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Hanford Waste Tanks-Light at the End of the Tunnel

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HANFORD WASTE TANKS – LIGHT AT THE END OF THE TUNNEL

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Tank Safety

The U.S. Department of Energy (DOE) faced several problems in its Hanford Site tank farms in the early nineties. It had 177 waste tanks, ranging in size from 55,000 to 1,100,000 gallons, which contained more than 55 million gallons of liquid and solid high-level radioactive waste (HLW) from a variety of processes. Unfortunately, waste transfer records were incomplete. Chemical reactions going on in the tanks were not totally understood. Every tank had high concentrations of powerful oxidizers in the form of nitrates and nitrites, and some tanks had relatively high concentrations of potential fuels that could react explosively with oxidizers. A few of these tanks periodically released large quantities of hydrogen and nitrous oxide, a mixture that was potentially more explosive than hydrogen and air.

Both the nitrate/fuel and hydrogen/nitrous oxide reactions had the potential to rupture a tank exposing workers and the general public to unacceptably large quantities of radioactive material. One tank (241-C-106) was generating so much heat that water had to be added regularly to avoid thermal damage to the tank's concrete exterior shell. The tanks contained more than 250 million Curies of radioactivity. Some of that radioactivity was in the form of fissile plutonium, which represented a potential criticality problem.

As awareness of the potential hazards grew, the public and various regulatory agencies brought increasing pressure on DOE to quantify the hazards and mitigate any that were found to be outside accepted risk guidelines. In 1990, then Representative, now Senator Ron Wyden (D-Oregon), introduced an amendment to Public Law 101-510, Section 3137, that required DOE to identify Hanford tanks that might have a serious potential for release of high-level waste.

In response, DOE placed some 60 tanks on a "Watch List." Also in 1990, the Defense Nuclear Facilities Safety Board (DNFSB), the Executive Branch oversight board for DOE's weapons production facilities, issued a finding (90-7) concerning the potential for explosive nitrate/ferrocyanide reactions in some tanks. DOE began an intensive program to identify high priority safety issues that could lead to the release of HLW and resolve these issues.

Background

To understand the safety issues we must first understand the processes that produced the waste. From Hanford's inception in 1944 until 1988, its primary mission was the production of plutonium for nuclear weapons. The basic processes consisted of irradiating uranium fuel elements in a nuclear reactor, dissolving the fuel in nitric acid, and separating plutonium from unwanted fission products. The unwanted fission product acid waste was made basic with

sodium hydroxide and stored in Hanford's large, steel, underground waste storage tanks. During wartime, high quality materials were scarce. Emphasis was on production, not on the storage tanks. The early tanks were built in a hurry, and were only intended to be used for a short time.

Three different chemical separation processes were used at Hanford to produce plutonium. Glenn Seaborg and associates at the Chicago Metallurgical Laboratory of the Manhattan Project invented the Bismuth Phosphate process. It was first used in 1942 to separate microgram quantities of plutonium produced by irradiation of natural uranium with deuterons in a cyclotron at Washington University in St. Louis. The process, which used bismuth phosphate to co-precipitate the plutonium from nitric acid solution, was scaled up and operated at Hanford from 1944-56. It had several disadvantages including batch operation, inability to recover uranium, large amounts of chemicals, and large volumes of waste. In retrospect, the bismuth phosphate process had one saving grace. The waste it produced, although voluminous, did not contribute to Hanford's tank safety issues of the nineties.

In 1948-49, Argonne National Laboratory developed a continuous solvent extraction method for the separation of plutonium and uranium called the REDOX (Reduction-Oxidation) process. Hexone, which is immiscible with water, was used to selectively extract uranyl, and plutonyl nitrate from aqueous solutions of fission products. The REDOX process was used at Hanford from 1952-67.

The PUREX (Plutonium-Uranium Extraction) process was developed by the General Electric Company at its Knolls Atomic Power Laboratory in Schenectady, New York and operated at Hanford from 1956-88. It is similar to the REDOX process. The major difference being that the solvent is a 70/30 mixture of normal paraffin hydrocarbon (NPH, kerosene) and tributyl phosphate (TBP). It has four major advantages over the REDOX process- lower waste volumes, lower solvent flammability, better solvent stability with nitric acid, and lower operating costs. However, substantial amounts of the TBP and NPH found their way to the waste tanks, adding to tank safety issues.

Three other processes contributed large amount of wastes and some troublesome chemicals to the waste tank mix. From 1952 –1957, a process based on PUREX was used to extract uranium from bismuth phosphate wastes stored in the tank farms. The wastes were dissolved in nitric acid and the uranium extracted with TBP/NPH. Several extraction cycles resulted in a pure product that was converted to reactor fuel and recycled for further plutonium production. The aqueous wastes from the contactor were neutralized and returned to the tanks along with insoluble solids left over from the dissolution process. Uranium recovery added more TBP and NPH to the tank wastes.

