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Flammable Gas Generation, Retention, and Release in High-Level Waste Tanks Physical and Chemical Models

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
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FLAMMABLE GAS GENERATION, RETENTION, AND RELEASE IN HIGH-LEVEL WASTE TANKS - PHYSICAL AND CHEMICAL MODELS

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ABSTRACT

The most evident dangers from flammable gas release in ventilated high-level waste tanks at Hanford are those caused by periodic release of gases generated and retained in depths of the tanks. In Hanford Tank 101-SY the flammable gases hydrogen, ammonia and methane are accumulated along with oxidizer nitrous oxide in bubbles while the ammonia and nitrous oxide are also deposited in solution. Accumulation of both the free and dissolved gases is enhanced by hydrostatic pressure. The free gases are apparently held by several mechanisms - viscous trapping of bubbles, stabilization in three-phase foams at hydrophobic surfaces, capillary channel gas accumulation, mechanical trapping in crystal clusters, and tight engulfment in 'armored bubbles.' Episodic release is brought about by ascension from the bottom of large conglomerates which release gases by bubble detachment and by slower diffusion-controlled mass-transfer processes. Density of the conglomerates increases in this process, whereupon they settle to repeat the cycle again.

The flammable gases are produced by a combination of radiolytic and non-radiolytic chemical processes in breakdown of water and organic and inorganic constituents. Hydrogen production is enhanced by organic destruction while radiolytic hydrogen production is depressed by nitrite ion. Most of the nitrous oxide and ammonia appear to be derived from reduction of nitrite by organics, with smaller amounts coming from amine nitrogen in chelators. Methane is produced in only small amounts. Formate, oxalate, and carbonate are refractory end-products from degradation of organic constituents such as the chelators ethylenediaminetetraacetate (EDTA) and N-(2-hydroxyethyl)ethylenediamine-triacetate (HEDTA).

THE FLAMMABLE GAS PROBLEM

Flammable gas production from radiolysis is always a concern for high-level radioactive waste storage. However, a special problem developed at Hanford when wastes were concentrated by evaporation to conserve space in large million-gallon storage tanks. The green slurry concentrate began to grow after being pumped into the tanks. This slurry growth defeated the purpose of volume reduction, but the real problem became evident when some tanks began to have rather large surface level drops accompanied by release of flammable gases noted to contain both fuel (hydrogen and ammonia) and oxidant (nitrous oxide). Tank 241-SY-101 (101-SY) exhibits the largest cyclic releases, and hydrogen concentrations in the tank dome space and ventilation header have exceeded the lower flammability limit in at least two instances, for short periods of time. Other Hanford waste tanks are being studied for potential flammable gas problems. The newer, double-shell, tanks such as 101-SY are air-purged and maintained under negative pressure. Tank 101-SY exhibits the largest episodic gas releases (as indicated by tank surface level drop and increase in tank pressure). The other actively ventilated double-shell tanks should not present such a great hazard as 101-SY, but they are to be monitored. A number of older, single-shell, waste tanks are to be monitored to determine whether flammable gas buildup could be developing, especially in those without active ventilation. A total of 25 Hanford high-level radioactive waste tanks are now considered have the potential of developing flammable gas concentrations, either through gas release events or through buildup of gases in the tanks not actively ventilated (even though Tank 101-SY is the only one which has definitely been shown to exceed the lower flammability limit).

CHEMICAL CONSTITUENTS OF LIQUID WASTES

Chemical analyses have been made on core samples from Tank 101-SY. The weighted average contents of major constituents for samples taken in December, 1991, (1) is shown in Table I. Concentrations of the predominant radionuclides calculated from a report by Reynolds (2) are: ^{137}Cs, 360 μCi/g and ^{90}Sr, 24 μCi/g.

