CRUST GROWTH AND GAS RETENTION IN SYNTHETIC HANFORD WASTE

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ABSTRACT

The focus of the work described here is to examine the principal contributing factors leading to slurry growth and gas retention within waste from a particular high-level waste tank on the Hanford Site. Laboratory studies of aged synthetic waste have shown that the waste retains gases in the form of bubble attachment to solid particles. This attachment phenomenon is related to the presence of organic constituents (HEDTA, EDTA, and citrate) added to the waste matrix. The mechanism for bubble attachment is related to the hydrophobic surface produced by the organic complexant. The formation of a stable gas bubble/solid interaction is believed to be responsible for crust flotation and gas retention in the synthetic waste used here.

INTRODUCTION

Out of 177 high-level waste storage tanks on the Hanford Site, 23 tanks have been placed on a safety watch list because the waste that they contain may produce flammable gases. One tank in particular, Tank 241-SY-101 (101-SY), has exhibited periodic releases of flammable gases at or near the flammable range since its initial filling in the late 1970s. Because of the possible consequences if the flammable gases were to ignite, this problem has been elevated to a priority safety concern by the U.S. Department of Energy (DOE). Currently, little is known about the chemistry regarding the production and retention of gases within this waste tank. To obtain information about the waste's chemistry, Pacific Northwest Laboratory (PNL) is conducting studies of the behavior of synthetic wastes that can be related to the chemistry of the actual waste. The information from these studies will be used to plan for short-term mitigation and long-term remediation of the tank waste.

The focus of this work is to examine the principal contributing factors leading to gas retention within the tank waste. Synthetic waste formulations have been produced based on actual, measured compositions of waste from Tank 241-SY-101. Laboratory studies using synthetic wastes have shown that gas generation occurs thermally at a significant level at current tank temperatures (1). Gas compositions include the same gases produced in actual tank waste, primarily N_2, N_2O, and H_2 (2), although in somewhat different relative amounts.

One possible mechanism of gas retention in the synthetic waste is by attachment of bubbles to solid particles. This attachment phenomenon is related to the presence of organic constituents (HEDTA, EDTA, and citrate) added to the waste matrix. The mechanism for bubble attachment is related to the hydrophobic surface produced by the organic complexant, as has been confirmed by increased contact angles observed for solid, gas, and liquid systems containing added organics. The formation of a stable gas bubble/solid interaction is believed to be responsible for crust flotation and gas retention in the synthetic waste. This paper discusses PNL's studies to determine how a crust forms and how gases are retained by the waste, and other related topics.

THEORY AND APPROACH

Mechanism of Gas Retention and Crust Formation

Flotation of solid particles having densities greater than the liquid phase in which they were originally immersed has been widely used by the mining industry. Solid particle buoyancy is gained by attachment of the particles to air bubbles. The tendency for particles to attach to air bubbles is largely controlled by the surface energy of the solid. The principles underlying mineral flotation technology provide some insight into the mechanism of crust formation in Tank 101-SY.

A solid particle immersed in a liquid will tend to become attached to an air bubble if the equilibrium contact angle between the solid and the liquid is greater than zero (or, at equilibrium, the solid is incompletely wetted by the liquid). The Young-Dupre' equation, Eq. 1 (3), describes expected trends in wetting behavior as a function of the interfacial tensions between the solid, liquid, and gas phases:

$$\cos\Theta = [\sigma_{SV}-\sigma_{SL}]/\sigma_{LV} \qquad \text{(Eq. 1)}$$

The contact angle, Θ, is measured between the solid and liquid phases. A value of $\Theta = 180°$ is indicative of completely wetted solids and no tendency for gas bubble retention, while a value of $\Theta = 180°$ is indicative of the absence of wetting and a great tendency for gas bubble retention. 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 contact angle between a gas, solid, and liquid interface is demonstrated in Fig. 1 for a surface that resists wetting and a surface that favors wetting. To minimize the surface energy of the system, a solid will seek a position at a liquid-gas interface such that the equilibrium contact angle Θ is achieved. Or, for any value of $\Theta > 0$, a stable position for a solid particle is at the liquid-gas interface.

Critical conditions for the flotation of solid particles in a less dense liquid phase have been calculated by Huh and Mason (3). Flotation is favored by a high value of the equilibrium contact angle , or an increasing degree of solid surface hydrophobicity. Flotation is diminished by high solid/liquid density ratios, large particle sizes, and decreases in the surface tension of the liquid phase.

