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STUDY OF PHYSICAL PROPERTIES, GAS GENERATION AND GAS RETENTION IN SIMULATED HANFORD WASTE

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Study of Physical Properties, Gas Generation, and Gas Retention in Simulated Hanford Waste

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ABSTRACT

The purpose of this study was to establish the chemical and physical processes responsible for the generation and retention of gases within high-level waste from Tank 101-SY on the Hanford Site. This research, conducted using simulated waste on a laboratory scale, supports the development of mitigation/remediation strategies for Tank 101-SY.

Simulated waste formulations are based on actual waste compositions. Selected physical properties of the simulated waste are compared to properties of actual Tank 101-SY waste samples.

Laboratory studies using aged simulated waste show that significant gas generation occurs thermally at current tank temperatures (~60°C). Gas compositions include the same gases produced in actual tank waste, primarily N_2, N_2O, and H_2. Gas stoichiometries have been shown to be greatly influenced by several organic and inorganic constituents within the simulated waste.

Retention of gases in the simulated waste is in the form of bubble attachment to solid particles. This attachment phenomenon is related to the presence of organic constituents (HEDTA, EDTA, and citrate) of the simulated waste. A mechanism is discussed that relates the gas bubble/particle interactions to the partially hydrophobic surface produced on the solids by the organic constituents.

INTRODUCTION

Of 177 high-level waste storage tanks on the Hanford Site, 23 have been placed on a safety watch list because they may produce flammable gases. One tank in particular, Tank 101-SY, has exhibited periodic slow increases in waste volume followed by rapid decreases accompanied by venting of large quantities of gases. Beginning in the early 1980's, these cycles have occurred every 8-15 weeks. The concentration of hydrogen in the space above the waste slurry has approached its lower flammability limit during some of the gas release episodes. Similar, but less frequent, rising and falling of the waste level has been observed in other tanks, presumably accompanied by gas release.

This report summarizes the results of studies conducted at Pacific Northwest Laboratory (PNL) to help establish the causes of generation, retention, and episodic release of flammable gases from Tank 101-SY. Physical properties of simulated Tank 101-SY wastes formed in laboratory tests are summarized, as are the results of gas generation measurements using these simulated wastes. Where possible, comparisons of properties between actual Tank 101-SY waste and simulated waste have been made. Microscopic-scale

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phenomena responsible for the retention of gases within the wastes are also discussed.

This work is part of a coordinated effort, sponsored by Westinghouse Hanford Company (WHC), for the understanding, mitigation, and remediation of flammable gas releases from high-level waste underground storage tanks. (Ashby et al. 1992)

RESULTS AND DISCUSSION

The results of this work have been divided into three areas for discussion. The first section is Waste Simulant Compositions, which details the waste composition and measures physical properties. Selected comparisons are made between physical properties of the simulated waste and actual Tank 101-SY waste. The second section is Gas Bubble/Particle Interactions in Simulated Waste. This section describes the chemistry by bubble attachment to particles in simulated waste. The third section is Gas Generation from Simulated Waste. This final section details gas production and gas product stoichiometry, as well as factors that influence gas production rates from simulated waste.

WASTE SIMULANT COMPOSITIONS

Several simulant compositions have been devised for use in laboratory studies in the place of actual waste from Tank 101-SY. The purpose of each was not necessarily to precisely reproduce the composition of the actual waste but rather were designed to aid in the conduction and interpretation of laboratory experiments. Simulant compositions used in this study are given in Table 1, identified by an alphanumeric code. Simulant SY1-SIM-91A contains the principal inorganic constituents of the actual waste in addition to 0.3 M organic complexants. Simulant SY1-SIM-92A more closely reproduces the composition of the actual waste. In addition to the principal inorganic components, this simulant contains minor components that have been found in actual waste, including transition metals, chloride, fluoride, sulphate, and phosphate ions. The composition of the latter simulant was based on a weighted average of analyses of actual waste cores obtained during "Window C" (Herting, 1992). Both SY1-SIM-91A and SY1-SIM-92A exist as slurries at tank temperature (~60°C). For results reported here, the complexants HEDTA and EDTA were used to simulate organic constituents of the waste. While those complexants are present in the actual waste, they represent a minority fraction of the total organic carbon present. The majority of organic waste constituents have yet to be identified.

