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Mechanics of Bubbles in Sludges and Slurries

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Research Objective

This project is focusing on key issues associated with the flammable gas safety hazard and its role in safe storage and in future waste operations such as salt-well pumping, waste transfers, and sluicing and retrieval of tank waste. The purpose of this project is to develop a basic understanding of how single bubbles (of flammable gases) behave in representative waste simulants and then develop a framework for predicting macroscopic full-tank behavior from the underlying single-bubble behavior.

The specific objectives of this research are as follows:

1. quantitatively describe the interaction of bubbles with waste materials (both sludges and slurries) to understand the physical mechanisms by which barometric pressure changes give rise to a hysteresis between level and pressure
2. develop improved methods for estimating retained gas by properly accounting for the interactions of bubbles with the waste
3. determine how to estimate waste physical properties from the observed hysteresis and the limitations of these estimates
4. determine how barometric pressure fluctuations induce slow upward migration and release of gas bubbles.

Problem Statement

Previous studies have established that the waste level of Hanford tanks responds to barometric pressure changes, the compressibility of retained bubbles accounts for the level changes, and the volume of retained gas can be determined from the measured waste level and barometric pressure changes. However, interactions between the gas bubbles and rheologically complex waste cause inaccurate retained gas estimates and are not well understood. Because the retained gas is typically a flammable mixture of hydrogen, ammonia, and nitrous oxide, accurate determination of the retained gas volume is a critical component for establishing the safety hazard of the tanks. Accurate estimates of retained gas from level/pressure data are highly desirable because direct in situ measurements are very expensive in an individual tank and impossible in many single-shell tanks. The elucidation of the bubble waste interactions will have a direct influence on improving the accuracy of gas volume estimates, provide for more accurate models for estimating waste properties from level/pressure data, and should quantify the effect of barometric pressure fluctuations on the slow rise and release of bubbles. The results of this research will support critical operations at the Hanford Site associated with the flammable gas safety hazard and future waste operations such as salt-well pumping, waste transfers, and sluicing/retrieval.

Research Progress

This research program, which began in FY 1998, is separated into four related activities on bubble behavior, as shown schematically in [Figure 1](#). Modeling studies on continuum materials (sludges) are being conducted from both the solid mechanics and fluid mechanics viewpoints. The solid mechanics

Figure 1. Interrelationship of the Individual Research Problems with the Overall Program Objectives

models are being developed by Terrones at Pacific Northwest National Laboratory (PNNL) and the fluid mechanics solution approach is being developed by Denn and Muller at the University of California at Berkeley. The modeling studies of bubble behavior in particulate materials (slurries) are being conducted by Rossen at the University of Texas at Austin. Finally, experimental studies on both sludges and slurries are being conducted by Gauglitz at PNNL. Bubbles retained in sludges and slurries have significantly different behavior, thus it is appropriate to approach modeling these materials from different viewpoints, though the experimental studies are more closely related. Progress has been made in each of these activities and is summarized in the following sections.

Experimental Studies on Single and Multiple Bubbles

The objective of this research activity is to quantify the effects of small pressure changes on bubble volumes in waste simulants. These experiments investigate both individual bubbles in a small apparatus and multiple bubbles in a larger apparatus. In this section, we describe the apparatus and simulants that we have investigated and some results that highlight the significant new findings.

The test stand for examining single bubbles and multiple bubbles is depicted in [Figure 2](#). For the single-bubble experiments, centrifuge tubes act as the vessel for the experiment and we use a centrifuge to remove extraneous bubbles from the simulant before testing. In the multi-bubble case, bubbly simulant is loaded into larger tanks. In both cases, a supernatant fluid of known density is used to fill the apparatus to the desired level where we can most accurately measure level changes. The apparatus is attached to a pressure regulation system to induce changes in bubble volume and hence level. In general, step changes or sinusoidal cycles of pressure are made and the level changes are tracked. For single bubbles, cameras are used to image bubble shape and changes and the meniscus in a capillary tube that stands over the vessel. The capillary magnifies level changes in the vessel itself. The position of the meniscus is determined with image analysis software (LabVIEW) to obtain the level as a function of pressure

Figure 2. Apparatus for Measuring dl/dp on Single and Multiple Bubbles

automatically. For multiple-bubble experiments, an Enraf (854 ATG) gauge is used to obtain the level. This gauge is identical to the level gauge used in the Hanford tanks. All measurements of pressure and level are automatically recorded using LabVIEW software.