The uranium recovery process created two gallons of waste for every gallon processed and threatened to overwhelm available tank storage space. To reduce the extra waste volume, sodium ferrocyanide and nickel sulfate were added to the waste to precipitate cesium as sodium cesium nickel ferrocyanide. The process generated a high activity, cesium containing sludge that was returned to (or in the case of in-tank precipitation, remained in) the tanks and a low activity liquid that was discharged into the ground. The fact that ferrocyanide could react explosively with nitrates was overlooked at the time.

Between 1967-76, strontium was recovered from PUREX tank waste sludge. It was later purified and stored in capsules that were used by DOE and the private sector for irradiation purposes. The sludges were dissolved in nitric acid and solvent extracted with a mixture of di-2ethylhexyl phosphate (D2EHP), TBP, and NPH. The strontium was purified by back-extracting into an aqueous solution containing complexants such as EDTA, HEDTA, glycolic acid and citric acid, reacidified and again extracted with D2EHP/TBP/NPH. The aqueous solution containing the complexants was then sent to the waste storage tanks. The strontium was mixed with sodium fluoride to precipitate strontium fluoride, dried, and loaded into stainless steel capsules. Some of the D2EHP, TBP, and NPH were entrained in the waste and added more potential fuel to the tanks. However, the real troublesome components that found their way to the waste tanks were the complexants that not only act as fuels but also break down under tank conditions to produce flammable gases.

Assessment

Hanford currently has one hundred seventy seven HLW tanks ranging in size from 55,000 to 1,160,000 gallons. Except for the sixteen 55,000-gallon tanks, all are 75 feet in diameter. The largest are ~47 feet high. All tanks are of welded carbon steel construction and have reinforced concrete outer shells. Twenty-eight of the largest are double shell tanks that have two carbon steel shells with a 2¹/₂-ft wide annulus in between the shells. The rest are single shelled. The tanks are buried under 5-10 feet of soil to provide shielding. Risers (2-48 inch penetrations) through the top of the tank provide the only access to the waste and are the means of inserting instrumentation, sampling equipment, and other devices. As can be seen from Table 1 the volume of Hanford tank waste is substantial.

Table 1 Tank Waste Volumes	
Process	Volume added (+) or subtracted (-) (gallons)
Processing waste fed to tanks (1944-88)	+ 496,000,000
Reprocessing of waste to extract uranium, cesium, and strontium	- 63,000,000
Low activity water from reprocessing fed to ground	- 86,000,000
Natural evaporation and evaporator campaigns (1944-88)	- 301,000,000
Operations since 1988	+ 8,000,000
Present Waste Volumes	
Sludge	15,000,000
Saltcake	19,000,000
Liquid	20,000,000
Total	54,000,000

From the early years of Hanford through the height of the Cold War, plutonium production was critical. Waste management was something that had to be done but waste treatment and storage practices were not up to present day standards. Generally, waste sent to the tanks was not analyzed. Waste was transferred from tank to tank and from tank to waste processing units and back again without substantial documentation. Record keeping was minimal,

especially prior to 1980. It was almost impossible to determine the fate of individual batches of waste.

Two practices were major contributors to the confusion. Underground 3-in. pipes offset by one foot of elevation were connected anywhere from two to six tanks in a cascade. Waste was allowed to fill the first tank in a cascade and overflow into succeeding tanks. Solids would settle in the first tanks in the cascade leaving liquid in the final tanks. No record was kept of the amount or composition of solids that dropped out in each tank. Evaporators were used to reduce waste volumes. Wastes from a number of tanks were mixed in waste receiver tanks, transferred to the evaporator, concentrated, transferred to bottoms receiver tanks, and redistributed back to the tank farms. In addition to redistributing wastes among the tanks, evaporator campaigns promoted chemical reactions, evaporated some organic species, and concentrated waste causing additional precipitation.

Complex Chemistry

To make matters still more complicated, the composition of waste changed over time. High concentrations of radioactive species released significant amounts of heat, causing evaporation of water and precipitation of a variety of compounds as solubility limits were reached. As radioactivity decayed off tank temperatures decreased, which caused additional precipitation. Organic solvents in the waste evaporated over time. Radiolysis of both organic and inorganic compounds led to formation of gases. Last but not least, more than 60 single-shell tanks leaked. Total leakage is unknown but is estimated to be in excess of a million gallons containing more than a million Curies and unknown quantities of chemicals.