<u>Physical Properties of Simulated and Actual Waste:</u> Physical properties of simulated waste have been examined to better understand the properties of the actual waste in Tank 101-SY. In an effort to determine how closely the simulated waste formulations mimic the actual Tank 101-SY waste, we compared selected simulated waste properties to those available from recent core samples of actual waste. (Herting et al., 1992; Tingey 1992) Settling velocities, densities, wt% centrifuged solids, shear strength, and wt% water were each determined as a function of temperature and dilution of the waste.

Table 1 Concentrations of Components from Tank 101-SY and Those Used in Synthetic Waste Formulations.

Component	Tank 101-SY wt%[a]	SY1-SIM-92A wt%	SY1-SIM-91A wt%
TOC	1.58	1.55[b]	2.37[b]
+assoc N,O,H in organic	3.16	2.09	3.39
Na	20.5	20.3	21.6
Al	3.5	3.55	3.9
+assoc O in AlO_2^-	---	4.2	4.6
Cr	0.368	0.35	---
Cu	---	0.00	---
Fe	0.028	0.026	---
Ni	0.008	0.008	---
Ca	0.021	0.021	---
K	0.37	0.37	---
Cl^-	1.5	1.56	---
PO_4^{-3}	1.1	1.1	---
NO_2^-	11.5	11.64	9.7
NO_3^-	10	10.1	15.1
CO_3^{-2}	1.6	1.53	2.4
F^-	0.1	0.1	---
OH^-	3.1	3.1	3.1
SO_4^{-2}	0.19	0.19	---
H_2O	38	38.1	33.9
total	100.86	99.95	99.98

a. Calculated from Herting et al. 1992
b. As HEDTA and EDTA.

Weight and Volume Percent Solids: The wt% centrifuged solids as a function of waste temperature (30 to 80°C) were measured for the simulated waste as well as for actual Tank 101-SY waste. The simulated waste has wt% solids (18 to 20 wt%) most comparable to that for actual Tank 101-SY samples taken from the convecting zone (upper half of the tank) of the waste tank, which were between 10 to 28 wt% centrifuged solids. The actual waste samples from the non-convecting zone (those from the lower half of the waste tank) were between 65 to 100 wt% solids.

Volume percent settled solid data for simulated waste and for Tank 101-SY samples were measured over a range of temperature (30 to 80°C). The simulated waste results (50 to 58 vol%) closely match results for actual Tank 101-SY samples taken from the convective zone of the tank. The settled solid data from the crust and nonconvective zone of the actual waste show essentially 100% solids with no settling behavior, quite unlike the simulated formulation. From these measurements, the simulated waste most closely represents the convective layer with respect to the property of wt% centrifuged solids and vol% settled solids.

Shear Strength: The shear strength of simulated and Tank 101-SY waste was measured as a function of temperature, 30 to 80°C for the actual waste, 25°C for the simulated waste. Actual waste samples from the nonconvecting layer of Tank 101-SY had the smallest shear strength values (~0 to 50,000 dynes/cm^2 while samples from the crust and non-convective layers had the highest measured shear strength values (5,000 to 250,000 dynes/cm^2). Simulated wastes generally yielded quite low shear strengths, between 10,000 and 20,000 dynes/cm^2. The simulated formulation shear strength data were taken at a lower temperature than Tank 101-SY samples so a direct comparison is not possible. But, by extrapolating Tank 101-SY data, we conclude that the relatively low values for the simulated waste formulations are more consistent with the convecting layer data than with the non-convecting layer data.

Density Measurements: Density measurements for the simulated waste and Tank 101-SY waste were taken at various temperatures. After centrifuging, the supernate was decanted from each sample before the densities of the solids and supernates were determined. The temperature had very little effect on the supernate or solids density, regardless of the source of the sample (convecting or non-convecting zone). There was also good agreement between the simulated waste and Tank 101-SY density data. The solids densities were 1.75 to 1.8 for the simulant, and 1.7 to 1.85 for the actual waste respectively; the supernate densities ranged 1.35 to 1.5 for the simulant, and 1.4 to 1.55 for the actual waste.