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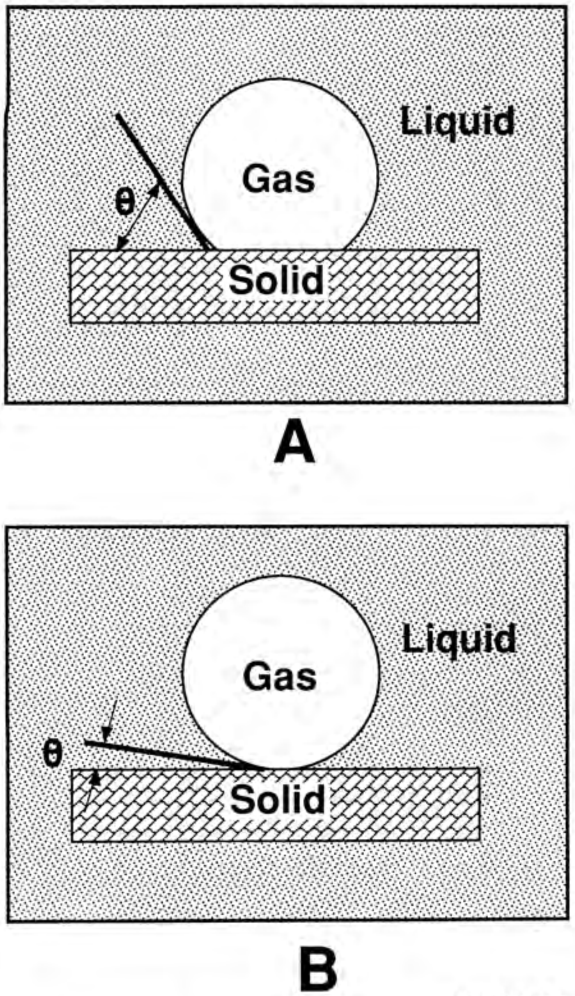

Fig. 1. Adsorption of organic waste components lowers the wettability of solids, and enhances gas bubble-particle adhesion. (A) A large contact angle is the result of reduced solids wettability with organics present. (B) Nearly complete wetting with organics absent results in a small equilibrium contact angle.

Fig. 2. Flotation of Polymethylmethacrylate (PMMA) Beads by Sparging with Nitrogen Gas: PMMA beads [density = 1.2g(cm^{-3})] in DI water before sparging with gas.

Fig. 3. The Flotation of PMMA beads by attachment of gas bubbles from a nitrogen sparge. The PMMA beads form a stable raft indefinitely after the cessation of the gas sparge.

Gas Retention and Solids Flotation Using PMMA Beads

Flotation of solid particles that are more dense than the liquid phase in which they are immersed is demonstrated quite simply in Figs. 2 and 3. Polymethylmethacrylate (PMMA) cylinders [typically 0.2-cm-diameter, 0.4-cm-length, density = 1.2 g(cm)$^{-3}$] were submerged in deionized water, as shown in Fig. 2. Although the equilibrium contact angle was not measured, it was clear that Θ was greater than zero because of the tendency of water droplets to form "beads" on the PMMA surfaces. The liquid was then sparged with nitrogen through a glass frit. As shown in Fig. 3, gas bubbles became attached to the surfaces of the PMMA beads, causing the solids to rise to the surface of the liquid.

Those PMMA beads that reached the surface were stable in that position indefinitely following the cessation of nitrogen sparging. However, those beads attached to nitrogen bubbles that were unable to reach the liquid-air interface were not indefinitely stable. Eventually, the nitrogen bubbles coalesced and were released to the atmosphere, and the PMMA beads, *no longer buoyant, sank to the bottom* of the beaker.

