accident event listed in the table is "Burping in Tank 101-SY Only." The accident sequence is described as "complexant degradation and radiolysis produce gases and crust entrains gases, which are released when liquid level decreases and hydrogen concentration exceeds 5% and ignition source is available." Under the corresponding column labeled "source term," the table states that the hydrogen concentration in the bubble may range from 5 to 50 percent.

The next accident event identified in the table is "Hydrogen Explosion and Dome Damage." The "preventative features" column for this accident notes that "taping of pits does not prevent in-leakage but restricts it; in-leakage to the pits will purge hydrogen into the ventilation system. Hydrogen generation rate is limited by fission product concentration of liquid and by the exhaust air." Under "mitigating measures" that can be taken to respond to the accident, the table states that the "hydrogen

Table 3. Storage Tanks Hazards Analysis^a

Event	Possible sequence	Source term ^b	Potential consequence(s)	Preventative features	Mitigating measures
Nuclear Criticality in Tank	High concentration plutonium solution is transferred to tank and a critical mass accumulates.	Fission products and gases, 10^{19} total fissions.	Environmental release; personnel radiation exposure; possible loss of continued tank usage.	Quantity of fissionable material and area over which it would precipitate makes the event not credible. Administrative control on concentration of fissionable material in transfers.	Batch transfer would be diluted by contents of tank, thereby creating an unfavorable environment for accumulation of a critical mass. Criticality specifications exist. SOP requires analysis. This event is considered incredible.
Acid Solution Transferred to DS Tanks	Operator error.	10 Cl/gal	Failure of pipelines, jumpers, NO _x fumes generated will be exhausted to atmosphere.	Administrative controls.	Batch transfer: would be neutralized by contents of tank. Tank contents are monitored and SOP and operation specification control content of solution to be transferred.
Burping and Liquid Level Increase	Complexant degradation reactions produce gases and rapid increase in liquid level occurs and explosive mixture is produced and reaction reduces nitrite, nitrate, or hydroxide concentration.	Gaseous products; NO ₂ , N ₂ O, CO, H ₂ , CO ₂ , CH ₄ , NH ₃ and NO _x are available. Entrained radioactive particles in vapor space.	Release of unfiltered toxic gases. Mechanical and thermal stress from liquid height. Corrosion rate enhanced by hydroxide reduction.	Sampling of tank content and liquid level allows operators to take action.	Control of organic content by SOP. Unfilterable noxious fumes are discharged from stack and allowed to disperse. Filter systems on exhausters remove filterable fumes and radioactive particulates.
Burping in Tank 101-SY Only	Complexant degradation and radiolysis produce gases and crust entrains gases, which are released when liquid level decreases and H ₂ concentration exceeds 5% and ignition source is available.	H ₂ concentration in bubble - 5 - 50%.	H ₂ concentration could exceed 5% in tank 101-SY resulting in ignition and burning. See Hydrogen Explosion.	Liquid levels and temperatures are monitored and the crust is lanced periodically. Waste can be transferred to a tank that has airlift circulators.	Exhauster or portable exhauster must be operated at all times to flush out emitted gases.

Table 3. Storage Tanks Hazards Analysis (continued)

Event	Possible sequence	Source term ^b	Potential consequence(s)	Preventative features	Mitigating measures
Fire/Explosion	Organic material is transferred to waste tanks and an electrical spark or short ignites the fumes, vapor explosion produces pressure, destroys ventilation system filters and produces structural damage to primary tank or vent system.	14 Cl/wk (0.0014 Cl/min) per tank Exposure time <1h >5,000 MPC	Environmental release; possible loss of tank use.	No source for electric spark in tank.	Control of organic concentration and temperature of transferred liquids by SOP.
Hydrogen Explosion and Dome Damage	Pits (sluice and pump) are seal taped to reduce in-leakage and maximize DP between tank and atmosphere. This creates a stagnant area in the pits or exhaust system fails and hydrogen builds up in the pit air space or the tank vapor space and a spark (electrical or mechanical) occurs igniting the hydrogen and the resulting explosion causes a portion of the pit or dome to fail.	14 Cl/wk (0.0014 Cl/min) per tank Exposure time <1h >5,000 MPC	Damage of instruments, vessels, or dome stress. Loss of tank containment; environmental release; personnel exposure and/or injury.	Taping of pits does not prevent in-leakage but restricts it; in-leakage to the pits will purge hydrogen into the ventilation system. H ₂ generation rate is limited by fission product concentration of liquid and by the exhaust air.	Tank farms are not normally occupied, reducing likelihood of personnel injury. Hydrogen accumulation rate (30 ft ³ /d) requires 23 d without ventilation to accumulate concentration of 2% H ₂ . Alarm indicates loss of vacuum immediately.

Table 3. Storage Tanks Hazards Analysis (continued)

Event	Possible sequence	Source term ^b	Potential consequence(s)	Preventative features	Mitigating measures
Primary Tank Failure	Excessive temperature rise and temperature gradients or excessive corrosion or tank overfills and hydrostatic head increases or vacuum in tank excessive causing bottom to uplift. Any one can cause the structural integrity of primary tank to collapse.	5,000 gal of liquid to annulus	Primary tank leaks and tank usage is lost.	Design limit exceeds operating specifications.	Temperatures monitored during hot transfers per SOP. Corrosion rate is minimized by waste chemical composition. Redundant high liquid level alarms exist. Minimum liquid levels are specified for primary tanks to prevent bottom from uplifting.

^a Source: Table 9-3, "Double-Shell Tank Farm Facility (241-AN, AW, AP, and SY) Safety Analysis Report (Rev. 1)," pp. 9-8, 9-9, 9-10. See R.T. Kimura, "Characterization of Shielded Double-Shell Tank Vapor Space Radionuclides," Internal letter 65950-85-586 to W.H. Trott, Rockwell Hanford Operations, Richland, Washington, January 1986, for source term definitions and assumptions.

^b The Cladding Removal Waste (CRW) feed >180 days cooled, but < 1 year.

accumulation rate (30 cubic feet per day) requires 23 days without ventilation to accumulate concentration of 2% hydrogen."

It is evident from the descriptions of these three accident sequences in Table 3 that the contractor knew and considered the following information in the 1986 SAR for double-shell tanks:

- Degradation of complexants in the waste produces gases under the salt crust that represent a potentially explosive mixture and include quantities of hydrogen and nitrous oxide.
- The hydrogen concentration in the gases can be 5-50 percent and is released from under the crust in what is referred to as a "burp."
- o The NS team found that a bounding analysis of a rapid burn of hydrogen and nitrous oxide was not performed. Until 1990, formal safety analyses for the tank farms did not consider a rapid burn of hydrogen and nitrous oxide as a credible event, even though an RHO engineer had calculated the large amount of energy that would be released in such a burn as early as 1979.¹¹
- o For the postulated hydrogen explosion, the analysis in the 1986 SAR assumed that the hydrogen generation rate was limited by the fission product concentration of the tank liquid and that 23 days with no ventilation would be required to accumulate a hydrogen concentration of 2 percent. Given what was known at the time (1986), this analysis of a hydrogen explosion presented an inaccurate and incomplete description of the potential risks involved.
- o Prior to March 1990, safety analyses governing operation of the double-shell tanks focused only on radiolytic decomposition of water as a potential source of hydrogen generation. Samples of the gases released during the April 19, 1990, pressurization event at tank 101-SY were obtained using more sophisticated instrumentation. The analysis of these samples revealed the presence of large concentrations of hydrogen and nitrous oxide. WHC incorporated this new and significant data into an analysis of the consequences of a hydrogen and nitrous oxide burn and its implications for the structural integrity of tank 101-SY. (WHC had initiated this process in late March 1990.) The preliminary results of this updated analysis indicate potentially severe yielding of the primary tank (plastic deformation), including possible failure or distortion of the dome, damage to the secondary tank, and considerable damage to the reinforced concrete tank (with breakup of the concrete, including yielding and distortion of the rebar).
- o Although the presence of hydrogen and nitrous oxide in double-shell tanks had been indicated in various documents since the late 1970's and the energetics of a hydrogen and nitrous oxide reaction was calculated in 1979,¹² insufficient action was taken to address the potential threat. A sample of the gases causing slurry growth could and should have been obtained years ago, a bounding analysis should have been performed when the possibility of a hydrogen/nitrous oxide combustion

event was first identified in 1978, and immediate, appropriate corrective actions should have been taken at that time to resolve the problem.

Finding II(A)3: The need for a tank sampling program stating how and when waste samples were to be taken and used was not analyzed in the SAR and not included in the OSR's.

- o The 1986 SAR relied on the sampling of tank contents as the basis for tank farm operators to take appropriate preventive action in response to potential hazards. However, if tank farm operations staff are to determine the correct preventive actions to take, then data on waste characteristics must be monitored on a continuing basis. The SAR must establish and define the basis for a formal waste sampling program to monitor waste characteristics in DST's. The OSR's must outline requirements for such a program, including sample frequency and the data required to be obtained from each sample. The Hanford SAR and OSR's for the DST's were deficient in these respects.

Finding II(A)4: The 1986 SAR did not identify dedicated tank space for the immediate transfer of waste in the event 101-SY were to leak, and the contractor did not ensure that a reserve tank was available.

- o Although the 1986 SAR takes credit for having spare tank space to mitigate leaks (it states that "spare tank space is maintained at all times to contain the normal volume from the leaking tank"), the only spare tank space available with respect to 101-SY was located in the East Area tank farms, a considerable distance from the West Area where tank 101-SY is located. Since 1980, when 101-SY was filled, there has been no means available to transfer waste to spare tanks in the East Area in the event of an emergency. The waste in 101-SY would first have to be diluted and a viable means of transferring it would have to be installed. Until the waste in 101-SY is properly characterized, any transfer of the waste ought to be to an empty tank, thus precluding further unanticipated problems owing to incompatible waste mixtures.
- o This deficiency was documented by a RH0 engineer in 1983 in response to pressurizations of tank 101-SY:

I do not know of any planned corrective action for the waste tanks. We could dilute and pump a tank. That is what was done in S and SX tanks when they grew. If all three tanks in the West area are filled, transferring [to the] east would be difficult. There is only the small tank for cross site transfers. Maybe pumping out directly from the [tank] is possible [but] it has not been attempted. These tanks become a [special] case of the question "What do you do when a DS tank leaks?"¹³

Finding II(A)5: The 1986 SAR did not analyze the detrimental effects of the mixture of waste materials (corrosive, radioactive, alkaline slurry plus organics) in tank 101-SY.

- o The documentation of additions to tank 101-SY indicates that there were no effective controls on the mixture of slurry and complexed concentrate wastes. The following is a summary of the additions to 101-SY:¹⁴

April 1977	274,000 gallons	Double-shell slurry
November 1977	365,000 gallons	Complexed concentrate
June 1978	131,000 gallons	106-SX complexed concentrate
August 1978	60,000 gallons	111-U complexed concentrate
November 1980	230,000 gallons	Double-shell slurry
September 1984 to May 1988	8,000 gallons	Water

- o The contractor did not take adequate precautions for the storage of radioactive wastes, such as conducting sufficient research and testing to determine the effects of waste mixtures that were expected to be stored in the tank. Controls over different waste combinations were never analyzed in any of the SAR's or subjected to OSR's.

Finding II(A)6: The 1986 SAR did not address the detrimental effects of crust formation nor provide contingency plans to ensure the performance of surveillance activities necessary for safe operations (e.g., liquid and sludge level measurements and waste-sampling requirements) if a crust were to form.

- o Accurate tank level measurements, sludge level measurements, and sampling of the tank contents were not being performed on a regular basis, presumably owing to the presence of a crust of undetermined thickness that had formed on the waste in tank 101-SY. Such data is necessary to ensure safe operations and to reduce the risks associated with the potential for corrosion, gas combustion, and changing waste characteristics. The only sampling of 101-SY after the tank was filled in 1980 occurred in late 1985, and the purpose for taking that sample had nothing to do with mitigating either slurry growth or hydrogen generation.
- o The frequency for measurements and for samples of the waste and its byproducts were not covered in the OSR's.
- o The 1986 SAR required some double-shell tanks to use airlift circulators. An airlift circulator provides sufficient movement to prevent "hot spots" from forming in the waste and tends to keep solids entrained. Such a device was used in the SST's to prevent the formation of a crust. Ample evidence existed to indicate that crusts would form in all of the DST's in which double-shell slurry was stored and that some amount of slurry growth would occur. Neither possibility was mentioned in either the FDC or the SAR for the double-shell tanks.

Finding II(A)7: The 1986 SAR did not establish requirements for monitoring systems to detect the presence of hydrogen and other flammable gases, and these phenomena were not addressed in the OSR's.

- o Hydrogen generation was known to occur both from radiolysis of water and complexant degradation, and it was known that other gases, including ammonia, were being generated from the waste. Flammable and toxic gases should have been addressed in the SAR, and methods for monitoring the emissions should have been specified in the OSR's.

Finding II(A)8: Although the 1986 SAR assumed a corrosion rate, the SAR did not identify or require any means (e.g., use of base-metal coupons) to determine the extent of corrosion of the primary tank below the surface of the waste.

- o Corrosion below the surface of the crust in tank 101-SY is of particular concern because the extent of such corrosion is essentially unknown. Storage of concentrated radioactive waste presents the potential for reactions that consume hydroxide and/or nitrate and thereby increase the corrosion rate. If the effects of corrosion were found to be significant, a re-analysis of the primary tank would be indicated. Such a re-analysis would have to address current corrosive effects and determine whether the tank was within design limits. The tank's structural integrity and its ability to withstand operating loads, loads that would be predicted from a seismic event, and loads from other extreme circumstances would need to be considered.

Finding II(A)9: Contrary to the 1986 SAR, only one conductivity probe was installed at one location in the annulus of tank 101-SY.

- o The 1986 SAR requires each of the SY tanks to have three leak detection devices (in the form of conductivity probes) extending into each tank annulus. These were to be installed 120 degrees apart, with 17 probes at each location. Data obtained from all 51 probes were to be read at the tank farm instrument building. However, tank 101-SY has only one string of conductivity probes installed in the annulus.

Finding II(A)10: The 1986 SAR requires only a single thermocouple tree. One thermocouple tree is insufficient to monitor the contents of tank 101-SY realistically.

- o Temperature detectors are a critical element of the overall design of any waste tank. The detectors used in all DST's to monitor temperatures are thermocouples. Only one thermocouple tree, located 20 feet from the center line of the tank and approximately 17 feet from the tank wall, serves to monitor the tank waste and vapor space of tank 101-SY. Therefore, only a portion of the primary tank and its contents can be monitored. Using a single thermocouple tree assumes that the thermal conductivity of the waste is such that equilibrium temperatures are achieved throughout the waste, effectively preventing hot spots from occurring. A technical basis for this assumption has not been made.

Until it is, more thermocouple trees would be needed to provide adequate temperature monitoring of tank 101-SY.

Operational Safety Requirements and the Operational Specifications Document

A November 1989 version of the OSD lists the limited set of OSR's for the SY Tank Farm as well as a series of other requirements that would be considered safety limits, limiting control settings, limiting conditions for operation, and surveillance requirements at other nuclear facilities.¹⁵ The actions that must be taken in response to violations of the specification limits are listed separately within the same document.

Finding II(A)11: Despite numerous revisions of the specifications document during the past 13 years, information on slurry growth and hydrogen generation was not incorporated or used to develop operating limits for the waste tanks.

- o The 1977 OSD listed a "specification limit" of 2 percent of total vapor space volume as the limit on concentrations of hydrogen. To provide an additional margin of safety, a lower operating "standard limit" of 1 percent was specified.¹⁶ Although information existed since at least 1983 that concentrations greater than 2 percent were being generated in tank 101-SY, hydrogen limits were not revised until 1986, when the limit for hydrogen concentration was replaced by a specification limiting how long the primary tank exhaust system could remain inoperable. This new limit was also based on prevention of a 2-percent concentration. The rationale for the new limit was:

Adequate analysis techniques for the determination of hydrogen concentrations are not readily available. By specifying a limit for exhauster downtime the specification can be readily monitored.¹⁷

- o The operating standard for hydrogen concentration was eliminated in 1982 and the operating specification limit on exhauster downtime was eliminated in 1988.¹⁸ Throughout this period, a 1980 document served as the technical basis of the hydrogen concentration limit. The relevant limits on hydrogen deriving from the 1980 document were based solely on radiolytic decomposition of water even though that document referred to the generation of hydrogen by other processes:

There have been several experiments conducted to verify mechanisms and rates of H₂ generation other than water radiolysis. [A January 1979 report]¹⁹ summarizes an experiment which confirms H₂ generation during double shell slurry growth. However, a quantitative H₂ generation rate equation has not been established. Experiments are being conducted to determine the factors which affect H₂ generation. The document to be issued on this subject will be evaluated and incorporated into the annual review.

Double shell slurry and concentrated complexant are being studied.²⁰

Contrary to assurances in the 1980 document, neither the technical bases nor the operating specifications were changed to reflect the results developed, and there was no "annual review" of the technical bases.

- o In November 1978, the Manager of Tank Farm Process Engineering wrote a memorandum stating that, on the basis of laboratory analysis of the slurry growth phenomenon, the vapor space in each SY tank should be sampled for hydrogen:

The test results indicated carbon dioxide and hydrogen concentration of 0.29 and 4.2 volume percent, respectively. The conclusion stated by the Chemical Science Group was that the surface level rise noted in TK-101-SY was due to gas entrapped within the slurry. Because the reported level for hydrogen [in the laboratory study] exceeded both the 1601 Section J [OSD] Specification and Standards limits (and was, in fact, within the explosive range), Tank Farm Process Engineering (TFPE) has concluded that the vapor spaces in tanks containing material of this type should be periodically checked regardless of the fact that they are connected to operating exhausters.²¹

Nevertheless, 18 months later this same manager approved use of radiolytic decomposition of water as the basis for the hydrogen concentration limit.²²

Finding II(A)12: OSD requirements have been written generically and therefore do not accurately portray or take into account the physical characteristics of the waste in many of the tanks. DOE and the contractor allowed operational specification limits to remain in effect that were unachievable and failed to provide a margin of safety.

- o Between 1977 and 1982, the limiting specification and standard for hydrogen concentration required that gas samples be taken and analyzed on a frequency established by Tank Farm Process Engineering. However, no means existed at that time for sampling or analyzing hydrogen concentration, and consequently a surveillance frequency was never established. After 1982, sampling was required only if the exhauster were inoperable for 23 consecutive days, with additional sampling required for each 23-day period of continued inoperability. A 23-day period was considered "adequate lead time to prepare for sampling... [and] to implement emergency procedures if H₂ [was] found in the tanks, before the concentration reached 4%."²³
- o Hydrostatic head is the pressure exerted by a column of liquid and is an important physical property to consider when determining tank integrity. The OSD revision of March 1988 changed the specified method for determining specific gravity of tank contents for the purpose of

calculating the hydrostatic head. Previously, it had been permissible to test just the feed material for specific gravity. This document and subsequent revisions (in June 1988 and November 1989) stated that "stored wastes are sampled periodically per FSS-T-080-00001 [Tank Farm Sample Schedule], and the waste SpG [specific gravity] is obtained from the sample analyses."²⁴ These documents also contained a recovery action section that stated that "hydrostatic head above the maximum shall be reduced by transfer of a portion of the stored waste to another tank, and dilution of the remainder to decrease the waste SpG, as necessary."²⁵

When these new requirements were approved in 1988, there was no readily available means either for sampling tank 101-SY for specific gravity or for transferring 101-SY contents to another tank. These deficiencies also existed for other tanks containing double-shell slurry on which a crust had formed. In fact, the referenced sample schedule, FSS-T-080-00001, called for sampling 101-SY and several other tanks only on an "as requested" basis.²⁶ The requirements remain in effect even though they cannot be met. Despite these problems, for most of 1989 the operating contractor had an active plan to transfer a portion of the contents of tank 101-SY to tank 103-SY. Safety analyses governing tank sampling, waste compatibility with the receiver tank, and waste transfer are only now in the process of being developed.

- o All OSD revisions since 1977 have contained specified limits on allowable concentrations of nitrate, nitrite, and hydroxide ions to inhibit corrosion and stress corrosion cracking of the various tank structures. Since 1980, the OSD specification on tank composition has stated that "tank contents must comply with the given composition limits. Sampling of the tank contents is performed per...[the] Tank Farm Sample Schedule."²⁷ This sampling requirement was not readily achievable for any tank containing waste with a solid crust. Nonetheless, contractor management neither changed the specification requirement nor developed alternative means for assuring that the composition of the tanks met specifications. Thus, the contractor failed to provide sufficient protection against corrosion and stress corrosion cracking in these tanks. Prior to consolidation of OSD requirements in 1982, it was considered acceptable to sample only the input feed to the SY Tank Farm. Such sampling was not capable of detecting changes in waste composition that might result from subsequent radiolytic and chemical degradation of waste solutions after the feed material was deposited in the tank.

Finding II(A)13: The technical basis for certain operational specifications in the OSD remain flawed because they do not take into account information that has become available regarding some of the stated limits.

- o Since 1977, the lower flammability limit of hydrogen in dry air (4 percent) constituted the technical basis for preventing hydrogen combustion in a waste tank. Even after contractor studies demonstrated that hydrogen, nitrous oxide, and other gases were being generated by the slurry growth phenomenon, no apparent effort was made to revise the

flammability limit to reflect actual conditions inside the tanks. A 1985 RHO study of equipment used at Three Mile Island referred to a 3-percent lower flammability limit of hydrogen in nitrous oxide.²⁸ An earlier 1979 assessment calculated the energy release from a hydrogen and nitrous oxide combustion event.²⁹ These studies and calculations should have triggered a reevaluation of the applicability of the 4-percent limit and its viability as a basis for operating 101-SY.

- o The OSD specification for the maximum hydrostatic head at the primary tank wall was designed to preserve tank integrity by preventing excessive dynamic loading during movement of tank contents resulting from a seismic event. The 1973 Functional Design Criteria for the SY Tank Farm specified a maximum hydrostatic head equivalent to 1 million gallons of liquid, with a specific gravity of 1.7. The 1977 SY Tank Farm OSD incorporated this limit, specifying a maximum liquid level of 365 inches and a maximum hydrostatic head of 617 inches water gauge.³⁰ A 1980 OSD revision changed these limits to 422 inches and 720 inches, respectively.³¹ The new 1980 limits were based on an analysis that apparently did not consider any of the following: (1) the presence of a sludge layer and a solid crust (each with its own specific gravity); (2) possible changes in the waste composition due to radiolytic and organic decomposition and polymerization; (3) inability to measure the respective heights of the sludge, liquid, and crust layers; and (4) possible changes in specific gravity due to the presence of solids.³² All these conditions were known to exist at the time of the analysis. The failure to consider how a seismic event might cause a solid crust of unknown thickness and density to break up and impinge on the tank walls is a significant deficiency. It is also significant that in 1980, within a few days of receiving the technical basis for new level limits with a specific gravity of 1.7, the contractor began filling tanks 101-SY and 103-SY with 230,000 and 365,000 gallons of slurry, respectively, with a specific gravity of approximately 1.85.³³

Finding II(A)14: Existing OSD limits relative to slurry growth and hydrogen concentration have been routinely violated.

- o Between 1977 and 1988, the hydrogen concentration specification was 2 percent; an operating standard limit of 1 percent was eliminated in 1982. Prior to 1983 laboratory studies noted the possibility that hydrogen concentrations could be higher than the limit. After 1983, the reality of hydrogen concentrations above the limit was recognized.
- o The November 1980 double-shell slurry campaign³⁴ resulted in additions of 230,000 and 365,000 gallons of waste with a specific gravity of approximately 1.85 in tanks 101-SY and 103-SY, respectively. This operation violated the OSD specific gravity limits (less than 1.7) for the two tanks. Indeed, a reduction of the specification for specific gravity to less than 1.7 was recommended for future double-shell slurry campaigns--not because the limits had been exceeded but because of concerns about the adequacy of available tank volume:

The tank growth phenomenon has the greatest bearing on the future of the DSS [double-shell slurry] process. If all DSS will grow, then the process needs to be examined carefully. Some method must be devised to predict and estimate the extent of growth. The growth will affect the number of tanks necessary to store waste. It may not be advisable to concentrate the waste past a certain point (perhaps a specific gravity of 1.7) if all or most of the space sayings are voided by [subsequent] growth [of the waste].³⁵

Finding II(A)15: The new OSR's developed by Westinghouse and under review by DOE-RL still contain many of the deficiencies outlined above. For example, they apply generically to all double-shell tanks and are therefore inappropriate because they are not uniformly achievable in all those tanks. Furthermore, these limits do not take into account the existing state of knowledge about the waste.

- o In May 1988, following the transition from Rockwell, Westinghouse sought permission from DOE-RL to update Chapter 11 [the OSR section] of the 1986 SAR to reflect its own organizational structure and to make a relatively minor technical change to the OSR for primary tank minimum liquid level.³⁶ On September 20, 1989, before this change could be implemented, DOE-RL responded to a Headquarters Technical Safety Appraisal finding that the OSR's for the tank farms were inadequate by directing WHC to expand the number, specificity, and coverage of the OSR's.³⁷ The development and approval of this new set of OSR's is still in progress. On May 21, 1990,³⁸ DOE-RL properly rejected the new OSR's that WHC had proposed on April 16, 1990.³⁹ New operating restrictions on tank 101-SY and other tanks have the status of interim OSR's until new OSR's have been approved by DOE.⁴⁰

B. CONTRACTOR MANAGEMENT

In a March 20, 1989, presentation to members of a DOE Headquarters Technical Safety Appraisal (TSA) team, the Manager of the WHC Defense Waste Management Division noted that safety performance at the Hanford Tank Farm was assured through "management overview, trend analysis, root-cause analyses (Event Fact Sheets, Critiques, and Unusual Occurrence Reports), independent safety assessments, oversight by independent quality assurance and safety functions, and external reviews."⁴¹ The Hanford "Oversight Management Approach" was said to include "systematic policies, requirements, manuals, procedures,...separate oversight organizations with strong review/approval authority,...[and] active performance evaluation and improvement programs."

In its review of safety issues related to tank 101-SY, the NS team found that WHC management performance in many of these specific areas was wanting. In fact, lack of management attention to tank farm operations extends back through the past several DOE operating contractors.

Background

The Hanford Tank Farm is currently operated by WHC under a cost-plus, award-fee contract signed in 1987 for a 5-year term. WHC assumed responsibility for operations from Rockwell Hanford Operations (RHO), which operated the tank farms for 10 years (1977-1987). The change in contractors in 1987 was part of an overall "consolidation" of the site, aimed at bringing all major Hanford operations under a single operating contractor. One impetus for site consolidation was to achieve an enhanced and more uniform level of environment, safety, and health performance for operations at Hanford.

Since 1987, when WHC took over, there has not been any significant infusion of new management at the tank farms.⁴² Staffing shortages persist, reflecting a high turnover of engineers, a work force reaching retirement age, and limited recruitment in certain technical trades. WHC organizational changes to enhance line program accountability for operations and safety have not fundamentally changed the way management addresses safety issues like those encountered at tank 101-SY, nor have they changed how those issues are communicated and reported. During and immediately after the transition, WHC reviewed all corporate-level policies, but lower level requirements and procedures are being revised more slowly. Training remains largely "on-the-job" and is not based on performance requirements.

One of the principal changes WHC made was to establish a safety oversight organization reporting to a Vice President for Safety, Quality Assurance, and Security (SQS). A nuclear safety division, WHC-NS, now reports to this vice president and provides nuclear safety oversight of WHC operations independent of the line programs that run Hanford's reactors and other nuclear facilities. Tank Farm Nuclear Safety (TFNS), which is a subdivision of WHC-NS, provides independent nuclear safety oversight of tank farm operations. TFNS consists of a supervisor and a four-person technical staff--two each for single-shell and double-shell tanks--who perform surveillance and safety review functions in oversight of tank farm operations. The NS team found the effectiveness of this overall approach hampered by lack of line performance and responsiveness to the safety organization, which was aggravated by the safety organization's lack of "clout." Upper management of the various safety organizations (TFNS, WHC-NS, and SQS) has failed to support lower level staff in their efforts to see that major safety concerns, such as 101-SY, were meaningfully addressed by tank farm operations and engineering.

This section of the Report examines line management's response to flammable gas concerns, the role of engineering and safety oversight, and the nature and evolution of contractor programs to report those concerns to upper management and to DOE.

Management Response To Safety Issues at Tank 101-SY

Finding II(B)1: The tank farm operating contractors have failed to resolve operational safety issues at tank 101-SY in a responsible period of time.

- o The issue of hydrogen generation at tank 101-SY dates to the mid-to-late 1970's (as chronicled elsewhere in this Report), and the issue of radionuclide and toxic gas venting during tank pressurizations dates to 1983:
- In 1983, a surveillance engineer noted that "the fact that the tank [101-SY] has pressurized and the pressurizations are cyclic...are major safety concerns relating to loss of containment."⁴³
 - In 1984, the frequency and degree of overpressurization of tank 101-SY led Rockwell Hanford Operations (RHO) to form a task force to recommend preventive measures. Although the task force recommended further investigation into the potential for release of airborne contamination, little was accomplished, aside from the collection of a few grab samples.
 - A series of internal letters in 1985 from Tank Farm Surveillance challenged inaction on the part of Hanford management to resolve the issue.⁴⁴ The NS team could find no response to these expressions of concern.
 - In 1985-1986, an RHO safety engineer conducted an assessment that concluded that "pressurizations, although not an emergency condition at the concentrations measured, may pose a health hazard and must be prevented."⁴⁵ Further characterization of tank contents was recommended, but the contractor failed to pursue it.
 - In April 1986, the Waste Management Health Physics Division noted that "detecting releases due to pressurization is uncertain; we have very low confidence in the negative results obtained to date. The best solution...is to prevent the problem in design.... Safety has been remiss in failing to apply [industry standards]."⁴⁶ The NS team could find no response to this memorandum either.
 - In 1988, the issue of radionuclide and ammonia venting during pressurization events resurfaced in a major review of tank 101-SY by a WHC engineer. He concluded that, "given enough pressure and time, discharge of the tank gas and radionuclides into the environment and subsequent contamination spread is inevitable."⁴⁷ He recommended increasing negative pressure and ventilation, sealing tank penetrations, increasing the height of the stack (to control ammonia concentrations at ground level), installing gas monitors, and placing workers in masks until physical improvements could be completed. These and other recommended actions were not vigorously pursued because tank farm engineering management gave them low priority.⁴⁸

WHC engineering staff believed that the venting of airborne radionuclides during pressurization events was not of concern, noting that personnel and area monitoring had not detected contamination. Similarly, the WHC staff

position on ammonia was that it was not an unresolved worker safety issue because dangerous concentrations would not be present until well after an odor was detected. The NS team could find no documentation reflecting a well-analyzed, technical basis for these positions. Nor did it find evidence that such issues were elevated either within the contractor organization or raised with DOE-RL.

Finding II(B)2: WHC failed to resolve safety issues at the Hanford Tank Farm in part because it failed to establish and maintain adequate staffing and funding.

- o Chronic shortages in technical staffing and budget have plagued the Hanford Tank Farm organization since the early 1970's. One reason for this situation has been the high turnover rate of engineers in several key categories, including cognizant engineers, process engineers, and safety support staff.⁴⁹ A shortage of experienced personnel in certain key disciplines (such as chemical engineering) has been yet another factor.

An obvious result of these shortages has been a persistent lack of the kind of technical expertise at the tank farms that is necessary to identify, address, and resolve problems such as those that arose at tank 101-SY. These shortages have also undercut the effectiveness of operations in such key areas as maintenance, surveillance, and engineering support. Although contractor management has recognized the gravity of the problem, particularly since the fall of 1988, resolution has been lacking, as illustrated by the following chronology:

- As part of a transition checklist during the 1987 contract consolidation under WHC, the question was posed: "Are engineering personnel available with defined responsibilities and objectives?" The response was that the "Tank Farms have experienced high turnover [30 percent or greater], inefficient use of manpower to provide mentors for training the new engineers, discontinuity of engineering support to operations, and a general lack of trained, experienced personnel."⁵⁰
- In connection with a 1987 transition question aimed at safety personnel staffing, the response was that "Safety Analysis Reports are out of date at both B Plant and tank farms, and their update is not receiving priority. Defense Waste Management support in these areas must receive priority or additional manpower must be assigned."⁵¹
- In a June 1988 assessment of fiscal year (FY) 1989 staffing for the Nuclear Facility Safety (NFS) organization, the manager of that organization raised concerns over the absence of adequate staff. She noted that "concern has been expressed about the quality, objectivity and independence of facility appraisals done by [safety] engineers" and estimated a need for an increase of 5.5 full-time positions equivalents (80 percent) in FY 1989 staffing.⁵²

- On November 4, 1988, in response to projected FY 1989 budget and staffing shortfalls, process engineering management provided a list of scheduled activities to be deferred.⁵³ Despite the serious safety concerns raised in the October 1988 memo discussed elsewhere in this Report, which had been reissued only 2 weeks earlier, the Manager of Process Engineering expressed the view that, unless upper management intervened, budgetary economies would include "reduced OSR/OSD compliance, no engineering studies/improvements, and no 101-SY slurry growth remediation [emphasis added]." A February 1989 memo from the same manager again reported to upper management that "no or minimal 101-SY slurry growth remedial actions" could be supported. The memo emphasized that "if process engineering is to produce quality products with the existing work scope, more money and people need to be made available."⁵⁴
- As a result of personnel transfers, the process engineering organization lost its cognizant engineer for 101-SY in early 1989. The Manager of Tank Farm Engineering attempted to issue a change request to initiate engineering services for a hydrogen monitoring system, but his request lacked cost data. This was information that the manager lacked but that a cognizant engineer would readily be able to provide. This served to delay implementation of the hydrogen monitor.⁵⁵
- In response to a query from the Manager of Defense Waste Management concerning the need for a "first-class review of options and hazards" associated with tank 101-SY, the head of Waste Management Engineering informed the manager in July 1989 that a study had been done the previous year, that some action items had been completed, and that some remained open.⁵⁶ He recommended completion of two outstanding items (installation of a hydrogen monitor and the transfer of 30 inches of waste to another tank) before any further actions at 101-SY were contemplated. The memo also provided the status of both the monitor and the pump needed to transfer any waste from 101-SY; the monitor was said to be "competing with a lot of other tank farm work for both funding and manpower."
- An April 1989 TSA of the Hanford Tank Farm noted "staffing inadequacies in the maintenance, cognizant engineering, personnel protection and safety organizations."⁵⁷ The TSA noted that "inadequate staffing in the WHC Nuclear Facility Safety Group limits the ability of this group to proactively pursue safety issues." The TSA concluded that "the Tank Farm is not considered to include high priority facilities relative to other Hanford facilities for additional personnel resource allocation." The DOE-RL's corrective action was "staffing for the [NFS] will be increased to projected levels."
- The Manager of Tank Farm Process Engineering sent a memo on September 11, 1989, to upper WHC management, providing

information intended to help them prioritize his work.⁵⁸ He stated that his engineers were capable of performing approximately 50,000 hours of work per year but currently had projected work that amounted to 100,000 hours. Accordingly, he outlined the work that was not going to be done, including 1,000 hours of 101-SY remediation, as well as routine engineering support for the SY Tank Farm.

- The Manager of Double-Shell Tank Engineering informed his supervisor in a memo dated November 2, 1989, that revisions to the OSR's required by DOE-RL would impact staffing of other efforts, including "routine operational engineering support to...SY Tank Farm."⁵⁹

- On November 30 and December 5, 1989, in response to projected FY 1990 budget and staffing shortfalls, the WHC program manager prepared two assessments of programmatic impacts.⁶⁰ In the second of these reviews, he noted:

Key projects have been deferred. Cross-site transfer line secondary containment has failed; four of the seven lines have failed. SY Tank Farm is subject to frequent ventilation pressurizations. The lines and the ventilation system must be replaced to avoid potential major environmental damage.

- Although NFS staffing levels were increased, a memorandum dated March 20, 1990, expressed concern over "inexperienced cognizant engineers in Tank Farm Nuclear Safety" who lacked experience in chemistry, radiation safety, or engineering.⁶¹

- o From the foregoing, it can be concluded that, despite the urgency expressed at the middle management and staff level about the need to resolve attendant safety concerns, the tank farms have continually received insufficient staffing and budget priority from upper WHC management, and that this situation has applied particularly to 101-SY slurry growth remedial activities. Inadequate staffing has been exacerbated by a management system that has not provided enough continuity to ensure that safety issues get resolved, regardless of whether an individual is transferred or management changes the priorities of particular engineers. Issues were in effect forgotten or "lost" until symptoms of the problem recurred, necessitating yet another round of response. Such a system sparked intermittent flurries of activity, but as tank 101-SY shows, without an established mechanism to evaluate progress and hold individuals and groups responsible, an issue could go unresolved for a long time. WHC has developed revised procedures for its cognizant engineers, which, if properly implemented, may help resolve one aspect of this particular problem.⁶²

Finding II(B)3: WHC middle and upper management failed to be responsive to tank farm safety issues raised by lower level staff and middle management.

- o The October 1988 WHC memorandum discussed elsewhere in this Report raised serious safety concerns with respect to 101-SY, including the potential for a hydrogen burn or detonation during a pressurization event, for unfiltered radionuclide emissions, and for emissions of ammonia gas.⁶³ The memo stressed the need for a permanent solution and, short of that, concerted actions to control the potentially hazardous effects of slurry growth. It identified certain corrective actions that should be implemented, including pumping out a portion of the waste and attempting to seal off all tank in-leakage points. It also called for the installation of additional level detectors and gas monitors, mandatory respiratory protection for operators, higher ventilation flow rates, and improved methods for air lancing. Management's response to this memorandum was wholly inadequate, as demonstrated by the following:

- After an initial meeting to discuss followup actions to the October 1988 memorandum, the author was transferred to another tank farm project and was no longer involved with the corrective action program.⁶⁴ (There is no indication that this transfer was related to the concerns he raised.)
- A change request to design and install a hydrogen monitor in 101-SY was approved by the operations department. However, the installation of the monitor was in competition with other tank farm work for funding and manpower and was not pursued. Oddly, an internal memo from the Manager of Waste Management Engineering to the Manager of the Waste Management Division suggested that increased priority for the monitor was needed,⁶⁵ as though the engineering manager lacked the authority to determine engineering priorities for 101-SY. The hydrogen monitor was not installed until March 1990.
- Management took limited action to address potential airborne emissions of radionuclides and ammonia during a pressurization event in tank 101-SY--a key concern repeatedly raised by four different engineers from the mid-to-late 1980's. Instead, management took the position that no measurable contamination had been detected in the SY Tank Farm, ignoring a number of studies that had questioned whether the existing monitoring program was capable of detecting such emissions. Management response was limited to pursuing grab samples for radionuclide analysis, obtained following pressurization events in 1984, and Draeger-tube readings for ammonia obtained during lancing operations.
- Prior to the proposed transfer of waste from 101-SY to 103-SY, a transfer pump had to be identified, modified, and tested. This was not completed until 1989. Cold weather further delayed any transfer of waste. (A safety analysis of such a transfer was initiated only after the issue of 101-SY became public.)
- Management rejected the 1984 and 1988 recommendations that the contents of 101-SY should be characterized by taking and analyzing

core samples of the waste. WHC management acknowledged the need to characterize 101-SY only after the issue became public. Core sampling is scheduled to begin in July or August 1990 as part of the WHC "Safety Improvement Plan" for the tank farms.

- o The WHC Manager of Defense Waste Management maintained that the 1988 memorandum distributed to over a dozen members of his staff was never provided to him.⁶⁶ He said that had he received it, he would have shared it with DOE and acted on it immediately. Apparently, the memorandum was elevated only to the level of the Manager of Waste Management Engineering several months after it was written. This official had no explanation of why he failed to share it with the manager.⁶⁷ Although the manager said that he did not receive the memo, he did inquire in the summer of 1989 about the status of corrective actions aimed at resolving the problems that were the subject of the memo and was notified at that time of its existence. The manager's inquiry about the status of options for remedying problems in 101-SY during the summer of 1989 indicates that he was aware of the problem, even if he was not aware of the memo. There is no evidence that, once having learned about the slowness of WHC's efforts at remediation, he did anything to expedite matters.
- o Management also did not review recommendations for addressing problems in tank 101-SY that had been made in 1984 or examine the effectiveness of previous corrective actions. Nor did it initiate an operational safety assessment, despite the seriousness of the issues discussed in the 1988 memo (i.e., potential hydrogen explosions and radionuclide and toxic chemical releases). Based on discussions with WHC engineers who were asked to develop a plan of action in response to the 1988 memorandum, it is apparent that emerging concerns over the level of waste in 102-SY, a DOE-RL requirement to revise Operational Safety Requirements (OSR's), and preparation for a cross-site transfer of waste were accorded higher priority than corrective actions at 101-SY.⁶⁸

Finding II(B)4: WHC's failure to respond effectively to the 1988 memorandum repeated RHO's failures during the mid-1980's.

- o On July 13, 1984, RHO formed a task force to address the problem of gas formation and pressurization in tank 101-SY.⁶⁹ The 1984 task force was directed to identify an innovative, cost-effective method to prevent or decrease the severity of gas buildup and to devise means for the subsequent release of the gas. The primary concern identified by the task force was the potential release of airborne contamination through unfiltered tank openings during a pressurization event. Short-term and long-term recommendations ranged from continued lancing of the crust in 101-SY to investigation of the potential for radionuclide emissions during pressurization events. Contractor management's response to the recommendations was ad hoc at best, with no formal tracking procedures for corrective actions and with little evaluation of the adequacy of actions implemented. These deficiencies are illustrated by the following:

- Management did not direct that any formal peer or safety review of the recommended corrective actions be conducted, nor that a tracking system be established to follow implementation and its results.
 - Management did not establish a formal funding mechanism to implement the recommendations of the task force. Corrective actions were carried out solely according to the good-faith efforts of individual team members.
 - In July 1984, RHO installed a temporary air sampler to determine whether radionuclides were being released through tank openings after pressurization events. When initial samples failed to reveal radioactive emissions, the air sampler was removed. A replacement has still not been installed.
 - A temporary hydrogen monitor was installed in the vent line from 101-SY. However, no formal engineering study was conducted to determine the appropriate operating specifications for the monitor or the proper placement of the monitor to ensure that representative samples were obtained. As a result, the wrong type of monitor was installed. With no preventive maintenance program in place, the monitor was frequently inoperable.
 - A core sample was taken in 1985 at different depths in tank 101-SY--not to understand slurry growth better, but in connection with a study of corrosion. Earlier attempts to take a sample using a "bottle-and-string" technique failed to penetrate the overlying crust, and two attempts were made to breach it physically by using a weighted sampling device. When lead weights of 11 and 22 pounds, respectively, proved unsuccessful, a truck-mounted drilling rig was used to obtain the needed samples. Throughout these successive attempts, no apparent consideration was given to the presence of hydrogen and the possibility that ignition might result from the procedures being used.
 - The six samples resulting from the waste coring operation were sent to Pacific Northwest Laboratories (PNL) for use in their studies of corrosion. Due to other priorities, slurry growth laboratory studies had previously been canceled, and the samples were not used to obtain analytic results characterizing 101-SY waste.
- o Management attention to the problem--as reflected in priority setting, resource evaluations, action-tracking systems, and regular progress reports--was generally ineffective. A formal safety evaluation was not conducted and a resource management plan was not put in place to identify priorities, establish schedules, and ensure funding. With the exception of a temporary hydrogen monitor and limited grab sampling, key recommendations, including characterization of tank 101-SY contents and radionuclide emissions as well as photographs of the tank surface, were not completed in a timely manner. Hence, although formation of the task

force in 1984 reflected a high degree of management attention, failure to follow through on the task force's findings reflected just the opposite.

Finding II(B)5: WHC failed to ensure that tank farm line management was fully responsive to concerns raised by its independent safety organization.

- o Safety oversight at Hanford independent of the line programs has been the responsibility of a series of successive organizations, including Tank Farm Surveillance Analysis (RHO, pre-1987), Defense Waste Storage Safety (WHC, 1987-1989), and Nuclear Safety (WHC-NS, 1989-present). These organizations have served an important function at the tank farms, providing management a self-assessment capability and access to an independent professional safety perspective on operations.

Management appears to view the current nuclear safety organization as more of a support organization than an oversight organization. Thus, management emphasizes "cooperation and negotiation" rather than the development of firm, technically sound positions on safety issues that have programmatic impacts. This appears to be true even in those instances in which WHC-NS staff have produced compelling technical documentation.⁷⁰

- o Management has failed to resolve the following list of issues that have been repeatedly raised by tank farm safety staff over a long period of time:
 - Reporting of deficiencies at 101-SY (scope, content, root-cause analysis, and corrective actions);
 - Flammable vapor sampling and monitoring deficiencies at 101-SY;
 - Control of modifications to essential components at the Hanford Tank Farm;
 - Evaluation of the potential for fire and chemical explosions in SST's; and
 - Review of electrical power failures at Hanford.
- o The following chronology relates to two 101-SY issues--radionuclide emissions during pressurizations and event reporting--and illustrates how legitimate issues raised by the safety organization were not resolved in a timely manner.

