C R E S P

The Consortium for Risk Evaluation with Stakeholder Participation III

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Ms. Shirley Olinger, Acting Manager
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Office of River Protection
P.O. Box 450 MSIN: H6-60
2440 Stevens Center Place
Richland, WA 99354

RE: CRESP Review Team Letter Report 3

Dear Ms. Olinger:

This letter report is in review of the Issue Response Plan for Effects of Anti-foam Agent on Gas Retention/Release (IRP; Sherwood, 2007) and the draft RPP-WTP Support Program Test Plan (Test Plan or TP; Guzman-Leong, undated). This review is also based on a presentation to us by Jain (2007), associated follow up discussion and documentation, our review of a prior report by Stewart (2006) and relevant literature, and our collective prior experience and expertise. Citations in this letter and additional recommended literature for consideration are provided as Appendix A.

Gas retention and release in waste slurries and the resultant potential impact on safety during a post-design basis event (e.g., plant upset condition, DBE[1]) serves as the basis for the planned follow-on evaluation to insure that Waste Treatment Plant (WTP) will not be operated under conditions that have the potential to exceed safety requirements. Ultimately, issue resolution must be achieved by either (i) demonstrating that the conditions that resulted in the initial issue identification are not plausible, (ii) modifying the WTP physical design to eliminate the potential for the plausible upset scenario that exceeded safety requirements, or (iii) developing operating protocols for WTP, either for operations during normal or upset conditions, that eliminate the potential for the plausible upset scenario that exceed safety requirements.

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[1] For discussion purposes in this letter report, the design basis event (DBE) refers to the upset event, such as a seismic event or loss of power, that would lead to failure of operating equipment and limit the availability of air, ***and*** the associated waste characteristics and operating conditions at the time of and subsequent to the upset event that cumulatively result in the potential to exceed safety limits.

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In the discussion that follows, we first examine the DBE, including inconsistencies and uncertainties in the underlying assumptions. We suggest considerations to be addressed to understand (i) the extent to which the DBE issue may be plausible, and if plausible, (ii) the fraction of planned WTP operations that may be impacted, and (iii) benefits and tradeoffs of alternative approaches to achieving issue resolution.

If on closer examination the DBE is plausible, there remains considerable uncertainty about the actual waste characteristics and operating conditions that would lead to the potential exceedance of safety boundaries. Given these uncertainties, the goals of the planned experimental program should be to (i) reduce uncertainty in the evaluation of the DBE, and (ii) provide guidance on waste characterization, to be carried out as part of WTP operations, to identify when and which operating conditions or operational constraints should be imposed to meet necessary safety requirements. In essence, the planned experimental program (if necessary) should provide the basis for a validated mathematical formulation that allows for predicting, within understood uncertainty bounds, the hydrogen retention and release during normal operating and upset conditions based on measurable waste and processing characteristics. With these goals in mind, we examine the underlying assumptions, experimental plans and data analysis presented in the IRP and Test Plan.

Definition of the Post-Design Basis Event

Primary documentation has not been available describing the postulated upset event, process management scenario to address the event, and associated calculations that resulted in the concern that release rates of in-situ bubbles containing hydrogen may be problematic (post-design basis event). Therefore, our understanding of the issue is based on secondary descriptions and discussions as follows (see Guzman-Leong, undated; and Stewart, 2006, p. 1.1):

> An event (such as a seismic event) occurs that results in loss of primary power at WTP, forcing reliance on emergency power. Limited availability of secondary power results in intermittent mixing of in-process tanks containing non-Newtonian waste mixtures that include anti-foam agent (AFA). Decomposition of waste mixture components results in gas generation (including hydrogen), which accumulates as dissolved gas and small bubbles within the waste slurry. Gas generation is the result of radiolysis of water, radiolytic decomposition of organic constituents in the waste mixture, and thermal reactions between organic and inorganic constituents. Hydrogen is only one of several gases generated. Other primary species are nitrogen and nitrous oxide, lesser amounts of ammonia and methane, and traces of many other gases. Air sparging also introduces dissolved gases into the liquid such that the small gas bubbles occurring within the waste contain air in combination with the gas generated by the waste itself. Intermittent mixing by a combination of air spargers and pulse-jet mixers (PJMs) is used to purge accumulated hydrogen from the waste slurry. Only a part of the accumulated hydrogen will be released from the waste slurry during intermittent mixing, with the extent of hydrogen release being dependent on mixing duration and waste characteristics. If accumulated hydrogen is not released sufficiently during intermittent mixing, concern exists that a change in waste