Experiments thus far have been challenging. Data on single bubbles is difficult to obtain because the simulant must be transparent, yet still have properties (shear strength and Young's modulus) that are close to tank waste. A variety of particulate-liquid systems have been employed. There are two systems that show promise, but each has limitations. The first system is carboxyl polymethylene (Carbopol)–water, which is a polymer solution rather than two-phase, and the second is a silica-oil system. The Carbopol solutions are crystal clear and have the desired yielding behavior (50 to 2000 Pa strength), but the Young's modulus is low, which results in accentuated elastic behavior. The oil-silica system has all the desirable properties, but air is quite soluble in the mineral oil that is needed to obtain a clear dispersion. This results in bubble volume changes from gas within the bubble dissolving, and this complicates data analysis. More detail on these phenomena will be discussed below. Data have been collected on both systems, and the search continues for a water-silica system (low gas solubility) that will have good yielding properties and a high Young's modulus.

Figure 3 shows the response of a water-based simulant and an oil-based simulant to a step change increase in pressure. Notice that the level in the water-based system steps down and remains constant while the level in the oil-based system steps down and slowly creeps lower. When the pressure is raised above the oil-based simulant, the pressure in the gas bubbles rise. Because the solubility of air is substantial in mineral oil, some of the gas within the bubble partitions into the liquid over time. In general, hydrogen has a low solubility in the actual tank waste, and partitioning of hydrogen across the surface of bubbles is not expected. However, many of the tanks have significant amounts of trapped ammonia gas, and ammonia is soluble in tank waste. Therefore, we believe the oil-based silica simulant are valuable for examining these phenomena further.

Figure 3. Step Changes in Pressure Show the Effects of Mass Transfer Across the Bubble Surface

Figure 4 shows normalized pressure and level (dL/dP) data from single- and multi-bubble experiments with the calculation for an ideal gas. Both data sets show hysteresis, but the corners of the hysteresis loop are rounded versus the square dL/dP profiles apparent in many actual tank data. The model developed under this program would predict that the reason for such smoothing is a lower Young's modulus of elasticity. The difference in the degree of hysteresis between the single- and multiple-bubble data is unexpected. Both sets of data were taken on a simulant with a shear strength of ~ 1000 Pa (4% Carbopol-water). At this time we cannot explain the discrepancy, but possible factors include relaxation of residual stresses and to a lesser degree bubble-bubble interactions.

Figure 4. Pressure Cycles Representative of Natural Weather Events Show Hysteresis in Pressure and Level Measurements

Solid Mechanics Modeling

The objective of this research activity is to model the effect of small pressure changes on bubble volumes. In this section, we summarize progress on developing this model and comment on the significance of the new findings. During last year, a general procedure was developed to find the stress and strain fields produced by periodic pressure variations (of frequency ω) for an internally or externally pressurized single bubble embedded in an elastic-plastic medium. With this procedure, analytic expressions can be obtained for the bubble radii as a function of applied pressure. Driving pressure amplitudes, p_A , are chosen so that finite plastic deformations occur during the expansion or the compression of the bubble. This choice of pressure amplitude leads to the development of residual stresses after each

pressure sweep. These stresses are taken into account to determine the stress field at the subsequent sweep. In the present parametric study, the following initial conditions (at $t = 0$) were used

$$\varepsilon_r(r; 0) = \varepsilon_\theta(r; 0) = 0, \quad \sigma_r(r; 0) = \sigma_\theta(r; 0) = -p_o$$

where, ε_r and ε_θ are the radial and angular strains, σ_r and σ_θ are the radial and angular stresses, and p_o is the reference pressure. Boundary conditions for an infinite as well as a finite medium were used. Solutions of the elastic-plastic equations were found by using the boundary conditions (for $t > 0$) shown in Table 1. Numerous cases have been computed for a series of different sets of parameters, including experimental data. A parameter set includes the yield stress of the material, Poisson ration, Young's modulus of elasticity, pressure amplitude, initial bubble radius, outer boundary radius, solubility of the gas in the medium, and reference pressure.

