

PHYSICAL CHARACTERISTICS OF HANFORD TANK WASTE RELATING TO FLAMMABLE GAS RETENTION AND RELEASE

Chuck Stewart, Pacific Northwest National Laboratory

Abstract

All Hanford high-level waste tanks generate flammable gas. Some tanks can accumulate gas and have the potential for a large, sudden release. A good understanding of how gas is retained in the waste and the important mechanisms for its release is required to manage the existing hazard and to prevent new hazards from being created in the future. Almost ten years of tank monitoring, analyses and experiments have shown that the physical characteristics of the waste are the dominant factor in determining tank behavior. This paper will show how the physical configuration and properties of the waste in Hanford tanks affect flammable gas retention and release.

Introduction

Approximately 285,000 m³ of high-level radioactive waste is stored at the U.S. Department of Energy's Hanford site. This volume would form a cube 65 m (216 ft.) on a side or fill a football field (360 x 160 ft.) to a depth of 53 m (175 ft.). The waste is stored in 177 carbon steel tanks with capacities from 190 - 4500 m³ (50 to 1200 kgal). Of these, 149 are single-shell tanks (SSTs) built in the 1940's, 50's and early 60's and 28 are newer double-shell tanks (DSTs) constructed in the 1970's. The SSTs were removed from active use in 1980. Since then, much of their pumpable liquid fraction has been transferred to the DSTs. This has generally left the SSTs with less waste per tank, much of which is solid, while the DSTs are generally filled closer to their capacity and contain more liquid. However, the liquid transferred to the DSTs was typically concentrated by evaporation which, in some tanks, formed relatively deep layers of settled solids by precipitation as the waste cooled.

All radioactive Hanford wastes generate flammable gas. Some tanks store this gas until a relatively large volume accumulates creating the potential for a sudden release into the tank headspace. A sufficiently large release could create a flammable concentration in the tank headspace for a few hours. If the gas is ignited the resulting high pressure may fail the containment and release radioactive material to the environment.

The amount of gas that a tank can store and the potential for a large, sudden gas release depends on the waste configuration and properties. The tanks of concern are generally those with the deepest layer of solids that are "wet," immersed in liquid. A good understanding of how gas is retained in the waste and the important mechanisms for its release is required to manage the existing hazard and to prevent new hazards from being created in the future. Almost ten years of tank monitoring, in situ measurements, analyses and laboratory experiments (1) have shown that the physical characteristics of the waste are the dominant factor in determining tank behavior. This paper will describe how the physical configuration and properties of the waste affect

flammable gas retention and release mechanisms. The relative magnitude of flammable gas volume that is stored in Hanford tanks and the potential for large releases are also evaluated.

The physical characteristics and properties of the waste that are most important to the understanding of gas retention and release mechanisms are identified by reviewing the mechanisms of gas bubble retention.

Gas Bubble Retention And Release

Gas is generated in the waste by radiolysis of water, and by thermal and radiolytic decomposition of organic complexants. The gases produced include mainly hydrogen, nitrous oxide, ammonia, and nitrogen with a small amount of methane and other hydrocarbons. Gas molecules form in solution in the liquid. However, except for ammonia, these gases are not very soluble in concentrated salt solutions. Therefore most of the gas comes out of solution as bubbles. Ammonia, on the other hand, is very soluble and most of it remains in solution. The dominant mechanism for ammonia release is evaporation from a stirred liquid surface. But since ammonia has a very high flammability limit, it is more a toxicological than a flammability hazard. Bubbles, which contain the most flammable of the gases, are the most important mode of gas retention and release concerning flammability.

The principal mechanisms of bubble retention can be grouped into three categories: bubbles retained by direct attachment to particles (e.g., armored bubbles, attached bubbles, agglomerates, etc.), bubbles retained between particles by capillary forces, and bubbles retained by the strength of the surrounding waste. In layers of settled solids, bubble retention is dominated by the waste strength and capillary forces; direct attachment of bubbles to particles plays a minor role. Gas release occurs upon failure of the gas retention mechanism. Since bubbles rise freely in a fluid, a liquid cannot retain bubbles and can only store dissolved gas. The dominant mechanisms are discussed below.

Bubble Retention by Capillary Forces

Bubbles can be held in the interstitial spaces or pores between particles by capillary forces when the lithostatic load is sufficient to hold the particles in contact against the force of the bubble's internal pressure trying to push them apart. This retention mechanism requires either relatively large particles, which reduces the internal bubble pressure, or a deep waste column, which increases the lithostatic load, or both. These bubbles assume an irregular, dendritic shape conforming to the passages between the particles. When the internal pressure of a bubble is sufficient to push the surrounding particles apart, it is restrained by the yield strength of the waste.