The Safety Issues

By now the reader should be convinced that Hanford tank waste is a pretty complex and confusing subject. The safety analysts of the early 1990's reached the same conclusion. There was a sense among regulators, DOE, and contractor safety professionals that a number of unreviewed safety questions (USQs) existed. This meant DOE could not demonstrate that the risk to workers and the general public from potential chemical and radioactive releases from the tanks was understood. Nor could DOE demonstrate that the risks were acceptable under DOE guidelines. After a series of studies, DOE concluded that there were six major safety issues: high heat, criticality, ferrocyanide, flammable gas, organic complexants, and organic solvents.

High heat: One tank (241-C-106) had sufficient concentration of radioactive cesium and strontium to cause heating of the tank wastes and rapid evaporation of water. Several other tanks required active ventilation to maintain tank temperatures. If temperatures were allowed to rise unchecked, tank structures could be damaged or a steam bump might occur that would release wastes to the environment. Temperatures in tank C-106 could be maintained by monthly addition of water, but this solution to keep the tank cold was not acceptable for the long run due to concerns that tank C-106 might eventually begin to leak.

Criticality: The quantity and distribution of fissile materials in the waste tanks could not be verified to be below criticality levels.

Ferrocyanide: Approximately 140 metric tons of sodium nickel ferrocyanide were used to precipitate cesium from the uranium recovery wastes. Appreciable quantities of ferrocyanide sludges found their way into 18 tanks. Under the right (or wrong) conditions, it was feared ferrocyanide and nitrates could react explosively.

Flammable gas: All aqueous radioactive waste generates flammable gas, and Hanford's waste is no exception. Studies showed that hydrogen, nitrogen, nitrous oxide, ammonia, and methane were being generated by the radiolysis of water and the decomposition of organic compounds. The generation rate was slow enough that no hazard arose if the gas was released as it was generated. However, the waste in some tanks accumulated the gas over months and years and suddenly released large quantities in minutes. One tank, SY-101, released large quantities of gas approximately every 90 days. Some of the releases produced concentrations of hydrogen in the tank headspace that were high enough to support combustion. Ignition of the gas could produce elevated pressures that could damage tank structures and release tank contents. DOE reviewed all of the high-level waste storage tanks and identified 25 tanks that could have potential flammable gas concerns.

Organic complexants: More than 800 metric tons each of glycolic acid, citric acid, and hydroxyethylethylenediaminetriacetic acid (HEDTA) and 200 metric tons of ethylenediaminetetraacetic acid (EDTA) were used during strontium recovery operations. The complexants were initially sent to single shell tanks. Subsequent tank farm operations, particularly evaporation campaigns, served to concentrate and redistribute the materials. Like ferrocyanide, the complexants are a fuel that can react with nitrate to produce an explosive propagating reaction. The reaction could be spontaneous (self-accelerating) or touched off by an ignition source.

Organic solvents: The principal solvents that found their way into the waste tanks are hexone (used in REDOX), tributyl phosphate (TBP), and normal paraffin hydrocarbon (NPH). TBP and NPH were used in PUREX, uranium recovery, and strontium recovery. A floating layer of organic solvent was observed in two tanks. Tank headspace sampling indicated the presence of significant amounts of solvents in eight other tanks. If the solvents were ignited, the resulting fire could cause over-pressurization of the tank and potential release of waste to the environment.

Resolution

After a number of false starts DOE and its contractors realized that closure of the USQs and resolution of the safety issues would require input from four major sources: historical records of plant processes and tank farm operations, sampling and analysis of tank waste, data from field instrumentation, and theoretical and experimental studies of actual and simulated wastes.

The job of analyzing the historical records fell to a group of scientists at Los Alamos National Laboratory (LANL). LANL used four models to calculate the composition and deposition of wastes in each tank. The first model used transfer records, tank level records, and models of tank farm operations to determine what wastes were placed where. The second model computed the accumulation of sludges from primary waste, the formation of saltcake, and the deposition of other solids. The third model described the processes such as precipitation and chemical reactions that occur when waste liquids from various sources

mixed. The fourth model used process flow sheets, lists of process chemicals, and analyses of characteristic wastes to determine the composition of the waste streams produced by each process. The output of LANL's calculations was a series of tables that predicted the layers and compositions of the waste in each tank. Although not reliable enough to fully and accurately assess safety issues, the LANL results have been useful for identifying tanks likely to have safety issues and for grouping tanks with similar wastes histories.

