Gas Retention and Release from Hanford Site Sludge Waste Tanks

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ABSTRACT

Radioactive wastes from nuclear fuel processing are stored in large underground storage tanks at the Hanford Site. Solid wastes can be divided into saltcake (mostly precipitated soluble sodium nitrate and nitrite salts with some interstitial liquid consisting of concentrated salt solutions) and sludge (mostly low solubility aluminum and iron compounds with relatively dilute interstitial liquid). Waste generates hydrogen through the radiolysis of water and organic compounds, radio-thermolytic decomposition of organic compounds, and corrosion of a tank's carbon steel walls. Nonflammable gases, such as nitrous oxide and nitrogen, are also produced. Additional flammable gases (e.g., ammonia and methane) are generated by chemical reactions between various degradation products of organic chemicals present in the tanks.

Six double-shell tanks (DSTs) containing saltcake wastes began showing signs of gas accumulation and buoyant instability in the form of periodic waste level drops in the 1980s. Studies in the 1990s indicated that gas would accumulate in the settled solids layer until its bulk density was lower than the supernatant liquid. The resultant gas release caused by this instability was termed a Buoyant Displacement Gas Release Event (BDGRE). Criteria were developed to prevent forming additional waste tanks that exhibited BDGREs. Significant gas accumulation and BDGREs were never observed in tanks containing predominantly sludge wastes.

Literature reviews, data from Hanford Site waste tanks, and experiments with waste simulants have led to new conclusions on gas retention and release in sludge waste. The data show similar overall behavior where initially the settled solids volume increases as gas bubbles form. Gas fraction in the settled solids increases to a peak concentration after which additional generated gas escapes through connected cracks and there is a balance between gas generation and gas release with little change in gas fraction. Experiments showed that this behavior does not change as sludge waste depth increases.

Sufficient data now exist to differentiate between gas retention and release behavior in Hanford Site sludge waste tanks and saltcake waste tanks. The saltcake criteria do not need to be applied to sludge waste tanks that exhibit certain gas retention and release behavior. Criteria for waste characteristics and process behavior have been defined that identify specific wastes and tanks that, based on previous operating experience, will have low gas retention and will not exhibit large, spontaneous releases.

The first criterion defines what waste is considered sludge and what waste is considered saltcake. If the mass ratio of soluble to insoluble constituents is below 2.5, then the waste is sludge. The second criterion is a density difference criterion that prevents tanks being operated in a region where sludge buoyancy might occur. For large gas releases to occur, the settled solids must accumulate sufficient gas to become less dense than the overlying supernatant (i.e., the settled solids would become buoyant). Based on previous operating experience, the ratio of liquid density to degassed settled solids bulk density ($\rho\ell/\rho B$) should be maintained at ≤ 0.84. This ensures that retained gas content in the sludge would need to exceed 16% by volume for the settled solids to become buoyant in the overlying supernatant. Tank waste that satisfies the mass ratio criterion, the liquid to bulk solids density criterion, and has process data supporting typical Hanford waste sludge behavior does not pose a significant risk for a large spontaneous gas release event.

ACRONYMS

BDGRE	buoyant displacement gas release event
DST	double-shell tank
SST	single-shell tank

INTRODUCTION

Radioactive wastes from nuclear fuel processing are stored in large underground storage tanks at the Hanford Site. There are 149 older single-shell tanks (SSTs) built in the 1940s through 1960s and 28 newer double-shell tanks (DSTs) built from 1968 through 1986. The SSTs contain only negligible amounts of liquid wastes, and the Tank Operations Contractor is continuing a program of moving solid wastes from SSTs to DSTs. Solid wastes can be divided into saltcake (mostly precipitated soluble sodium nitrate and nitrite salts with some interstitial liquid consisting of concentrated salt solutions) and sludge (mostly low solubility aluminum and iron compounds with relatively dilute interstitial liquid). Some DSTs store only liquid waste, while others contain both liquid and settled solids.

Waste generates hydrogen through the radiolysis of water and organic compounds, radio-thermolytic decomposition of organic compounds, and corrosion of a tank's carbon steel walls. Nonflammable gases, such as nitrous oxide and nitrogen, are also produced. Additional flammable gases (e.g., ammonia and methane) are generated by chemical reactions between various degradation products of organic chemicals present in the tanks.