Weight Percent Water: The wt% water measurements were performed for the simulated waste samples and Tank 101-SY samples. The simulated waste sample had approximately the same wt% water (40 wt%) as Tank 101-SY convecting-layer samples (36 to 39 wt%). The nonconvecting-layer and crust samples had ~30 and 15 wt% water respectively, which was considerably less wt% water than the simulated waste formulation.

Solids Settling Behavior for Simulated Waste: Information on solid settling rates is needed to predict how the solids will settle after a gas release event, or during waste mixing for mitigation. Any remediation of the tank likely will include pumping of waste from the tank to a treatment facility or to another tank, such action will require understanding of solids settling behavior.

Settling rate data for simulated waste SY1-SIM-92A (Table 1) without added organics are presented in Figure 1 as volume settled solids versus time at 60°C. The settling rate could be described by first order kinetics. The solid curves in Figure 1 are calculated fits of the data to Equation 1:

$$y = a*\exp(-kt) + b \qquad \text{(Eq. 1)}$$

where a, b, and k are fitted constants, t is time, and y is the observable volume of settled solids. The constant k is the first order rate constant for settling. Experiments were repeated for simulated wastes at 60°C. Figure 2 shows the rate constant data for 60 and 80°C with temperature. The value of the settling rate constant increased as the simulated waste was diluted with 2 M NaOH at both temperatures.

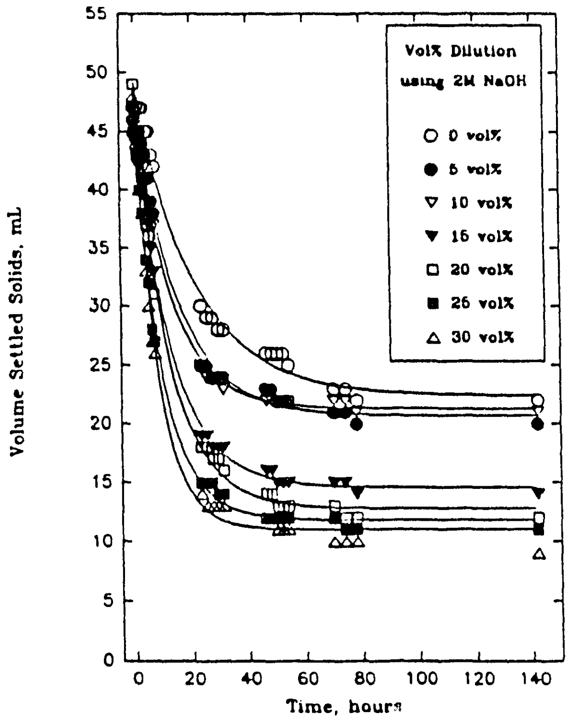

Figure 1 Settling Rate Data for Simulated Waste SY1-SIM-92A at 80°C as a Function of Dilution with 2 M NaOH. This simulated waste contains no added organics.

The effects of added organics on the settling behavior of the simulated waste solids were observed by repeating the settling experiment using simulated waste with EDTA and HEDTA added to the formulation. The settling behavior of the simulated waste with organics added displayed first order settling behavior similar to that observed for the waste without organics present. The value of the settling rate constant increased as the simulated waste formulation was diluted with 2 M NaOH. Values of the settling rate constant for the simulated waste containing no organic were consistently higher than those for the simulated waste containing 0.2 M organic complexant.