> chemistry, heterogeneity within the waste in the vessel or a physical disturbance would result in the rapid (near instantaneous) release of the accumulated hydrogen, overwhelming the tank headspace air purge system and resulting in a transient of hydrogen concentration in the headspace that exceeds safety limits. No specific mechanism for a spontaneous gas release is given in the references and none is assumed in the safety basis. It is simply a conservative assumption of a complete, instantaneous release of all gas bubbles in the slurry with no pre-cursor mechanism specified[2].
>
> During intermittent mixing, it is expected that the accumulated hydrogen in non-Newtonian waste mixed with AFA will be expelled more slowly than the WTP design allowed. This is based on observations made using waste simulants that showed greater gas bubble retention and slower bubble rise velocity for simulants containing AFA relative to those without AFA. To compensate for slower hydrogen release during mixing, increased frequency or duration of intermittent mixing would be required, potentially exceeding current power design capacity for Important-to-Safety systems (ITS).[3] Changes to planned operating conditions may be required to overcome this potential problem. These changes may be (i) selection of an alternative AFA that reduces foaming satisfactorily but does not unacceptably increase the rate of hydrogen production or inhibit the release of hydrogen during intermittent mixing, (ii) an increase ITS power generation capacity to increase the design air supply during upset conditions to either increase purge air flow rate or facilitate longer operating periods for the air spargers and PJMs to purge hydrogen from the waste, (iii) to impose additional restrictions on the in-process waste quantity or characteristics (e.g., rheology) [4], or (iv) to revise the safety strategy (such as by refining the underlying assumption of instantaneous hydrogen release or the calculation of hydrogen release rate during intermittent mixing).

The IRP focuses on an experimental program proposed to reduce uncertainty associated with the release of dissolved hydrogen and hydrogen within small bubbles from WTP tanks containing antifoam agent (AFA) during upset conditions. Additional testing is planned without AFA for comparison with tests containing AFA. Sensitivity or trade-off analyses are needed that examine (i) the assumptions (including identifying a plausible mechanism that potentially may lead to the postulated instantaneous release given the presumed waste characteristics) and calculations that resulted in issue identification and postulated safety exceedance, or (ii) the impact or possibility of alternative operating conditions to avoid the postulated safety exceedance.

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[2] This assumption may be unrealistic and too conservative given the rheological properties of the waste slurry and the difficulty in releasing the small gas bubbles under aggressive mixing. Based on the experience of the CRESP review team, it seems unusual to specify an event without an underlying mechanism. For example, in nuclear reactor system probabilistic risk assessments, all event mechanisms are characterized in order to establish a basis for frequency.

[3] Post-DBE Scenario (page 26, Guzman-Leong, undated). The full-scale PJM and sparger ON and OFF times for the post-DBE scenario have changed radically since the half-scale tests (Stewart, 2006) without justification. A full-scale Post-DBE now consists of 3 hours of PJM and sparging operation followed by 220 hours of idle sparging.

[4] See Sherwood (2007, p. 4).

The Committee has been told that the gas management system does not have the capacity to safely handle an instantaneous release of all entrapped hydrogen during an emergency or in the recovery period after an emergency. How far is the current estimate from the safety boundaries? No mechanism has been postulated or proven for the instantaneous hydrogen release and the Committee questions the likelihood of such an occurrence. The Committee notes that the IRP states that *"Gas bubbles are essentially immobile when the mixing system is not operating in non-Newtonian materials so the rate of gas retention is equal to the generation rate; this static condition is unaffected by the AFA* (Sherwood, 2007)*."* The set of assumptions that lead to instantaneous release of hydrogen accumulated between mixing intervals seems inconsistent with the apparently very slow release of hydrogen from the same waste slurry during mixing. Simply stated, if you cannot get the hydrogen out of the waste during aggressive mixing, how does it all release instantaneously in the absence of mixing?

Further questions arise that include:

- What was the safety margin in prior analyses? How close is the postulated DBE to the safety limit?
- What is the time interval during which WTP would have to function on only secondary power?
- What fraction of the waste inventory requiring processing would be impacted by any new constraints on the in-process waste quantities (i.e., batch sizes) or waste characteristics (e.g., rheology) necessary to avoid the postulated safety concern?
- How sensitive is the postulated event to the amount of AFA used or waste characteristics (e.g., total mass of organic compounds)?
- During WTP operation, how will the operators know if gas retention exceeds some acceptable threshold or if the hydrogen release rate during mixing is less than some acceptable level? What response actions would they take?
- Can alternative operating strategies for intermittent mixing, such as pumped waste recirculation (e.g., using the ultrafiltration circulation circuit) result in more efficient hydrogen release? Can a strategy be developed that reduces hydrogen holdup or improves hydrogen release during a design basis event (such as dilution with water)? Can a strategy be developed that under certain upset conditions, the in-process waste is flushed back to the large-scale feed tank?

