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CHEMICAL PROCESSING DEPARTMENT
HAZARDS EVALUATION
IN-TANK WASTE SOLIDIFICATION
PROJECT CAC-965

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CHEMICAL PROCESSING DEPARTMENT
HAZARDS EVALUATION
IN-TANK WASTE SOLIDIFICATION
PROJECT CAC-965

I. INTRODUCTION

A fundamental objective of the Chemical Processing Department Waste Mangement Program is the immobilization of radioactive fission products that are contained in separations plant liquid waste streams. For certain of the liquid wastes containing fission products and various chemical salts, the immobilization method chosen is in-tank solidification, a process by which millions of gallons of wastes will be concentrated to solid salts in existing underground waste storage tanks and will be permanently stored in these vessels.

Candidate wastes for in-tank solidification are those liquid wastes with fission-product concentrations too great to be discharged directly to the ground, but not so great as to be hazardous by virtue of excessive fission-product self-heating at any time during or following the solidification process. Of the liquid wastes presently being stored in underground tanks in the chemical separations areas, about 80 per cent can probably be processed by in-tank solidification. Additional volumes will become eligible for treatment after removal of the long-lived radioisotopes by the B-Plant Phase III process facility.

The equipment designed for the initial in-tank solidification processing effort is prototypical. The unit is principally a single liquid circulator installed within an existing 750,000-gallon underground waste storage tank. It will be operated by the passage of electrically heated air to agitate the tank contents and to evaporate the liquid from the waste. The required air flow will be supplied by means of a compressor-exhauster system, with controls provided to maintain temperatures and pressures within the prescribed safe operating ranges. The effluent vapor phase from the underground tank will be exhausted through de-entrainment and filter devices to a condenser. From the condenser, the liquid phase will flow to a crib, and the cooled effluent air will be exhausted to the atmosphere. Candidate wastes will be added from other storage tanks while maintaining the operating level of the solidifying waste within a specified range. The concentration operation will be continued until a maximum safe allowable load is reached in the tank.

The in-tank solidification prototype was authorized as Project CAC-965 for construction and installation in the underground storage tank, TK-241-BYR-101. Reference (1) established a hazards evaluation team to prepare a review of that project. In February 1964, a preliminary review was submitted by the team (2) in which additional instrumentation was recommended for the purpose of insuring against possible over-heating in the vapor space of the underground tank. Subsequently, a more detailed study of possible hazards has been completed. This report presents the findings of the study.

Future in-tank solidification units and/or future wastes that might be processed by this technique have not been considered in this report, since the design and processing details for future installations have not yet been sufficiently defined to permit accurate analysis. It is hoped that the findings of this present review may be of some value in guiding the development of future units.

II. SUMMARY AND RECOMMENDATIONS

In the course of evaluating possible hazards associated with the in-tank solidification unit, detailed reviews were made of the solidification process, the facility design, and the operating plans. In particular, the safety considerations with respect to each of these areas of review were investigated. The considerations pertinent to hazards evaluation and the conclusions regarding the potential for a hazardous condition are summarized below:

(a) Basic process design is consistent with the practical limitations of the equipment elements. Thus, temperature, pressure, and operating load requirements are reasonable. Under a reasonable range of conditions that might be anticipated on the basis of the original process design, administrative control of the process within the limitations imposed by postulated safety conditions is practicable.

(b) The underground tank structural considerations limit the allowable operating pressure, temperature, and load. The design of the in-tank solidification unit provided adequate instrumentation and other equipment elements necessary for ordinary control within these limitations. Safety devices are adequate for providing necessary backup protection against temperature and pressure excursions that are not explosive in nature.

(c) The nature of the waste being solidified, under the predicted processing conditions, is not expected to increase the possibility for developing a leak in the operating underground tank as compared to other waste storage tanks. A major benefit of the solidification process is the reduction of the potential hazard of storing liquid wastes.

(d) The presence of kerosene-type solvent has been noted in wastes considered candidates for in-tank solidification. If processed in the in-tank solidification unit, a flammable atmosphere in the vapor space of tank might occur. The ignition temperature for the solvent is probably about 490° F. Potentially, the external insulated surfaces could reach this value, and the uninsulated surface temperatures could be considerably higher. To an extent, the surfaces should be cooled by the spraying action of the liquid being circulated, but development studies thus far have not fully defined the degree of such cooling over the possible range of operating conditions in the tank.

(e) A principal constituent of the wastes to be processed is sodium nitrate. Under proper conditions of temperature, sodium nitrate in contact with organic material is explosive. Assuming a sufficiently high temperature (see (d), above), a nitrate-organic explosion could potentially be caused in the in-tank solidification tank by the accumulation of nitrate on a hot surface in the presence of an organic material such as solvent or cyanide. Cyanide compounds were introduced to HAPO underground storage tanks in tonnage quantities during the waste scavenging program, approximately 6 years ago. Subsequent radiolytic decomposition of the cyanide may have occurred, but sufficient evidence to confirm this possibility has not been developed.

Compared to many other CPD processing operations, the radiological consequences of postulated incidents involving the in-tank solidification unit are small.