In the early 1990's, sampling and analysis of the tank wastes seemed to be all that might be required to determine the composition and behavior of tank wastes and the nature and extent of the safety issues. Unfortunately, real life was not that simple. The wastes in the tank are not homogeneous. They vary vertically, reflecting the tank's transfer history and the various chemical and physical processes that have occurred over time. They vary horizontally over the 75-ft. diameter of the tank, reflecting the location of fill and withdrawal pipes. Most sampling devices remove a 1-in. diameter sample that represents a little more than one millionth of the waste in the tank. A statistically reliable picture of waste composition can require more than a dozen samples per tank. Sample numbers are limited by (1) the cost (\$1,000,000 to retrieve and analyze a core), (2) access (only 2 -3 risers are available for sampling in most tanks), and (3) time (core sampling takes a week and analysis take months).

Field instrumentation and monitoring data was helpful but limited. Thermocouples inserted in the wastes gave temperature profiles and aided in determining heat generation and loss behavior. Level gauges determined the waste height in the tanks and helped identify potential flammable gas tanks. Instrumentation such as gas chromatographs and mass spectrometers monitored the tank dome space gases and vapors and augmented data obtained by sampling and laboratory analysis. Dome space gas composition proved critical to understanding the nature and extent of the organic solvent and flammable gas safety issues.

Tank waste has undergone rigorous characterization and analysis. Of the 177 Hanford waste tanks, 132 have been characterized, providing the critical information needed to resolve complex safety issues. Theoretical and laboratory studies at Georgia Tech, Argonne National Laboratory, and the Pacific Northwest National Laboratory (PNNL) provided understanding of the mechanisms of gas generation and retention. Studies of waste simulants at Federal and private laboratories, later confirmed with real waste, determined the conditions under which ferrocyanide and organic compounds reacted with nitrates. These studies have proved to be very important in resolving the USQs and getting the waste cleaned up.

Safety Issues Resolved

Resolving the USQs and closing the safety issues has proved difficult and involved, at times sorely trying the patience of DOE, its contractors, and the regulators. However, at present all issues are either closed or in the final stages of closure.

High Heat: Except for tank C-106, all tanks that require active ventilation for cooling would take months or years to heat up to dangerous levels if ventilation was lost. That is more than enough time to repair or replace failed equipment and restore ventilation. As for tank C-106, DOE has transferred the heat generating sludge waste out of tank C-106, a single-shell tank, into a double-shell tank where dilution and higher heat removal capacity has eliminated the problem.

Criticality: Historical data and sampling and analysis results from more than 130 tanks have been analyzed for the concentration and distribution of fissile and neutron absorber materials. The analysis concluded that fissile material in the waste was distributed at subcritical concentrations and that there were no mechanisms that could concentrate it. The criticality USQ was closed in 1994.

Ferrocyanide: Closing the USQ and safety issue required a combination of historical data, simulant studies, some analytical detective work on tank cores and laboratory tests on waste samples. Most of the 18 ferrocyanide tanks identified from the historical records were core sampled. Analysis of the sludge samples yielded some interesting results. Although the anticipated concentrations of nickel were found, the cyanide concentrations were much lower than were expected. Laboratory tests on waste simulants showed that cyanide degraded at the temperatures and gamma radiation intensities found in the tanks. Tests also showed that the high pH of the waste accelerated the degradation process. Tests on tank samples designed to determine whether the wastes could sustain an explosive reaction confirmed the simulant studies- they could not. Special care was taken to test wastes from tanks with the highest original concentrations of ferrocyanide, lowest temperatures, lowest gamma intensity, and lowest pH (i.e., tanks that represented bounding condition). None of the samples could be made to sustain a reaction. The safety issue and USQ were closed in 1996.

Flammable gas: A USQ for flammable gas was declared in 1990 and a series of studies were then performed on the generation, retention, and release of flammable gas. Twenty-five tanks were identified as potential flammable gas concerns. Controls aimed at eliminating potential ignition sources in the tanks were instituted. Tank headspace monitoring studies showed that tank SY-101 was the only tank having gas releases that were potentially explosive.

The simplest reaction that generates hydrogen is the radiolysis of water. Of greater concern is the degradation of complexants. Aluminate and nitrite ions present in the waste are thought to initiate and catalyze degradation. The gaseous products of the decomposition reaction are predominantly hydrogen and nitrogen containing molecules such as ammonia, nitrous oxide, and nitrogen. Nitrous oxide can react violently with hydrogen and ammonia. As shown in Table 2, H₂, N₂, and N₂O are produced in roughly equal amounts in SY-101.