Radionuclide emissions during pressurizations:

- In a September 1983 internal communication on tank 101-SY, a safety engineer advised a WHC project manager of "major safety concerns relating to loss of containment (airborne contamination released to the environment)."⁷¹

- In 1984, a safety engineer identified lack of redundant exhausters components, uncontrolled tank penetrations, and uncharacterized waste contents.⁷²
- In a January 1985 internal memo, the Manager of Tank Farm Surveillance reported a "potential airborne release which was unsampled and unmonitored."⁷³
- In May 1985, the Manager of Tank Farm Surveillance asked the Tank Farm Manager why airborne contamination during a pressurization event had not yet been sampled.⁷⁴
- In July 1985, the Manager of Tank Farm Surveillance informed his supervisor that the "general attitude toward this issue [containment of airborne radionuclides] appears to be that it would be too expensive to address."⁷⁵
- In 1986, a safety engineer recommended rejection of the 1986 SAR revision because it did not adequately treat radionuclide emissions.⁷⁶
- In a 1988 review of an Event Fact Sheet, a safety engineer noted that possible releases of radionuclides during tank pressurizations needed to be addressed.⁷⁷
- In 1989, a safety engineer included "unsampled, unmonitored, and unreported" radionuclide emissions among a list of outstanding, significant safety issues.⁷⁸

Event reporting:

- In a June 1988 internal memo to the Tank Farm Manager, a safety engineer expressed the view that events exceeding operating limits should at least be reported as Event Fact Sheets.⁷⁹
- In August 1988, a safety engineer advised the Tank Farm Manager that an event reported on an Event Fact Sheet should be reported as a Critique.⁸⁰
- In December 1988, a discrepancy report stated that nonconformance with operating limits for tank 101-SY would be reported in discrepancy reports and not Event Fact Sheets because slurry growth was an ongoing problem.⁸¹
- In a January 1989 weekly report, a WHC staff engineer cited the Tank Farm Manager's approval to downgrade reporting of 101-SY nonconformances with specification limits.⁸² (This was disapproved by upper WHC management after consultation with DOE-RL.)

- In a March 1989 review of an Event Fact Sheet, a safety engineer noted that the rise in 101-SY's level above the 422-inch specification limit should have been reported as a Critique.⁸³
- In March 1989, a safety engineer noted that a pressurization event at 101-SY should have been reported in a Critique instead of an Event Fact Sheet.⁸⁴
- o Contributing to the lack of progress on safety issues identified by the safety organizations was an apparent adversarial relationship that was allowed to develop between the WHC-NS staff and the various engineering and operating groups at the Hanford Tank Farm. This problem is documented in WHC internal letters during the 1988-1989 timeframe.⁸⁵ One source of the problem apparently was the tendency for the safety organization to attempt to work problems with line management, rather than to provide independent findings to which they must respond. In June 1989, tank farm management attempted to promote better relations between the two groups, as evidenced by an internal memorandum entitled "Teamwork," which was sent from the Manager of the Defense Waste Management Division and the Manager of the Safety Division to tank farm personnel.⁸⁶ However, recent discussions with tank farm staff indicate that the problem persists.⁸⁷

Incident Reporting Program

From August 1981 to November 1984, the criteria for reporting unusual events were contained in DOE Order 5484.2, "Unusual Occurrence Reporting System." This order was replaced by DOE Order 5000.3 on November 7, 1984, and remained in effect until May 30, 1990. (DOE Order 5000.3 was replaced by DOE Order 5000.3A on that date). The NS team evaluated the WHC incident reporting program against the standards in DOE Order 5000.3, which listed examples of events that organizations should use in developing their reporting programs. Among the examples of events that must be reported are the following:

- o Failure of effluent monitors, high radiation alarms, and evacuation signals;
- o Degradation of a barrier designed to contain radiation or toxic material, or unplanned release of radioactive or toxic materials past this barrier;
- o Release of toxic material that results or could result in exposure of personnel;
- o Leaks from pipes, valves, tanks, cells, or drains that could create on-site, off-site, or public concerns and failure of control or isolation valves; and

- o Unplanned or unexpected change in a process condition or variable of importance to performance, reliability or safety, whether abrupt or long term.

All of these examples applied to events at 101-SY.

When Westinghouse became the principal operating contractor at the Hanford site in 1987, it established a reporting system that included the reporting of events of lesser significance in Event Fact Sheets. WHC procedure GA-2.18 replaced RHO procedure RHO-GM-MA-2, establishing requirements and responsibilities for analyzing, reporting, and developing actions in response to design criteria deviations, surveillance anomalies, and suspect trends in waste tank leak and intrusion surveillance data.⁸⁸ The procedure states that, "in general, if there is a satisfactory explanation for the anomaly, only an Event Fact Sheet (EFS) will be required. An Unusual Occurrence Report (UOR) is to be issued only if there is no satisfactory explanation for the anomaly."

WHC Manual WHC-CH-1-3 defines the procedure for reporting events that could adversely affect or potentially affect the health and safety of WHC employees, visitors, or the public; the environment; equipment or facilities; or programs. An Event Fact Sheet is defined as a brief report on an event and includes a description of the event, recovery actions, consequences, and management decisions on the need for further investigation and corrective actions, using the best information available to ensure prompt reporting (within one working day). A Critique is defined as an evaluation of those events that do not meet the criteria for an Unusual Occurrence Report but require investigation beyond that identified in the EFS. An Unusual Occurrence is defined as any unusual or unplanned event having programmatic significance such that it adversely affects or potentially affects the performance, reliability, or safety of a facility. An Event is defined as a deviation from planned operations that may have significant safety, quality, environmental, programmatic, or public implications.

DOE Notice N5480.4 was issued in June 1988. It directs that contractors must promptly notify DOE of any nonroutine events with potential safety significance. The notice was issued in light of continued failure by some contractors and operations offices to divulge safety incidents and issues to DOE Headquarters promptly.

Finding II(B)6: The identification of unusual events at the Hanford Tank Farm has frequently resulted in underreporting. Events meeting the requirements for a UOR have been routinely identified and reported in Critiques or EFS's.

- o Events related to slurry growth and hydrogen gas formation occurring at Hanford fall into one of several categories listed in DOE 5000.3 pertaining to Unusual Occurrence Reports. Past failures of equipment, such as the recent failure of the isolation valve on 103-SY and its associated supports, appear to be similarly reportable as UOR's.
- o In August 1987, it was determined that a vacuum monitor had never been installed on the SX Tank Farm exhaust system, although the Operational Safety Requirements required daily readings of such a monitor. Similar

discoveries had been reported at the Hanford Tank Farm between 1987 and 1989, and the Unusual Occurrence Report describing those nonconformances was even referenced in the Critique for the SX event.

- o Another example of inconsistent reporting involves reporting of worker exposures to toxic vapors, such as ammonia. Several events have been reported in the last few years, yet some of them, such as a September 1989 worker exposure, were subjected only to Critiques when UOR's should have been issued.
- o A note dated January 10, 1989, from the Manager of Tank Farm Surveillance to the Tank Farm Manager, stated that continuously writing Event Fact Sheets on multiple occurrences of slurry growth in 101-SY was not recommended and subsequent occurrences should only be reported in a discrepancy report--a document that is customarily not transmitted to DOE-RL.⁸⁹ This position was accepted by the Tank Farm Manager. Such an approach violated WHC procedures related to event reporting.⁹⁰
- o The first Unusual Occurrence Report related to problems in tank 101-SY since 1979 was issued on April 4, 1990, after the problems in the tank had become public. WHC did not issue a separate Unusual Occurrence Report to record the pressurization event of April 19, 1990, arguing that none was needed because the April 4 UOR was "open." Such an interpretation of UOR reporting requirements violated DOE policy and ignored the fact that UOR's serve to inform DOE Headquarters and other DOE sites of significant events.⁹¹
- o An internal memo dated June 29, 1988, from a TFNS engineer to the Tank Farm Manager regarding a review of a recent Event Fact Sheet,⁹² noted that the event violated a limiting condition for operation (actually it violated a design limit, which was a more severe safety violation).⁹³ The engineer pointed out that the report should have been elevated to the attention of WHC management and required immediate action.
- o The findings above are supported by a 1989-1990 self-assessment by the Hanford contractors and DOE-RL, which found:

Inadequate reporting and guidance for trend analysis exists at Hanford; problems exist in the discipline of operation at the Hanford facilities; in many cases, safety documentation and, to a lesser extent, procedures for Hanford facilities, are inadequate.⁹⁴

Finding II(B)7: Root-cause analyses and corrective actions described in Event Fact Sheets, Critiques, and UOR's are seldom comprehensive; corrective actions frequently take years to implement, and as a result, events recur.

- o In June 1989, WHC staff completed a review of WHC Critiques and Unusual Occurrence Reports issued since July 1987.⁹⁵ As part of this review, reports were reexamined to ensure that closeout documentation did in fact support the belief that corrective actions had been completed. The reexamination was completed in early 1990.⁹⁶ A February 1990 DOE-RL

audit of WHC Defense Waste Management found that the earlier review of event reports had been ineffective.⁹⁷

- o The NS team reviewed root-cause analyses of several events and found them to be weak. Often the real root cause had not been determined. In some cases, the first and most obvious cause was addressed but deeper, underlying factors were never considered. In instances where a detailed review of event reports by the WHC Tank Farms Nuclear Safety staff had revealed significant deficiencies in the content of the root-cause analysis, the team found no evidence that those individuals responsible for the original work had made the requisite corrections or that WHC-NS management required line management to make any improvements. For example, one event involved breaker tripping in an exhaust circuit, which caused loss of facility ventilation. The breaker was checked and, when no problem was found, reinstalled. Shortly thereafter, it tripped again, causing the same loss of facility ventilation. Events frequently have been repeated several times before action was taken to expand the investigation to determine the root cause.
- o A February 1990 DOE-RL audit of WHC Defense Waste Management found the following:
 - "The requirements for identification of root cause and actions to preclude recurrence of events/deficiencies reported on event reports are not being effectively implemented at the tank farms."
 - "Lower tier procedures describing the application of root cause analysis and for recording, monitoring, assessing and reporting the status of corrective action items have not been developed."⁹⁸
- o Even when the root cause has been properly identified, there have been problems with corrective actions. Corrective action tracking systems have recently been established; however, the actions taken are poorly documented. These kinds of reporting-system deficiencies at Hanford were cited by the EH site safety representative in a December 1989 report.⁹⁹
- o The NS team found instances in which a hardware configuration had been determined to be inadequate to meet design or SAR requirements, and management changed the requirement instead of fixing the broken equipment. For example, a letter from the Tank Farm Manager to DOE-RL, dated August 1988, included an attachment that stated:

Investigation also determined that an error existed in the basis of the OSR [SAR] for double shell tanks. The OSR indicated that three conductivity probes were installed in the double shell tank annulus. However, the three tanks in SY farms were built with only one conductivity probe. A change to the OSR is in progress.¹⁰⁰

This observation was reported in a Critique.

- o The NS team findings concerning weaknesses in the WHC reporting system are supported by a 1989-1990 self-assessment by the Hanford contractors and DOE-RL.¹⁰¹ The self-assessment team observed that:
 - "An effective sitewide corrective action program has not been implemented."
 - "Root cause analysis has been a long-standing weakness at Hanford."
- o Until recently, there was no effective mechanism in place at Hanford to track the closeout of Unusual Occurrence Reports, Critiques, or Event Fact Sheets. Until the recent revision of WHC Manual WHC-CM-6-1, EP-5.2,¹⁰² the responsibilities of the tank farm cognizant engineers were either vague, nonexistent, or ill-defined with respect to coordination of interdisciplinary interfaces, specific responsibilities, documentation of decisions, and transfer of responsibilities.

Finding II(B)8: Contractor policies and procedures pertaining to the incident reporting program fail to provide the necessary elements to ensure adequate review and resolution of safety issues.

- o Current WHC procedures do not require safety review of all events, nor do they ensure that comments by safety reviewers are reflected in the final disposition of the reporting documentation.¹⁰³ There is no requirement that safety reviewers concur in actions taken by the cognizant engineer.¹⁰⁴
- o Cognizant engineers have the responsibility to assign Impact Levels, which determine the extent of review required, for actions taken to resolve events. Such a system could be used to avoid proper review by other organizations.¹⁰⁵ In the view of one senior WHC engineer, abuses of this type have in fact been occurring at the Hanford Tank Farm.¹⁰⁶
- o WHC middle and upper management have deleted or ignored safety concerns expressed by the WHC safety organization during internal reviews of events reported in the incident reporting program. Technical peer review of concerns expressed by reviewers are not always performed prior to WHC management's decision to accept or reject those concerns.¹⁰⁷
- o The 1989-1990 self-assessment by the Hanford contractors and DOE-RL included findings similar to the above:¹⁰⁸
 - "A significant need exists at Hanford for a more proactive approach to completing corrective actions."
 - "Safety features required to be operational by DOE Orders are generally not identified within the SAR and managed (e.g., designated as safety class systems) in a manner that assures a high degree of reliability."

- "A significant number of lesser known Hanford nuclear facilities currently have OSR packages that place no formal limits of any kind on facility operations. Reference to a lower-tier document is usually used to help define the facility safety envelope."

Responses to DOE Appraisals

A significant amount of the interaction between the tank farm operating contractor and DOE has been through the routine reporting system and responses to DOE-RL and DOE Headquarters surveillances and appraisals. The NS team examined WHC responsiveness to three significant reviews: two surveillances conducted by the DOE-RL Waste Management Division in June and October 1989 and a 1989 Technical Safety Appraisal conducted by DOE Headquarters.

Finding II(B)9: WHC has been insufficiently responsive to DOE safety concerns.

- o DOE-RL issued a surveillance report on June 13, 1989, citing findings of a surveillance inspection conducted at 101-SY.¹⁰⁹ The surveillance noted that the tank was being operated outside of approved limits, specifically the limit on the maximum liquid level of the waste in the tank. The report noted that the technical basis for operating beyond mandated limits was not established and that the resolution of outstanding operational issues at 101-SY was receiving low priority.

As discussed elsewhere in this Report, the contractor did not respond to the DOE-RL report until January 29, 1990, well beyond the 30-day requirement. When WHC's response was received, DOE-RL judged it to be wholly inadequate; among other things, the submission included an engineer's sketch as a technical basis for the 422-inch specification for maximum waste height. WHC was also not responsive to concerns that had been raised regarding formal remedial actions for 101-SY, the need to maintain continuity of process engineering support, and the lack of a master plan for 101-SY. DOE-RL informed WHC that "WHC quality on responding to this surveillance needs greater improvement. This surveillance has been outstanding by WHC since June 13, 1989."¹¹⁰ (The planned safety analysis activities encompassed in the WHC Safety Improvement Plan include provision of a technical basis for 101-SY operating limits and specifications.)¹¹¹

- o Another surveillance report was issued by DOE-RL on October 31, 1989. This report included findings of a surveillance of tank 244-BX ventilation requirements.¹¹² DOE-RL questioned the technical basis for the operating specification that required active ventilation only if waste temperatures equaled or exceeded 140° F and requested the relevant operating and surveillance procedure.

The contractor responded to the aforementioned DOE-RL report on December 5, 1989, submitting a 1981 internal letter describing the basis for the operating specification and providing a copy of the operating specification document.¹¹³ DOE-RL responded by objecting to the

outdated status of the standards referenced in the 1981 letter, the lack of any surveillance requirement, the failure to resolve whether a study recommended in 1981 to establish better ventilation requirements had ever been conducted, and the open status of a requirement for hydrogen monitoring of the tank vapor space.

Thus, this response also was judged by DOE-RL to be inadequate and unresponsive to the concerns raised. A revised response was requested, and WHC transmitted it to DOE-RL on March 16, 1990.¹¹⁴ The revised WHC response acknowledged the lack of a surveillance procedure, the lack of hydrogen monitoring, and the inappropriateness of the table of standards referenced in the original response. It acknowledged that the study referred to in the earlier response had not, in fact, been performed; WHC maintained that operating experience suggested that such a study was no longer necessary.¹¹⁵

- o As noted earlier, the TSA for the Hanford Tank Farm was conducted by the DOE Headquarters Office of Environment, Safety, and Health from March to April 1989. Operational safety performance was appraised against 12 performance objectives, including maintenance, radiological protection, training, and emergency readiness. The appraisal resulted in a total of 68 concerns that DOE-RL subsequently addressed in a corrective action plan submitted to DOE-HQ in July 1989.¹¹⁶

A March 1990 NS review of WHC and DOE-RL followup to the July 1989 commitments found that a formal program for verifying corrective actions did not exist at the tank farms.¹¹⁷ Actions that had been portrayed to DOE-RL as having been completed were not verified. (A subsequent DOE-RL review rejected over 50 percent of the WHC actions that had previously been submitted as complete.) The NS assessment showed that WHC also lacked a management system to track and verify completion of externally generated safety concerns, and little attempt was being made to identify the root causes of safety deficiencies as a means to develop more lasting institutional solutions to problems. Thus, deficiencies found by the TSA team in April 1989 were also observed by the NS team during its on-site walkthrough in April 1990. These deficiencies included problems with equipment and instrument maintenance, lack of monitoring of flammable and toxic gases, manpower shortages, and improper control panel labeling.

C. DOE MANAGEMENT

For reasons discussed below, this section of the Report deals almost wholly with DOE field office management of the Hanford Tank Farm. The DOE field office that manages the Department's many diverse facilities at Hanford is the Richland Operations Office (DOE-RL). The senior official in this office is the DOE-RL Manager, who reports to DOE Headquarters in Washington, D.C. Reporting to him are the Deputy Manager and the heads of the principal administrative units--the Assistant Managers for Administration, Operations, Research and Projects, and Safety, Environment, and Security.

The NS team's findings with respect to DOE's management of issues related to slurry growth, especially in tank 101-SY, are discussed below. Those findings largely parallel the findings discussed in the Contractor Management section of the Report. It should be emphasized that although this section focuses on weaknesses in field office management, the line program offices at DOE Headquarters--in this case the Office of Defense Programs and, more recently, the Office of Environmental Restoration and Waste Management--are responsible for the conduct of field office oversight at the tank farms. The NS team found almost no evidence of program office leadership of, involvement in, or responsibility for the day-to-day operations of the tank farms.

Finding II(C)1: DOE-RL failed to establish formal systems to ensure that safety issues were routinely raised to DOE-RL upper management either by lower level DOE-RL officials or by the tank farm contractor.

- o Until just before his press conference of March 23, 1990, the DOE-RL Manager was not aware of key developments with respect to gas generation in the double-shell tanks, particularly in tank 101-SY. He had not learned about a WHC study that highlighted the possibility of explosions below the slurry crust until the day before the press conference, although WHC had informed a middle level and an upper level DOE-RL manager about the results of that study on March 6, 1990, 2 weeks earlier.¹¹⁸ The DOE-RL Manager was also unaware that documented tank pressurizations had occurred repeatedly since 1983, that tank limits had routinely been exceeded, that potentially flammable concentrations of hydrogen had been measured in the vapor space of tank 101-SY at least as early as 1985, and that concerns had been expressed within WHC about dangers to workers arising from pressurizations and other phenomena associated with gas generation in the tank farms.¹¹⁹

In part, the DOE-RL Manager's lack of knowledge about these issues reflected the contractors' failure to keep DOE-RL fully informed, as well as their failure to convey important information in a manner that clearly communicated the significance of the information to DOE-RL personnel. For example, the agenda of the meeting held on March 6, 1990, at which WHC briefed DOE-RL on the problems in 101-SY, was unrelated to the hydrogen issue; the briefing materials that WHC brought to the meeting failed to discuss it. WHC raised and discussed the issue with DOE-RL in a manner that did not convey its seriousness.¹²⁰

- o Nevertheless, sufficient information was communicated to DOE-RL to have alerted it much sooner to safety issues associated with gas generation in tank 101-SY. Through 1985, DOE-RL received status reports on various contractor experiments concerning slurry growth, and after 1987 Event Fact Sheets were routinely written documenting the tank's repeated pressurizations. In January 1984, Rockwell Hanford Operations (RHO) formally briefed DOE-RL managers on the slurry growth problem, including the fact that when the tank pressurized the potential existed for unfiltered releases of radioactive material.¹²¹ Additionally, DOE-RL had staff assigned to the tank farms as monitors, and the NS team was informed that these monitors routinely attended contractor meetings at

which hydrogen generation and slurry growth were in all likelihood discussed.¹²² Former DOE-RL monitors acknowledged to the NS team that they were aware of the pressurization events.¹²³

- o Despite the fact that DOE-RL's managers had multiple sources of information concerning tank 101-SY, none of them viewed gas generation as serious enough to require protective measures until March 1990, when outside groups focused attention on the issue. Most of the DOE-RL managers were under the impression that hydrogen released into the vapor space above the crust was controlled by dilution and venting. For them, the significance of the issue was not heightened until WHC's "discovery" that both hydrogen and a strong oxidizer (nitrous oxide) were present below the crust and that combustion could occur there.¹²⁴ As discussed in detail elsewhere in this Report, the generation of nitrous oxide and hydrogen below the crust had been known and documented by the contractors over a period of many years. This information was apparently not transmitted to DOE-RL personnel in a manner that would reasonably put them on notice of its significance.
- o The below-the-crust phenomenon, however, was not the only, or even necessarily the most important, safety issue related to gas generation at the Hanford Tank Farm. Other phenomena (such as tank pressurizations, potential radionuclide and hazardous gas releases, and flammable concentrations of hydrogen in the vapor space) were indicators of potentially hazardous conditions in the waste tanks that were known to at least some DOE-RL managers.¹²⁵ These managers apparently did not view these issues as serious enough to present to upper DOE-RL management--for example, as an Unreviewed Safety Question requiring additional analysis and precautions.
- o DOE-RL's overall handling of the gas generation issue suffered from lack of a formal, systematic method for ensuring that potential safety issues were properly evaluated and brought to the attention of upper management.

Finding II(C)2: DOE-RL lacked adequate staffing, expertise, and training to ensure adequate oversight of the waste management facilities.

- o DOE-RL managers frequently cited lack of expertise resulting in dependence on information provided by their contractors as a key reason the "new" issue brought out at the March 1990 press conference--the below-the-crust phenomenon--was not spotted earlier.¹²⁶
- o Lack of sufficient expertise was compounded by inadequate staffing. DOE-RL's line overseer for the DST's was greatly overburdened even in that job, yet at one point he was also responsible for oversight of the single-shell tanks.¹²⁷
- o DOE-RL's inadequate staffing and expertise were noted in a 1989-1990 self-assessment by the Hanford contractors and DOE-RL as follows:

There is a shortage of personnel in the safety area who have adequate or above adequate experience and site knowledge to fulfill the staffing requirements both at the DOE-RL and contractor levels.¹²⁸

Finding II(C)3: DOE-RL lacked a formal surveillance program that provided regular coverage of the tank farm facilities.

- o Over the past year, the lead engineer for DOE-RL's Safety and Environment Division conducted no surveillances at all.¹²⁹ The cognizant engineer for DST's in the Waste Management Division was supposed to do 20 surveillances per year, as specified in a plan developed in 1987, but was only able to do a few surveillances in response to events at the tank farms.¹³⁰ The absence of a systematic and adequately staffed surveillance program reduced the likelihood that DOE-RL would discover safety issues that the contractor had not communicated to DOE-RL.
- o The DOE-RL's Office of Nuclear Facility Safety has a staff of only four safety engineers for the entire Hanford site.
- o Members of the DOE-RL staff seldom visit the Hanford Tank Farm, partly because of the distance from the DOE-RL offices and partly because of the heavy workload of safety reviews and other administrative duties. Individual staff members are attempting to make as much impact as possible in selected areas, but they are generally overburdened.
- o Occasionally, individual staff members have had a positive impact on overall performance. One such example is a 1990 DOE-RL directive to WHC concerning the need to improve the revised operational safety requirements under development for the DST's.
- o DOE-RL permitted WHC to respond slowly and incompletely to DOE-RL safety concerns. Inadequate WHC responses to significant issues were not rapidly elevated to higher management for resolution.

Finding II(C)4: DOE-RL failed to properly manage its support services contractor.

- o Findings from an August 1988 DOE-RL surveillance were not responded to until approximately 6 months after the surveillance was conducted. DOE-RL had delegated the responsibility to review WHC's response to the surveillance to its support services contractor, Stone & Webster Engineering Corporation. Stone & Webster, which had been retained because of a DOE-RL manpower shortage, was expected to report the results of its review to DOE-RL. Instead, the contractor incorrectly closed out the surveillance and did so without obtaining DOE-RL approval.¹³¹ Allowing one contractor to close out a surveillance of another contractor's work amounted to an abdication of DOE-RL's oversight role.

Finding II(C)5: DOE-RL middle and upper management attention to operational safety issues, both within the line and in the independent safety organization, has been inadequate.

- o As noted above, the DOE-RL staff member who monitored the DST's was overburdened, conducted few surveillances, and in general was unable to provide adequate oversight of contractor operations. In addition, the key overseer of the tank farms in the DOE-RL safety organization conducted no surveillances during the past year. These deficiencies are symptomatic of an overall lack of attention by DOE-RL's upper and middle management to operational safety issues.
- o The monitor for DST's was essentially on his own, receiving little apparent support or direction from higher level DOE-RL management to assist him in ensuring prompt resolution of safety issues by the contractor.¹³² The DOE-RL independent safety organization was unable to compensate; between December 1989 and March 1990, there was no mention of tank 101-SY in their weekly reports.

Finding II(C)6: DOE-RL's sensitivity to safety issues was generally inadequate.

- o DOE-RL management failed to recognize the safety implications of information provided by the contractor. A prime example occurred on March 6, 1990, when DOE-RL managers were told by WHC that Westinghouse engineers at the Department's Savannah River site had expressed concerns related to the potential for combustion below the crust in tank 101-SY. A DOE-RL manager at the briefing properly inquired whether the new development constituted an Unreviewed Safety Question. The Acting Assistant Manager for Operations and the Branch Chief of the Waste Management Division, along with the other DOE-RL personnel present, were erroneously assured by WHC that the matter was not an Unreviewed Safety Question. However, the DOE-RL officials present did not explore the implications of the new information--such as whether, reviewed or not, a significant hazard was present that required corrective measures, briefing of upper management and external groups, reporting to Headquarters, or other action.¹³³ One week later, when the contractor provided written notification that safety restrictions had been taken at the tank farms, DOE-RL middle management again failed to bring the issue to the attention of the DOE-RL Manager.¹³⁴

Finding II(C)7: DOE-RL failed to investigate root causes of problems properly.

- o Although the contractor's communication of problems associated with slurry growth in tank 101-SY was in many respects deficient, DOE-RL did not adequately investigate the problems that were communicated. Numerous pressurization events that occurred in tank 101-SY were documented by WHC in Event Fact Sheets, and these were distributed to DOE-RL managers.¹³⁵ Notice of these repeated pressurizations did not trigger an attempt to determine the root cause of the problems.

Finding II(C)8: DOE-RL did not ensure adequate reporting by its contractors to DOE Headquarters.

- o DOE-RL tolerated widespread nonreporting and underreporting of tank farm conditions, demonstrating in the process that it did not appreciate the importance of operating information to DOE Headquarters and to other DOE facilities.

Finding II(C)9: DOE-RL has been overly dependent on external pressure to heighten the priority of safety issues.

- o As noted elsewhere in this Report, documented pressurizations of tank 101-SY occurred as early as 1983. In 1985, a concentration of at least 5-percent hydrogen was measured in the tank's ventilation area, indicating a much higher concentration below the crust.¹³⁶ The repeated pressurizations of the tank and other phenomena associated with slurry growth were known to some DOE-RL personnel, but no decisive action was taken to mitigate these hazards until March 1990, when the possibility of an explosion below the crust became the focus of attention.
- o This possibility of an explosion was highlighted in the December 1989 WHC issue paper discussed earlier. However, DOE-RL's knowledge of the concerns engendered by that paper did not elevate DOE-RL attention to the issue. It was not until consultants to the Defense Nuclear Facilities Safety Board (DNFSB) asked for and received a briefing on the matter that DOE-RL felt compelled to act.¹³⁷ The DNFSB briefing took place on March 20-21, 1990, and it covered both the history of the slurry growth phenomenon--including the 1985 5-percent reading--and the potential for below-the-crust explosions.¹³⁸ More than anything else, it was the DNFSB consultants' reaction to this briefing--they openly referred to the handling of the issue as equivalent to NASA's handling of the O-ring problem prior to the Challenger disaster--that triggered a call to the DOE-RL Manager, who was then in Washington, D.C., and the subsequent public release of information.¹³⁹ Until the DNFSB consultants raised the issue, DOE-RL management did not treat slurry growth as a priority concern.

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III. OVERVIEW OF EXOTHERMIC REACTIONS IN SINGLE-SHELL TANKS

This section of the Report discusses the NS team's findings concerning DOE-RL and contractor handling of issues related to the potential for exothermic reactions in single-shell tanks (SST's), especially the possibility of ferrocyanide explosions. Although the ferrocyanide issue is distinct from the slurry growth problem discussed in previous sections of this Report, they are related in that public discussion of the ferrocyanide issue led to contractor studies, which eventually surfaced the fact that hydrogen and nitrous oxide generation was a serious potential hazard in tank 101-SY.

Identification of the Safety Issue

In the 1950's, ferrocyanides were added to some single-shell tanks (SST's) as part of a cesium recovery campaign.¹ Under certain conditions, ferrocyanides can react exothermically with other chemicals present in the tanks and cause a runaway reaction or explosion.² This can occur when the temperature inside the tanks is sufficiently high.³ Actual tank temperatures have generally been considerably less than what is required to precipitate such a reaction, in part because of the liquid present in the wastes.⁴

In a 1983 report, the then-Manager of the Pacific Northwest Laboratories' (PNL) Analytical Chemistry Laboratory expressed concern that "recent planned or ongoing activities involving stored wastes have possibly increased the potential" for exothermic reactions in the waste tanks.⁵ Although he did not believe that a ferrocyanide explosion or other hazardous exothermic reaction was likely under then prevailing tank conditions, he was concerned about the potential for such reactions if conditions changed. If, for example, all remaining liquids in the wastes were removed and the tanks were backfilled with rock--steps that were under active consideration because the SST's were leaking--temperatures might increase to the point where exothermic reactions would be possible.⁶

He and other PNL chemists recommended studies to evaluate the potential for exothermic reactions under various tank conditions.⁷ Although there was a divergence of opinion among contractor organizations about the need for such studies,⁸ the recommendation eventually won approval from PNL, Rockwell Hanford Operations (RHO), and DOE-RL. DOE-RL provided PNL with funding to conduct a literature review, which was to be the first phase of the studies.⁹ In addition, beginning in December 1983, the planned studies were included in the Hanford Waste Management Technology Plan (HWMTP), signifying that the concerns raised by the PNL chemist would be tracked until satisfactorily resolved.¹⁰

The Burger and Martin Reports

The literature review was carried out in two parts. The first part, which focused on the potential for a ferrocyanide explosion, resulted in a November 1984 report by PNL chemist L. Burger (a document known as the Burger Report).¹¹ A second report, dated June 1985 and authored by E. Martin, dealt with organic complexants in the tanks and is referred to here as the Martin Report.¹²

The Burger Report discussed a worst-case scenario in which "a possible energy release equivalent to 36 [tons] of TNT is calculated."¹³ Although the report stated that the sequence of steps needed to produce such an explosion was "highly improbable,"¹⁴ it stressed that knowledge about both the nature of the reactions and relevant tank conditions was incomplete. Accordingly, the report recommended followup laboratory work and tank sampling.¹⁵ In contrast, the Martin Report concluded that the potential for explosive combinations of the complexants studied was "nonexistent or negligible" and that "the presence of organic material in the high-level defense waste does not constitute undue hazard under the present storage conditions."¹⁶

The Martin Report was cleared by DOE-RL for publication and was cited as a reference in a 1987 Environmental Impact Statement (EIS) issued by DOE-RL.¹⁷ The Burger Report, as discussed below, was denied clearance by DOE-RL, and no reference to it appeared in the EIS.

DOE-RL Denial of Clearance to the Burger Report

The Burger Report had been cleared by PNL and RHO for limited dissemination "to DOE and DOE contractors,"¹⁸ but even with this limitation, the then-EIS Program Manager for DOE-RL recommended that the clearance request be disapproved. He provided no explicit written justification for his recommendation, and when interviewed by a member of the NS team, he could not recall why the request was disapproved.¹⁹ However, on May 18, 1985, in a handwritten note to the DOE-RL's Director of the Waste Management Division, he wrote:

Report PNL-5441 [the Burger Report] has been submitted for clearance and I recommend that it be disapproved. The safety significance of the issue, however, must be considered by Rockwell/PNL. I recommend that Rockwell/PNL develop a R&D plan to technically address subject issue and then after results are available, publication of facts (not speculations) be considered. We should assure ourselves that this issue is visibly tracked by contractors and [DOE-]RL. I see potential problems with (interim) tank drying and ISD [in situ disposal] as well. Meanwhile, the HDW [Hanford Defense Waste]-EIS considers a similar explosion scenario. P.S.--I believe PNL should have handled this smoother [sic].²⁰

The Director of the DOE-RL Waste Management Division accepted his recommendation for disapproval and addressed the following handwritten note to PNL's Manager for Nuclear Waste Technology:

If such a potential exists PNL should propose the work necessary to evaluate the potential. However, to publish an open report which speculates on such an explosion without any real basis is to invite misuse of the data and concept. I do not want to hide this if this is a real potential issue but let's channel it in a direction to resolve the questions not just raise them.²¹

Pacific Northwest Laboratories' Manager for Nuclear Waste Technology, in turn, made the following handwritten comment about the Burger Report:

After looking through this report I can well understand why DOE did not approve it. (The summary alone leaves you hanging.) We need to establish some guidelines for handling such sensitive information (e.g. the work was done for Rockwell--a report and proposal to Rockwell might have been the best route). Do we report things openly just for the sake of science?²²

At some point during consideration of the Burger Report clearance request, the EIS Program Manager for DOE-RL consulted the DOE-RL Chief Counsel about the possibility that disapproval of the request might be viewed as a cover-up.²³ The Chief Counsel later expressed his view in a handwritten note as follows:

OCC [Office of Chief Counsel] doesn't have any legal objection to the proposed handling of this provided it is clear that PNL must follow up with a study proposal. It must be demonstrated that DOE is not suppressing this report, but merely redirecting the effort.²⁴

Attempts to Fund Followup Studies to the Burger Report

The cumulative effect of the notes described above was to suggest that the Burger Report was incomplete, speculative, and in need of followup studies before it could be cleared for publication. In apparent response to this suggestion, PNL prepared a June 1985 proposal for followup work. This or a similar proposal was sent to RHO in December 1985. A cover letter transmitting the proposal stated:

A proposal to evaluate the hazards was prepared in response to a DOE-RL request and is attached for your consideration. We would be glad to make the appropriate staff available at your convenience to discuss the matter.²⁵

These were not the first attempts to obtain funding for the followup work recommended in the Burger Report. In April 1984, after the report was essentially complete (though not yet in final form), DOE-RL approved \$50,000 for that purpose.²⁶ A week later, however, after a mid-year budget meeting, RHO shifted all but \$10,000 of these funds to another project.²⁷ The remaining \$10,000 was not sufficient to undertake the laboratory and sampling work recommended in the report.²⁸ Thus, when the Burger Report was disap-

proved for publication in 1985, the recommended followup work was neither complete nor in progress.

The 1984 withdrawal of funds for followup studies led to some consternation within the contractor organizations among the project's backers, but this was tempered by a realization that there was no immediate need for the studies as long as tank conditions remained stable. Moreover, because a tank sampling project was scheduled to commence that summer, at least one supporter of the ferrocyanide studies agreed that it made sense to wait for the results of the sampling and to proceed with the followup work on the basis of the new data.²⁹

The sampling project was delayed for more than a year, however, and when it finally began, ferrocyanides had been dropped from the list of substances to be sampled.³⁰ Some ferrocyanide sampling was finally undertaken in December 1988, after the issue was revived earlier that year.

Removal of Exothermic Reaction Project from the HWMTP

The prospects for conducting the followup studies recommended in the Burger Report suffered another blow when the exothermic reaction project was listed as "completed"--and therefore effectively "closed out"--in the December 1984 HWMTP.³¹ The project was again listed as "completed" in the September 1985 HWMTP.³² Listing of the project was dropped entirely from the 1986 and 1987 HWMTP's.³³ Thus, despite suggestions offered by DOE-RL (as expressed in notes accompanying the denial of clearance for the Burger Report) that followup studies be proposed, such proposals were made but were not funded and the entire project was closed out of the HWMTP.

Persistence of the Safety Issue

During this period when the ferrocyanide studies were being discontinued, DOE-RL and the contractor continued to evaluate plans for removing as much of the remaining liquid as possible and backfilling the tanks. As discussed earlier, these plans were part of the impetus for the Burger Report because such actions would change tank conditions and could elevate tank temperatures to the point where a ferrocyanide explosion was possible.³⁴

In January 1985, PNL initiated a test plan for RHO that would examine the suitability of using basalt as a backfill material in the SST's. This plan stated:

The reference plan for disposal of the single-shell tank wastes is on-site stabilization and isolation....RHO currently plans to demonstrate in-situ disposal of...single shell tank wastes by filling the tanks with basalt gravel (McKenny 1984). When Murthy et al. (1982) assessed in-situ disposal of single-shell tank wastes, they concluded that dome collapse was a credible accident which could result in a significant radiation dose to the public. To eliminate or mitigate the effects of dome

collapse, it was proposed that the tanks be filled with rock (Rouston 1983).³⁵

This study was finalized in October 1986 and concluded that basalt was not a good choice for the backfill material.³⁶ A September 1986 letter, transmitting the final draft report to RHO and requesting clearance for publication, reported that "additional experimental studies are required before a final domefill is selected."³⁷ Therefore, almost 3 years after the issue was "closed out" in the HWMTP and after funding was canceled for the recommended followup studies, DOE was continuing its SST stabilization program without resolving the associated ferrocyanide safety issue.

Treatment of the Issue in the 1987 EIS

A ferrocyanide explosion in an SST was treated as the worst-case accident in the 1987 EIS.³⁸ While conceding the possibility of such an explosion, the EIS stated that "the presence of [ferrocyanide] in quantities sufficient to produce a large explosion is still the subject of some debate," and that a "recent PNL report [the Martin Report] suggests that the [ferrocyanide] explosion is highly unlikely".³⁹

The EIS reference to the Martin Report was erroneous.⁴⁰ That report did not address the potential for ferrocyanide explosions. Instead, much of the data underlying the EIS discussion of ferrocyanide came from another PNL report.⁴¹ That report, in turn, relied on the Burger Report but, because of DOE-RL's denial of clearance, could not cite it.⁴² The erroneous reference to the Martin Report in the ferrocyanide section of the EIS was apparently an editorial mistake.⁴³ At least two persons in the contractor organizations noticed and pointed out the mistake during the draft stages of the EIS, but the error remained in the final version.⁴⁴

Rockwell resisted having to refer to a possible ferrocyanide explosion, even as a hypothetical worst-case accident in the EIS.⁴⁵ A PNL manager stated that it was included only after he "went to the mat" over the issue.⁴⁶

Renewed Attention to Ferrocyanide Issue in 1988

In 1988, several factors combined to focus renewed attention on the ferrocyanide/exothermic reaction issue. First, the December 1987 EIS had elicited public comments during its draft stage and was subjected to further public scrutiny after its publication. Some comments were directed toward the ferrocyanide section of the EIS.⁴⁷

Second, in early 1988, during the preparation of the SAR for the SST's, the ferrocyanide issue was brought up for discussion.⁴⁸ In order to address questions arising from these discussions and the EIS comments by mid-1988, Westinghouse Hanford Company (WHC), which had replaced RHO as the lead contractor at Hanford, had agreed to fund limited ferrocyanide studies, including a literature review and preliminary laboratory experiments. This work was completed between July and October of 1988.⁴⁹

Third, in late October 1988 a private citizen, who had previously worked at Hanford for the Nuclear Regulatory Commission (NRC), appeared before a local civic group and presented a critique of certain statements in the 1987 Hanford Defense Waste Environmental Impact Statement (EIS).⁵⁰ He astutely focused on the passage from the EIS that mentioned the potential for a ferrocyanide explosion as "still a subject of some debate."⁵¹ He also noted that the EIS reference to the Martin Report was erroneous:

EIS CONFUSES ISSUE--However, not to purposely confuse the reviewers of the EIS I am sure, the referenced PNL (1985) report, PNL 5453, DOES address the likelihood of an ammonium nitrate explosion, but DOES NOT mention the possibility of a ferro/ferric cyanide explosion.⁵²

Public attention to the error, however, triggered a series of events culminating in the "rediscovery" of the Burger Report by DOE-RL and the eventual public release of that document. This occurred after the former NRC employee's critique was processed through DOE-RL's Employee Concerns Program, which prompted a joint PNL-WHC inquiry into the history and status of the ferrocyanide issue.⁵³ The inquiry confirmed that the EIS reference to the Martin Report was in error. With respect to the Burger Report, the PNL-WHC team stated: "The report [was] disapproved by DOE-RL in May 1985. The reason for disapproval given to the author [was] that the studies were incomplete and therefore questions were left unanswered."⁵⁴

This focused attention on the ferrocyanide issue and resulted in the prioritization of the followup studies recommended in the Burger Report, with a timetable set for their completion.

Whatever the exact reasons for the 1988 revival of the ferrocyanide issue, the October 1988 critique by the former NRC employee appears to have ensured that the issue would receive a high priority. The ferrocyanide issue was restored to the HWMTP in December 1988.⁵⁵

1989 Release of the Burger Report

Following the concerns raised in 1988 and the internal investigation they prompted, DOE-RL requested that the contractors coordinate their efforts "in updating and issuing [the Burger Report]."⁵⁶ A reply from WHC stated:

Because of its speculative nature, PNL-5441 [the Burger Report] was not originally cleared and released. It will be revised to include the results from the investigations recommended in [a November 1988 letter from WHC to DOE-RL].⁵⁷

In January 1989 at DOE-RL's request, WHC submitted a plan to "revise and issue" the Burger Report by February 1990.⁵⁸ The plan called for completing laboratory work and analyses before releasing the Burger Report, which was rechristened a "draft," apparently reflecting DOE-RL's and WHC's position that the report had not been cleared in 1985 because it was "incomplete" or "speculative."⁵⁹ By the spring of 1989, however, the State of Washington's

Department of Ecology had become aware of the report's existence and had requested a copy.⁶⁰ Faced with a specific request, DOE-RL accelerated the clearance process and provided Washington State officials with a copy of the Burger Report in the summer of 1989.⁶¹

A congressional committee and the news media obtained copies of the report soon thereafter, and in October 1989, news articles appeared about the ferrocyanide issue. DOE-RL's earlier disapproval of the Burger Report was prominently featured in these articles.⁶²

DOE-RL Response to 1989 Publicity Concerning the Ferrocyanide Issue

The release of the Burger Report and the attendant publicity about possible ferrocyanide explosions generated numerous requests for information directed toward DOE-RL from governmental and news media organizations.⁶³ In response, DOE-RL informally made inquiries about the history of the issue and focused more attention and resources on current studies of ferrocyanide in the tanks.⁶⁴ (As discussed earlier in this Report, the result of one such study was identification of a hydrogen explosion in the double-shell tanks, rather than a ferrocyanide explosion in the SST's, as the greatest potential hazard.)

A key issue arising from the news media and governmental inquiries was DOE-RL's reason for disapproving the Burger Report in 1985. Initial statements by DOE-RL staff were that the Burger Report had failed peer review and had been refuted by a 1985 report.⁶⁵ In a letter to a U.S. Senate committee, the DOE-RL Manager conceded that this statement was incorrect. He stated that the Burger Report "was not made public until recently, in part because of expectations that additional studies would verify that the conditions necessary for explosion were neither present nor expected during interim storage."⁶⁶

The pressure from outside sources focused additional managerial attention on both the history and current status of the ferrocyanide issue. In December 1989, DOE-RL requested that WHC do a probabilistic risk assessment on the ferrocyanide issue, with the deadline set for January 16, 1990.⁶⁷ In February 1990, DOE-RL requested a detailed schedule for revising and updating the Burger Report;⁶⁸ the schedule was ready on March 17.

As the events of 1988 and 1989 demonstrate, the former NRC employee's critique and other external pressures were not the sole reasons for the revival of ferrocyanide studies in SST's. Public pressure did, however, provide the impetus for reexamining the Burger Report, and this pressure ensured a thorough consideration of the recommendations made in that report.

Current Status of Ferrocyanide Studies

At the request of DOE-RL, WHC and PNL have prepared a detailed plan to close the ferrocyanide issue.⁶⁹ This plan, which consists of approximately 50 tasks and subtasks keyed to a timetable extending into 1991, includes explosives testing, energetics work, and analysis of tank contents.⁷⁰ The work was planned for completion by February 1991 but has been delayed.⁷¹

Finding III(1): The NS team believes the evidence indicates that the ferrocyanide issue was revived more in reaction to external events than as a result of an orderly closing out of an unresolved safety concern.

- o Although the evidence found by the NS team did not warrant a finding that DOE-RL personnel intended to suppress the information in the Burger Report, their handling of the report itself and their overall management of the ferrocyanide issue from 1985 to 1990 helped to create the appearance of a cover-up. The key actions and circumstances contributing to this appearance are discussed under the findings below.

Finding III(2): In 1985 DOE-RL disapproved the release of the Burger Report for further dissemination, ostensibly because it required followup work. Yet when PNL requested funding for such work none was provided.