Mechanisms for Hydrogen Release From Waste Coupled to Bubble Rise Phenomena During Mixing

In-situ formation of hydrogen is expected to result in small bubbles containing hydrogen and other radiolytically and chemically generated gases, while air sparging (during mixing) is expected to result in the formation of larger bubbles comprised predominantly of nitrogen and oxygen. Many of the small hydrogen containing bubbles and some of the smaller sparge air bubbles remain entrapped in the waste during periods between mixing. Multiple mechanisms may be responsible for the release of hydrogen (dissolved and as one component in gas within small bubbles) from the waste mixtures during mixing with air spargers and Pulsed-Jet Mixers (PJMs). Potential bubble rise and associated hydrogen release mechanisms include:

1. Stripping. This phenomenon is the diffusion of dissolved gases, including hydrogen from the waste slurry into the momentum dominated sparge air bubbles. The bubbles rise to the free surface of the waste slurry in the tank and burst, releasing air and the contained gases, including hydrogen, to the tank headspace. As the liquid phase becomes depleted in dissolved gases, the small bubbles may dissolve back into the liquid to feed the stripping mechanism.
2. Coalescence. During mixing, small hydrogen containing bubbles may join to form larger bubbles that have a greater bubble rise velocity because of the resulting larger buoyant force. They may also coalesce with sparge air bubbles. This also increases the overall bubble rise velocity. Larger bubbles reaching the surface burst, releasing the contained gases, including hydrogen.
3. Drafting. Small hydrogen containing bubbles and the smaller sparge air bubbles may be carried to the surface in the upward moving flow field and wake created by the rising larger sparge air bubbles. These smaller bubbles may or may not burst when reaching the free surface of the waste slurry.
4. Tip streaming (detachment). Small bubbles are formed by breaking off from sparge air bubbles in the presence of AFA. These small bubbles may only contain a small amount of hydrogen.
5. Bulk convection cells. Operation of the air spargers and PJMs will likely result in bulk fluid circulation that will bring small bubbles to the free surface of the waste slurry, potentially liberating entrained gases if they burst.

The above phenomena are complex, coupled and the relative importance of each mechanism in the WTP tanks is unclear. However, it is clear that overall gas release, including hydrogen, is not a function of a single mechanism and should not be assumed to be solely a function of bubble rise velocity or a single mechanistic representation.[5] Thus, measurement of overall gas retention and bubble rise velocity should not be taken as representative of hydrogen release without verification of this assumption. Measurements should relate the rate of release of dissolved gas and gas contained in the small bubbles (e.g., oxygen under test conditions when sparging with nitrogen rather than air containing oxygen) to the various postulated mechanisms during mixing.

The IRP, the presentation by Jain (2007) and additional materials provided for review present inconsistent analyses of the mechanisms for removal of hydrogen from non-Newtonian waste mixtures. The presentation by Jain emphasizes evaluating the effect of large momentum

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[5] In the Test Plan, p. 8, it states: *"In either case, because mass conservation dictates that the average vertical velocity of the non-gas portion of the slurry is zero, the gas release rate is determined only by the relative rise speed of the bubbles relative to the slurry. The complexity and intensity of the slurry circulation is immaterial."* This statement is only true if bubbles do not burst when brought to the free surface of the waste by slurry circulation. In reality, it is likely that sparge bubbles will burst when brought to the free surface of the waste, and uncertain whether the small bubbles will burst when circulated to the free surface of the waste.

dominated sparge air bubbles in removing the much smaller in-situ generated bubbles containing hydrogen via coalescence. However, this mechanism is discounted in the Jain Response Document (p. 4, 5)[6]. Little is said about stripping of dissolved gases including hydrogen by mass transfer to the sparge air bubbles. The IRP presents both coalescence and stripping as viable mechanisms, but provides no context to evaluate their relative importance. It is stated on Page 23 of the IRP that the Task 4 data (mass transfer coefficients) will be used to help interpret the Task 3 (gas retention/release) results. In fact, the results from Task 4 data should contribute to the basis for the design of experiments being carried out under Task 3 (i.e., the current Task 4 should precede Task 3). In all of the documents mentioned above, the coalescence mechanism is believed to be associated with coalescence between the in-situ generated small bubbles and the large sparge air bubbles. The coalescence of small bubbles with each other is discounted. This may be the case for small bubbles in the presence of AFA since they behave like rigid spheres (see below). However, in general, bubbles of similar size are more likely to coalesce that those of greatly dissimilar size.

There is no mention of drafting as a potentially significant gas release mechanism. Presumably it can be discounted by the same argument that would prevent coalescence of small bubbles with a large one.[6] The drafting of cells, which are analogous to small bubbles, has been observed in the upward flow created by sparge air bubbles in fermentation vessels; for instance, see Bavarian et al. (1991) and Chalmers and Bavarian (1991).

