

Gas Releases During Saltcake Dissolution for Retrieval of Single-Shell Tank Waste

CW Stewart

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

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Abstract

It is possible to retrieve a large fraction of soluble waste from the Hanford single-shell waste tanks (SST) by dissolving it with water. This retrieval method will be demonstrated in U-107 and S-112 in the next few years. If saltcake dissolution proves practical and effective, many of the saltcake SSTs may be retrieved by this method. Many SSTs retain a large volume of flammable gas that will be released into the tank headspace during retrieval as the waste dissolves. This report describes the physical processes that control dissolution and gas release. Calculation results are shown describing the headspace hydrogen concentration transient during dissolution. The observed spontaneous and induced gas releases from SSTs are summarized, and the dissolution of the crust layer in SY-101 is discussed as a recent example of full-scale dissolution of saltcake containing a very large volume of retained gas. The report concludes that the dissolution rate is self-limiting, and gas release rates are relatively low.

Executive Summary

Saltcake dissolution is a proposed method for retrieving water-soluble salts from the Hanford SSTs. Water will be sprayed on the waste surface to dissolve the soluble fraction of the waste while the resulting brine is pumped out of the tank with an existing saltwell pumping system. Because a large fraction of typical saltcake waste is soluble, most of the waste in an SST can, in principle, be retrieved with almost the same time and cost as a typical interim stabilization campaign. A proof-of-concept test (limited to approximately 100,000 gal of brine) is planned in U-107 during the fall of 2001. A full-tank retrieval demonstration system is being planned for S-112 in 2002. If saltcake dissolution proves practical and effective, many of the saltcake SSTs may be retrieved by this method.

Many of the SSTs contain a large volume of flammable gas that will be released into the tank headspace as the waste dissolves. U-107 contains 180 ± 60 cubic meters ($6,400 \pm 2,000$ scf) of retained gas, and S-112 is estimated to retain a much smaller volume of 46 ± 23 cubic meters ($1,600 \pm 800$ scf). This report investigates the potential hazard of flammable gas that will be released during the dissolution process.

Dissolution is expected to release this gas in proportion to the fraction of the waste in which the soluble solids are dissolved. This process is self-limiting and controllable. Water or dilute brine capable of dissolving solids is less dense than the saturated liquid in equilibrium with the solids. Therefore, the solvent cannot penetrate below the pre-existing interstitial liquid in the waste; and dissolution can only occur in waste that is not saturated with liquid. Once the solvent has become saturated, it is no longer capable of further dissolution and forms a barrier to the less dense liquid from above.

This means that dissolution, and the associated gas release, can proceed no faster than the interstitial liquid can drain away. This is the primary mechanism that limits dissolution-induced gas releases. This self-limiting behavior makes gas release by dissolution controllable. The dissolution rate can be reduced relatively quickly by terminating pumping (accumulating brine forms a barrier to fresh solvent) and by shutting off the water spray (terminating the supply of fresh solvent). The most effective control is achieved if dissolution is local, and the inventory of excess solvent is kept to a minimum.

The predicted gas release rates in both U-107 and S-112 are relatively low. At least two days are required for the hydrogen concentration to reach the action level in the worst case and almost two months to reach the lower flammability limit (LFL). The U-107 proof-of-concept demonstration calls for addition of a maximum of 2,400 gallons of water per day. Assuming all of this water dissolves waste and all the brine is removed by saltwell pumping, ignoring in-line dilution, the dissolution rate is 4,392 gal-waste/day, equivalent to an average saltwell pumping rate of 3.58 gpm. The corresponding gas release is estimated at 117 scfd, assumed to be 50% hydrogen. Assuming that the ventilation rate in U-107 is $2.5 \text{ ft}^3/\text{min}$, the hydrogen concentration will reach the action level of 6,250 ppm in 8 days. The maximum hydrogen concentration would eventually reach 1.4 vol%, or 35% of the LFL if water addition were continued until all the wastes were removed.

The S-112 retrieval demonstration may employ an improved saltwell pump with a capacity of 10 gpm. Assuming brine is removed continuously at this rate, the dissolution rate will be about 12,000 gal-waste/day. Conservatively assuming the same gas fraction as in U-107, the gas release rate from S-112 is 328 scfd, again assumed to be 50% hydrogen. Assuming a ventilation rate of 2.5 scfm, the action level of 6,250 ppm hydrogen should occur in 2.5 days; and the hydrogen concentration eventually reaches a maximum 4.2%, just over the LFL. However, the LFL would not be reached for 57 days.

The small gas releases and the waste behavior during the dissolution of the crust layer in SY-101 qualitatively validated our understanding of the physics of solvent flow and saltcake dissolution. The initial 120-inch crust layer in this tank was comparable in thickness to the non-supernate waste in U-107 but contained almost twice the gas. The crust was dissolved in a series of three waste transfers and back dilutions that eventually added 525,000 gal of water. The bulk of the crust dissolution and gas release occurred in the second back-dilution when the headspace hydrogen concentration peaked at about 3,000 ppm. This concentration represents a sudden release of about 200 scf of hydrogen, much larger than can be expected during dissolution of SST waste.

All the saltcake tanks contain some dissolved ammonia in the liquid waste that is released mainly by evaporation. Dilution reduces the ammonia evaporation rate significantly, because the solubility of ammonia increases greatly as the pH decreases with dilution. Spraying water on the waste surface for retrieval will effectively prevent significant ammonia releases and will probably reduce ammonia concentrations below the historic baseline values.

The overall conclusion is the gas releases accompanying saltcake dissolution can be expected to correspond roughly to those already experienced during saltwell pumping. The gas release rates are relatively low, and the dominant mechanisms are self-limiting so that the process is controllable by adjusting the pumping and water addition rates. There is no known mechanism that can create large sudden gas releases during this process.

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1.0 Introduction

Saltcake dissolution is a proposed method for retrieving water-soluble salts from the SST. A proof-of-concept test is planned to transfer at least 100,000 gal of brine from U-107 to the double-shell tank (DST) system during the fall of 2001. The operations are intended to provide key information to reduce the technical risk of a full-tank retrieval demonstration system in S-112 planned for 2002. If saltcake dissolution proves practical and effective, many of the saltcake SSTs may be retrieved by this method.