Gas Retention and Crust Flotation in Synthetic Waste

Flotation of precipitated solids by nitrogen sparging of Tank 101-SY synthetic wastes was also demonstrated, as shown in Figs. 4 and 5. Table I contains the details of the components and concentrations used in this recipe. This reference formulation was originally proposed by D. Herting of WHC. One solution, labeled the control in Figs. 4 and 5, contained only the inorganic components. Three other

TABLE I

Synthetic Waste Formulation

Component	mol/L, (M)
NaOH	2.3
$NaAlO_2$	2.2
$NaNO_3$	3.7
$NaNO_2$	3.2
Na_2CO_3	0.6
Organic	0.3

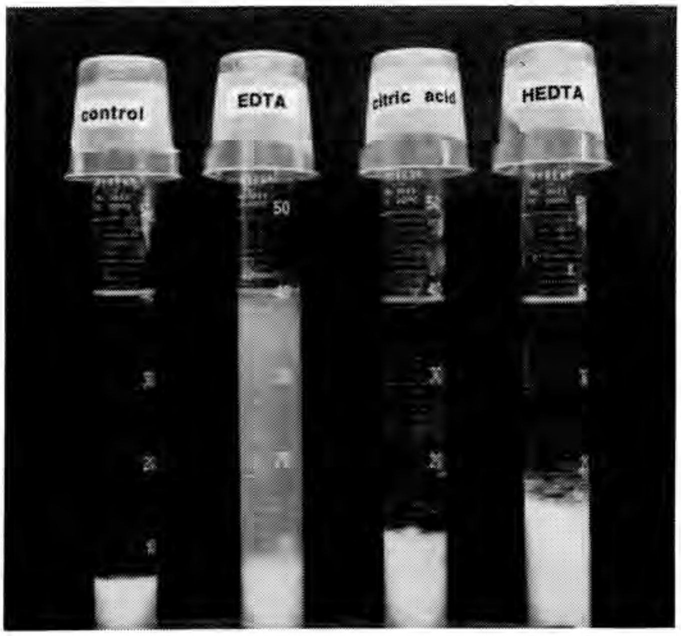

Fig. 4. Synthetic waste formulations before sparging with nitrogen gas.

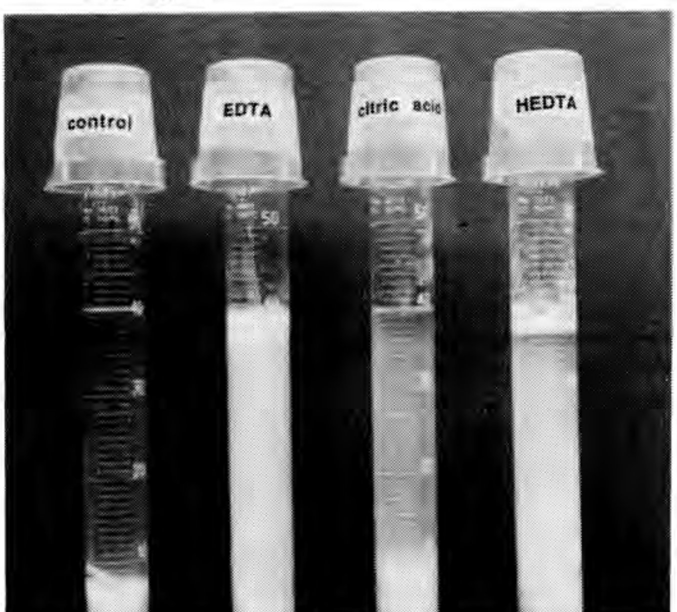

Fig. 5. Synthetic waste formulations 30 minutes after sparging with nitrogen gas.

solutions contained either EDTA, *citric acid, or HEDTA*, such that the final solution was 3.0 M in total organic carbon.

As is shown in Fig. 4, the apparent volume of solids prior to nitrogen sparging was greatest for the sample containing HEDTA and least for the control (containing no organic carbon). The control gave a relatively hard monolithic solid that could be broken up only with difficulty. The other three solutions yielded solids that were easily dispersed by stirring.

The four solutions were then sparged with nitrogen gas through a glass frit and allowed to stand at room temperature for 30 minutes. A considerable quantity of precipitated solids remained in suspension for the synthetic waste containing EDTA and HEDTA, as is shown in Fig. 5. Both of these samples additionally gave a stable crust composed of solid particles and adhering gas bubbles. Neither the control nor the sample containing citric acid yielded a floating crust. The phenomena of bubble attachment to solids is shown dramatically in Fig. 6, which shows several bubbles attached to a single particle in the organic-containing synthetic waste.