Table 1. Boundary Conditions for Parametric Study

	Radial Stress at the Bubble Radius	Radial Stress at the Outermost Boundary
1	$\sigma_r(a(t)) = -p_o - p_A \sin(\omega t)$	$\sigma_r(\infty) = -p_o$
2	$\sigma_r(a(t)) = -p_o - p_A \sin(\omega t)$	$\sigma_r(b(t)) = -p_o$
3	$\sigma_r(a(t)) = -p_o \left(\frac{a_o}{a(t)} \right)^3$	$\sigma_r(\infty) = -p_o - p_A \sin(\omega t)$
4	$\sigma_r(a(t)) = -p_o \left(\frac{a_o}{a(t)} \right)^3$	$\sigma_r(\infty) = -p_o - p_A \sin(\omega t) $
5	$\sigma_r(a(t)) = -p_o \left(\frac{a_o}{a(t)} \right)^3$	$\sigma_r(b(t)) = -p_o - p_A \sin(\omega t)$
6	$\sigma_r(a(t)) = -p_o \frac{a_o^3 + \text{SRT}(b_o^3 - a_o^3)}{a(t)^3 + \text{SRT}(b(t)^3 - a(t)^3)}$	$\sigma_r(b(t)) = -p_o - p_A \sin(\omega t)$

In Table 1, $a(t)$ is the bubble radius as a function of time (a_o at $t = 0$), and $b(t)$ is the outer radius of the spherical medium (b_o at $t = 0$). When the outer boundary is finite, the number of equations for the elastic and plastic deformations is twice that of infinite media. At each pressure sweep, the expressions for these deformations (elastic and plastic) are obtained analytically and solved numerically because they involve transcendental functions. Boundary conditions 1 and 2 correspond to an internally pressurized bubble in which the amount of gas inside the bubble would be continually changing to maintain a periodic pressure cycle. Although these conditions are not realistic in modeling bubbles inside sludge, they were used to generalize the solution of the elastic-plastic equations for an arbitrary number of pressure cycles (these conditions reduce the algebra considerably). Conditions 3 to 5 correspond to realistic boundary conditions because the internal bubble pressure is implicitly coupled to the bubble radius and the pressure fluctuations are externally applied to the medium. It was assumed the bubbles contain an ideal gas (R is the universal gas constant) and that the compression/expansion of the bubble is isothermal (at temperature T). Boundary condition 6 is a generalization of conditions 3 to 5 to include the effect of gas solubility in the elastic-plastic medium. Under the assumption of thermodynamic equilibrium, this condition is

derived by equating the number of moles of gas inside the bubble and in the medium at $t = 0$ to that at any other time. The product of the solubility coefficient S (in mol/bar/m³) and the bubble gas pressure gives C the gas concentration inside the bubble.

In the present study, the effects that the parameters have on bubble deformations have been studied. Interesting and new topologies for the bubble radius as a function of pressure have been observed for different combinations of parameters and boundary conditions. As an example, the effect of the solubility S on an expansion-compression sweep is shown in Figure 5. This parameter has a significant influence on the plastic deformations and thus the bubble radius.

The current model is significantly more rigorous than previous studies. This more careful analysis has resulted in two significant new results. First, the rounded corners of the pressure level hysteresis loops, as was mentioned in the experimental section above, results from elastic behavior and are directly associated with the Young's modulus of the simulant. Second, our estimate of material strength from level-pressure hysteresis is about 10-fold smaller than previous calculations that neglected residual stresses and did not have a rigorous inclusion of elastic and plastic regions.