TABLE I

Overall Average Tank 101-SY
Waste Composition, Wt.%

Na	20.7
Al	3.2
Cr (total)	0.41
Cr(VI)	0.002
Ca (acid digest)	0.023
Fe	0.028
K	0.326
Ni	0.015
Zn	0.002
NO_3^-	11.7
NO_2^-(by IC)	10.5
OH^-	2.47
TOC	1.53
TIC	0.63
PO_4^{3-}	0.64
SO_4^{2-}	0.40
Cl^-	0.79
F^-	0.03
H_2O	35.5

Samplers for trapping and retaining volatile materials such as volatile organics and ammonia were not utilized for these analyses. Such samplers are now under development. Analytical methods are being developed at Pacific Northwest Laboratories for use in analysis of the organic constituents representing the Total Organic Carbon (TOC).

CONSTITUENTS OF RELEASED GASES

The major constituents of gases released from Tank 101-SY are hydrogen, nitrogen, nitrous oxide, ammonia, and water vapor. Methane is usually only a trace component. Composition of the released gas is quite variable, depending on several parameters, viz., whether bubble release or diffusion mass transport is controlling or whether barometric pressure is increasing or declining. The tank is continuously ventilated with a purge air flow of about 550 cfm (0.26 m^3/s). In a dome space of about 35,000 cubic feet (9.9×10^2 m^3), gas releases are rapidly diluted. Analysis indicates that the dome space is well mixed within less than one minute following a gas release. The air purge flow displaces released gases with a time constant slightly over one hour. Nitrogen is a component common to both the released gas and the purge air. This presents some difficulties in estimation of actual compositions of gas releases, since nitrogen contents of the gas releases are certain to be variable. Approximate ranges of concentrations during an episodic gas release event are presented in Table II. The released gases are saturated with water at tank conditions. Ammonia and nitrous oxide concentrations in the tank exhaust are now monitored with a Fourier-transform infrared analyzer. A short period of operation before installation of the mitigation test mixer pump was available for analysis of baseline exhaust gas compositions. Following the gas release event, concentrations of hydrogen, nitrous oxide, and ammonia gradually decreased over a period of days to reach levels as low as 10 ppm (vol.) hydrogen, 12 ppm nitrous oxide, and 20-25 ppm ammonia. However, the ammonia concentration, and to a lesser extent the nitrous oxide concentration, rose during pronounced drops in barometric pressure. Ammonia concentrations rose up more than 100 ppm in synchrony with barometer declines. The high ammonia concentrations measured in the gas release events as well as in the interim periods led to some rethinking of the importance of ammonia as a participant in the chemistry of the tank, as well as in flammability and toxic release consequences. The pronounced barometric pressure effect indicated that the 101-SY wastes could be saturated with ammonia, a gas which has relatively high solubility, even in aqueous systems with high pH and high salt concentrations (3). Since the ratios of hydrogen to soluble gas concentrations underwent large changes during the release cycles, at least two different release mechanisms were indicated. Whereas the hydrogen/ammonia ratio approached 3/1 in gas release events (where rapid release of bubbles and large gas pockets could be seen), the ratio approached 1/6 in

TABLE II

Tank 101-SY Gas Release
Components, Dry Basis

Component	Content, Vol. %
H_2	30-35
N_2O	25-30
N_2	20-25
NH_3	12-18
CH_4	<1

water lancing operations preparatory to insertion of the mixing pump into the waste. This change in ratios can be due to a change from the process predominated by simple release of equilibrium bubbles to one predominated by mass-transfer-controlled release of dissolved gas.

GAS RETENTION

Gas is retained in 101-SY in bubbles (gas phase) and in solution (liquid phase). Possibly some, especially ammonia, is also retained by adsorption on crystals and colloidal metal particles (Pd, Rh) in the slurry. For ammonia, chemical combinations in ammines and ammoniates is also likely. The liquid and gas phase contents are assumed to be those causing safety issues.