The believed role of organic constituents in the waste is to adsorb into the solid surfaces, rendering them more hydrophobic than the clean surfaces. This surface alteration enhances the tendency for gas bubbles to adhere to the solid particles, and may cause the solid particles to rise to the surface of the liquid. The exact nature of the solid-adsorbate bonds in strongly alkaline solutions is not known, but probably involves linkage through carboxylate and/or alcohol groups for EDTA and HEDTA. The situation is, of course, complicated by the decomposition of organic chelators into other fragments in the actual waste.

It is somewhat surprising to us that citric acid was ineffective in promoting crust growth in synthetic waste, given the presence of carboxylate and alcohol groups that should form surface adsorbate bonds. It was noted, however, that NO_x was evolved when synthetic wastes containing citric acid were concentrated by heating. When citric acid was added as a solid to a solution containing only the inorganic components at

Fig. 6. Light micrograph of synthetic waste showing the attachment of gas bubbles to solid particles.

80 - 100°C, NO_x was evolved vigorously, indicating extensive oxidation of the organic molecules. Thus, the finding that citric acid did not promote crust growth may be more a result of extensive decomposition under conditions of these experiments than the ability of the citric acid to increase the hydrophobicity of solid particles through adsorption.

Surface Wetting Studies

Surface *tension and* wetting phenomena in Tank 101-SY synthetic wastes were examined as part of an ongoing study to determine how gases are retained in the wastes. 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 manipulating wetting behavior, it may be possible to allow the gases produced in the wastes to be vented continuously rather than go through buildup and release cycles.

As an indicator of the forces of interaction between solids and gas bubbles, minimization of the wetting angle is expected to be of benefit in Tank 101-SY. If the wetting angle can be minimized, it may be possible to prevent or eliminate gas retention in the waste. In consideration of Eq. 1, this could be accomplished by lowering the value of either σ_{LV} or σ_{SL}. The magnitude of σ_{SV} is largely fixed by the identity of solid phases that are present, and cannot be altered substantially in the temperature range of interest. Surfactants are commonly used to lower σ_{LV} in industrial applications, whereas the term σ_{SL} is sensitive to the surface adsorption of small quantities of compounds from the liquid phase. The following subsections describe preliminary efforts to assess the terms of the Young-Dupre' equation and implications of wetting phenomena for mitigation of the gas retention problem in Tank 101-SY.

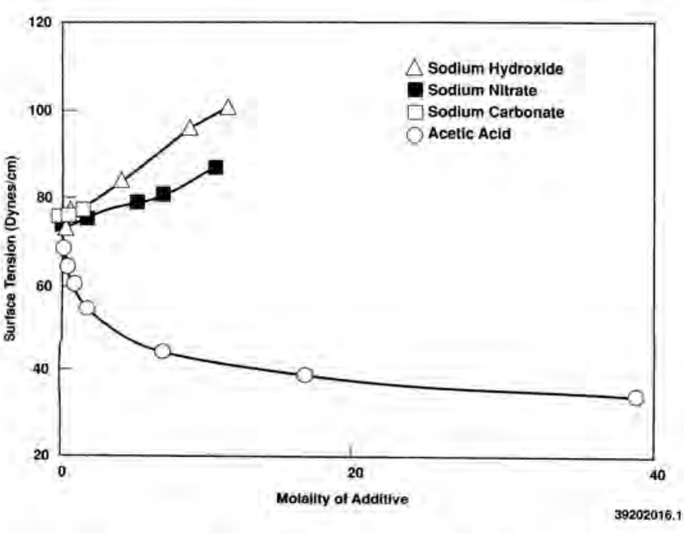

Fig. 7. Literature Surface-Tension Data for Sodium Carbonate, □; Sodium Hydroxide, Δ; Sodium Nitrate, ■; and Acetic Acid, O.

Liquid Surface Tension

The term σ_{LV}, the liquid/vapor surface tension (usually referred to as the liquid surface tension and 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, organic compounds such as acetic acid tend to decrease the magnitude of the surface tension (4). Trends in σ_{LV} for several solutes versus concentration are given in Fig. 7. In consideration of the relatively high concentrations of inorganic salts in Tank 101-SY compared with those of organic components, one would expect σ_{LV} for the waste solutions to be much greater than that of water (72 dynes/cm at 25°C).