Six DSTs containing low shear strength saltcake wastes began showing signs of gas accumulation and buoyant instability in the form of periodic waste level drops in the 1980s. As illustrated in Figure 1, gas would accumulate in the settled solids layer until its bulk density was lower than the supernatant liquid. The resultant gas release caused by this instability was termed a buoyant displacement gas release event (BDGRE).

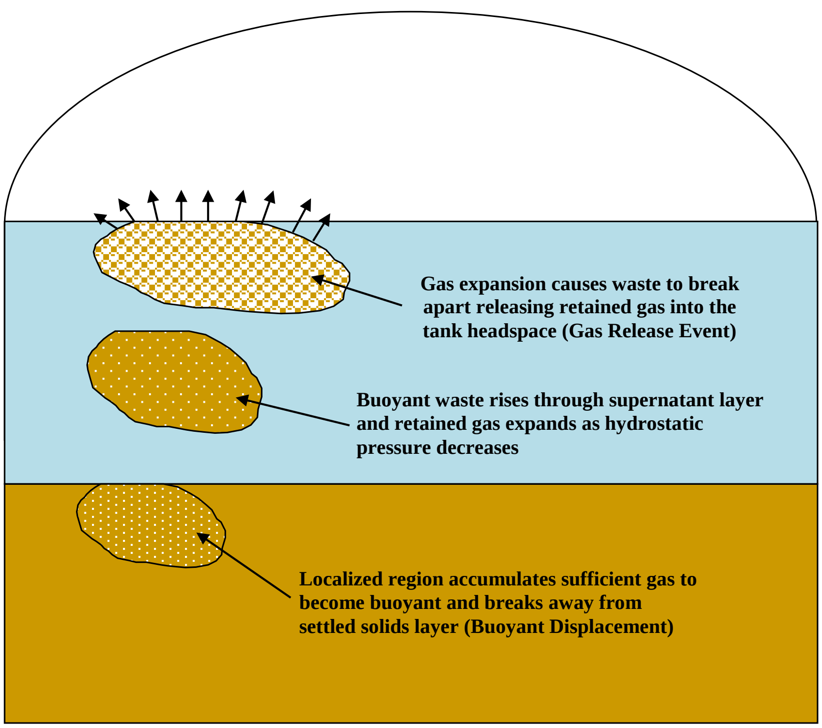

Figure 1. Illustration Showing Gas Accumulation Leading to a Buoyant Displacement Gas Release Event in a Low Shear Strength Saltcake Waste

Criteria were developed to prevent forming additional BDGRE tanks [5 and 7] and these criteria are based on the behavior observed in saltcake waste in the six DSTs that historically had BDGREs. When the criteria were extended to higher strength sludge wastes, constraints were placed on waste volumes resulting in using only some of the DST storage capacity. Significant gas accumulation and BDGREs were never observed in tanks containing predominantly high shear strength sludge wastes.

METHODS

Some Hanford Site saltcake waste has shown the propensity to accumulate gas fractions sufficient for the settled solids to become buoyant in the overlaying supernatant [1]. Criteria derived from saltcake behavior waste were applied to all waste types even though high gas accumulation has never been observed in Hanford Site sludge waste. The criteria limit the volume of settled solids and liquid waste that can be stored in DSTs. New criteria for Hanford Site sludge waste were developed based on data from the open literature, waste simulant experiments, and Hanford Site sludge waste process data.

The overall expected behavior in Hanford Site strong sludge materials is for bubbles to grow as slits and cracks, at all depths, and interconnect to form pathways for gas release (Figure 2). A gas release channel may temporarily be blocked, but a local increase in the pressure of a gas bubble will either reopen the previously open channel or will expand by extending a fracture in some other direction and eventually connect with an open channel. This behavior would occur at all DST plausible sludge sediment depths, because bubbles/cracks will expand and interconnect. This keeps overall gas content low in the sludge settled solids and a BDGRE is not possible.