In the saltcake dissolution retrieval concept, water is sprayed on the waste surface to dissolve the soluble fraction of the waste. The resulting liquid drains to a centrally located saltwell and is pumped out of the tank with a saltwell pumping system. Because sodium salts (e.g. sodium nitrite, nitrate and phosphate) and some other soluble species comprise a large fraction of typical saltcake waste, the water spray is expected to rapidly dissolve the solids it contacts. With this method, the retrieval of most of the soluble waste in a tank can, in principle, be accomplished in about the same time as an interim stabilization campaign.

Saltwell pumping, or interim stabilization, has been performed for many years in the SSTs to minimize the amount of liquid waste that could potentially leak into the surrounding soil. Drainable liquid in the interstitial pores in the solid waste is being removed from all SSTs as part of the tank interim stabilization process. In saltwell pumping, a long cylindrical metal screen (the saltwell screen) is installed as a well casing in the solid waste. In most tanks, the saltwell screen is installed near the center of the tank and extends virtually to the bottom of the tank. A jet pump located inside and at the bottom of the saltwell screen is used to pump liquid out as it drains into the saltwell screen. At the onset of pumping, any supernatant liquid (i.e., free liquid above the solids) drains quickly into the saltwell, and the rate of liquid removal is limited by pump capacity. As the liquid inventory is depleted, the pumping rate eventually exceeds the rate that liquids drain into the saltwell screen; and the pumping rate is reduced to approximately match the liquid drainage rate to prevent the jet pump from running dry. Saltwell pumping ends when the drainage rate falls below a specified minimum value.

Many of the SSTs contain a large volume of flammable gas (Mahoney et al. 1999; Hedengren et al. 2001) that will be released into the tank headspace as the waste dissolves. If the flammable gas were released during the dissolution process more rapidly than it could escape by passive ventilation, the gas mixture in the headspace could become flammable.

This report describes the physical processes that control the rate of dissolution of the solids and consequent rate of gas release. The observed behavior of spontaneous and induced gas releases from SSTs is summarized, and the dissolution of the crust layer in SY-101 is discussed as a recent example of full-scale dissolution of saltcake containing a very large volume of retained gas. The conclusion is that the dissolution rate is self-limiting and gas release rates will be slow.

Section 2.0 describes the spontaneous and induced gas releases in SSTs observed since 1995. Section 3.0 discusses the specific issues involved with gas release induced by saltcake dissolution, and Section 4.0 states the main conclusions. References are listed in Section 5.0.

2.0 Spontaneous and Induced Gas Releases in SSTs

Some of the Hanford SSTs that have not been saltwell pumped, including several of those on the Flammable Gas Watch List and a few others, store a significant volume of flammable gas and some occasionally release a small volume of it into the tank headspace. Disturbing the waste can also induce gas releases. Some of the largest induced releases are associated with saltwell pumping. A gas release event (GRE) is characterized by an increase in measured headspace hydrogen concentration to a peak at least 100 ppm above the steady state value over several hours or days followed by a more gradual decrease back to the steady-state concentration (McCain 2000). The passive (or active) ventilation of the tank headspace primarily controls the return to steady-state concentration in SSTs.

This section summarizes the gas releases observed in the hydrogen monitoring data in terms of volume, duration, frequency, and their trends. Section 2.1 discusses the spontaneous gas release histories and trends, gas releases induced by saltwell pumping are discussed in Section 2.2, and a summary is given in Section 2.3.

2.1 Spontaneous Gas Releases

The exact mechanism by which spontaneous gas releases occur in SSTs is not known. The upward motion of pore-filling or particle-displacing bubbles by “percolation” is a probable explanation (Stewart et al. 1996). In a pore-filling bubble, this occurs when the bubble grows to the point that hydrostatic pressure difference exceeds surface tension holding the bubble in the throat between pores. Similarly, particle-displacing bubbles percolate when they grow such that hydrostatic pressure difference exceeds the waste strength, pinches off the bottom of the bubble, and pushes the top of the bubble upward. Neither of these mechanisms has the potential to produce large sudden releases nor is there any other mechanism known by which such a release can occur spontaneously in SSTs.

Though the release mechanisms are not completely understood, the releases that have been observed are uniformly small and slow. Over two hundred spontaneous GREs have been observed in SSTs between 1995, when the Standard Hydrogen Monitoring Systems (SHMS) were installed in SSTs, and July 2000 (McCain 2000, Hedengren et al. 2001). The mean estimated hydrogen release volume of all these releases is only 0.5 cubic meters. The upper bound hydrogen release volume (99.9 percentile) is only about three cubic meters, which corresponds to about 5% of the hydrogen volume required to make a tank’s headspace flammable. These data imply that the probability of a spontaneous release creating flammable conditions is far less than 0.001. The median time to peak hydrogen concentration for these releases is about one day, and the total release duration is about five days. The shortest time to peak hydrogen concentration, recorded in five GREs, was about four hours. Many require several days to reach the peak concentration.

It can be concluded that spontaneous releases from SSTs do not represent a significant hazard during a saltcake dissolution waste retrieval campaign.

2.2 Induced Gas Releases

Retained gas can be expected to escape from a volume of waste that is disrupted. Disturbances are generally classified as local or global. Local disturbances are caused by activities such as core sampling, lancing in a liquid observation well (LOW) or installing a thermocouple tree. A global disturbance is one that affects a large fraction of the waste such as a large volume water addition, saltwell pumping, or operation of large mixer pumps. There is no known mechanism in SSTs whereby a local disturbance can “trigger” a large, global release (Stewart et al. 1996).

2.2.1 Local Disturbances

No large releases have been induced by local waste disturbances and the probability of even a small release is relatively low. In 1996, an informal study of 77 waste intrusive activities in 47 separate SSTs showed only three probable occurrences of small gas releases associated with the waste disturbance. An additional examination of 61 core sampling events and four LOW installations monitored with a hand-held combustible gas meter showed a significant (though much less than flammable) rise in the hydrogen concentration in only three of these events (Hedengren et al. 2001).