Fluid Mechanics Modeling on Continuum Materials and Rheology of Simulated Waste Materials

The slurries in the Hanford storage tanks are complex fluids that exhibit a yield stress and most likely deform elastically below the yield stress. We are studying the behavior of bubbles in these slurries under the influence of gravity and changing barometric pressure through a computational and theoretical effort. Specifically, we are interested in how multiple bubbles suspended in a yield-stress fluid interact, coalesce, and move. The issues involved are intuitively clear: an expanding single bubble strains the surrounding fluid to a point where the yield stress is exceeded, the fluid structure within that yielded region collapses,

Figure 5. Effect of Solubility on Plastic Deformation ($\rho_0 = 1$ atm, $f_{\max} = -10$, $\sigma_y = 500$ Pa, $E = 80$ kPa, $b_0 = 10a_0$, $SRT = 0.01$)

the fluid around the bubble flows but remains surrounded by a region that continues to deform elastically. The yielded region will continue to grow in size as the bubble grows. In an array of bubbles, the yielded regions will interact. How this interaction occurs and what happens when the yielded regions intersect is the heart of the problem. When there is a fully connected yielded region, bubbles can move about, coalesce, and rise.

We chose to begin our study of the flow of fluids exhibiting a yield stress with squeeze flow, or flow between converging planes, which contains some of the same issues regarding singularities and unyielded regions as we expect to find with flow around submerged bubbles. Numerical studies using the commercial finite-element code POLYFLOW gave results consistent with those published by O'Donovan and Tanner (1984). We encountered numerical problems with the commercial code, however, when the simulation was extended to the unbounded flow around a rigid sphere. We then focused on the development of a specialized finite-element code to deal specifically with the Bingham plastic.

Bingham plastics pose an interesting computational problem because of a discontinuity in the stress-deformation rate constitutive relation at the yield stress. The conventional computational fluid mechanics approach is to introduce a smooth "regularized" constitutive relation which converges to the analytical Bingham material when a regularization parameter becomes infinite. This is the approach employed in POLYFLOW and in our own finite-element code. From the point of view of understanding the mechanics of the fluid around a submerged bubble, we are most interested in determining which regions are yielded (and thus act like viscous liquids) and which regions are unyielded (and thus act as solids). Our method of determining the numerical solution is to solve the regularized equations and to gradually increase the regularization parameter until convergence is attained in the flow field. The method has been validated in pipe flow and squeeze flow.

Flow around a rigid sphere captures many of the relevant features of flow past a bubble, without adding the complexity of the mobile interface; the flow requires approximation of an unbounded domain and the presence of a yielded region surrounding the sphere. Moreover, some prior numerical work exists for this problem (Beris et al. 1985, Blackery and Mitsoulis 1997). One of the issues of concern to us is the effect of a finite computational regime on the solution of the unbounded problem. In the work of Blackery and Mitsoulis (1997), for example, we see an effect of altering the radius of an enclosing cylinder (i.e., the extent of the computational boundary) even when the apparent yielded region does not reach this boundary. Physically, this cannot be correct, because the unyielded region should, in principle, act as a rigid solid and thus make the presence of the outer boundary irrelevant. We seek to determine why this discrepancy exists and whether the general method used by Blackery and Mitsoulis (1997) (which closely parallels our current method) is equivalent to the free boundary problem solved by Beris et al. (1985).

We are now applying our code to flow around a submerged rigid sphere. We are able to obtain solutions that show unyielded regions near the sphere surface and at a distance from the sphere, but the outer yield surface is sensitive to the choice of the regularization parameter, and it is not clear that it is converging. We have identified several possible sources of this problem, including the proper criterion to use for convergence and the relative tradeoff between convergence of the continuity (mass balance) and momentum (velocity and stress) equations. In addition, we are exploring issues associated with roundoff error and the possible need for selective mesh refinement.

