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### Parametric Effects of Anti-foam Composition, Simulant Properties and Noble Metals on the Gas Holdup and Release of a Non-Newtonian Waste Slurry Simulant

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#### ABSTRACT

Gas holdup tests were performed in bench-scale and small-scale mechanically-agitated mixing systems at the Savannah River National Laboratory (SRNL) for a simulant of waste from the Hanford Tank 241-AZ-101. These featured additions of DOW Corning Q2-3183A anti-foam agent. Results indicated that this anti-foam agent (AFA) increased gas holdup in the waste simulant by about a factor of four and, counter-intuitively, that the holdup increased as the non-newtonian simulant shear strength decreased (apparent viscosity decreased). Such results raised the potential of increased flammable gas retention in Hanford Waste Treatment and Immobilization Plant (WTP) vessels mixed by air sparging and pulse-jet mixers (PJM) during a Design Basis Event (DBE). Additional testing was performed to determine the effects of simulant properties, composition of alternate AFAs, and presence of trace noble metals.

Key results are that:

- Increased gas holdup resulting from addition of Q2-3183A is due to a decrease in surface tension that supports small bubbles which have low rise velocities.
- Dow Corning 1520-US AFA shows it to be a viable replacement to Dow Corning Q2-3183A AFA. This alternative AFA, however, requires significantly higher dosage for the same anti-foam function.
- Addition of noble metals to the AZ-101 waste simulant does not produce a catalytic gas retention effect with the AFA.

#### INTRODUCTION

The Waste Treatment Plant at the Hanford Site in Washington state utilizes combined Pulse Jet Mixers and spargers for mixing of radioactive waste slurries and release of hydrogen gas. The anti-foam agent DOW Corning Q2-3183A will be added to waste streams in the WTP to prevent foaming. These waste streams with finely divided solids are subject to foaming due to a phenomenon called particle-stabilized foaming [1]. Previous Phase I (P-I) tests at SRNL [2] with the DOW Corning Q2-3183A in a 60 liter mixing stand (1/9<sup>th</sup> scale<sup>1</sup>) using a mechanical agitator indicate that additions of this AFA to waste simulant increase gas holdup by as much as a factor of four in AZ-101 simulant. These results also show that gas holdup in non-Newtonian simulants containing this AFA:

- (i) increases with increasing superficial velocity<sup>2</sup>  
(that is, increasing bubble generation rate), and

<sup>1</sup> The vessel dimensions are 1/9<sup>th</sup> linear scale of the plant but no other geometrical similarities exist with the plant.

<sup>2</sup> *Superficial Velocity* = *Gas Generation Rate Per Unit Volume* ÷ *Slurry Surface Area*; the *slurry surface area* being the area of the slurry at the surface level of the vessel.

(2) increases with decreasing shear strength.

The increased holdup of up to 10% voids, observed in the P-I tests if extended to the WTP would hamper operations and increase gas retention in the waste slurry in the event of a Design Basis Event (DBE). In a DBE, air supply to the PJMs and spargers is interrupted. Radiolytically generated hydrogen gas bubbles are essentially immobile in the non-newtonian waste when it is not being mixed, which increases the potential flammable gas release when the air supply is restored. A Phase II (P-II) test program was initiated to identify:

- (i) parametric effects of waste properties and anti-foam agent additions to Hanford waste simulants have on gas retention and release,
- (ii) components of anti-foam agents responsible for such effects, and
- (iii) alternative AFA products and formulations that do not exhibit deleterious gas retention/release behavior when added to the AZ-101 simulant.