2.2.2 Saltwell Pumping

The removal of drainable liquid by saltwell pumping can induce gas releases by various mechanisms. The hydrostatic pressure within the waste decreases as liquid is removed, which causes trapped gases to expand and some of the dissolved gases to evolve to the gas phase. Both of these effects result in bubble growth, which may cause either bubble disengagement or percolation gas release. Particle-displacing bubbles not released by these mechanisms may “pop” when the liquid eventually drains away from around them (Peurrung et al. 1997). However, even after the bulk liquid has been drained away, some gas may remain trapped between particles in small, pore-filling bubbles surrounded by liquid held by capillary forces. Gas that remains trapped in this way is eventually released when the surrounding liquid evaporates or gradually drains away.

The highest headspace hydrogen concentrations in SSTs were recorded during saltwell pumping. The highest hydrogen gas concentration ever measured in an SST was 7,200 ppm, detected in BY-106 during saltwell pumping in 1995 (Watrous et al. 2000). The next highest was 4,950 ppm in U-103 in 1999 (McCain 2000).

The general relation between saltwell pumping and gas releases has been fairly well established (for some tanks) by headspace monitoring data. There appears to be about a one-day lag between pumping and the corresponding gas release, but the lag is greater in several cases.

Sometimes pumping activities are not accompanied by increased gas release rates at all (Huckaby et al. 1999).^(a)

Available headspace gas monitoring data suggest that the highest induced gas release rates occur shortly after saltwell pumping begins when the waste drains rapidly. As the drainage rate decreases, gas release rates decline correspondingly. In this second phase, a temporary cessation in pumping has little immediate effect on the drainage rate far from the saltwell; and the response of the gas release rate is correspondingly damped.

After pumping ceases, liquid continues to drain from the outer regions of the waste, as well as from the upper layers not completely drained during pumping. This slow drainage continues to release trapped gases. The headspace hydrogen and nitrous oxide concentrations in tank S-106, for example, appear to have been significantly higher for months after completion of saltwell pumping than before it was started.^(a)

Saltwell pumping releases some, but not all, of the trapped gas. Data of sufficient quality and quantity are available to quantify the total volume of gas released by saltwell pumping in only three SSTs: S-106, U-105, and U-103. These data indicate that 25 - 50% of the initial retained hydrogen volume was released. This corresponds roughly to the fraction of total liquid pumped from the tank (Johnson et al. 2001). The small spontaneous releases typical of unpumped SSTs continued after pumping in at least two tanks, though they appeared to have ceased in several other pumped tanks.

Following saltwell pumping, a large region of the waste should contain pore-filling bubbles from which gas releases should be small and slow. However, as gas rises into the upper layers with lower lithostatic loading, the bubbles may again displace particles. The particle-displacing bubbles may then create small spontaneous releases similar to an unpumped tank. The only potential mechanism for a significant gas release from a pumped tank has been postulated to be the waste subsidence that has been assumed to cause the large craters or depressions seen in the waste surface of some tanks months or years after completion of saltwell pumping. Gas still trapped in the subsiding region would hypothetically be subject to release. No subsidence related gas releases have yet been observed, and the physics of the process leading up to subsidence would appear incompatible with gas retention (Stewart et al. 1996). In addition, the historic waste level drops that have been attributed to subsidence occur over weeks or months, indicating the potential for a significant gas release is remote.

In summary, gas releases at least as large as have been observed during saltwell pumping can be expected during saltcake dissolution. The effect dissolution has on accelerating or impeding gas releases is discussed in the next section.

^a Peurrung LM and JL Huckaby. 2000. *Gas Release Behavior During Saltwell Pumping*. PNNL letter report TWS00.039 from J Brothers to GD Johnson, CH2M Hill Hanford Group, Inc., March 10).

3.0 Gas Releases Induced by Dissolution

This section provides estimates of the gas release rates induced by dissolution and describes the resulting behavior of the headspace hydrogen concentration for the two tanks of immediate concern and for retrieval of a “typical” SST using dissolution. Section 3.1 summarizes the conditions and retained gas volume in U-107 and S-112 tanks with their estimated passive ventilation rates in Section 3.2. Section 3.3 not only shows that dissolution is a slow and self-limiting process but also that the gas release rate induced by dissolution is not likely to exceed levels of concern given the passive ventilation rates in the tanks. Estimates of the gas release rates resulting from dissolution are in Section 3.4, and the resulting headspace hydrogen concentrations are forecast in Section 3.5. Section 3.6 summarizes the dissolution and gas release behavior during the recent remediation of the crust layer in SY-101 which is the only large-scale saltcake dissolution operation performed to date. Potential ammonia releases are discussed in Section 3.7.

3.1 Conditions in Candidate Tanks

Hedengren et al. (2001) describe the conditions in U-107 and S-112 as of December 2000, which are very different. Tank U-107 contains excess liquid (supernate), and the solid waste is completely saturated with liquid. In contrast, S-112 has a relatively deep layer of “dry” unsaturated zone on top of liquid-saturated waste. U-107 contains a much greater volume of flammable gas. The nature and extent of the planned dissolution in each tank is also quite different.

The waste level in U-107 is 157 inches, of which the upper 1 to 2 ft is thought to be supernate. The tank headspace is about $1,670 \text{ m}^3$ ($59,000 \text{ ft}^3$). The level has risen very gradually (about 0.1 in./year) since 1990. Fourteen small spontaneous GREs have been recorded by the tank’s standard hydrogen monitoring system (SHMS-B) since March 1995. During the six years of SHMS monitoring, the maximum hydrogen concentration was 1,900 ppm; and the average was 840 ppm. The best estimate of the retained gas volume is 180 ± 60 cubic meters ($6,400 \pm 2,000$ scf) (Hedengren et al. 2001). The waste level has risen 6 inches since 1981 (Whitney 1995) indicating a gas accumulation of 75 m^3 at 1 atm assuming an in situ pressure of 1.2 atm.