Whether a bubble is held by yield strength or capillary force depends on a Bond number criterion developed by Gauglitz et al. (2, 3, 4). This dimensionless group contains two parameters, a ratio of gravitational force to surface tension force and a ratio of waste strength force to surface tension force. If the number exceeds unity a bubble is held by capillary forces between particles in the pore-filling configuration. The Bond number is expressed as:

$$N_{Bo} = \frac{\Delta\rho g H_S D_p}{4\sigma} + \frac{\tau_y D_p}{4\sigma} \left(\frac{A_2}{A_1} \right) > 1 \quad \text{Eq. (1)}$$

where H_S = the height of the lithostatic column above the bubble
 D_p = the mean pore diameter through which a bubble must pass to escape retention. Assumed to be represented by the particle diameter.
 $\Delta\rho$ = the difference between solid and liquid density
 σ = the surface tension
 τ_y = the yield stress
 A = A_2/A_1 is a ratio related to how the yield stress resists bubble expansion; it was estimated at 2.8 by (3).

The upper limit on the vertical size of a pore-filling bubble can be derived from the balance of capillary forces and the hydrostatic pressure difference between the top and bottom of the bubble (5). As the bubble grows, the depth and curvature radii of the liquid-gas interfaces continually readjust themselves in response to the uniform and increasing gas pressure inside the bubble. When the bubble internal pressure overcomes the restraining force of surface tension, gas pushes out of the top of the bubble and liquid flows into the bottom of the bubble causing the bubble to move upward. The gas volume fraction at which this motion occurs is called the percolation threshold. The maximum height, Δh , that a pore-filling bubble can attain before percolating is expressed as

$$\Delta h = 4\sigma/\rho_L g D_p \quad \text{Eq. (2)}$$

where σ is the surface tension and ρ_L is the liquid density.

Pore-filling bubbles, though they may represent a considerable gas volume, are not a flammability concern because there is no mechanism for them to release the gas rapidly. In order for gas in a pore-filling bubble to move, liquid must be displaced from the pores the bubble enters and flow into the pores the bubble vacates. Flow of the liquid through a porous medium is a very slow process. Also, before a pore-filling bubble can be released into a tank's headspace, it must rise into decreasing lithostatic load and eventually become a particle-displacing bubble whose characteristics are described below.

Bubble Retention by Waste Strength

If a bubble is retained by the strength of the waste, as determined by the Bond number in Eq. (1), the bubble shape is determined by a balance of surface tension and waste strength. With relatively weak waste or small bubbles, surface tension pulls bubbles into an approximately spherical shape. If the effect of waste strength is greater than surface tension forces, the bubble grows into the weakest area of the waste surrounding it and assumes a dendritic shape. Particle-displacing bubbles that are not dendritic are called "round" bubbles, even though they may be ellipsoidal or similarly distorted from a truly spherical shape.

There are two basic constraints on the size of round particle-displacing bubbles: 1) a bubble can be approximately spherical only when the forces defining its surface are dominated by surface tension, and 2) a bubble can grow vertically only until its buoyancy exceeds the ability of the waste to hold it in place. The first criterion is derived from simple scaling of the relative importance of strength to surface tension. The maximum diameter of round bubbles before they begin to assume a dendritic shape is given by.

$$D_b < \frac{\sigma}{\tau_y} \quad \text{Eq. (3)}$$

Where τ_y is the yield stress, σ is the surface tension, and D_b is the bubble diameter.

In the second criterion, the ability of the material to resist the bubble's buoyancy limits the size. A criterion for incipient motion of a solid sphere immersed in a Bingham fluid can be derived in terms of a critical gravity-yield number, Y_G . The resulting limiting diameter is expressed as

$$D_b < \frac{\tau_y}{\rho_w g Y_G} \quad \text{Eq. (4)}$$

where ρ_w is the bulk waste density and g is the acceleration of gravity. The number Y_G is estimated at 0.2 for use with yield strengths as measured at Hanford. The maximum round bubble diameter is essentially constant at about 1/2-1 cm. This size is quite consistent with observations in waste and simulants. A very large round bubble that could contain a hazardous amount of gas simply cannot exist.

Eq. (4) also gives the limiting height of dendritic particle-displacing bubbles. When they grow to the limiting size, the increased hydrostatic pressure difference pinches off the bottom of the bubble and pushes the top of the bubble upward in a manner similar to migration of pore-filling bubbles. However, motion of particle-displacing bubbles is much faster since it does not require liquid flow through a porous medium. If the waste is moderately strong, the bubbles do not collapse completely and dendritic bubble networks form to provide continuous gas release (4).

Buoyant Gas Release

It is possible for gas releases to occur while individual bubbles remain confined within the waste. This can happen in tanks with a deep layer of supernatant liquid when a portion, or "gob," of the settled solids accumulates sufficient gas to become buoyant with respect to the liquid above it, breaks away and rises through the liquid. The stored gas bubbles expand as the gob rises, failing the surrounding waste so a portion of the gas can escape into the headspace. After releasing gas until it is no longer buoyant the gob sinks back to the bottom of the tank. This gas release process has been identified as a buoyant displacement gas release event. Meyer and

Wells (6) have derived models that determine whether buoyant displacements can occur and predict the volume of gas released. These models are summarized briefly below.