Tank 101-SY temperature profiles are studied to gain insight as to the physical nature of tank contents. Fig. 1 shows the typical type of profile which develops prior to a gas release event (GRE). The consensus is that three major zones are present, namely, crust, a convecting zone, and a non-convecting zone. The 'crust' is on the order of four feet thick and consists of floating three-phase

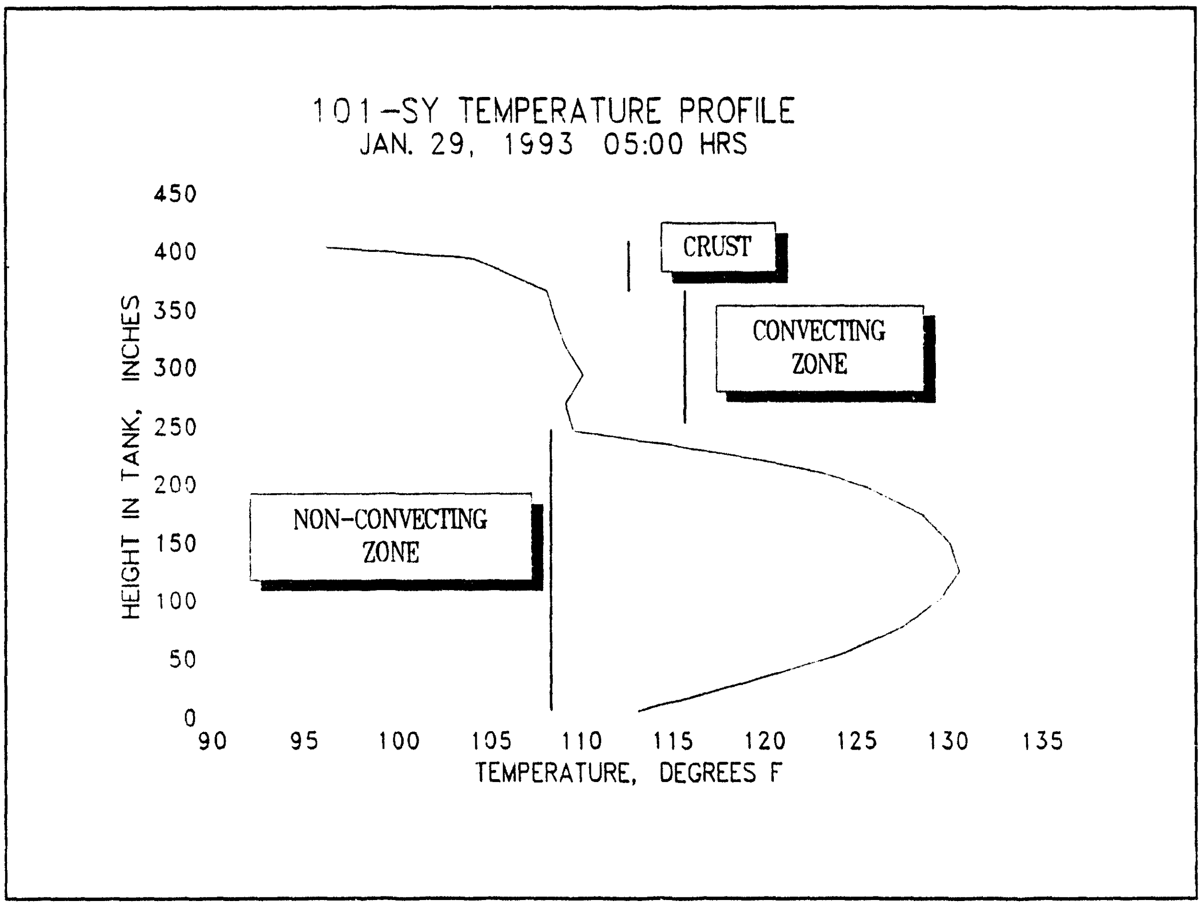
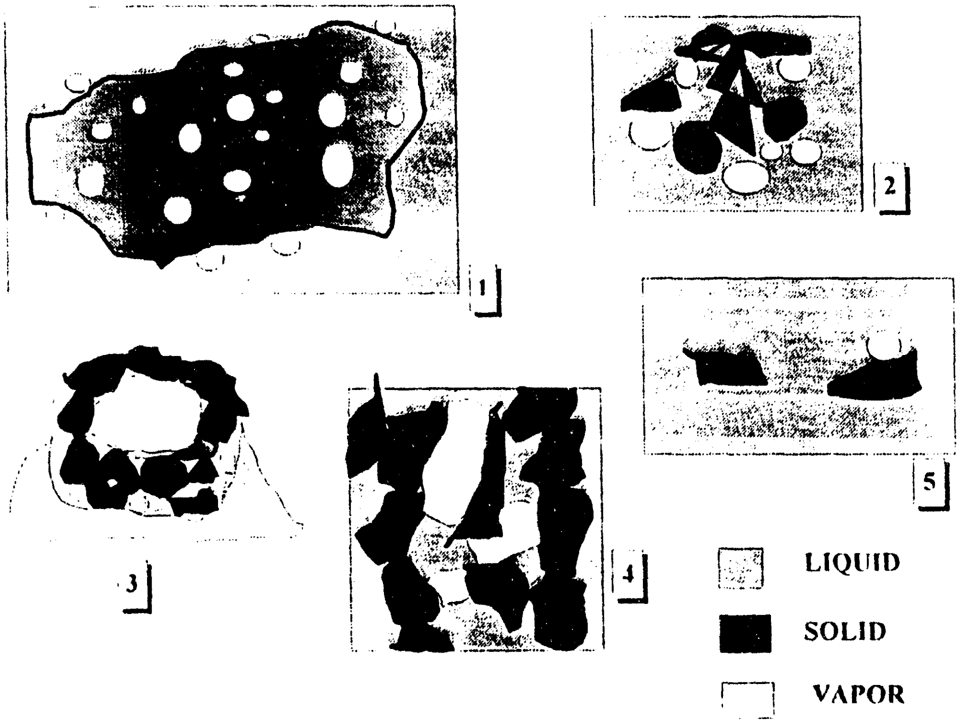