- o In recommending that the clearance request for the Burger Report be disapproved, DOE-RL's EIS Program Manager acknowledged that the "safety significance" of the issue raised in the report "must be considered by Rockwell/PNL."⁷² He recommended that the contractors "develop a [research and development] plan" to address the issue and stated: "We should assure ourselves that this issue is visibly tracked by contractors and [DOE-]RL."⁷³

The Waste Management Division Director agreed, stating that PNL "should propose the work necessary to evaluate the potential."⁷⁴ He further stated that he did not want to "hide" the ferrocyanide issue but wanted to "channel it in a direction to resolve the questions not just raise them."⁷⁵ A similar recommendation was made by DOE-RL's Chief Counsel when the EIS Program Manager took the unusual step of consulting him about the possible appearance of a cover-up if the report were denied clearance.⁷⁶ The Chief Counsel's reply stressed that it must be "clear that PNL must follow up with a study proposal."⁷⁷ He added: "It must be demonstrated that DOE is not suppressing this report, but merely redirecting the effort."⁷⁸

These comments implied that the Burger Report consisted of unsupported speculations and that no plan existed to conduct the technical analyses required to evaluate the actual risks posed by ferrocyanides in the SST's. In fact, the Burger Report contained recommendations that followup analyses be performed, and these recommendations became the focal points for the ferrocyanide studies that were eventually funded, beginning in 1988, and that are still in progress.⁷⁹ Additionally, more than a year prior to the 1985 DOE-RL disapproval, PNL had submitted a formal proposal to conduct the kinds of followup technical studies recommended in the Burger Report. As noted earlier, the proposal was initially funded in April 1984, but most of the funding was withdrawn a few weeks later in order to fund another project. Thus, PNL had already attempted to do what DOE officials suggested needed to be done before the Burger Report could be cleared for publication.

- o Nevertheless, in response to the DOE-RL suggestions, PNL prepared new proposals to conduct the followup studies called for in the report.⁸⁰ These proposals were never funded.⁸¹

Extensive interviewing and document searches failed to establish why the proposals went unfunded. By itself, the denial of funding to a particular project is unremarkable--other projects might legitimately have been given a higher priority. However, because DOE-RL personnel used the need for followup studies as a reason to disapprove the Burger Report and urged that the issue be "visibly tracked," the later denial of funding for reasons that were not highly visible contributed to the appearance of irregularity in DOE-RL's management of the issue. As discussed below, other events and circumstances enhanced this appearance.

Finding III(3): Both prior to and after DOE-RL's disapproval, the ferrocyanide issue was erroneously listed as "complete" in the Hanford Waste Management Technology Plan, indicating that no additional funding was intended.

- o Just as important as the lack of funding for the followup studies was the absence of any "visible tracking" of the issue by DOE-RL and the contractors, as recommended by the EIS Program Manager when he denied the clearance request. The Hanford Waste Management Technology Plan was designed to be a mechanism for such tracking. Inclusion in the HWMTTP was supposed to ensure that an issue would be monitored until it was satisfactorily resolved.⁸² The exothermic reaction/ferrocyanide issue, which included the Burger and Martin studies, had been in the December 1983 and April 1984 HWMTTP's but was inexplicably listed as "completed" in the December 1984 HWMTTP.⁸³ The Burger and Martin Reports had in fact been completed by that time (although the Martin Report was not finalized until 1985), but the followup laboratory work and other analyses recommended in the Burger Report, which were contemplated when the issue was first put in the HWMTTP, had not been done because of lack of funding.⁸⁴
- o Although it could not be determined who made the specific decision to close out the ferrocyanide issue, the evidence indicated that no item was listed as "completed" or otherwise closed out of the HWMTTP without DOE-RL knowledge and approval.⁸⁵ Thus, DOE-RL's disapproval of the Burger Report in May 1985, ostensibly because it needed followup work and "visible tracking," occurred after DOE-RL and the contractor had already denied funding for the work and removed the issue from the most obvious tracking mechanism, the HWMTTP.
- o This apparent mistake was compounded when, after the May 1985 disapproval of the Burger Report, the September 1985 HWMTTP contained an identical listing of "completed" next to a listing of the issue.⁸⁶ Thereafter, the issue disappeared from the HWMTTP altogether, until some ferrocyanide studies reappeared in it in December 1988.⁸⁷

Finding III(4): When the Burger Report was disapproved in 1985, DOE-RL's Chief Counsel advised DOE-RL managers to ensure that steps were taken to make it clear that DOE-RL was not "suppressing" the report but was merely "redirecting the effort." Instead of being "redirected," however, the issue was apparently dropped until 1988.

- o As noted above, DOE-RL and the contractor had already "redirected" the ferrocyanide issue in 1984 (before DOE-RL disapproved the Burger Report) by withdrawing funding that was for intended followup studies and by closing the issue out of the HWMTF. The only way to "redirect" it again in 1985 would have been to reverse these decisions, and that was not done.
- o In addition to the repetition of the "completed" entry in the September 1985 HWMTF and the absence of any reference to the ferrocyanide studies in later editions of the HWMTF, PNL's requests for funding--which had been prepared in response to DOE-RL suggestions--went unheeded and were apparently not "tracked" by DOE-RL. Moreover, ferrocyanide was removed from the list of substances to be sampled in the SST's.⁸⁸ Awaiting the results of such sampling had earlier been advanced as a reason to delay the followup studies recommended in the Burger Report.⁸⁹
- o In a note dated May 18, 1985, recommending disapproval of the Burger Report, the EIS Program Manager wrote that the draft EIS "considers a similar explosion scenario."⁹⁰ When interviewed by a member of the NS team, he suggested that a reason for disapproving the report might have been that the ferrocyanide issue was being handled in a more rigorous manner as part of the EIS process.⁹¹ The evidence, however, does not support the conclusion that the ferrocyanide studies were in any meaningful sense "redirected" into the EIS. On the contrary, the authors of the ferrocyanide section of the EIS and the PNL report (which provided key data underlying that section) relied on the Burger Report's data but could not cite the report itself because of DOE-RL's refusal to clear it.⁹² No followup studies to the Burger Report were conducted during the preparation of the EIS; indeed, that document's discussion of the conditions that could potentially cause a ferrocyanide explosion was far less detailed than that of the Burger Report.⁹³

Finding III(5): The NS team believes the evidence indicates that the ferrocyanide issue was revived, funded, and elevated in priority in 1988 and 1989, principally in reaction to external pressures.

- o The followup studies recommended in the Burger Report were eventually funded. The actual work started in 1988. These studies were elevated in priority as a result of publicity and official inquiries that accompanied the release of the Burger Report in 1989.

The revival of this issue, and the provision of sufficient resources and management attention to resolve it, occurred principally in reaction to external pressures and events, not as a result of the "visible tracking" or "redirection of efforts" envisioned in the comments accompanying DOE-RL's 1985 disapproval of the Burger Report.

Finding III(6): The NS team believes the evidence indicates that the actual reason for DOE-RL's May 1985 disapproval of the request to clear the Burger Report was concern about the public relations impact of the report's discussion of the potential for a ferrocyanide explosion.

- o When interviewed by the NS team, both the EIS Program Manager and the Manager of the Waste Management Division, the principal DOE-RL managers involved in the decision to disapprove the report, stated that they could not recall the decision itself or the reasons for it.⁹⁴ On the basis of his review of the pertinent documents, however, the division manager acknowledged that the Burger Report was not technically flawed but that, in his opinion, it could have been misinterpreted if made public.⁹⁵ This is consistent with the recollection of a former RHO and WHC employee who reviewed the Burger Report during the 1984-1985 DOE-RL clearance process. She recalled that there was a concern that the public would be alarmed by the worst-case scenario discussed in the report.⁹⁶

Excerpts from the notes written at the time support the conclusion that public relations considerations, not technical deficiencies, were behind the report's disapproval. The DOE Division Manager wrote that "to publish an open report which speculates on such an explosion without any real basis is to invite misuse of the data and concept."⁹⁷ The EIS Program Manager stated cryptically: "I believe PNL should have handled this smoother [sic]."⁹⁸ And the PNL manager, who agreed with the position taken by the EIS Program Manager, asked the rhetorical question: "Do we report things openly just for the sake of science?"⁹⁹

- o Moreover, the public relations sensitivity of the report was revealed by repeated denials in the handwritten notes of an intention to "hide" or "suppress" anything and by the EIS Program Manager's visit to DOE-RL's Chief Counsel to discuss his concern about the appearance of a cover-up.

Finding III(7): In response to governmental and media inquiries about the Burger Report, DOE-RL and the contractor provided inaccurate and misleading information concerning the reasons for its disapproval in 1985.

- o When the reasons for the Burger Report's disapproval became an issue, beginning in late 1988 after the public critique of the EIS's treatment of a ferrocyanide explosion, DOE-RL requested that the contractor investigate and provide a response.¹⁰⁰ That response, which was based upon a cursory investigation that did not include interviews of the DOE principals or examination of the contemporaneous notes made in connection with the disapproval,¹⁰¹ stated that the "reason for disapproval [of the Burger Report] given to the author is that the studies were incomplete and therefore questions were left unanswered."¹⁰² This suggested that a technical deficiency, rather than public relations considerations, was the principal reason for the report's disapproval. Moreover, the suggestion that the report was "incomplete" ignored the fact that DOE-RL and the contractor withdrew funding, removed the issue

from the HWMTP, and failed to carry out the followup actions recommended in the report.

- o The theme that the Burger Report was "incomplete" or "speculative" was repeated in later DOE-RL and contractor statements, especially after the report was made public in 1989. A 1989 DOE-RL press statement, for example, contained the inaccurate statement that the Burger Report had been disapproved because it had failed peer review and was contradicted by a later report. In a letter to a committee member of the U.S. Senate staff, the DOE-RL Manager corrected this error. In doing so, however, he again put forward the "incomplete" rationale for the report's disapproval, which does not accord with the available evidence.¹⁰³

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6. Interview with H. Van Tuyl, Pacific Northwest Laboratories, by H. Anderson and T. Heitman, U.S. Department of Energy, Office of Nuclear Safety, 26 April 1990; interview with L. Morgan, Pacific Northwest Laboratories, by T. Heitman, U.S. Department of Energy, Office of Nuclear Safety, 11 April 1990.
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20. M. Shupe, internal handwritten note to J. White, U.S. Department of Energy, Richland Operations Office, 18 May 1985.
21. J. White, U.S. Department of Energy, Richland Operations Office, handwritten note to J. McElroy, Pacific Northwest Laboratories, undated.
22. J. McElroy, internal handwritten note to R. Liikala, Pacific Northwest Laboratories, 29 May 1985.
23. Interview with E. Pride, U.S. Department of Energy, Richland Operations Office, by H. Anderson and T. Heitman, U.S. Department of Energy, Office of Nuclear Safety, 24 April 1990.
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26. P. Rasmussen, U.S. Department of Energy, letter enclosing Class I change package CIN-5130 to General Manager, Rockwell Hanford Operations, 24 April 1984.
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29. Telephone interview with G. Beitel, formerly of Rockwell Hanford Operations, by H. Anderson, J. Fitzgerald, and T. Heitman, U.S. Department of Energy, Office of Nuclear Safety, 12 April 1990; Van Tuyl interview, 26 April 1990.
30. Van Tuyl interview, 26 April 1990; Schulz interview, 20 April 1990; Hanson to Wojtasek, 23 December 1985.
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32. HWMTP, September 1985.

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99. McElroy to R. Liikala, 29 May 1985.
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101. Mihalik interview, May 1990; White interview, May 1990; Shupe interview, April 1990.
102. Wodrich to Gerton, 22 November 1990.
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82. Interview with M. Kupfer, Westinghouse Hanford Company, by H. Anderson, U.S. Department of Energy, Office of Nuclear Safety, 2 May 1990; Zinsli interview, 9 May 1990; Van Tuyl interview, 26 April 1990.
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IV. RISK COMMUNICATION

Because the NS investigation was in part prompted by concerns about the reliability and candor of DOE-RL and contractor statements concerning the risks posed by slurry growth and exothermic reactions, the NS team examined these statements and compared them to findings resulting from the investigation. In so doing, the team attempted to evaluate DOE-RL and contractor statements within their proper context, recognizing that the persons who made them did not have the benefit of the in-depth factual record developed during the NS investigation. Even with this understanding, however, the team found preventable deficiencies in DOE-RL and contractor risk communications. These findings are discussed below.

The hazards associated with slurry growth in double-shell tanks (DST's) and potential exothermic reactions in single-shell tanks (SST's) were communicated in a variety of ways within the contractor organizations, from the contractors to the Department of Energy's Richland Operations Office (DOE-RL), and ultimately from DOE-RL to DOE Headquarters, Washington State officials, the news media, external oversight groups, and the general public. The NS team examined the accuracy, completeness, and timeliness of these communications. Although the team focused on communications relating to slurry growth and exothermic reactions, the findings have general implications for DOE-RL's overall management of information concerning safety issues.

The findings set forth below are organized to reflect three areas of analysis: first, the extent to which the contractor provided DOE-RL with accurate, complete, and timely information; second, the adequacy of DOE-RL's investigation of safety issues prior to briefing the public or external agencies; and third, the accuracy, completeness, and candor of DOE-RL briefings.

Finding IV(1): The contractor failed to transmit significant information to DOE-RL regarding the potential hazards associated with slurry growth in double-shell tanks.

- o On July 19, 1988, the acting head of Tank Farm Process Engineering asked an engineer to conduct a review of files pertaining to slurry growth in tank 101-SY.¹ The engineer responded on September 7 with a nine-page memorandum, plus charts and a photograph.² The memorandum identified four principal safety concerns associated with slurry growth and trapped gases in tank 101-SY: (1) hydrogen flammability and detonation; (2) tank level in excess of specifications; (3) overpressurization of tank vapor space, with the potential for subsequent contamination spread to the environment and personnel; and (4) ammonia releases potentially above threshold limits at the stack.³

The WHC engineer stated that tank 101-SY "has been studied long enough and characterized enough to be able to justify taking action to correct the gas generation problem now, if the risk warrants the cost of doing so."⁴ In the remainder of his memorandum, he analyzed the potential hazards and proposed steps to address each one of them.

On the basis of his analysis of data covering the previous 5-year period, he stated that "in all likelihood, portions of the vapor space go above the 4 percent flammability limit [for hydrogen]; further, it is likely that, at some point, the whole vapor space could go above 4 percent."⁵ He summarized with the statement that "this is an identified hazard that should not be left unattended."⁶

The engineer also discussed the pressurization events that were occurring in tank 101-SY, concluding as follows:

Given enough pressure and time, discharge of the tank gas and radionuclides into the environment and subsequent contamination spread is inevitable....It is obvious to most observers...that it is just a matter of time until a burp contaminates the area. The attendant publicity and cleanup combined with our eight-year advance notice may prove embarrassing. [Emphasis added.]⁷

He also pointed out the potential risks to workers at the site, analyzed the potential effects of ammonia production within the waste, and outlined a series of recommended corrective actions to ameliorate the risks. Concerning these proposed actions, he stated that "taking no corrective action to at best control the symptoms is not defensible in view of the risks."⁸

- o The September 7 memorandum was circulated within WHC, and one of the engineer's colleagues made the following comment:

I suggest that the distribution [of the memorandum] be broadened--the more champions you can get into your corner, the more likely this work will go forward. I agree with [you that] WHC is at risk on this problem that we have recognized for a long time. [Emphasis added.]⁹

- o The September 7 memorandum was reissued on October 25, 1988, with essentially the same content, except that the passage about the possible embarrassment to the corporation that might result from a contamination incident was deleted.¹⁰ The revised memorandum was circulated widely within WHC. It was formally distributed to eight persons in the WHC Waste Management Division,¹¹ but interviews conducted by the NS team revealed that many others also reviewed it.¹²

One such WHC official was the Manager of Defense Waste Engineering.¹³ He did not advise DOE-RL of the report's conclusions, and when

interviewed, he could not recall whether he had discussed them with his supervisor, the WHC Manager of the Defense Waste Management Division.¹⁴ The latter, however, was unequivocal in his denial that he had ever seen the report, contending that he would have taken immediate corrective actions if he had been aware of it.¹⁵

- o Regardless of the level of knowledge concerning the report within WHC's management ranks, the evidence indicates that DOE-RL personnel did not receive a copy of the report, nor were they otherwise briefed on its conclusions, until after the slurry growth issue became widely publicized in March 1990. When the DOE-RL manager was shown a copy of the report for the first time, he indicated that had he been aware of its conclusions earlier, he too would have directed that corrective actions be taken earlier.¹⁶

By failing to make DOE-RL personnel aware of the contents of the 1988 memorandum until external events forced its disclosure, the contractor deprived DOE-RL and DOE Headquarters of significant information about risks associated with tank farm operations. Apart from the specific technical analyses contained in the document, its tone and conclusions emphasized both the serious consequences that could result from slurry growth and the fact that the contractor did not have the phenomenon under control and needed to take corrective action. These facts were in direct contradiction to the prevailing impression among DOE-RL personnel that slurry growth presented no safety hazards and that the situation was being adequately handled by the contractor.

- o Another instance of the contractor's failure to transmit significant information to DOE occurred in the fall of 1989, approximately a year after the 1988 memorandum. In late October 1989, Westinghouse initiated a "detailed review of organic materials decomposition and potential for gas pocket generation," as well as a study of the "potential for explosive vapors in DST's."¹⁷ The resulting issue papers, along with other issue papers, were transmitted in January 1990 to Westinghouse engineers at the Savannah River site for their review--but not before references to the 1988 memorandum and other internal WHC documents on 101-SY were deleted.

A Westinghouse Savannah River Company representative informed the WHC Manager of Waste Management Engineering on February 6, 1990, of the significance that Savannah River reviewers attached to the flammability of slurry growth gases in the presence of an oxidizer in tank 101-SY. A WHC engineer assigned to get more details from Savannah River did not attempt to contact the Savannah River reviewers until February 9 and actually failed to speak to anyone there until February 12. After learning the bases of the Savannah River concerns, the WHC engineer spent several days attending a training course and did not brief the Manager of Waste Management Engineering on what he had learned until February 27--2 weeks later. Yet another week passed before a briefing was arranged for upper WHC management. Meanwhile, the WHC Manager of Waste Management Engineering failed to mention the issue to the Advisory Committee on Nuclear Facility Safety at a meeting held on February 8, to

members of a State investigation team, or to DOE-RL staff with whom he spoke prior to March 6.

Finding IV(2): DOE-RL based some public statements and briefings on inadequate investigation of the facts.

- o Although the contractor did not always provide accurate and timely information to DOE-RL about the safety issues associated with slurry growth, the information it did provide should have alerted DOE-RL personnel to the significance of the issues. Because DOE-RL failed to recognize the situation promptly and because an adequate investigation of the slurry growth phenomenon was delayed, the information conveyed to the public in hastily prepared briefings and statements contained inaccuracies and distortions.
- o The NS team recognizes that it was not always possible to delay public briefings until all facts relating to a given issue were known. In some cases, however, DOE-RL and WHC apparently were unaware of certain facts only because they failed to investigate the matter sufficiently.
 - As detailed elsewhere in this Report, the WHC briefing of DOE-RL lower and middle level managers on March 6, 1990, should have triggered a thorough reexamination of the safety implications of the slurry growth phenomenon. Instead, the DOE-RL officials in attendance kept the information to themselves, so that the DOE-RL Manager was not made aware of the contents of the March 6 briefing until more than 2 weeks later.
 - As detailed in the section on exothermic reactions, inaccurate public statements were made concerning the reasons for DOE-RL's disapproval of the 1984 Burger Report. Although the DOE-RL Manager corrected these misstatements, he did so on the basis of a cursory investigation of the facts. As a result, his correction was itself incomplete and misleading.

Finding IV(3): DOE-RL and the contractor provided inaccurate and misleading information to the news media and other external groups.

- o The provision of inaccurate and misleading information about slurry growth ranged from minor misstatements of little consequence to statements capable of seriously misleading the public about the nature of the hazards involved. Among the relatively minor inaccuracies, for example, was the statement made on March 22, 1990, during a presentation to the Defense Nuclear Facilities Safety Board, that the "tank vapor space pressure first increased above atmospheric from [the] July 4, 1983, gas release event."¹⁸ Contrary to this statement, the first overpressurization event at tank 101-SY occurred in January 1983.¹⁹

Another statement made as part of the same briefing advised that the contractor had implemented a lancing operation in September 1984 in an effort to control slurry growth. Lancing was actually initiated in October 1983.²⁰

- o These inaccuracies, however, were less responsible for misrepresenting the hazards posed by slurry growth than were others that, although they may have been technically true, omitted important information. Note, for example, the March 1990 DOE-RL presentation to the Defense Nuclear Facilities Safety Board (DNFSB) indicating that since 1981, tank 101-SY had experienced a 3-9 inch rise of the crusted surface over about a 3-month period.²¹ DOE-RL failed to point out, however, that the level had risen 9 percent since 1980 and that the upward trend continued through early 1989. WHC had projected in late 1988 that if this trend continued unabated, by 1993 waste levels would routinely exceed tank operating limits. Similarly misleading data indicated that three gas releases were monitored for hydrogen in 1985.²² In fact, five releases were monitored, and two were not recorded because operations personnel failed to follow proper procedures.

At the March 1990 briefing of the DNFSB, it was also stated that the lancing operations conducted between 1984 and 1988 were not very successful. What went unsaid was that lancing continued for more than 4 years after contractor personnel had concluded that lancing was ineffective. Yet another example of statements that were factually correct, but left out important data on the nature and extent of the hydrogen gas phenomenon in tank 101-SY, was the observation that "laboratory slurry growth estimates of hydrogen in gases released ranged from 4.8 percent to 21.1 percent." In fact, estimates of hydrogen levels based on laboratory studies were significantly lower than later estimates based on calculations that assumed gases were generated near the bottom of the tank. When conservative assumptions were applied to the same results, the 4.8-percent estimate of hydrogen concentration based on laboratory studies was calculated to be 34 percent.

- o Both WHC and DOE-RL officials made other statements to the press that underestimated potential hazards and reflected an inaccurate view of the potential dangers posed by slurry growth and potential exothermic reactions in the waste tanks. For example, a DOE spokesman was quoted as drawing a questionable comparison between tank wastes and flour: "To say that [wastes] can explode is as useful as saying the flour in the kitchen can explode, which it can under the right conditions."²⁴

Although not intentionally inaccurate, such statements had the potential to mislead the public about the nature of the potential hazards and the circumstances under which these risks were discovered.

Finding IV(4): In its statements and briefings to external groups and the public concerning the safety issues discussed in this Report, DOE-RL sometimes failed to make clear what was known, what was not known, and what was uncertain.

- o DOE-RL's handling of information concerning potential exothermic reactions in SST's, particularly the 1984 Burger Report, provides examples of DOE-RL's management of uncertain or incomplete data.

Statements to the press and oversight groups were characteristically upbeat.

- A Seattle Post Intelligencer article dated October 24, 1989, stated that the Director of the Washington State Department of Ecology complained that the DOE-RL Manager had assured her that tank temperatures were being monitored. She is quoted as having said, "I took that to mean, frankly, that temperatures were being monitored in every tank, not just four out of 22."²⁵ She recommended that Governor Booth Gardner commence a full State investigation of the matter.²⁶
 - A DOE spokesman stated that "constant monitoring ensures the safety of the tank material."²⁷ This is another example of how the false impression that temperature monitoring at the tank farms was frequent, complete, and accurate was encouraged. In fact, temperatures for only 4 SST's were being monitored on a monthly basis; the remaining 18 SST's in question were monitored every 6 months.
 - In fact, thermocouples in many tanks were either defectively calibrated or inoperable. In some tanks, where thermocouples were operating properly, temperatures were being monitored only twice per year.²⁸
- o Another example of a statement capable of creating a misleading impression occurred during an October 1989 meeting with a representative of the Washington State Department of Ecology. WHC's Manager of Defense Waste Engineering stated that "operating conditions...do not allow the presence of these explosives [including ammonium nitrate] in the tanks."²⁹ In view of the facts that ammonium nitrate was known to have accumulated in the riser of one single-shell tank and that waste characterization studies had not been done on several tanks, such a statement could not be supported.³⁰
- o An October 1989 article reported in the Seattle Times attributed similar categorical statements to DOE that were technically inaccurate:
- In hearings early this year about a multibillion-dollar cleanup of Hanford, the Energy Department wrote that "there is little hazard" and the presence of certain chemicals does not pose a hazard under the current tank operating conditions. The potential...to form explosive substances is nonexistent.³¹

This last sentence is false. It is well documented that some of the waste tanks at Hanford contain substances that are potentially explosive. More important, however, is the implication that sufficient information existed to support such a categorical statement. In fact, as discussed elsewhere in this Report, studies to address this very issue are only now being completed.

- o A presentation by an RHO senior chemist at the "Waste Management '85" conference provides yet another example of how public discussion of safety issues was conducted in a manner that could have created a misleading impression. In January 1985, RHO measured hydrogen concentrations in tank 101-SY exceeding 4 percent, the lower flammability limit in air. Throughout 1985, RHO conducted various studies to find a method to resolve the hydrogen problem. These studies and subsequent efforts failed to achieve that goal. Nonetheless, at the conference referred to above, the chemist offered the following assessment:

Slurry growth, although not completely eliminated, is being safely and effectively controlled, ...the parameters affecting slurry growth have been defined, and predictive equations have been established.³²

As has been pointed out previously in this Report, there was no justification for such a blanket assurance. In reality, the slurry growth phenomenon was not well understood and was not under control. Inexplicably, the RHO presentation at the Waste Management '85 conference received prior review and approval from DOE-RL as well as RHO and its senior management.³³

NOTES

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5. Ibid.
6. Ibid.
7. Ibid.
8. Ibid.
9. K. Carothers, internal handwritten note to G. Dunford, Westinghouse Hanford Company, undated (September? 1988).
10. K. Fein, "Tank 101-SY Slurry Growth," internal note to D. Baide, Westinghouse Hanford Company, 25 October 1988, p. 3.
11. Ibid., p. 1.
12. Interview with D. Wodrich, Westinghouse Hanford Company, by S. Blush, U.S. Department of Energy, Office of Nuclear Safety, May 1990; interview with K. Carothers, Westinghouse Hanford Company, by S. Blush, U.S. Department of Energy, Office of Nuclear Safety, May 1990.
13. Wodrich interview, May 1990.
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29. D. Wodrich, "Single Shell Tank Waste Stability," visual presentation package, Westinghouse Hanford Company, 16 October 1989.
30. Westinghouse Hanford Company, "Single Shell Tank Waste Stability," visual presentation package for presentation to Washington State Nuclear Waste Board, 26 October 1989.
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33. Interview with M. Jansky, Westinghouse Hanford Company, by D. Hagerty, U.S. Department of Energy, Office of Nuclear Safety, 24 May 1990.

V. CONDUCT OF TANK FARM OPERATIONS

Background

Operations activities should recognize that safety, the environment, and productivity are compatible goals. To achieve these goals, DOE facility operations must be formally implemented and controlled. Experience has shown that the better operating facilities have well-defined, effectively administered policies and programs to govern the conduct of operations. Effective control of operating activities is primarily achieved by establishing operating standards, communicating operating standards to the working level, ensuring that personnel are well trained, monitoring performance in operations closely, and holding workers and their supervisors accountable for their performance.

Operations

Overall responsibility for operation of the SY Tank Farm is assigned to the Tank Farm Surveillance and Operations Department. Within this department, Tank Farm Processing Operations is responsible for the following tasks: (1) receipt of waste transfers into the tank farm facilities, (2) shift coverage for the tank farms, (3) collection of surveillance data from waste storage tanks, (4) control and operations of the Computer Automated Surveillance System, and (5) surveillance of tank farm processing facilities. Tank Farm Services is responsible for providing support for radioactive waste storage and disposal, for contamination control operations, and for maintenance operations. The tank farm facility is manned 5 days per week, from 8 a.m. to 4 p.m. Off-shift coverage is provided by the Computer Automated Surveillance System and by centrally located operations personnel. Although the day-shift operations supervisor is responsible for activities within the SY Tank Farm, in fact several different organizations exercise control over specific activities, including health physics, maintenance, and process engineering.

Finding V(1): The SY Tank Farm does not have a well-integrated, central organization in which one individual is responsible for establishing work priorities and allocating resources. This shortcoming has resulted in conflicting requirements among different groups who control activities at the site and in the diminution of the authority of the facility's central Control Room.

- o During its inspections, the NS team found that operations personnel were not fully cognizant of the reason for each alarm condition within the Control Room. In addition, some alarm annunciator window light bulbs

were inoperable, effectively rendering the annunciator itself inoperable.

- o Logsheets in the 242-S Evaporator Control Room, where many of the alarms for the SY Tank Farm are monitored, were incomplete. It could not be determined from the logs whether an alarm was valid or invalid, whether corrective action was required, or whether such action had been undertaken to correct the deficiency.
- o Several strip charts for active equipment had been out of paper for several weeks.
- o It was unclear which instruments on the control board were abandoned in place and which were operable. Furthermore, it was not clear whether instruments judged to be operable were properly calibrated.
- o The area behind the control board was extremely cluttered with loose wiring, miscellaneous instruments, and equipment in various stages of disassembly. Additionally, significant quantities of dust and dirt were evident in and around electrical devices.

Audits and appraisals of the tank farms have been conducted on a regular basis for several years. These evaluations have included quality assurance, safety, and program appraisals, both internal and external. They have identified significant deficiencies in material conditions and programs in all areas of the Hanford Tank Farm. Many deficiencies have been repeatedly identified.

Finding V(2): Weaknesses in tank farm operations identified by past audits and appraisals still exist, particularly with respect to the inoperability and overall poor condition of monitoring systems.

- o In some cases, important plant equipment, including some safety equipment, is not reliably maintained; in other cases, the equipment's ability to perform its function is indeterminable.¹
- o Equipment performance cannot be assured due to inadequate procedural controls and manpower for maintenance and calibration activities.²
- o The calibration and preventive maintenance programs are inadequately implemented. Inoperable instruments are frequently not repaired within the calibration interval.³
- o Inaccurate readings and erroneous alarms from the exhaust stack monitors, liquid level monitors, and radiation level monitors may occur due to the equipment's exposure to weather.⁴

In order to mitigate the effects of gas formation and subsequent pressurization in tank 101-SY, tank farm personnel have conducted in-tank operations under the direction of Tank Farm Engineering, including tank sampling, lancing, and photographic observations. The only sampling of waste since tank 101-SY was filled, however, was conducted in connection with a study of corrosion. Lancing operations were conducted to break the waste crust and

provide a vent path for gases to escape, and photographic observations were conducted to determine the profile of the crust and to assess the effectiveness of lancing operations.

Two different sampling methods were used to obtain samples of the tank's contents. The first method involved a weighted (11 pound) "bottle-and-string" sampler, designed to sink through the viscous slurry to a desired depth. Once at the desired level, a string attached to a cork stopper on the sample bottle would be pulled, allowing the bottle to fill. In an effort to accommodate the presence of the solid crust, this sampling method was modified by adding a second 11-pound weight to the bottle and string. This modification proved unsuccessful, even after repeated attempts.

The currently approved method for tank sampling involves positioning a truck-mounted drill over the tank. As the drill is lowered into the tank, it is pushed or rotated into the waste, where it obtains a waste sample 1 inch in diameter and 19 inches long. This method or a similar one was used to obtain the 1985 samples.

Different lancing methods were used to create vent paths for accumulated gases. Theoretically, lancing creates eddies within the slurry, which in turn create pathways and allow trapped gases to escape. Early lancing operations involved inserting a portable lance (a 50-foot steel tube) through one of the tank's conduit "risers." Once inserted into the tank and prior to penetrating the crust, the portable lance was pressurized with water and forced through the crust to a specific depth. Routine lancing operations led to the installation of three permanent lances, each set at different depths. Water was initially used as the primary medium for tank lancing. Concern over how adding water might affect the waste level of the tank, however, forced operations staff to switch to air as a lancing medium. Air lancing was continued until 1989, when (5 years after it began) lancing of all kinds was determined to be counterproductive.

In-tank photographs were taken on several occasions to help determine the profile of the crust and to assess the effectiveness of lancing operations. Photographs were obtained by opening a riser on the tank above the area to be photographed and lowering a remote-controlled camera and flash into the tank.

Finding V(3): Operating procedures for the tank farms do not contain "notes" or "cautions" warning operators about gas generation within individual tanks and the potential safety implications.

- o The only safety precautions undertaken during in-tank operations were those designed to prevent the spread of contamination resulting from physical contact with waste.
- o Overpressurization of the tank vapor space, with subsequent contamination of the environment and potential radiation exposure of personnel, was not satisfactorily addressed by plant management. When the pressure in 101-SY exceeds "0" inch water gauge, the normal downward flow of air through vents, drains, and plugs is reversed. Given enough pressure and time, the discharge of the tank gases and radionuclides into the

environment and a subsequent spread of contamination is inevitable. Since the timing of the "burps" is not sufficiently predictable, operators who periodically perform maintenance and surveillance around the tank could be inadvertently contaminated.

- o There are no precautions in the in-tank procedures controlling the timing of in-tank operations. If a tank "burp" occurred during an in-tank operation, the open riser would provide a relatively large unfiltered and unmonitored vent path for escaping gases and entrained particles.
- o Despite documented concerns about the flammability of trapped gases, no evidence could be found that precautions were taken prior to 1990 to prevent the introduction of ignition sources.

Surveillance

Surveillance-related systems include a Process Instrumentation Surveillance, Calibration, and Evaluation System (PISCES); a Preventive Maintenance System; a Job Control System; and the Computer Automated Surveillance System (CASS). PISCES was implemented at the Hanford Tank Farm in 1985 to provide a tracking system for scheduled calibration and maintenance activities. The Preventive Maintenance System has been in effect since 1976 and is being incorporated into PISCES. The Job Control System was implemented in June 1989 to track work orders for repair and corrective maintenance. CASS has been implemented to record readings from process instrumentation and transmit certain alarms. Process instrumentation, which is monitored by CASS, includes the liquid level monitors and the radiation monitors on both annulus exhausters and leak detection pits.⁵

Finding V(4): Surveillance activities at the Hanford Tank Farm do not have a high priority or receive the necessary support from WHC management to maintain the operability of current surveillance equipment and instrumentation or to obtain additional data-collection equipment and instrumentation.

- o Historically, the surveillance program at the Hanford Tank Farm has not had adequate equipment to obtain the data necessary to characterize the reactions and contents of the wastes stored in the different tanks. The surveillance equipment that has been installed has not been included in a preventive maintenance program, nor has it received timely maintenance when it has become inoperable. Surveillance equipment has not been upgraded or replaced as new problems and events have occurred in the various tank farms. This has been the case for both single-shell and double-shell tanks. Some obsolete equipment has not been upgraded or replaced.
- o During the April 1989 Technical Safety Appraisal (TSA) of the Hanford Tank Farm, findings and concerns were expressed regarding the lack of a preventive maintenance program or effective predictive maintenance activities. The appraisal team considered the procedural controls and manpower for maintenance and calibration activities to be insufficient.

The appraisal team found that proper and updated requirements for instrumentation and equipment were not provided and that procedures, documentation, and reference materials for maintenance activities were lacking. Concern was also expressed by the appraisal team regarding inadequacies in the Operational Safety Requirements (OSR's), the existing inconsistencies for incorporating the OSR's into procedures, and the relationship of the limiting conditions for operation and the surveillance requirements in the OSR's.⁶

o The results of this general neglect of surveillance at the Hanford Tank Farm can be illustrated by the following events at tank 101-SY:

- Photographs of the tank contents were taken routinely until 1987. Photos requested in June 1988 were not obtained until April 1989 because of problems at the tank site, lack of personnel (specifically radiation protection technologists), and other delays. (Photographic surveillance in the tank has recently been suspended due to concern over hydrogen detonation from stray ignition sources.)⁷
- Surveillance equipment failure and time out-of-service has been excessive for the tank, but this situation has been typical for the surveillance equipment at the Hanford Tank Farm. For example, the Gastech hydrogen monitor/chart recorder installed in January 1985 malfunctioned on February 11, 1985, and was out-of-service for over a month. In April 1985, maintenance of the hydrogen monitoring system was suspended due to other manpower requirements. From January through September 1985, the hydrogen monitoring system was operable for only 69 days. The system was removed from service in February 1987.⁸
- Currently, Tank Farm Surveillance Analysis and Support provides a Daily Surveillance Analysis Anomaly Report to the Tank Farm Operations Manager, listing all out-of-service equipment.⁹ The list dated May 1, 1990, included a critical radiation monitoring instrument in the tank annulus that had read "0" since March 26, 1990.¹⁰ In 1989, this instrument was out-of-service from April through July. This same group provides a similar list to all Hanford Tank Farm and WHC management on a monthly basis and arranges a monthly meeting to discuss the Tank Farm Surveillance Analysis and Support investigations. Members and former members of this group indicated to the NS team that the level of maintenance for Hanford Tank Farm surveillance equipment and instrumentation has not improved during the past 25 years.¹¹

o In the April 1989 TSA, several concerns were expressed that relate to the surveillance program:¹²

- The CASS is not under configuration control in accordance with WHC-CM-6-1, Procedure EP 2.1, "Configuration Control."

- Administration of the Job Control System by shift managers and plant engineers has a negative effect on their duties.
- o A February 1990 audit of WHC Defense Waste Management by DOE-RL found the following deficiencies:¹³
 - "Important plant equipment including some safety equipment is not maintained in a reliable condition or the equipment's ability to perform its function is indeterminate." The NS team found five instances of this deficiency at the tank farms.
 - "Internal surveillances are not always performed, tracked, or closed out by the operations organization as required by administrative procedures." The NS team found 12 instances of this deficiency at the tank farms.
- o In a 1989-1990 self-assessment performed by the Hanford contractors and DOE-RL, the self-assessment team made similar findings:¹⁴
 - "Hanford facilities continue to be hampered by inadequate maintenance of equipment and facilities."
 - "Funding has not been adequate to properly maintain and update either facilities or the basic infrastructure at Hanford."

Finding V(5): WHC management does not support staff efforts (operations, maintenance, radiation protection, and surveillance) to obtain needed data and analysis for the evaluation of events and anomalies being reported for the Hanford Tank Farm.

- o In the April 1989 TSA,¹⁵ the appraisal team found that the cognizant engineer was no longer involved in or required to track performance once an instrument or equipment was logged into the PISCES, nor was he required to recommend preventive maintenance unless a work request was prepared. The assessment also found that there was no assignment of responsibility to maintenance, maintenance engineering, or operations organizations for tracking performance. At that time, the cognizant engineer did not schedule periodic reviews of instrument and equipment performance. Some of these deficiencies still exist, even though procedures associated with the responsibilities of cognizant engineers were revised on August 21, 1989.¹⁶ (It should be noted that 7 months may not have been sufficient time to fully implement the new procedures.)
- o Inadequate surveillance equipment and instrumentation has long been a problem at the Hanford Tank Farm. Tank 101-SY has only a single thermocouple tree for monitoring tank activity. As noted above, the radiation monitoring in the annuli of double-shell tanks is accomplished by a single instrument with no backup capability. The OSR that applies to leak detection instrumentation does not require backup radiation monitoring, restrict time out-of-service, or require grab sampling during inoperable periods.¹⁷ When sampling has been recommended in

order to understand more completely the events occurring in 101-SY, the WHC staff has been told that the acquisition and installation of the requested surveillance equipment was too expensive or not needed, since a safety concern had not been absolutely demonstrated.¹⁸

Finding V(6): Staffing levels for operations, maintenance, and radiation protection are insufficient to maintain the equipment and instrumentation required for surveillance of safety-related parameters in waste tanks at the Hanford Tank Farm, including 101-SY.

- o There is a severe shortage of certified radiation protection technologists (RPT's) supporting the operations at the Hanford Tank Farm. With the recent implementation of the Radiation Area Management Program, RPT resources will be further strained, resulting in adverse impacts on the ability to conduct operations and maintenance in the tank farms. The Radiation Area Management Program has been designed to upgrade radiation protection activities; however, the lack of RPT's reduces not only the effectiveness of the program but also affects the ability of the operating organizations to initiate needed corrective actions. The staff of RPT's currently assigned to the tank farms is highly qualified and, like that of maintenance, is being forced to provide expanded services without a commensurate increase in support.
- o There is a severe shortage of qualified staff within both the maintenance group and the operations organization.

Maintenance

The maintenance staff for the 200 West Area at Hanford Tank Farm is responsible for all SY, SX, S, U, TY, TX, and T Tank Farms as well as T-Plant, the evaporators, vaults, diversion boxes, transport lines, and laundry facilities. The 200 West Area includes 83 single-shell tanks and 3 SY double-shell tanks.

Three systems are used to schedule and conduct maintenance activities: PISCES, the Preventive Maintenance System, and the Job Control System. PISCES and the Preventive Maintenance System are used for scheduled calibration and maintenance activities, and the Job Control System is used for repair and corrective maintenance.

Finding V(7): Field inspections of the SY Tank Farm revealed that material conditions have not improved and that numerous deficiencies identified during previous inspections remain unresolved.

- o Members of the NS inspection team performed field inspections at the SY Tank Farm to assess the current status of its material conditions. At the SY instrumentation building, wiring behind the instrument panel was in complete disarray. Numerous wires were cut off or loose. Wires were not run in cable trays or conduits and many were unsupported. The floor and the lower wiring behind the instrument panel were covered with about an inch of feathers, dirt, and bird droppings.

- o Few of the numerous valves and devices in the building were supplied with any permanent labeling. Many had no labeling at all, and some were identified by taped or handwritten notes affixed to adjacent structures. Handwritten scale changes appeared on or near several instruments.
- o A design modification had been made to supply air to the 101-SY lancing system. This 100-psi (pounds per square inch) air-piping assembly, which included valves and instrumentation, was supported by a roll of heavy tape and a wooden wedge; a permanent pipe support had not been installed.
- o In the primary (K-1) and annulus (K-2) exhaust areas, sample pumps were unbolted and lay on the bottom of every continuous air monitor (CAM) cabinet. These and other cabinets were all found with a significant accumulation of dirt, trash, and debris, including at least one tumbleweed. Cabinet doors are routinely left open, effectively bypassing cabinet air filtration. Additionally, three vent-and-balance sample ports upstream of the K-1 and K-2 exhaust CAM's were missing, allowing potential dilution of air samples.
- o The portable exhauster inlet valve was found partially open, with the fan windmilling as the K-1 system drew air backwards through the portable exhaust fan and subsequently through the ducting into tank 101-SY. The condensate drain line back to tank 101-SY was also open. Both provide unmonitored release paths in the event of a tank pressurization.
- o Several structural supports have "settled," causing failures of the supported structure. Two significant examples are provided by the K-1 exhaust duct from tank 103-SY and the annulus air-inlet ducts on tank 101-SY. Settlement of at least two adjacent supports has caused failure of the isolation valve in tank 103-SY's K-1 duct. This valve is now leaking and is wrapped in plastic to control the spread of contamination. Although the valve has been broken for about 8 months, a new one has not yet been obtained. This situation constitutes a failure of primary tank containment, and since all three tanks are interconnected, it could result in an unmonitored release in the event of a pressurization in tank 101-SY.
- o All junction boxes and instrument cabinets in the SY Tank Farm show weather damage that varies from minor to substantial. Enclosures are frequently left uncovered, with exposed, frayed, or loose wiring. The cabinet for the specific gravity instrumentation for tank 102-SY was so badly deteriorated that it is being abandoned.
- o The gas sample lines entering the primary exhaust duct on tank 101-SY were found detached, allowing air leakage that could dilute actual gas samples. If this occurred during the pressurization event of April 19, 1990, the 3.9-percent hydrogen reading in the duct may have been unreliably low. As a temporary corrective action, the connection has since been taped. However, no permanent, leak-tight connection has been made. Furthermore, the instrumentation has not yet been calibrated.

Finding V(8): A program to track equipment performance and failures does not exist. No predictive maintenance is performed. The equipment at SY Tank Farm thus has a history of neglected corrective maintenance.

- o The manual tape level indicator for tank 101-SY was out-of-service for at least three extended periods: from July 24, 1985, to September 17, 1985; from July 19, 1986, to February 19, 1987; and from July 20, 1987, to June 20, 1988.
- o The first hydrogen monitor installed on tank 101-SY in 1985 was functional for only 69 days in the 8 months between January 11, 1985, and September 11, 1985. It was finally removed in February 1987.
- o The leak detector probes in the annuli of tanks 101-SY and 103-SY were inoperable from at least July 1987 through August 1988.
- o A formal equipment performance testing, monitoring, trending, and analysis program is not implemented for all aspects of the tank farms, even though such a program was scheduled for completion by the end of July 1989.¹⁹

The maintenance staff consists of about 25 electricians, millwrights, welders, instrument technicians, and fitters. Due to training, vacation, and nonmaintenance duties, the number of workers available during any given day is reduced by about half. Several staffers are on loan to the 200 East Area for a special project, and a few additional specialists (such as sheet-metal workers) are available from the central shop for specific jobs. When radiological dress-in/dress-out and other health physics and industrial safety requirements are met, each worker is able to provide a maximum of 5-6 hours of productive work per day. After allocation of personnel to all tank farm facilities, the three tanks in the SY Tank Farm can expect to receive less than 10 man-hours of maintenance support per day.

Technical and Engineering Support

Technical and engineering support for all activities and facilities associated with the SY Tank Farm is the responsibility of Waste Management Plant Engineering. Waste Management Plant Engineering is divided into two groups: process technology, which has responsibility for long-term issues, and process engineering, which has responsibility for day-to-day activities at the tank farm. Activities performed by these groups include the following: (1) to prepare engineering studies defining the needs of and scope for new or modified facilities, to evaluate alternatives, and to recommend appropriate actions; (2) to provide process engineering and technical support for tank farm operations; (3) to provide overall design engineering and technical direction for the design, fabrication, and installation of electrical and mechanical plant systems and components; (4) to maintain design configuration control of production facilities; and (5) to develop and coordinate reviews, provide comment resolution, and assure issuance of engineering instructions.