Gas accumulation in the settled solids layer is a balance between gas generation and steady gas release. Gas release is assumed to occur by the slow migration of bubbles that qualitatively obeys the form of Stokes' Law. Based on in-situ measurements, the waste viscosity (determining bubble rise velocity) is assumed to increase linearly with waste depth from zero at the top of the layer. The resulting gas fraction (also termed "void fraction") profile is given by

$$\alpha(\eta) = \frac{C_B}{\rho_w} \left(\frac{GT}{p_s} \right)^{\frac{1}{3}} H_s^2 \eta(1 - \eta) \quad \text{Eq. (5)}$$

where T is the average waste temperature, p_s is the average pressure in the retained gas, G is the volumetric gas generation rate, H_s is the depth of the settled solids layer and $\eta=z/H_s$. If the average gas fraction predicted by Eq. (5) exceeds the neutral buoyancy gas fraction, a buoyant displacement gas release will occur. The coefficient C_B is adjusted to ensure that the tanks currently exhibiting buoyant displacements are predicted to exceed neutral buoyancy. The neutral buoyancy gas fraction is defined by the waste densities as follows:

$$\alpha_{NB} = 1 - \frac{\rho_L}{\rho_w} \quad \text{Eq. (6)}$$

Once it is known from Eqs. (5) and (6) that a buoyant displacement can occur, the volume of gas released is determined from the size of the gob, the neutral buoyancy void fraction, and the pressure, which is a function of the depth of liquid above the settled solids layer. The gob size is estimated from a form of Rayleigh-Taylor instability and a balance of buoyant force to the restraining effect of the waste strength. This leads to the following expression for the release volume:

$$V_{REL} = C_R \left(\frac{p_s}{p_A} - 1 \right) \alpha_{NB} H_s \frac{\tau_y}{\rho_L} \quad \text{Eq. (7)}$$

where p_A is the ambient barometric pressure. The leading coefficient, C_R , is adjusted so the predicted release volume best fits the historical data of the group of tanks known to exhibit buoyant displacements.

Important Physical Properties for Bubble Retention and Release

Based on the foregoing discussion and inspection of Eqs. (1) through (8), the list of physical parameters important for determining gas retention and release characteristics is straightforward. The models require the following parameters:

H_S	thickness of the settled solids layer
H_L	thickness of the supernatant liquid layer (if any)
D_P	effective solid particle diameter, represents the pore diameter between particles
ρ_S	density of solid particles
ρ_L	density of the supernatant or interstitial liquid
ρ_W	bulk density of the waste (solid-liquid matrix)
σ	surface tension
τ_y	waste yield stress

Measuring Waste Physical Properties

Measurement of the waste properties in Hanford tanks is challenging. Samples of the toxic, radioactive waste cannot be handled except by remote manipulation in a specially designed hot cell. Also, since the solubility of the dissolved solids in the saturated salt solution is highly temperature dependent and samples cannot be kept at tank temperature, what is measured in the lab may not represent the waste as it exists in the tank. The most useful measurements are made in situ, though development and deployment of any hardware in the tanks is extremely difficult and costly. Notable successes of in-situ measurement include the ball rheometer for density, waste layering and rheology, the void fraction instrument (VFI) for retained gas volume and its distribution, the retained gas sampler (RGS) for gas composition and volume, and the neutron and gamma probes for gas fraction and layering.

The ball rheometer uses a 16 lb, 3.6-inch diameter tungsten ball that is fixed to a cable. The ball is lowered or raised at a constant speed by rotation of the drum on which the cable is wound. A load cell records the tension in the cable. The ball position is known from the amount of cable let out from the drum. Analysis of the force vs. position data coupled with a model for fluid behavior yields the requisite information for viscosity, yield strength and density. Additional details on the operation of the ball rheometer are given by Stewart et al. (7).

The VFI was designed to measure the volume fraction of free (undissolved) gas at specific locations in a tank. The gas is determined by compressing waste that has been captured in a small sample chamber about the size of a soup can. The sample chamber is mounted on a pivoting arm at the end of a long mast that is positioned in the tank by a crane. Gas measurements are typically made every 12 - 24 inches through two or more tank risers. Details of the VFI operation are also provided in (7).

The RGS is a version of the universal core sampler specifically designed to capture the waste and gas under a leak-tight seal so that they can be analyzed in a hot cell laboratory. RGS samplers are spaced at intervals in a normal core sampling operation. Three to six 19-inch long, 1-inch diameter RGS samples are typically obtained in a tank. Information obtained from the RGS include gas volume fraction and gas composition, as well as the dissolved gas (ammonia) concentration. Operational details of the RGS are given by Mahoney et al. (8).