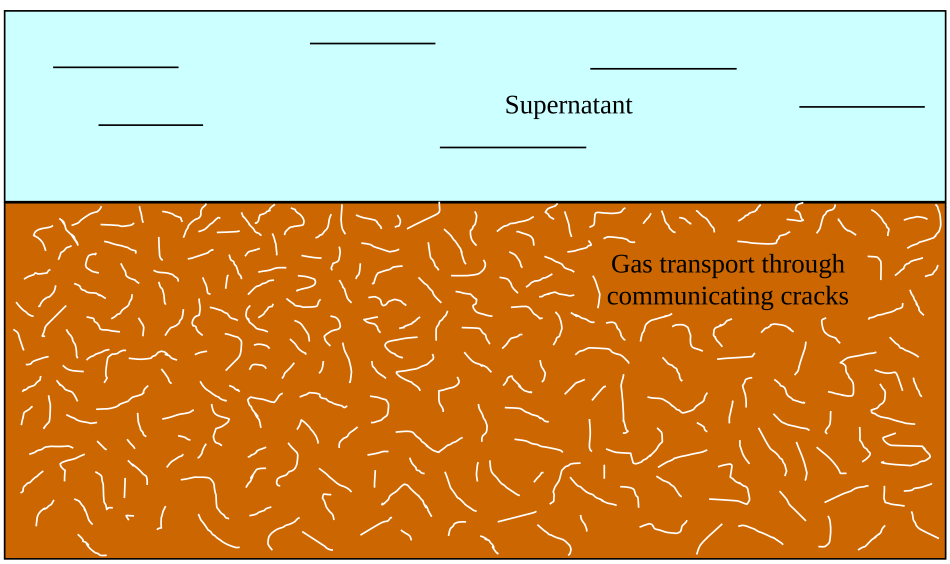

Figure 2. Illustration Showing Gas Transport through Gas Bubble Cracks in Sludge Waste

DISCUSION

Literature reviews, data from Hanford Site waste tanks, and simulant experiments were used to investigate gas retention and release behavior in sludge waste tanks.

Literature Review

Gas retention in fine-grained materials has been studied for many decades. In the 1990s and early 2000s, studies examined gas retention and release in Hanford Site waste [2, 3, 4, 5 and 6]. Efforts focused on understanding why settled solids in a few tanks stored significant gas and occasionally experienced BDGREs. Gas transport could be described through a bubble percolation model [5, 7] where the volume of gas stored increased approximately with the square with the settled solids height. This model was conservatively applied to both low strength saltcake waste and higher strength sludge waste.

Experiments showed that stronger sediments retained gas in the form of long dendritic bubbles formed by local mechanical failure of the solid matrix [2, 8, 9, 10, 11, and 17]. These failures form cracks and provide a connected pathway that allows gas to rapidly escape at relatively low overall gas fractions. Some studies suggested there was a limit to the depth of the connected pathways (this depth is referred to as d_{max}) that allow gas to escape and limit gas retention [8]. Therefore, efforts focused on showing that Hanford Site sludge waste contained relatively low gas fractions and that increasing sludge waste depth would not lead to high gas fractions and possible large sudden gas releases.

Differentiating between Hanford Site Saltcake and Sludge Waste

Hanford site settled solids can be divided into two distinctive waste types based on solubility, saltcake and sludge. Saltcake solids were mostly formed by concentrating liquid waste through evaporators until precipitates formed, and are predominantly sodium nitrate with some amount of sodium phosphate and sodium fluoride and fluorophosphates. The sludge wastes were formed via acid neutralization and are comprised of mostly low soluble aluminum compounds [e.g., $Al(OH)_3$, $NaAlSiO_4$, AlOOH, $NaAlCO_3(OH)_2$] [12]. As a result of acid neutralization, sludge interstitial liquid is sodium nitrate brine with a specific gravity falling between 1.05 and 1.30.

Saltcake wastes have a mass ratio of soluble analytes (e.g. potassium and sodium) to insoluble analytes (e.g. aluminum, bismuth, iron, calcium, manganese, lanthanum, nickel, silicon, uranium and zirconium) greater than 2.5. Sludge waste has a ratio of soluble to insoluble analytes in the bulk settled solids (the bulk settled solids includes both the liquid and solid fractions) of less than 2.5 [13].