### WASTE SIMULANT

The waste simulant had similar chemical species as the actual waste, but without radioactivity. It had a pH of 12. The dilution curves (yield stress as a function of total wt % solids) for Phase I and Phase II simulants are shown in Fig. 1. Phase I simulant was prepared in our laboratory, using settling for solids separation. This apparently resulted in large size particles but which were not measured. Foaming was not experienced with this simulant. Phase II simulant was produced by a commercial vendor, using a centrifuge. Particle sizes distribution included a high fraction (63%) of fine, 0.65  $\mu\text{m}$  particles, which resulted in foaming, similar to the real waste. Fig. 1 gives the rheological characteristics of both simulants, which agree with those of the real waste. Both simulants however did not include the noble metals portion of the real waste due to their low concentrations. However, there is a possibility that the noble metals could catalyze reactions between the waste components and the anti-foam. Consequently, Palladium, Rhodium, Ruthenium and Silver were added in trace amounts to the simulant and testing was conducted to determine the effect of noble metals on gas holdup.

Testing was performed at nominal 30 Pa, 13 Pa, and 3 Pa yield stresses. The corresponding apparent viscosities were 15 mPa-sec, 9 mPa-sec and 5 mPa-sec, respectively.

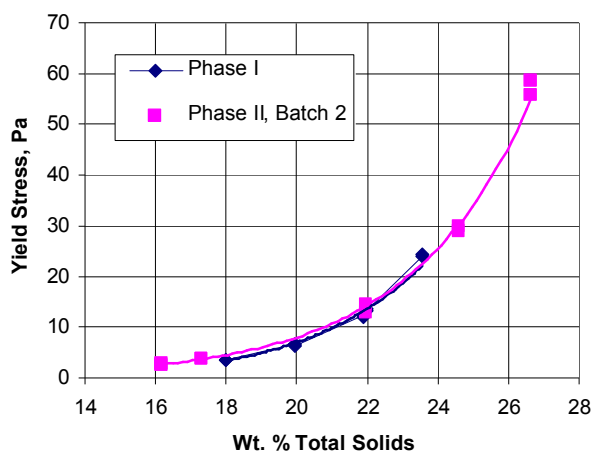


Fig.1 Rheological Properties of AZ-101 Waste Simulants

### Alternate Anti-foam Compositions

The AFAs tested have the following components:

Dow Corning Q2-3183A (base AFA)

Polypropylene glycol (PPG)	40-70%	Treated silica	3-7%
Polydimethyl siloxane (PDMS)	40-70%	Polyether polyol	3-7%
		Octylphenoxy polyethoxy ethanol	3-7%
		<i>Active ingredients</i>	100%
<u>Dow Corning AF-7500</u>		<u>Dow Corning 1520-US</u>	
Water	30-60%	Water	>60%
PDMS	30-60%	PDMS	15-40%
Reaction product of dimethyl Siloxane, methyl hydrogen Siloxane	10-30%	Methylated silica	1-5%
Polyethelene glycol stearate ether	7-13%	Polyethelene glycol sorbitan Tristearate	1-5%
Other siloxane	3-7%	Methyl cellulose	1-5%
<i>Active ingredients</i>	20%	<i>Active ingredients</i>	20%

(diluted from pulpate concentrate)

The major anti-foam ingredients are PPG, PDMS, and treated silica, with the associated other ingredients added to make the emulsions stable.

### EXPERIMENTAL APPARATUS

Two types of experimental equipment were used in this testing. The first was a bench-scale test setup, Fig. 2, used to determine the relative effects of the components of the base AFA, Q2-3183A on gas holdup and thus isolate the component that is responsible for increased gas holdup. It was also used to quickly evaluate different alternate anti-foams that did not incorporate the suspect component. The test rig consisted of a clear Plexiglas vessel, 178 mm in diameter and 610 mm high, filled up to the 419 mm