Neutron and gamma probes have been used for many years in the liquid observation wells in single shell tanks for monitoring of the interstitial liquid level. The neutron probe detects the presence of water (actually hydrogen) and the gamma probe responds to the presence of

radioactive isotopes that emit gamma radiation. A new-generation neutron/gamma probe has been deployed that operates inside the central well in multi-function instrument trees (MIT) in double shell tanks. In SY-101, the neutron probe has become the instrument of choice for determining the thickness of the floating crust layer and the distribution of retained gas within it (9, 10). The MIT neutron/gamma probes will be used to survey several other DSTs in 2000.

These and other methods that are typically used to monitor and measure the physical properties and parameters listed above and methods to directly measure gas retention are described in the balance of this section.

Waste Configuration

For the purposes of estimating retained gas volumes and release behavior we must know not only the overall waste depth, but the thickness of each waste layer. Several direct and indirect methods are available to determine this.

Waste surface level is, by definition, the height of the uppermost layer. The waste level monitoring instrument has traditionally been a reel type conductivity gauge (made by the Food Instrument Corporation, thus the gauges were termed "FIC"). These units have had a history of maintenance problems, mainly the buildup of a long "wastecicle" on the probe from repeated wetting and evaporation of the salt solution. The FIC units are being replaced with a buoyancy-tension wire gauge manufactured by Enraf-Nonius®. The "ENRAF" gauges now provide accurate data for a large number of tanks. Since they do not require repeated making and breaking of contact with the waste they have not been subject to wastecicle buildup.

The vertical temperature profile provides a good picture of the waste configuration. A liquid layer is termed convective because thermally-driven convection occurs there and the settled solids is called the nonconvective layer because the strength of the solids inhibits convection. This creates the characteristic uniform temperatures in the convective layer and a parabolic profile in the nonconvective layer. The thickness of the layers can be inferred by noting the elevation where the profiles shift from one pattern to another. Each tank has thermocouple trees to measure waste temperatures. New thermocouple systems were installed in DSTs called multi function instrument trees (MIT). These units have an internal well so that a calibration probe can be inserted to provide data at more locations than the fixed location thermocouples.

Since the neutron probe detects the presence of water (actually hydrogen), its profiles can be interpreted to describe the waste configuration. A liquid-rich convective region exhibits a high neutron count while a somewhat dryer, gas retaining layer shows a lower count. Similarly, the gamma probe responds to the presence of radioactive isotopes that emit gamma radiation. In Hanford waste, this is mainly cesium which is present in both liquid and solid. Thus the gamma profile can be compared to the neutron profile to determine whether a low neutron count indicates gas or solids.

Finally, the ball rheometer defines the boundaries between waste layers very accurately since it is sensitive to small changes in waste viscosity, density and yield stress. However, the

device can only be operated in relatively weak waste that the ball can penetrate by its own weight. This effectively limits its operation to the DSTs.

Particle Size

Particle size is typically measured by laser diffraction in the hot cell laboratory. A small sample of waste is suspended in its own supernate to prevent dissolution. A laser beam is directed through the sample and the particle size distribution is inferred from the diffraction pattern. This method is useful only with relatively insoluble solids or soluble solids where the tank temperature is approximately equal to the hot cell temperature to ensure that particle size doesn't change by temperature-induced precipitation or dissolution. The particle sizes in DSTs and sludge tanks typically favor micron to sub-micron diameters with a few larger ones in the 10 - 100 micron range (11, 12, 13).

Particle size can also be roughly estimated by the visual appearance of waste core samples as they are extruded from the sampler in the hot cell. Most waste has a fine clay- or mud-like appearance suggesting micron-sized particles or smaller. A more granular texture similar to fine sand occurs in single-shell salt cake tanks which indicates particles of 10 - 100 microns. A few samples have a "snow-cone" appearance with particles several millimeters in diameter.

Density of Particles, Liquid and the Bulk Waste

Densities of the individual solid and liquid phases are determined in the laboratory from core samples or grab samples of the waste. However, the results are subject to the same caveat on tank temperature versus lab temperature as was particle size measurement. If the hot cell temperature is lower than tank temperature, the density of the liquid will generally be too low since solids will leave the liquid as solubility decreases. The solids density may be low or high depending on which soluble components precipitate as the temperature changes. The bulk density of a waste sample, however, is unaffected by temperature changes since volume changes accompanying precipitation and dissolution are small in the highly concentrated saturated salt solutions typical of the waste.

The density of fluids can also be measured quite accurately with the Ball Rheometer. A modified ENRAF level gauge can also be lowered beneath the waste surface to measure the density of the liquid beneath. Neither device, however, can measure density in a material with a yield stress.