Surface tension values for a dilute synthetic waste solution were obtained as a function of temperature. The waste com-

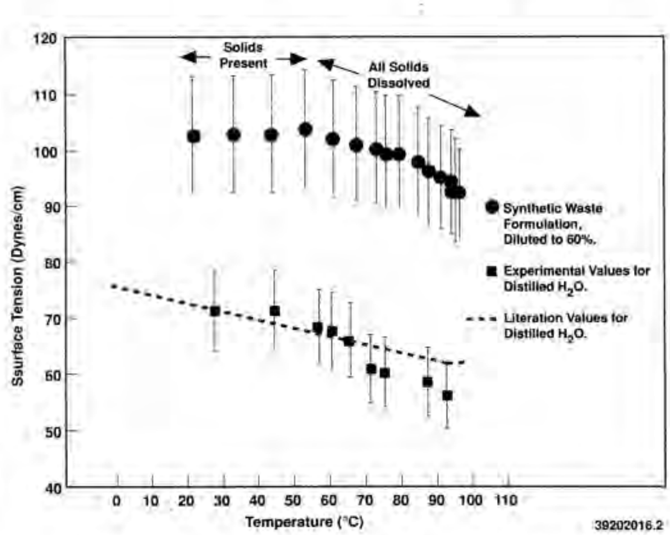

Fig. 8. Surface-Tension Data Versus Temperature for Synthetic Waste Formulation, Diluted to 60%, ●; Experimental Values for Distilled Water, ■; and Literature Values for Distilled Water, ...

position was diluted to 60% to dissolve essentially all the solids at room temperature (a small quantity remained, however). This was done so that the concentration of dissolved solids did not change appreciably as the waste was heated.

Results, determined using the capillary rise method, are given in Fig. 8, along with literature results for water. Surface tension did not change measurably versus temperature from 25-50°C, corresponding to the range over which the remaining solids dissolved. Above 50°C, a slow decrease with increased temperature could be seen. The overall change in σ_{LV} in the temperature range of interest *for the dilute synthetic waste* was sufficiently small that little impact on wetting behavior is expected due to that term.

Similar measurements of σ_{LV} were made for undiluted synthetic wastes as a function of temperature by the capillary rise method. The results were irreproducible, presumably because rapid cooling within the capillary led to precipitation reactions. Because considerably higher concentrations of dissolved inorganic salts are present in undiluted wastes, surface tensions should be higher than shown in Fig. 8 for dilute

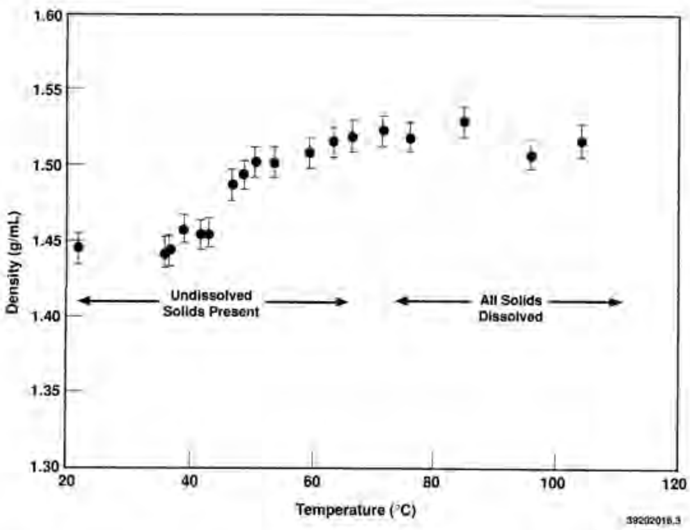

Fig. 9. Density changes in synthetic waste as a function of temperature.

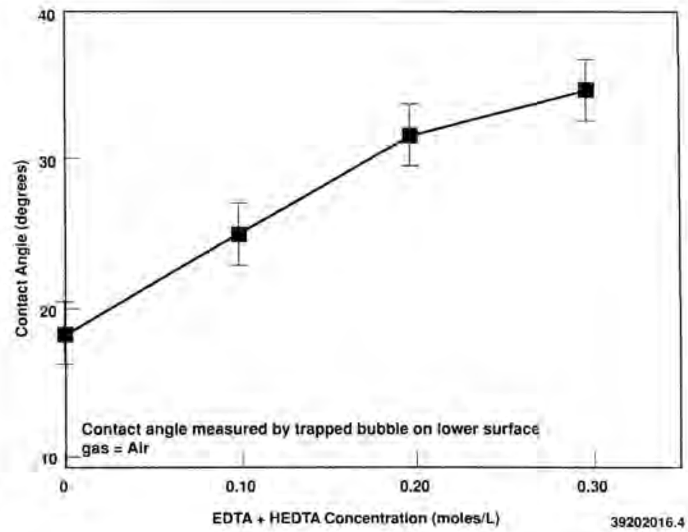

Fig. 10. Contact Angle on Sapphire Versus Complexant Concentration in Synthetic Waste.

wastes. High values of σ_{LV} favor lower solids wettability and enhanced gas bubble retention.