Each Hanford Site waste tank has a unique alpha-numeric identifier and the tanks were binned into either saltcake or sludge waste so that gas retention and release characteristics could be compared and contrasted [14]. Results showed significant differences in gas retention and release behaviors between the two waste types.

Hanford Tank Waste Process Data

Empirical data indicate that Hanford Site saltcake wastes can contain significantly high gas fractions. Average gas fractions in some saltcake settled solids exceed 20% by volume [15]. Six tanks that contained both a deep bed of saltcake settled solids and a deep supernatant layer experienced BDGREs, indicating that gas generation exceeded gas release in these settled solids. Saltcake tanks also showed slow gas transport through the settled solids during waste transfers operations [14].

The Hanford Site has processed and stored sludge waste for decades. Sludge waste does not accumulate large gas fractions and have never exhibited sudden large gas releases [14]. Average retained gas content (gas fraction) in sludge tanks has been estimated and these estimates are shown in Table 1. The maximum average gas fraction in sludge waste is below 8% by volume. Waste storage and waste transfer data showed that all the sludge waste tanks reached an equilibrium between gas generation and release and that gas transport through the sludge settled solids is fast [14].

Tank	Estimated Gas Fraction (dimensionless)
AN-106	0.079
AW-103	0.069
AY-101	0.042
AY-102	0.073
BX-101	0.020
BX-103	0.012
BX-104	0.075
BX-107	0.025
BX-112	0.005
C-103	0.006
S-107	0.024
SY-102	0.009
T-110	0.036
TX-101	0.009
TY-104	0.017

Table 1. Estimated Average Sludge Waste Gas Fractions

Tall column experiments were conducted with waste simulants to determine whether low gas fractions and rapid gas transport would continue as sludge waste depths increased.

Waste Simulant Experiments

The principal objective of the tall column tests was to test the theory that gas retention and release would change as waste depths increased (the d_{max} theory described in reference [8]). In the tall column tests, the theory was directly tested by determining whether there was any significant change in gas transport at sludge depths deeper than d_{max}. The objectives were to measure the retained gas fraction in a column with a simulant depth greater than 310 inches (the maximum postulated sludge depth at the Hanford Site Tank Farms). The tests also used lower shear strengths than expected for Hanford Site sludge waste to ensure test conditions would convincingly confirm or refute d_{max} theory applicability. The testing allowed visual observation of gas transport at different heights from multiple video cameras that recorded bubble growth and movement.

A total of three tall column experiments were conducted at the Cold Test Facility at the Hanford Site. The first experiment was conducted using a kaolin-water-zerovalent iron simulant with a target shear strength of ~500 Pa. The second experiment was designed as a replicate of the first test to demonstrate that the results are repeatable. The third experiment was designed to use a higher target shear strength of ~900 Pa using a kaolin-water-zerovalent iron simulant.

Tests were conducted in a 45-ft tall carbon steel column with a nominal diameter of 60 inches (Figure 3). The column wall was ⅜-in. thick and the column interior was painted to provide a smooth surface. Inside the column, an approximately 1-ft by 1-ft square column (also painted on its exterior) was installed to house ten cameras. One side of the viewing column was made up of acrylic windows, the majority of which were approximately 2-ft in height. These windows faced the interior of the column and allowed video to be collected during testing. Of the ten cameras, nine were at fixed elevations in the viewing column and the tenth was a mobile rover camera. The primary use of the rover camera was to monitor changes in water and slurry level as the test progressed. Each camera had a field of view with the approximate dimensions of about 10 in. (height) by 8 in. (width) with two scales visible on either side of the viewing area (see Figure 4). Test details are provided in reference [16] and results are summarized here.