Component	Mol %
Hydrogen	29
Nitrous oxide	24
Nitrogen	33
Ammonia	11
Methane	0.4
Carbon monoxide	0.3
Water	2.4

At the high pH found in the tanks most of the ammonia dissolves into solution. Simultaneous release of large quantities of ammonia is unlikely unless it is swept out of solution by a large

release of other gases. The mechanism of retention for other gases involves the attachment of small gas bubbles to fine particles of waste in the lower layer of the tank. When enough gas is retained so that the density of the lower layer becomes less than the layer above it, inversion occurs (i.e., the lower layer starts to rise toward the surface). As it rises, the decreased pressure on the bubbles causes them to rapidly expand and combine leading to the release of the gas at the surface.

Studies have shown that two conditions must be met for a tank to be capable of a large gas release. First, large enough quantities of organic complexants and nitrates must be present to produce appreciable amounts of gas. Second, the waste must have a liquid layer of sufficient thickness and density above the gas retention layer to provide the pressure required to retain significant quantities of gas.

In 1993, the large flammable gas releases in tank SY-101 were stopped by the installation of a pump that reduced gas buildup by periodically stirring the lower layer and making a near homogenous mixture in the tank. This allowed for lower continuous levels of gas release.

The pumping action appears to have caused crust growth in the tank and steps are now being taken to eliminate that problem by pumping an appreciable amount of the waste out of the tank. Dilution of the waste remaining in tank SY-101 and in the receiving tanks should also eliminate the potential for retention of substantial quantities of gas and remove the gas issues from this tank.

Flammable gas is not a problem in single-shell tanks because they lack the dense liquid layer required for gas retention. Several double-shell tanks other than tank SY-101 do exhibit small periodic gas releases. However, none of these tanks is believed capable of a release large enough to exceed the lower flammability limit in the dome space. There is still a concern that disturbances of the waste in some tanks caused, for example, by insertion of sampling equipment into the waste, could release localized gas concentrations that could ignite and harm instrumentation. DOE's strategy is to manage the risks by eliminating gas storage in tank SY-101, monitoring other flammable gas tanks, and maintaining controls on all tanks to eliminate potential ignition sources.

Organic complexants: Historical data, laboratory tests, and core sampling analysis results led to the determination that twenty tanks had levels of complexants high enough to constitute a potential hazard. Theoretical studies and laboratory tests conducted on actual and simulant wastes, and chemical analysis of tank cores led to the following conclusions and the resolution of the USQ.

- Spontaneous, self-accelerating reactions are not possible. The wastes in the tanks have aged and decomposed to safer states and are cooling down rather than heating up.
- Small ignition sources are not enough to start an explosive propagating reaction under any conditions.
- Wastes that contain more than 20% water cannot sustain a propagating reaction. A minimum of about 4.5 wt% total organic carbon is required to support propagation in dry waste. The total organic carbon required to support propagation increases with increasing water concentration. Propagation cannot occur for any mixture containing more than 20 wt% water.

- Most of the complexants are water-soluble and have been transferred to double shell tanks that have >> 20% water.
- Substantial fractions of the complexants have decomposed into less energetic forms that do not sustain a propagating reaction.

Tests on waste samples from more than 130 tanks have confirmed that the conditions for a propagating complexant/nitrate reaction no longer exist in any tanks at Hanford. The USQ and safety issue are now closed.

Organic solvents: Dome space sampling and analysis of tank cores have failed to find appreciable quantities of hexone (which is an indication of organic solvents in the tank). It appears that any hexone (boiling point 116 °C) that was released to the tank farms has evaporated. NPH and TBP have higher boiling points of 175-235 °C and 289 °C respectively. Although a 70/30 NPH/TBP ratio was used in the PUREX process, a 30/70 ratio was found in samples of the organic layer from tank C-103 indicating that there has been substantial evaporation of the NPH. Vapor sampling found eight more tanks that might have appreciable amounts of solvents entrained in the solid waste.

Extensive modeling has shown that solvent fires can only be started by large initiating events such as lightning strikes or a vehicle accidents that pour burning gasoline into a tank. Studies also show that pressure build up in the tank dome due to solvent fires would be insufficient to cause dome failure. The worst case consequence is limited dome cracking followed by release of a very small quantity of radioactivity. The risk to workers and the general public for this accident is extremely small. The organic solvent safety issue and USQ are also closed.

The Present

Five of the six safety issues are closed. The flammable gas safety issue cannot be closed until the wastes are removed from the tanks and disposed. DOE has instituted controls to reduce flammable gas hazards in all tanks and is mitigating flammable gas problems in tank SY-101; the flammable gas concentration is below the lower flammability limit.

In late 1998, the U.S. Department of Energy Office of River Protection was established via public law to manage cleanup of the Hanford Site waste tanks. DOE has also signed a multi-billion dollar contract with BNFL Inc. for the construction and operation of a vitrification plant to treat Hanford's tank waste. The glass made by the plant will trap radioactive and chemical materials and keep them from easily escaping, providing safe storage and disposal.