Fig. 1

foam with the heavier-than-liquid solids buoyed by their contained and attached gas bubbles. The 'convecting' zone is assumed from its usually uniform temperature to be freely convecting and mostly liquid. The 'non-convecting' zone, like the crust, must be free to transport heat only through conduction; it contains over 60 vol. % solids. A gas release event, many times triggered by a barometric depression, goes through the following process:

1) An initial increase in ammonia release over a period of hours or days,
2) A sudden increase in liquid level up to several inches
3) A 'rollover' during which high surface movements can be seen and during which surface level drops and an inversion in the tank temperature is seen. This process is accompanied by the gas release and an increase in tank pressure.

The nature of the rollover and gas release, as well as the nearly complete temperature inversion indicates that large amounts of non-convecting layer are suddenly transported to the top of the tank in the occurrence. Thus it appears that the gas release events are caused by buildup of gas in the non-convecting layer until buoyant forces overcome gravitational and rheological constraining forces. It can be seen that the depth of heavy liquid in the tank contributes to intensify the associated problems. The high hydrostatic head compresses bubbles in the lower levels so that more gas has to be accumulated to overcome given restraining forces, since buoyant force is dependent on gas volume. When the restraining forces are finally overcome, and the bottom layer rises, the rise is accelerated as the bubbles inflate as they experience lower hydrostatic pressures as they rise. In addition, the soluble gases, ammonia and to a lesser extent, nitrous oxide held in solution at the tank depths will be released through interfacial mass transport as the liquid is brought to the surface. The nature of physical gas retention has been deduced through study of photomicrographs of tank slurry, as well as through conjecture based on physical properties of the slurry. The nature of the rollover events is such that solid has to be carried from the bottom to the top of the tank in rather large conglomerates. Possible types of bubble retention are illustrated in Fig 2. The