For each tank farm, there is a single engineer who is assigned as the cognizant person through whom tank farm operations and tank farm engineers communicate. Over the past 8 years, five individuals have held the post of cognizant engineer for tank 101-SY.

Finding V(9): Although the cognizant engineer is clearly vital to effective communication between tank farm operations and the engineering groups, his/her importance was not adequately recognized or supported by line management.

- o The cognizant engineer's post in Waste Management Plant Engineering is considered an entry-level position. Five of the six engineers assigned to the role were recent college graduates with little or no experience.
- o A formal training program was never implemented for engineers assigned to this position. Furthermore, a formal turnover process did not exist to relieve cognizant engineers of their duties. As a result, the tank farms have failed to develop an historical "corporate knowledge" of operational problems and solutions.
- o Cognizant engineer support for activities not directly associated with the tank farms has taken precedence over support for actual tank farm activities, as exemplified by the delay in identifying a suitable pump for use in slurry removal during preparations for the 1988 cross-site transfer.

In 1984, after concern was raised over the continuing pressurization of 101-SY, a task force was formed to identify and implement corrective actions. The corrective actions included lancing the surface of the tank to provide an escape path for accumulated gases, monitoring the vent path for the presence of hydrogen, and sampling the tank in order to determine the chemical consistency. The responsibility for implementing the task team's corrective actions was assigned to Waste Management Plant Engineering.

Finding V(10): Waste Management Plant Engineering implemented the 1984 task force recommendations in an ad hoc manner.

- o No formal mechanism was established by Waste Management Plant Engineering to support the implementation of corrective actions.
- o Lancing was ordered and supervised by Waste Management Plant Engineering without a formal evaluation of the operation in light of the unique operational history of the tank and the suspected presence of flammable gas.
- o The hydrogen sampling monitor installed at the direction of Waste Management Plant Engineering was a lab monitor, not an industrial monitor suitable for the application. As a result, spare parts were unavailable and the detector was soon declared nonfunctional.

Finding V(11): Despite documented concerns about the flammability of trapped gases and about possible tank pressurization and subsequent spread of

contamination, no formal safety evaluations were conducted to assess in-tank operations for potential ignition sources.

- o No formal evaluation was conducted to determine the ignition potential of the weighted "bottle-and-string" sampling rig; the truck-mounted, high-speed sampling drill; or the portable lance. In addition, no evaluation was conducted to determine the effect of a photographic flash on flammable gases in the vent space.
- o A 1988 review of 101-SY noted that a 9-inch drop in liquid level is sufficient to produce an 11-percent hydrogen mixture in the vapor space.²⁰ The report concluded that if the hydrogen should find an ignition source, the vapor space pressure would rise above atmospheric pressure. If tank pressurization occurred, the open tank riser, through which in-tank operations are conducted, would provide an unfiltered and unmonitored vent path for the tank's contents.

Finding V(12): Despite concern over the rising level of waste in the tank, no formal safety evaluation was conducted to determine the effects of water and air as a lancing media.

- o Lancing of tank 101-SY on a regular basis was recommended by a letter dated October 7, 1983.²¹ Between October 20, 1983, and April 17, 1986, at least 27 separate lancing operations were conducted with a portable lance. Each operation added approximately 400 gallons of water to the tank. The only evaluation to address the safety implications of these operations was an engineering study conducted to determine the maximum flow rate for water running through the lance. (The engineers were concerned about exceeding the capacity of the tank's ventilation exhaust system.) Waste Management Plant Engineering did not conduct a formal safety evaluation of the procedure because lancing was accepted as a routine operation.
- o The effects of the added water and the usefulness of air lancing were first discussed in a memo dated April 1, 1985. Investigation of the air-lancing option resulted from concern that 101-SY was approaching the maximum liquid level permitted by specifications. The memo noted that the relationship between water lancing and the observed increase in 101-SY's liquid level was unknown. It further stated that "additional water would contribute to an increase in slurry volume," noting:

Air lancing instead of water [lancing] had the advantage of not adding to the total amount of waste in the tank but...it raises some safety concerns that should be addressed before air is added to 101-SY. Lancing using air instead of water could increase the chance of tank pressurization or cause an increase in liquid level due to air entrapment. I don't know if using air would increase the risk of the tank burping during lancing.²²

- o On August 7, 1986, a WHC engineer stated:

Lancing is currently the only means used to control or limit the impact of gas release. It had usually been effective in lowering the liquid level but not in preventing pressurization. The permanent, stationary, lances...do not appear to be as effective as the portable lances...Alternative lancing methods should be investigated.²³

- o On July 18, 1986, another WHC engineer concurred that permanent lances had not been as effective as the temporary lances and suggested that this could be because of differences in lance nozzles or because of the low volume of water used.²⁴
- o On November 25, 1986, following increased concern about the effects of water lancing on 101-SY's waste level, the tank was lanced with air using the permanent lances. No formal safety evaluation was conducted prior to conducting the air lancing; instead, only an engineering study was performed to determine the maximum airflow rate that would not exceed the capacity of the tank's discharge ventilation system.
- o In 1988, as a result of the concern about the continued rise in tank level and after an incident in which a gas release resulted in a positive pressure event, a second task force was formed to identify and implement corrective actions. As was the case with the 1984 task team, Waste Management Plant Engineering was responsible for drawing up and implementing the associated corrective actions. No formal review of the effectiveness of the 1984 task team corrective action was conducted by Waste Management Plant Engineering management.

Finding V(13): As with the 1984 task team recommendations, the 1988 corrective actions were implemented by Waste Management Plant Engineering in an ad hoc manner.

- o A hydrogen monitor was removed from the Hanford T-Plant and reinstalled in 101-SY using duct tape. The sampling configuration was fabricated from available spare parts and can only be described as an "interim fix." The configuration employed could not have provided valid quantitative results and can only have indicated whether a particular gas was or was not present.
- o Alternate methods were studied to improve the efficiency of lancing. However, lancing was halted at the direction of tank farm engineers after the cognizant engineer expressed the view that lancing itself might contribute to the rise in tank level. No formal safety evaluation of the decision to begin or the decision to terminate lancing was performed by the management of Waste Management Plant Engineering.
- o The identification and installation of a pump for use in the removal of waste from 101-SY was delayed by Waste Management Plant Engineering owing to other work priorities. The process for setting priorities was informal and not risk based.

Worker Safety

Worker safety at the Hanford Tank Farm focuses in large part on ensuring tank containment, providing appropriate instrumentation and monitoring equipment for personnel, applying conventional occupational safety practices, and instituting emergency preparedness programs. Although deficiencies have been cited in each of these areas of worker safety (e.g., in the 1989 DOE Technical Safety Appraisal), those associated with the first two categories are particularly important in minimizing the potential for exposure of workers to hazardous levels of radioactive and toxic materials.

For tank 101-SY, operational anomalies, including slurry growth, pressurization events, and gas "burps," were not addressed in the original design and were not covered by the prevailing Safety Analysis Report (SAR). As a result, derivative operating requirements, limits, procedures, and instrumentation for protection of the public and the workers were not based on a valid assessment of risk. The issues raised by 101-SY involved unpredicted and uncontrolled operational behavior to which management was obliged to respond promptly in order to mitigate potential hazards. By the same token, management should have thoroughly evaluated the potential risk and demonstrated whether such risks were adequately mitigated in the existing SAR.

Tank 101-SY demonstrates a failure by management at the Hanford Tank Farm to act promptly when it encountered worker safety issues. Although some action was taken, no formal resolution was achieved and the issues resurfaced.

Finding V(14): Radionuclides and potentially dangerous concentrations of ammonia and other toxic fumes may be vented during pressurization events at tank 101-SY.

Radionuclides

- o The single-shell tanks at Hanford were not originally designed to prevent unfiltered leakage of in-tank gases to the atmosphere from pump pits, sampling and monitoring pits, and other penetrations. A number of incidents involving radionuclide venting from passively ventilated single-shell tanks occurred in the 1970's and early 1980's.²⁵ In 1981, there was "substantial evidence that tank vapor radioactivity concentrations sometimes exceed [RHO-MA-139, Part D, Standards Pertaining to Radioactive Airborne Emissions] Table II [where technically and economically practical] and perhaps Table I [mandatory] limits."²⁶ Further parametric studies of slurry growth were recommended and included as an FY 1980 award-fee objective for Rockwell Hanford Operations (RHO). The objective was addressed through a two-phased sampling program consisting of vent space radionuclide sampling of 42 single-shell tanks and through quantifying emissions from selected tanks. Phase I results indicated that SST vent spaces contained "significant radionuclide concentrations."²⁷ Based on these and other confirmatory studies, actions were initiated in 1982 to install high-efficiency particulate air (HEPA) filters and to strengthen controls (e.g., tape pit block crevices), thus preventing direct radionuclide

venting. Due to what were judged to be higher priorities, Phase II of this program (emission quantification) was not funded.²⁸

- o Unlike single-shell tanks, double-shell tanks were designed with HEPA-filtered ventilation systems to maintain a negative pressure in the vent space. However, containment integrity is defeated (through penetrations similar to those noted above) when sufficient in-tank pressurization takes place to displace vent space gases. Pressurization events were common for double-shell tanks: 131 incidents occurred in 1984, though the number progressively declined to about 30 verifiable incidents in 1989.²⁹ Most pressurization events have been attributable to exhauster failures or to overpressurization associated with inappropriate waste slurry feed rates. For tank 101-SY, however, the cyclical pressurization observed since 1982 has been due to in situ gas generation, which builds up under and periodically breaches the crust overlying the waste.
- o The safety implications of pressurization as it pertains to radioactive gaseous emissions have been raised repeatedly over the past 7 years. The following chronology illustrates this fact:
 - The question of radionuclide venting during pressurization events at 101-SY was first raised in 1983 by the Manager for Tank Farm Surveillance, who also had conducted the Phase I study that characterized vent spaces in single-shell tanks. He noted that "the fact that the tank [101-SY] has pressurized and the pressurizations are cyclic...[presents] major safety concerns relating to loss of containment (airborne contamination released to the environment)."³⁰ These concerns were raised to the responsible program office manager for Rockwell Hanford Operations. NS interviews with those involved indicate that in 1983 an informal proposal by RHO to upgrade the ventilation systems for existing double-shell tanks and to design new systems for those tanks yet to be built, thus preventing overpressurization, was rebuffed by the Department of Energy's Richland Operations Office as too costly.³¹ A related proposal to sample and analyze gases vented from 101-SY during a pressurization event was also rejected.³²
 - In 1984, the frequency and degree of overpressurization in 101-SY led to the formation of an RHO task group to recommend preventive measures. Recommendations included (1) periodic lancing of the crust to release gas pressure and (2) further investigation into the potential for release of airborne contamination. A particulate sampler was subsequently used to monitor venting during a pressurization event, and the results were within emission requirements.³³ Because of the technique used, however, questions were raised about the validity of these grab samples.
 - A subsequent series of internal letters from Tank Farm Surveillance challenged tank farm management's failure to resolve the issue of airborne radionuclide emissions.³⁴ On July 8, 1985, this exchange culminated in a request that the Tank Farm Surveillance

Division assume responsibility from process engineering for sampling tanks (including 101-SY) for containment. A surveillance engineer suggested using the sampling technique proposed in 1984.³⁵ In response, a joint audit by Tank Farm Surveillance and process engineering was requested to devise a common characterization plan for airborne radionuclide emissions. The resulting plan established two operational phases: the first phase sampled radionuclide particulate concentrations in the AN and AW Tank Farms, and the second attempted to calculate potential leakage rates due to pressurization events. Tank 101-SY was sampled in Phase I and calculated to emit up to 14 percent of the maximum instantaneous concentration for ²³⁹Pu and 3 percent for ¹³⁷Cs. The lead investigator concluded that the calculated maximum releasable concentrations were well within "emergency environmental limits."³⁶ He also noted that "pressurizations, although not an emergency condition at the concentrations measured, may pose a health hazard and must be prevented."³⁷ Further work to characterize radioactive gases was also recommended but had not been performed.³⁸

- According to several sources, the minimum particulate size that Hanford is capable of sampling (3 microns) precluded the complete sampling of radioactive gases and other respirable aerosol emissions.³⁹ This limitation was first identified at Hanford in the late 1970's and was the basis for a 1981 feasibility study to determine whether a newly developed cryogenic gas collection system could lower detection thresholds and provide better monitoring for radionuclide gases. These recommendations and a 1986 applied-research proposal for improved airborne radionuclide monitoring were set aside because of budgetary priorities.⁴⁰ In 1987, the issue was again raised when the Westinghouse staff noted that existing samplers were incapable of effectively collecting radioactive gases other than iodine isotopes and cesium gas, leaving tritium, carbon-14, tellurium, technetium, and selenium unmonitored.⁴¹ Again, the recommendations included real-time gas-sampling systems. In-house and industry surveys were conducted by WHC, and it was concluded that existing sampling programs in the tank farms were adequate and that they were consistent with state-of-the-art technology.⁴²
- Although the study mentioned above is referenced in the 1986 revised SAR for the tank farms, the Manager of Tank Farm Surveillance had "strongly recommended rejection of the proposed [SAR] revision" because of inadequate discussion of pressurizations and because the SAR identified significant radionuclide venting as "incredible for a single event."⁴³
- An April 1986 position statement on behalf of the Waste Management Health Physics Division noted as follows:

Detecting releases due to pressurization is uncertain; we have very low confidence in the

negative results obtained to date. The best solution...is to prevent the problem in design. To accomplish this, the first step is to define ventilation as an 'essential safety system' and provide special design criteria.... Safety has been remiss in failing to apply...industry standards [DOE Order 6430.1 and Nuclear Air-Cleaning Handbook] to tank farms in the absence of specific guidance.⁴⁴

- The issue of radionuclide and ammonia venting during pressurization events at 101-SY resurfaced among a number of other safety concerns discussed by a WHC engineer in his October 1988 review of 101-SY.⁴⁵ He concluded that, "given enough pressure and time, discharge of the tank gas and radionuclides into the environment and subsequent contamination spread is inevitable." His claim was that "this tank [101-SY] has been studied and characterized sufficiently to be able to justify taking action to correct the gas generation problem now." Recommended actions included increasing the negative pressure and ventilation in tank 101-SY in order to minimize the potential for pressurization during periodic "burps." Other recommendations entailed sealing penetrations open to the atmosphere, installation of a controlled filtered-air inlet, increased stack height (to control ammonia concentrations at ground level), installation of gas monitors, and placing workers in masks until physical improvements can be made. The first recommendation, apparently originally suggested in 1982, has not been implemented. The rest have only recently been under active study for implementation at 101-SY. As discussed in the main body of the Report, these corrective actions were not of sufficient priority to receive support.⁴⁶
- o WHC engineers currently believe that the venting of airborne radionuclides during pressurization events is not a major concern for the following reasons: (1) contamination has not shown up on smear samples taken after pressurization; (2) air-monitoring stations have produced negative results for airborne radioactive particulates; and (3) no biological uptakes have taken place in the work force.⁴⁷ This position has been regularly challenged by members of the WHC safety staff at the tank farms, who have cited past assessments to support their positions. In a November 1989 listing of key safety issues at the tank farms, a WHC engineer in the nuclear safety group noted:

A recent study by PNL [Pacific Northwest Laboratories] demonstrates that more than 90 percent of the radionuclides discharged in some waste streams may not be detected by current sampling equipment. The radioactive particles are smaller than the 0.3 micrometer filters and can pass through the filter to the environment. These discharges would be classified as unsampled, unmonitored, and unreported.⁴⁸

To date, the only samplings that have been conducted to characterize radionuclide venting at 101-SY and other DST's have been the "particulate" grab samples taken in 1984 (after pressurization at 101-SY) and in 1985 (for selected DST's, including 101-SY). Those taken in 1984 constitute the only attempt to monitor radionuclide venting during a pressurization event at 101-SY, and they yielded negative results. However, the length of time of the sampling, its isokinetic nature, and the lack of sensitivity of the technique to lower micron particulate sizes raises questions about the validity of those results.

Ammonia and Other Toxic Gases

- o Ammonia is a prevalent constituent of waste stored at the tank farms. Sources of ammonia include neutralized PUREX decladding wastes generated from the processing of zirconium-clad fuel elements, as well as chemical degradation of concentrated complexant and double-shell slurry mixtures.
- o The safety implications of ammonia for waste management operations at Hanford were evaluated by an RHO engineer in 1983. Ammonia buildup in the tank vapor space and ammonia nitrate buildup on HEPA filters were projected to be "far below" explosive levels. Occupational and environmental hazards were likewise ruled out in consideration of the containment and ventilation system provided, and the "pungent" odor of ammonia was found at concentration levels below the hazard threshold for workers.⁴⁹
- o Notwithstanding the conclusions of that hazards assessment, ammonia and other organic chemical fumes have proven to be a frequent occupational concern at the tank farms. On July 3, 1987, two electricians complained of nose and throat irritation after inhaling fumes near tank C-103.⁵⁰ A similar incident occurred on July 15, 1987. On November 9, 1987, workers detected ammonia fumes at the SY Tank Farm after lancing operations were performed in tank 101-SY.⁵¹ More recently, on September 28, 1989, an employee near the same farm was overcome by what was assumed to be organic chemical fumes.⁵² The most recent hydrogen "burp" at 101-SY, on April 19, 1990, reportedly included the release of ammonia fumes that were detectable by workers.⁵³
- o Despite evidence of ammonia emissions during lancing operations and periodic hydrogen "burps" at 101-SY, remedial measures have been directed primarily at aging waste tanks in the AP and AW Tank Farms, where the more serious incidents have occurred. However, the 1988 memorandum on tank 101-SY once again raised concern about hazardous ammonia releases during pressurization events, particularly during atmospheric inversions, which are common at Hanford. Recommendations for continuous ammonia monitors and for the distribution of masks to workers were not implemented at 101-SY, apparently because of budget priorities and because of the perception that ammonia at the concentrations released was not dangerous.⁵⁴

- o A DOE Headquarters Technical Safety Appraisal conducted in April 1989 at the Hanford Tank Farm found that "WHC has not implemented a periodic monitoring program, as required by DOE 5480.10, to assure the continued effectiveness of controls for physical and chemical stresses [to workers]." ⁵⁵
- o Two WHC task teams have recently evaluated necessary corrective actions in response to overall ammonia hazards at the tank farms. Both concluded that the AP, AW, and C Tank Farms are of primary concern. (Tank 101-SY was excluded because the calculated instantaneous release concentration at 4 percent of the permissible limit for ammonia was not considered a potential problem during pressurizations.) Recommendations included increasing the height of the exhaust stacks and the use of carbon absorption canisters for tank filtration. ⁵⁶
- o As a result of the NS team assessment, the 1988 recommendations have been given renewed attention and appropriate compensatory actions were ordered at the tank farm on May 14, 1990. These actions included a requirement for all workers in the proximity of 101-SY to wear filtered masks and a recommendation for further investigation into the risk posed by the presence of ammonium nitrate on the waste crust in tank 101-SY.

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VI. MANAGEMENT OF LABORATORY SUPPORT

As described in the Historical Overview section of this Report, a series of laboratory studies on slurry growth was conducted first by Atlantic Richfield Hanford Company (ARCO) and later by Rockwell Hanford Operations (RHO). These studies were initiated to investigate the causes of slurry growth, to develop methods for predicting the extent of the potential problem, and to implement control measures.

Analyses of slurry growth actually predated the observation of growth in double-shell slurry (DSS), including that observed in tank 101-SY. However, it was the extent of the growth of DSS in tank 101-SY that led RHO to conduct the first of several parametric experiments on synthetic and actual slurry compounds. These studies, conducted from 1978 to 1983, found that gases were being generated through chemical reactions, that gases could be trapped under the waste surface, and that this entrapment was responsible for the observed "growth" of the waste. These early studies also concluded that hydrogen was among the gases generated and that it was present at flammable and potentially detonable concentrations. The simultaneous generation of significant concentrations of nitrous oxide was also identified as early as 1979, and at least one RHO engineer and two RHO chemists were aware that nitrous oxide was capable of increasing the likelihood and consequences of a hydrogen burn.

The generation of hydrogen through radiolysis of water was a well-known phenomenon in high-level wastes. Studies at Hanford that predated the 101-SY issue had raised questions about the safety significance of radiolytic hydrogen accumulation and whether there was any need to maintain tank vapor spaces below the prevailing 1-percent operating limit for the tanks; operating experience demonstrated that natural ventilation of the vapor space in SST's could keep these limits from being exceeded. Then-current understandings about hydrogen generation rates and maximum concentrations of hydrogen in the vapor spaces of SST's were used to develop design criteria and safety analyses for double-shell tanks. Operating limits, requirements, and procedures for DST's (including tank 101-SY) were derived from these basic documents. Although later laboratory experiments undermined the technical bases for those criteria by showing that radiolysis of water was neither the sole nor the principal source of hydrogen generation, the base documents were not revised to take that into account. Thus, the early discovery that flammable gases were associated with slurry growth did not lead to immediate steps to remove the potential hazard.

Finding VI(1): The early Hanford analytical research program for studying slurry growth consisted of a disjointed series of individual research projects. Contractor management failed to develop a coherent approach to research aimed at resolving the slurry growth problem in a timely manner.

Research was undermined by a weak quality assurance program that failed to assure valid results or to preclude avoidable difficulties in data collection and interpretation. Key safety information (e.g., the significance of nitrous oxide as an oxidizer for hydrogen flammability) was neither widely recognized by RHO nor conveyed to DOE-RL.

- o Between 1974 and 1977, Hanford chemists made few laboratory efforts to determine the origin of hydrogen detected in the vapor spaces of single-shell tanks. This was apparently because radiolysis of water was believed to be the sole source of the hydrogen, and radiolysis was generally well understood. There was little focus to this early work, which was primarily concerned with how much hydrogen could be generated by radiolytic means and whether tank ventilation could sufficiently handle the amount generated.
 - In 1974, an ARCO researcher evaluated hydrogen evolution from salt cake in single-shell tanks. He concluded that "atmospheric pressure changes may provide enough tank breathing to assure hydrogen dilution at low evolution rates." However, he cautioned that this mechanism may not provide adequate ventilation for high evolution rates.¹
 - In 1975, another ARCO researcher recommended a "literature survey and some preliminary calculations to determine the scope of the radiolytic [emphasis added] hydrogen problem in waste tanks."²
 - A 1976 report discounted potential exothermic reactions between sodium nitrate and the organic compounds left in the salt cake that remained in SST's after water was removed. The report noted that "the greatest explosion hazard, if any exists, is a hydrogen-oxygen explosion resulting from radiolysis of water in the waste."³
 - In 1977, an RHO researcher from the Chemical Sciences Department hypothesized that radiolytic hydrogen might be accumulated as bubbles under the waste crust of certain tanks, leading to the "liquid level cycling phenomenon" then being observed. He discounted earlier RHO evaluations that the maximum hydrogen concentrations that could be generated were less than 2 percent.

We must assume that H_2 concentrations do exceed the LEL [lower explosive limit] of four percent in localized areas near the top of the tanks, unless further study yields contrary evidence. It has already been calculated that the smallest of such explosions would collapse the dome of any tank.⁴

- Later in 1977, the Manager of RHO Chemical Sciences noted that "gas produced by radiolysis and trapped beneath the crust is potentially more dangerous" than growth of the crust as the cause of waste level variations. He noted that his investigations to

date were "unfunded exploratory work" and that there was a need for a "refined experiment for Tank 101-SY."⁵

- o In 1977, double-shell slurry was produced and deposited in 101-SY. The rapid and sizable increases in the volume of this material led to more focused laboratory research on slurry growth. As a result, radiolysis of organics replaced radiolysis of water as the postulated source of hydrogen and cause of slurry growth. Studies from 1979 to 1980 confirmed this hypothesis.
- In early 1978, an RHO researcher submitted a laboratory proposal to study "liquid level variation in Tank 241-SY-101."⁶ One of three experiments proposed was to determine "the rate of radiolysis of the organic complexants N-hydroxyethylene-diaminetriacetic acid (HEDTA)/ethylenediamine-tetraacetic acid (EDTA) and the rate of CO₂ evolution."
 - In an assessment of experiments on slurry growth performed in 1978, a senior chemist observed that these experiments demonstrated that gas trapped in the slurry caused volume growth.⁷ He further noted that "a diluted gas sample was analysed as 4.2% hydrogen....[B]ecause this level of hydrogen is potentially explosive, the air space in Tank 101-SY should be checked for hydrogen build-up periodically." He recommended further gas identification experiments, determination of gas generation rates, gas sampling of 101-SY, and investigation of "salt-complexant" interactions and gas retention mechanisms.
 - The minutes of the 15th Waste Management Consultants' Meeting of October 17-18, 1978, indicate that the consultants were critical of the RHO gas analyses that served as the basis of RHO's explanation for the cyclic nature of slurry growth. The consultants noted that "if it is verified that...the gases from these complexant residues do contain hydrogen in significant fraction among the gases generated, then a real hazard may exist."⁸
- In response to the consultants' concerns, RHO initiated a "hazards assessment" of the hydrogen problem, assigning the work to a young engineer recently graduated from college. The engineer worked on the assessment during 1979, but his report was never formally issued. The NS team found among his papers a calculation of the amount of energy that would be released should a hydrogen and nitrous oxide burn occur. This calculation indicates that he was not only aware of the presence of nitrous oxide, he also understood that nitrous oxide was an oxidizer that would enhance the flammability of hydrogen.
- A January 1979 assessment of synthetic slurry growth experiments performed over the previous year indicated that off-gases from the experiments were "high in hydrogen," with concentrations of 12 percent, based on mass spectroscopy, "well above the lower explo-

sive level (4 percent hydrogen)."⁹ A nitrous oxide concentration of 21 percent was based on the same analysis.

- An evaluation of laboratory studies that same month by a senior operations engineer addressed the question of whether atmospheric breathing alone would maintain the hydrogen concentration within the tanks at less than half the LEL for hydrogen or whether some form of monitoring or additional exhaust system would be required.¹⁰ Calculations in this study were based on hydrogen generation resulting from radiolysis of water, not from chemical degradation. The evaluation concluded that there was not "conclusive evidence requiring exhausting of any tanks during isolation; however, enough evidence does exist to indicate a potential hydrogen problem." A parametric study of hydrogen formation and a confirmatory process test on a selected tank were recommended.
- A 1980 RHO summary of laboratory studies of slurry growth in tank 101-SY again reported that slurry growth was "due to gas generation caused by the oxidative degradation of the complexant HEDTA....The reaction products are an unidentified complexant and several gas species; principally N_2 , N_2O , and H_2 ."¹¹
- o By 1981, the impetus behind the contractor's laboratory studies of slurry growth shifted from identifying the gases being generated and the cause of the problem to predicting the potential extent of the growth. Slurry growth had become a threat to waste minimization, which was a centerpiece of the Hanford waste management program. Inadequate quality assurance was a major problem that plagued the contractor's laboratory work, producing results that were often invalid and not reproducible.
- In a review of prior slurry growth experimental data, a senior member of Waste Processing Technology concluded that only 15 percent of measured slurry growth for four tanks--101-SY, 103-SY, 101-A, and 101-AX--could be accounted for on the basis of experimental results. He recommended further data analyses and laboratory experimentation.¹²
- A May 1981 review of recent RHO studies of slurry growth criticized studies reported in December 1980 and February 1981 on the basis of inadequate laboratory procedures.¹³
- A July 1981 assessment of plans for future slurry growth experiments noted that "past slurry growth studies cannot fully explain or predict slurry growth."¹⁴ Prediction of "slurry growth was considered important for "projecting future waste volumes and to safely achieve the maximum double-shell tank fill volume." A series of experiments was recommended to establish a "firm basis for deciding whether to let the slurry grow and, if not,...the best method of reducing or eliminating the growth."

- An August 1981 request to perform experiments for determining gas production rates from organic degradation was forwarded to Tank Farm Process Engineering for approval. It noted that the "relationship between gas production and chemical composition is not clear."¹⁵
- A December 1981 report on the just-completed "Double-Shell Slurry Campaign" acknowledged that "the tank growth phenomenon has the greatest bearing on the future of [the] DSS process." The author concluded that "some method must be devised to predict and estimate the extent of growth....[T]he growth will affect the number of tanks necessary to store waste." He recommended that key aspects of tank growth be studied before the next DSS campaign.¹⁶
- A January 1982 assessment of "gas production/slurry growth scouting experiments" stated that "no conclusion can be drawn from the analytical data at this time."¹⁷
- A month later, the same researcher proposed "a laboratory study to examine, in a detailed yet timely fashion, quantitative measurements of slurry growth."¹⁸ He noted that information gathered in this study, plus data from gas generation experiments, would allow a quantitative prediction for slurry growth by April 1982.
- A 1982 statistical analysis of previous slurry growth experiments found basic deficiencies with the experiments.¹⁹ The statistician who did the analysis recommended that, while quantitative predictions of slurry growth were needed, qualitative results ought to be emphasized due to weaknesses in experimental procedure, documentation, and "progression of logic."
- Late in 1982, a senior RHO chemist observed that "a significant amount of laboratory work has been done, attempting to provide data for a predictive, quantitative model of slurry growth."²⁰ He went on to note that "many problems were encountered during the study." These problems included mechanical difficulties with laboratory apparatus (e.g., plugging of lines with slurry), uncontrolled gas releases during experimentation, and varying slurry composition. These problems affected the reproducibility of the experiments and even led to small-scale explosions in the laboratory.
- Pilot studies of slurry growth in 1982 were subject to other problems, including discrepancies in sample labeling and documentation, as well as lack of coordination between the researchers and the engineering staff who performed the actual sampling.²¹
- A July 1982 memorandum noted that "conclusions are difficult to generate from this study. The product samples were virtually solid after sitting in the oven for a month."²²

- o In July 1983, tank pressurizations and flammable gas releases in tank 101-SY finally began to be seriously viewed as safety issues that needed to be addressed. Laboratory studies designed to better predict and mitigate or eliminate slurry growth, as well as characterize in situ hydrogen concentrations, continued. Rockwell began to look to external contractors for analytical support. Formal research programs on slurry growth were initiated in FY 1984 and 1985. Although one objective of these research programs was to find solutions to 101-SY, that objective went unfulfilled.
- On June 14, 1983, the DOE-RL Director of the Waste Management Division requested that monthly technology reports be submitted to him by Rockwell. These monthly reports provided the status of laboratory studies being conducted, including progress to date, major problem areas, and planned work. Slurry growth studies, including efforts to develop methods to control it, were routinely referenced in these monthly reports.²³
 - An October 1983 internal letter on the safety of double-shell slurry admitted that, although much had been learned about slurry growth from past experiments, "some aspects, including that of slurry collapse and tank pressurization, have not been studied."²⁴ The letter noted that "gas generation occurs at all levels in the waste, with major gaseous products being N_2O , H_2 , and N_2 ." It also noted that no corrective actions were planned at that time for the SY tanks and that regular lancing or crust breaking offered the most likely means to "control the severity of gas releases and minimize the likelihood of loss of containment."
 - An informal note from a senior chemist in October 1983 responded to an internal RHO letter that expressed safety concerns with respect to slurry growth and pressurizations in tank 101-SY. The note began by observing that "many of the [safety] issues brought up are true. Technology has not been following the actual process very close [sic]." He pointed out that he was "unaware that the tank had pressurized three times" and that he did not know of any planned corrective action for the waste tanks. He concluded:

This points out that we have been trying to predict how much the slurry growth will grow. Little or no effort has been spent on how well we control it when it grows. I feel that the pressurizations are a complete surprise. Perhaps we could have predicted that if more attention had been paid to the process rather than the lab.²⁵
 - Another October 1983 RHO memorandum outlined objectives and proposed approaches to sampling the vapor space of 101-SY. One objective was to permit a comparison of actual gas composition with experimental results. Another objective was to measure maximum hydrogen concentrations in the vapor space after

pressurizations occurred. The memo noted that the use of automatic gas chromatography had been ruled out as too costly "due to the problems encountered in comparing gas compositions to those observed in laboratory experiments and since a flammable H₂-air mixture is unlikely to occur."²⁶

- A November 1983 memo criticized the technical basis for production of double-shell slurry, noting that "the existing studies provide insufficient information about slurry growth and...cast uncertainties on the present [waste management] program plan to make DSS."²⁷

A subsequent memo during that same month noted that the RHO chemical laboratory had recently performed additional experiments to characterize more accurately specific gases generated during slurry growth.²⁸ It noted that "slurries that contain glycolic acid (hydroacetic) generate hydrogen and N₂O." Mass spectroscopy of DSS-generated gases were found to be as high as 15 and 13 percent volume for hydrogen and nitrous oxide from decomposition of HEDTA and 32 and 10 percent, respectively, from decomposition of glycolic acid.

- In response to a request for additional DSS analyses, an RHO chemist summarized the situation at the tank farms in January 1984 as follows:

The complete composition of each and every waste in each and every tank is not known. Chemical reactions have occurred in-situ, spurred by radiolysis, thermal impetus, and catalysis. The reactions have caused changes, of unknown nature, in the wastes. Throughout the years, wastes have been blended, processed, transferred to and fro; generally creating a hodgepodge of nuclear waste.²⁹

- Thermal destruction of the organic complexants that had been mixed with DSS was one of the potential measures to control slurry growth then being studied. Based on a meeting held in March 1984, the contractor planned to proceed with a "scouting" effort to examine the effects of heating prior to concentrating the DSS feed material.³⁰ This scouting effort was completed and reported on June 29, 1984, and the results indicated that complexant destruction did not occur until temperatures reached 240° C (with 77 percent reduction in total carbon, complete destruction of HEDTA and EDTA, and no slurry growth observed after 48 hours). Significant gas generation was observed, although the identity and source of the gases were not identified.³¹
- Results of ongoing gas generation experiments were reported in a March 1984 memorandum.³² The memo noted that five studies "showed that there were large quantities of gases generated during growth"; however, it emphasized that these results were in doubt

because of poor experimental controls (e.g., reaction vessels were not airtight and gas analysis was not sensitive enough). Gases generated from decomposition of glycolic acid were as high as 53 and 7 percent (volume) for hydrogen and nitrous oxide, respectively, and as high as 63 and 5 percent (volume) from HEDTA. A somewhat higher value was recorded for hydrogen generation from glycolic acid (72 percent) but was considered suspect because of an equipment miscalibration on the day of the measurement.

- An August 1984 report titled "Slurry Growth Scale-Up Results" described the production and growth of synthetic slurry during experiments designed to address observed discrepancies between laboratory slurry growth results and actual observed growth in the tank. Slurry growth measurements were obtained for use in correlating slurry growth with vessel volume and geometry to allow scale-up effects to be incorporated into equations for waste volume prediction.³³
- A November 1984 memorandum noted that "slurry-growth caused gas entrapment and sudden gas releases observed in Tank 101-SY create two safety concerns"--releases of airborne radionuclides during pressurization events and elevated hydrogen concentrations in the vapor space as a result of a tank burp. The memo observed that there was "uncertainty about the amount of hydrogen produced and how the amount varied with reaction conditions and slurry composition." It further noted that recent work with synthetic DSS had shown hydrogen concentrations of about 50 percent. Nitrous oxide was listed among the gases being generated.³⁴
- The objective of an RHO "Technology Program Plan for Fiscal Year 1985" was to "monitor and evaluate slurry growth and problems associated with...101-SY and other slurry-containing tanks" and to "evaluate possible long-term solutions to Tank 101-SY pressurizations."³⁵ The plan noted that slurry growth studies would continue at Pacific Northwest Laboratories (PNL) and would address waste characterization (using actual and synthetic DSS), gas compositions, and slurry growth control techniques.
- RHO terminated FY 1985 support for analytical work aimed at resolving the problem in tank 101-SY. The second quarterly report of laboratory work for FY 1985 noted that no hydrogen had been detected in tank 101-SY's vapor space and that, "due to higher priority work on another task, the planned pilot plant work will not be done and other laboratory studies have been postponed indefinitely."³⁶
- PNL completed its work, submitting a "Double Shell Slurry Growth Milestone Report" to RHO, on September 27, 1985. The report summarized the results of experiments using actual and synthetic waste that were aimed at determining the influence of temperature, inorganics, and stirring on observed slurry growth. Further studies were recommended to augment what PNL scientists considered

an "insufficient" data base on slurry growth. The report noted that "accurate predictions of the cause and magnitude of the phenomenon are not possible" and that "all previous studies have omitted the effects of radiolytic decomposition on the rate of DSS growth."³⁷

- RHO had budgeted funds to support further analytical work in 1986. An August 1986 summary of the status of slurry growth studies noted that work conducted in 1985 by PNL was discontinued because of "cost and schedule overruns."³⁸ It pointed out that "studies of slurry growth control methods have not been performed." An RHO chemical engineer recommended an FY 1987 program to study methods to control slurry growth, but that work was not pursued.

In 1986, coincident with water and steam lancing, RHO achieved a measure of success in minimizing slurry growth in tank 101-SY. However, this success was short-lived, and laboratory efforts to characterize the waste in 101-SY were not reinitiated until after the problem of 101-SY was made public in 1990.

Finding VI(2): Nitrous oxide can lower the threshold concentration at which hydrogen will burn. Despite current claims by WHC staff that it had only recently recognized the role of nitrous oxide as an oxidizer of hydrogen, a number of former RHO engineers, scientists, and consultants to the tank farms had explicit knowledge of the chemistry of oxidative reactions involving hydrogen and nitrous oxide as early as 1976.

- o In a December 1976 review of hydrogen flammability concerns associated with tank 105-A, a consultant observed that "assuming that the trapped gas is essentially hydrogen, then the introduction of an oxidizing atmosphere (HNO_3 , NO_2 , NO , O_2 , etc.) even in small quantities could cause local ignition under the bulge" of 105-A's steel liner, which had been distended due to steam-induced pressure.³⁹ One of his conclusions was that "if it could be demonstrated that the assumption of oxygen present below the [tank] liner is not a credible one then the penetration through the top could be made [only] if the quantity of oxidizer in the tank is limited." These same considerations would apply to hydrogen and nitrous oxide below the crust of tank 101-SY.
- o In a January 1979 report summarizing results of studies to identify slurry growth gases, a senior RHO chemist noted that the "hydrogen was well above the lower explosive limit in air. Hydrogen combustion can also be supported by N_2O , which was present in significant quantities."⁴⁰
- o A Rockwell engineer who was asked to do a hazards assessment of 101-SY in 1979 calculated the energy release that would result from combustion of hydrogen and nitrous oxide, clearly indicating that he understood the oxidative nature of nitrous oxide in the presence of hydrogen.⁴¹
- o A December 1985 report prepared by an RHO chemist addressed in some detail "hydrogen reactions with various oxidants."⁴² His report cited a 1964 Bureau of Mines report dealing with the flammability of hydrogen in

the presence of oxidants. The report included a table of the lower and upper flammability limits of hydrogen in the presence of nitrous oxide. This report was extensively distributed within RHO, including key tank farms managers and engineers. It was also sent to members of the DOE-RL Waste Management Division staff.

Finding VI(3): Scientific peer review of the contractor's experimental research program that was aimed at understanding slurry growth was allowed to lapse for over a decade.

- o In the early 1970's, ARCO established a Tank Farm Consultants' Panel to provide review of Tank Farm Waste Management issues. Between April 1977 and October 1979, the panel met five times and made repeated recommendations related to hydrogen generation and slurry growth, including the following:
 - 1977--Perform studies of radiolytic decomposition and carry out 101-SY hydrogen analysis;
 - 1978--Hydrogen generation was an "overwhelming" potential hazard and therefore should be investigated;
and
 - 1979--Various experimental approaches should be explored to characterize slurry growth and flammable gas generation.
- o A standing peer review committee was not reestablished at the tank farms until April 1990, when WHC formed a Senior Chemists' Panel in response to an earlier proposal growing out of the Washington State's investigation of potential exothermic reactions in single-shell tanks.

NOTES

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2. C. Delegard, "Program to Determine Hydrogen Evolution from Salt Cakes," internal letter to M. Kupfer, Atlantic Richfield Hanford Company, 8 January 1975.
3. G. Beitel, "Chemical Stability of Salt Cake in the Presence of Organic Materials," report prepared for the U.S. Energy Research and Development Administration, Contract No. E(45-1)-2130, Atlantic Richfield Hanford Company, April 1976.
4. J. Starr, "Progress Report--Liquid Level Cycling Phenomenon," internal letter to M. Smith, Rockwell Hanford Operations, 23 September 1977.
5. M. Smith, "Liquid Level Variation in Storage Tanks," internal letter to J. Deichman, Rockwell Hanford Operations, 2 November 1977.
6. F. Jungfleisch, "Laboratory Proposal for Study of Liquid Level Variation in Tank 241-SY-101," internal letter to J. Deichman, Rockwell Hanford Operations, 18 January 1978.
7. T. Lane, "Synthetic Double Shell Slurry Gas Identification," internal letter to K. Carothers, Rockwell Hanford Operations, 10 November 1978.
8. J. Honeyman, "15th Waste Management Consultants Meeting," internal letter to R. Zinsli, Rockwell Hanford Operations, 8 January 1979.
9. T. Lane, "Synthetic Double Shell Slurry Gas Identification," internal letter to K. Carothers, Rockwell Hanford Operations, 24 January 1979.
10. G. Dukelow, "Hydrogen Generation in Isolated Tanks," internal letter to R. Zinsli, Rockwell Hanford Operations, 22 January 1979.
11. C. Delegard, "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101," Rockwell Hanford Operations, RHO-LD-124, December 1980.
12. L. Gale, "Slurry Growth Occurring in Tanks 101SY, 103SY, 101A, and 101AX," internal letter to D. Wilkins, Rockwell Hanford Operations, 17 February 1981.
13. D. Reynolds, "Some Observations on Predicting Tank Growth," internal letter to D. Wilkins, Rockwell Hanford Operations, 1 May 1981.
14. L. Gale, "Future Slurry Growth Experiments," internal letter to D. Wilkins, Rockwell Hanford Operations, 7 July 1981.
15. T. Lane, "Experiments for Determining Gas Production Relating to Slurry Growth as a Function of Chemical Composition," internal letter to M. Jansky, Rockwell Hanford Operations, 13 August 1981.

16. D. Reynolds, "Double-Shell Slurry Campaign," RHO-CD-1268, Rockwell Hanford Operations, December 1981.
17. M. Jansky, "Gas Production/Slurry Growth Scouting Experiments," internal letter to L. Gale, Rockwell Hanford Operations, 8 January 1982.
18. M. Jansky, "Slurry Growth Experiments," internal letter to L. Gale, Rockwell Hanford Operations, 12 February 1982.
19. M. Rees, "Statistical Analysis Done to Date on the Slurry Growth Experiment," internal letter to L. Gale, Rockwell Hanford Operations, 20 March 1982.
20. M. Jansky, "Statement of Laboratory Data on Gas Generation/Slurry Growth," internal letter to L. Gale, Rockwell Hanford Operations, 5 April 1982.
21. M. Jansky, "Pilot Plant--Slurry Growth Data," internal letter to L. Gale, Rockwell Hanford Operations, 23 July 1982.
22. M. Jansky, "Slurry Growth Studies: Chemical Compositions," internal letter to L. Gale, Rockwell Hanford Operations, 27 July 1982.
23. For example, see J. Womack, Richland Hanford Operations, "High-Level Waste Technology Monthly Reports to Lead Site," monthly report submitted to J. White, U.S. Department of Energy, Richland Operations Office, Contract No. DE-AC06-77RL01030, 14 June 1985.
24. L. Sasaki, "Letter on Safety of Double-Shell Slurry Storage," internal letter to D. Ellingson, Rockwell Hanford Operations, 7 October 1983.
25. D. Reynolds, "Letter from Ellingson on safety of DSS," internal letter to K. Carothers, Rockwell Hanford Operations, undated (October 1983).
26. L. Sasaki, "Gas Sampling and Analysis of Tank 101-SY," internal letter to K. Carothers, Rockwell Hanford Operations, 18 October 1983.
27. J. Albaugh, "Slurry Growth," internal letter to D. Wilkens, Rockwell Hanford Operations, 7 November 1983.
28. M. Jansky, "Composition of Gases Generated During Slurry Growth," internal letter to L. Sasaki, Rockwell Hanford Operations, 22 November 1983.
29. M. Jansky, "Extensive Analyses of Hanford Wastes: Double Shell Slurry and Customer Waste," internal letter to J. Goldin, Rockwell Hanford Operations, 12 January 1984.
30. M. Jansky, minutes of meeting on "Thermal Destruction of Complexants," Rockwell Hanford Operations, 1 March 1984.
31. M. Jansky and B. Meissner, "Thermal Destruction of Complexants," internal letter to L. Sasaki, Rockwell Hanford Operations, 29 June 1984.