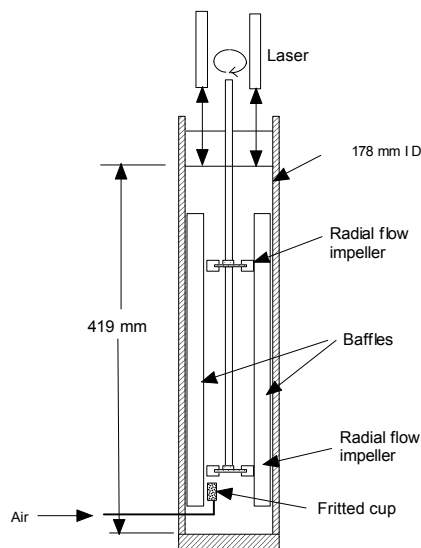


Fig. 2 Bench-scale Test Rig

level with waste simulant. The simulant was mixed with upper and lower radial turbines on a common shaft. The mechanical agitators were powered by a three-quarter hp motor with a variable speed drive. Air was injected through a 6.35 mm tube fitted with a 5 m fritted stainless steel cup at its end. The injected bubbles were directed at the tip of the lower agitator to break up the large gas bubbles into small bubbles. The slurry level in the test vessel was monitored by 3 laser distance meters focused on the surface from above. The laser distance measuring devices were Disto 4 and 4a manufactured by Leica Instruments, calibrated to an accuracy of +/-1.5 mm. This provided a gas holdup accuracy of +/-0.36% void.

The second test setup (Fig. 3) had a vessel with an ID of 438 mm with clear acrylic sides (9.5 mm thick) and a stainless steel elliptical bottom. The height of the side wall was 978 mm; the overall height was 1090 mm. Four equally spaced baffles were installed in the vessel. The agitators consist of a 133 mm diameter axial mixing impeller (low shear hydrofoil model 3LS39) for the upper shaft, and a 133 mm radial flow mixing impeller (Smith Turbine model 6DS90) for the lower shaft. Power to the agitators was provided by a ¾ hp variable torque motor (Philadelphia Mixers model PD-34) connected to a variable frequency drive. A schematic of the test facility is shown in Fig. 3. The 1/9<sup>th</sup> scale test rig utilized 4 laser distance meters positioned at different radii and azimuthal locations.

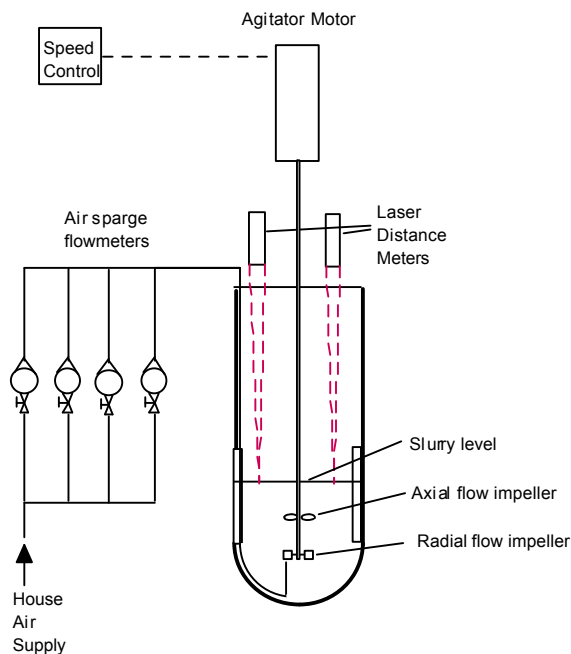


Fig. 3 1/9<sup>th</sup> scale Test Rig

## PROCEDURE

A typical test run involved air sparging at a constant air flow with agitation lasting for ten minutes, followed by ten minutes of agitation for gas release. Then the air flow would be changed for the next data point, and so on. A series of test points for a given set of simulant rheology and AFA dose would be obtained during a day's testing. Data was obtained at a sampling rate of 1 sample/sec and the data were averaged to provide a single data point on the charts.

## TEST RESULTS

### Gas Holdup with and without AFA in Non-foaming and Foaming Simulants

Measured gas holdups in non-foaming Phase I (P-I) and foaming Phase II (P-II) simulants at three rheologies are given in Figs. 4 - 6. Holdup is defined as the increase in simulant volume due to gas addition divided by the initial volume. The non-foaming P-I simulant with Q2-3183A AFA showed increased gas holdup relative to the no AFA case up to a factor of 4 at low superficial velocities (0.01 mm/s) at 13 Pa expected in the plant. As the yield stress decreases (apparent viscosity decreases) from 30 Pa to 13 Pa, the holdup doubles. The foaming P-II simulant showed increased foaming with decreasing yield stress, up to nearly 100% holdup at an air superficial velocity of 1 mm/s at 3 Pa. Addition of Q2-3183A AFA to P-II simulant resulted in similar to a slightly higher value than for P-I simulant with AFA. This shows that foaming did not affect the gas holdup characteristics in the presence of AFA.