Liquid densities were measured as a function of temperature for synthetic wastes and are given in Fig. 9. Densities are needed to calculate the liquid surface tension values from capillary rise measurements. Organic components were excluded for the waste solutions corresponding to Fig. 9 to minimize measurement error due to gas bubble formation, particularly at the highest temperatures.

Liquid densities were found to increase as a function of temperature from approximately 40-80°C because of increased dissolution of solids. No clear trends were found from 20-40°C or for 80-110°C. By 80°C, all solids appeared to be dissolved, in agreement with trends in the density. Because surface tension values rise with the concentration of dissolved inorganic salts, as shown in Fig. 7, trends in surface tension versus temperature for undiluted wastes are expected to follow the trends in density versus temperature shown in Fig. 9.

In terms of mitigating Tank 101-SY, one can conclude that heating of the bottom of the waste tank is not a viable method to induce circulation within the wastes. Rather, waste layers should be stabilized with heating.

Equilibrium Contact Angles

Contact angles, Θ, were measured directly in synthetic waste solutions as a function of the concentration of organic complexant HEDTA and EDTA. Measurements were made by injecting gas bubbles into the liquid waste, such that the bubbles were trapped on the underside of a sapphire substrate that was completely immersed in the liquid. This approach is considered superior to the usual method of placing a liquid drop onto the surface of a solid in air (3).

Contact angles were determined manually using a goniometer. Sapphire (Al_2O_3) in the form of a 1-in.-dia. polished disk was intended to simulate the surface of sodium aluminate. The sapphire substrate was conditioned for several hours in the waste solution before measuring the contact angles. Given that the crusts in the actual tank and in the synthetic waste studies have been found to contain a mixture of solids in rough proportion to their abundance in the wastes, the identity of the solid phase may not be critically important. Air was used in the place of hydrogen or nitrous oxide. Because of the dilute nature of the gas compared to the liquid or solid phases, it is not anticipated that the identity of the gas will affect solid/liquid equilibrium contact angles. Ongoing studies will verify this expectation.

Equilibrium contact angles were seen to increase as the concentration of organic complexants was increased, as shown in Fig. 10. The surface adsorption of organic complexants is believed to be responsible for the increase inΘ. By binding the solid surfaces through the polar end of the molecules, less polar groups may project outwards from the particle, thereby reducing the wettability of the solids and increasing the tendency for gas bubbles to adhere to the solid particles. The term σ_{SL} should be the most affected by the surface absorption of organic compounds.

Crust formation and gas retention in Tank 101-SY synthetic wastes is caused by the adherence of gas bubbles to the surface of solid precipitates. These solids were made partially hydrophobic by the adsorption of organic complexants. Gas bubbles adhered to the solid particulates in an attempt to establish an equilibrium contact angle between the solid and the liquid. Once buoyed to the surface, and through the contact of a gas bubble with several particles (and vice versa), a stable crust can be formed.

CONCLUSION

Our studies support the hypothesis that gas retention and crust formation in Tank 241-SY-101 could be caused by bubble attachment to hydrophobic solid particles. The hydrophobic particles result from adsorption of organic chelators on their surface. Gas retention and bubble attachment is governed by the Young-Dupre' relationship, which relates surface wetting to interfacial tensions between the solid, liquid, and gas phases.

Conditions required to promote crust growth and flotation as well as gas retention in Hanford's radioactive waste tank 241-SY-101 have been demonstrated to exist in a *synthetic tank* waste. These conditions are (A) solid phases present to which gas bubbles can adhere. The waste simulants are all saturated with respect to solutes, and solid phases are present; (B) an increased hydrophobic surface on the solids to produce a positive contact angle for bubble attachment. It was shown that by adding organics to the synthetic wastes, a hydrophobic surface (equilibrium contact angle >0) was formed on the solids. The contact angle increased with increasing organic complexant concentration in the synthetic waste.

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