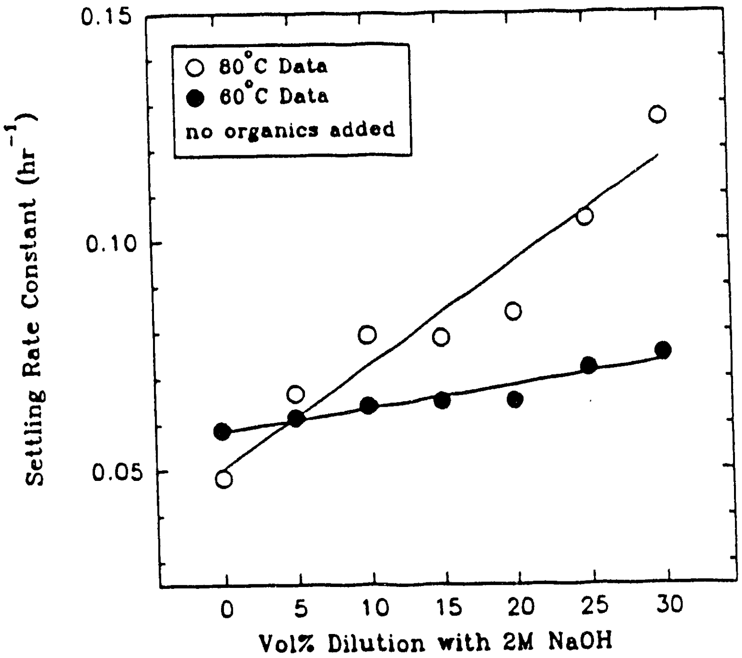

Figure 2 Settling Rate Constants Measured at 80°C and 60°C on Synthetic Waste as a Function of Dilution Using 2 M NaOH. This formulation does not contain organics.

GAS BUBBLE/PARTICLE INTERACTIONS IN SIMULATED WASTE

Surface tension and wetting phenomena in simulated Tank 101-SY waste were examined as part of an ongoing study to determine how gases are retained in the waste. Densities, liquid surface tensions, and equilibrium solid/liquid contact (wetting) angles were determined as a function of temperature and organic complexant concentrations in the waste. The principal hypothesis being tested is that gases are retained as bubbles that are attached to solid particles as a result of surface tension forces. By manipulation of wetting behavior, it may be possible to continuously vent the gases produced in the waste rather than allow them to undergo buildup and release cycles.

The Young-Dupré relationship (Huh and Mason 1974), Equation 2, describes expected trends in wetting behavior as a function of the interfacial tensions between the solid, liquid, and gas phases:

$$\cos \theta = [\sigma_{SV} - \sigma_{SL}] / \sigma_{LV} \qquad \text{(Eq. 2)}$$

The contact angle, θ, is that measured between the solid and liquid phases. A value of $\theta = 0°$ is indicative of complete solids wetting and no tendency for gas bubbles to adhere to solids, while a value of $\theta = 180°$ is indicative of the absence of wetting and a large tendency for gas bubble adherence to solids. The terms σ_{SV}, σ_{SL}, and σ_{LV} refer to interfacial tensions at the solid/vapor, solid/liquid, and liquid/vapor interfaces, respectively. The terms of Equation 2 are illustrated in Figure 3.