Figures and Photographs

Figures

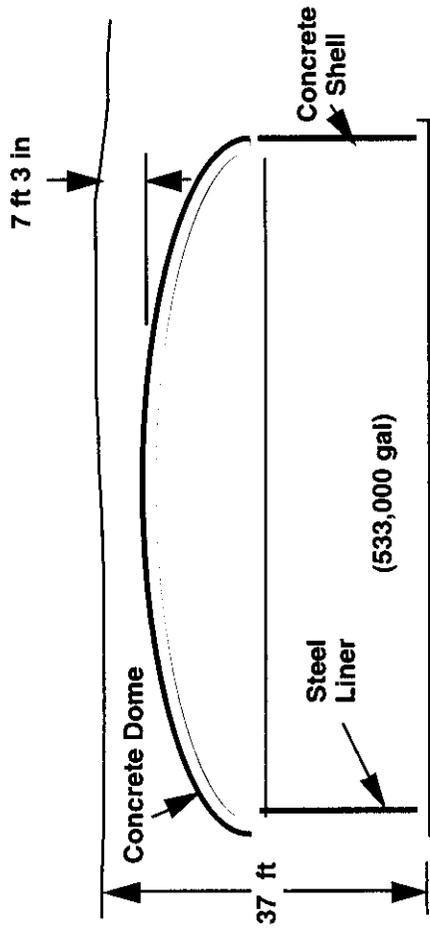
1. Single-shell tanks

Photographs

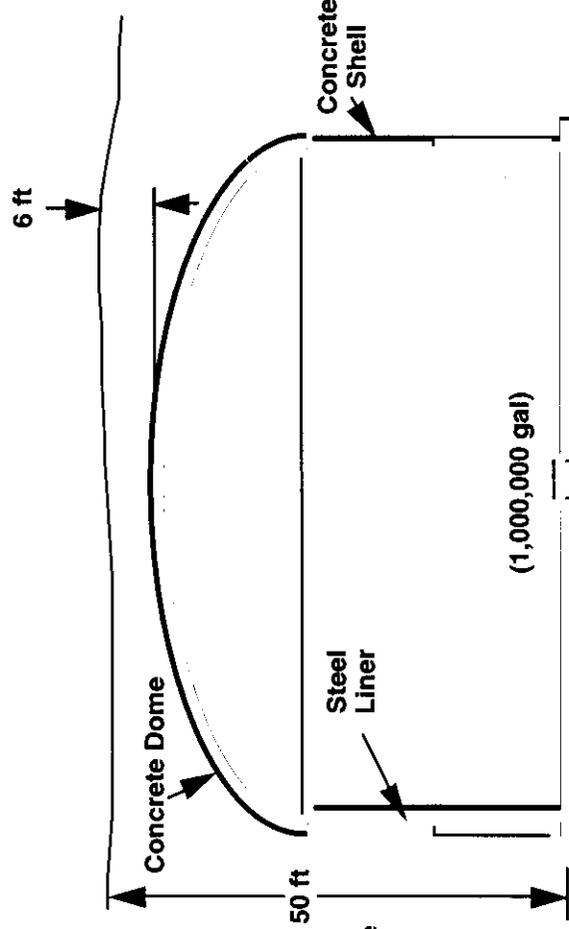
1. TX-Tank Farm construction
2. Pump insertion into tank 101-SY
3. Core sampling

4. Saltcake and supernatant liquid in tank S-106 (the liquid has since been pumped out)
5. Saltcake in tank U-104
6. Saltcake buildup on the sides of a tank
7. Surface view of SX-Tank Farm

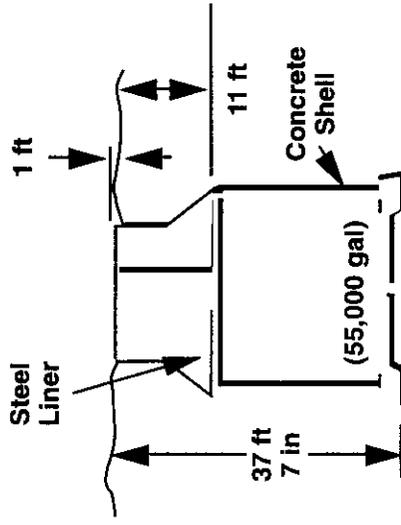
Cross-Sectional Views of Hanford Single-Shell Tanks