Modeling of Bubbles in Particulate Materials (Slurries)

We are investigating the mechanics of bubble movement in representative particulate waste layer (slurry) in a Hanford tank using a one-dimensional biconical-pore network model. The goal of this work is to determine the effective compressibility of the gas in the slurry. With this information, one could

determine the volume of gas in the slurry from changes in waste level upon fluctuations in barometric pressure. The compressibility of the gas depends on its pressure, which is the sum of barometric pressure (known as a function of time), hydrostatic pressure from the liquid in the tank (also known), and capillary pressure in the porous medium formed by the slurry. Accordingly, determining gas compressibility requires determining the average capillary pressure of the population of bubbles responding to gas generation and changes in barometric pressure over time.

Three time scales are involved in the process of gas accumulation and response to barometric pressure. Over a period of months or years chemical reactions in the liquid create volatile components that diffuse to and accumulate in the bubbles. During this period, bubble mass and volume increase slowly at fixed liquid pressure. This process determines the initial states of bubbles when barometric pressure changes. On a shorter time scale of hours, bubble volume responds to changes in barometric pressure at fixed mass. It is on this time scale that effective compressibility is observed. On a still-shorter time scale, of seconds or less, interfaces advance or retreat impulsively, driven by capillary forces. These jumps occur at fixed barometric pressure and bubble mass. Impulsive jumps occur from pore throat to (near) pore throat for expanding bubbles, whether due to accumulation of mass over a period of months or to a short-term decrease in barometric pressure. In contrast, interfaces jump from pore body to pore body during pressure increases.

These jumps are crucial to the effective compressibility of gas in the slurry for two reasons. First, because these jumps have occurred during the slow growth of bubbles over months, most bubbles are lodged at pore throats. In particular, for large bubbles occupying many pores, expanding bubbles jump from one pore throat nearly to the next pore throat. As a result, the population of bubbles present as barometric pressure changes is biased toward bubbles poised in pore throats, ready to jump again if pressure decreases. However, these same bubbles do *not* jump backwards if pressure increases, until their interfaces first retreat to pore bodies.

Second, the outward jumps of interfaces as pressure decreases implies 1) an infinite compressibility for individual bubbles at the moment of the jump and 2) a comparatively large effective compressibility for a population of bubbles that includes a few that do jump and many that do not. On the other hand, upon an increase in pressure, the effective compressibility is small until interfaces retreat to pore bodies. This implies a significantly higher effective compressibility for a population of bubbles upon a pressure decrease than upon a pressure increase.

Our model can fit tank data with level-pressure hysteresis from the Hanford Site such as shown in [Figure 6](#) (Whitney et al. 1996). One might idealize the trend of these data as a linear increase in tank level during the initial decrease in pressure, no change at first in tank level upon an increase in pressure, and thereafter a linear drop in tank level, with the same slope as for the initial increase in tank level. Fitting these data requires that bubbles be long, occupying many pores. Unfortunately, it is impossible to determine capillary pressure directly from these data. That is, one can fit this trend with either narrow pores (high capillary pressure) or wider pores (lower capillary pressure) depending on pore geometry. One can also fit the data with pores modeled as smooth cylindrical tubes, if contact-angle hysteresis is introduced into the model. Further study is needed to resolve the apparent indeterminacy of capillary pressure to determine gas compressibility from tank data. Independent data on pore geometry and contact-angle hysteresis could resolve this problem. It is also possible that a more sophisticated analysis of tank-level data might identify subtle features that could be used to fit the capillary pressure unambiguously. This is indeed an objective for the coming year.

Figure 6. Variation of Tank Waste Level with Changes in Barometric Pressure (from Whitney et al. 1996)

Insights from other research on tank waste may provide the independent information on pore geometry needed to identify gas compressibility unambiguously. We will work with other groups involved in research on the slurry to provide this information. In addition, we will analyze the pressure-level data more completely, looking for features with which we can fit the capillary pressure with less ambiguity than the data in Figure 6.