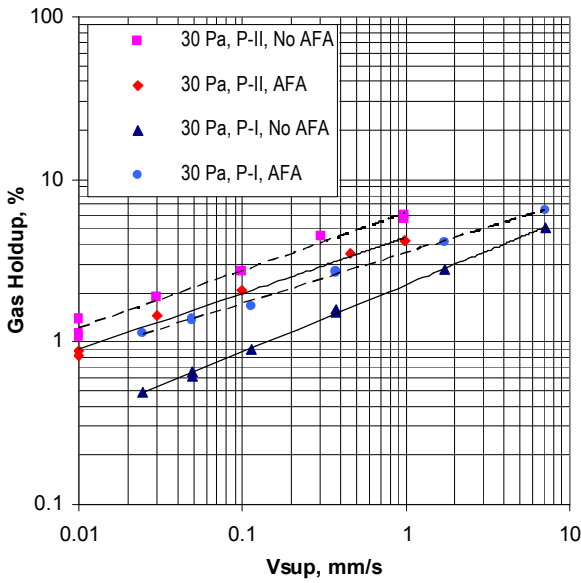


Fig. 4 Gas Holdup in 30 Pa P-I and P-II AZ-101 Simulants with and without Q2-3183A AFA

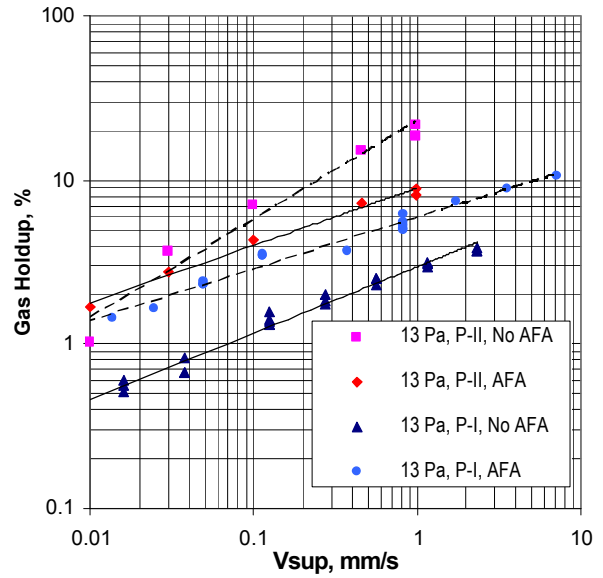


Fig. 5 Gas Holdup in 13 Pa P-I and P-II AZ-101 Simulants with and without Q2-3183A AFA

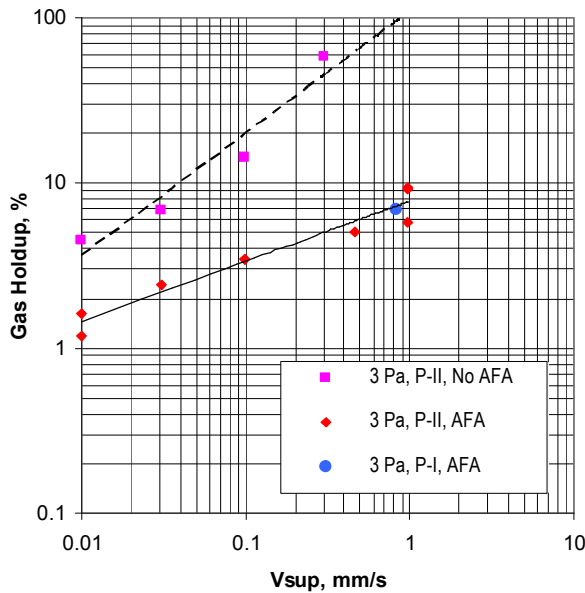


Fig. 6 Gas Holdup in 3 Pa P-I and P-II AZ-101 Simulants with and without Q2-3183A AFA