Figure 3. Tall Column Installed at the Cold Test Facility being filled with Simulant

Figure 4. Photo from the Interior 1 ft by 1ft Viewing Column

Figures 5 through 7 show the retained gas content and gas generation rate as a function of time for the three tall column tests. In Test #1, gas content peaked at about 8.3% by volume at about 60 hr and was about 7.1% at the end of the test. Peak gas generation rate was about 21 mole/m^3·day also at about 60 hr. In Test #2, gas generation rate was near its peak soon after the column was loaded and the water level increased steadily immediately after the loading was completed. A peak retained gas content of about 9.1% by volume was reached after approximately 47 hours and gas content at the end of the test was about 7.6% by volume. Estimated peak gas generation rate in Test #2 (~32 mole/m^3·day) was higher than the peak gas generation in Test #1, and was reached at just a few hours into Test #2.

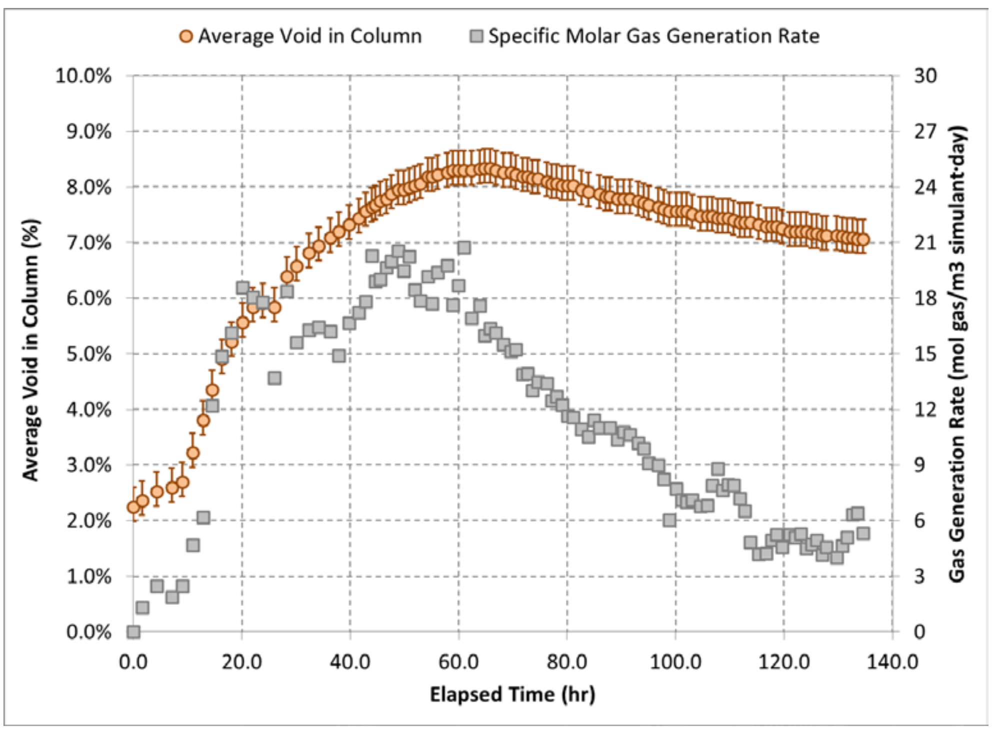

Figure 5. Tall Column Test #1 Average Gas (Void) Content and Gas Generation Rates