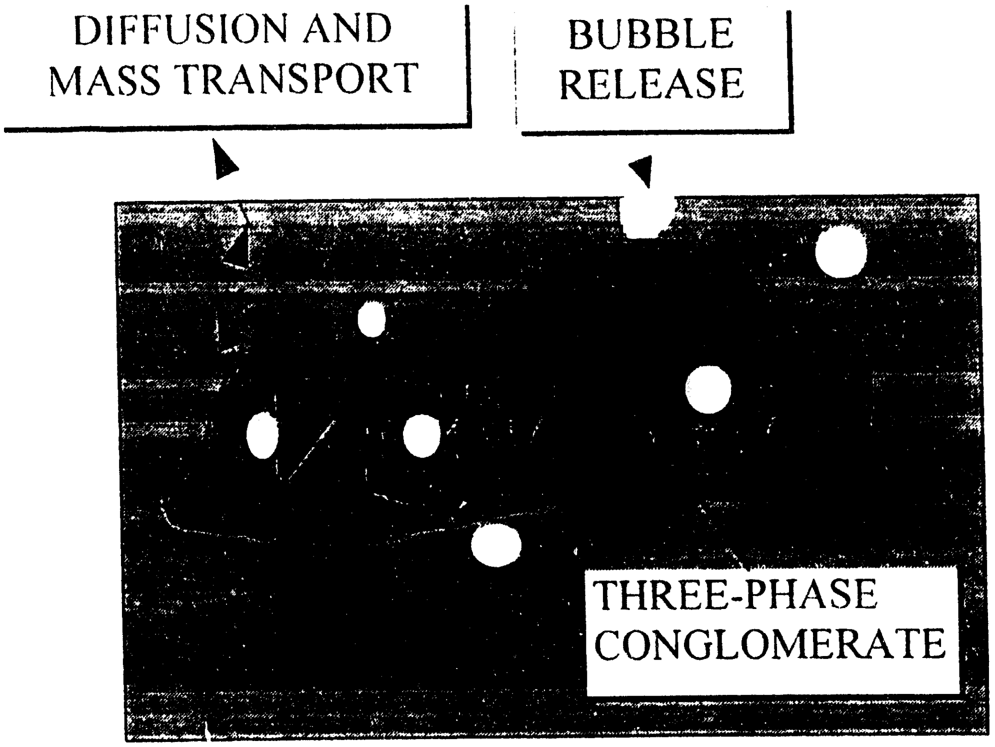
TYPES OF VAPOR RETENTION

Fig. 2

various types of vapor or gas bubble retention as illustrated are as follows:

1) Viscous trapping of bubbles in a gel or highly viscous slurry,
2) Retention of bubbles in aggregates of crystals,
3) Bubble structures held tightly in 'armored bubbles' as shown by Gaudin (4) in minerals flotation processes,
4) Retention of vapor in capillaries or larger channels in settled solids layer, and
5) Individual bubble-particle attachment.

It appears likely that all of these mechanisms are operative in Tank 101-SY. The gas-solid interactions will be controlled by interfacial tension effects at hydrophobic surfaces. The GRE, initiated as above, then will involve movement of conglomerates to the surface, releasing some bubbles as they rise. As the conglomerate touches the surface (as illustrated in Fig. 3), bubbles on the top



MECHANISMS FOR VAPOR RELEASE

Fig. 3

will burst, with dissolved gases continuously being transported into bubbles and to and through the liquid top surface. When the conglomerate reaches a neutral buoyancy through this vapor release, it will begin to sink, with the downward velocity accelerating due to bubble compression with increasing depth and consequent hydrostatic head.

EFFECT OF SLURRY SHEAR STRENGTH

The slurry in the non-convective layer has a high shear strength (2, 5), which increases exponentially with decreasing temperature below 60 °C (5). This high shear strength has a strong effect, not only on individual bubble retention, but on the physical behavior of the three-phase conglomerates. A simplistic analysis of the forces on a right circular cylindrical element of tank contents yields a force balance such that upward buoyant force, F↑, is countered by shear resistance, F↓, the forces being defined by Eq. 1 and Eq. 2, respectively, in which ρ_l is liquid density, ρ_s is conglomerate density, g is acceleration of gravity, r is cylinder radius, h is cylinder height and τ_s is shear strength of the slurry.