Surface Tension

The only applicable measure of surface tension available is from laboratory studies of chemical simulant by Norton and Pederson (14). The surface tension values measured range from 0.07 to 0.10 N/m, which is only slightly higher than that of water. The surface tension also appears not to be very sensitive to salt concentration and temperature. Therefore, a constant value of 0.08 N/m is typically used as the best estimate for surface tension in tank applications.

Waste Yield Stress

The ball rheometer was designed specifically to measure yield stress and has provided good data in six DSTs. The data show that the yield stress and apparent viscosity varies approximately linearly, increasing from zero at the top of the nonconvective layer to 200 - 300 Pa at the tank bottom. Unfortunately, the ball rheometer cannot be used in stiffer wastes because a yield stress on the order of 1000 Pa is sufficient to support the ball.

An alternate method is available for tanks where the ball rheometer cannot be used. Gauglitz and Aiken (15) calibrated the deformation of the cylindrical core samples during extrusion by observing the behavior of equal sized samples of clays with known yield stress. This method has shown that typical SST waste has yield stress of a several hundred to a few thousand Pa. Only the driest, most brittle samples appear to approach 10,000 Pa in strength.

Yield stress measurements by traditional viscometers and shear vanes in the laboratory have not been particularly successful. The results are, again, subject to the temperature difference problem already mentioned as well as the disturbance of the waste necessary to bring it from the tank to the measurement device.

Direct Measurement of Gas Retention

As discussed above, the VFI and RGS were designed specifically to measure local in situ gas volume fractions from which the overall retained gas volume in a tank can be estimated. An analytical method that deduces the total retained gas volume directly from the response of the waste to barometric pressure effects (BPE) is also useful in tanks in which neither instrument has been operated. The characteristics of each are described below.

A VFI deployment produces a relatively large number of data points in the vertical direction, but only from two risers. We must assume that the data from these two risers represent the entire tank in computing the average gas fraction from the individual data points. In five of the six double-shell tanks sampled with the VFI, RGS samples from two additional risers and the BPE method have provided independent corroboration that this assumption is generally valid. Uncertainties in the average gas fraction derived from VFI data range from 10 - 30% standard deviation due mainly to variability in the data (16).

A single RGS gas fraction measurement is made on each 19-inch core sample segment. The gas value from an RGS segment is generally as accurate as a single VFI data point, but there are usually only three to six RGS measurements per tank, one to three per riser, compared to 20 - 40 VFI data points. Therefore, the RGS measurements are less likely to be representative of the entire tank. In the single-shell tanks the waste is much less uniform and the sparcity of RGS samples makes the uncertainty even higher. However, since the waste is too strong to use the VFI in single-shell tanks, the RGS and BPE are the only methods available.

The barometric pressure effect (BPE) model estimates stored gas volume from the response of the waste surface level to fluctuations in barometric pressure. Gas bubbles trapped in a weak solid-liquid matrix expand and compress as the barometric pressure changes. In its

simplest form the model applies the ideal gas law, assuming isothermal conditions, to determine the in situ gas fraction as:

$$\alpha = -\frac{p_{\text{EFF}}}{L_G} \frac{dL}{dp_0} \quad \text{Eq. (8)}$$

where p_{EFF} is the average pressure felt by the gas and dL/dp_0 is the rate of change of waste level with barometric pressure derived from the monitoring data using statistical methods developed by Whitney et al. (17). L_G is the thickness of the waste layer(s) containing gas. A more general form of the model also considers the effect of waste strength (18). A much more detailed model is being developed and compared to experiments by Gauglitz et al. (19). The overall uncertainty in the BPE volume fraction varies from 20–50%. However, the BPE method has a rather high detection limit of 1000–1500 ft³ of gas and the conditions where it can be applied are somewhat restrictive (16).

Effect of Waste Configuration on Gas Retention and Release

Besides physical properties, gas retention depends on macroscopic parameters describing the waste type and configuration. The characteristics and implications of each configuration in view of flammable gas retention and release are reviewed below.

The three waste types of interest are liquid (no or little solids present), sludge (insoluble solids) and saltcake (solids precipitated from saturated liquid on cooling). Liquid, by definition, is a dilute or concentrated solution of dissolved solids, water and a small fraction of soluble organics that contains at most a small fraction of suspended solid particles. Sludge consists of fine insoluble particles which are mostly metal oxides. Saltcake forms by the settling of sodium and aluminum salts precipitated from a saturated solution by cooling. Saltcake particles are generally larger than sludge particles. However, a “salt-slurry” waste type is also which consists of finer particles than typical saltcake. Salt slurry is typically found in DSTs. Some tanks contain a mixture of sludge and saltcake that can be considered a “mixed” waste type. However, the mixed waste appears to behave as saltcake in most cases and will not be separated here.