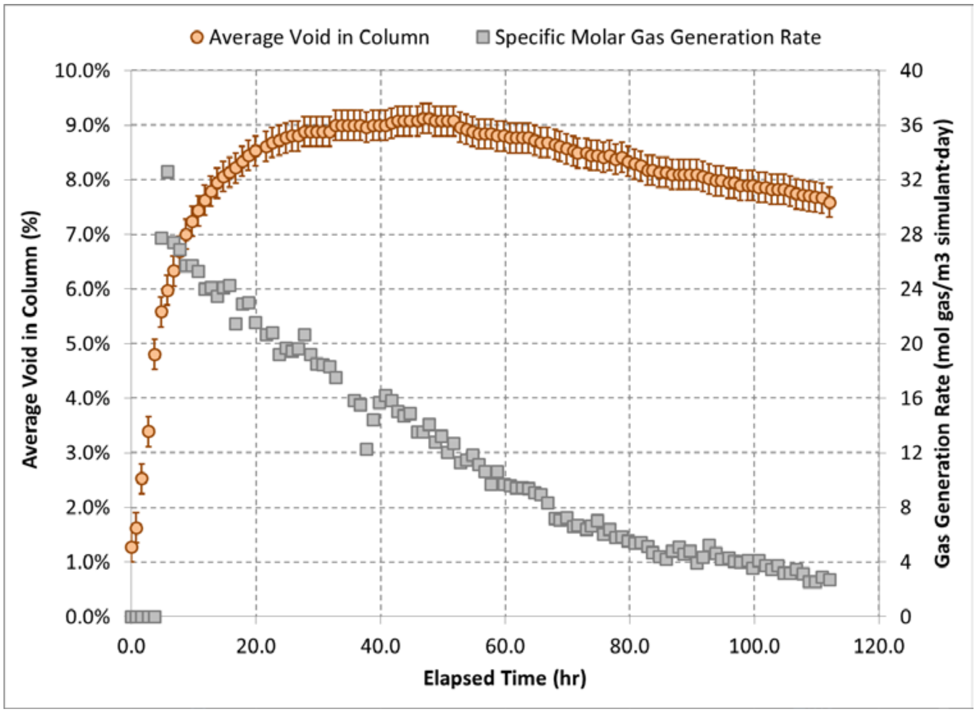

Figure 6. Tall Column Test #2 Average Gas (Void) Content and Gas Generation Rates

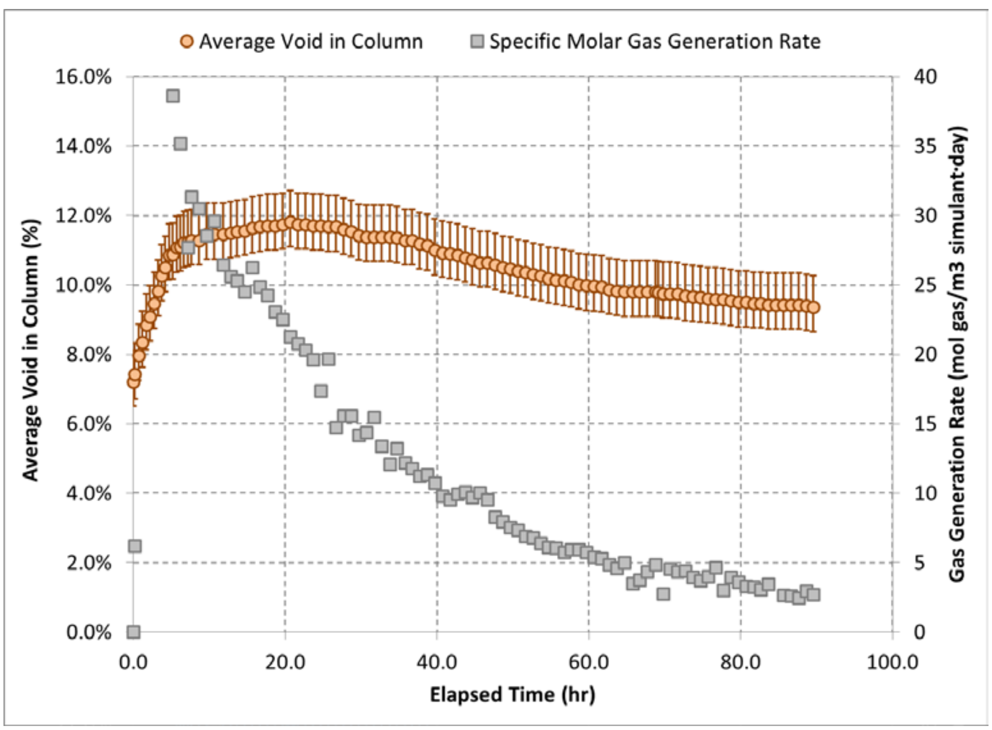

Figure 7. Tall Column Test #3 Average Gas (Void) Content and Gas Generation Rates

In Test #3, gas generation rate was near its peak soon after the column was loaded and the water level increased steadily immediately after the loading was completed. A peak retained gas content of about 11.8% by volume was reached after approximately 20 hr and gas content at the end of the test was about 9.4% by volume. Estimated peak gas generation rate in Test #3 was the highest of the three tall column tests, ~39 mole/m^3·day. The peak gas generation rate was reached at just a few hours into Test #3.