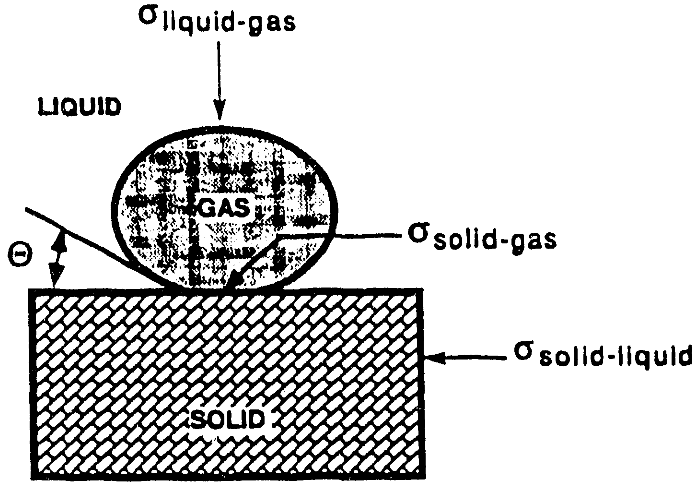

Figure 3 Schematic Terms of the Young-Dupré Equation

Minimization of the wetting angle, an indicator of the interaction forces between solids and gas bubbles, may be of benefit in Tank 101-SY. In consideration of Equation 2, minimization could be accomplished either by lowering the value of σ_{LV}, the liquid surface tension, or by lowering σ_{SL}, the solid/liquid interfacial tension. The remaining term, σ_{SV}, is largely fixed by the identity of solid phases that are present, and probably cannot be substantially altered within the temperature range of interest. Surfactants are commonly used to lower σ_{LV} for aqueous solutions in industrial applications to a small fraction of that of pure water. The term σ_{SL} is sensitive to the surface adsorption of small quantities of compounds; the adsorption of complexants onto solid surfaces in the actual waste is thought to raise σ_{SL}, thereby promoting gas bubble retention. The following section describes efforts to assess the terms of the Young-Dupré equation for simulated waste and implications of wetting phenomena for mitigation.

<u>Liquid Surface Tension:</u> The term σ_{LV}, the liquid/vapor interfacial tension (usually referred to as the liquid surface tension that is measured against air), is strongly affected by dissolved solids. Electrolytes such as sodium hydroxide, sodium carbonate, and sodium nitrate tend to increase the value of σ_{LV} through tightly held waters of hydration . In contrast, many organic compounds such as acetic acid tend to decrease the magnitude of the surface

tension (Handbook of Chemistry and Physics, Chemical Rubber Co. 1969). In consideration of the relatively large concentrations of inorganic salts in Tank 101-SY compared to those of organic components, one would expect σ_{LV} for the waste solutions to be much larger than that of water (72 dynes/cm at 25°C).

Surface tension values for a dilute simulated waste solution were obtained as a function of temperature. These were measured using the capillary rise method. The waste composition was SY1-SIM-91A, but was diluted by 60% to dissolve essentially all the solids at room temperature (a small quantity remained). Dilution ensured the concentration of dissolved solids would not change appreciably as the waste was heated. Dilution also improved wetting of the capillary tube by the liquid.

For the dilute simulated waste at temperatures above 50°C, trends in surface tension as a function of temperature were similar to distilled water, although displaced to higher values. Surface tension did not change measurably as the temperatures was increased from 25° to 50°C, corresponding to the range over which the small quantity of remaining solids dissolved. The overall change in σ_{LV} in the temperature range of interest for the dilute simulated waste was sufficiently small that little impact on wetting behavior is expected due to temperature.

Equilibrium Contact Angles: An attempt was made to determine the contact angle, θ, directly in simulated waste solutions as a function of the organic complexant concentrations of HEDTA and EDTA. Measurements were taken by injecting gas bubbles into the liquid waste, so that the bubbles were trapped on the underside of a sapphire substrate that was completely immersed in the liquid. The sapphire substrate was conditioned for several hours in the waste solution before taking contact angle measurements. Air was used in place of hydrogen or nitrous oxide.

Equilibrium contact angles were found to increase as the concentration of organic complexants was increased (as is shown in Figure 4). The surface adsorption of organic complexants is believed to be responsible for the increase in θ. By binding to solid surfaces through the carboxylate groups, the less-polar remainder of the molecule may project outward from the particle, thereby reducing the wettability of the solids and increasing the tendency for gas bubbles to adhere to solid particles. These results are consistent with earlier observations, where it was shown that stable, floating crusts could be formed by sparging inert gases into waste solutions containing various organic complexants, whereas waste solutions containing no organics did not form a stable crust (Bryan et al. 1992a and 1992b).