Waste configuration is the arrangement of waste types in layers within a tank. The waste types are distributed within the tanks in only a few different ways, depending mainly on the amount of liquid. In order of decreasing amount of liquid, the main waste configurations are: “liquid” containing almost entirely the liquid waste type, “liquid-over-solid” where a relatively deep layer of supernatant liquid overlies an equally deep layer of liquid-saturated settled solid particles, “wet solids” where the settled solids are saturated with liquid but there is little or no supernate, and “pumped,” where interstitial liquid has been reduced by saltwell pumping such that the interstitial liquid level is well below the waste surface.

Two other waste configurations are also of interest: “crust,” a solid-over-liquid arrangement consisting of a floating layer of gas-bearing solids, and “mixed slurry” in which most of the solid particles and small gas bubbles are kept in suspension mechanically. A crust exists only with the more concentrated saltcake wastes in a few DSTs as a modification of the liquid-over-solid configuration. The SSTs A-101 and AX-101 are unique in that, based on core

sample evidence, the entire mass of undissolved solids in the tank floats on a very dense liquid layer. However, this cannot be treated as a true “crust.” Mixed slurry currently exists only in SY-101 due to the action of the mixer pump. The characteristics of gas retention and release in each of the four main waste configurations, liquid, liquid-over-solid, wet solids and pumped, are discussed in more detail below.

Liquid Waste Configuration

Only a few of the DSTs currently contain essentially all liquid. In these tanks, gas generated in solution by radiolysis nucleates to form small bubbles on suspended micro-particles or on the tank walls. Once these bubbles grow large enough to become buoyant they rise immediately to the surface, release into the headspace and are removed by ventilation. This continuous release mechanism makes retention of a significant volume of free gas physically impossible in this configuration.

Liquid-Over-Solid Configuration

The liquid-over-solid waste configuration is represented by eighteen DSTs. These include those with a floating crust but excludes SY-101 because the mixer pump has changed its configuration to mixed slurry. In twelve tanks the nonconvective layer consists of sludge with saltcake in the other six. All but one of the saltcake tanks have a crust.

Except for the few tanks with a thick crust layer, gas is retained mainly in the nonconvective layer. The settled solids are relatively weak with a consistency similar to a thin milkshake, creamy peanut butter in the middle and stiff peanut butter at the bottom. The yield stress increases roughly linearly from zero at the upper surface to 200-300 Pa at the bottom (16). This strength is sufficient to hold bubbles up to about a centimeter in diameter. The particle size is relatively small so that Eq. (1) predicts only particle-displacing bubbles. The material strength is also sufficiently low such that the bubbles remain approximately round per Eq. (2).

Measurements made by the VFI and RGS in five DSTs with the liquid-over-solid configuration show that gas volume fraction in the nonconvective layer increases with depth from near zero at the top. In three tanks the gas fraction shows a parabolic profile. The peak gas fraction ranges from 0.1 to 0.16 with averages from 0.04 to 0.11 (20). Similar average gas fraction are estimated using the BPE model for other DSTs containing sludge.

The liquid-over-solid waste configuration is subject to buoyant displacement gas releases described above. Buoyant displacements are the largest and fastest releases known to occur in Hanford tanks and the only ones that are known to have created flammable conditions in a tank's headspace (21). Before the mixer pump was installed in SY-101, its buoyant displacements typically released over 5,000 scf of gas over a period of 10 - 20 minutes three times per year. At least two of these releases exceeded 10,000 scf, enough to make the tank headspace just flammable. This has only occurred in SY-101. The releases from the other five tanks that exhibit buoyant displacements are much smaller, slower and less frequent: typically 1,000 scf of gas released over two hours once per year.

Future operations transferring waste in and out of DSTs could potentially create waste configurations and conditions that could lead to buoyant displacements. Large releases can happen in tanks with several meters of nonconvective and convective layer depth, a low neutral buoyancy volume fraction (implying a small difference between nonconvective and convective layer densities), and relatively high gas generation rates. These conditions are easily avoided by keeping the waste relatively dilute. Applying the models derived by Meyer and Wells (6) as described above can also show whether buoyant displacement gas release might be a concern.

Wet Solids Configuration

Most of the tanks other than DSTs that retain a significant volume of gas consist entirely of wet solids (i.e., solid matrix saturated with liquid) with little or no supernatant liquid. Eighty-one tanks have this configuration, 25 with mixed or saltcake waste and 56 with sludge. However, 3 of the mixed or saltcake tanks and 30 of the sludge tanks are essentially empty with less than one meter of waste.

In the saltcake waste type, assuming 30-micron particles, Eq. (1) states that the upper several meters will retain individual round bubbles while the bottom few meters will contain pore-filling bubbles due to the high lithostatic load. Sludge waste, assuming a 1-micron particle diameter, will retain gas as particle-displacing bubbles at any depth attainable in SSTs. The wet solids tanks with saltcake waste type have the highest gas fraction and deepest waste so they account for most of the total retained gas volume.