In all three tall column tests, gas was transported freely from all depths in the column, even before the peak gas fraction was achieved, and the gas morphology was not a function of the simulant depth, i.e., the gas voids had a similar appearance (primarily slits and cracks) from the top of the simulant layer to the bottom. The tall column experiments demonstrated that gas retention and release do not change at plausible Hanford Site sludge waste depths.

Sludge Waste Criteria

Two criteria are applied to Hanford Site waste to distinguish between saltcake and sludge gas retention and release behavior if specific process data are available for that waste. The first criterion is based on waste chemical composition and defines what waste is considered sludge and what waste is considered saltcake. If the mass ratio of soluble to insoluble constituents is below 2.5, then the waste is sludge, if the ratio is greater than 2.5, then the waste is saltcake. The available data showed all tanks with a mass ratio of soluble to insoluble constituents below 2.5 (i.e., all sludge waste tanks) had low overall gas fractions (<8% by volume) and rapid gas transport through the settled solids [14].

Although sludge wastes were shown to have low gas fractions, it remains theoretically possible to have a high density supernatant above the settled solids such that even a low gas fraction might make the settled solids buoyant. The second criterion is a density difference criterion that prevents tanks being operated in a region where sludge buoyancy might occur. For large gas releases to occur, the settled solids must accumulate sufficient gas to become less dense than the overlying supernatant. Based on previous operating experience, the ratio of liquid density to degassed settled solids bulk density (ρ_ℓ/ρ_B) should be maintained at ≤ 0.84. This ensures that retained gas content in the sludge would need to exceed 16% by volume (more than twice the maximum of 7.9% by volume observed to date) for the settled solids to become buoyant in the overlying supernatant [14].

Before applying the criteria to a newly formed sludge waste tank, process data are necessary to confirm gas retention and release characteristics. The process data are the following:

- Has no evidence of large spontaneous gas release events.
- Has reached a balance between gas retention and release at a retained gas content of about 8% by volume or less.
- Has rapid gas transport.
- Exhibited rapid settling to a configuration similar to that of the source tank.

Tank waste that satisfies the mass ratio criterion, the liquid to bulk solids density criterion, and has process data supporting typical Hanford waste sludge behavior does not pose a significant risk for a large spontaneous gas release event.

CONCLUSIONS

Literature reviews, data from sludge waste tanks and simulant experiments have led to new conclusions on gas retention and release in Hanford Site sludge waste. The data show similar overall behavior where initially the settled solids volume increases as gas bubbles form. Gas fraction in the settled solids increases to a peak concentration after which additional generated gas escapes through connected cracks. There is a balance between gas generation and gas release with little change in gas fraction. Experiments show that this behavior does not change as waste depths increased.

Sufficient data now exist to differentiate between gas retention and release behavior in Hanford Site sludge waste tanks and saltcake waste tanks. The BDGRE criteria that were based on gas retention and release characteristics in some saltcake waste tanks do not need to be applied to sludge waste tanks that exhibit certain gas retention and release behavior. Criteria for waste characteristics and process behavior were defined that identify specific wastes and tanks that, based on previous operating experience, will have low gas retention and will not exhibit large, spontaneous releases.

If the mass ratio of soluble to insoluble constituents is below 2.5, then the waste is sludge. For large gas releases to occur, the settled solids must accumulate sufficient gas to become less dense than the overlying supernatant (i.e., the settled solids would become buoyant). Based on previous operating experience, the ratio of liquid density to degassed settled solids bulk density (ρ_ℓ/ρ_B) should be maintained at ≤ 0.84. This ensures that retained gas content in the sludge would need to exceed 16% by volume for the settled solids to become buoyant in the overlying supernatant.

Based on process data history, tank waste that satisfies the mass ratio criterion, the liquid to bulk solids density criterion, and has process data supporting typical Hanford waste sludge behavior does not pose a significant risk for a large spontaneous gas release event.

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