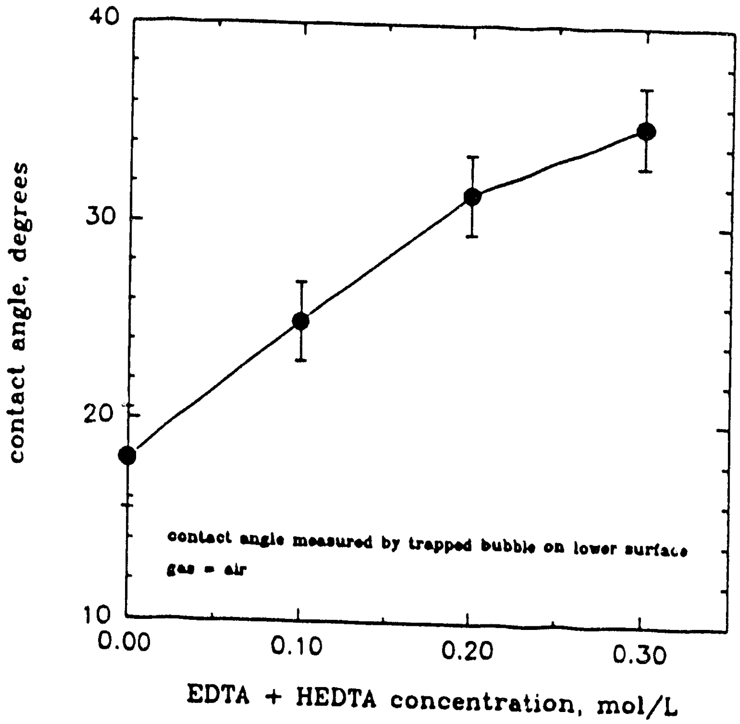

Figure 4 Equilibrium Contact Angles measured on a Model Aluminum Oxide (sapphire) Surface. Wettability is lowered by the presence of many organic waste components.

GAS GENERATION FROM SIMULATED WASTE

The extent to which the stoichiometry and rates of gas generation obtained in laboratory tests using simulated wastes agree with the behavior of actual waste is of considerable interest. The rates of gases evolved from Tank 101-SY have been observed to be in a ~1:1:1 mole ratio of N_2, H_2, and N_2O. (Ashby et al. 1992 and Erhart 1991) In contrast, nitrous oxide was by far the predominant degradation product in a number of laboratory studies, as reviewed by Ashby et al. (1992). We have found that gas generation rates and stoichiometry can be affected to a large degree by relatively small change in composition of the simulant.

Gas Production Resulting from Changes in Simulated Waste Formulation: Figure 5 is a plot of moles of gas (H_2, N_2, and N_2O) produced under thermal conditions for two simulated formulations, SY1-SIM-91A and SY1-SIM-92A (Table 1). Each of these formulations was treated in the same fashion by using the same total mass of reactants (20 g), the same reaction vessels, and same temperature and time of reaction (90°C, 5 d). The product gas compositions were determined by mass spectral analysis. The only differences between experiments are the differences in simulated waste formulations. The simulated waste SY1-SIM-92A produces gases in the (decreasing) order $N_2O > N_2 > H_2$, but the simulated waste SY1-SIM-91A generates product gases in the (decreasing) order $N_2 > N_2O > H_2$. The major differences between the two simulated wastes are the concentration of halides (chloride and fluoride) and transition metals.

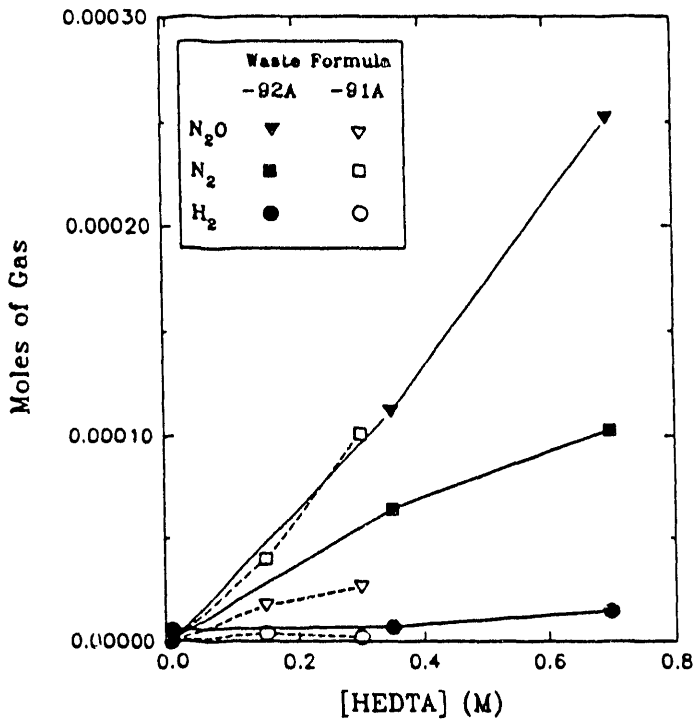

Figure 5 Comparison of Thermal Gaseous Products from Different Formulations (SY1-SIM-92A and SY1-SIM-91A)