(a) The maximum credible incident would be a chemical explosion originating in the underground tank, for example, an explosion of organic vapor. Under the worst conditions of explosion, it is considered highly unlikely that off-site personnel would be exposed to greater than maximum permissible concentration of radioisotopes.

(b) In the event of a leak in the tank, radioisotopes could escape to the soil. In the case of liquid wastes, it appears likely that the waste would remain in the soil column rather than penetrate to the ground water. Certainly this would be true if the volume loss were controlled by normal remedial actions. Following solidification, the potential for radioisotopes to reach the ground water is virtually nil. Leaching by volumes of water far in excess of normal Hanford precipitation would be required.

This in-tank solidification unit is judged to be basically adequate for its intended service of solidifying certain Hanford radioactive wastes for permanent storage. Based on the reasoning outlined above, however, some additional measures for the control of possible hazards are recommended:

(a) It is recommended that the introduction of any volume of solvent as an immiscible phase to the in-tank solidification unit be prevented by positive means such as decanting.

(b) It is recommended that the presence or absence of cyanide in the waste feed material be determined. In the event that the presence of cyanide is concluded, or that its absence cannot be assured, laboratory development studies to determine the conditions and to evaluate the potential for a reaction are recommended.

III. FACILITIES AND PROCESS DESCRIPTION

A. Functional Description and Flow Diagram (3, 4)

The in-tank solidification unit is installed in Tank 241-BYR-101, a 75-foot, diameter, 758,000-gallon underground waste storage tank. The installation is designed to concentrate candidate high-salt wastes by sparging hot air into the liquid in the tank and permitting the water vapor to be carried from the tank, to be condensed and routed to a crib. As evaporation progresses, more liquid wastes will be added to the in-tank solidification unit, within the space and structural limitations of the tank. To make room for further additions, increments of the hot concentrate will be transferred by pumping, if possible, to an underground storage tank receiver for cooling and solidification as permanently stored waste. If transfer under these conditions is not possible, the concentrated waste will be permitted to cool and solidify in Tank 241-BYR-101. In either case, volume reduction of existing high salt wastes by approximately a factor of four is expected. As soon as the use of the concentration equipment at Tank 241-BYR-101 is complete, the above-grade equipment will be moved to another site. It is estimated that the initial concentration operation will require about 6 months to complete.

Figure I shows a schematic flow diagram for the unit. Air at a rate of 4200 SCFM is drawn through an inlet air filter, AF-1, into a compressor, C-1. The air is compressed to an estimated 15 to 20 psig, sufficient to overcome the hydrostatic head of the waste solution, and is then heated to 1200° F by passage through a 1400-KW air heater, EH-1. A small portion of the heated air is recycled to the compressor inlet in order to control the inlet air temperature and assure good compressor operation. The hot air is conducted to the circulator, discharging through the circulator beneath the surface of the waste. The circulator is designed to provide mild agitation, by the action of the hot air, and to provide heat transfer between the hot inlet air (1200° F) and the circulating liquid phase during passage of the air through the circulator. As the hot air discharges from the circulator and rises through the solution, it loses additional heat by the evaporation of water.

An exhauster, EF-1, in the exit vapor system is used to control the normal operating pressure in the waste tank at a slightly negative value. The exhauster pulls the moisture-laden air from the tank via a vent line which is routed to a de-entrainer, DM-1, and a high efficiency filter, FT-1, in series. The de-entrainer separates entrained water from the off-gas, thereby reducing the load on the filter. A condenser, EX-1, removes most of the evaporated water, after which the dehumidified air passes through the exhauster to the atmosphere. It is intended that separated condensate be cribbed; however, it can also be routed back to Tank 101-BY or to Tank 105-BY in the unlikely event that equipment or operational failure causes high condensate activity.

B. Feed Materials

Approximately 50,000,000 gallons of wastes are available as possible candidates for the in-tank solidification program. The principal types include coating wastes, aged high-level salt wastes, and wastes generated during the U Plant recovery of uranium from original $BiPO_4$-process wastes. Approximately 15,000,000 gallons are the product of a waste scavenging operation, run in conjunction with the U Plant recovery operation, in which nickel ferrocyanide was used to scavenge fission products, principally cesium-137, from waste supernates. Additional candidate wastes for the in-tank solidification program will be generated by the processing of the current and stored high-level (boiling) wastes in the B-Plant Phase III facility. Processing of Phase III wastes was not considered in this study because at the time they will become available (about 1967), improvements in the design of the in-tank solidification equipment and better definition of the wastes themselves will have changed the study bases

The waste volume in each storage tank includes a liquid (supernate) phase and a solid (sludge) phase. Proportions of the two phases vary widely among the many tanks.(5) Although the principal constituents of these wastes can be predicted on the basis of known HAPO separations programs and a limited sampling program, the accurate and detailed compositions cannot be practically determined. Some tanks contain wastes from several programs. On behalf of some programs, parts of the waste inventories have been transferred among tanks, and tanks have been refilled on the basis of availability of space. Consequently, in general there is no reliable and accurate inventory of a tank's content.