The saltcake dissolution proof-of-concept in U-107 will employ a variety of nozzles and flow rates to place approximately 38,000 gal of water on the waste after saltwell pumping has removed the supernate and some of the interstitial liquid (Estey et al. 2001). The test is limited to production of 100 kgal of brine in excess of the estimated pumpable liquid available. This is predicted to result in the retrieval of about 50 kgal or about 15% of the original 340 kgal of waste, excluding supernate. After the saltcake dissolution test is completed, saltwell pumping will continue until the interim stabilization criteria are met.

Tank S-112 contains 189 inches of saltcake. The tank headspace is about $2,000 \text{ m}^3$ ($70,600 \text{ ft}^3$). The tank was saltwell pumped in 1979, which removed 125,000 gal of liquid (Kupfer et al. 1997). The interstitial liquid level (ILL) is about 123 inches, 66 inches below the waste surface

level. Since 1981, the waste surface level has subsided about 5 inches while the ILL has increased about 10 inches (Whitney 1995). This indicates a gradual gas accumulation, probably in pore-filling bubbles. The neutron log clearly shows a very “dry” region from the waste level down to the ILL where the liquid content increases abruptly to approximately full saturation. No GREs have been recorded since the SHMS-B was installed in 1995. Neutron log integration yields a retained gas volume estimate of $46 \pm 23 \text{ m}^3$ ($1,600 \pm 800 \text{ scf}$). If the rise in ILL were assumed to be the result of gas accumulation, the recorded 10-inch rise would indicate 54 m^3 of gas assuming a porosity of 0.4 and a gas pressure of 1.3 atm.

The goal of the saltcake dissolution retrieval demonstration in S-112 is to retrieve the waste to the limit of the method. Currently, the water application system includes nozzles that can forcibly mobilize the insoluble solids to potentially retrieve over 90% of the approximately 430,000 gal waste volume.^a

3.2 Estimated Ventilation Rates

The tank ventilation rate must be included in assessing the potential for the gas release to make the headspace flammable. The lower the headspace ventilation rate, the higher the hydrogen concentration resulting from a given release. Except for the SX-Farm tanks, all of the SSTs potentially to be retrieved by saltcake dissolution are passively ventilated. This means ventilation is driven by natural convection which is affected by temperature differences between the waste and ambient air, changes in barometric pressure, and various other micrometeorological effects (e.g., gusting winds, solar heating of the ventilation riser, etc.). The situation is further complicated by the flow paths between tank headspaces (e.g. cascade lines), seasonal and diurnal temperature variations, and variability in the leakage paths to the atmosphere around risers. Due to these factors, passive ventilation rates cannot be predicted with any certainty.

However, ventilation rates of 13 passively ventilated tanks were determined by measuring the decay in the concentration of a tracer gas injected into the tank headspace. Tracer gas studies indicate passive ventilation rates can vary significantly by tank and from day to day. Tanks with large inter-tank connections (e.g., A-farm tanks are interconnected via a defunct underground ventilation system) tend to exhibit higher ventilation rates, and tanks with few leak paths or blocked cascade lines tend to exhibit lower rates. A similar technique, in which the decay in the concentration of hydrogen after a small GRE is used to estimate ventilation rates, has provided generally similar results (Wilkins et al. 1997, Sklarew and Huckaby 1998).

The passive ventilation rates of U-107 and S-112 have not been measured, but approximate rates can be inferred from the measured ventilation rates of similar tanks. Gas tracer studies have been conducted to determine the passive ventilation rates of U-102, U-103, U-105, U-106, and U-111 over periods of one to two months (Huckaby et al. 1997, 1998). The tracer test results for

^a S-112 Saltcake Dissolution Retrieval Demonstration Value Engineering Study Report, June 1-7, 2001. Facilitated by Richard Harrington, CH2M Hill Hanford Group, Richland, Washington.

the U-farm tanks range from 1.3 to 5.2 ft³/min with an average of 2.5 ft³/min. The tracer tests on S-102 showed a range of 1.2 to 3.4 scfm with an average of 2.1 scfm. The SHMS gas release studies for S-111 (Sklarew and Huckaby 1998) give a range of ventilation rates of 1.6 to 15 scfm with an average of 5.4 scfm.

Considering all the available data above, a conservative ventilation rate of 2.5 scfm can be assumed for both U-107 and S-112. The lower bound for the average ventilation rate is the ventilation resulting from natural “breathing” due to barometric pressure fluctuations. This has been estimated to be 0.45% of the headspace volume per day (Crippen 1993). For U-107, barometric breathing is 266 scfd or 0.18 scfm for the 59,000 ft³ headspace. The barometric breathing rate for the 70,600 ft³ headspace in S-112 would be 317 scfd or 0.22 scfm, approximately an order of magnitude less than the 2.5 scfm estimated from measurements.

3.3 Gas Release Behavior During Dissolution

Gauglitz et al. (1994, 1995, 1996), Stewart et al. (1996), Stewart (2000), and Hedengren et al. (2000; 2001) describe in detail the analyses and experiments on the mechanisms of gas retention. The following is a summary of the applicable facets of this work.

Gas that is potentially releasable at sufficient volume and rate to present a hazard is stored as bubbles surrounded by a matrix of solid particles saturated with liquid. If the solid matrix around the bubbles is not saturated, pathways exist to the tank headspace; and the gas generated in the waste is dissipated rapidly by diffusion and is not flammable (Stewart et al. 1996). Therefore, potentially significant gas releases can only occur by disrupting the liquid-saturated solids.

The balance of waste strength, surface tension, and hydrostatic pressure gradients to a relatively small size limit the individual bubbles that exist in this form. Large bubbles or “caverns” containing a hazardous volume of flammable gas cannot exist. No plausible mechanism is known by which a local disruption affecting a few bubbles can propagate to trigger the release of a large fraction of the retained gas in the tank.