Transition Metal Concentration Effects on Gas Production: The effect of changes in the transition metal concentration in simulated waste on gas generation was measured by using SY1-SIM-91A simulated waste as the base formulation. Transition metals were added in increasing amounts to a series of reaction vessels containing SY1-SIM-91A. The transition metals in this study were Cr, Cu, Fe, and Ni nitrate salts. These were used since they were showr to be present in chemically significant levels in Tank 101-SY. They are also the same as those included in simulated waste formula SY1-SIM-92A. The relative concentration of these metals was varied from 0 to 3 times that found in Tank 101-SY. This range of concentrations was chosen to bound the concentration of these metals in order to see the effect, if any the variation of these constituents would have on the simulated waste gas production.

The moles of gas produced as a function of the relative transition metal concentration added to the simulated waste formulation is depicted in Figure 6. The production of N_2O and N_2 drops quickly with increasing concentration of added transition metals to the formulation. The production of N_2O and N_2

is relatively constant at high concentrations of added transition metal salts. The hydrogen production is low throughout the entire concentration range of added metal salts.

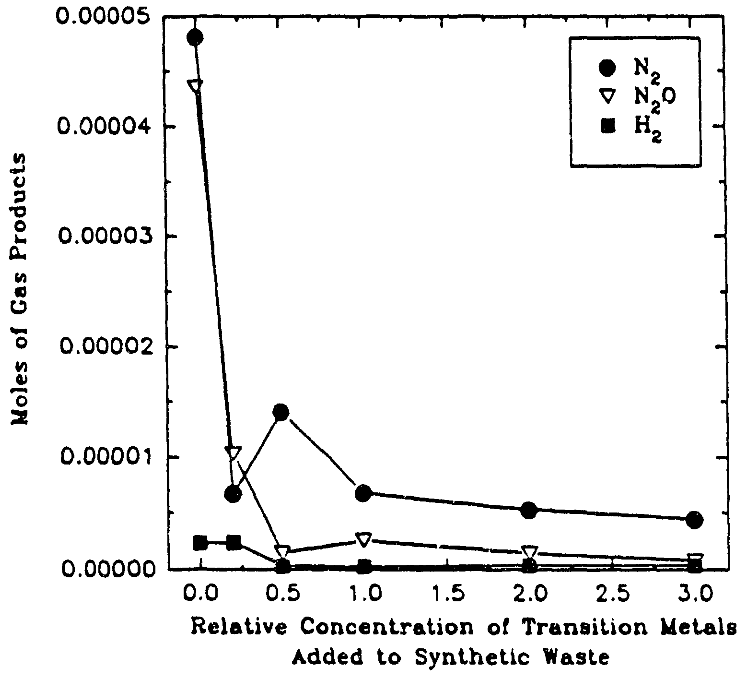

Figure 6 Moles of Gas Produced as a Function of Concentration of Transition Metals Added to Simulated Waste Formulation SY1-SIM-91A. The relative concentrations of metals are based on Tank 101-SY actual waste analyses.

The value of the N_2O to H_2 molar ratio for the gaseous products varies from approximately 20 for the simulant with no added transition metals to approximately 2 for the simulant with 3X transition metals added. The N_2O to H_2 ratio shows a general decrease with increasing transition metal concentration in the simulated waste formulation.

Chloride Concentration Effects on Gas Production: Chloride ions, a component in Tank 101-SY waste, appears to influence both the rate at which flammable gases are produced and the stoichiometry of those gases. Tests have been conducted using simulated wastes containing varying concentrations of sodium chloride to establish bounds for these effects.

The effect of changes in the chloride concentration in simulated waste on gas generation was measured by using SY1-SIM-91A simulated waste as the base formulation. Sodium chloride was added in increasing amounts to a series of reaction vessels containing SY1-SIM-91A. The NaCl concentration was varied from 0 to 2M in order to bound the known concentration of chloride (~ 0.5M) in Tank 101-SY.