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33. W. Robertson, "Slurry Growth Scale-Up Results," Rockwell Hanford Operations, SD-WM-TRP-006, 28 August 1984.
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35. L. Sasaki, "Technology Program Plan for Slurry Growth, Fiscal Year 1985," Rockwell Hanford Operations, SD-WM-TPP-007, 21 December 1984.
36. L. Sasaki, "Fiscal Year 1985 Second Quarterly Report on Slurry Growth," internal letter to K. Carothers, Rockwell Hanford Operations, 18 April 1985.
37. M. Hanson, Pacific Northwest Laboratories, "Double Shell Slurry Growth Milestone Report," letter to G. Beitel, Rockwell Hanford Operations, 27 September 1985.
38. L. Sasaki, "Slurry Growth Status and Recommendations," internal letter to J. Womack, Rockwell Hanford Operations, 26 August 1986.
39. C. Grelecki, Hazard Research Corporation, letter to C. Walker, Atlantic Richfield Hanford Company, 21 December 1976.
40. T. Lane, "Synthetic Double Shell Slurry Gas Identification," internal letter to K. Carothers, Rockwell Hanford Operations, 24 January 1979.
41. L. Vanselow, handwritten calculations, Rockwell Hanford Operations, undated (found in 1979 files).
42. J. Henrie and D. Flesher, "Hydrogen Control in the Handling, Shipping and Storage of Wet Radioactive Waste," Rockwell Hanford Operations, December 1985.

Another view of the contents of tank 101-SY. The riser on the right is used for the manual tape level indication. A previously used tape was inadvertently dropped into the tank and is visible on the crust surface. (False color photograph)

Double-shell tanks under construction.

SY Tank Farm annulus ventilation filter unit. Extensive damage to insulation from filter changing operations and weather.

Junction box in SY Tank Farm damaged by mobile crane.

Tank 103-SY primary exhaust duct isolation valve inoperable due to settlement of supports. Taped and covered to limit spread of contamination.

SY Tank Farm instrument panel showing damaged thermocouple instrument cable for tank 101-SY.

Connection tubing for the 101-SY hydrogen analyzer, showing use of duct tape to seal the tubing to the primary exhaust duct. The NS-EH team originally found it unsealed.

The 101-SY pump pit—confinement boundary for the primary tank—showing damage to the concrete structure. Partially sealed with duct tape to control leakage.

Top view—concrete pump pit on 101-SY. Cover block partially sealed with duct tape.

Tank 102-SY specific gravity instrument enclosure. Severe deterioration from steam leak over an extended period of time. Currently inoperable

APPENDIX A:
CONDUCT OF THE INVESTIGATION

The Offices of Nuclear Safety (NS) and Environment, Safety, and Health (EH) of the U.S. Department of Energy began this investigation on April 10, 1990, when members of the NS team assembled in Richland, Washington. During the first phase of the investigation, the team attended briefings given by DOE-RL and contractor personnel, conducted preliminary interviews and began to collect and analyze relevant documents.

In succeeding weeks, based upon the results of the preliminary shape of the investigation, the team was able to identify more precisely the major and subsidiary issues that required additional fact-gathering and analysis. More comprehensive interviews and document searches were conducted in an attempt to resolve those issues.

By May 18, 1990, when the field investigation ended, the team had gathered approximately 2,000 documents and had interviewed over 100 individuals. Most of those interviewed were current or former employees of DOE-RL or one of the contractor organizations. Extensive notes were taken of these interviews, and many witnesses were contacted two or more times for the purpose of clarifying statements or obtaining additional information.

The members of the NS team are:

S. Blush	Director, Office of Nuclear Safety
F. Anderson	Nuclear Engineer, Office of Nuclear Safety
H. Anderson	Attorney, Stier, Anderson & Malone, Consultant to the Office of Nuclear Safety
C. Burger	Nuclear Engineer, Office of Nuclear Safety
J. Fitzgerald	Director, Performance Assessment Division, Office of Nuclear Safety
D. Hagerty	Staff Assistant to the Director, Office of Nuclear Safety (detailed from Lawrence Livermore National Laboratory)
T. Heitman	Special Assistant to the Director, Office of Nuclear Safety
M. Hillman	Nuclear Engineer, Office of Nuclear Safety
J. Keating	Program Support Specialist, Office of Nuclear Safety
D. Ruscitto	Senior Resident Inspector at Richland, Office of Environment, Safety, and Health
J. Stefano	Deputy Director, Division of Resident Programs, Office of Environment, Safety, and Health

APPENDIX B:

EXCHANGE OF LETTERS BETWEEN SECRETARY WATKINS
AND GOVERNOR BOOTH GARDNER

STATE OF WASHINGTON
OFFICE OF THE GOVERNOR

OLYMPIA
88504-0413

BOOTH GARDNER
GOVERNOR

March 27, 1990

Admiral James D. Watkins (Retired)
Secretary of Energy
1000 Independence Avenue
Washington, D.C. 20585

Dear Jim:

Last Friday, Department of Energy officials at Richland announced that hydrogen buildup in the Hanford waste tanks was potentially explosive. This is the second time in six months Washington citizens have had to consider the potential for explosion in waste storage tanks. This incident is only the latest in a series of revelations about safety and health risks at Hanford. I am troubled that safety concerns frequently appear to be revealed only after they are raised by independent reviewers.

This pattern undercuts the progress we have made at Hanford. It stymies our efforts to resolve nuclear waste issues. It jeopardizes our emphasis on new research and development activities on the site. It impedes our effort to attract people and businesses into adjacent communities. And it is deadly to the credibility of the Department of Energy.

Your call for a cultural change emphasizing safety and candid behavior in the Department of Energy has not reached all levels of the agency at Hanford. It appears that upper level management is far more attentive to these concerns than those farther down the organization. We need to heighten the sensitivity of Hanford staff and contractors to health and safety concerns. The alternative is to leave the public perpetually alarmed about Hanford.

What we need is really very simple. We need to know all there is to know about Hanford problems. We need to be assured that the Department of Energy is vigorously pursuing all leads regarding potential safety and health problems. We need concurrent analysis and assessment by outside parties, including the state. We need a cooperative means of communicating about these sensitive health and environmental issues with the public.

Secretary James D. Watkins
March 27, 1990
Page 2

Now is the time for some intercession on your part. I am requesting that you take the following actions:

- Immediately take the steps necessary to mitigate any danger from tank explosion at Hanford, including committing the necessary additional resources. The additional funds needed for this effort should not come at the expense of the cleanup effort now underway.
- Conduct a thorough, independent, and public review of the procedures, as well as the management structure, for handling health and safety issues at Hanford.
- To assure that all potential dangers are brought forward in a timely, coordinated, and responsive way, create a communication and decision structure of Hanford and non-Hanford people to accomplish the following: (1) technical evaluation of health and safety risks; (2) policy evaluation; and (3) coordinated dissemination of public information.

Involving the State of Washington more actively in these issues would greatly improve the way the Department of Energy conducts its business at Hanford, and would help deal with the issue before us.

I appreciate your personal attention to this matter.

Sincerely,

A handwritten signature in dark ink, appearing to read 'Booth Gardner', with a horizontal line extending from the end of the signature.

Booth Gardner
Governor

cc: Washington Congressional Delegation
Mike Lawrence

The Secretary of Energy
Washington, DC 20585

April 2, 1990

The Honorable Booth Gardner
Governor
State of Washington
Olympia, Washington 98606-0413

Dear Governor ^{Booth} Gardner:

I believe you realize how hard we have been working within the Department to change the manner in which we deal with States and the public. Given this effort, it is especially regrettable that we did not do a better job of coordinating last Friday's announcement on gas generation in a Hanford high-level waste storage tank. We were anxious to inform the public as soon as we realized that we had a potentially serious problem to address.

Before making the announcement, however, we contacted the Director of the Washington Department of Ecology and your personal representative on Tri-City issues. We assumed -- incorrectly, it would appear -- that you had already been advised of the situation since the head of the State review group investigating the presence of ferrocyanide in Hanford high-level waste tanks had been present at a briefing we conducted on hydrogen buildup in Hanford waste tanks three days prior to our public announcement.

The lack of specific answers on the risk and potential impact of gas buildup in the Hanford storage tanks is frustrating. As you know, we have studied gas buildup in these tanks for many years and an attempt was made to address a maximum credible accident in our 1986 Safety Analysis Report on double-shell tanks. Since that report analyzed hydrogen buildup in the vapor space, but not in the waste salts, we need to revise our documentation to address this concern.

I have identified a group of experts to help me assess whether there really is a problem in the double-shell tank in question. I have also directed that we reassess whether this situation could occur within waste storage tanks at the Savannah River Site. We do not fully understand why hydrogen gas is being generated, and I am taking immediate action to develop those answers. We will work with your staff every step of the way.

I believe we have taken all the steps available at this time to mitigate any danger from a tank explosion at Hanford. In addition, I have directed the Office of Environment, Safety, and Health and the Office of Nuclear Safety to form an independent

investigative team to provide me with an interim evaluation of the management structure for handling information concerning gas generation in the Hanford waste tanks. A broader review of Hanford safety procedures and management structure for handling health and safety concerns will be conducted in May, when my "tiger team" arrives. State officials will be asked to observe this assessment of environment, safety, and health activities at Hanford.

I have directed that the Department do whatever is needed to identify problems early on and then develop aggressive work plans and schedules to resolve them. Due to the nature of the problems we are finding, there will be occasions when we have to inform the public of our findings promptly. More can be done to coordinate these announcements better with State and community officials, and I agree that we must do a better job in the future. I am convinced that the best way to avoid confusion in the future is for your staff to establish a permanent presence in Richland to monitor our efforts first-hand. I am encouraged to hear that you are considering this, and I promise to do my part by expediting as best I can the processing of security clearances for your staff. I believe this is the most productive "next step" in our joint efforts to improve environmental monitoring and waste management operations at Hanford.

The Department is continuing to pursue improvements leading to excellence in its waste management operations. The full cooperation and openness of personnel at the Hanford Reservation is an indication of how I want all employees to conduct themselves. I regret that we did not do the best job coordinating last Friday's announcement, but intend to use this lesson well-learned to improve our relationship in the future.

Sincerely,

James D. Watkins
Admiral, U.S. Navy (Retired)

cc:
Senator Brock Adams
United States Senate
Washington, D.C. 20510

Senator Slade Gorton
United States Senate
Washington, D.C. 20510

Honorable Sid Morrison
House of Representatives
Washington, D.C. 20515

APPENDIX C:

KEY DOCUMENTS*

Dukelow, G. "Request for Vapor Space Air Sampling in Selected UGS Tanks." Internal letter to D. Washenfelder. Rockwell Hanford Operations. November 17, 1978.

Vanselow, L. Handwritten calculations. Rockwell Hanford Operations. Undated (found in 1979 files).

Lane, T. "Synthetic Double-Shell Slurry Gas Identification." Internal letter to K. Carothers. Rockwell Hanford Operations. January 24, 1979.

Dukelow, G. "Hydrogen Gas Evaluation in Underground Storage Tanks." Internal letter to C. Carter. Rockwell Hanford Operations. April 20, 1979.

Ehli, T. "Hydrogen Concentration Process Specifications Basis." Internal letter to TFPC File. Rockwell Hanford Operations. March 25, 1980.

Delegard, C. "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101." Rockwell Hanford Operations, RHO-LD-124. December 1980.

Van Tuyl, H. "Potential for Exothermic Chemical Reactions in Waste Tanks." Report for Pacific Northwest Laboratories. February 3, 1983.

Reynolds, D. "Letter from Ellingson on safety of DSS." Internal letter to K. Carothers. Rockwell Hanford Operations. Undated (October 1983).

*All contractor files related to the operation of the Hanford Tank Farm are maintained by the current operating contractors in Richland, Washington.

Albaugh, J. "101-SY Tank Pressurization Prevention." Internal letter to Distribution. Rockwell Hanford Operations. July 13, 1984.

Bell, N. "Short-Term Solution of Tank 101-SY Pressurization Problem." Internal letter to distribution. Rockwell Hanford Operations. July 23, 1984.

Bell, N. "Long-Term Recommendations of the Task Force on Pressurization of Tank 101-SY." Internal letter to distribution. Rockwell Hanford Operations. August 13, 1984.

Burger, L. "Complexant Stability Investigation Task 1--Ferrocyanide." Pacific Northwest Laboratories. November 1984.

Dickman, J. "Double-Shell Tank Pressurization." Internal letter to G. Dukelow and W. Heine. Rockwell Hanford Operations. January 9, 1985.

Shupe, M. Handwritten memorandum to J. White and J. Krupar. U.S. Department of Energy, Richland Operations Office. May 18, 1985.

White, J. Handwritten memorandum to J. McElroy. Pacific Northwest Laboratories. Undated (between May 18 and May 29, 1985).

Pride, E. Handwritten memorandum. Rockwell Hanford Operations. May 24, 1985.

McElroy, J. Handwritten memorandum to R. Liikala. Pacific Northwest Laboratories. May 29, 1985.

Sasaki, L. "Results of Hydrogen Monitoring in Tank 101-SY." Internal letter to K. Carothers. Rockwell Hanford Operations. September 16, 1985.

Hanson, M. "Cyanide Analysis in TY Tank Farm Samples." Letter to R. Wojtasek. Pacific Northwest Laboratories. December 23, 1985.

Fein, K. "Tank 101-SY Slurry Growth." Internal memorandum to D. Baide. Westinghouse Hanford Company. October 25, 1988.

Brush, P. U.S. Department of Energy, Office of Environment, Safety, and Health. "Special Report: Office of Environment, Safety and Health Review of Hanford Tank Farm Flammable Gas Issues." Attachment to Transmittal Letter to S. Blush. U.S. Department of Energy, Office of Nuclear Safety. June 6, 1990.

Internal Letter

Rockwell International

Date November 17, 1978

60411-78-

TO (Name, Organization, Internal Address)
D. J. Washenfelter
Tank Farm Operations
2750-E/200 East

FROM: (Name, Organization, Internal Address, Phone)
G. T. Dukelew
Tank Farm Process Engr'g
2750-E/200 East
Ext. 211

Subject Request for Vapor Space Air Sampling in Selected UGS Tanks

Ref: (a) SOP 200.1.25.2, "H₂ Analysis Using Vacuum Pump and Redundant Systems"

(b) Letter, November 10, 1978, T. A. Lane to K. G. Carothers, "Synthetic Double Shell Slurry Gas Identification"

It is requested that Tank Farm Operations (TFO) schedule testing of vapor space air in the tanks listed below per SOP 200.1.25.2 [Reference (a)] and prior to December 20. The process equipment to be used in conjunction with this procedure is mounted on a plywood panel stored in Building 801-C (Ref. H. L. Winters, 942-2820).

TK-101-SY	TK-102-SX	TK-101-AX
TK-102-SY	TK-103-SX	TK-101-A
TK-103-SY	TK-104-SX	
	TK-105-SX	

Note: SOP 200.1.25 has been voided and only the Reference (a) procedure is now applicable.

The tanks listed above have received evaporator-crystallizer slurry of the type described in Reference (b), which states results of a laboratory test undertaken by the Chemical Sciences Group to determine the cause for increasing surface levels in TK-101-SY. Here, synthetic DSS feed was processed per the evaporator flowsheet to produce a simulated TK-101-SY slurry. The pot was sealed after evaporation and held in a controlled temperature bath for a period of sixty days, and the contained gas was then sampled for mass spectrographic analysis. The test results indicated carbon dioxide and hydrogen concentration of 0.29 and 4.2 volume percent respectively. The conclusion stated by the Chemical Science Group was that the surface level rise noted in TK-101-SY was due to gas entrapped within the slurry.

Reference Doc

Ignored N2O

D. J. Washenfelter
Page 2
November 17, 1978

Because the reported level for hydrogen exceeded both the 1601 Section J Specification and Standards limits (and was, in fact, within the explosive range), Tank Farm Process Engineering (TFPE) has concluded that the vapor spaces in tanks containing material of this type should be periodically checked regardless of the fact that they are connected to operating exhausters.

The Reference (a) procedure was developed for application in conjunction with the Tank 105-A bulge penetration program, and was based upon requirements stated by outside consultants having expertise in the area of hydrogen hazards. Minor revisions are being made to render it suitable for general use. However, it can be used as now issued if a PDA is attached to state these minor changes.

G. T. Dukelow, Manager
Tank Farm Process Engr'g

GTD/CMW/db

cc:

H₂ ; H₂O REACTION

8% H₂ - CAPACITY FILLED

$$\text{VOLUME H}_2: 3636 \text{ FT}^3 \quad 0.08(45446) = 3636 \text{ FT}^3$$

$$\text{VOLUME N}_2\text{O}: 3636 \text{ FT}^3 \quad 0.08(45446) = 3636 \text{ FT}^3$$

$$~~45446 - 3636 \times 2 = 38174 \text{ FT}^3~~$$

$$45446 - 2(3636) \text{ FT}^3 = 38174 \text{ FT}^3 \quad (\text{ASSUME THIS IS ALL AIR})$$

$$\text{H}_2 \text{ VOLUME} : 0.08(38174) = 30539 \text{ FT}^3$$

$$\text{O}_2 \text{ VOLUME} : 0.20(38174) = 7635 \text{ FT}^3$$

$$\frac{\eta}{V} = 1.09 \frac{\text{gmole}}{\text{FT}^3}$$

$$\text{H}_2: 3636 (1.09) = 3963 \text{ gmoles}$$

$$\text{N}_2\text{O}: 3636 (1.09) = 3963 \text{ gmoles}$$

$$\text{H}_2: 30539 (1.09) = 33288 \text{ gmoles}$$

$$\text{O}_2: 7635 (1.09) = 8322 \text{ gmoles.}$$

$$\Delta H_r = \Delta H_f (\text{PROD}) - \Delta H_f (\text{REACTANTS})$$

$$\Delta H_r = 3963 \left(\overset{-57.8}{\cancel{19.55}} \text{ Kcal} \right) - [3963 (19.55)] = -3.07 \times 10^5 \text{ Kcal}$$

$$Q = MC_v \Delta T$$

C_v

ELEMENT

$$6.1 \text{ cal/gmole}^\circ\text{K}$$

N₂

$$8.7 \text{ cal/gmole}^\circ\text{K}$$

H₂O

$$6.4 \text{ cal/gmole}^\circ\text{K}$$

O₂

$$3.07 \times 10^8 \text{ CAL} = 3963 \text{ gmols} \left(\frac{8.1 \text{ cal}}{\text{gmole}^\circ\text{K}} \right) \Delta T + 8322 \text{ gmols} \left(\frac{6.4 \text{ cal}}{\text{gmole}^\circ\text{K}} \right) \Delta T + 37251 \text{ gmols} \left(\frac{6.1 \text{ cal}}{\text{gmole}^\circ\text{K}} \right) \Delta T$$

$$3.07 \times 10^8 = 314970 \Delta T \quad \Delta T = 975^\circ\text{K} \quad T_f = 316.33 + 975 = 1291^\circ\text{K}$$

$$\frac{37251 + 8322 + 3963}{453.6} = 109 \text{ lbmoles}$$

$$P = 109 \text{ lbmoles} \left(\frac{1.314 \text{ ATM ft}^3}{\text{lbmole}^\circ\text{K}} \right) \frac{1291^\circ\text{K}}{45496 \text{ ft}^3} = 4.07 \text{ ATM}$$

LANE 1979-JAN

Rockwell International

Internal Letter

Date: January 24, 1979

60120-79-012

TO: K. G. Carothers *Left July 1, 1979*
Waste Process Engineering
2750-E, 200 East
2-7811

FROM: T. A. Lane
Chemical Sciences Group
222-S, 200 West
2-1571

Subject: Synthetic Double Shell Slurry Gas Identification

Ref: (A) Letter, November 10, 1978, T. A. Lane to K. G. Carothers, Same Subject

(B) Monthly Report, June, 1978, T. A. Lane

(C) Letter, January 18, 1978, F. M. Jungfleisch to J. L. Deichman, "Laboratory Proposal for Study of Liquid Level Variation in Tank 241-SY-101"

A rise in the surface level of the Double Shell Slurry (DSS) in Tank 101-SY has been observed. Experiments to model the growth using synthetic feed have been completed. The results, reported in Reference B, showed the growth could be modeled with cold synthetic material. They also showed the rise was due to gas being trapped in the slurry. Based on this information, an experiment was designed to identify the gas(es) causing the rise. Preliminary results, reported in Reference A, indicated the gas was high in hydrogen.

A quantitative experiment to determine the amount of hydrogen present, as well as other gases, has been completed. The gas from this experiment has been analyzed by mass spectroscopy. The analysis shows it contains 12 percent hydrogen, which is well above the lower explosive level (4 percent hydrogen). Nitrogen compounds, which will support hydrogen combustion, N_2O were also identified. The full gas analysis is shown in Table I. Details of the gas identification experiment are presented below.

A synthetic feed of the composition shown in Table II was prepared. The feed was reduced 25 volume percent at 70 torr following the evaporator flowsheet. The evaporator pot was then removed from the rest of the evaporator system, sealed, reevacuated to 70 torr, and placed in a constant temperature bath at 70° C. A gas sample was removed 47 days later and analyzed by mass spectroscopy. The analysis showed there were several components in the gas (see Table I). The hydrogen was well above the lower explosive limit in air. Hydrogen combustion can also be supported by N_2O , which was present in significant quantities.

RECEIVED
FEB 02 1979
D. G. HARLOW

RECEIVED
JAN 31 1979

Henry Van der
Reference Doc.
11/21/78. Failed to take action for H₂ > 2%.

K. G. Carothers
Page 2
January 24, 1979

Recommended future work includes studies of "salt-complexant" interactions and gas retention mechanisms. A run to verify that the growth phenomenon is not light sensitive will also be run.

Thomas A Lane

T. A. Lane, Advanced Chemist
Waste Chemistry Unit

TAL:jkr

Attachment

Information: H. . Babad
J. S. Buckingham
J. O. Honeyman
F. M. Jungfleisch *FmJ*
D. L. Merrick *←*
M. J. Smith
R. A. Zinsli

Starting Pressure = 70 torr

Ending Pressure = 82 torr

36%
.00032 gmols GAS total
gm in 47 DAYS 250 mL
= ↑ diff growth gas

1 cu ft = 28,317 cc.

21.82 cu ft / 1000' run

617,877 cc max

.00032 gm molar (2471.5)

47 days 21.82 ft³

67909825 gm molar
47 days 21.82 ft³

+ relative to
3.2 E-6 gm molar
3.2 E-6 gm molar

3.2 E-6 gm molar
59.43 days 21.82 ft³

3.2 E-6 gm molar
3.2 E-6 gm molar
3.2 E-6 gm molar

1 gm molar

59.43 days 21.82 ft³

≈ 2.0016 gm

6 gm molar gas
1 gm molar gas

Table I
MASS SPECTROSCOPIC GAS ANALYSIS RESULTS
(Mole Percent)

—CO ₂	< 0.01
Ar	0.40
O ₂	2.39
N ₂	62.8
CO	< 0.10
He	< 0.01
—H ₂	11.8
—CH ₄	< 0.01
—N ₂ O	20.7
—NH ₃	1.89

Table II
SYNTHETIC FEED ANALYSIS

Al ₃ ⁺	1.50 <u>M</u>
OH ⁻	2.50 <u>M</u>
NO ₂ ⁻	2.70 <u>M</u>
NO ₃ ⁻	2.47 <u>M</u>
CO ₃ ²⁻	0.26 <u>M</u>
TOC*	58.8 g/l

*Total Organic Carbon

CC

April 20, 1979

60411-79-0284

. C. R. Carter	. G. T. Dukelow
. Tank Farm Surveillance & Operations	. Tank Farm Process Control
. 2750-E/200 East	. 2750-E/200 East

Hydrogen Gas Evaluation In Underground Storage Tanks

- Ref: (a). Rockwell Hanford Occurrence Report 79-17, February 2, 1979, "TK-103-SY Liquid Level Decrease."
- (b). Letter, January 24, 1979, T. A. Lane to K. G. Carothers, "Synthetic Double-Shell Slurry Gas Identification." ✓

Reference (a) dealt with the sudden decrease in TK-103-SY surface level readings taken at two different locations on February 2, 1979. The significant features of the occurrence were the general subsidence as evidenced by the widely spaced data points (manual and FIC are 45 feet apart), the very short duration of about ten hours as compared with a prior long term increase trend, and the existence of a hard surface crust. The report described the investigations of the tank leak detection systems, which failed to identify any leak mechanism. Also discussed was the possibility that the prior surface level increases and the sudden subsidence were the results of gases generated by radiolytic and organic decomposition, and their entrapment in or below the surface crust. The fact that this TK-103-SY crust had been penetrated by efforts to obtain deep liquid samples on the day preceding the occurrence was discussed.

The occurrence itself is not the concern addressed by this letter. In-stead, the real problem is the possibility that the gaseous release theorized to have caused the liquid level decrease could present a potential explosion hazard, jeopardizing the tank structure and overall system containment. Reference (b) describes tests that were performed to identify and quantify the gases evolved by decomposition of the organic constituents in 242-S Evaporator products. The test material was radiologically cold synthetic Double-Shell Slurry (DSS) based upon TK-101-SY assay data, and having a Total Organic Carbon (TOC) of 58.8 grams per liter. After 25% volume concentration to simulate the evaporator product, the test material was sealed for 47 days and then gas sampled. The mass spectroscopy results indicated 11.8% hydrogen, 1.9% ammonia and 20.7% nitrous oxide. These data, while based upon very high complexant content sample, are considered applicable to all tanks that have received evaporator slurries and have varying quantities of organic constituents. These tanks are listed in the attachment.

Reference Doc.Ignored N₂ORECEIVED
APR 27 1979

DL MERRICK

101-SY 135,000 GALT
 737 WU LIQ
 122 WU SPACE IN 260,000 GALT = 34,760 ft³

$$180 \text{ CFM} = 10,800 \text{ ft}^3/\text{h} = 259,200 \text{ ft}^3/\text{day}$$

C. R. Carter
 Page 2
 April 20, 1979

The implied presence of flammable air-hydrogen/ammonia concentration in the tanks themselves must be tempered by the consideration of certain facts. First, the slurry receivers are connected to vessel ventilation systems which normally provide sufficient dilution air to prevent formation of an explosive mixture. In the case of TK-101-SY where the laboratory data indicated a hydrogen generation rate of 19 ft³/day, the normal air flow rate of 180 cfm is calculated to reduce the H₂ concentration to less than 70 parts H₂ per million parts air. The negative results obtained by gas sample analysis (i.e. no needle deflection for a 0 to 4% H₂ scale range) of the tank's vapor space support the conclusion that no explosive air-hydrogen mixture exists. Similar tests performed on the vapor spaces of TK-102-U, TK-103-U, TK-105-U and TK-106-U, after 121 days without forced exhausting also showed no measureable hydrogen concentrations. The second fact is that the TOC of 58.8 grams per liter is not typical of all tanks. Classifications on the basis of TOC has not been finalized, but preliminary assessments indicate that most of the subject tanks contain material with less than 10 grams per liter TOC. The existence of air-gas mixtures in excess of lower explosion limits is therefore not considered to be a viable probability.

However, the test results do suggest a possibility for flammable gas generation that must be investigated until a data based conclusion of no hazard potential can be developed. The questions to be answered are the following:

1. Do the vessel ventilation systems provide adequate dilution air to the tank vapor spaces to prevent the buildup of explosive mixtures, including the theorized 103-SY gas release situation?
2. What is the nature of the gas(s) entrapped within the surface crust, and can a potentially explosive mixture of air and H₂/NH₃ exist within or at the surface crust that is not detectable by vapor space sampling?
3. Can a critical limit for TOC be assigned on the basis of gas generation rate, and is it possible to predict a point where flammable gas generation by organic phase decomposition would be insignificant when compared to radiolytic decomposition?

C. R. Carter
Page 3
April 20, 1979

The tanks identified in the attachment will be the subject of an investigation designed to provide a basis for evaluation of the gases evolved from evaporator slurry. All tanks that have been in evaporator bottom service are included, regardless of their product designation and the time that they were last used as receivers. The investigation will include the following:

1. Routine vapor space gas analysis per SOP 200.1.25.2, "Hydrogen Analysis Using Vacuum Pump And Redundant Systems." The tanks will be sampled at the frequency denoted in the attachment. Those identified for quarterly analysis are either designated as "High Complexant" material storage tanks or have no capability for measurement of vessel vent air flow rates. The tests will require the installation of special gas sample ports on designated tank risers. However, these fixtures are of simple construction, and can be installed prior to June 1, 1979 if supported by the Surveillance And Maintenance Program Office.
2. The Waste Processing Technology Unit (D. L. Merrick) is presently investigating techniques designed to characterize the gases generated by organic phase decomposition in an actual tank environment. The development effort involves preparation of a process for extracting samples directly from the waste surfaces without interaction of the tank vapor spaces. Tank Farm Process Control will provide assistance as requested. A report of this work is scheduled for issue by September 1, 1979.

G. T. Dukelow

G. T. Dukelow
Tank Farm Process Control

GTD/CIW/meo

att:

cc: J. W. Bailey
G. T. Dukelow
J. H. Garbrick
D. L. Merrick
J. E. Mirabella
R. J. Thompson
C. M. Walker
LB

242-A AND 242-S EVAPORATOR SLURRY RECEIVER TANKS

Group I (1)

Group II (2)

1). Waste designates High Complexant.

2). Vessel Ventilation flow rate cannot be measured.

East Area Tanks

TK-101-A (a) (b)

TK-103-A (b)

TK-101-AX (a) (b)

TK-102-AX (a) (b)

TK-103-AX (a) (b)

TK-101-AZ (b)

TK-102-AZ (b)

West Area Tanks

TK-101-SX (a) (b)

TK-101-SY (a) (b)

TK-103-SY (a) (b)

TK-102-SX (a)

TK-103-SX (b)

TK-104-SX (b)

TK-105-SX (b)

TK-106-SX (b)

TK-106-U (a)

TK-111-U (a)

West Area Tanks

TK-101-S

TK-102-S

TK-106-S

TK-107-S

TK-108-S

TK-109-S

TK-110-S

TK-111-S

TK-112-S

TK-102-U

TK-103-U

TK-105-U

TK-108-U

TK-109-U

Group I: Tank vapor space sample analysis for hydrogen to be scheduled at a quarterly frequency.

Group II: Tank vapor space sample analysis for hydrogen to be scheduled at a semi-annual frequency.

Notes: 1). All tanks shall be sampled by June 1, 1979 per SOP 200.1.25.2.

2). Sampling frequency to be reviewed annually.

Internal Letter

C.H.L.I. MAR 25,
Rockwell International

Date March 25, 1980

No. 65260-80-0898

TO: Name Organization Internal Address
TFPC File

FROM: Name Organization Internal Address Phone
• T. J. Ehli
• Tank Farm Process Control
• 2750-E/200-East
• 942-1149

Subject: Hydrogen Concentration Process Specification Basis

The attachment supports the following limit, which is presented in
RHO-MA-151, Section G, Process Specification 2.1.1.

<u>Variable</u>	<u>Specification Limit</u>
Hydrogen	Maximum: 2 vol %

This limit applies to the primary tank vapor space.

TJ Ehli

T. J. Ehli
Tank Farm Process Control

TJE/ljo

Approved By *G. T. Dukelow* Date 3/24/80
G. T. Dukelow-Manager TFPC

cc: G. T. Dukelow
T. J. Ehli
D. L. Merrick
T. B. Veneziano
LB

Hydrogen Generation Rates

To simplify calculations, it will be assumed that all H₂ generated will remain in the tank (no diffusion out of the tank). This is a conservative assumption due to the fact that H₂ will diffuse out of the tank.

A "worst case" condition of a full tank with material generating 100,000 BTU/hr and complete failure of the HVAC System will be assumed. Maximum heat generation of material to be stored in the AW Tanks is estimated at 100,000 BTU/hr (Reference 1). A full tank will give the minimum volume thus minimum time for reaching the maximum concentration. The following H₂ generation rate equation is taken from Reference 2. Radiolysis of water is assumed to be the predominant mechanism of H₂ generation.

$$\begin{aligned}\text{ft}^3 \text{ H}_2 \text{ evolved/hr} &= (1.26 \times 10^{-5} \frac{\text{ft}^3}{\text{BTU}}) (\text{Heat Generation}) \\ &\quad \text{Rate, BTU/hr} \\ &= 1.26 \text{ ft}^3/\text{hr}\end{aligned}$$

$$\text{Volume of H}_2 \text{ generated per day} = \underline{\underline{30.2 \text{ ft}^3}}$$

There have been several experiments conducted to verify mechanisms and rates of H₂ generation other than water radiolysis. Reference 3 summarizes an experiment which confirms H₂ generation during double shell slurry growth. However, a quantitative H₂ generation rate equation has not been established. Experiments are being conducted to determine the factors which affect H₂ generation. The document to be issued on this subject will be evaluated and incorporated into the annual review. Double shell slurry and concentrated complexant are being studied.

The 30.2 ft³/day H₂ generation rate with no leakage out of the tank is a reasonable worst case condition. This rate is higher than the H₂ generation rates for a concrete material made up of Hanford sludge and for Purex shipping casks (Reference 4). Reference 2 also states that the H₂ generation rate used is higher than encountered under normal conditions.

The maximum liquid level assumed is 1.16 million gallons, or a liquid height of 35' 2". Although at the present time the 1.0 million gallon limit is used, there exists the possibility that the tank will be filled to the 1.16 million gallon mark. This limit was chosen also because it provides a more restrictive analysis (smaller vapor volume). The vapor space above the liquid forms half of an ellipsoid. The 35' 2" height is at the primary tank tangent line.

Ellipsoid: Major semiaxis = 37.5 ft = a

Minor semiaxis = 11.6 ft = b

$$\begin{aligned}\text{Volume} &= \frac{4}{3} \pi a^2 b \\ &= 68,330 \text{ ft}^3\end{aligned}$$

$$\text{Vapor Space Volume} = \frac{1}{2} \text{ Ellipsoid Vol.} = \underline{\underline{34,165 \text{ ft}^3}}$$

Reference 5 states that the lower flammability limit for H_2 is 4% concentration. Incorporating a safety factor, the tanks will be checked before the H_2 concentration reaches 2% per Standard Operating Procedure TO-080-240.

A H_2 concentration of 2% in the tank vapor space would amount to:

$$0.02 \times (34,165 \text{ ft}^3) = 683 \text{ ft}^3 H_2$$

NOTE: The calculations are for a tank generating 100,000 BTU/hr.

If the exhauster for the primary tank becomes inoperative, H_2 sampling should be done according to the following schedule (gives worst case situation):

$$683 \text{ ft}^3 H_2 / 30.2 \frac{\text{ft}^3 H_2}{\text{day}} = 23 \text{ days}$$

The tanks should be sampled if the exhauster has been inoperative for twenty-three (23) consecutive days. Additional sampling should be conducted once every twenty-three (23) days if the exhauster continues to be inoperative.

The high diffusion rate of H_2 ensures equal mixing within the tank. Therefore, a sample taken at any point in the vapor space would represent the condition of the entire vapor space.

If the heat generation rate of the tank is not 100,00 BTU/hr or the vapor space volume is greater than 34,165 ft^3 , the sampling schedule can be calculated with the equation mentioned previously.

The 2% H_2 limit was set to provide adequate lead time (3 weeks) to prepare for sampling. Three weeks will also be available to implement emergency procedures, if H_2 is found in the tanks, before the concentration reaches 4%. The lead time for emergency procedures is calculated for a heat generation rate of 100,000 BTU/hr. It should be noted that no H_2 has yet been detected in the tanks with the existing sampling equipment (lower detection limit of 1000 ppm or 0.1%).

References

- 1) ARH-CD-362, June 1975, K. H. Tanaka, "Functional Design Criteria-Additional High Level Waste Storage Facilities"
- 2) ARH-CD-267, February 1975, J. S. Garfield. "Maximum Anticipated H₂ Concentration In Underground Tank Atmosphere From Radiolysis of H₂O"
- 3) Letter, January 24, 1979, T. A. Lane to K. G. Carothers. "Synthetic Double Shell Slurry Gas Identification"
- 4) Letter, January 22, 1979, G. T. Dukelow to R. A. Zinsli, "Hydrogen Generation In Isolated Tanks"
- 5) NBS Technical Note 690, October 1976, J. Hord, "Is Hydrogen Safe?"

Laboratory Studies of Complexed Waste Slurry Volume Growth In Tank 241-SY-101

Calvin Delegard
Chemical Sciences Group
Research Department

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International

Rockwell Hanford Operations
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Richland, WA 99352

Rockwell International

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PRELIMINARY REPORT

This report contains information of a preliminary nature. It is subject to change and therefore does not represent a final report. It was prepared primarily for internal use within Rockwell Hanford Operations. Any expressed views and opinions are those of the author(s) and not necessarily of the Company.

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RHO-LD-124

LABORATORY STUDIES OF COMPLEXED WASTE SLURRY
VOLUME GROWTH IN TANK 241-SY-101

Calvin Delegard
Chemical Sciences Group
Research Department

December 1980

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International
Rockwell Hanford Operations
Energy Systems Group
Richland, Washington 99352

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INTRODUCTION

In early April 1977, a new Hanford waste tank, 241-SY-101, was put into service. Two batches of Hanford waste slurry were introduced to this tank from concentration of waste liquor by the 242-S evaporator-crystallizer. The first batch showed a steady growth in waste depth, and thus waste volume, of about 0.8% per month. When the second batch was added, the total growth rate remained about 0.8% per month. Analysis of the evaporator feed for the second batch showed it contained significant organic carbon.

Previous laboratory studies were successful in simulating the growth behavior using synthetic waste containing the complexants EDTA and HEDTA* as the sources of the organic carbon.⁽¹⁾ These earlier studies briefly explored the effect of temperature on the reaction rate and noted the reaction's production of H_2 and N_2O .

The objective of the following study was to determine the characteristics of this growth reaction and, if possible, to determine its kinetics and mechanism.

SUMMARY AND CONCLUSIONS

The growth of waste volume in complexant laden Hanford waste slurry was found to be due to gas generation caused by the oxidative degradation of the complexant HEDTA. The complexant EDTA was found to be stable in this slurry. The degradation proceeds according to first order kinetics in both $NaAlO_2$ and HEDTA concentration and requires nitrate and/or nitrite to proceed. The dependence of reaction rate on NaOH concentration goes through a maximum implying the formation of an aluminum-HEDTA-hydroxide intermediate reactive species. The reaction products are an unidentified complexant and several gas species; principally N_2 , N_2O and H_2 . At 120°C HEDTA has a half-life of ~100 hours in simulated Tank 101-SY slurry. The reaction shows an Arrhenius dependence of reaction rate on

* EDTA: ethylenediaminetetraacetic acid, tetrasodium salt.
HEDTA: N-(2-hydroxyethyl) ethylenediaminetriacetic acid, trisodium salt.

temperature in the range 60-120°C implying that the reaction mechanism is unchanged in that span. The Arrhenius activation energy is 24.5 Kcal/mole. The growth rate of the genuine waste in Tank 101-SY is consistent with the rate predicted from the Arrhenius plot.

EXPERIMENTAL

REAGENTS

Synthetic waste slurries were used in these studies. The slurries were made using distilled water, technical grade NaAlO_2 and reagent grade NaOH , NaNO_3 , NaNO_2 , Na_2CO_3 , EDTA and HEDTA.

The synthetic waste slurries were formulated based on the composition of the second batch of Tank 101-SY complexed waste. The concentrations of the complexants in Tank 101-SY were inferred from the total organic carbon (TOC) concentrations of the waste. This is deemed valid as the complexants EDTA and HEDTA are the predominant source of organic carbon in Hanford high-level waste. The mole ratio of HEDTA:EDTA is 2:1 in accordance with B Plant process flowsheets. However, earlier B Plant flowsheets did not call for EDTA and, therefore, other wastes may have higher HEDTA:EDTA ratios.

The composition of the simulated waste slurry used for most of these studies is given in Table 1. The components NaNO_3 , NaNO_2 and Na_2CO_3 comprise the solids in the simulated Tank 101-SY slurry.

TABLE 1. Composition of Simulated Tank 101-Sy Slurry.

Component	Concentration, moles/l
NaAlO_2	2.27
NaOH	3.49
NaNO_2	3.55
NaNO_3	3.89
Na_2CO_3	0.31
EDTA	0.17
HEDTA	0.35

PROCEDURES

The synthetic waste slurries were reacted in 100 ml flasks which were connected, via a three-way stopcock with gas sampling sidearm, to a 100 ml gas measuring buret. To minimize absorption of product gas, the fluid used in the gas measuring buret was saturated aqueous NaClO_4 solution. The flask was held in a thermostatted oil bath at the reaction temperature. The experimental apparatus is diagramed in Figure 1.

RCP8003-16

FIGURE 1. Experimental Apparatus.

At high reaction temperatures (100 or 120°C), reaction progress was followed by measuring the volume of product gas evolved as a function of time. The volume of gas was measured by noting the liquid displacement in the buret. Corrections due to the rapid initial thermal expansion of the reactant slurry and enclosed gas were made. At low reaction rates, corrections due to atmospheric temperature and pressure changes become significant and were also made.

At lower reaction temperatures (60 or 70°C), the slurry entrapped product gases. Reaction progress was followed by measuring the volume of expansion of the slurry caused by the gas production. The slurry volume was followed by using 100 ml reaction flasks having volume calibrated necks (Cassia Flasks).

Gas product samples were taken in evacuated 100 ml gas sampling bulbs through the gas sampling sidearm.

Reaction progress was also followed through analyses of EDTA and HEDTA concentrations in the slurry. For reactions in which gas generation was not followed, the synthetic slurries were reacted in tightly capped glass vials.

The effect of light on the reaction was determined by comparing reaction progress under fluorescent light and dark conditions.

ANALYSES

Reaction progress is expressed as volume expansion (either as evolved gas or slurry expansion through entrapped gas) per unit slurry volume per unit time. Reaction progress is more conveniently expressed as volume percent increase per unit time.

The EDTA and HEDTA concentrations were determined through a high performance liquid chromatographic (HPLC) separation of their ferric iron complexes. The separation was followed by UV absorption and, occasionally, iron atomic absorption spectrometric determination of the respective Fe(III) complexes. This technique also allowed observation of the in-growth of an HEDTA decomposition product.

Analyses of the gaseous products were done by mass spectrometry. The contribution of air to the composition of the gas sample was deducted based on the argon contents of air and the sample.

RESULTS AND DISCUSSION

PARAMETRIC STUDY

A fractional factorial design of experiments was undertaken to determine which components were responsible for the slurry expansion reaction observed in Tank 101-SY. The seven components studied were NaAlO_2 , NaOH , NaNO_3 , NaNO_2 , Na_2CO_3 , EDTA and HEDTA.

A series of 16 experiments were run in accordance with a Plackett-Burman factor matrix. High and low concentration combinations of the various components, values of which are shown in Table 2, were run according to the Plackett-Burman factor matrix given in Table 3. Each of the reactions was run about one week at 100°C . The gas production rate was recorded and a gas sample taken for mass spectrometric analysis for each experiment.

Three experimental responses were used as measures of reaction progress. They were gas production rate, hydrogen production rate and $\text{N}_2:\text{O}_2$ ratio in the product gas. Earlier studies had shown that nitrogen was produced and oxygen consumed in this reaction. Thus, the $\text{N}_2:\text{O}_2$ ratio is a measure of reaction progress.

According to the Plackett-Burman analysis, the factors (components) most responsible for gas production are, in order, NaAlO_2 , NaNO_2 , HEDTA and NaOH . The factors contributing most to H_2 production rate are, in order, NaAlO_2 and NaOH . The factors yielding highest $\text{N}_2:\text{O}_2$ ratio are, in order, NaAlO_2 and NaNO_2 . Unfortunately, none of the factors' effects were statistically significant at the 0.90 significance level in the t-distribution. However, the data were useful in determining on which slurry components further experimentation should be done.

TABLE 2. Factor Concentrations
in Plackett-Burman
Factor Matrix.

Component	Concentration, moles/l	
	+	-
NaAlO ₂	2.27	0
NaOH	3.49	2.0
NaNO ₂	3.55	0
NaNO ₃	3.89	0
Na ₂ CO ₃	0.31	0
EDTA	0.17	0.0067
HEDTA	0.35	0.013

TABLE 3. Plackett-Burman Factor Matrix.

Trial	Component						
	NaOH	NaAlO ₂	NaNO ₂	NaNO ₃	Na ₂ CO ₃	EDTA	HEDTA
1	-	-	-	+	+	+	-
2	+	-	-	-	-	+	+
3	-	+	-	-	+	-	+
4	+	+	-	+	-	-	-
5	-	-	+	+	-	-	+
6	+	-	+	-	+	-	-
7	-	+	+	-	-	+	-
8	+	+	+	+	+	+	+
9	+	+	+	-	-	-	+
10	-	+	+	+	+	-	-
11	+	-	+	+	-	+	-
12	-	-	+	-	+	+	+
13	+	+	-	-	+	+	-
14	-	+	-	+	-	+	+
15	+	-	-	+	+	-	+
16	-	-	-	-	-	-	-

EFFECT OF COMPONENT CONCENTRATIONS

Following the parametric study, studies of the effects of component concentrations on reaction rates, as measured by gas generation, were begun. To study the effects of component concentrations on reaction rate, the concentration of the component of interest was varied while the concentrations of the remaining components were held constant. The reaction rates were noted as a function of component concentration. The components studied in this manner were NaAlO_2 , NaOH and NaNO_2 . Sodium nitrate was also studied when experiments showed that the reaction proceeded in the absence of NaNO_2 . Initial reaction rates were used in this study to eliminate possible interferences due to interactions of products or reaction intermediates as well as effects due to decreasing reactant concentrations. Values for the initial rates at various initial concentrations are given in Table 4.

The kinetic reaction orders for EDTA and HEDTA were determined by isolation. That is, the concentrations of the other reaction components (NaAlO_2 , NaOH , NaNO_2 and NaNO_3) were kept high, and therefore constant as the reaction progressed, relative to the complexant concentrations. This is the condition found for Tank 101-SY slurry. The change in complexant concentration with respect to time was then determined.