Dissolution is expected to release this gas in proportion to the fraction of the waste in which the soluble solids are dissolved. This process is self-limiting and controllable. Water or dilute brine capable of dissolving solids is less dense than the saturated liquid in equilibrium with the solids. Therefore, the pre-existing interstitial liquid in the waste forms a barrier that prevents solvent from penetrating below the interstitial liquid level. Dissolution can only occur in waste that is not saturated with liquid where the solvent can penetrate. Once the solvent has dissolved sufficient solids to become saturated, it is no longer capable of further dissolution and forms a barrier to the less-dense liquid from above.

Thus, dissolution can proceed no faster than the interstitial liquid (original or newly created) can drain away. This is the primary mechanism that limits dissolution-induced gas releases. In fact, gas is first released by draining the liquid away before solvent can enter and dissolve the solids

that retained gas while liquid-saturated. Attempting to add water faster only re-saturates the solid matrix with liquid and prevents penetration sooner.

This self-limiting behavior makes gas release by dissolution controllable. Though some lag may be expected, the dissolution rate and gas release rate can be reduced relatively quickly by terminating pumping (accumulating brine forms a barrier to fresh solvent) and by shutting off the water spray (terminating the supply of fresh solvent). The most effective control is achieved if dissolution is local and the inventory of excess solvent is kept to a minimum. Though the actual response time of the gas release to changes in pumping and water addition rates are not currently known, saltwell pumping experience (see Section 2.2.2) indicates that it would be reasonable to expect the gas release to lag cessation of pumping and spraying by about a day. However, the more local the dissolution the lag time is shorter.

These limitations indicate that saltcake dissolution should not produce much larger gas releases than those expected during saltwell pumping without concurrent dissolution. The largest saltwell pumping-induced gas releases occur relatively soon after saltwell pumping begins, when nearly all the supernate has been removed. If this behavior is a pattern for U-107, an elevation of the hydrogen concentration on the order of 5,000 ppm can be expected in the first month of pumping based on the gas releases recorded in the other U-tanks during saltwell pumping. Other saltcake tanks that have not been saltwell pumped should behave similarly to U-107 during retrieval by dissolution.

S-112 has no supernate, so the upper 66 inches of unsaturated waste should dissolve rapidly. However, this waste has had over 20 years to drain and contains little liquid. Therefore, it also contains little or no flammable gas that could be released, regardless of how fast water is added. When the upper layer is removed and dissolution becomes limited by draining, gas releases can be expected; but much smaller than in U-107 because S-112 contains only about 1/4 the gas. In fact, it is thought that there is insufficient gas in S-112 to make the headspace flammable even if all the gas was released instantaneously (Johnson et al. 2001). The behavior of S-112 during retrieval should be similar to other saltcake tanks that have been saltwell pumped for several years.

3.4 Estimation of Gas Release Rates

Based on the fact that dissolution, and therefore gas release during dissolution, is limited by the rate at which brine drains from the waste, a bounding gas release can be computed given the saltwell pumping rate. Water is assumed to be added at a rate, Q_{WIN} , such that the resulting brine production rate is equal to the brine capacity of the saltwell pump, Q_{BOUT} . Based on the waste composition, the added water dissolves the original waste at a rate, $Q_{DSL N}$, which can be expressed as

$$Q_{DSL N} = [F_{DSL N}/F_{BRINE}]Q_{BOUT} \quad (3.1)$$

where $F_{DSL N}$ is the volume of original waste in which soluble solids are dissolved per unit volume of water added and F_{BRINE} is the volume of total brine produced (water added plus

dissolved solids plus interstitial liquid liberated) per unit volume of water added. Assuming that dissolution immediately releases all the gas stored in the waste being dissolved, the gas release rate, Q_{GAS} , is the product of the gas volume fraction, α , and the dissolution rate as follows,

$$Q_{GAS} = \alpha Q_{DSL N} = \alpha [F_{DSL N}/F_{BRINE}]Q_{BOUT} \quad (3.2)$$

The solubility of U-107 waste is such that $F_{DSL N} = 1.83$ and $F_{BRINE} = 2.15$ and the gas volume fraction averages 0.17 (Estey et al. 2001). The U-107 proof-of-concept demonstration will apply a maximum of 2,400 gallons of water per day during one 8-hour shift while the saltwell pump operates continuously. Assuming all of this water dissolves waste, the dissolution rate is 2,400 gal-water/day $\times F_{DSL N}$ gal-waste/gal-water = 4,392 gal-waste/day. This is equivalent to an average saltwell pumping rate of 2,400 gal-water/day $\times F_{BRINE}$ gal-brine/gal-water = 5,160 gal-brine/day or 3.58 gpm. Eq. (3.2) indicates a corresponding gas release of 879 gal/day or 117 scfd. If the released gas is 50% hydrogen, as may be expected for saltcake waste, the release rate would be 59 ft³ of hydrogen per day.

Core samples from S-112 have not yet been analyzed. However, the waste composition from the Best Basis Inventory (CHG 2001), which is based on the waste transfer history, is similar to that of U-107 so that the same values of $F_{DSL N}$ and F_{BRINE} can be assumed to apply to S-112 waste. The S-112 retrieval demonstration may employ an improved saltwell pump with a capacity of 10 gpm. Assuming brine is removed continuously at this rate, the dissolution rate will be 8.5 gpm or 1,580 scfd according to Eq. (3.1). Conservatively assuming a void fraction of 0.2, the gas release rate from S-112, after the unsaturated waste is dissolved, would be 328 scfd via Eq. (3.2). Assuming a hydrogen fraction of 0.5, this amounts to 164 scfd of hydrogen.