Unlike the liquid-over-solid waste configuration, the gas retention characteristics of sludge and saltcake in wet solids tanks appear to be quite different. The median gas fraction for sludge tanks is only 0.01, but is 0.12 for all saltcake tanks. An average gas fraction exceeding 0.25 has been measured in a saltcake tank; the sludge tanks only reach 0.12. A large group of the sludge tanks exhibit a barely detectable gas fraction (20). This difference likely results from the generally lower waste depth, lower gas generation rate per unit volume and the smaller particle size of the sludge.

The characteristics of non-buoyant displacement gas releases from the wet solids configuration depend to a great degree on how the gas is stored. For example, pore-filling bubbles require liquid to flow through the porous media in order to migrate. This makes gas release a very slow process. Gas release from particle displacing bubbles may be somewhat faster but is believed to be limited to a small region of a tank. This is confirmed by headspace gas monitoring data which shows these tanks typically release on the order of 10 - 100 scf of gas over a period of several days. These tend to occur when the barometric pressure falls rapidly during storm passage in the late fall and early spring. Flammability is not a major concern except possibly for releases induced by a highly unlikely severe earthquake.

Pumped Configuration

There are 53 tanks of the pumped configuration, all SSTs. Of these, there are 35 of the mixed/saltcake waste type and 18 sludge tanks. Five of these tanks (four mixed/saltcake and one sludge) are essentially empty with less than one meter of waste. In pumped tanks the interstitial

liquid level is well below the waste level. The portion of the waste above the liquid level exerts a disproportionately high lithostatic load on the waste below. Applying Eq. (1) with the density difference set equal to the solid density, only one meter of unsaturated salt cake above the liquid level is required to force the entire column into the pore-filling bubble configuration. However, the small particle size of sludge maintains particle-displacing bubbles regardless of the depth of overburden above the liquid level. The small particles also make it difficult to remove interstitial liquid from sludge effectively.

Gas fraction information for pumped tanks is available only for sludge waste. The limited data shows that there is essentially no reduction in gas fraction after pumping a sludge tank (30). The maximum gas fraction observed is 0.12. We assume for lack of data that the gas fractions below the interstitial liquid level are also the same for both pumped and unpumped saltcake tanks.

The only potential mechanism for a significant gas release from a pumped tank might be a sudden waste subsidence months or years after saltwell pumping is completed. The removal of the interstitial liquid greatly increases the lithostatic load on the particle column. Apparently the continued slow migration of liquid eventually leads to a failure and compaction of the column. Any gas still trapped in liquid saturated waste in the subsiding region would be subject to release. While no such gas releases have yet been observed, craters and depressions on the surface of pumped tanks clearly show subsidence has occurred. However, since a large fraction of the stored gas is known to be removed by saltwell pumping, the volume of a post-pumping subsidence release is expected to be small.

Summary

We understand the mechanisms of gas retention, we have identified which of the Hanford tanks store significant volumes and have determined how large these volumes are. Operations are underway that will reduce retention in many of them. We understand what causes gas retention and can avoid creating new tanks that retain hazardous volumes of gas.

We also understand the mechanics and magnitudes of gas release as it occurs in the various Hanford waste configurations. Over 50 tank-years of monitoring flammable gas concentrations in the most hazardous tanks tends to confirm the theory that spontaneous gas releases are generally small and slow except for buoyant displacements which occur only in tanks with the liquid-over-solid waste configuration. However, we can predict conditions that cause buoyant displacements and how large a potential release might be so that this hazard can be avoided.

We are confident that we have identified and can control existing flammable gas hazards in Hanford tanks through understanding gas retention and release processes, backed up by a large body of confirming measurements, experimental results and in-tank observations. We are also confident we can avoid creating new hazardous tanks as waste is transferred and processed for cleanup.