The plot of the natural logarithm, $\ln$, of the initial gas generation rate versus $\ln[\text{NaAlO}_2]$ gives a straight line with slope 0.91 (Figure 2). The reaction rate, therefore, depends linearly on the NaAlO_2 concentration. The reaction does not proceed, either through gas generation or decomposition of complexant, in the absence of NaAlO_2 .

The effect of NaOH concentration on initial gas generation rate is more complex (Figure 3). The initial gas generation rate increases linearly with NaOH concentration to about 1.5M NaOH . At NaOH concentrations $>1.5\text{M}$, the rate decreases with increasing NaOH concentration. The significance of this maximum in reaction rate with changing NaOH concentration will be discussed in the section on the proposed reaction mechanism.

TABLE 4. Initial Reaction Rates, 120°C.

Component ^a	Concentration, moles/l	Initial Reaction Rate, Percent Volume Increase/Hour
NaAlO ₂ ^b	2.27	1.09, 1.14
NaAlO ₂	1.13	0.66
NaAlO ₂	0.57	0.40
NaAlO ₂	0.28	0.153
NaAlO ₂	0	0
NaOH ^b	3.49	1.09, 1.14
NaOH	2.87	1.49
NaOH	2.26	2.12
NaOH	1.38	2.30
NaOH	1.02	1.85
NaOH	0.51	0.80
NaNO ₂ ^b	3.55	1.09, 1.14
NaNO ₂	1.78	1.00
NaNO ₂	0.89	0.83
NaNO ₂	0.44	0.91
NaNO ₂	0	0.39
NaNO ₃ ^b	3.89	1.09, 1.14
NaNO ₃	0	2.31
NaNO ₂ /NaNO ₃ ^b	3.55/3.89	1.09, 1.14
NaNO ₂ /NaNO ₃	0/0	0

^aThe concentrations of the other components are as stated in Table 1. Slurry volume = 100 ml.

^bSimulated Tank 101-SY slurry, Table 1.

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FIGURE 2. Reaction Order for NaAlO₂.

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FIGURE 3. Dependence of Initial Reaction Rate on [NaOH].

The effects of NaNO_2 and NaNO_3 concentrations on the gas generation reaction rate are not easily assessed since, for the Tank 101-SY slurry, these components exceed saturation. Varying the NaNO_2 concentration from about 0.5 to 3.5M had little effect on the gas production reaction rate (Figure 4). However, even at zero NaNO_2 concentration, the reaction as measured by gas generation and complexant decomposition proceeded. These rates were, however, slower than the rates found when both NaNO_2 and NaNO_3 were present.

FIGURE 4. Dependence of Initial Reaction Rate on $[\text{NaNO}_2]$.

Gas generation and complexant decomposition also occurred in the absence of NaNO_3 , provided NaNO_2 was present. In fact, these two measures of reaction progress proceeded at higher rates than occurred when both NaNO_3 and NaNO_2 were present. Presumably this was due to increased dissolution of the solid NaNO_2 in the reactant slurry.

Neither gas generation nor complexant decomposition occurred to a significant extent when both NaNO_2 and NaNO_3 were absent. Other experiments showed that both small amounts of N_2O and H_2 were generated and slight evidence of complexant decomposition occurred in nitrate and nitrite-free simulated Tank 101-SY slurry. Nitrate and nitrite ions, when present, are chemically consumed in this reaction.

Plots of $\ln$ (fraction EDTA remaining) and $\ln$ (fraction HEDTA remaining) versus time are linear for reactions in which these species are kinetically isolated, that is, at low concentration with respect to other reactant components (Figure 5). First order kinetics are observed for HEDTA decomposition with a half-life, $t_{1/2}$, of about 100 hours at 120°C for synthetic Tank 101-SY slurry. The complexant EDTA does not measurably react in these conditions.

FIGURE 5. Logarithm Fraction Complexant Remaining Versus Time.

Use of high performance liquid chromatography complexant analysis allowed observation of the in-growth of an HEDTA decomposition product. The plot of $\ln[(P_{\infty} - P_t)/P_{\infty}]$ versus time (where P_t = product absorbance at time, t , and P_{∞} = product absorbance at infinite time) is also linear and coincides closely with the HEDTA decomposition plot (Figure 6). Thus, the HEDTA decomposition product is relatively stable and grows in directly from HEDTA according to first order kinetics. The HEDTA decomposition product complexes Fe(III) as shown by its atomic absorption signal.

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FIGURE 6. Logarithm (Fraction HEDTA Remaining) and Logarithm $[(P_\infty - P_t)/P_\infty]$ Versus Time.

The location of the product peak in the chromatogram coincides with a trace impurity peak found in unreacted reagent HEDTA. The impurity is most likely N-(2-hydroxyethyl) ethylenediaminediacetic acid, disodium salt (HEDDA). That the HEDTA decomposition product is HEDDA has not yet been confirmed. However, chromatograms of other possible decomposition products; acetic acid, glycolic acid ($\text{HOCH}_2\text{CO}_2\text{H}$), ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), iminodiacetic acid $[\text{HN}(\text{CH}_2\text{CO}_2\text{H})_2]$, N-(2-hydroxyethyl) iminodiacetic acid $[\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]$ and nitrilotriacetic acid $[\text{N}(\text{CH}_2\text{CO}_2\text{H})_3]$; have shown that the decomposition product is not one of these compounds. The HEDTA impurity, HEDDA, is not commercially available in separated form.

EFFECT OF LIGHT

Additional kinetic experiments were conducted in the absence of light. These experiments, using simulated Tank 101-SY slurry, generated gas and decomposed HEDTA at essentially the same rate as the experiments conducted in light (see Figure 6). Photon induced free radical reaction pathways are therefore not significant for this reaction.

EFFECT OF TEMPERATURE

The effect of temperature on the reaction rate as measured by gas generation was determined at 60, 70, 100 and 120°C using simulated Tank 101-SY slurry. The initial gas generation reaction rates found at each temperature are given in Table 5.

TABLE 5. Effect of Temperature
on Initial Reaction Rate.

Temperature, °C	Initial Reaction Rate, Volume Percent Increase/Month
55 ^a	1.2
60	2.5, 3.15
70	11.6
100	215
120	798, 814

^aRate observed in Tank 101-SY for second layer of complexed waste slurry, corrected to atmospheric pressure.

A plot of $\ln$ rate versus $1/T$, $^{\circ}\text{K}^{-1}$, gives a straight line (Figure 7). The slope of this line was obtained by a least squares fit of the data points. The Arrhenius activation energy calculated from this slope is 24.5 kcal/mole. The linearity of the Arrhenius plot implies that the reaction mechanism does not change in the temperature range studied.

The expansion rate of the second layer of the genuine Tank 101-SY material in the tank is also presented in Table 5 and Figure 7. This rate was derived from surface level measurements and is thus a measure of the physical expansion of the slurry. The rate as shown has been corrected for hydrostatic pressurization of the product gas lying under the slurry surface as well as expansion of the first layer of slurry. As seen in Figure 6, the reaction rate for the Tank 101-SY slurry is consistent with the laboratory derived rate data.

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FIGURE 7. Arrhenius Plot for Reaction.

GASEOUS DECOMPOSITION PRODUCTS

The identity and quantity of the gaseous decomposition products are shown in Table 6 for three simulated waste slurries. For simulated Tank 101-SY slurry, the principle gaseous products are N_2 and N_2O . Oxygen gas is consumed in this reaction. A similar slurry, but lacking $NaNO_3$, produced a similar distribution of products but did not consume O_2 . A simulated Tank 101-SY slurry containing no $NaNO_2$, however, produced primarily H_2 and did not consume O_2 .

PROPOSED REACTION SEQUENCE

The presence of a maximum in the reaction rate as a function of NaOH concentration, taken with the first order reaction kinetics of $NaAlO_2$ and HEDTA, suggest the formation of a specific hydroxide substituted aluminum-HEDTA complex as the reactive species.

TABLE 6. Product Gas Compositions.

Product Gas Component	Gas Concentration, Mole Percent		
	Sim. Tank 101-SY	Tank 101-SY NaNO ₃ Withheld	Tank 101-SY NaNO ₂ Withheld
N ₂ O	56.5	47.5	13.8
N ₂	19.2	41.1	2.0
CO	11.4	-	-
H ₂	4.8	11.2	84.0
CO ₂	3.3	-	-
CH ₄	2.3	-	-
NH ₃	2.0	-	-
NO _x	0.4	0.28	0.15
Relative Amount O ₂ Consumed ²	7.4	0.22	0.55

A series of hydroxide coordinated aluminum HEDTA complexes have been studied and their formation constants evaluated.⁽²⁾ The simple (Al HEDTA) complex is found between pH 2.2 and 4.8. The dominant species found between pH 4.9 and 9.1 is (Al HEDTA OH)⁻. Above pH 9.2 and to at least pH 10, the species [Al HEDTA (OH)₂]²⁻ becomes dominant. No data for aluminum HEDTA species above pH 10 were found in the literature.

However, analogous iron (III) HEDTA hydroxide complexes have been studied.⁽³⁾ The [Fe HEDTA] complex is found below pH 3.8. The complex [Fe HEDTA OH]⁻ prevails from pH 3.9 to 9.0. From pH 9.1 to 10.2, the species [Fe HEDTA (OH)₂]²⁻ is dominant. Above pH 10.3 and to at least pH 11.3, the species [Fe HEDTA (OH)₂]³⁻ prevails. Due to the similar behavior of the hydroxide substituted aluminum and iron (III) HEDTA complexes, therefore, the existence of [Al HEDTA (OH)₃]³⁻ appears likely at pH >10. Further hydroxide coordination is not unreasonable at the high NaOH concentrations used in this study.

Thus, the formation of a specific reactive aluminum-HEDTA-hydroxide complex such as $[Al\ HEDTA\ (OH)_4]^{4-}$ probably accounts for the reaction rate increase found as NaOH concentration increases to 1.5M. Reactions (1) summarize the aluminum-HEDTA-hydroxide equilibria leading to the formation of the postulated reactive complex.

The decrease in reactivity as NaOH concentration exceeds 1.5M could be due to formation of the next aluminum-HEDTA-hydroxide complex; for example, $[AlHEDTA(OH)_5]^{5-}$. This equilibrium is shown in Reaction (2).

Alternatively, the reactivity decrease found with increasing NaOH concentration $>1.5M$ could be due to dissociation of the reactive aluminum HEDTA complex caused by the formation of a more stable solvated aluminum species.

The solvated aluminum species presented in uncomplexed basic solution is generally believed to be tetrahedral $Al(OH)_4^-$.⁽⁴⁾ Laser Raman and nuclear magnetic resonance studies have shown that, in systems having 0.75 to 3.2M NaOH, increasing aluminum concentration from ~ 0.5 to 6M favored condensation of $Al(OH)_4^-$ to form the dimer $[(HO)_3AlOAl(OH)_3]^{2-}$.⁽⁴⁾

Similar laser Raman evidence for dimerization was found when NaOH concentrations were increased from ~ 1 to $10M$ in $1.7M$ $NaAlO_2$ solutions.⁽⁵⁾ Therefore, dissociation of the reactive complex caused by formation of the aluminum dimer may be responsible for the decreasing reaction rate shown as NaOH concentration exceeds $1.5M$. The formation of the dimer may also explain the slightly decreasing dependence of reaction rate on increasing $NaAlO_2$ concentration shown in Figure 2. Reaction (3) describes the dissociation of the reactive complex and formation of the aluminum dimer.

The kinetic studies in this report show that the reactive complex of aluminum, HEDTA and hydroxide undergoes oxidation by nitrate and nitrite. The products of this reaction are a stable complexant, which may be HEDDA, and various gases; principally N_2O , N_2 and H_2 . Reactions (4) summarize the kinetic and chemical observations.

SUGGESTED FUTURE WORK

Further investigations on the roles of O_2 , nitrate and nitrite in this reaction should be undertaken.

Identification of the stable complexant decomposition product should be done. A preparative scale HPLC could be used to separate the product complex. Mass spectrometric analysis of the complex and nuclear magnetic resonance study of the corresponding acid should be sufficient to identify this product complexant species.

Other metal ion catalysts should be tried. These metal ions should have higher HEDTA formation stability constants at the waste slurry's basic conditions than aluminum (III). Such metal ions might be Fe(III), Cu(II), Ca(II) and Zn(II).⁽⁶⁾

Most importantly, laboratory verification of this reaction's behavior with full-level complexed waste slurry should be done. This verification would necessarily include the HPLC analysis of the complexants present in the waste.

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POTENTIAL FOR EXOTHERMIC CHEMICAL REACTIONS IN WASTE TANKS

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Background

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

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

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

A later preliminary safety analysis⁴ noted on p. 14 a maximum permissible salt cake temperature of 260°C, and stated, "Prior to evaporation, a representative sample of the contents from each tank will be collected, dried,

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

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

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

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

Explosion Studies

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

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

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

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

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

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

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

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

The fourth item, also by Beitel¹⁰, refers on p. 1 to the SRI tests (item 1 above) and states, "No evidence of detonation was seen in any of the samples, a finding in agreement with the literature which states that black powder (a nitrate plus charcoal type explosive) is shock insensitive (cannot be triggered by a shock wave)." This statement seems to be at variance with the statement quoted above from the SRI report.

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

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

Exothermic Reactions

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

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

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

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

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

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

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

Potential Consequences

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

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

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

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

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

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

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

Reaction Probabilities

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

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

The most recent report by Beitel that I have found¹³ says on page 8, "Although sodium nitrite may be present and is more reactive than sodium nitrate, it is less energetic and to the extent it is present, reduces the worst possible hazard." While this is true, the presence of sodium nitrite may be expected to increase the probability of an initiating event.

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

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TO: KGC

FROM: DAR

SUBJ; letter from Ellindson on safety of DSS.

Many of the issues brought up are true. Technology has not been following the actual process very close.

COMMENTS:

1) I was unaware that the tank had pressurized three times. Are we prepared to do anything the next time it pressurizes? It looks like it should happen in the Nov-Dec time period. What are the signs that lead up to the pressurization? Are we going to sample the gas? Measure how much the tank pressurizes? Assure ourselves as to the calibration of the instruments?

2) What do we know for sure about slurry growth. This is my summary and may be disputed.

a -- Tank growth occurred in single shell tanks. This phenomena is not unique to double-shell slurry. However, tank growth has occurred in both double-shell slurry campaigns

b -- Organics seem to be important to the growth. The tank that had complexed concentrate has pressurized. The tank that did not have the complexant heel has not.

c -- Temperature appears to have a large affect on the rate of gas generation

d -- The gasing is a chemical reaction. Radiation may play a role but only a contributing one.

e -- We do not know for sure what organic is involved. We are just beginning to know what gases may be involved.

3) We do not know at what level in the tank this reaction occurs. Gas generation may take place throughout the tank. However, gases are more soluble under pressure. There may be some level in the tank under enough pressure

~~bubbles~~
that ~~bubbles~~ are not present. I personally feel that the tank is much like a "Tootsie Roll Pop". It has a crust around the cool sides, top and bottom and a fairly liquid center. I have suggested that a neutron probe either in the annulus or a drywell be used to look at the moisture profile.

4) We don't know what the maximum credible level. We only have a 13% estimate based on past experience.

5) Large pressurizations may release contamination. I personally doubt that the pressurizations are large enough to damage the tank but I have no basis for that belief.

6) The gasing reaction has been going on for three years now. The tank is cooling which will slow the reaction. However, the cold cap seems to trap the gas better so that pressurizations may continue. The chemical reaction could continue until the temperature cools or the organics are used up. This could take decades.

7) Elimination of organics may minimize the problem but may not completely solve the problem. We have seen at least in the lab, that there is gasing without organics.

8) I do not know of any planned corrective action for the waste tanks. We could dilute and pump a tank. That is what was done in S and SX tanks when they grew. If all three tanks in the West area are filled, transferring to the east would be difficult. There is only the small tank for cross site transfers. Maybe pumping out directly from the tank is possible but it has not been attempted. These tanks become a special case of the question "What do you do when a DS tank leaks?"

In one sense, this points out that we have been trying to predict how much the slurry will grow. Little or no effort has been spent on how well we control it when it grows. I feel that the pressurizations are a complete surprise. Perhaps we could have predicted that if more attention had been paid to the process rather than the lab.

542

Internal Letter

Rockwell International

Date July 13, 1984

No . 65900-84-416

TO: (Name, Organization, Internal Address)
Distribution

FROM: (Name, Organization, Internal Address, Phone)
J. F. Albaugh, Manager
Process Engineering Dept.
2750-E/A203/200-E
3-1095

Subject: 101-SY TANK PRESSURIZATION PREVENTION

A task force is being formed to address the problem of gas formation and subsequent tank pressurization in Tank 101-SY. A confined layer of organic containing waste produces gas which, unable to escape, lifts the surface crust until a fissure develops which allows gas release. If the pressure has built up sufficiently before the release, tank pressurization may occur. Efforts to increase tank ventilation and lance the surface to provide an escape path have not always been successful. The task force should attempt to identify an innovative, cost effective method for preventing or decreasing the severity of gas pressure buildup and subsequent release.

The task force is charged with the following actions:

1. Implement a short-term solution that will prevent further tank pressurizations (July 20, 1984).
2. Identify tasks necessary for implementing long-term solution (August 3, 1984).
3. Hold an organizational meeting in Room A111, 2750-E Building at 9:00 A.M., July 17, 1984, to assign all actions and responsibilities.
4. Hold daily update meetings until Item 1 is complete.

Assigned task force members and their responsibilities are:

- N. E. Bell - Chairperson
- W. J. Powell - Procedures and Hardware
- L. M. Sasaki - Technology and Laboratory Support
- R. E. Van der Cook - Technical Consultant
- C. M. Walker - Surveillance
- R. A. Van Meter - Research and Engineering Interface
- O. Strunk - Operations Support
- D. R. Ellingson - Health, Safety and Environment Support

Rockwell
International

Distribution
Page 2
July 13, 1984

Management briefings on task force progress will be held as required.

J. F. Albaugh, Manager
Process Engineering Department

JFA:bjb

cc: N. E. Bell
D. R. Ellingston
W. J. Powell
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Internal Letter

Rockwell International

Date July 23, 1984

No . 65950-84-449

TO: (Name, Organization, Internal Address)

. Distribution

FROM: (Name, Organization, Internal Address, Phone)

. N. E. Bell

. Tank Farm & Evaporator

. Process Engineering

. 3-1151

Subject . SHORT-TERM SOLUTION OF TANK 101-SY PRESSURIZATION PROBLEM

The task force on prevention of pressurization in Tank 101-SY makes the following recommendations as a short-term solution:

1. Tank 101-SY should be routinely lanced when the liquid level is between 408.5 and 409.0 inches. Water should be used during lancing to soften the crust. The previous lancing criterion was 411 inches. Lancing at a lower liquid level should result in release of a smaller volume of gas, which is less likely to pressurize the tank.
2. A modified lancing head (like that used for LOW installation) should be used during the next lancing (expected in 4-6 weeks). This type of lance injects water horizontally as it is lowered and makes a bigger hole. The modified lance should be installed in riser 17C, which is on the far side of the tank from the existing lance (riser 14A).
3. The next lancing should be performed in stages in order to determine the depth of the gas bubbles in the waste. The tank is believed to have three layers - a surface crust, a liquid center, and a solid bottom. The lance should be stopped at six feet under the surface and held 36 to 48 hours. If no gas release occurs, the lance should be lowered to four feet from the bottom and held 36 to 48 hours. If no release occurs, the lance should be lowered to the tank bottom. If the modified lance is unsuccessful, the existing lance should be used to release gas from the waste.
4. In-Tank photography of the waste surface should be taken as soon as possible since the tank liquid level is now at the lowest level in four years. Photographs should also be taken just after lancing.
5. Readings at all thermocouple points in the waste and in the tank bottom should be taken weekly. Preliminary data show a correlation with temperature and liquid levels.

W. J. Powell (Tank Farms and Evaporator Process Engineering (TF&EPE)) and O. Struck (Tank Farm Surveillance and Operations) will be responsible for fabrication and installation of the modified lance. C. M. Walker (TF&EPE) will be responsible for obtaining and evaluating photography and temperature readings.

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Distribution
July 23, 1984
Page 2

Task Force members and their responsibilities are:

- N. E. Bell - Chairperson
- W. J. Powell - Procedures and Hardware
- L. M. Sasaki - Technology and Laboratory Support
- D. M. Tulberg - Technology Support
- R. E. Van der Cook - Technical Consultant
- C. M. Walker - Surveillance
- R. A. Van Meter - Research and Engineering Interface
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N. E. Bell, Engineer
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Internal Letter

Rockwell International

Date August 13, 1984

No . 65950-84-486

TO: (Name, Organization, Internal Address)

. Distribution

FROM: (Name, Organization, Internal Address, Phone)

. N. E. Bell
. SIS Unit/TF&EPE

. 3-1151

Subject . LONG-TERM RECOMMENDATIONS OF THE TASK FORCE ON PRESSURIZATION OF TANK 101-SY

Reference: Letter, July 23, 1984, N. E. Bell to Distribution, "Short-Term Solution of Tank 101-SY Pressurization Problem"

Pressurization of Tank 101-SY is believed to be caused by the reaction of organics in the waste to form gases. These gases collect in the waste, causing the waste surface to rise until a sudden gas release occurs and the liquid level drops. Sharp rises in radiation readings on the SY-Farm exhaust filters after pressurization are strong evidence that release of airborne contamination through unfiltered tank openings may be occurring. Calculations show that airborne contamination exceeding release limits probably would not be measurable as increases in ground contamination. Based on the composition of gases generated during laboratory experiments and calculations of the volume of gas released during Tank 101-SY pressurizations, there is also a possibility that hydrogen concentrations in the tank void space exceed tank operating specifications during pressurization.

Several methods have been suggested to provide continuous, low-volume gas release in Tank 101-SY. The existing ventilation system should be capable of controlling low volume emissions, thus preventing pressurization, release of air borne contamination, and high hydrogen concentrations. However, all these methods depend on the location of the gas buildup in the waste, which is unknown. Temperature readings in the waste and radiation readings in the annulus indicate that the original waste layers have mixed and then separated to form a crust, a middle liquid layer, and a bottom solids layer. In this case, gases could be collecting either just under the crust or in the solids layer.

The task force recommends the following actions:

1. As a short-term solution, the tank should be routinely lanced before the liquid level reaches 409 inches to prevent pressurization. Hot water should be used.
2. No long-term solution should be implemented until more is known about gas buildup in the tank.
3. The location of gas buildup should be further investigated.
 - a. The tank should be lanced with a modified lance held in stages to determine the depth of the gases. This staged lancing should begin when the tank liquid level reaches 408 inches. The first lancing should be done to a depth of six feet under the surface

4th Lancing with
modified lance
begin when tank
liquid level
reaches 408
inches. The
first lancing
should be done
to a depth of
six feet under
the surface

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in three different risers. If the gas has not released after a 36 to 48 hour wait, the tank should be lanced to a depth of 15 feet from the top in three risers. This should be the center of the liquid layer. If the gas has not released after a 36 to 48 hour wait, the tank should be lanced to a depth of four feet from the bottom in three risers. This should be the center of the solids layer. If this is unsuccessful, the tank should be lanced to the bottom and the existing lance be used to force a gas release.

- b. Temperature readings should be collected at all available locations weekly.
 - c. Photographs of the tank surface should be taken just after lancing.
 - d. A steel LOW should be installed just after the next lancing. Gamma and neutron scans of the tank should be performed once every two weeks to show changes in the waste. Installation of a fiberglass LOW for acoustic (density) readings should be investigated. Density readings should indicate how thick the various layers are and where the gas is collecting.
- 4. The potential for release of airborne contamination should be further investigated. An air sampler should be placed over a release point in time to measure the next release.
 - 5. The potential for high hydrogen concentration should be further investigated. A hydrogen detection device, preferably a meter with stripchart recorder should be placed over a release point or at the exhaust filters.
 - 6. A core sample should be taken at each of the three layers. The physical properties and chemical composition of each layer are important in determining which engineering solutions will be effective.
- C. M. Walker (TF&EPE) will be responsible for continued surveillance and evaluation of Tank 101-SY, W. J. Powell (TF&EPE) will be responsible for installation of equipment at Tank 101-SY.

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Task Force members and their responsibilities are:

- o N. E. Bell - Chairperson
- o W. J. Powell - Procedures and Hardware
- o L. M. Sasaki - Technology and Laboratory Support
- o D. M. Tulberg - Technology Support
- o R. E. Van der Cool - Technical Consultant
- o C. M. Walker - Surveillance
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COMPLEXANT STABILITY INVESTIGATION
TASK 1 - FERROCYANIDE SOLIDS

L. L. Burger

November 1984

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Up to 140 metric tons (t) of cyanide is contained in the early single shell Hanford waste storage tanks with possibly as much as 30 t in a single tank. The material was added as potassium ferrocyanide during the cesium scavenging campaign which began in 1954. The goal of this campaign was to produce additional tank storage space by concentrating the wastes and cribbing the supernate. The program continued through 1957.

Mixed with nitrates or nitrites, both of which are present in the tanks, cyanide has been shown to undergo explosive reactions when heated. The chemical and radiolytic reactions of the ferrocyanides and the cyanide ion are examined in this report along with the thermodynamic calculations for potential reactions. A worst case scenario is considered which assumes that all of the cyanide in one tank - along with sufficient nitrate-nitrite for reaction - is concentrated in one region; a possible energy release equivalent to 36 t of TNT is calculated.

It is not known whether such localized concentrations are possible nor is it known whether any initiating event, i.e., temperature $>350^{\circ}\text{C}$, is likely. Dilution with inert material may change the reaction to a thermal excursion, raise the initiating temperature or otherwise modify, perhaps even prevent, the reactions. Not enough is known about the nature of the reactions to make such a prediction.

Sludge sampling of tanks known to have large quantities of cyanide will help answer some of these questions. Questions regarding the kinetics will require laboratory testing of mixtures.

It is possible that hydrolysis, oxidation, and radiolysis may have destroyed most of the cyanide over the 25-30 year span. Unfortunately, neither the conditions in the tanks, amount of aqueous phase, solubility of the cyanide, etc., nor adequate basic chemical information are known to substantiate such a conclusion. However, simulated laboratory tests may provide the necessary information.

Recommendations for laboratory work and for tank sampling are made.

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INTRODUCTION

Large quantities of ferrocyanide (hexacyanoferrate (II)) precipitates were placed in the 200 Area single-shell waste tanks over a period of several years. The question of the long-term safety of these residues has been raised. To assist in making decisions regarding the management of these tanks, it is desirable to review the safety aspect. In order to predict conditions that might lead to rapid exothermic reactions between these solids and nitrate salts, it is necessary to review the chemistry of the cyanide complexes and the thermodynamics and kinetics of the possible reactions. It is also necessary to determine the amounts of cyanide solids in a given tank along with the concentration, i.e., dilution with inert materials, that may exist.

The purpose of this report is to review the existing information on these precipitates, on the potential reactions that may occur and to make recommendations for a study which would better establish the chemistry involved, determine the precise location of the cyanide precipitates and thus permit the development of a long-range storage plan.

CONCLUSIONS AND RECOMMENDATIONS

Up to 900 kmols of ferrocyanide precipitates (~140 t of CN^-) are known to have been placed in Hanford waste tanks about 25 to 30 years ago. Although the records show that large amounts were placed in at least 14 tanks, at present, we are unable to conclusively state the quantities that reside in individual tanks. The composition of the other constituents in the waste tanks containing ferrocyanides is also unknown. Similarly, no information exists on the possible layering of ferrocyanide precipitates in the waste tanks or the potential for their intimate contact with nitrate salts.

The energy released by the reaction of cyanide ion and nitrate ion is significant. The "worst case" scenario described in this report predicts the energy release from a single waste tank could be equivalent to that of 36 tons of TNT. The conditions necessary for reaction (or for "rapid" reaction) are not known, nor are any kinetic parameters known.

At present, there is insufficient information to state that the hazard of a potentially violent cyanide reaction does not exist. A better information base is required to permit a safe program for long term tank management.

The following actions are required to obtain the information necessary for a definitive hazard evaluation and are listed in order of decreasing priority:

- (1) Obtain and analyze the available information on tank histories for those tanks known to have held $\text{Fe}(\text{CN})_6^{4-}$ in large quantities at one time.
- (2) Conduct radiolysis tests under simulated tank conditions to determine the rate of disappearance of CN^- and to identify the radiolysis products. The radiolysis tests should be conducted both with an aqueous phase present and on settled sludges alone.
- (3) Determine the kinetic parameters of the CN^- and NO_3^- reaction by both experiment and calculation. The effect of inert materials is especially important and must be included in these studies. The information obtained from these studies would allow realistic

conclusions to be made regarding the potential for rapid exothermic reactions in waste tanks containing ferrocyanide solids. In addition, the conditions for potentially hazardous reactions would be known and could be precluded by tank management practices.

- (4) Obtain tank samples and conduct chemical analyses for soluble and insoluble cyanides, cyanate, nitrate, fission products, and water content.
- (5) Obtain the temperature profile of the tank to give information on temperature maxima and on possible layering of solids.
- (6) Obtain the γ profile to provide much the same information as (5) above.

It is our recommendation that continued studies be directed to obtaining the information indicated in the above list.

HISTORICAL PERSPECTIVE

In the early 50's it became apparent that the impending shortage of underground storage could be alleviated by concentrating the active wastes and cribbing the supernate. Ferrocyanide scavenging was a practical solution to the problem (Burns 1953) and began with active operation in the uranium recovery plant in September 1954 (Smith and Coppinger 1954; Schulz 1955). The flowsheet was described by Sloat (1954). T-Plant was still operating, and scavenging of T-Plant wastes probably began there in December 1954. Both U-Plant and T-Plant scavenging processes were carried out in-plant, and the wastes sent to available underground tanks. In general, the tanks were chosen to be easily accessible to usable crib sites.^(a)

In-farm scavenging started in East Area with the C-farm in November 1955 and began in West Area the following year (Sloat 1955a).

During this period, other decisions regarding Hanford production impacted waste storage. For example, because of special production runs a decision was made in June 1955 to continue T-Plant through June 1958 and run B-Plant from July 1955 to June 1957 (Peterson 1954). Direct evaporation was also employed to develop new storage space. Evaporations were started on dilute wastes in January 1955 (Abrams 1956), although some evaporation was apparently practiced as early as 1949.

During a portion of the time, calcium or strontium salts were added to increase the strontium decontamination by carrying it on the phosphate precipitate (Sloat 1955b). The first calcium additions were made in March 1955 (Abrams 1956). Occasionally, phosphate was added to the tanks.

During the scavenging campaigns more than 100 tons of cyanide were added to the tanks (Backman et al. 1964). The final disposition of these wastes is largely unknown, because of the method of routing and rerouting of wastes. However, some tanks can be designated as probably having considerable quantities of cyanide precipitates.

(a) R. J. Sloat - personal communication, January 1984.

The scavenging flowsheet varied somewhat depending on the application, but basically it consisted of the following steps (Sloat 1954, Schmidt and Stedwell 1954):

1. add $K_4Fe(CN)_6$ to obtain a concentration of 0.005 M
2. adjust the pH to 8-10, preferably about 9
3. add $NiSO_4$ to obtain a concentration of 0.005 M
4. agitate 10 minutes
5. discharge by jetting to underground storage.

A settling time of about 7 days was generally adequate to permit the supernate to be pumped to the cribs. Specifications were set on the activity permitted to be transferred to the cribs.

CHEMISTRY

The transition metal cyano complexes are very strong. In the case of Fe(II), the hexacyano complex is strong enough that the salts are often considered nontoxic.

Metals such as Ni and Co also form strong anionic complexes. Most of the heavy metal salts of these complex acids are insoluble in water. Thus, nickel, zinc, and copper ferrocyanides are easily precipitated. In early laboratory studies a variety of ferro- and ferricyanide precipitates were tested and found to be excellent Cs carriers. These included Fe(II), Fe(III), Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) ferrocyanide and Fe(II) Ni(II), and Co(II) ferricyanide. All but the Co and Ni ferrocyanides were rejected because of inferior behavior in the pH range required. Cobalt was ruled out because of cost (Stedwell 1956).^(a)

Sillén (1964) gives the solubility product of $\text{Ni}_2\text{Fe}(\text{CN})_6$ as $\log K = -13.1$ to -14.9 . This gives a $\text{Fe}(\text{CN})_6^{4-}$ concentration in water at 25° of $(0.7-3) \times 10^{-5}$ mol/L. The simple cyanide salts of the heavy metals are also quite insoluble, but most form anionic complexes with excess CN^- . The solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ has not been reported.

Reactions of interest include hydrolysis to form the CN^- ion, oxidation of the ferro complex to the ferri complex, replacement of one or more CN^- ligands by H_2O , NO , NO_2^- , etc., and oxidation of CN^- to CNO^- .

No data were found for the free energies or enthalpies of the cyanide solids of interest. However, it is useful to examine the aqueous species. (Data are from Wagman et al. 1982). The reaction

(a) Later studies concerned with Cs recovery from Purex wastes (Van Tuyl 1957a, 1957b) involved zinc ferrocyanide. Cobalticyanides were also briefly considered.

represents a free energy change of + 8.2 kcal. For the hydrolysis reactions:

and

the free energies at 298K are +40 kcal and + 19 kcal, respectively. Using the entropy values, the free energies at 350K were estimated as 33 kcal and 14 kcal. Using these data, the equilibrium constants of Table 1 were calculated.

TABLE 1. Hydrolysis Constants for Hexacyanoferrates

$$K = \frac{(\text{CN}^-)^6}{(\text{Fe(CN)}_6^{x-})} \frac{1}{(\text{OH}^-)^{(6-x)}}$$

Species	Hydrolysis Constant as a Function of Temperature	
	298 K	350 K
Fe(CN)_6^{3-}	1.2×10^{-14}	1.8×10^{-9}
Fe(CN)_6^{4-}	3.8×10^{-30}	2.5×10^{-21}

At a pH of 10 and assuming that the Fe(CN)_6^{4-} concentration is equivalent to that given by the solubility product of $\text{Ni}_2\text{Fe(CN)}_6$, about 2×10^{-5} M, the concentration of CN^- at 350 K is of the same order of magnitude, i.e., 10^{-6} to 10^{-5} M. Both solubility and hydrolysis increase with temperature.

It is possible that much of the ferrocyanide has been oxidized to ferricyanide by the results of radiolytic decomposition of the water-nitrate mixture, thus increasing the tendency for decomposition in the highly alkaline

environment. However, the maximum CN^- concentration will be controlled by the complexes resulting from the presence of Ni^{2+} and Fe^{2+} in the tanks.

Another process that contributes to the decomposition is the formation of complexes such as $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ (I), $\text{Fe}(\text{CN})_5\text{NO}^{3-}$ (II), $\text{Fe}(\text{CN})_5\text{NO}_2^{4-}$ (III), etc. Formation of I is promoted by radiation. II is reported to convert to III in hydroxide solutions (Sharpe 1976).

Removal of CN^- and hence of the cyanide complexes depends on subsequent CN^- reactions. This can occur through oxidation or as a result of radiolysis. Oxidation produces the cyanate ion and can occur by

for which $\Delta G = -46 \text{ kcal}$. Thus, at a pH of 10

$$\frac{(\text{CNO}^-)}{(\text{CN}^-)} = 5.4 \times 10^{25}. \quad (5)$$

However, the reaction is apparently slow under ordinary conditions. An important driving force tending to solubilize and permit the destruction of cyanide ion is the stability and insolubility of ferric hydroxide.

RADIOLYSIS

One of the reasons for considering the solubility is the potential for radiolysis which is probably a maximum in the aqueous phase. Several studies have been carried out on radiolysis of dilute CN^- solutions over a wide pH range. (Touhill et al. 1969; Ogura et al. 1972; Behar 1974; Bielski and Allen 1977; Liaw and Woodbridge 1977; Draganic, Draganic, and Niketic 1977; and Shen-chu, Shao-hua, and Ji-lan 1981). Radiolytic destruction is quite effective and G values for destruction in the vicinity of 6 are consistently reported. (a)

The compounds formed include CNO^- , NH_3 , CHONH_2 , $\text{NH}_2\text{CH}_2\text{COOH}$, and smaller amounts of COOH^- , CO_2 , urea, and probably N_2 . The initial mechanism is apparently the attachment of the OH radical (from the radiolysis of water) to the CN^- ion. It is perhaps surprising that the free radical complex rearranges to form a high yield of organic compounds rather than mostly CNO^- since the OH radical is an excellent oxidant.

The cyanate ion is quite stable while the organic compounds will be gradually decomposed.

Using a G value of 6, a radiation dose of 10^6 rad would destroy 6 mmol/L. A rough calculation will illustrate the effectiveness of radiolysis:

Assume 10^6 g CN^- in 1/10 tank volume, i.e. 2×10^5 L of water-saturated sludge. Then the bulk cyanide concentration is 0.02 mol/L. If the aqueous phase is 10% of the waste volume, 3.3×10^7 rad would be required to destroy the cyanide.

The assumption is made that the radiolysis at cyanide concentrations of 10^{-6} - 10^{-5} M has the same efficiency as at 10^{-4} - 10^{-3} M where most of the measurements have been made. The data of Liaw and Woodbridge (1977) and of Ogura et al. (1972) suggest that the G value may drop as the concentration

(a) The G value is the number of molecules destroyed (or formed) by the absorption of 100 eV of energy, in the present case, energy absorbed by the solution. A "normal" value for a pure substance is about 1.

does. On the other hand, no credit is taken for decomposition of the solid phase. Unknowns include the radiolytic yields from complexed CN^- and the effect of NO_3^- radiolysis on the overall reaction.

It is seen that a radiation dose of 10^7 to 10^9 rad, depending on the localized concentration, could convert most of the cyanide to CNO^- , and other low energy compounds. 10^8 rad over a period of 25 years would require an in-tank dose rate of about 450 r. This is approximately what 1 Ci of $^{137}\text{Cs/L}$ would produce.

As mentioned above, no credit is given to radiolytic decomposition of the solid. A brief mention was made of experiments with $\text{Cs}_2\text{ZnFe}(\text{CN})_6$ by Hepworth, McClanahan, and Moore (1957). Surprisingly little decomposition was indicated. The conditions used were not typical of the waste tank environment.

Thus, while the radiation received over the 25-30 year period could have destroyed the cyanide under ideal conditions, it is not known what the effectiveness has been. Besides the unknown effects of NO_3^- and of complexing of the CN^- mentioned above, other uncertainties are the amount of aqueous phase and the actual cyanide solubility. Laboratory experiments are required to answer these questions.

ENERGETICS

It is apparent from the enthalpies and free energies of formation shown in Table 2, that most cyanide compounds are thermodynamically unstable. Little work has been reported on kinetics, but it is quite likely that the activation energies are quite high. However, for the present it must be assumed that the temperature is adequate or that some other mechanism will permit the reaction. We are then only concerned with the heat of reaction, ΔH .

Experience with explosive reactions of the ferrocyanide precipitates was briefly reviewed in RL-SEP-65 (Backman et al. 1964). The work was reported by Wirta and Koski (1957) and by Hepworth, McClanahan, and Moore et al. (1957). A second comment appears in a Chemical Research and Development Section Monthly Report (Cooper 1957) to the effect that for an aqueous phase of greater than 0.09 M NO_3 , in contact with solid $\text{Cs}_2\text{ZnFe}(\text{CN})_6$, the threshold temperature was 375°C . If solid nitrates were added to the dry Cs compound, localized explosions and flames accompanied by dense white fumes were observed.

As further evidence that the reactions are potentially violent, patents exist for explosives, e.g. (Eiter, Vogl, and Michl 1954):

- (a) Mixtures of NaNO_2 and $\text{K}_4\text{Fe}(\text{CN})_6$ (47%) or with $\text{Hg}(\text{CN})_2$ (73%)
- (b) $\text{Ba}(\text{NO}_2)_2 + \text{NaCN}$ (28%)

The patent abstract does not give further information. The explosive reaction of molten NaNO_3 and NaCN is mentioned by the National Board of Fire Underwriters, Research Report No. 2 (1950) and by Sax (1957). Thus, there is no question that the reaction of cyanide compounds with either solid nitrates or nitrites may be explosive provided the concentrations and temperatures are adequate.

The products of potential explosive reactions are uncertain, but plausible ones can be assumed and ΔH values calculated. Two examples are given

TABLE 2. Thermodynamic Properties of Compounds
(Wagman et al. 1982)

Compound ^(a)	ΔH_f	ΔG_f	S°
	<u>kJ mol^{-1}</u>	<u>kJ mol^{-1}</u>	<u>$\text{J mol}^{-1} \text{K}^{-1}$</u>
$\text{Fe}(\text{CN})_6^{3-}$	561.9	729.4	270.3
$\text{Fe}(\text{CN})_6^{4-}$	455.6	695.08	95.0
$\text{K}_4\text{Fe}(\text{CN})_6$	-594.1	-453.0	418.8
$\text{K}_3\text{Fe}(\text{CN})_6$	-249.8	-129.6	426.1
$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$	1184.	--	--
$\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$	--	-163.0	--
$\text{Cu}_2\text{Fe}(\text{CN})_6$	--	736.5	--
NaCN	-87.49	-76.43	115.6
CN^-	150.6	172.4	94.1
OCN^-	-146.0	-97.4	106.7
OII^-	-229.99	-157.24	-10.75
$\text{H}_2\text{O}(\text{l})$	-285.83	-237.13	69.91
$\text{H}_2\text{O}(\text{g})$	-241.82	-228.57	188.82
NaNO_2	-358.65	-284.55	103.8
NaNO_3	-467.85	-367.0	116.52
NaOH	-425.61	-379.49	64.45
Na_2O	-414.22	-375.46	75.06
$\text{Fe}(\text{OH})_3$	-823.0	-696.5	106.7
$\text{Fe}(\text{OH})_2$	-569.0	-486.5	88
FeO	-272		
Fe_2O_3	-824.2	-742.2	87.4
$\text{NO}(\text{g})$	90.25	86.55	210.76
$\text{NO}_2(\text{g})$	233.18	51.31	240.06
$\text{CO}(\text{g})$	-110.52	-117.76	132.6
$\text{CO}_2(\text{g})$	-393.51	-394.36	213.74

(a) The states not indicated are crystalline solids except for the ions where the reference state is the 1 m solution.

below. $K_4Fe(CN)_6$ is not the best choice as the reactant since it is not present as a solid, and because it represents a reasonably stable compound. However, it is one for which there are reliable data. The other extreme may be $Fe_4(Fe(CN)_6)_3$ which is a possible reactant and probably represents the stability of other potential ferro or ferricyanides.

$$\begin{aligned}\Delta H &= -2056 \text{ kJ} \\ &= -82 \text{ kcal per mol } CN^- \end{aligned}$$

$$\begin{aligned}\Delta H &= -7398 \text{ kJ} \\ &= -98 \text{ kcal per mol } CN^- \end{aligned}$$

$$\begin{aligned}\Delta H &= -403.6 \text{ kJ} \\ &= -96.5 \text{ kcal per mol } CN^- \end{aligned}$$

Substitution of ferricyanides results in an increase of energy release of 40-60 kJ per mol of CN^- . Substitution of sodium nitrite for nitrate increases the energy by about 20-40 kJ per mol of CN^- . Nitrite is present in the tanks as a result of the long-term radiolysis of nitrate. If NO is produced in place of N_2 , the energy is greatly reduced - a factor of about 3. If Na_2O is produced in place of NaOH, the energy is reduced by 40-80 kJ per mol CN^- . The latter must result if the mixture is dried. Thus, a maximum energy of about 400 ± 60 kJ (95 kcal) per mol of CN^- may be expected. For comparison, conversion of 1 mol of carbon to CO_2 by the $NaNO_3$ reaction will release about 365 kJ (85 kcal).

The heat capacities of the sludge components are small. Typical values, (Table 3) J/mol-K, are: $NaNO_3$, 93; NaOH, 59; $AlPO_4$, 93; $Al_2(SO_4)_3 \cdot 6 H_2O$, 493; $H_2O(l)$, 75; $H_2O(g)$, 34. An estimated C_p for hydrated sludge is 1.2-2 J/g-K.

TABLE 3. Heat Capacities of Typical Compounds^(a)

	<u>J mol⁻¹ K⁻¹</u>	<u>J g⁻¹ K⁻¹</u>
NaOH	59.5	1.5
NaNO ₃	92.5	1.1
NaNO ₃ (l)	154.8	1.8
Fe(OH) ₃	101.6	1.0
Fe ₂ O ₃	103.8	0.6
Al(NO ₃) ₃ ·6 H ₂ O	433.0	1.4
Al ₂ O ₃ ·3H ₂ O	183.5	1.2
AlPO ₄	93.2	0.8
Al ₂ Si ₄ O ₁₀ (OH) ₂	294	0.8
H ₂ O(l)	75.3	4.2
H ₂ O(g)	33.6	1.9
N ₂	29	1.0
NaOH(l)	87.8	2.2
Fe(OH) ₂	97.0	1.1
NaCN	68.5	1.3

(a) Typical temperature effects would increase C_p by 10-30% at 1000 K. 20% was used as an average in the ΔT estimate.

Other heat sinks are: volatilization of water, 40 kJ/mol; fusion of NaNO₃, 15 kJ/mol; and fusion of NaOH, 7 kJ/mol.