In general, stored supernates are composed principally of the nitrate, nitrite, and aluminate salts of sodium in a saturated alkaline solution. (6, 7) Some carbonates, sulphates, phosphates, and, perhaps, cyanides are present in certain wastes, as well as lesser or trace, amounts of other salts, e.g., silicates and chlorides. The only fission product of any practical significance in the supernates is cesium-137. The results of a recent sampling program (6) indicate the composition of a typical candidate supernate to be approximately as follows:

NaOH	-	2.1 M
$NaAlO_2$	-	0.5 M
$NaNO_2$	-	1.5 M
$NaNO_3$	-	1.1 M
pH	-	12.5
Specific Gravity	-	1.14
Cs-137	-	0.03 curies/gal.

The associated precipitated waste sludges in the underground tanks generally are expected to contain salts made up of ions common to the supernate, with greater proportions of the less soluble constituents, such as the silicates, carbonate, etc. Also, the alkaline-precipitated heavy metals, (e.g., iron, nickel) are in the sludge layers. Fission-product content will include insoluble strontium-90 and rare-earths, not found in the supernate. (8, 9) Sludge and supernate sample pairs taken from the same tank also have shown a proportion of cesium-137 in the sludge higher than would be expected on the basis of solubility considerations in a simple alkaline nitrate system. Of course, this condition would be expected in a tank that had been treated with nickel ferrocyanide. Normal plutonium and uranium isotopes are also precipitated in the sludge layer. The concentrations of these materials are so low as to be of no practical concern.

Under the normal conditions of the underground storage tanks, the ferrocyanide salts used in the waste scavenging program would be expected to be stable. Decomposition will reportedly result from strong radiolysis with liberation of cyanide. (10) The cyanide would no doubt recombine in the alkaline waste system. Based on work with cesium zinc ferrocyanide, radiation decomposition of cyanide to its basic elements may also occur under irradiation from an external source but there is some uncertainty regarding the exact extent of degradation which would result from self-irradiation. (11) Analyses of three recent sludge samples from the 241-C Tank farm (200 East Area) showed no ferrocyanide. (12) These results cannot be considered conclusive, however, due to the limited extent of the program. More than 100 tons of cyanide (calculated as cyanide ion) were added during the waste scavenging program and distributed among various tanks.(13) This represents a considerable stoichiometric excess compared to the fission products scavenged, and no evidence has been developed that would give assurance that the cyanide has decomposed to any substantial degree.

The presence of a light organic solvent phase has been noted in at least one supernate sample.(6) This would probably have been discharged during the solvent-extraction uranium recovery program at U Plant and would therefore be expected to contain a degraded mixture of TBP and kerosene diluent. The extent of the organic solvent content in the tanks would be very difficult to determine with certainty.

C. Facility and Site Description

The 75-foot diameter underground tank being used for the first waste concentration experiment is Number 101 in the 241-BYR Tank Farm, located in the 200-East Area. A 5,000-cfm compressor draws air through an intake filter and blows it through an electric heater for delivery through an insulated 10-inch pipe to the circulator which is suspended from the central riser and immersed in the waste solution. Air is exhausted from a riser located in the northwest quadrant near the outside edge of the dome. The exhauster draws air out of the riser through a de-entrainer, filter, and condenser for delivery to the atmosphere through a short stack. A pressure-vacuum water-seal tank is connected to the riser along with the exhaust system.

The hot air supply equipment and the exhaust system equipment are mounted on skids for portability. All of this equipment is located on solid ground between the tanks except for connections to the tank riser.

Electrical power is provided from two systems. The 500-HP compressor is connected directly to a 2400-V.A.C., 3-phase line through a full voltage starter. All other equipment, including the four 360-KW heaters, is supplied from a 1500-KVA, 13.8-KV to 480-volt, 3-phase transformer and unit substation.

D. Operation

The over-all operating plan for the in-tank solidification unit will provide for a gradual warm-up (not greater than 3° F per day) of the existing tank contents, after which operating temperatures and pressures will be adjusted to the normal values, and evaporation of water at approximately 10 gal./min. will be commenced. As evaporation proceeds, supernate solutions from other storage tanks will be added to the operating tanks. The additions will be scheduled to control the tank liquid depth between a minimum of approximately 16 feet and the maximum based on the hydrostatic limitation (see tabulation, page 9).

The transfer of increments of hot concentrated "product" waste by pumping to another receiver tank will also be attempted. If a transfer system is successful, the use of tank 101 as a concentrator will be prolonged, and costs for moving and installing the equipment at other sites will be reduced.

Detailed operating procedures for the unit have provided for start-up, normal operation, and for shutdown, as summarized below:

1. Start-up

The equipment pieces involved all require some pre-start-up checking. There are also certain jobs to be performed that involve the unit as a whole, such as turning on the trace heating in the winter time, filling of seals, and activation of the sampling equipment.

Start-up of major equipment pieces commences with the exhauster. With the tank pressure in the 101-BY tank controlled in the range of -0.05 to -0.1 psig, the compressor is then started and the input air flow is adjusted to about 3,000 cfm. Further adjustments to the air flow are based on the desired mass flow rate, in order to control heat input, and will depend on the operating temperature and pressure. Initially, the tank contents will be gradually heated (3° F per day, maximum) by maintaining the air flow and very gradually adjusting the electric heaters, or by intermittent daily operation at higher operating temperatures. In either event, the air heaters are started up bank by bank, starting with up to three on-off banks and using the fourth adjustable bank for adjusting the temperature to the desired value.