Two important factors not accounted for here alter the initial distribution of bubbles that then respond to changes in barometric pressure. First, bubbles grow over a period of months or years, not at constant barometric pressure but with barometric pressure fluctuating over the period of bubble growth. This factor can be introduced into the model of bubble growth. Second, bubble growth depends on diffusion, which, in turn, depends on chemical potential and thereby on bubble pressure. Thus bubbles pushing into pore throats with relatively high capillary pressure grow more slowly than bubbles with interfaces farther from the throats. This would tend to bias the distribution of bubbles more toward more bubbles in pore throats and thereby toward higher effective compressibility for the population as a whole. We will also introduce insights from the study of growth of gas bubbles in oil reservoirs under primary production.

A three-dimensional (3D) pore network differs from the 1D biconical pore network assumed here, especially in the amount of liquid stored in the crevices and corners of pore bodies occupied by gas bubbles. This reservoir of liquid affects the jumps bubbles make and thus the effective compressibility of gas in the bubbles. We will test the sensitivity of the model to geometric factors to make it reflect 3D pore-network geometry more accurately.

Planned Activities

From an overall viewpoint we are midway through the second year of this project and are ready to shift to comparing experimental and modeling results from the initial focus of developing the computational frameworks and experimental apparatuses and methods. We are planning to complete the main

experimental studies of bubble expansion and compression toward the end of this year and the first part of the third year and will also be making detailed comparisons between experimental and modeling results during this period. Towards the end of this year, as planned, we also expect to start our experimental study on the mechanisms of slow bubble rise. This topic continues to be a crucial, but yet unexplained, issue in understanding gas migration in the actual waste tanks. We still expect that much of the third year will be devoted to reconciling the differences between theory and experiment, which will likely require additional experiments and numerical simulations.

References

Beris AN, JA Tsamopoulos, RC Armstrong, and RA Brown. 1985. "Creeping motion of a sphere through a Bingham plastic." *J. Fluid Mech.* 158:219-244.

Blackery J and E Mitsoulis. 1997. "Creeping motion of a sphere in tubes filled with a Bingham plastic material." *J. Non-Newtonian Fluid Mech.* 70:59-77.

O'Donovan EJ and RI Tanner. 1984. "Numerical study of the Bingham squeeze film problem." *J. Non-Newtonian Fluid Mech.* 15:75-83.

Whitney PD, PA Meyer, NE Wilkins, NE Miller, F Gao, and AG Wood. 1996. "Flammable gas data evaluation progress report." Pacific Northwest National Laboratory, Richland, Washington.

Publications

Denn MM and G Marrucci. "Squeeze flow between finite plates." *J. Non-Newtonian Fluid Mechanics* (submitted).

Kam SI and WR Rossen. "Anomalous capillary pressure, stress and stability of solids-coated bubbles." *J. Colloid Interface Sci.* (in press).

Kam SI. 1998. "Interactions between bubbles and solids: Three applications." Department of Petroleum and Geosystems Engineering, The University of Texas at Austin.

Presentations

Gauglitz PA, G Terrones, CL Aardahl, DP Mendoza, and LA Mahoney. 1999. "Mechanics of bubbles in sludges and slurries: Experimental studies and solid mechanics modeling results." Engineering Foundation Conference on Rheology in the Minerals Industry II, Oahu, Hawaii, March 14-19.

Gauglitz PA, G Terrones, DP Mendoza, CL Aardahl, MM Denn, SJ Muller, and WR Rossen. January 1999. "Mechanics of bubbles in sludges and slurries." Presented to Hanford Site Technology Coordinating Group - Tank Subgroup, Richland, Washington.

Gauglitz PA, G Terrones, DP Mendoza, MM Denn, SJ Muller, and WR Rossen. June 1998. "Mechanics of bubbles in sludges and slurries: Initial progress." Hanford Technical Exchange, Richland, Washington.

Web Site Address

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