Three adiabatic reaction cases were calculated, I-pure reactants, II-pure reactants plus 1 mol H₂O per mol of CN⁻, and III-2 mols of H₂O per mol of CN⁻ plus 2 extra mols of NaNO₃. Maximum calculated temperature rises are roughly 1800°C, 1200°C, and 500°C, respectively. The effect of increasing C_p with T was only estimated. The melting and vaporization of various components would reduce the temperature rise especially for the upper values. It may be significant that the materials having the greatest heat capacity (including phase transitions) are those that may be present in appreciable amounts, such as H₂O and NaNO₃. NaOH and the product gases contribute to the heat capacity of the reaction products. It is seen that even with appreciable dilution, the

potential temperature rise is great. The real impact of the diluents is not so much the reduction of temperature rise - since even a ΔT of 500°C would seem serious - but rather on the rate of reaction. The latter determines to a large extent the ultimate consequences of the exothermic reaction. Unfortunately, nothing is known of the reaction mechanism.

Another question is the initiation of the reaction. Any source of heat that could produce a temperature of 350 to 400°C is the most likely. This has not been identified although a sludge temperature as high as 315°C has been measured (Dahlke and DeFigh-Price 1983). Shock waves and contact friction are two additional methods that could give temperatures in this range, maybe only in a very small region.

Kinetic data and the effects of dilution can be obtained from laboratory tests. The question as to whether a sufficient quantity of ferrocyanide is concentrated in one place to be a hazard can perhaps be answered by tank sampling and by laboratory radiolysis tests.

TANK SURVEY

A brief review of early HW documents and discussions with present and former Hanford personnel indicates that the cyanide scavenged waste was spread over many tanks in many tank farms in both E and W Areas. The available information gave no obvious pattern for the disposal of cyanide sludges. The decision to use a particular tank, or to empty a given tank, was influenced by special tests, location of the scavenging operation, available crib sites, etc. A number of tanks have been identified that at least at one time contained sizable amounts of nickel ferrocyanide sludge. These include 101C, 108C, 109C, 112C, 105BY, 106BY, 107BY, 108BY, 110BY, 112BY, 101T, 101TY, 103TY, 104TY, 105TY, and 106TY.

An effort was made by F. M. Jungfleisch of Rockwell Hanford Operations to determine the state of some of these tanks through the records used for the TRAC program. The initial results were encouraging, and suggested the actual records are better than the information contained in the early Hanford documents. As this report was being completed, results of this tank survey were made available (Pickett 1984). Some 59 in-plant tributyl phosphate (TBP) waste campaigns, one in-plant test, and 29 in-tank campaigns were reviewed. Table 4 lists the effective scavenging volumes and the amounts of hexacyanoferrate (II) that could be present. Twelve tanks received the solutions just after treatment and it is assumed that all of the iron precipitated in these tanks. Two tanks, BY-104 and BY-105 received cyanide by transfer from BY-106, BY-107, BY-108, and BY-110. The total amount of hexacyanoferrate that is presumed to have been added is 9×10^5 moles or 5.4×10^6 moles of CN (140 t).

TABLE 4. Hexacyanoferrate(II) Additions

<u>Tank</u>	<u>Volume of Solution (Liters)</u>	<u>Fe(CN)₆⁴⁻ (Moles)(a)</u>	<u>Campaign Type</u>
BY-104 ^(b)	4E+7	2E+5	TBP Process
BY-105 ^(b)	3E+7	1E+5	TBP Process
BY-106	7E+6	3E+4	TBP Process
BY-107	2E+7	8E+4	TBP Process
BY-108	1E+7	7E+4	TBP Process
BY-110	2E+7	9E+4	TBP Process
BY-112	7E+5	3E+3	TBP Process
C-108	4E+6	2E+4	In-Tank
C-109 ^(c)	9E+6	5E+4	In-Tank
C-111 ^(c)	6E+6	3E+4	In-Tank
C-112 ^(c)	1E+7	7E+4	In-Tank
T-101	2E+6	1E+4	T-Plant Test
TY-101	6E+6	3E+4	1C Process
TY-103	5E+6	3E+4	1C Process
TOTAL	2E+8	9E+5	All

(a) Assumes that solutions are brought to 0.005M in Fe(CN)₆⁴⁻ during scavenging and that all Fe(CN)₆⁴⁻ settles in the first tank that received it.

(b) Received as solids transfers from BY-106, BY-107, BY-108 and BY-110.

(c) Corrected for supernates of BY-Farm that were not treated with Fe(CN)₆⁴⁻

"WORST CASE" SCENARIO

Greater than 10^5 kg (100 metric tons) of ferrocyanide was placed in underground waste storage during a few years starting in 1954. It is known that it is spread over many tanks, but it is not known whether a large quantity remains in any one tank. It can be deduced from the flowsheet that greater than 10^5 moles of CN^- could have been placed in one tank per scavenging sequence. The total nitrate available is not known because the supernate was pumped off. However, a second or more batches of scavenged waste could have ended up in a given tank.

The most hazardous sequence (worst case scenario) would seem to be:

- 1) The $\text{Ni}_2\text{Fe}(\text{CN})_6$ sludge representing the Cs from, for example, 3 tanks containing large amounts of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ was transferred to another tank. The total amount of ferrocyanide precipitate could amount to $(6-8) \times 10^4$ moles of $\text{Fe}(\text{CN})_6$.
- 2) The sludge settled in a pocket of $\sim 100 \text{ m}^2$ area, 10-20 cm deep.
- 3) The other major constituent in the sludge was a nitrate salt which deposited with the ferrocyanide precipitate.
- 4) Without further mixing, the material compacted and dried before appreciable decomposition could take place.
- 5) Heat from the Cs and other activities increased the temperature as the water was removed.
- 6) The ignition point was reached, and the 1.5×10^8 kJ (from 85 kcal/mol CN^-) is released in less than a second, (equivalent to 36 tons TNT).^(a)

The complete sequence is highly improbable. Any of steps 1 through 5 might have occurred.^(b)

(a) Whether the energy is released as a "detonation" or a "deflagration" is a matter of rate of propagation of the reaction. The question is not addressed at this time. Likewise, the efficiency of the reaction is not considered. 100%, which is very unlikely, was assumed in the estimates.

(b) It should be noted that the tank survey (Pickett 1984) indicated that a process similar to step one, did in fact, occur and resulted in more CN in one tank than the assumption made here. Five tanks possibly contain as much CN as the example.

An equally reasonable sequence is that the sludge settled in 2-7 days with the ferrocyanide precipitate diluted by a factor of 2-10 with other solids. A reasonably uniform deposit may have resulted. Early laboratory tests indicated that a fine precipitate was formed which settled slowly (Coppinger and Smith 1954). If the deposit were 50% ferrocyanide it might be of the order of 5-10 cm thick over the entire area of the tank. Calculations have not been done to assess the geometry effect for the system.

If other conditions are favorable for a reaction, then the drying step may be critical. Although it is reassuring that nothing has happened in 25-30 years, it must be emphasized that there are no data to indicate the actual in-tank condition as it relates to cyanide deposition or chemical environment.

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Internal Letter

Rockwell International

Date January 9, 1985

No. 72420-85-004

TO Name Organization Internal Address

G. T. Dukelow
W. F. Heine

FROM Name Organization Internal Address Phone

J. F. Dickman
Tank Farm Surveillance
Analysis
2750E/200E/3-1008

Return

Subject Double-Shell Tank Pressurization

- Ref: a) Letter, D. R. Ellingson to G. F. Boothe, "Effluent Sampling October 18, 1984
- b) Department of Energy Order 5484.1, Chapter 3, "Effluent and Environmental Monitoring Program Requirements," February 24, 1981.

Attached for your information is a summary of the double-shell tank pressurization events which were identified from pressure strip chart reviews during 1984. Eighty-three of the two hundred and forty pressure strip charts (approximately 35%) generated during 1984 were reviewed. The remaining one hundred and fifty seven strip charts were not submitted for review.

Review of the pressure strip charts revealed 131 indicated pressurization events. The maximum indicated pressurization occurred in Tank 101-AZ (the aging waste tank) on September 14, 1984. The pressurization averaged 3 inches water gauge (w.g.) for 11 hours and had a peak pressure of 60 inches w.g. that lasted for approximately 10 minutes. The cause of the indicated pressurization is unknown.

The maximum indicated duration of a pressurization also occurred in Tank 101-AZ. The pressurization apparently lasted for four days from November 1 to November 4, 1984. The indicated positive pressure during this time varied from 0.5 inches w.g. to 2.0 inches w.g. The cause of the pressurization was reported to be a plugged ventilation loop seal drain resulting in isolation of the tank from the ventilation system.

Each of the indicated 131 pressurization events represents a potential airborne release which was unsampled and unmonitored. Department of Energy Order 5484.1, Chapter III (Ref. ^a) requires all effluents to be monitored to determine "whether containment and control of release of radioactivity from site operations are functioning as planned." Reference ^b provided a description and an attached sketch of a sampling system which may assist in determining the significance of potential releases. Another sketch is provided with this letter. In order to increase the visibility and tracking of the problem to a satisfactory solution, Tank Farm Surveillance Analysis will enter two findings on AATS. The first finding will contain words to the effect that funding is required to develop and implement sampling of potentially significant effluent releases from tank farm pressurizations. A due date of April 1, 1985 will be assigned and action assigned to W. F. Heine. The second finding will be listed as follows: "Implement sampling of tank space concentrations during pressurization events to determine the

Rockwell
International

G. T. Dukelow/Heine
Page 2
January 9, 1985

significance of potential airborne releases as required by DOE 5484.1, Chapter 3. A due date of May 1, 1985 will be assigned and the action assigned to G. T. Dukelow.

J. F. Dickman, Manager
Tank Farm Surveillance Analysis

JFD/dj

Att.

cc: G. F. Boothe AB
J. C. Fulton
W. D. Killand
R. P. Knight
R. H. Sudmann

Double Shell Tank Pressurizations

1984

Note: January through May data was not received for review.

	<u>AN</u>	<u>AW</u>	<u>AY</u>	<u>AZ</u>	<u>SY</u>
JUNE	18	24	CNS	CNS	CNS
JULY	5	7	0	0	CNS
AUG	14 ⁽¹⁾	2 ⁽³⁾	1	1	CNS
SEPT	CNS	CNS	CNS	9	CNS
OCT	0 ⁽²⁾	21	2	6 ⁽⁴⁾	CNS
NOV	0	9	0	7 ⁽⁴⁾	CNS
DEC		3	2		

Maximum indicated pressure - 60 inches water gauge (w.g.) (101-AZ, Sept. 14, lasted approximately 10 min. at this pressure)

Maximum indicated duration - 4 days (Aging waste tank, 101-AZ, November 1-4, pressure varied from 0.5 to 2 inches w.g.)

CNS - Charts not submitted for review

(1) - 5 of 7 charts submitted for review

(2) - 3 of 7 charts submitted for review

(3) - 4 of 6 charts submitted for review (101 & 102 AW charts missing)

(4) - All pressurization occurred in the Aging Waste Tank (101-AZ)

SKETCH STATIC AIR SAMPLER

NOTE: IT MAY BE NECESSARY TO INSULATE SAMPLER TO MINIMIZE COLD LEG EFFECT AND POSSIBLE FREEZING CONDITIONS

THE MASS FLOW SENSOR SHOULD BE DELETED WHERE THE SAMPLER IS USED TO MEASURE POTENTIAL RELEASE CONCENTRATIONS RESULTING FROM PRESSURIZATIONS (ACTIVE DOUBLE SHELL TANKS).

DON'T SAY IT ... Write It!DATE 5/18/85TO Jerry White - CMD
JOE Knupara 5/20/85FROM Mel Shupe - NWT

Report PNL-5441 has been submitted for clearance and I recommend that it be disapproved. The safety significance of the issue, however, must be considered by Rockwell/PNL. I recommend that Rockwell/PNL develop a R&D plan to technically address subject issue and then after results are available, publication of facts (not speculations) be considered. We should assure ourselves that this issue is visibly tracked by contractor and RL. I see potential problems with (interim) tank drying and ISD as well. Meanwhile, the HDW-EIS considers a similar explosion scenario. P.S. I believe PNL should have

+ handled this smoother.

TO MAKE LIFE LAST, PUT SAFETY FIRST

+

To: Jack McCleary From Jerry White JFW

If such a potential exists ^{we} ~~we~~ should propose the work necessary to evaluate the potential. However, to publish an open report which speculates on such an explosion without any real basis is to invite misuse of the data and concept. I do not want to hide this if this is a real potential issue but let's channel it in a direction to resolve the questions not just raise them

RICHLAND OPERATIONS OFFICE
P.O. BOX 550
RICHLAND, WASHINGTON 99352

5/24

OCC doesn't have any
legal objection to the
proposed handling of
this provided it is
clear that PNL must follow
up with a study propo-
sal. It must be demon-
strated that DOE is not
suppressing this report,
but merely redirecting
the effort.

4-2000-
RL-5
GEP

RCL

RCL

Battelle

Pacific Northwest Laboratories

Date: 5/29/85

To: Ron

From: JACK L. McELROY

After looking through this report & can well understand why DOE did not approve it. (The summary alone being ^{very} ~~long~~ ^{long}.)

We need to establish some guidelines for handling such sensitive information. (eg the work was done for Rockwell - a report and proposal to Rockwell might have been the best route).

Do we report things openly just for the sake of science?

Date:

To:

From: JACK L. McELROY

Pass it this back through the approval chain with appropriate action for followup.

JHS, CAG, TDC, GGM,
LLB

Charlette could help define the action.

Internal Letter

Rockwell International

Date September 16, 1985

No. 65611-85-157

TO: (Name, Organization, Internal Address)

K. G. Carothers

KAC

FROM: (Name, Organization, Internal Address, Phone)

L. M. Sasaki

Waste Management Process

Technology Unit

2750-E/A-2271/3-3429

Subject: Results of Hydrogen Monitoring in Tank 101-SY

Refs: (a) Letter, 65611-84-211, November 26, 1984, L. M. Sasaki to K. G. Carothers, "Tank 101-SY Hydrogen Concentration Calculations"

(b) J. O. Henrie, Personal Communication, September 13, 1985.

Introduction

Results of calculations performed earlier (reference a) indicated that sudden release of accumulated slurry growth gases might cause the hydrogen concentration in the vapor space of Tank 101-SY to exceed the 2% specification. Monitoring of the tank vapor space was recommended. This letter describes the results of the hydrogen monitoring which began in January of this year.

Description

The monitoring system consisted of a Gastech hydrogen monitor and a chart recorder to continuously record the hydrogen concentration. The monitor was set to measure hydrogen concentration up to four percent, which is the lower flammability limit of hydrogen in air. Samples were pulled continuously from the 8-inch ventilation line on Tank 101-SY.

Several problems were encountered during the hydrogen monitoring period. After a few days of operation, the cold weather caused the reading to drift downward. Low concentrations of hydrogen would not have been detected during this period. Concentrations of two percent or above would have been detected but would have appeared to be of much lower concentration. However, no gas releases occurred during this time. On February 11, the chart recorder began malfunctioning; about one month passed before a replacement recorder could be found, tested, and installed. In April, the sample tube was found disconnected from the tank vent line; it is estimated that the line had been disconnected for as long as a month. Finally, due to other manpower requirements, maintenance of the recorder was suspended until the work was formally scheduled; about two months passed before maintenance of the recorder was resumed. As a result, hydrogen concentration data was obtained for only sixty-nine of the days between January 11 and September 11.

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Other data available for Tank 101-SY were liquid levels (measured three times a day for the FIC and daily for the manual tape), tank temperature profiles (taken weekly), and vapor space pressure.

Results

Since the hydrogen monitoring began, five gas releases have occurred in Tank 101-SY. They took place on January 31, March 15, April 14, May 31, and July 16. Two of these have caused pressurization of the vapor space. Hydrogen concentration information is available for three of the gas releases; problems with the monitoring resulted in no information on the hydrogen concentration after the other two releases. Figure 1 shows the liquid levels as a function of time during the gas releases. This and other information are also included in the table.

Liquid levels and temperatures for the monitoring period are shown in Figure 2. Both FIC and manual tape liquid level readings are shown and the temperatures are those recorded from thermocouples located 28, 76, and 124 inches from the bottom of the tank. This graph was provided by H. A. Anderson of the Tank Farm and Evaporator Processing Engineering Group (TF&EPE). The liquid levels are not graphed as frequently as in Figure 1 but the temperature drops that occur with gas releases are shown. The fact that temperatures at the bottom of the tank rise and fall with the liquid level suggest that gases accumulate at the bottom of the tank. The temperatures dropped after all the gas releases except the one in July. The temperature fell at two of the thermocouple locations but rose at the thermocouple nearest the bottom of the tank. There has also been a noticeable decline in the average liquid level and temperature in the tank over the last eight months.

The three gas releases for which there is hydrogen information are the ones which occurred in January, March and July. The first two gas releases were a result of lancements in the tank; no hydrogen was detected after these releases. Hydrogen was detected after the last gas release. The gas release in July may have been the largest of the three; the liquid level drop is comparable to the January drop and the change in pressure was the largest.

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Figure 3 shows the hydrogen concentration as a function of time for the July 16 gas release. A sharp peak occurred about 22 hours after the pressurization. The sharpness of the peak indicates that gas was released at a location almost directly below the vent line and that a gas plume must have entered the vent line, mixing very little with the air in the vapor space (reference b). The hydrogen concentration reached a maximum of 5%. The concentration dropped rapidly to 0.2 to 0.3% and remained at this level for over a day. This concentration most likely represents the maximum hydrogen concentration reached throughout the vapor space. The fact that the hydrogen concentration remained level for so long indicates that the gases were not released all at once but over a number of hours. Very low concentrations of hydrogen may have been present after the other gas releases although they were not detected.

It is estimated that about 1000 ft³ of hydrogen was released during a forty hour period. Using a rough estimate of the total volume of gases released (3800 ft³), the hydrogen concentration in the gases released would be about 26%. These numbers are comparable to those calculated in reference a and observed in laboratory slurry growth experiments. The average hydrogen concentration in the vapor space remained small because gases were released over a long period of time. If the gas release had been instantaneous, a hydrogen concentration of 2.5% might have been reached.

Summary

Of the three gas releases which were monitored for hydrogen, only one had detectable levels of hydrogen in the vapor space. After the July 16 gas release, the vapor space hydrogen concentration was 0.2 to 0.3%, well below the flammability limit and tank specifications. Similar concentrations would be expected from other gas releases in the tank. However, as the peak concentration of 5% indicates, small "pockets" of gases at higher hydrogen concentrations may exist until they become mixed with the air in the vapor space.

Because of the fairly large amounts of gases which can be released, it is important that the ventilation system for Tank 101-SY not be shut down when gas releases are expected. Continuous operation of the ventilation system will remove hydrogen and other slurry growth gases and minimize the possibility of hydrogen accumulating in the vapor space.

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Monitoring of liquid levels, temperature, and hydrogen concentrations in Tank 101-SY will continue in order to gather more information about slurry growth.

L. M. Sasaki

L. M. Sasaki, Engineer
Waste Management Process Technology Unit

LMS:wrj

Att. (3)

cc: D. R. Bratzel
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H. E. McGuire
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Hydrogen Concentrations After Gas Releases

Date	<u>Overall L.L. Drops</u>		Pressurization	Maximum H ₂ Conc.
	<u>EIC</u>	<u>Manual Taps</u>		
1-31-85	~1.4 in.	3.0 in.	-1.5 to +0.01"wg	not detected
3-15-85	1.2 in.	0.5 in.	none	not detected
4-14-85	4.2 in.	2.75 in.	none	no data
5-31-85	~3.2 in.	1.25 in.	none	no data
7-16-85	~3.9 in.	1.0 in.	-2.65 to > 0"wg	approx. 4%

*The sudden rise in L. L. that often occurs before a gas release was not included when determining overall liquid level drops.

Some L. L. drops were difficult to measure because instrumentation had been flushed before or after the gas release.

— FIC
- - - - - Manual Tape

Figure 1. Liquid Levels in Tank 101-SY During Gas Releases.

LIQUID LEVEL, inches

FIGURE 2

LIQUID LEVEL/TEMPERATURE:TK-101-SY

January 7, 1985 Through Sept 9, 1985

Hydrogen Concentration

FIGURE 3
HYDROGEN CONCENTRATION
IN IK101-SY VENT LINE

Calculation of Volumes of Gases Released

Volume of H_2 Released

Assumed: $T = 100^\circ F = 310.8^\circ K$

vent rate = $185 \text{ ft}^3/\text{min}$

H_2 monitoring showed:

1. One peak w/ 5% maximum H_2 conc
measuring area under the peak $\Rightarrow 32.2 \text{ ft}^3 H_2$
2. H_2 conc. was $\sim 0.25\%$ for $28 \frac{1}{2} \text{ hr}$ and
3. H_2 conc. was $\sim 0.15\%$ for $10 \frac{1}{2} \text{ hr}$

$$\begin{aligned} \text{Vol } H_2 \text{ released} &= 32.2 \text{ ft}^3 + [(0.0025)(28.5 \text{ hr}) + (0.0015)(10.5 \text{ hr})] (60 \frac{\text{min}}{\text{hr}}) (185 \frac{\text{ft}^3}{\text{min}}) \\ &= 32.2 \text{ ft}^3 + 165.7 \text{ ft}^3 \\ &= 197.9 \text{ ft}^3 \end{aligned}$$

Vol H_2 released $\approx 1000 \text{ ft}^3$ @ $100^\circ F$, 1 atm

Volume of gases released

Assumed: gases are trapped at the bottom of the tank (34 ft below the surface)

Sp. Gr. of DSS = 1.8 $\Rightarrow$ pressure at bottom = $1141.2 \text{ "w} = 2.8 \text{ atm}$

T at tank bottom = $139^\circ F = 332.4^\circ K$

Liquid Level drop = 3.9 ft ($-\Delta h$)

from reference a: $\Delta V = \frac{150,870.1}{409.8} \Delta h \text{ ft}^3$ (change in volume of waste, volume of gas trapped at bottom)

$$\text{volume of gas trapped at tank bottom} = \frac{150,870.1}{409.8} (3.9) \text{ ft}^3$$

$$= 1435.8 \text{ ft}^3 \text{ @ } 139^\circ F, 2.8 \text{ atm}$$

$$\text{volume of gas released} = (1435.8 \text{ ft}^3) \left(\frac{2.8 \text{ atm}}{1 \text{ atm}} \right) \left(\frac{310.8^\circ K}{332.4^\circ K} \right)$$

Vol of gas released = 3759.0 ft^3 @ $100^\circ F$, 1 atm

$$\text{Concentration of } H_2 \text{ in slurry growth gases} = \frac{1000}{3759} \times 100\% = 26.6\%$$

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bcc: DH McKenzie
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file/lb

December 23, 1985

Mr. R. D. Wojtasek
Program Manager
Applied Technology and Strategic Planning
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington 99352

Dear Mr. Wojtasek:

Subject: Cyanide Analysis in TY Tank Farm Samples

Reference: Letter, L. G. Morgan to C. J. Geier, Same Subject, March 29, 1985

During the TRAC Team meeting on December 6, 1985, it was announced that a number of elements had been deleted from those to be analyzed in the single-shell tank samples. Among those deleted was Cyanide.

As was stated in the reference letter, PNL feels there may be potential hazards involved in those tanks which received significant quantities of ferrocyanides. Large quantities of cyanide are involved; up to 140 tons estimated. Implementation of the reference disposal technology on the single-shell tanks may increase the hazard.

We recommend that analysis of samples from those tanks predicted to contain large quantities of ferrocyanides include cyanide, and that additional studies to fully determine potential hazards be completed prior to implementation or testing of dome filling techniques.

A proposal to evaluate the hazards was prepared in response to a DOE-RL request and is attached for your consideration. We would be glad to make the appropriate staff available at your convenience to discuss the matter.

Very truly yours,

M. S. Hanson, Program Manager
Defense Waste Technology
Hanford Environmental and Technology
Applications

MSH:gmh

cc: WW Schulz

From: Double-Shell Tank Process Engineering Unit
Phone: 3-3816 2750E/200E R1-51
Date: October 25, 1988
Subject: TANK 101-SY SLURRY GROWTH

13331-88-476

To: D. G. Baide R1-51

cc: R. J. Baumhardt R2-40 G. E. Dunford R1-51
F. E. Boyd S5-04 T. A. Carlson R1-51
T. E. Blankenship R2-40 L. M. Sasaki R2-11
D. E. McKenney R2-11 KOF: LB/File

References: See attached reference section.

SUMMARY

In accordance with a request of July 19, 1988, the Tank 101-SY "slurry growth" files have been studied. This tank has not been at its original fill level for the past eight years due to trapped gas bubbles that have the effect of increasing the volume of material in the tank. The breakdown of the organics and production of gases have been documented in various studies (references 9, 10) and correspondence (references 1, 2, 3). These gases raise several concerns:

- o flammability/explosion of hydrogen;
- o tank level rising above specifications;
- o over-pressurization of tank vapor space with subsequent contamination spread to environment, and personnel radiation exposure;
- o NH₃ potentially above threshold limit values at stack.

This tank has been studied and characterized sufficiently to be able to justify taking action to correct the gas generation problem now, if the risk warrants the cost of doing so. A rationale for "fixing" the problem is presented below. Several suggestions for possible fixes that can be individually or collectively accomplished to address the slurry growth are included. Each option would require a cost estimate to be prepared, and better definition of what is involved prior to proceeding.

HYDROGEN

Currently the 101-SY tank has a gas release event approximately every 8.5 weeks (the most recent was October 9, 1988) in which the liquid level drops on average approximately 4.5 inches. If that was all that occurred with this tank, there probably would not be a problem, but occasionally the

liquid level drops 9 inches with a coincidental release of considerably more gas than 4.5 inches can produce. Reference 2 indicates that if all the gas were to exit at once (which in the past has taken several hours), the tank vapor space could rise to 3.6 percent hydrogen for a 2.9-inch liquid level drop (based on bubbles at the bottom of the tank). With a 9-inch drop, an 11 percent hydrogen gas mixture could occur in the tank vapor space. Figure 5 shows the last 5 years of liquid level drops as taken from the raw data recorded by the surveillance system. The trend, although slow, is toward increasingly large liquid level drops. Figure 6 is the display of the linear regression calculation (by the computer program "STATGRAPHICS"). On Figure 6, B0 is the "Y" intercept, and B1 is the slope of the line fitting the data by the methods of linear regression (or least squares fit). The bounds represents the 95 percent confidence level that the slope will be inside the inner bounds, and that a new data point will be inside the outer bounds. According to the data then, large liquid level drops can be expected. Reference 3, which was reporting the results of actual in-tank hydrogen levels (as opposed to the calculations of reference 2), shows that overall tank hydrogen is lower than the theoretical maximum. This is probably due to the extended duration of the event (a few hours) and to continuous ventilation of the vapor space. It is possible, however, that the tank could burp bigger and faster and exceed the flammability limit of 4 percent hydrogen. (The 4-percent limit is based on dry air. A high water content will affect this and may warrant further study.) In all likelihood, nothing will happen; but, if the hydrogen should find an ignition source in a pump or fan or static discharge, the vapor space overpressure will rise considerably above 0 inch of water.

As seen on Figure 1, the overall high point of the tank is rising, as is the average tank height taken from the weekly surveillance data. Average tank height in 1988 was 412.5 inches, and the tank low in 1984 was 403 inches. Possibly, over a period of time, the tank is burping less and less completely and is retaining more and more gas. There is no guarantee that, at some point, an event will not occur in just the right order to more completely eject the gas. This could result in a liquid level drop of 15 to 20 inches which, as above, may yield considerably more than a 4 percent (the minimum flammability limit) hydrogen vapor space. Finally, the hydrogen monitor has detected what was called a "plume" of hydrogen at 5 percent (reference 3). It seems clear that, at numerous times during the year, Tank 101-SY could have been technically out of compliance with the 2 percent hydrogen limit (reference 7). In all likelihood, portions of the vapor space go above the 4 percent flammability limit; further, it is likely that, at some point, the whole vapor space could go above 4 percent. This is an identified hazard that should not be left unattended.

TANK LEVEL SPECIFICATIONS

Figure 1, and the associated linear regression calculated and graphed in

Figure 2, would indicate a long-term threat to the 422-inch limit on the tank level. From Figure 2, the upper bound of the 95 percent confidence level intersects the 422-inch point in early 1990. And the expected maximum tank height (heavy line on Figure 1) will cross 422 inches in approximately October of 1993. In other words, the 422 inches will be in occasional jeopardy during the next year or so, and by 1993 will be in frequent jeopardy. The 101-SY tank will not fail structurally at 422 inches, making the risk of exceeding 422 inches primarily a problem of analysis and paper work to document this occurrence.

PRESSURIZATION OF TANK VAPOR SPACE

The tank is normally maintained at -1.85 inches water and approximately 550 cfm of air. A ventilation safety switch turns off the ventilation at -6.0 inches. The maximum ventilation flow rate from SY-101 is 700 cfm (reference 5).

Risk to Environment

A few months ago and several times during the past few years, Tank 101-SY burped sufficiently to pressurize the vapor space above 0.0 inches. This has the effect of reversing flow that is normally down through vents, drains, plugs, and leaks. Ultimately, given enough pressure and time, discharge of the tank gas and radionuclides into the environment and subsequent contamination spread is inevitable. The tank farm grounds are surveyed after each positive burp and no contamination above background level has yet been detected. It is obvious to most observers, however, that it is just a matter of time until a burp contaminates the area.

Work Exposure

Operators are periodically performing maintenance, taking readings, etc., above the tank, and remain in that area for many minutes.

With larger "burps" occurring, it is possible to expect several pressurizations per year. Since the lancing is not working predictably now (reference 4FB/4BC) the timing of the burps is unknown and could catch people in the area unaware. This would release a radiation exposure that has not been quantified. Analysis of the potential source term and exposure to workers should be calculated.

NH₃ Potential

Reference 11 indicates that ammonia production may be a part of the break down of the HEDTA in the 101-SY tank. The report shows there is wide variability in relative distribution of gases between NO_x, NH₃, H₂, and others. One data point indicates NH₃ will be present at approximately 40 percent of the level of hydrogen. Therefore, an ammonia concentration

spike in the tank vapor space may be occurring with the tank burps at the same time the hydrogen puffs out. Ammonia concentrations of 0 to 4 percent might be expected in these puffs. At these levels, the flammability potential is very low (reference 12), but ammonia will detonate (reference 12) at higher concentrations and may therefore add some energy to any hydrogen burn that might occur. Over a two-week period in which lancing was conducted bi-weekly, the average concentration of NH_3 was found to be 102 ppm. This yields 5 pounds per day on a continuous basis.

Two other ammonia considerations warrant mention. The environmental reporting requirements have been stated (reference 4RW) as: "a 100 pound/day release of ammonia must be reported per CERCLA". At a 4-percent concentration puff (which is about the largest possible puff, but not necessarily the largest relative abundance of hydrogen/ammonia that might occur), approximately 100 pounds of ammonia will be discharged. There is some chance, therefore, that the tank would qualify as an ammonia generator under the CERCLA, which would entail additional reporting requirements.

The other consideration is the potential for personnel occupational hazard from ammonia fumes. These fumes will primarily be exhausted through the ventilation stack at high velocity and dissipate in the air. Any reverse pressurization of the vapor space may push a portion of the ammonia into the occupied areas. The 0 to 4 percent concentration in the tank vapor space equates to up to 40,000 ppm concentrations. At 140 ppm, ammonia is extremely irritating to the eyes and mucuous membranes (reference 12). The Occupational Safety and Health Administration (OSHA) limits occupational exposure to 50 ppm and continuous exposure should be kept under 25 ppm (reference 12). It would appear that worst case circumstances could make the ammonia hazard a significant problem. Occasional atmospheric inversion conditions in the tank farms brings stack ammonia down to grade level in concentrations that are detectable by the operators.

RECOMMENDATIONS

It seems that, at this time, precise knowledge of the root cause of the slurry growth is not as important as defending against its effects. Obviously it is desirable to know exactly what is happening to avoid reoccurrences and perhaps eliminate the problem. However, the nature and location of gas production, the trip mechanism, the release of puffs, the hydrogen content, and the contamination levels of the vapor space have been examined for 8 years and may never be exactly known. What is known is that:

- the tank level is rising;
- gas forms in the slurry and is irregularly discharged;
- the gas discharge is contaminated, contains hydrogen and ammonia, and can overpressurize the ventilation.

These effects are tolerated because they were unplanned. We would not receive nor would we ask for authority to set up a similar situation in another tank. In view of the risks to the tank, the environment, and the working personnel, it is recommended that the effects of the tank's burps, if not the cause, be eliminated. Actions that could be taken to ameliorate these effects are listed below.

The short-term, low-cost options are listed first, followed by long-term more expensive that are "should do" choices, followed lastly by long-term expensive options that "should be considered".

Short-Term, Low-Cost

- o Reduce tank level by pump out to approximately 400 inches.
- o Reduce leakage points for positive pressure to escape.
- o Reduce the slurry viscosity (by dilution with water or other wastes) to allow bubbles to rise more readily.
- o Install additional level detectors.
- o Place all 101-SY area workers on mask.

Long-Term "Should Do"

- o Increase the negative pressure and flow capacity for 101-SY ventilation.
- o Mechanically break holes in the crust in several locations.
- o Improve lancing techniques.
- o Install gas monitors.

Long-Term "Consider"

- o Initiate a recirculating pumped degassification system.
- o Install mixer/agitator near tank bottom to disengage bubbles.
- o Increase air flow from lances or install ALC's to cool tank and thereby reduce tank gas production rate.
- o Photograph tank before and after a gas event (during an event would also help).

DISCUSSION OF CORRECTIVE ACTIONS

Increase Negative Pressure and Ventilation

For Tank 101-SY, no outage of the ventilation system is acceptable. An operating ventilation system is undoubtedly responsible for minimizing the effects of previous positive burps. A highly reliable, dedicated ventilation system that could maintain 4 inches negative and when necessary exhaust air in the range of 3000 cfm should be installed. A high capacity fan with a flat vacuum curve could accomplish this. The higher vacuum will provide some room before the tank is overpressurized and the larger air flow rate (when air is available) will flush hydrogen and ammonia at a much faster rate. At 3000 cfm, the vapor space will be exchanged (or withdrawn) in about 10 minutes, as opposed to the 40 to 50 minutes it currently requires. Increasing the stack height would also reduce the likelihood of having ammonia drop back to grade level in the tank farms. The system may have to be redundant and have local emergency power available.

Reduce Tank Level

This tank and its slurry are headed up in height. The low level of 403 inches has not been seen since 1984. The average tank height for 1988 is 412.5 inches. If the crust is mostly level, the margin for expansion has been reduced by 9.5 inches since 1981, and at a minimum the tank ought to be lowered by that amount. Projecting that the slurry will continue to generate gas to 1995 (reference 1) and that the slurry will continue to increase its viscosity (and/or the gas retention mechanisms), the tank level could rise an additional 8.5 to 9 inches between 1988 and 1995. This will put the average tank height at 421 inches with peaks and valleys of ± 4.0 inches. If a destination for part of the slurry can be found, the tank should be reduced in level to a point at which a later future and additional reduction is not necessary.

Reduce Leakage Points

Attention could be directed to sealing drains, gaskets, and leaks into the tank to defend against atmospheric/environmental releases during a pressurization event. If most of the unfiltered flow paths are sealed the affects of the event will be minimized. This would ensure that the environment and the operators would be passively protected in the event that all the mechanical system proved inadequate. This would require installation of a controlled filtered air inlet which does not now exist.

Break Crust

There is some possibility that the crust is temporarily catching the bubbles that seem to spontaneously come out of the slurry every 8 weeks. By capping the gas and then puffing it out in bursts, (see photographs - Figures 9,10,11, and 12 for evidence of puffs at the sidewalls) the release may be exacerbated. If a "vent" can be put into the crust by

mechanically breaking the crust in perhaps 3 places and renewed periodically, the puffing might be minimized. Several floating vents with a probe reaching 4.0 feet down could possibly be dropped in or pushed into the crust as an alternative. This corrective action, breaking the crust, is not guaranteed to have any affect. Most of the others will.

Reduce the Slurry Viscosity

With a high enough viscosity, bubbles can grow and be imbedded in the slurry and will not migrate. Eventually, enough bubbles agglomerate and the large bubble's tendency to rise overpowers the slurry. If the bubbles grew at the same rate all over the tank, the shock wave from the air lances or from the collapse behind the first large bubble leaving could initiate an area or the whole tank to suddenly release the gas. This trapping effect can only occur in viscous or "chunky" material. It does not occur to an great extent in water. Unfortunately, reducing the viscosity by dilution will probably double the volume of waste which would require a second tank to hold the excess. This would be a better-than-nothing solution, however, and could be verified in the laboratory prior to beginning a program.

Improve Lancing

With the lancing currently being done daily and burps coming every 8 weeks, it is obvious that lancing has become ineffective. The lances may have isolated themselves (reference 4BC) in encapsulating columns of waste. Regardless of the mechanism, they are not tripping the tank until the tank is ready. When they are working, it was the lancing that caused at least one instance (October 20, 1983) of overpressurization. If the tank will not trip until there is a hazard, the trip mechanism needs to be examined. New lances could be installed in new locations, or perhaps a larger effect system could be installed in the existing nozzles (more air, lateral piping, pulsed air).

Recirculating Degassification

A small quantity of slurry could be pumped through a vacuum degassification chamber (or other suitable approach such as heating and recooling or just returning to the top of the crust) and reinjected into the tank on the opposite side. By processing the tank volume every 4 to 8 weeks, it should be possible to completely avoid any future burping. This would take a 12- to 25-gpm system that could accommodate the physical and chemical properties of the slurry. This approach has been recommended (reference 4WE) for somewhat analogous water systems having outgassing events.

Increase Air Flow

The gas generation rate is reported to be highly temperature dependent (reference 8). Since airlift circulators are routinely utilized to remove tank heat, it is possible that airlift circulators could be installed (in

conjunction with the larger ventilation system) to cool the tank contents and reduce the gas generation rate. Perhaps the air lances now in place could partially serve this function if continuously input air was sufficiently cool (or cooled). If temperatures could be reduced by 20°F, the gas generation rate would drop by as much as 50 percent (reference 9). The disadvantage is that cooler slurry is more viscous. It was suggested (reference 4BV) that heating the tank to reduce the viscosity would be beneficial to enabling bubbles to escape. More laboratory work and an examination of the literature relating to retained bubbles in a viscous medium would be in order to define this subject.

Install Gas Monitors

Equipment should be permanently installed and properly housed to continuously monitor the ventilation stream for hydrogen and ammonia. It is important to know the specific hazard to be dealt with after the documentation that a hazard exists.

Place Workers on Mask

Masks/respirators that are capable of filtering both particulate and ammonia could protect workers from the inhalation of hazardous material. Considering the uncertainty of the timing of the burps and the potential for risk from released material, masks are probably warranted. However, masks will not protect operators from the external gamma dose received from being in a potential cloud of release contaminated air.

Install Level Detectors

The single FIC level detector should be backed up by a minimum of one and preferably several additional level detectors (all uniformly calibrated and operating on the same principles). More data on tank level, hydrogen levels, and temperature will prove useful in tracking the eventual demise of the gas problem.

Take Photographs

Photographs of the inside of the tank just before, during, and after an outgassing event could provide information on the role of the crust during an event. Perhaps an automatic trip could be placed on the camera, or the tank panned continuously with a closed circuit TV that records its viewing on video tape. The tape would be visually scanned and recycled if it did not contain pertinent information.

CONCLUSION

Although Tank 101-SY is among several tanks that have had some slurry growth, the problem at 101-SY is presently uncontrolled. The tank burps in its own time and to its own extent. Taking no corrective action to at least control the symptoms is not defensible in view of the risks discussed above. Westinghouse Hanford Company should investigate the cost of the options listed, identify funding, and implement a solution. The minimum actions to be taken should include pumping out a portion of the tank volume, and attempting to seal all tank in-leakage points. In addition, installing more level detectors and gas monitors, and placing operators on mask should be considered as possible short-term actions.

Two of the long-term "should do" options warrant attention: higher ventilation flow rate and improved air lance. This will not cure the problem, but it will keep the tank from achieving over-height limits, defend against a hydrogen problem, and protect the workforce and environment from any contamination loss. Tank 103-SY may have room for some of the solution (reference 4BP), and the ventilation need not be elaborate to tie into existing piping and conform to existing quality levels. In the long-term "consider" options, the idea most likely to eliminate the burping is the pumped degassification. This, of course, will be fairly expensive, but it is the one option that treats the problem and not the symptoms.

K O Fein

K. O. Fein, Engineer
Double-Shell Tank Process Engineering Unit

bjb

attachment

ATTACHMENT TO 13331-88-476

REFERENCES

1. Letter, L. M. Sasaki to D. R. Ellingson, "Safety of Double Shell Slurry Storage (101-SY)", October 7, 1983.
2. Letter, L. M. Sasaki to K. G. Carothers, "Tank 101-SY Hydrogen Concentration Calculations", November 26, 1984.
3. Letter, L. M. Sasaki to K. G. Carothers, "Results of Hydrogen Monitoring in Tank 101-SY", September 16, 1985.
4. Personal Conversations, July 1988:
 - o DE = Darrel Ellingson, Nuclear Safety
 - o FB = Fay Boyd, Tank Farm Surveillance and Operations.
 - o HA = Hank Anderson, Tank Farm Surveillance. Analysis and Support
 - o LS = Leela Sasaki, Tank Waste Characterization
 - o BC = Brett Campbell, Double Shell Process Engineering
 - o RB = Rex Bendixsen, Tank Waste Retrieval
 - o HP = Hurshal Powers, Waste Management Planning
 - o WE = William Evans, United States Geologic Survey
 - o TC = Terry Carlson, Double Shell Process Engineering
 - o BP = Bill Powell, Tank Farm Process Technology
 - o RW = Ron Wheeler, Environmental Assurance
 - o BV = Bob Van der Cook, Chemical Processing Division
5. SY Ventilation Drawings:
 - H-2-37747
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6. Letter, D. R. Ellingson to Distribution, "Vapor Space Pressurization of Double Shell Tank 241-SY-101", July 12, 1983.
7. Operating Specification Document, OSD-T-151-0007, "241-AN-AP-AW-AY and AZ and SY Farms", March 17, 1988.
8. Supporting Document, SD-WM-TPP-007, "Technology Plan for Slurry Growth, 1985", December 21, 1984.

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9. Supporting Document, SD-RE-TI-062m, C. H. Delegard, "Identity of the HEDTA Decomposition Product in Synthetic Hanford High Level Waste", C. H. Delegard, January 24, 1983.
10. Supporting Document, SD-WM-TI-049, L. A. Gale, "Summary of Slurry Growth Experiments 1982", March 3, 1983.
11. Document, RHO-LD-124, D. H. Delegard, "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101", December 1980.
12. Dangerous Properties and Industrial Materials, H. Irvin Sax, Sixth Edition, Van Nostrand Reinhold Company, 1984.

Gen.
Sent copy
to DS with HOFelder

Rec 9/19

2nd Draft

Copies To:

9/21
Kelly
PCS Review
THIS For me
I saw the
Gary
9/15/88

Brett Campbell

Gary Sanford

Dan Bader

Terry Carlson

Comments to

K & Fern
-3 & 16
R-51

Gary
This letter is right on!
Ken has organized it well,
developed his main points/
ideas well, and provided
a sound rationale for action.
I suggest that the distribution
be broadened—the more
champions you can get into
your corner, the more
likely this work will go
forward. I agree with Ken.
WHC is at risk on this
problem that we have
recognized for a long time.
Kelly

to Bill Clark
KOF READ 12/25/88

Westinghouse
Hanford Company

Internal
Memo

From: Tank Farm Operations
Phone: 3-1071 S5-04
Date: November 17, 1988
Subject: TANK 101-SY SLURRY GROWTH

13230-88-FEB-145

To: D. G. Baide R1-51

cc: R. J. Baumhardt	R2-40	J. S. Lee	T4-01
T. D. Blankenship	S5-04	D. E. McKenney	R2-11
G. L. Dunford	R1-51	T. K. Orgill	T4-01
P. Hinojosa	S5-04	D. J. Washenfelder	R1-43

REF: Letter, K. O. Fein to D. G. Baide, "Tank 101-SY Slurry Growth", dated 10/25/88

In accordance with recommendations of corrective actions stated in the referenced letter by K. O. Fein, the actions listed as short-term and long-term need to have cost estimates. Actions required to control slurry growth effects should have high priority.

Please prepare estimates for the actions listed and discuss at a meeting Tuesday, November 22, 1988, in the 272-AW conference room at 10:00 a.m. If you have questions, call F. E. Boyd on 3-1071.

F. E. Boyd

F. E. Boyd
Asst. Manager

pld

Rec'd 9:30 AM
11/18/88

Ken + Brett -

Please respond to this request to support our unit at the 10 AM meeting. Ken please take the lead, but have Brett help you as appropriate.

Thank, Don 11/18/88

United States Government

Department of Energy

memorandum

DATE: June 6, 1990

REPLY TO
ATTN OF:

EH-322

SUBJECT:

Review of the Hanford Tank Farm Flammable Gas Issues

TO: Steven Blush, Director, NS-1

The attached EH Report, prepared by Dave Ruscitto and John Stefano who participated in the joint ONS/EH investigation of the subject matter, is hereby forwarded. Please note that the photographs referenced in Paragraph D.2.a. of the report are being developed and will be furnished at a later date. A similar set of photographs was provided to you by Dave Ruscitto during your most recent visit to the Hanford site.

A copy of the report has been furnished to the Tiger Team appraising the Hanford site.