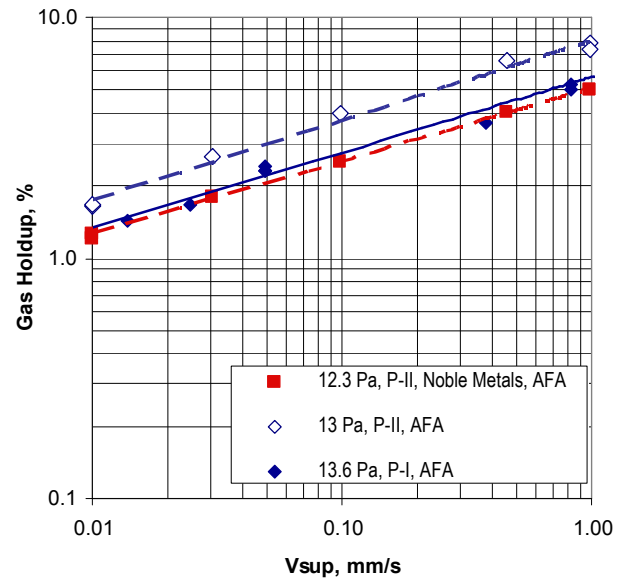


Fig. 7 Gas Holdup in 12.3 Pa P-II AZ-101 Simulants with Noble Metals

### Effect of Noble Metals

Fig. 7 shows that addition of noble metals to P-II simulant with AFA has no effect on the gas holdup. In fact, noble metals reduced the holdup down to the same level as for the non-foaming P-I simulant. Similar behavior was observed at 30 and 3 Pa. Thus, noble metals have no catalyzing effect on gas retention.

### AFA Component Testing

The major components of Q2-3183A, PDMS and PPG, were tested individually in water and AZ-101 simulant to determine the component responsible for increased gas holdup, or the relative effects of