The total amount of N_2O, N_2, and H_2 gas produced from these formulations (over a four week period) is shown in Figure 7 as a function of NaCl added to the simulated waste formulation. This figure indicates that the production of N_2O and N_2 are influenced a great deal by the change in the chloride concentration. The production of N_2O shows a maximum at approximately 0.5M chloride concentration in this simulated waste. This concentration is significant since it is approximately the concentration of chloride reported in Tank 101-SY. The production of N_2O drops off dramatically by increasing or decreasing the chloride concentration from this value. The effect of chloride addition on the H_2 production is not as pronounced as for the other gases.

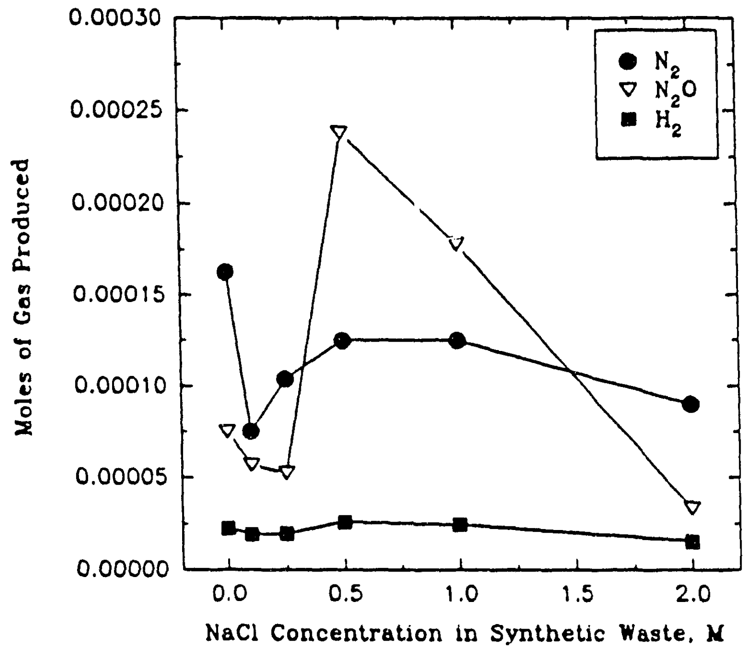

Figure 7 Moles of N_2O, H_2, and N_2 Gases Produced After Four Weeks Reaction Time in Synthetic Waste SY1-SIM-91A as a Function of Added NaCl.

CONCLUSIONS

There is close correlation between the measured properties of the simulated waste formulations and the convective slurry layer (the upper one-half) of Tank 101-SY. This was an unexpected result since the simulated waste formulations were based on tank analytical data from all zones of the tank. These data imply the simulant is a good match for the convective slurry layer of Tank 101-SY. It may not, however, be a good match for the nonconvecting layer of the tank, where there is concern about gas retention. The simulated waste formulations were prepared based on analytical data based on the average composition of Tank 101-SY. It would be predicted then, that the simulated waste should best match an average or composite sample from Tank 101-SY.

Liquid surface tension, supernate density, and equilibrium solid/liquid contact angles were each measured as a function of temperature and organic complexant concentration. These measurements were part of a study to determine how wetting phenomena affect gas retention in Tank 101-SY and how gas retention might be reduced or prevented. Surfactant addition may be a viable means to reduce the liquid surface tension, if a surfactant of appropriate chemical and radiation stability could be found. Equilibrium contact angles, measured by trapping gas bubbles on the bottom side of a flat alumina substrate, were found to increase substantially with the concentration of organic complexants in the waste. Complexant adsorption is believed to lower the wettability of the solids, thereby enhancing the tendency for gas bubbles to be retained in the waste.

Gas generation results are significant because they indicate that the fuel-oxidant ratio of the product gases can be greatly altered by subtle shifts in chloride, transition metal, or hydroxide concentration in the waste. This information is important in terms of changing the concentration of these reagents during mitigation schemes including dilution of the waste and organic destruction. On-going work is being conducted to determine the gas generation effects of other components of the waste matrix.

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