Peter N. Brush
Acting Assistant Secretary
Environment, Safety and Health

Attachment:
As stated

cc w/attachment:
L. Duffy, EM-1
M. Lawrence, RL
J. Fitzgerald, NS
J. Hulman, EH-32
R. Poe, EH-342
O. Lynch, EH-331
R. Bowser, EH-321
R. Hanson, EH-342
O. Thompson, EH-331

SPECIAL REPORT

OFFICE OF ENVIRONMENT, SAFETY AND HEALTH REVIEW

OF

HANFORD TANK FARM FLAMMABLE

GAS ISSUES

PRE-DECISIONAL INFORMATION"

A. INTRODUCTION

1. Purpose

The purpose of this inspection was to evaluate the circumstances surrounding the discovery of potentially flammable gases in the Hanford double-shelled tanks (DST). The inspectors were participants in a joint investigation team composed of members of the DOE Office of Nuclear Safety (NS) and Office of the Assistant Secretary of Environment, Safety and Health (EH). The participation of EH representatives was two-fold:

- a. Evaluate worker health and safety response on the part of the Richland Operations Office (DOE/RL) and the principal contractor, Westinghouse Hanford Company (WHC).
- b. Provide technical input in several functional areas to the combined overall NS/EH investigation. In this respect, safety performance as well as areas indirectly related to safety were evaluated.

This report is a combined assessment covering both areas.

2. Scope

The charter of the NS/EH Team was to evaluate all relevant aspects of the hydrogen generation issue which would allow understanding of how technical information, particularly as it relates to safety issues, flows between DOE/RL and both DOE Headquarters and WHC.

The EH representatives were assigned to evaluate contractor and DOE-RL performance in the functional areas of safety, operations, maintenance, design control and event reporting. The evaluation was primarily focused on the hydrogen generation issue, but also involved the West Tank Farms and the SY farm in particular.

Activities undertaken in response to the current understanding of the problem are not within the scope of this report. This report is concerned with lessons to be learned from how the issue was handled from the time of its initial identification until the recent concerns were expressed.

"PRE-DECISIONAL INFORMATION"

3. Background

In March 1990, DOE/RL reported that potentially explosive gases, primarily hydrogen (H_2) and nitrous oxide (N_2O), were being evolved within certain double shell tanks (DSTs) in the Hanford Tank Farms. These tanks store nuclear wastes resulting from the reprocessing of nuclear fuel. Reprocessing operations have been conducted at Hanford since the time of the Manhattan Project. The gases are the product of decomposition of complex organics in the tanks. Some gases are also produced by radiolytic action.

The most troublesome tank has been DST 241-SY-101, referred to as 101-SY, which is located in the SY Tank Farm in the 200 West Area, approximately in the center of the 560 square mile Hanford Reservation. Tank 101-SY contains a mixture of double shell slurry (DSS) and complexant concentrate (CC). The DSS was generated during a pilot project which was designed to reduce the volume of single-shelled tank (SST) wastes through evaporation. The CC was produced during the waste fractionization process at the Hanford B-Plant in which long-lived fission products were removed from certain waste streams. Tank 101-SY is nearly full and contains about one million gallons of waste. The radioactive content is approximately three million curies of mixed-fission products and transuranic elements. Over the past several years a phenomenon known as slurry growth has been observed in the tank. A hard crust has formed over the top of the tank contents. This crust is floating on the liquid tank contents which are suspected to have stratified into several distinct layers. As the gases evolve and collect underneath the crust, the crust rises and a gas pocket is formed. Periodically the tank will "burp" and the gases will be released from beneath the crust which will settle back down. The gases are normally released out the tank ventilation system. Sometimes, however, 101-SY, as well as its neighbor tanks, which share the same ventilation system, are pressurized and the gaseous mixture is released out of any available leakage path. It is the composition, volume and behavior of this gas bubble that has caused concern because of the potential for a hydrogen explosion inside the tank.

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B. FACILITY OVERVIEW

1. Tank Structure

The SY Tank Farm consists of three steel tanks, designated as Tank 101-SY, 102-SY and 103-SY. Each steel tank is surrounded by an outer tank of concrete lined with steel. The area between the tanks is referred to as the annulus. Any leakage from the primary tank will be collected in the annulus preventing an inadvertent release of radioactivity to the environment. The upper portion of the tank is not doubly contained. The concrete shell and dome is monitored for temperature with numerous thermocouples. Openings in the concrete dome are called risers and provide access to the primary tank and annulus space for pumping connections, instrumentation and ventilation. There are several spare risers available for future use. The risers generally terminate below ground in non-airtight enclosures called pits. These pits are covered with concrete shield blocks. Due to the nature of Tank 101-SY contents, there is presently no capability for inserting a pump into the tank through the pump pit riser. The annulus area drains to an adjacent leakage detection pit. Within the farm there are also several additional pits containing valves and other ancillary equipment.

2. Ventilation System

Both the primary tank and the annulus are exhausted through similar exhaust systems. An exhaust fan draws air from the tank or annulus through a steam-heated moisture remover, roughing filter and two high efficiency particulate air (HEPA) filters. A continuous air monitor (CAM) samples the air downstream of the filters prior to its release out the short exhaust stack. The main tank only breathes through air leaking into pits. The annulus is ventilated by design to allow cooling of the tank shell. There are four inlet air ducts which direct outside air below the primary tank through cooling channels in the concrete primary tank base located between the two tanks. Additionally there is a single annulus air inlet which provides a flowpath directly into the annulus area without passing under the tank. All five annulus air inlet lines are fabricated out of sheetmetal and are equipped with a HEPA filter on the inlet. Ventilation flows in both exhaust systems are controlled to maintain both areas at a vacuum and the primary tank at a negative pressure relative to the annulus.

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Unlike most other DST farms, there is no backup ventilation system permanently installed on either the annulus or the primary tank. A portable exhaust unit is currently installed on a temporary basis on the primary tank.

3. Instrumentation and Monitoring Systems

a. Instrument Building

Most of the process instrumentation and alarms are routed to the 241-SY-271 Instrument Building located inside the SY Tank Farm fenced enclosure. A main instrument panel, an air compressor and a motor control center are the primary components inside the building. Certain alarms are also transmitted to the Computer Automated Surveillance System (CASS) located in Building 2750-E in the 200 East Area. Other alarms and indications read out in the adjacent 242-S Evaporator control room. Although the Instrument Building is not normally manned and the evaporator control room is only manned on day shift, the CASS is staffed around-the-clock.

b. Radiation Monitoring Systems

The farm area contains five area radiation monitors mounted on poles. They provide overall radiation detection coverage for the farm area. The 271-SY Instrument Building contains an area radiation monitor. There are CAMs on each separate tank annulus exhaust outlet as well as the above described CAMs on the exhaust stacks. The stack CAMs are interlocked with their respective fans to stop the fans in the event radiation is detected in the exhaust stream. The leak detection well and the 241-SY service pit are both equipped with a radiation detector.

c. Hydrogen Monitoring Systems

The first temporary hydrogen monitor was installed in January of 1985 on the Tank 101-SY exhaust duct. It was simply a portable combustible gas indicator temporarily installed in a cabinet with a chart recorder. It was not designed specifically to monitor for hydrogen and only recorded from zero to four percent hydrogen. From the outset the assembly experienced difficulties and was removed from service in February 1987.

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Although plans were made to replace the hydrogen monitor with a more reliable and accurate device, no progress was made until the issue resurfaced in February 1990. At that time an instrument was removed from the Hanford T-Plant and installed similarly to the old monitor. It also has a chart recorder and has a zero to 10 percent and zero to one hundred percent scales. The switch between scales is manual and it is left set on the lower scale. The current configuration was fabricated from available parts and can only be described as an "interim fix." The sample tubes are not iso-kinetic and are inserted into the duct and held in place by a sealant. They have been removed in the past and left disconnected as was the case during a Team field walkdown conducted on April 24, 1990. In its present configuration, this installation cannot be relied upon to provide any quantitative results other than to indicate whether, via the grab sample, a particular gas was present.

d. Level Instrumentation

Each tank is monitored by a semi-automatic liquid level instrument which is manufactured by Food International Corporation, and referred to as the FIC. It consists of a conductivity-actuated plummet which is lowered until liquid level is reached. At that time, the conductivity change actuates a depth reading. A manually lowered conductivity probe referred to as the manual tape is used as a back-up. A portable sludge level indicator consisting of a drop weight on a reel tape was designed for use in detecting the solids level below the supernatant. This can no longer be used because of its inability to penetrate the crust.

e. Pressure Instrumentation

Tank pressure is monitored and recorded on a high range and low range scale. The high pressure alarm (insufficient vacuum) warns of impending ventilation flow reversal. The low pressure alarm(excessive vacuum) warns of insufficient downward force on the tank bottom. This condition, when combined with a minimum liquid level, could be insufficient to counteract uplift that could damage the tank bottom.

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f. Temperature Instrumentation

A thermocouple tree is inserted into the tank to measure temperature at various levels. As the crust rises and falls, it also apparently twists. From in-tank photographs, it appears that the thermocouple tree has been bent. It has not been determined whether this has damaged the tree and is impacting the reliability of the data. There are also thermocouples located in the tank concrete walls. Their purpose is to monitor for undue thermal stresses in the tank structure. This is currently not a concern in the SY Tank Farm because the waste is not generating enough heat to cause a sensible temperature increase. Numerous instrument leads from thermocouples to the Instrument Building are so badly deteriorated that the signals are not detectable. Although instrument calibration is specified, it was not apparent that instrument calibration has or is currently being checked.

4. Electric Power Systems

There is a single normal power source for all of the SY Tank Farm. One exception is the air system which is supplied with an emergency power supply from the 242-S Evaporator. On a loss of power all ventilation and nearly all instrumentation is lost. The portable exhaustor would also lose power. Although some other DST Farms are equipped with a back-up diesel power supply, the SY Tank Farm is not.

5. Auxiliary Systems

a. Air System

An air compressor and associated piping and valves is located in 271-SY. The air supplies instrumentation needs as well as the air lift circulator system in Tank 102-SY. The circulator was used when Tank 102-SY was the feed tank for the 242-S evaporator. Since the evaporator is no longer in service, the circulator is not used. A modification for the air lancing system was made to the piping in the Instrument Building. It appears that this modification was never fully installed based upon a lack of pipe supports. (Refer to paragraph D.2.a.)

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b. Lancing Systems

A system of air and water lances was temporarily and later permanently mounted in Tank 101-SY. The purpose of the lancing was to agitate the space below the crust and force a venting of the trapped gases. Neither air nor water lancing proved successful and both operations were discontinued although the hardware is still in place. Three of the four installed lances have been severely bent by the twisting crust and most likely cannot be removed without great difficulty.

C. OPERATIONS

1. Previous Audits and Appraisals

Audits and appraisals conducted in the Tank Farms over the past several years have identified numerous weaknesses in the conduct of operations. Some of the areas among those most frequently cited include deficiencies in key control, control of procedure changes, logkeeping, alarm status and internal surveillance.

2. Conduct of Operations

The administrative procedures for the conduct of operations in the tank farms and associated facilities address many of the good practices now identified within the commercial nuclear industry. However, implementation of these procedures is not yet complete. For example, logsheets in the 242-S Evaporator Control Room, where many of the SY Tank Farm alarms are received, were incomplete. It could not be determined from the logs whether an alarm was valid or invalid, or whether corrective action was required or taken. Some alarm annunciator window light bulbs were burned out and by internal WHC understanding may not be changed by an operator. Several strip charts for active equipment were out of paper and have been that way for weeks. The operators were not fully cognizant of the reason for each alarm condition that existed although the area supervisor was very knowledgeable. It was unclear which instruments on the control board were abandoned in place and which were operable. Furthermore, it was not clear whether instruments which were required to be operable were in calibration. The area behind the control board was extremely confused with loose and determinated wiring, miscellaneous instruments and equipment in various stages of disassembly and large quantities of dirt in and around electronic devices.

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3. Operations Interface With Other Groups

Although the Day Shift Operations Supervisor is responsible for activities within the SY Tank Farm area, in fact several organizations exercise control of specific activities. Some examples include health physics, vent and balance, maintenance and process engineering. There is no integrated organization control by one individual who can prioritize work and resources on a scheduler basis. As a result, conflicting requirements among different groups often lead to lost productivity and contributes to the inability to rapidly respond to safety issues. This continuing lack of coordination is combined with a lack of certified operators to support these outside groups. The operators are very knowledgeable about the farms and is a valuable resource. The operators have been the primary identifiers of material problems.

4. Conclusions

Tank Farm operations weaknesses identified by past audits and appraisals continue to exist, particularly with respect to the operability status and overall poor condition of the SY Tank Farm monitoring instruments, indicators, and alarms. There is ample evidence of equipment neglect and abuse, and these material problems have been consistently identified to WHC management by the facility operators. However, judging from the generally poor condition of the facility equipment and the SY Tank Farm overall, it can reasonably be concluded that neither the contractor's management nor DOE/RL (in its oversight role) have reacted positively or timely in getting the equipment deficiencies corrected. Other findings in support of this are discussed in Paragraphs D. (Maintenance) and E. (Safety) of this report. Additionally, there appears to be no integrated organization controlled by one individual who can prioritize work and resources at the Tank Farms. This has resulted in conflicting requirements among the different groups who control activities at the site which is believed to have contributed to the inability of contractor or DOE/RL management to respond to safety issues, in a timely manner, such as the issue addressed by this report.

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D. MAINTENANCE

1. Previous Audits and Appraisals

Previous audits and appraisals of the Tank Farms have been conducted continuously over the past few years. These include quality assurance, safety and program appraisals, both internal and external. These efforts have identified significant deficiencies in material conditions and programs in all of the Hanford tank farms. Many deficiencies are repeatedly identified with no apparent corrective action taken. Some typical assessment findings are summarized below:

- a. A plant labeling program needs to be implemented. (Reference: Tank Farms Operations Proficiency Assessment Report, January 1989)
- b. Instrumentation in the farms is suffering from exposure to the elements resulting in erroneous readings from the exhauster stack monitor, liquid level monitors and radiation level monitors. (Reference: Technical Safety Appraisal, May 1989)
- c. The calibration and preventive maintenance program is inadequately implemented. Instruments which have failed may not be repaired within the calibration interval. The maintenance work list was cut on a priority basis due to lack of resources. (Reference: Tank Farms Operations Assessment Report, January 1989)
- d. Important plant equipment including some safety equipment is not maintained in a reliable condition or the equipment's ability to perform its function is indeterminate. (DOE/RL Audit of Defense Waste Management, February 12-28, 1990)
- e. Equipment performance cannot be assured due to inadequacies in procedural controls and manpower for maintenance and calibration activities. (Technical Safety Appraisal, May 1989)
- f. A formal equipment performance testing, monitoring, trending and analysis program is not implemented for all aspects of the tank farm, however, it was scheduled for completion by the end of July 1989. (Reference: Technical Safety Appraisal, May 1989)

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2. Corrective Maintenance

a. Field Inspection Findings

Inspections of the SY Tank Farm were conducted in April and May, 1990. These tours revealed that the material condition within the SY farm has not improved since the time of the most recent appraisals described above. Additionally, a brief inspection of the adjacent S farm revealed a significant radiological hazard. The purpose of the inspection was not to perform a comprehensive assessment of facility conditions, but to sample selected areas to develop an overall assessment of material status. A summary of the findings by area follows:

241-SY-271 Instrument Building

- The floor and lower wiring behind the instrument panel was covered with about one inch of feathers, dirt and bird droppings. (Photo No. 1)
- A design modification was made which supplied air to the lancing system. This 100 psi air piping assembly which included valves and instrumentation was supported on a roll of heavy tape and a wooden wedge rather than a permanent pipe support. (Photo No. 2)
- Few of the numerous valves and devices had any permanent labeling associated with them. Many had no label and some were identified with tape or with a handwritten note on an adjacent structure. Several instruments had handwritten scale changes. (Photo No. 3)
- The dual-pen recorder associated with radiation instruments RR-EXH-K1-1 and RR-EXH-K2-1 was out of paper. (Photo No. 4)
- Wiring behind the instrument panel was in complete disarray. Numerous wires were cut off, determined or loose. They were not run in cable runs or conduits and many were unsupported. (Photo No. 5)

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K-1 and K-2 Exhauster Area

- Differential pressure(DP) gage DPI-EXH-K1 was pegged high on the continuous air monitor(CAM) for the K-1 system. The corresponding gage on the K-2 system was on scale. (Photo No. 6)
- Three vent and balance sample ports upstream of the K-1 and K-2 exhaust CAMs were missing, allowing potential dilution of the air sample. (Photo No. 7)
- The insulation on the K-1 and K-2 airflow heaters was severely damaged and there were steam leaks present. (Photo No. 8)
- Sample pumps were unbolted in the bottom of every CAM cabinet. These and other cabinets were all found with a significant accumulation of dirt, trash, debris and in one case a tumbleweed. Cabinet doors are routinely left open, bypassing cabinet air filtration. (Photo Nos. 9, 10, 11)

Portable Exhauster Area (Temporarily Installed at Tank 101-SY)

- There is an active bird nest inside the exhauster inlet enclosure(outside the main ductwork).
- The portable exhauster inlet valve was found partially open with the fan windmilling as the K-1 system drew air backwards through the portable exhaust fan and ducting into Tank 101-SY. The condensate drain line back to Tank 101-SY was also open. These are both unmonitored release paths in the event of a tank pressurization. (Photo No. 12)
- Several instrument panel labels had deteriorated from exposure to the elements and were unreadable. (Photo No. 13)
- As a result of the directive to eliminate ignition sources in the SY Tank Farm, the electric air heaters on the portable exhauster are locked out. Should this unit be required to operate, it would be forced to run in a degraded mode (i.e. with moist inlet air to the filters). This is not an analyzed configuration. (Photo No. 14)

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General SY Tank Farm Yard Area

- Numerous junction boxes, panels and conduits exhibited damage from vehicle impact. The most common source of this damage is crane activities. (Photo No. 15)
- Several structural supports have settled causing failures of the supported structure. Two significant examples are the K-1 exhaust duct from Tank 103-SY and the annulus air inlet ducts on Tank 101-SY. Settlement of at least two adjacent supports has caused failure of the isolation valve in the Tank 103-SY K-1 duct. This valve is now leaking and is wrapped in plastic to control the spread of contamination. Although it has been broken for about eight months a new valve has not been procured. This is a failure of primary tank containment and since all three tanks are interconnected, could result in an unmonitored release in the event of a pressurization in Tank 101-SY. (Photo No. 16) The K-2 air inlet for the Tank 101-SY annulus is not welded as is the K-1 system but is fabricated from sheetmetal. Each of the four inlet risers which channel air under the primary tank bottom is supported by a single column fixed in a concrete base. Settlement of the free end relative to the end of the duct fixed to the tank has caused a twist resulting in cracked seams. Some cracks are currently wrapped with duct tape. Others are not and show signs of continuing deterioration. This is a breach of secondary containment and is a flowpath which bypasses the HEPA filters located on the breather inlet. (Photo No. 17)
- All junction boxes and instrument cabinets revealed weather damage varying from minor to substantial. Enclosures are frequently left uncovered with wires exposed, frayed or loose. The cabinet for the specific gravity instrumentation on Tank 102-SY was so badly deteriorated that it is being abandoned. (Photo No. 19)

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Temporary Hydrogen(H₂) Monitor

- The sample lines entering the primary exhaust duct on Tank 101-SY were found detached, allowing air leakage which could dilute the actual sample. If this was the case during the April 19, 1990, pressurization event, the 3.9 % hydrogen reading in the duct may be unreliably low. As a temporary corrective action, the connection has been taped, however no permanent, leak-tight connection has been made. (Photo No. 20)
- The instrument has not yet been calibrated due to a lack of appropriate span gas. A 2.0 % functional check has been conducted.
- Some of the equipment internal to the cabinet is not permanently secured and is lying among various fittings and debris. (Photo No. 21)

b. Equipment Maintenance History

The SY tank farm equipment has a history of neglected corrective maintenance as evidenced by the following:

- The Tank 101-SY manual tape level indicator was out of service for at least three extended periods; July 24, 1985 - September 17, 1985, July 19, 1986 - February 19, 1987 and July 20, 1987 - June 20, 1988.
- The first hydrogen monitor installed in 1985 on Tank 101-SY was functional for only 69 days in the eight months between January 11, 1985, and September 11, 1985. It was finally removed in February 1987 due to continuing operability problems.
- The leakage detector probes in Tanks 101-SY and 103-SY annuli were inoperable from at least July 1987 through August 1988.

There is no machinery history program to track equipment performance and failures. No predictive maintenance is done.

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3. Preventive Maintenance

Preventive maintenance programs at the tank farms involves both instrument calibration and testing and equipment preventive maintenance activities. The Process Instrumentation Surveillance, Calibration and Evaluation System (PISCES) and Preventive Maintenance (PM) are the two systems in use. The Job Control System (JCS) is associated with corrective maintenance activities.

A brief review of PISCES was conducted on a sampling basis and several weaknesses were noted. One PISCES functional test on a leakage detection instrument had been performed with unsatisfactory results in each of the last six months. The alarm was failing to be registered by the Computer Automated Surveillance System (CASS) which is located in the 200 East Area in Building 2750-E. The PISCES card indicated every month that the deficiency would be repaired under a specific JCS work order. The work order was reviewed and found to have been cancelled in January, 1990 because all required work had been completed under another activity. The JCS records were too vague to determine what the actual deficiency was and what action had been taken to correct the problems. There was no tie between the JCS and PISCES. Each PISCES that is completed is recorded as being accomplished regardless of whether there were any failures. There is no indication that any programmatic controls existed to eventually facilitate a repair of this device. Furthermore, there are no plans at this point to initiate action to determine how many other similar situations exist. This problem is similar to one identified by DOE-RL in the Hanford Plutonium-Uranium Extraction (PUREX) Plant PISCES. Corrective action was made a restart issue with PUREX prior to the recent stabilization run. (Refer to Critique Report WHC-C-90-003-PUREX-01.) There is no evidence that the lessons learned from this critique have been or will be transferred to the tank farms either by WHC or DOE/RL. Currently there are some PMs and PISCES that are overdue for accomplishment in addition to those which have been performed with unsatisfactory results.

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4. Maintenance Resources

a. Manpower

The maintenance staff for the 200 West Area is responsible for all the S, T, and U tank farms as well as T-Plant, the evaporators, vaults, diversion boxes, transport lines and laundry facilities. There are 83 single-shelled tanks (SST) in addition to the three SY double-shelled tanks (DST) in the 200 West Area. The average staff of electricians, millwrights, welders, instrument technicians and fitters is about twenty-five. The number available for work during any given day is about one-half of that due to training, vacation and non-maintenance duties. Several are on loan to the 200 East Area for a special project and a few additional specialists such as sheetmetal workers are available from the central shop for specific jobs. When radiological dress-in/dress-out and other health physics and industrial safety requirements are met, each worker can provide a maximum of five to six hours of productive work per day. When divided up among all the facilities, the SY Tank Farm can expect to receive less than ten man-hours of maintenance support per day. This is not sufficient to even meet basic PM and PISCES requirements. It is clear that corrective maintenance suffers as a result. This lack of manpower resources is the primary reason for the poor material condition of the SY farm. Those maintenance technicians interviewed were noted to be technically competent and highly experienced. With increased sensitivity to tank farm operations on the part of DOE-RL and WHC, the maintenance group is being forced to accomplish more without the requisite increase in resources. As a result the condition of the SY Tank Farm continues to deteriorate.

b. Spare Parts

Implementation of quality standard NQA-1 over the last year resulted in disposal of a majority of Tank Farm spare parts and equipment. This occurred because few of the existing spares had traceability for quality purposes that conformed to NQA-1 standards. This has seriously impacted the capability to make repairs in a reasonable time frame. A phased implementation of NQA-1 standards allowing use of existing spares with requisite controls would have been a better solution. In the effort to speed compliance, safety was sacrificed.

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5. Conclusions

The maintenance program at the SY Tank Farm is inadequate. Maintenance, like Operations, is suffering from a serious lack of attention from directly responsible management groups and oversight groups such as radiological controls and quality control. The deficiencies observed in maintenance have left installed barriers to radioactive release, vital instrumentation and equipment in unanalyzed and degraded conditions. The ability of the system as a whole to perform its design function in the manner intended under both normal and accident conditions is questionable.

E. SAFETY

1. Safety Oversight

a. Contractor Oversight

The Westinghouse Hanford Company (WHC) Nuclear Facility Safety (NFS) organization is responsible for safety oversight of the Tank Farms. The Tank Farms Nuclear Safety (TFNS) group consists of a supervisor and four technical staff, two each for SSTs and DSTs. The senior DST safety reviewer is a senior qualified chemist who is knowledgeable and experienced. The DST workload involving reviews of event reports, program plans and procedures, safety analysis reports (SAR), etc., is significantly more than two individuals can be expected to handle and provide an acceptable level of oversight.

More disturbing, however, were inferences made by operating staff interviewed that WHC NFS managers have attempted to isolate staff who raise safety issues from the WHC program groups as well as their counterparts at DOE/RL. A review of documentation, personnel interviews and field inspections revealed that numerous valid safety-related concerns raised by TFNS staff have been systematically ignored and/or watered down. No evidence was found of a single instance where WHC NFS management aggressively pursued a staff-developed safety issue with the program groups. Significant examples of longstanding, issues which were not acted upon include the following:

- Tank 101-SY reporting deficiencies including report scope, content, root cause analysis and corrective actions.

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- Flammable vapor sampling and monitoring deficiencies in the vapor space of tank 101-SY.
- Control of modifications to essential tank farm components.
- Evaluation of fire and chemical explosion potential in Hanford SSTs.
- Review of tank farm electrical power failures.

It appears that WHC NFS does not provide an independent oversight function at the tank farms. They consider themselves to be a support organization rather than an oversight organization. Management emphasis is placed on "cooperation and negotiation" rather than taking firm, technically sound positions on safety issues with programmatic impact. This is true even when provided with compelling technical documentation. There is no evidence that the concerns of the WHC TFNS staff are ever communicated directly to DOE/RL NFS managers.

b. Richland Operations Office Oversight

The DOE/RL NFS organization is slightly more successful in contributing to a safer operation. With a staff of only four qualified safety engineers for the entire Hanford Site, direct involvement with any issue at the tank farms is unusual. DOE-RL NFS staff seldom visit the farms due to the heavy workload of safety reviews and other administrative duties in the Federal Building in Richland. They are attempting to make as much impact as possible in selected areas but they are totally overloaded. Recent attempts to utilize the services of the General Support Services Contractor, Stone and Webster Engineering Corporation (SWEC) have been somewhat helpful, however this is a short-term solution and does not alleviate the overall shortfall of qualified staff. Occasionally, however the DOE-RL NFS group will positively impact overall performance. One example is the RL direction to the contractor concerning the revised Operational Safety Requirements (OSR) which are under development for the DSTs. Frequently, WHC NFS response to DOE-RL safety concerns is sluggish and programmatic impact is negligible.

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c. Oversight Coordination, Interface and Effectiveness

In both organizations, the severity and priority of issues is eventually diluted to the point that the significance of the issue is lost. The hydrogen generation problem in the DST is a representative example of how an issue which was recognized in the late 1970's and repeatedly resurrected throughout the 1980's by diligent staff members was never resolved by management. There is no formal mechanism to track this sort of safety issue from discovery to resolution. Issues like this tend to reside with a cognizant staff member. If that individual is transferred or has his priorities changed, the issue may be forgotten until the symptoms, never properly treated, are once again recognized. This transient process may spark intermittent flurries of activity but without an established mechanism to evaluate progress and hold individuals and groups responsible, the basic issue may never be adequately addressed.

2. Safety Analysis

The current Safety Analysis Report (SAR) for the DST Farms was published in 1986. In reviewing the SAR and selected design drawings several inconsistencies were noted. Some examples include the following:

- a. The contents of the tank are not completely characterized.
- b. Instrumentation described in the SAR is not installed or is inoperable.
 - Annulus leakage detectors.
 - Specific gravity instrumentation.
 - Solids level detectors.
 - Tank thermocouples.
- c. Temporary modifications exist which have not been analyzed.
 - Lancing installation.
 - Portable exhauster installation.
 - Temporary hydrogen monitor.

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- Radiation detector temporary wiring run after original underground wiring failed.
- d. Tank pressurizations which have occurred since 1983 are not addressed.
- e. In an effort to maintain tank vacuum, inleakage is minimized by taping leaking joints. This process causes variable exhaust flowrates, often well below design criteria.
- f. There is no existing mechanism to transfer tank contents to any other tank.

3. Radiation Protection

a. Contamination Control

The primary containment boundary has numerous penetrations located upstream of the high efficiency particulate air (HEPA) filters in the K-1 ventilation system. Tank design allows inleakage through the various pits to provide a ventilation flowpath. These same unmonitored flow-paths provide routes for the release of contamination during pressurization. The SY farm is not heavily contaminated at this time and has not been seriously contaminated by recent pressurizations. This does not ensure, however that this will be the case for all potential incidents including an ignition of a flammable material. The presence of the solid crust on the surface of tanks such as Tank 101-SY may be acting as an additional barrier to fission product release. This is not in any way an analyzed barrier and future attempts, if any, to break up or dissolve the crust must take this into consideration.

In the SY Tank Farm adjacent to the SY Farm a serious radiological condition exists which affects safety in both farms and potentially beyond the farm boundaries. The inactive K-1 ventilation system for the S farm is heavily contaminated. Fixed and smearable contamination exceeded the capability of the survey instrument in use (greater than 100,000 cpm). Local dose rate readings exceeded 100 mR/hr and the area was posted as a High Radiation Area. The ability to fix loose contamination not only on this unit, but throughout the Hanford Site, has been

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recently hindered by the prohibition on use of a fixative known as Fabri-Film. This material has proven highly effective as a temporary remedial action, especially on vertical surfaces. Concerns over hazardous constituents in Fabri-Film has precluded its continued use. An outstanding Radiological Problem Report (RPR) was issued several months ago but no corrective action has been taken.

b. Staffing

As is the case with operations and maintenance personnel, there is a severe shortage of certified radiation protection technologists (RPT) to work the tank farms. With the recent implementation of the Radiation Area Management (RAM) Program, RPT resources will be further strained with the resultant adverse impact on the ability to conduct operations and maintenance in the tank farms. The RAM program has been designed to upgrade radiation protection activities, however the lack of RPTs is reducing not only the effectiveness of that program but also impacting the ability of the operating organizations to initiate needed corrective actions. The staff of RPTs currently assigned to the farms is of high quality and like the maintenance group are being forced to provide expanded services without a commensurate increase in support.

4. Conclusions

There is no effective mechanism in place to track safety issues from "cradle to grave." The current systems rely on the initiative of the few individuals who are cognizant of each separate issue. Both contractor and operations office staffs are severely under-staffed further exacerbating existing weaknesses. Safety Analysis Reports and their attendant Operational Safety Requirements have been systematically watered down over the past several years to the point where they do not accurately reflect the true safety risks of their associated facility. Finally, from interviews conducted with Tank Farm operators, there were inferences that safety issues communicated to contractor management are usually ignored. This suggests that a more in-depth investigation be performed to either substantiate or negate such inferences.

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F. DESIGN CONTROL

1. Configuration Control

The control of design changes in the tank farms since construction has not been a rigorous process. The only method currently available to determine the design configuration of any component or system is to walk down the system in the field. Design drawings have not been updated with any consistency. This contributes to the exceptionally long turn-around time in preparing and reviewing design changes. Although it appears that recent programmatic changes have been made in this area, there has been no attempt to bring existing design record drawings up to date. A field review was conducted on selected design drawings in the SY farm. Instrumentation, electrical, riser and piping drawings were all found with deviations from the as-built configuration. There is no facility description or systems description for the SY Tank Farm other than the generic discussions in the SAR for DST.

2. Temporary Modifications

The program to control temporary modifications is weak. There is no programmatic control of temporary electrical jumpers and lifted leads. For example, the electrical leads for area radiation monitor RE-241-SY-3 are lifted behind the 271-SY instrument panel. The original wires buried underground have failed and have been replaced with a temporary cable run into the instrument. Handwritten modifications to safety-related instrument scales is common. Tape is used to seal leakage paths through tank pits. The temporary hydrogen monitor is not permanently mounted and is connected to the ventilation duct with tape. There is no safety evaluation required to determine whether this or any other temporary modification raises an unreviewed safety question. No program exists to periodically review temporary modifications to determine whether they are still required or remain properly configured.

3. Design Weaknesses

The SY Tank Farm was designed in the early 1970s after several other DST farms had already been completed. The most significant design weaknesses involve a lack of redundancy that is not found in some other farms. It is not clear why some of these design features were omitted from the SY design.

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a. Back-Up Ventilation

There is currently no permanently installed back-up exhaust capability. The portable exhauster which is now temporarily installed is no more reliably supplied with electric power than the permanent exhauster. It is not rigged to provide any annulus back-up and it is not available to back-up any other tank or farm in the event of a remote failure. Additionally, a large truck-mounted vacuum cleaner assembly, normally used to suck up contaminated soil, is parked in the SY Tank Farm and has, in the past, been rigged to draw air out of the primary tank by inserting the flexible hose down the exhaust stack and turning on the suction. It appears that use of this equipment as described above has not been analyzed and may violate ignition source restrictions currently in effect.

b. Emergency Electric Power

A loss of electric power will de-energize the entire tank farm with the exception of the air compressor. This includes a loss of monitoring, instrumentation and ventilation. Depending on the type of failure, a portable generator would have to be brought in. The availability of the limited few generators onsite would be questionable during a large power outage.

c. Toxic and Flammable Gas Monitoring

DOE Order 5820.2A requires that a capability exist to monitor for combustible vapors in the DST. No such capability currently exists and the temporary monitor on Tank 101-SY is inadequate with respect to monitoring known tank vapors. Some combustible gases may not even register on the present instrument. Additionally, the documented presence of ammonia and other toxic substances in the DSTs warrants a monitoring capability beyond what exists today. Currently, sample tubes are used on a case basis when workers smell unusual odors. There is no continuous on-line monitoring capability of any type for toxic substances.

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d. Environmental Protection of Equipment

The equipment in the SY Tank Farm is subject to a host of environmental effects including damage from weather and vehicles. Wind-blown dust is the greatest threat. All cabinets and enclosures have received damage from dust and debris to some extent. Although cabinets are frequently left open in spite of operational requirements, cabinet and filter design allows ingress of contaminants even with doors closed. Many structures and components in the farm have been struck by trucks and cranes. Although much of the damage must be attributed to carelessness, farm configuration significantly contributes to the probability of impacting structures during maintenance.

4. Conclusions

Configuration control and control of temporary modifications is unacceptable at the SY Tank Farm. Programs do not exist to provide for upgrading and/or developing design documents that match existing installations. Several significant design weaknesses exist which could have impact on the ability of the facility to withstand certain failures. Although evidence of this unacceptable situation is visible and obvious, neither WHC nor DOE/RL has acted to correct the matter.

6. EVENT REPORTING

1. Reporting Criteria and Threshold

The criteria for reporting unusual events is contained in DOE Order 5000.3A, "Unusual Occurrence Reporting System." Attachment 1 of this order lists typical examples of events to assist field organizations in determining whether an event meets the criteria of the order. Among some examples given are the following:

- a. Failure of effluent monitors and high radiation alarms.
Degradation of barriers designed to contain radiation or toxic material, or releases of the above past such barrier.
- b. Release of toxic material which results or could result in personnel exposure. Personnel contamination.

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- c. Leaks from pipes and tanks which could create on-site, off-site or public concerns. Failure of control or isolation valves.
- d. Unplanned or unexpected changes in process conditions or variables of importance to performance, reliability or safety whether abrupt or long term.

2. Tank Farms Compliance With Reporting Requirements

Events related to slurry growth and hydrogen gas formation fall into one or several of the above categories. Additionally, failures of equipment both past and current such as the isolation valve on Tank 103-SY and its associated supports appear to be reportable. For example, in August 1987 it was determined that no vacuum monitoring equipment had ever been installed on the SX farm exhaustor system although the OSR required daily readings. Similar discoveries between 1987 and 1989 had been reported and the Unusual Occurrence Report (UOR) describing those similar non-conformances was even referenced in the Critique Report for the SX event. Another example of inconsistent reporting involves the exposure of workers to toxic vapors such as ammonia. Several events have been reported in the last few years yet some, such as the September 29, 1989 worker exposure were only afforded Critique Reports.

3. Root Cause Analysis

Root cause analysis of several events was reviewed and in most cases found to be weak. Often the real root cause was never determined. In many cases, the first, and most obvious cause, was addressed and deeper, underlying problems were never addressed. In some cases, detailed review of event reports by the WHC TFNS staff revealed significant deficiencies in the content of the analysis. There is no indication that the individuals responsible for the report made corrections or that the WHC NFS management required improvement. An example involved breaker tripping in an exhaustor circuit. The breaker was checked, no problem was found and reinstalled. Shortly thereafter it tripped again causing the same loss of facility ventilation. Events frequently are repeated several times before any action is taken to expand the investigation of root cause.

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4. Corrective Action

Even when the root cause is properly identified, there are problems with the application of corrective actions. Corrective action tracking systems have recently been established. However, the actions taken to attain the milestones are poorly documented. In many cases when a hardware configuration is found inadequate to meet design or SAR requirements, the requirement is changed rather than fixing the broken equipment. For example, in 1988 a Critique Report indicated that a DOE/RL inspector had noted missing leak detection probes in the SY Farms Tanks. Notwithstanding the fact that this should have been a reportable event, the corrective action was to modify the SAR to reflect the actual configuration. This sort of action is routinely approved by DOE/RL. Discussion with DOE/RL safety and program staffs indicate that there is no program in place for routine review of Event Fact Sheets (EFS), Critique Reports and UORs. A recent review of reporting deficiencies at the Hanford site was published by the EH Site Safety Representative in December, 1989. Site-wide findings revealed similar deficiencies in timeliness, root cause analysis, corrective actions, and a failure to report events.

5. Conclusions

The identification of unusual events in the Tank Farms frequently results in under-reporting. Many events meeting the requirements for a UOR are made a Critique Report or simply an EFS. Recent EFSs have shown an improved threshold for reporting. However, a decision was made not to report future tank burps as an EFS. Root cause analysis and corrective actions are seldom comprehensive and corrective actions frequently take years to implement. As a result, events often recur. Lessons learned elsewhere are seldom effectively utilized in the SY Farm.

APPENDIX D:
LIST OF INTERVIEWEES

<u>Name</u>	<u>Affiliation</u>
E. Anderson	Pacific Northwest Laboratories
S. Anderson	Westinghouse Hanford Company
J. Antonnen	U.S. Department of Energy, Richland Operations Office
W. Baumgartner	Pacific Northwest Laboratories
R. Baumhardt	Formerly of Westinghouse Hanford Company
D. Beers	Westinghouse Hanford Company
G. Beitel	Formerly of Rockwell Hanford Operations
R. Bendixsen	Westinghouse Hanford Company
G. Boothe	Westinghouse Hanford Company
F. Boyd	Westinghouse Hanford Company
E. Bracken	U.S. Department of Energy, Richland Operations Office
G. Bracken	U.S. Department of Energy, Richland Operations Office
J. Broderick	U.S. Department of Energy, Richland Operations Office
J. Buckingham	Formerly of Rockwell Hanford Operations
L. Burger	Pacific Northwest Laboratories
J. Burnham	Formerly of Pacific Northwest Laboratories
B. Campbell	Westinghouse Hanford Company
K. Carothers	Westinghouse Hanford Company
J. Clark	U.S. Department of Energy, Richland Operations Office
H. Daugherty	Westinghouse Hanford Company
B. Decker	Formerly of Rockwell Hanford Operations
C. DeFigh-Price	Westinghouse Hanford Company
J. Deichman	Formerly of Westinghouse Hanford Company
J. Dickman	Westinghouse Hanford Company
R. Dios	Westinghouse Hanford Company
G. Dukelow	Westinghouse Hanford Company
G. Dunford	Westinghouse Hanford Company
D. Ellingson	Westinghouse Hanford Company
K. Engelhardt	Westinghouse Hanford Company
K. Fein	Westinghouse Hanford Company
R. Fleishman	Pacific Northwest Laboratories
D. Forehand	Westinghouse Hanford Company
L. Gale	Formerly of Westinghouse Hanford Company
L. Garner	Westinghouse Hanford Company
C. Geffen	Pacific Northwest Laboratories
C. Geier	Westinghouse Hanford Company
R. Gerton	U.S. Department of Energy, Richland Operations Office
B. Hamilton	Westinghouse Hanford Company

M. Hanson	Pacific Northwest Laboratories
D. Harlow	Westinghouse Hanford Company
D. Herting	Westinghouse Hanford Company
M. Hevland	Formerly of Westinghouse Hanford Company
M. Jansky	Westinghouse Hanford Company
S. Johnson	Formerly of Rockwell Hanford Operations
F. Jungfleisch	Westinghouse Hanford Company
J. Kaser	Formerly of Pacific Northwest Laboratories
E. Kasioncic	Westinghouse Hanford Company
R. Kimura	Westinghouse Hanford Company
R. Knight	Formerly of Rockwell Hanford Operations
J. Krupar	Formerly of U.S. Department of Energy, Richland Operations Office
M. Kupfer	Westinghouse Hanford Company
T. Lane	Westinghouse Hanford Company
J. Latkovitch	Pacific Northwest Laboratories
M. Lawrence	U.S. Department of Energy, Richland Operations Office
R. Liikala	Pacific Northwest Laboratories
D. Lindsey	Westinghouse Hanford Company
D. Maupin	Westinghouse Hanford Company
J. McElroy	Pacific Northwest Laboratories
H. McGuire	Westinghouse Hanford Company
D. McKenney	Westinghouse Hanford Company
S. Metcalf	Westinghouse Hanford Company
L. Mihalik	Formerly of Westinghouse Hanford Company
J. Mishima	Pacific Northwest Laboratories
K. Morgan	U.S. Department of Energy, Richland Operations Office
L. Morgan	Pacific Northwest Laboratories
S. Moy	U.S. Department of Energy, Richland Operations Office
J. Mudg.	Kaiser Engineers Hanford
L. Muhlestein	Westinghouse Hanford Company
J. Newson	U.S. Department of Energy, Richland Operations Office
D. Nguyen	Westinghouse Hanford Company
B. Opitz	Westinghouse Hanford Company
B. Powell	Westinghouse Hanford Company
E. Pride	U.S. Department of Energy, Richland Operations Office
R. Prosser	Rockwell Hanford Operations
D. Provost	Washington State Department of Ecology
P. Rasmussen	U.S. Department of Energy, Richland Operations Office
D. Reynolds	Westinghouse Hanford Company
L. Rodgers	Westinghouse Hanford Company
B. Rutherford	U.S. Department of Energy, Richland Operations Office
L. Sasaki	Westinghouse Hanford Company
D. Saueressig	Westinghouse Hanford Company
A. Schade	Westinghouse Hanford Company
R. Scheele	Pacific Northwest Laboratories
P. Schuette	Pacific Northwest Laboratories
W. Schulz	Formerly of Rockwell Hanford Operations
P. Scott	Pacific Northwest Laboratories
M. Shannon	Westinghouse Hanford Company
M. Shupe	Formerly of U.S. Department of Energy, Richland Operations Office

S. Slezak	Sandia National Laboratories
J. Starr	Formerly of Rockwell Hanford Operations
J. Steach	Westinghouse Hanford Company
D. Stepnewski	Westinghouse Hanford Company
D. Strachan	Pacific Northwest Laboratories
R. Stupka	Rockwell Hanford Operations
S. Sutter	Formerly of Pacific Northwest Laboratories
W. Trott	Rockwell Hanford Operations
T. Vail	Westinghouse Hanford Company
H. Van Tuyl	Pacific Northwest Laboratories
R. VanderCook	Westinghouse Hanford Company
L. Vanselow	Westinghouse Hanford Company
D. Varley	Pacific Northwest Laboratories
T. Veneziano	Formerly of Rockwell Hanford Company
N. Vermeulen	Westinghouse Hanford Company
C. Walker	Rockwell Hanford Operations
D. Washenfelter	Westinghouse Hanford Company
B. Weaver	Westinghouse Hanford Company
E. Wheelright	Pacific Northwest Laboratories
J. White	U.S. Department of Energy, Richland Operations Office
D. Wodrich	Westinghouse Hanford Company
R. Wojtasek	Westinghouse Hanford Company
J. Womack	Westinghouse Hanford Company
J. Wukelik	Formerly of U.S. Department of Energy, Richland Operations Office
J. Zimmer	Westinghouse Hanford Company
R. Zinsli	Westinghouse Hanford Company

Note: Many of the interviewees listed above were employed first by Rockwell Hanford Operations and later by Westinghouse Hanford Company. These individuals are listed in this appendix according to their current affiliation. However, the endnotes in this Report carry the pertinent affiliation for the time period referenced.

APPENDIX E:
COMMONLY USED ACRONYMS

DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DOE-RL	Department of Energy, Richland Operations Office
DSS	Double-Shell Slurry
DST	Double-Shell Tank
EH	DOE Office of Environment, Safety, and Health
EM	DOE Office of Environmental Restoration and Waste Management
NS	DOE Office of Nuclear Safety
OSD	Operations Specifications Document
OSR	Operational Safety Requirement
PNL	Pacific Northwest Laboratories
RHO	Rockwell Hanford Operations
SAR	Safety Analysis Report
SST	Single-Shell Tank
TSA	Technical Safety Appraisal
WHC	Westinghouse Hanford Company

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