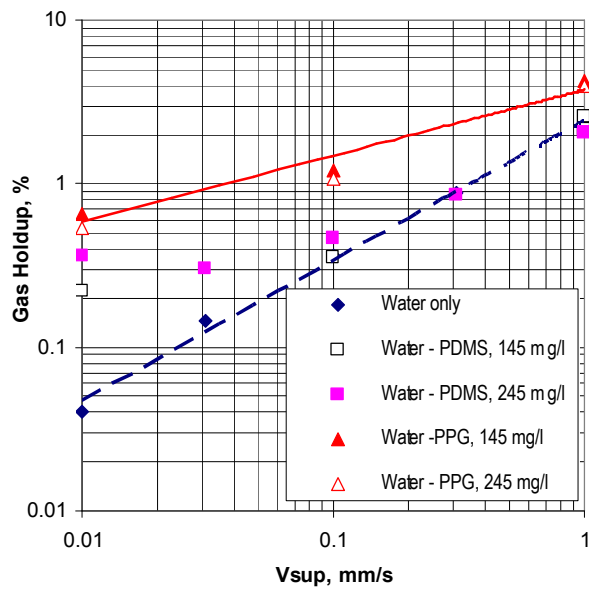


Fig. 8 Gas Holdup in Water with and without PDMS or PPG

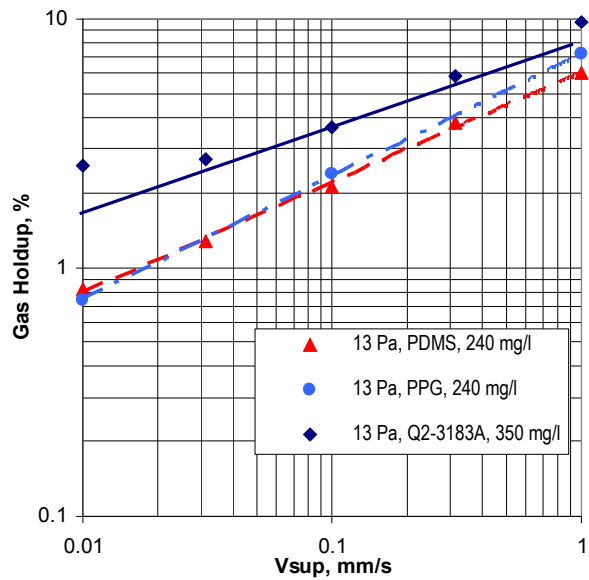


Fig. 9 Gas Holdup in AZ-101 Simulant with PDMS or PPG

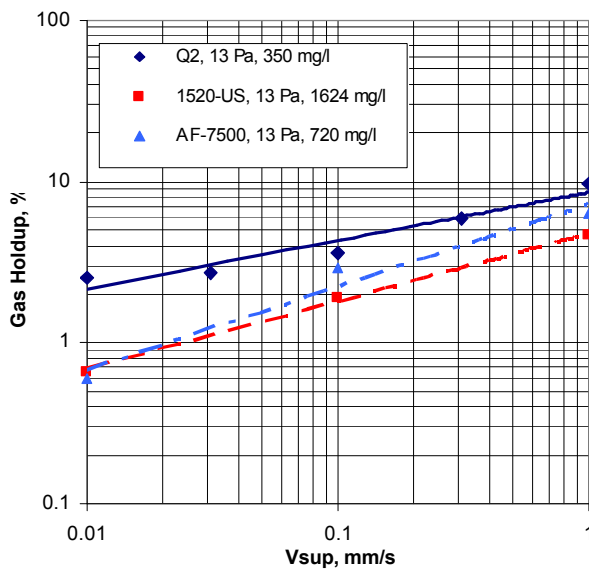


Fig. 10 Gas Holdup in AZ-101 simulant with Alternate AFAs 1520-US and AF7500 in Bench-scale Apparatus

each of these components. Fig. 8 shows the results in water, where PPG generates high holdup and PDMS has no to low holdup increase compared to water only. The concentration of 245 mg/l corresponds to 70% concentration of PDMS or PPG in Q2-3183A (total concentration of 350 mg/l).

In AZ-101 simulant, the behavior of PDMS and PPG are similar, Fig. 9, with PPG having only slightly higher holdup than PDMS at high superficial gas velocities at 13 Pa. Both individual components have lower holdups than the combination in Q2-3183A. As an anti-foamer, Q2-3183A is more effective than either PDMS or PPG at the same concentrations, according to the vendor. Thus, at this concentration of 350 mg/l, the anti-foam property of Q2-3183A leads to high bulk holdup, rather than suppressing it.

## DISCUSSION

The search for an alternative AFA in place of Q2-3183A should properly start at an understanding of why an anti-foam agent would paradoxically increase gas holdup. The anti-foam agent Q2-3183A contains surfactants such as PPG and PDMS which are used both as frothers and anti-foams. PDMS is used as a frother in the production of polyurethane foam [3] and PPG is used as a foamer for minerals separation [4]. The mechanisms by which a surfactant controls foaming also occur in the bulk fluid and some of these also affect bulk gas holdup [4,5].

An anti-foam consists of a surface-active but insoluble oil, such as PDMS or PPG, and usually includes hydrophobic solids such as treated silica. The surface active materials spread rapidly onto any air-water interfaces, and thin the liquid films between adjoining foam bubbles. The hydrophobic solids rupture the foam bubbles, causing them to coalesce to form bigger bubbles. Larger bubbles rise more rapidly than small bubbles, and so a gas emulsion of larger bubbles would tend to have lower holdup. The surface active property directly reduces surface tension. The surface tension in water, AZ-101 simulant, and AZ-101 supernate with the addition of Q2-3183A was measured by Pacific Northwest National Laboratory (PNNL), given in Fig. 11. This shows a dramatic 40% decrease with just a small 100 mg/l addition, leveling at a 58% decrease at 350 mg/l. The surface tension decrease leads to production of small bubbles, which rise slowly, increasing holdup. Therefore the two properties, bubble coalescence and small bubble generation counteract each other and actual gas holdup depends on concentration of the anti-foam.