3.5 Headspace Hydrogen Concentration

The change in hydrogen concentration with time, including the effect of passive ventilation in dissipating the gas release, can be modeled by a simple expression. It is assumed the volumetric rates of gas release, ventilation, water addition and brine removal are constant, and the headspace is well mixed at all times. The well-mixed headspace assumption appears to be justified for most tanks (Huckaby et al. 1998). Equations for the volume fraction of hydrogen in the headspace, C_H , at any time t and for the time to reach a given headspace hydrogen concentration under these assumptions are derived in Appendix A. The time required to reach a given C_H is expressed as:

$$t = \frac{V_{HS0}}{Q_B} \left[1 - \frac{\left(C_H - \frac{Q_{GAS} \chi_H}{Q_A} \right) \frac{Q_B}{Q_A}}{\left(C_0 - \frac{Q_{GAS} \chi_H}{Q_A} \right)} \right] \quad (3.3)$$

where C_0 = initial headspace hydrogen concentration
 V_{HS0} = initial headspace volume

and χ_H = hydrogen fraction of the retained gas in the waste

$$Q_A = Q_{VIN} + Q_{GAS}$$

$$Q_B = Q_{WIN} - Q_{BOUT} - Q_{GAS} \frac{P_{HS}}{P_{GAS}}$$

where P_{HS} = pressure in the headspace atmosphere (~ 1 atm)
 P_{GAS} = pressure at which the gas is retained in the waste
 Q_{VIN} = headspace ventilation rate

The headspace concentration at a given time, t, is defined by

$$C_H(t) = \frac{Q_{GAS}\chi_H}{Q_A} + \left(C_0 - \frac{Q_{GAS}\chi_H}{Q_A} \right) \left(1 - \frac{Q_B}{V_{HS0}} t \right)^{\frac{Q_A}{Q_B}} \quad (3.4)$$

For long times, the second term on the right side of Eq. (3.4) approaches zero so that

$$C_H \approx \frac{Q_{GAS}\chi_H}{Q_A} \quad (3.5)$$

U-107 is estimated to have a headspace volume of about 59,000 ft³. Assuming that the ventilation rate in U-107 is 2.5 scfm, $Q_{GAS} = 117$ scfd, $\chi_{H2} = 0.5$, and $C_0 = 500$ ppm, Eq. (3.3) indicates that the time required for the hydrogen concentration to reach the action level of 6,250 ppm would occur in 8 days, or 6 days with only barometric breathing. With a 2.5 scfm ventilation rate, the hydrogen concentration would eventually reach a maximum of 1.4 vol% (14,000 ppm), or roughly 35% of the LFL if water addition were continued until all the wastes were removed. This would theoretically occur in 119 days. With only barometric breathing the concentration would reach the LFL in 78 days and about 7 vol% hydrogen (~2 times the LFL) at complete retrieval.

Now assume that a “typical” unpumped single-shell tank, with properties represented by those of U-107 and the 70,600 ft³ headspace of S-112, is being retrieved with the higher-capacity, 10 gpm, saltwell pump. With a gas release rate of 328 scfd and a ventilation rate of 2.5 scfm, Eq. (3.4) indicates a hydrogen concentration of 3.1% (31,000 ppm) after 51 days when all the waste is removed. It would take 2.9 days to reach the action level of 6,250 ppm. For only barometric breathing, it would take 2.6 days to reach the action level and 27.4 days to reach the LFL. The hydrogen concentration at complete retrieval with barometric breathing would be 8 vol% or twice the LFL.

Two further limiting cases need to be mentioned. First, possibly delaying water addition until saltwell pumping has drained all possible liquid. In this case, the dissolution rate would be initially limited only by the water addition rate. Thus dissolution and coincident gas release could potentially be much faster than when limited by the draining rate, depending on the

capacity of the water spray system. However, 25 - 50% of the retained gas is released during saltwell pumping, probably more than 50% in the upper half of the waste, so less gas remains to be released by dissolution. To put this in perspective, assume that the water spray system has a capacity of 20 gpm and operates continuously on freshly drained waste containing a void fraction of 0.1, half of its original gas content. Assume that the other waste properties remain as specified earlier. With only barometric breathing, the gas release of 705 scfd corresponding to this flow rate of water would increase the headspace hydrogen concentration to 6,250 ppm in 24 hours and reach the LFL in about 12 days. Thus the reduced retained gas volume coupled with limited water pumping capacity prevents large, sudden gas releases in this case.

Second, a large volume of excess water might be added that would continue to mix with the brine and dissolve waste even after both saltwell pumping and the water spray were terminated. The continued dissolution would also continue to release gas and could potentially compromise the control of headspace flammability. However, with both the pumping and water spray shut off, the only mechanisms available to mix the water with the brine and continue dissolution are diffusion and natural convection. Diffusion is extremely slow in a liquid, and convection is limited to thin layers by the density gradient until mixing is almost complete (Rassat et al. 2000). Therefore, while the presence of excess solvent could delay and reduce the response of gas release to cessation of pumping and water addition, the physical mechanisms involved in the mixing process dictate that gas release would fall far below the rate induced during pumping.

3.6 Gas Releases During Dissolution of SY-101 Crust

The gas releases observed during the remediation of the SY-101 crust are consistent with the limitations described in Section 3.3. Rassat et al. (2000), Mahoney et al. (2000) and Johnson et al. (2001) describe in detail the process, theory, and events. The initial 120-inch crust layer in this tank was comparable in thickness to the non-supernate waste in U-107 but contained almost twice the gas. However, in contrast to the waste in U-107 and most other SSTs, the SY-101 crust layer was buoyant and floated on a deep reservoir of liquid similar to the floating solids layers in SSTs A-101 and AX-101. Addition of water to a floating layer produces an upward buoyant force that pulls the floating layer up into the dilute liquid (Stewart 1999). This mechanism keeps the solids in contact with the solvent and maintains a higher dissolution rate than would occur in non-buoyant SST waste.

The crust was dissolved in a series of three waste transfers and back dilutions that eventually added 525,000 gal of water. The bulk of the crust dissolution and gas release occurred in the second back-dilution. Relatively little gas was released from the crust as it descended as a piston in a cylinder during transfers. Larger gas releases occurred during dissolution with the largest occurring during and after the second top dilution when the bulk of the crust dissolved. Temperature profiles and in-tank video clearly shows dilution water remained on top of the existing liquid until it had dissolved sufficient solids to exceed the net density of the floating crust.