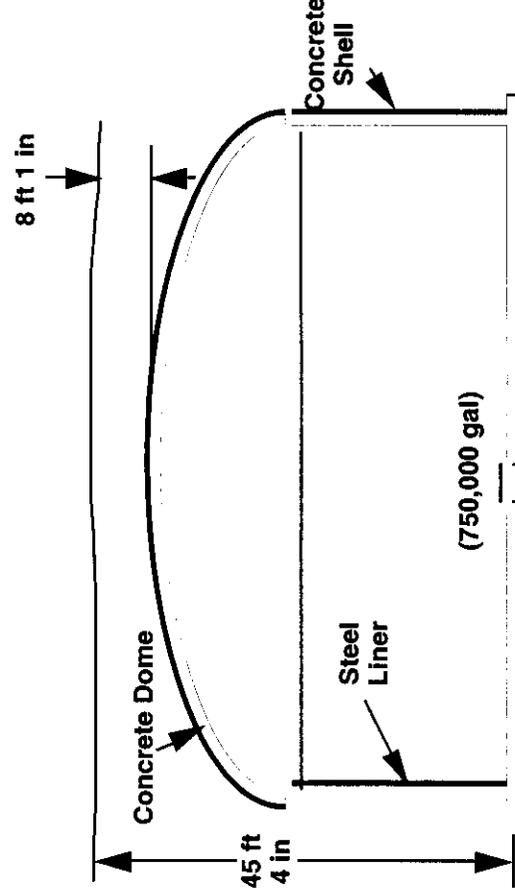
75 ft Diameter Single-Shell Tank



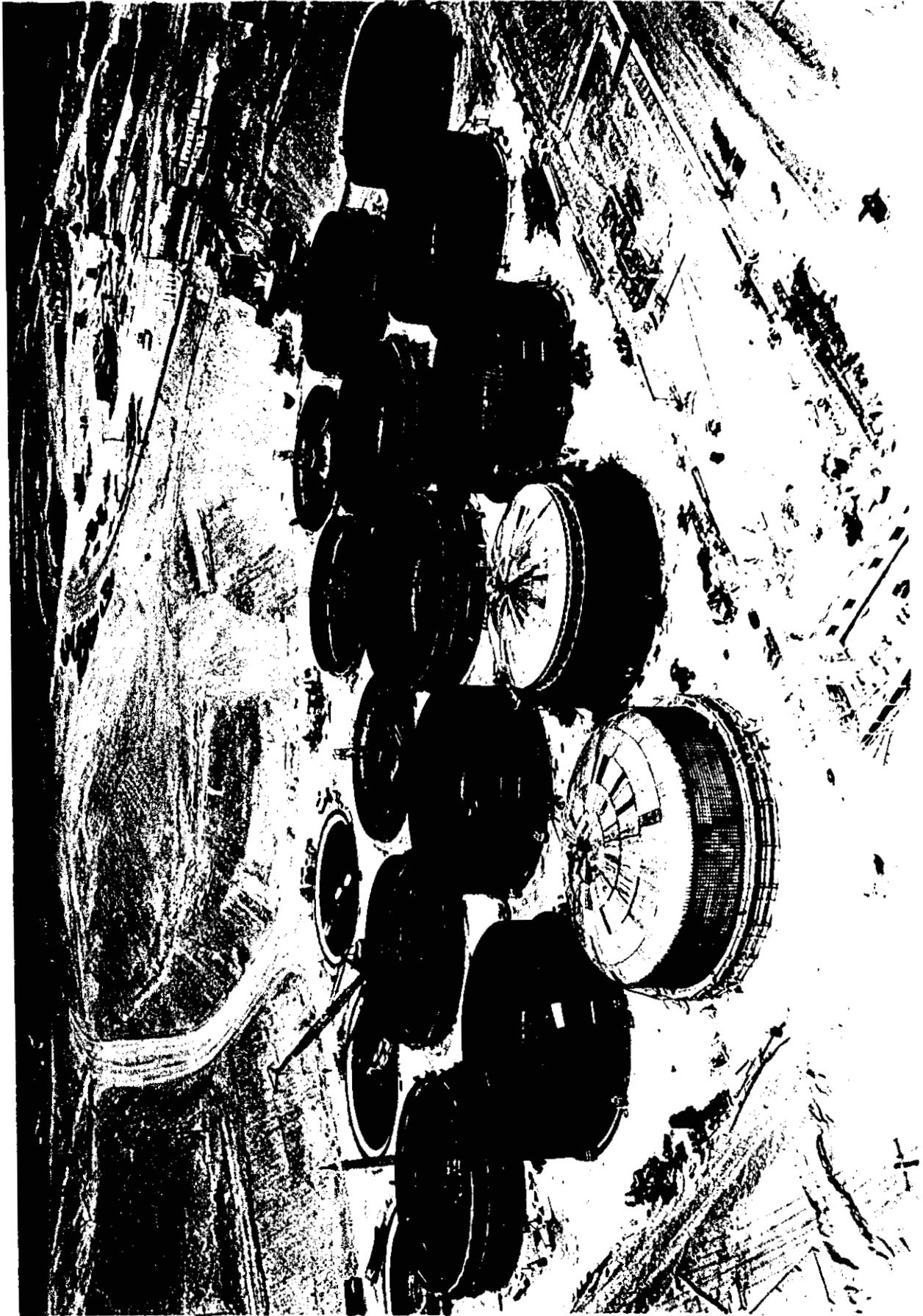
75 ft Diameter Single-Shell Tank

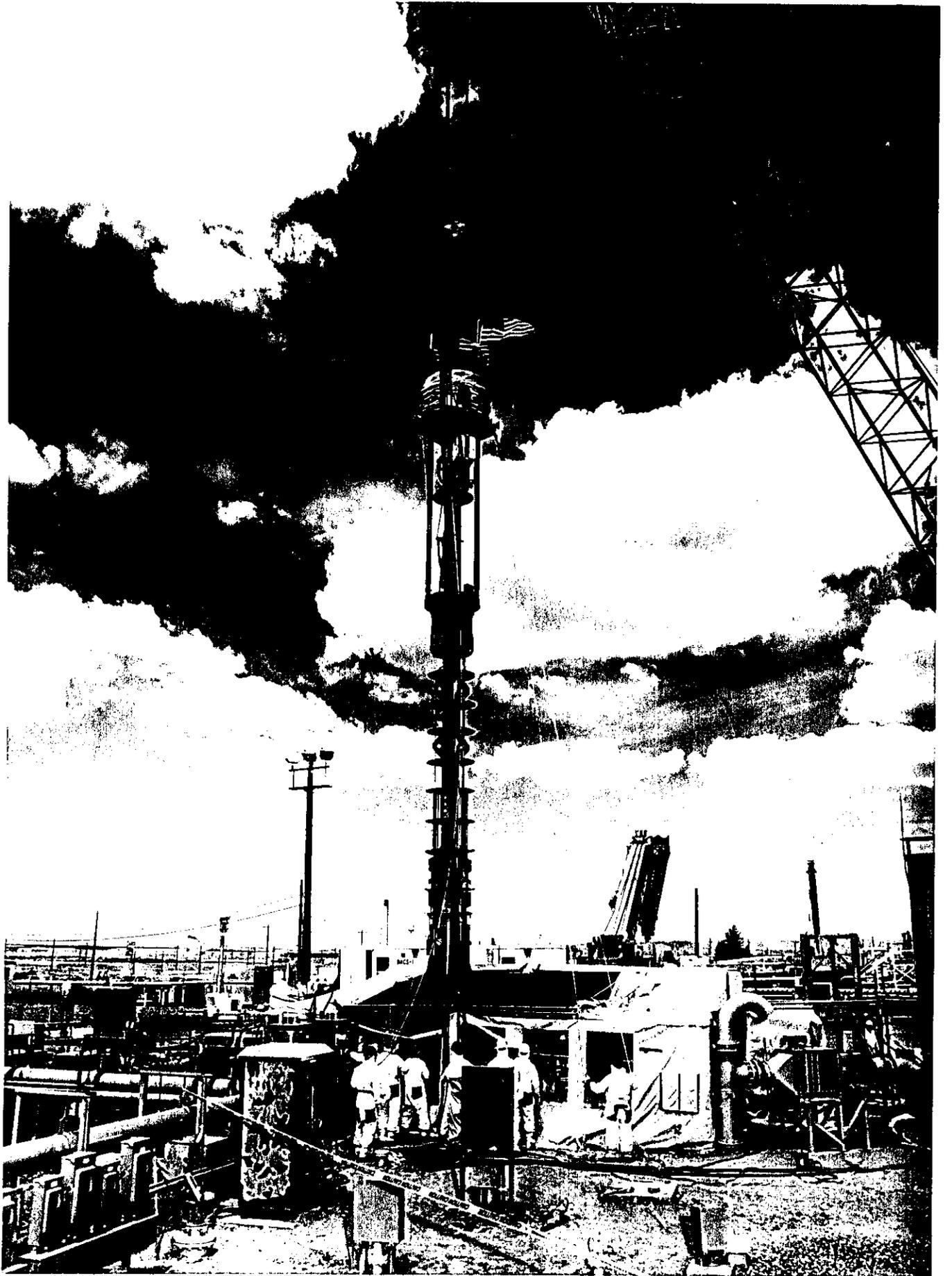


20 ft Diameter Single-Shell Tank



75 ft Diameter Single-Shell Tank







Tank 106-S 3/17/89



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Tank 104-U (5/16/84)