Laboratory tests indicate an endpoint specific gravity of 1.9 will result in a salt mass that will essentially solidify following cooling. The 17.5 foot depth indicated for 1.9 specific gravity corresponds to about 550,000 gallons of material in the tank.

2. In order to insure the inherent structural qualities of the construction materials, the maximum allowable temperature of the tank is 300° F*. The allowable rate of temperature increase is 3° F per day.(15)

3. The maximum safe internal pressures allowable are +1.5 psig and -15 inches W.G.(14)

B. Significant Process Considerations

1. Operating Temperatures

In addition to the operating temperature limitations imposed by the tank structural considerations, operating temperature limitations are imposed by other requirements for safety and efficiency. Process design considerations were aimed at insuring the necessary temperature control.

Early development studies showed entrainment from a concentration operation to be a function of the temperature of the air being discharged from the circulator.(16) For this reason, the in-tank solidification unit was designed for a maximum temperature of 700° F at the circulator discharge. (See Figure 1). Temperature control depends on control of heat input to the circulator and by the heat transfer that will take place in the circulator.(17) In order to insure adequate heat transfer, the effective heat transfer area of the prototype circulator was greatly increased by the installation of stud fins in the annular air passage.(18)

At the anticipated temperature of the circulator discharge air, (700° F), the equilibrium bulk solution temperature during the early stages of concentration is estimated to be 170° F. This value will increase as the increased salt concentration affects the vapor pressure and the heat transfer characteristics of the wastes. A maximum bulk temperature at less than 300° F (see item 2, above) is expected, and can be limited by control of the temperature of the input circulator air. The rate at which the temperature is permitted to increase at start-up (3° F per day) can also be readily controlled by input air temperature.

*Tests are being conducted currently that may become the bases for increasing this value.

With the circulator input air temperature at 1200° F, the external skin temperature of the insulated portion of the circulator piping in the vapor space of the tank has been estimated to be in the range of 450° to 500° F, maximum. Potentially, the three uninsulated air take-offs to the circulator itself could reach a metal temperature near the temperature of the input air whenever the operating level did not cover the take-offs. Circulator development studies have shown, however, that under some conditions the operating circulator will discharge vertically a volume of liquid that will drench and cool the take-off piping.

The somewhat limited extent of the development studies of the in-tank solidification system causes some questions regarding the maintenance of circulation and of the control of temperatures within a concentrating tank. Development has been conducted primarily with systems in which the operating circulator has been completely submerged, with several feet (or "feet-equivalent," in the case of scaled-down demonstrations) of liquid above the circulator.(19) In actual practice, the circulator will not always be completely submerged, and liquid levels inadvertently lower than planned are possible. The effect of these conditions, particularly over a range of salt concentrations, cannot be predicted with certainty, but some effect on circulation patterns, salt deposition, and temperature patterns would be expected.

Upon completion of the in-tank solidification operation in TK-241-BYR-101, the circulator will be shut down and the tank contents will be permitted to cool. During this period, the fission products in the waste will continue to furnish heat. Based on heat transfer calculations, the bulk temperature of the tank contents can be readily controlled at approximately 200° F, or less, by proper selection of waste feed materials.(20) From actual experience with an existing filled waste storage tank, a maximum temperature of approximately 250° F has been predicted for solidified wastes with a heat generation rate in the range of 0.5 to 1.0 Btu/hr./cu.ft.(21) (0.15 to 0.3 watt/cu.ft). This range of values is several fold larger than will result from concentration of present candidate wastes

2. Chemistry

The basic sodium salt composition described under III B, above, is a stable system over a wide range of temperatures and pressures. Similar salt systems, both as aqueous solutions and as sludges, have been stored in CPD high-level boiling tanks for many years. In aqueous solutions, boiling temperatures have been maintained routinely, and as salt cake, temperatures in excess of 330° F have been observed.(22)

Sodium nitrate, a principal component of stored wastes, is a stable salt under the conditions of storage. It is commonly heated to above 300° C (572°) for industrial heat treating applications. However, sodium nitrate is an oxidizing agent, and mixtures of the salt with reducing agents, such as organic materials, can be fire and explosion hazards [10] A mixture of sodium nitrate with cyanide can be explosive.

At HAPO, limited studies of nitrate-cyanide explosions were conducted in connection with development of processes for the conversion of cesium zinc ferrocyanide to a cesium chloride product, for purposes of fission-product packaging[11, 23]. Cesium zinc ferrocyanide ($Cs_2ZnFe(CN)_6$) was found to decompose exothermically after being heated to about 500° C (932° F). Mixtures of solid salts at nitrate-to-$Cs_2ZnFe(CN)_6$ mole ratios in the range of about 0.4 to 6, exploded when heated to approximately 350° C (660° F). Other cyanide-containing salts could also form explosive mixtures with nitrates, with the conditions depending on the particular system.