The headspace hydrogen concentration peaked at about 3,000 ppm during these events, far below 25 % of the LFL. This concentration represents a sudden release of about 200 scf of hydrogen or

700 scf of retained gas (which was about 30% hydrogen), such that the peak value was not significantly affected by ventilation. However, these releases are larger than can be expected during dissolution of SST waste. Local bubble slurry flows, crust capsizing and sinking, and “landslides” of waste from the tank walls were observed during this period creating much more severe crust disruptions than the dissolution itself.

The small gas releases and the waste behavior during this relatively aggressive series of events qualitatively validated our understanding of the physics of solvent flow and saltcake dissolution. This provides confidence that gas releases during retrieval of SST waste by saltcake dissolution will be small and controllable as predicted.

3.7 Ammonia Release

All the saltcake tanks contain some dissolved ammonia in the liquid waste that is released mainly by evaporation. During and after saltwell pumping, ammonia is released at a somewhat elevated rate. The remaining liquid in the pores between the solid particles after draining greatly increases the surface area for evaporation (Peurrung et al. 1997).^(a)

Dilution reduces the ammonia evaporation rate significantly because the solubility of ammonia increases greatly as the pH decreases with dilution. A water spray is also a very effective way to scavenge ammonia vapor from the headspace. This was clearly demonstrated during back-dilution in SY-101 where the headspace ammonia concentration decreased from around 400 ppm to less than 100 ppm in a matter of minutes after back dilution began (Mahoney et al. 2000). Spraying water on the waste surface for retrieval will effectively prevent significant ammonia releases and will probably reduce ammonia concentrations below the historic baseline values.

^a Also discussed by Peurrung LM and JL Huckaby. 2000. *Gas Release Behavior During Saltwell Pumping*. PNNL letter report TWS00.039 from J. Brothers to GD Johnson, CH2M Hill Hanford Group, Inc., March 10).

4.0 Conclusions

Saltcake dissolution is expected to temporarily increase the gas release rate from the waste, because it eliminates the solid matrix in which waste gases are trapped. However, dissolution can only occur in waste that is not saturated with liquid and only where pathways exist that the solvent can penetrate. Thus, dissolution can proceed no faster than the interstitial liquid (original or newly created) can drain away and gas releases are correspondingly limited. Adding water faster than it can drain away only re-saturates the solid matrix with liquid and prevents solvent penetration. Therefore, gas releases can be controlled by reducing the saltwell pumping rate as well as the water addition rate.

The estimated passive ventilation rate of U-107 is expected to prevent the hydrogen concentration from reaching its LFL, given the current 2,400 gal/day water addition (equivalent to approximately 3.6 gpm pumping rate) limit in the proof-of-concept demonstration plan. Assuming all the added water is effective at dissolving waste, and the passive ventilation rate is 2.5 scfm; it would take 8 days for the hydrogen in the U-107 headspace to reach the action level of 6,250 ppm. The hydrogen concentration would eventually reach a maximum of 1.4 vol% (14,000 ppm), or roughly 35% of the LFL if water addition continued until all the waste was removed. This would theoretically occur in 119 days. At the higher pumping rate of 10 gpm currently planned for full scale retrieval, gas releases could potentially raise the headspace hydrogen concentration to the action level in about 2.9 days. The hydrogen concentration would reach 3.1% (31,000 ppm) after 51 days when all the waste is removed, assuming the same ventilation rate and other properties as in U-107.

In the case where water addition is delayed until after saltwell pumping, the dissolution rate and coincident gas release could potentially be much higher than when limited by the draining rate. With only barometric pressure breathing, a water spray rate of 20 gpm (about 4 times the nominal rate) on freshly drained waste with half its original gas content would increase the headspace hydrogen concentration to 6,250 ppm in 24 hours. While somewhat faster than the normal operation case, the reduced retained gas volume coupled with limited water pumping capacity prevents large, sudden gas releases.

It is also possible to accumulate a volume of excess solvent that would slowly dissolve waste and release gas after pumping and water spray were shut down. However, because diffusion is extremely slow in a liquid and convection is extremely limited, the presence of excess solvent cannot induce gas release at rates comparable to that during pumping.

Since water spray is a very effective ammonia scavenger and dilution greatly increases the solubility of dissolved ammonia; releases are expected to be minimal. In fact, the concentration of ammonia in the headspace is expected to decrease during retrieval by saltcake dissolution.

There is no supernate in S-112, so the upper layer of unsaturated waste should dissolve very rapidly and contain little flammable gas. When dissolution becomes limited by draining, gas releases are anticipated but expected to be much smaller than in U-107 since S-112 contains only

about 1/4 as much gas. In fact, the total estimated retained gas volume in S-112 is not sufficient to make the headspace flammable if all of it were released suddenly.

The small gas releases and the waste behavior during the relatively violent series of events accompanying the dissolution of the crust layer in SY-101 qualitatively validated our understanding of the physics of solvent flow and saltcake dissolution. This provides further evidence that gas releases during retrieval of SST waste by saltcake dissolution will be small and controllable as predicted.

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APPENDIX A

Headspace Hydrogen Concentration Model

Headspace Hydrogen Concentration Model

Consider a tank containing variable volumes of waste and headspace with inflows and outflows as indicated in Figure A.1. The ventilation inflow, Q_{VIN} , and outflow, Q_{VOUT} , carry air into and the headspace atmosphere out of the tank headspace volume, V_{HS} , respectively. During dissolution, water is added to the waste volume, V_W , at a volumetric flow rate of Q_{WIN} and brine is pumped out at the rate Q_{BOUT} . Gas is released from the waste to the headspace at the volumetric rate Q_{GAS} . The headspace atmosphere and the liquid/gas/solid mixture in the waste volume are both assumed to be incompressible.