$$F\uparrow = (\rho_l - \rho_s) g \pi r^2 h \qquad (Eq.\ 1)$$

$$F\downarrow = 2\tau_s \pi r h \qquad (Eq.\ 2)$$

As gas is accumulated in this element, liquid is expelled, and density of the element decreases. Ultimately the buoyant force may equal and then exceed the shear resistance. The point at which this occurs can be found by equating F↑ to F↓. It can be seen that this will be most likely to occur for large values of r, in other words, for large conglomerates. The actual tank situation is more complex. For one thing, even if the gas content is uniform, the gas void volume fraction will decrease with increasing depth due to hydrostatic compression. Furthermore, the shear strength is not uniform - both due to variable gas void volume and to variable temperature. With currently measured shear strengths, the predominant control for gas buildup is attainment of neutral buoyancy in the non-convecting layer. However, the contribution of shear strength to gas retention increases as the shear strength increases with declining tank temperature. Secondary effects due to contribution of bubbles to increasing shear strength may compound this temperature effect. In December, 1991, a very large GRE occurred, along with a vigorous rollover. It was noted that the tank was cooling, apparently at a higher rate than before due to increased tank ventilation. The need to counteract this cooling trend and the related increasing gas retention was obvious, and this gave even more impetus to mitigation efforts.

RADIOLYSIS

Radiation chemistry studies have been performed at Argonne National Laboratories and at Pacific Northwest Laboratories. Recent results have been summarized by Meisel et al. (6). Apparently the major reactions producing gases are reactions of H, O^-, and e^-_{aq} produced in spurs in the aqueous medium. Meisel et al. (6) propose that molecular hydrogen is produced by H recombination and by hydrogen abstraction from organic compounds as well as by secondary production from organic compound reaction with NO_2 (from O^- plus nitrite and e^-_{aq} plus nitrate) and from ultimate oxidation of formaldehyde and glyoxylate produced in chemical degradation of chelator fragments. They propose that radiolytic production of N_2O results from reduction of nitrite by H, while other secondary nitrite reduction pathways also contribute to N_2O production. The most important contributions to understanding of the flammable gas production are that hydrogen production (as compared to that from water radiolysis) is influenced negatively by nitrite and nitrate and positively by organics. Preliminary work by Meisel et al. indicates that ammonia is produced radiolytically from amine nitrogen in chelator (such as HEDTA) molecules.

CHEMICAL PRODUCTION OF GASES

The flammable gas problem at Hanford is further complicated in that gases can be produced by non-radiolytic chemical degradation of organics in the highly alkaline wastes. This was recognized early on in Hanford studies; some of the most recent work has been reported by Ashby et al. (7). The studies show that, as an example, HEDTA can undergo slow reaction in synthetic waste similar in chemical content to 101-SY waste to produce hydrogen, ammonia, and nitrous oxide. The series of reactions requires organic (HEDTA), $Al(OH)_3$ (in anionic hydrated forms), nitrite, and OH^-. They show further that hydrogen comes from the organic and nitrous oxide about 85% from organic reduction of nitrite and 15% from HEDTA. Preliminary studies show that ammonia is produced predominantly from reduction of nitrite. Current analysis of Tank 101-SY actual wastes (8) show that about half of the organic carbon present is in the form of refractory (at tank conditions) formate and oxalate. HEDTA is nearly depleted, while more refractory EDTA is still present to some extent along with chelator fragments such as iminodiacetate (IDA) (or its N-nitroso derivative) and ethylene diaminetriacetate (ED3A). Carbonate is also found, but it is contributed from atmospheric CO_2 as well as from organic degradation.

SUMMARY

The major flammable gas concerns in regard to twenty-five Hanford high-level radioactive waste tanks are related to gas release events in double-shell tanks and possible flammable gas buildup in single-shell tanks. The primary gases of concern are hydrogen, ammonia, and nitrous oxide, and to a lesser extent, methane. Sources of hydrogen are radiolysis of water, organics and ammonia, as well as non-radiolytic degradation of organic compounds. Sources of ammonia determined to date are radiolysis of chelators and reduction of nitrite by organics. Nitrous oxide is produced through reduction of nitrite and by oxidation of chelator nitrogen (both radiolytic and non-radiolytic).

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