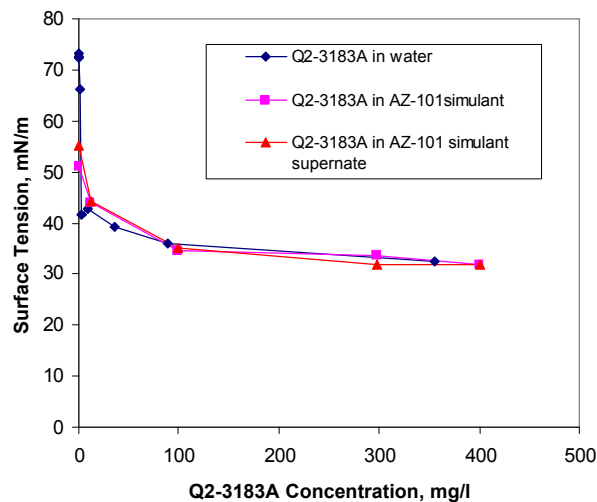


Fig. 11 Surface Tension in Water, AZ-101 Simulant, and Supernate with Addition of Q2-3183A

The increase in gas holdup with decrease in yield stress (decrease in apparent viscosity) may be explained as a function of solids content of the slurry. The increasing apparent viscosity of the slurry with increasing total solids content promotes formation of large bubbles. Krishna, et al. [6], for example, found that increasing the solids content of air/paraffin oil/silica slurries from 0-36% reduced gas holdup from 28-2%.

Tan [4] found that at low concentrations, surface foaming increased with increasing concentration of the anti-foam. Then a plateau region is reached where Marangoni effects counteract film thinning effects of the surfactant and foaming characteristics remain constant with AFA concentration. Finally, a critical point is reached at a higher concentration where the surfactant exceeds its solubility limit and phase separation occurs as solid particles. PPG forms polymeric solid particles [5] that act as anti-foamer to rupture films between coalescing bubbles. Similar behavior in the bulk fluid that affects bulk holdup would be expected.

The effect of adding AFA appears to favor high holdup at low concentrations and then to decrease it at high AFA concentration. This is supported by bench-scale testing where the cumulative dose of Dow Corning 1520-US was progressively increased (simulant diluted from 30 Pa to 3 Pa). At 100 mg/l, the gas holdup was initially high at 6% then decreased to less than 4% at 750 mg/l. After a rest interval, the holdup jumped up from its previous value. The AFA appear to have degraded, requiring new additions to rejuvenate its anti-foam property, after which the holdup decreased again.

Results of the noble metals testing also indicate that increasing the Q2-3183A concentration decreases the gas holdup. In this test, the 3 Pa P-II simulant with noble metals was retested after a month of layover. The gas holdup increased by 50% over the initial value at the same Q2-3183A concentration. This was apparently due to degradation of the AFA, where in previous testing it was shown that the PDMS and PPG components separated leading to less effective anti-foam action. Adding 50% of the initial concentration to 525 mg/l brought the gas holdup back down to its original value.

## **SUMMARY**

Results of gas holdup tests with bench-scale and small (1/9<sup>th</sup>) scale, mechanically-agitated test systems with WTP waste slurries demonstrate that:

- Both foaming and non-foaming simulants exhibit similar increased gas holdups with the addition of Q2-3183A AFA up to a factor of four. Decreasing the yield stress increased the gas holdup, although the apparent viscosity decreased.
- The increased gas holdup with addition of AFA to the simulant is believed to be due to the decrease in surface tension generating small bubbles with low rise velocities.
- Dow Corning 1520-US was shown to be a viable alternative to Q2-3183A. However, much higher concentrations are required for the same anti-foam function.
- Noble metals do not catalyze an increased gas holdup characteristic of the simulant. Gas holdups were similar with and without addition of noble metals.

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