Also of significance to hazards analysis is the known presence of organic solvent with some of the stored waste. The solvent probably originated with the U-Plant Uranium Recovery Program, which employed a mixture of TBP (up to 30% by volume) in a kerosene-type diluent. The minimum and maximum concentrations for diluent flammability in air are about 0.6 per cent and about 6 per cent by volume, respectively.[24]

The minimum limit corresponds to a vapor pressure of approximately 4.5 mm. of Hg which, for the TBP-diluent system of interest, corresponds to a temperature of about 129° F. In a water-solvent system, the solvent vapor is not flammable under any conditions if greater than 33 volume per cent water vapor is also present. This corresponds to a temperature of 162° F; consequently, the danger region for a water-diluent-air system is between 129° F and 162° F. The effect of a solute in the aqueous phase is to increase the upper temperature of the danger region through decreasing the vapor pressure of the water and, therefore, the volume of the water vapor in the system. The ignition temperature of the kerosene-type diluent is estimated to be about 490° F.[24]

3. Radiological Considerations

As described under Section III B, the single isotope of any significance in wastes to be subjected to in-tank concentration is cesium-137. On the basis of recent samples, a typical concentration might be 0.03 curie/gal. However, on the basis of the allowable fission-product heat generation rate, estimated to be as high as 0.3 watts per cu. ft. for the final solidified waste, future candidate wastes could contain somewhat higher fission-product levels. Assuming Cs-137 only, and four-fold volume reduction during concentration, the value of 0.3 watt per cu. ft. corresponds to a beginning Cs-137 concentration of 2 c/gal. At this rate, in a full tank of concentrated waste the final cesium-137 content might be as high as 4,000,000 curies, or 8 curies per gallon.

Existing stored sludges also contain a relatively small rare-earth and strontium-90 content.[8, 9] On the basis of recent sludge analyses and assuming a Cs-137 content in the supernate in the range of 0.03 to 2 curies/gallon, the total fission-product content of 550,000 gallons of solidified waste could be approximately as follows:

Component	Total Curies
Cs-137	60,000 to 4,000,000
Sr-90	5,000
Pm-147	2,000

As indicated above, plutonium concentrations in the underground storage tanks are confined to the sludge layers, and the amounts involved have never been a criticality concern. For the assumption of a tank full of Purex coating waste at the normal level of plutonium losses to this stream, the concentration of plutonium in a typical sludge layer would be of the order of 0.01 gram per liter. A local accumulation of plutonium equivalent to a concentration increase of greater than would be required to approach the conditions required for a criticality.[25] No mechanism available or imaginable could result in such an increase in concentration.

C. Process Control Equipment

Consistent with the structural and process limitations required for reasons of safety, the design of the in-tank solidification unit included features aimed at insuring process control consistent with these limitations. In general, the important process control elements include those having to do with control of:

(a) The load in the tank;

(b) Temperature;

(c) Pressure; and

(d) Stream composition.

Four dip-tube and temperature-well assemblies are provided, one each in the four quadrants of the tank circular cross-section. Each assembly has four dip-tubes and four temperature elements. The sixteen dip-tubes vary in length from 3 feet to 25.5 feet above the tank bottom. The 16 temperature elements vary in length from 3 feet to 21.5 feet above the tank bottom. These instruments will be used for bulk specific-gravity, liquid-level, and temperature measurements during the course of the solidification operation. The temperature elements, of, course, will be useful in monitoring the tank temperature following shutdown of operations. Openings are also

provided in the dip-tube assemblies that could be used for taking liquid measurements manually or for taking dip samples of the tank contents. Also, pipe wells extend into the tank that could be used for taking radiation profiles vertically through the waste volume.

An electrode that was in place on the original tank will remain available for taking tank liquid-level measurements, also.

Other principal temperature measurements required for safe operation of the unit include:

(a) The input air temperature;

(b) Vapor-phase off-gas temperatures;

(c) Condenser and condensate temperatures; and

(d) Pressure-vacuum relief temperatures.

Temperature-operated electrical switches are provided both for equipment and process safety. These switches operate in conjunction with an electrical interlock system that provides for automatic shutdown of the electrical heaters if the compressor is shut down, and automatic shutdown of the compressor if the exhauster is shut down. The actuating switches of principal interest from the process-safety viewpoint provide for protection as follows:

(a) Excessive input air temperatures will shut down the electrical heaters.

(b) Excessive vapor temperature in the tank dome will shut down the compressor and electric heaters.

The tank operating pressure is controlled from a measuring element in the tank that automatically controls a butterfly valve in the exhauster inlet line. An excessively high tank pressure shuts down the input air compressor and an excessive vacuum shuts down the exhauster. Backup protection is provided by a pressure-vacuum relief tank that will relieve the 101-BY tank through filters to the atmosphere in the event of pressures outside the range of 8 inches water gauge negative to one psig positive. At shutdown of the in-tank solidification operation, pressure in the piping from the air heater to the circulator is relieved automatically to the dome of the tank.

Installed sampling equipment is provided in the off-gas train for measuring the degree of entrainment and the effectiveness of off-gas clean-up following the individual off-gas equipment pieces. A timing device automatically takes a composite off-gas condensate sample.