References

1. Bonner WF, RA Brouns and RK Quinn. 2000. *Application of Science and Technology at Hanford*. Proceedings of Waste Management 2000, February 27 - March 2, 2000, Tucson, Arizona.
2. Gauglitz PA, LA Mahoney, DP Mendoza, and MC Miller. 1994. *Mechanisms of Gas Bubble Retention*. PNL-10120, Pacific Northwest National Laboratory, Richland, Washington.
3. Gauglitz PA, SD Rassat, MR Powell, RR Shah, and LA Mahoney. 1995. *Gas Bubble Retention and Its Effects on Waste Properties: Retention Mechanisms, Viscosity, and Tensile and Shear Strengths*. PNL-10740, Pacific Northwest National Laboratory, Richland, Washington.
4. Gauglitz PA, SD Rassat, PR Bredt, JH Konynenbelt, JM Tingey, and DP Mendoza. 1996. *Mechanisms of Gas Bubble Retention and Release: Results for Hanford Waste Tanks 241-S-102 and 241-SY-103 and Single-Shell Tank Simulants*. PNNL-11298, Pacific Northwest National Laboratory, Richland, Washington.
5. Stewart CW, ME Brewster, PA Gauglitz, LA Mahoney, PA Meyer, KP Recknagle, and HC Reid. 1996a. *Gas Retention and Release Behavior in Hanford Single-Shell Waste Tanks*. PNNL-11391, Pacific Northwest National Laboratory, Richland, Washington.
6. Meyer PA and BE Wells. 2000. *Understanding Gas Release Events in Hanford Double-Shell Tanks*. Proceedings of Waste Management 2000, February 27 - March 2, 2000, Tucson, Arizona.
7. Stewart, CW, JM Alzheimer, ME Brewster, G Chen, RE Mendoza, HC Reid, CL Shepard, and G Terrones. 1996b. *In Situ Rheology and Gas Volume in Hanford Double-Shell Waste Tanks*. PNNL-11296, Pacific Northwest National Laboratory, Richland, Washington.
8. Mahoney LA, ZI Antoniak, JM Bates and ME Dahl. 1999. *Retained Gas Sampling Results for the Flammable Gas Program*. PNNL-13000, Pacific Northwest National Laboratory, Richland, Washington.
9. Stewart CW, SD Rassat, JH Sukamto and JM Cuta. 1999. *Buoyancy and Dissolution of the Floating Crust Layer in Tank 241-SY-101 During Transfer and Back-Dilution*. PNNL-13040, Pacific Northwest National Laboratory, Richland, Washington.
10. Cannon NS, DA Barnes and FS Strong. 2000. *Neutron and Gamma Probe Application to Hanford Tank 241-SY-101*. Proceedings of Waste Management 2000, February 27 - March 2, 2000, Tucson, Arizona.
11. Herting DL, DB Bechtold, BE Hey, BD Keele, L Jensen, and TL Welsh. 1992. *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank*

241-SY-101. WHC-SD-WM-DTR-026, Westinghouse Hanford Company, Richland Washington.

12. Lumetta GJ, MJ Wagner, FV Hoopes and RT Steele. 1996. *Washing and Caustic Leaching of Hanford Tank C-106 Sludge*. PNNL-11381, Pacific Northwest National Laboratory, Richland, Washington.

13. Herting DL. 1998. *Results of Dilution Studies with Waste from Tank 241-AN-105*. HNF-SD-WM-DTR-046, Numatec Hanford Corporation, Richland, Washington.

14. Norton JD and LT Pederson. 1995. *Solubilities of Gases in Simulated Tank 241-SY-101 Wastes*. PNL-10785, Pacific Northwest National Laboratory, Richland, Washington.

15. Gauglitz PA and JT Aikin. 1997. *Waste Behavior During Horizontal Extrusion: Effect of Waste Strength for Bentonite and Kaolin/Ludox Simulants and Strength Estimates for Wastes from Hanford Waste Tanks 241-SY-103, AW-101, AN-103, and S-102*. PNNL-11706, Pacific Northwest Laboratory, Richland, Washington.

16. Meyer PA, ME Brewster, SA Bryan, G Chen, LR Pederson, CW Stewart, and G Terrones. 1997. *Gas Retention and Release Behavior in Hanford Double Shell Waste Tanks*. PNNL-11536 Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

17. Whitney PD, G Chen, PA Gauglitz, PA Meyer, and NE Miller. 1997. *Estimating Retained Gas Volumes in the Hanford Waste Tanks Using Waste Level Measurements*. PNNL-11693, Pacific Northwest National Laboratory, Richland, Washington.

18. Whitney PD, PA Meyer, NE Wilkins, F Gao, and AG Wood. 1996. *Flammable Gas Data Evaluation Progress Report*. PNNL-11373, Pacific Northwest National Laboratory, Richland, Washington.

19. Gauglitz PA, G Terrones, DP Mendoza and CL Aardahl. 2000. *Behavior of Flammable Gas Bubbles in Hanford High Level Waste*. Proceedings of Waste Management 2000, February 27 - March 2, 2000, Tucson, Arizona.

20. Barker SA, WB Barton, DR Bratzel, M Epstein, PA Gauglitz, GD Johnson, SN Maruvada, CE Olson, ML Sauer, SE Slezak, CW Stewart and J. Young. 1999. *Flammable Gas Safety Analysis Data Review*. SNL-000198, Sandia National Laboratory, Albuquerque, New Mexico.

21. Johnson GD, WB Barton, JW Brothers, SA Bryan, PA Gauglitz, LR Pederson, CW Stewart and LM Stock. 1997. *Evaluation of High-Level Nuclear Waste Tanks Having a Potential Flammable Gas Hazard*. Proceedings of Waste Management 1997, March 2-6, 1997, Tucson Arizona.