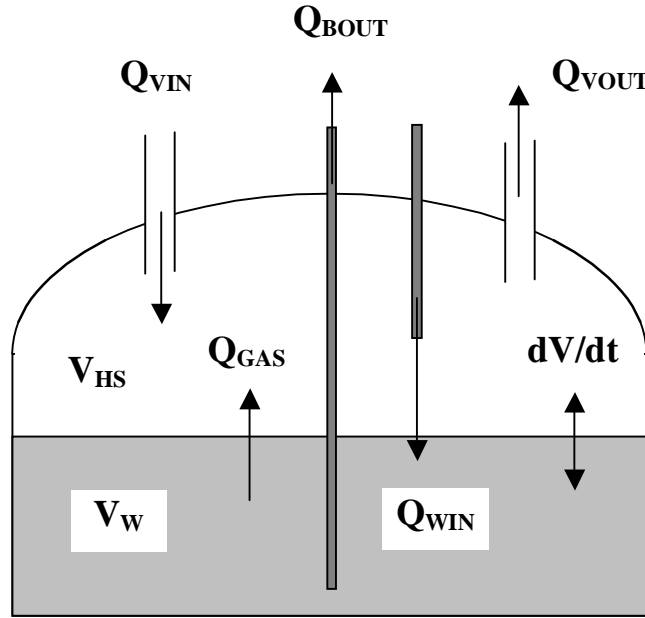


Figure A.1. Schematic of Tank Flow Paths

Let the volume of the tank be fixed but allow the headspace volume and waste volume to vary. The incompressible fluid assumption requires that:

$$\frac{dV_{HS}}{dt} = -\frac{dV_W}{dt} \quad (A.1)$$

Continuity on the headspace volume can be expressed as:

$$\frac{dV_{HS}}{dt} = Q_{VIN} - Q_{VOUT} + Q_{GAS} \quad (A.2)$$

Assuming the released gas leaves the waste with the pressure at which it was retained, P_{GAS} , that the volume change during dissolution is negligible, and that gas expansion in the waste due to decrease in hydrostatic pressure is minimal, continuity on the waste volume is written as:

$$\frac{dV_W}{dt} = Q_{WIN} - Q_{BOUT} - \frac{P_0}{P_{GAS}} Q_{GAS} \quad (A.3)$$

Substituting Eqs. (A.2) and (A.3) into Eq. (A.1) provides an expression for the ventilation outflow, Q_{OUT} , as a function of the other known inflows and outflows.

$$Q_{VOUT} = Q_{VIN} + Q_{GAS} \left(1 - \frac{P_{HS}}{P_{GAS}} \right) + Q_{WIN} - Q_{BOUT} \quad (A.4)$$

The continuity equation for hydrogen in the headspace, assuming that the hydrogen concentration remains small, can be written as:

$$\frac{d}{dt} (C_H V_{HS}) = Q_{GAS} \chi_H - Q_{OUT} C_H \quad (A.5)$$

where C_H is the headspace hydrogen concentration (vol%) and χ_H is the volume fraction of hydrogen in the waste gas. Expanding the derivative and substituting Eqs. (A.3) and (A.4) via Eq. (A.1) yields

$$V_{HS} \frac{dC_H}{dt} = Q_{GAS} \chi_H - C_H (Q_{VIN} + Q_{GAS}) \quad (A.6)$$

Note that, even though it appears outside the time derivative, the headspace volume is a function of time. Assuming that the water inflow, brine-pumping rate, the gas release rate and pressure are constant, Eqs. (A.3) and (A.1) can be solved for the headspace volume as a function of time as follows:

$$V_{HS}(t) = V_{HS0} - \left(Q_{WIN} - Q_{BOUT} - Q_{WIN} \frac{P_{HS}}{P_{GAS}} \right) t \quad (A.7)$$

where V_{HS0} is the headspace volume at $t = 0$. To simplify further steps, define the following terms:

$$\begin{aligned} Q_A &= Q_{VIN} + Q_{GAS} \\ Q_B &= Q_{WIN} - Q_{BOUT} - Q_{GAS} \frac{P_{HS}}{P_{GAS}} \end{aligned} \quad (A.8)$$

Now, substituting these definitions and Eq. (A.7) into Eq. (A.6) and rearranging yields the following ordinary differential equation:

$$\frac{1}{C_H - \frac{Q_{GAS}}{Q_A}} \frac{dC_H}{dt} = -\frac{Q_A}{V_{HS0} - Q_B t} \quad (A.9)$$

Eq. (A.9) can be solved under the initial conditions that $C_H = C_0$ at $t = 0$ to yield

$$C_H(t) = \frac{Q_{GAS}\chi_H}{Q_A} + \left(C_0 - \frac{Q_{GAS}\chi_H}{Q_A} \right) \left(1 - \frac{Q_B}{V_{HS0}} t \right)^{\frac{Q_A}{Q_B}} \quad (A.10)$$

The time at which the hydrogen concentration reaches a specified value, C_H , is given by

$$t = \frac{V_{HS0}}{Q_B} \left[1 - \left(\frac{C_H - \frac{Q_{GAS}\chi_H}{Q_A}}{C_0 - \frac{Q_{GAS}\chi_H}{Q_A}} \right)^{\frac{Q_B}{Q_A}} \right] \quad (A.11)$$

If the headspace volume is assumed constant, the solution to Eq. (A.9) for the hydrogen concentration as a function of time under the same initial conditions becomes

$$C_H(t) = C_0 e^{-\frac{Q_{VIN}}{V_{HS}} t} + \frac{Q_{GAS}\chi_H}{Q_A} \left(1 - e^{-\frac{Q_{VIN}}{V_{HS}} t} \right) \quad (A.12)$$

Letting $t \rightarrow \infty$ Eq. (A.12) gives the steady state hydrogen concentration as

$$C_H = \frac{Q_{GAS}\chi_H}{Q_A} \quad (A.13)$$

Solving Eq. (A.12) for t , the time to reach a given hydrogen concentration can be calculated by

$$t = -\frac{V_{HS}}{Q_{VIN}} \ln \left[\frac{C_H - \frac{Q_{GAS}\chi_H}{Q_A}}{C_0 - \frac{Q_{GAS}\chi_H}{Q_A}} \right] \quad (A.14)$$

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