V. POSTULATED INCIDENTS

Postulated incidents that could lead to hazardous conditions can be grouped into (1) those that would release radioisotopes to the soil, and (2) those that would release radioisotopes to the air. Under some conditions, a significant fraction of the radioisotope inventory would be released, and therefore the analyses of these conditions are of particular interest. The postulated incidents that could lead to release of radioisotopes to the air or ground, and the controls available to prevent such occurrence, are described below. Possible radiological consequences of such releases are discussed in Section VI.

A. Excessive Temperatures

Temperatures or rates of temperature increase that exceed the structural limitations of the underground waste storage tanks (Section IV A, Item 2) could result from:

(1) Loss of operational control by mechanical or human failure;

(2) Failure of circulator piping, with discharge of hot air into top of tank;

(3) Failure of instrumentation that closes vent valve to tank at start-up allowing leak of hot air into tank vapor space; and

(4) Excessive fission-product inventory in the final waste.

The bulk liquid temperature at the start of concentration is predicted to be near 170° F. As concentration proceeds, this value will increase, reading a value of as high as 270° F[26] near the endpoint of the concentration. The large volume of solution in the storage tank will permit a good control of comparatively small temperature variations, and a 30° F difference between the operating temperature and the maximum allowable temperature (300° F) is considered to be ample for control purposes.

In the event of an increase in the tank vapor-space temperature, adequate instrumentation has been provided for shutdown of the electrical heaters before the temperature becomes excessive.

On the basis of the analyses of samples of candidate feed wastes, the fission-product heat generation rate of the final concentrated waste could be of the order of 100 fold below an estimated allowable maximum (Section IV B 3). This range is ample to insure a safe temperature in the stored solid waste with any reasonable control to a reasonable process specification of maximum heat generation.

B. Storage Tank Loading

Excessive storage tank loading could result from:

(1) Heavy equipment over the tank dome during the concentration operation; and

(2) An excessive weight of wastes within the tank.

Administrative controls should prevent heavy equipment from operating over the tank dome during waste concentration as a precautionary measure to prevent a combination of live-load stresses and temperature stresses on the tank.

The allowable waste load within the tank was specified as a liquid-level specific gravity relationship under Section IV A 1, above. On the basis of past experience, it is expected that accurate measurement of liquid level and specific gravity will not be simple due to the heterogeneous nature of the wastes while being solidified. Control of this initial operation can be assured, however, by a properly conservative approach.

C. Corrosion of Tank

A small number of HAPO storage tanks are known to have developed leaks, apparently as a result of corrosion in the alkaline waste system. In the case of TK-241-BYR-101, if a leak were to occur, some fraction of the fission-product inventory of the liquid phase (Cs-137) would escape to the soil, depending on the size of the leak.

By HAPO experience, the incidence of leaking tanks has been very small, 4 possible or known leakers out of a total of 145 tanks.[27] The effects of the leaks have not been severe; the leak rates have been in the range of 100 to 700 gallons per day, and no resulting radioactivity in the ground water has been observed. The leaks have been determined by the use of liquid-level measuring instruments, and remedial action has been possible.

The possibility of developing a leak in TK-241-BYR-101, operating as an in-tank concentrator under the prescribed operating conditions, is not significantly different from other HAPO storage tanks. The effects of a leak will be minimized by successful operation of the in-tank solidification program through the elimination of the liquid phase from the tanks.

D. Excessive Pressures

1. Failure of Exhaust System Power

If the exhaust system power fails, the supply air blower would tend to cause a pressure build-up in the tank. However, the electrical circuitry is arranged such that a loss of exhaust power will shut down the supply air. In addition, a water seal is provided on top of the tank to relieve either pressure or vacuum and to maintain the tank atmosphere in the range between one pound per square inch and -8 inches W.G.

2. Excessive Pressure Drop on Exhaust Filter

If a filter restriction interfered with the air flow while the supply and exhaust systems were operating, the increased pressure drop across the filter would tend to cause excessive pressure in the underground tank. Assuming the condition were not corrected by normal operating surveillance, an over-pressure sensing element would shut down the air flow systems. Finally, if this system failed, the tank water seal would relieve the pressure.

3. Failure of Water Seal

Failure of the water seal due to freezing in cold weather is prevented by electrical strip heaters installed in the seal tanks. In case of power failure to the heaters, the complete water system and water seals would have to be drained during cold weather. The entire in-tank solidification unit would be shut down under these conditions.

4. Solvent Explosion

A solvent explosion in the 101-BY Tank could potentially be caused by the volatilization of solvent during circulator operation resulting in the formation of an explosive mixture of vapors above the liquid surface in the tank. The estimated maximum temperature of the insulated portion of the circulator piping (450° F - 500° F) is in the same range as the estimated ignition temperature of the kerosene-type organic diluent (490° F) that could be introduced to the tank.

Under normal operating conditions, the volume of diluent, as liquid, corresponding to the minimum explosive concentration in the tank vapor space would be approximately 25 gallons. It is conceivable that the condition necessary for this explosive condition could be reached if a reasonable volume of solvent --- say, of the order of 200 gallons --- were introduced to the in-tank solidification unit. At a reasonable and normal range of operating temperatures, which would be increased if the vapor pressure of the water phase were suppressed by the solute in the tank, the amount of water vapor present with the diluent vapor would be insufficient to prevent ignition.

To prevent the possibility of a solvent explosion, the introduction of any volume of solvent as an immiscible phase should be prevented by positive means, such as by decanting.

5. Nitrate-Organic Explosion

A nitrate-organic explosion in the 101-BY Tank could potentially be caused if a dried nitrate salt cake were to accumulate on a hot surface in the presence of an organic material. The temperature required for an explosive reaction could vary with the particular conditions of composition and concentrations of reacting materials, but a study of systems of this type indicates

that temperatures at least as low as those that might be encountered in 101-BY Tank --- of the order of 500° F --- could be dangerous. While such hot surfaces may not be available for solid deposition and drying under normal operating conditions, there is no positive assurance that operating conditions could not prevail that would permit a dangerous concentration of nitrate and heat. The organic material required to make a reactive mixture could be either a solvent phase, or it could be a cyanide-containing salt.

It is likely that additional development efforts could prove conclusively that the conditions of deposition and temperature required for a nitrate-organic reaction cannot occur simultaneously. In any event, additional development would be valuable in determining the possible extent of this problem.

Another approach to the elimination of a possible nitrate-organic hazard would be to develop the assurance that a hazardous organic material could not be introduced. Thus, a positive decanting system would eliminate the possibility of introducing a liquid organic phase.

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.

VI. RADIOLOGICAL CONSEQUENCES

All events postulated except for a solvent or organic-nitrate explosion would cause radiation exposure only in the immediate vicinity and primarily from inhalation of contaminated air, with possibly some external radiation exposure from the content of the tank itself. If it were assumed that the liquid in Tank 241-BYR-101 contained about 8 curies per gallon and was at a temperature of approximately 170° F, the radiation level at the liquid surface would be on the order of 800 R/hr and the air contamination level approximately 10^{-5} uc/cc. The air contamination in the immediate vicinity of a ruptured or leaking line leading from the dome or in the event of a rupture or leak in the dome itself would therefore be approximately 10^{-5} uc/cc. People in the vicinity without respiratory protection for an 8-hour day could receive internal deposition that would ultimately result in a radiation dose of 3 rads. The air contamination would be of consequence only very near the rupture or leak unless there were an air sweep through the tank. If the supposition were made that the air sweep of 4200 scfm continued through the liquid and was exhausted through the leak, and that atmospheric conditions would cause the dilution to be at a minimum, concentrations of approximately 6×10^{-8} uc/cc (maximum permissible concentrations in air for Cs-137) would probably be detected at distances of 3600 meters from the tank. This would dilute rapidly, of course, if the air sweep were discontinued.

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In the event of inadvertent entry of a kerosene-type organic such as that used as a diluent for TBP in the U Plant Uranium Recovery program, the possibility exists that an explosion might result from the organic vapor being ignited by contacting the hot circulator piping (estimated temperature of 450 - 500° F). Under worst conditions, estimated to be 60,000 ft^3 of dome space saturated with kerosene-type vapor at 158° F, an explosion could result causing estimated gas temperatures of 5500° F and pressures of 190 psia.

This pressure, which is considerably in excess of the 10 psig estimated limiting internal pressure on the dome (HW-37519), would probably cause the dome to rupture at its centerpoint, the pump pit.[28] Such a detonation would be expected to be on the order of a muffled explosion with the vapors rapidly escaping to the atmosphere through cracks and openings in the dome concrete and soil overburden. The escaping gas would contain radioactive aerosols and droplets resulting from vaporization and containment of the waste. Large entrained droplets would fall out on the ground immediately adjacent to the tank, as would any waste liquor splashed out of the vessel by falling debris. It would therefore be expected that significant radiation levels would be encountered within approximately 50 feet of the tank due to fallout of large droplets, splashes, and possible exposure of the tank contents through openings in the ruptured dome.

If an accident should occur under worst meterological conditions, approximately 1,000 curies of Cs-137 would have to be entrained as a fine aerosol before the closest off-plant area would be contaminated to 11 uc of Cs-137 per square meter. Milk from cows grazing on foliage from this area might contain 100% of the maximum permissible concentration of Cs-137 recommended for non-radiation workers. Radiation doses to off-plant people from inhalation and from external exposure from the radioactive cloud would be on the order of 150 and 0.3 mrads, respectively. Since, in the type of explosion visualized, the gas pressure on the liquid surface is almost uniform in the downward direction until the pressure is substantially back to atmospheric, it is most unlikely that sufficient activity could be entrained in aerosols to cause off-plant ground contamination of this magnitude. If all the postulated energy went into vaporizing liquid, about 1,000 gallons would be evaporated. If it were further assumed that Cs-137 was at the maximum concentration and that 1% entrainment occurred, the total content in the escaped material would be only 800 curies.

No attempt was made to evaluate the results of a nitrate-cyanide explosive reaction since there is not enough information available as to the amount (if any) of the cyanide that might be in the tanks to be processed and as to the required reaction conditions.

In the event of a rupture of the tank lining below the liquid level of the tank, an unknown quantity of the liquid would escape into the soil before any remedial action could be taken. None of the studies that have been conducted on waste tank leakage are completely applicable to the waste being processed in the in-tank solidification program. However, it appears likely that the waste would remain in the soil column rather than penetrate through to the ground water. Certainly this would be

true if volumes were on the order of 50,000 gallons. In any case, a comparison between a rupture in a tank presently being used for storage of the waste to be processed and the tank being used for in-tank solidification indicates that the rupture is more likely to seal itself and the radioactive materials are more likely to be retained in the soil column in the case of a leak in the latter tank.

Once the salt cake is formed, the integrity of the tank is much less important. Precipitation in the Hanford area is very low; the yearly average for 47 years is 6.40 inches, with a maximum of 11.45 inches.(29) Studies during the history of the plant have shown that on the 200-Area plateau, where all the tank farms are located, none of the precipitation penetrates through to the ground water; instead, it is returned to the atmosphere through plants and through capillary action in the soil.(30) Therefore, there is no mechanism for transporting activity to the ground water.

At the likely concentrations of radioactive isotopes in the solidified wastes, the decay of these isotopes to innocuous levels would take very many years. It would be important to assume that no uncontrolled liquid streams traverse this area during this period. In the unlikely event that meteorological conditions changed to cause a significant increase in precipitation, it would be necessary to control the possibility of leaching the solidified waste, such as by providing an impermeable cap over the tank area.

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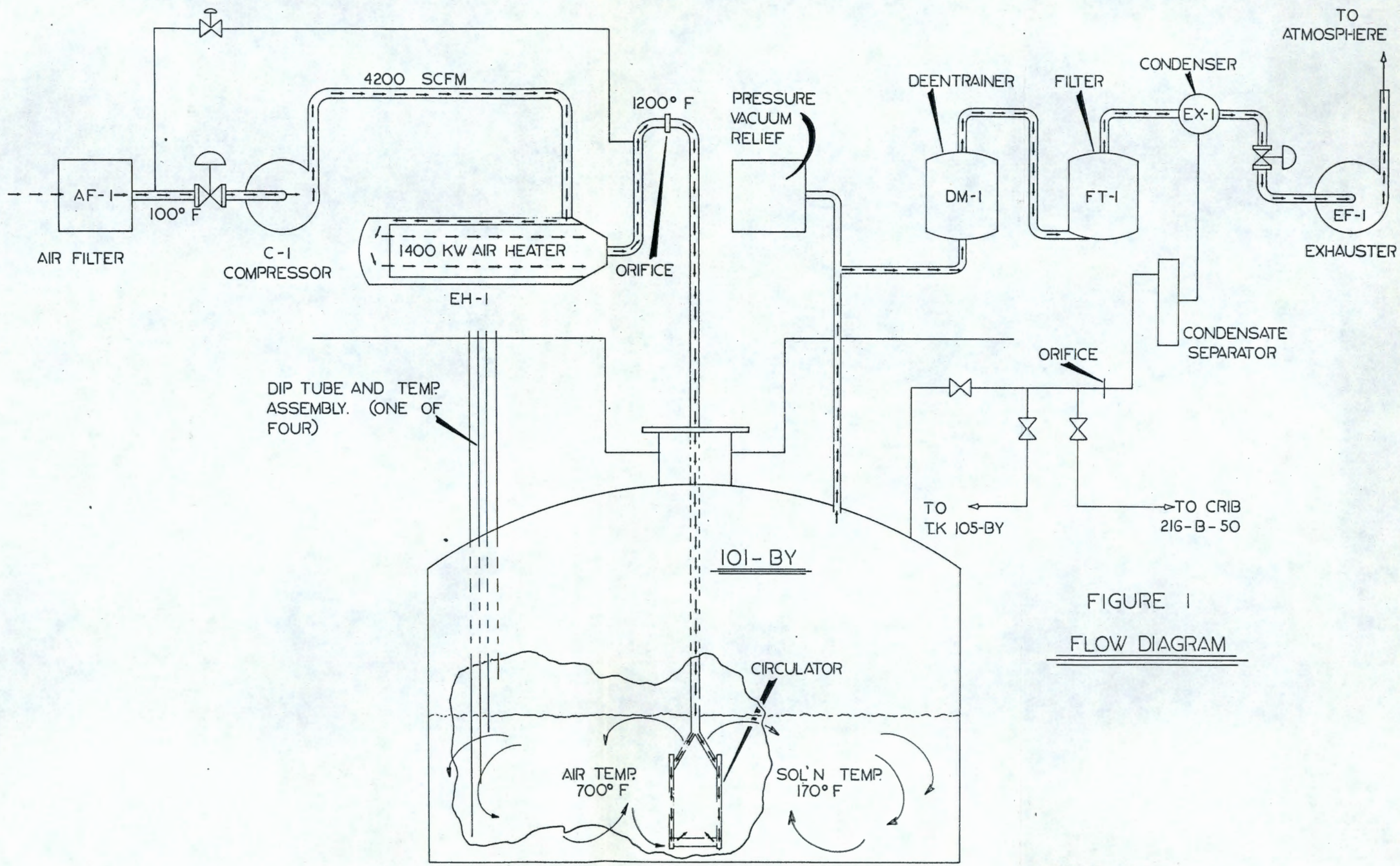

FIGURE 1

FLOW DIAGRAM