For turbulent flow, the Test Plan assumption is that in regions where the time averaged yield stress is exceeded on the macro-scale, the fluid behaves in a “Newtonian like” manner. That is, the shear stress versus shear rate relationship is linear (Bingham fluid), with a non-zero (yield stress) rather than a zero intercept. Once the yield stress is exceeded, the material behaves as a fluid with a Newtonian viscosity. A full turbulence spectrum continues to exist, although turbulent stresses at smaller scales (on the order of the small in-situ bubble diameters and less) may be less than the yield stress. This would result in localized regions of zero velocity gradient (plug flow) around the bubbles. There is also the real possibility that shear thinning behavior may occur on the macro-scale. This would just further complicate micro-scale phenomena.

It is reported in the Jain presentation (slide 12) that smaller and more stable in situ gas bubbles are generated in the presence of an anti-foam agent due to a lowering of surface tension. There is evidence in liquid-liquid systems[7] Padron (2005) that dependent upon surfactant concentration, static interfacial tension plays a very small role in affecting drop size in agitated dispersions. Rather Marangoni phenomena oppose breakup of drops by imparting surface elasticity. The common belief that adding surfactant produces smaller drops by lowering interfacial tension is not always true. Rather, the surfactant immobilizes the interface and prevents coalescence. This should also be the case here for the in-situ bubbles. However, the

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[6] The Jain Response Documentation (provided to CRESP without title pages, authors, report numbers or dates) pp. 4, 5 indicates that small bubbles would be trapped in the streamlines around large rising sparge air bubbles, thereby being swept away from the bubble surface and trailing wake. This would preclude both coalescence and wake drafting.

[7] Low viscosity dispersed drops in liquid-liquid systems behave analogously to small gas bubbles in liquid-gas systems.

situation is even more complex for small rising bubbles. The papers by Bando & Takemura (2006) and Magnaudet & Eames (2000), referenced in the IRP, both report that Marangoni effects cause small gas bubbles to exhibit rigid sphere (immobilized interface) behavior. This increases the drag coefficient and lowers the rise velocity, increasing holdup.

In the presence of AFA, surfactant on the surface of the large, rapidly rising sparge air bubbles is convected along the surface from the top to the sides of the bubble. As the surfactant becomes concentrated there, instabilities arise that can cause tip streaming of small satellites from the large sparge air bubbles. There is little discussion of this phenomenon in the Jain Response Documentation. It is mentioned that lowering surface tension lowers the resistance to nucleation thereby producing more nucleation sites and a larger number of smaller gas bubbles. We have not assessed this potential mechanism.

As is evident, the phenomena at play are complex and coupled. It is not surprising that project personnel differ on which are more relevant. We recommend that all potential mechanisms be considered. Such basic understanding is certainly required in data interpretation to distinguish among competing mechanisms, and to allow extrapolation (scale-up) to the plant-scale. For instance, preliminary calculations can be performed to assess the relative importance of stripping using mass transfer correlations for sparged stirred vessels and bubble columns.

Selection and Use of Simulants (Tasks 1 and 6)

Task 1 of the IRP is to develop a baseline simulant for Envelope B/D waste from Hanford Tank 241-AZ-101[8]. However, the report by Stewart (2006) documents use of a simulant for waste from the same tank. Thus, the need for new simulant development, and the basis for the new simulant (e.g., the properties to be reflected by the new simulant that differ from the previous simulant) is not clear. The criteria and basis for new simulants are not provided. Testing is proposed to examine gas retention differences as a function of the preparation method of the AZ-101 simulant without any rationale for why this is needed. Subsequent dialogue has indicated that Task 1 does not develop a baseline simulant and no new simulant development is planned in any task. AZ-101 simulant as developed in years past and used in the 2006 tests at SRNL will be used. Task 1 is to 1) obtain baseline gas retention data on the as-received simulant, and 2) assess the effect on gas retention of excluding noble metals from the recipe because of high cost. This clarification and associated testing should be reflected in the test plan. In addition, the relationship of simulant development under Task 1 of the IRP to waste characterization and simulant development currently being carried out under other ORP-WTP research and development programs should be clarified.

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[8] Sherwood (2007) states (p. 15-16):

"3.2.3.1 Develop Baseline Simulant (Task 1, SRNL)

Testing will be conducted with the Small-Scale Test Stand at SRNL. The objective of these tests is to determine the best recipe to simulate waste from Tank 241-AZ-101. The optimized simulant recipe emerging from these tests will then be used in subsequent, small scale testing (Tasks 5 and 6) and larger scale testing (the ¼ or ½-scale prototypic test vessel recommended by Task 3, and the mass transfer tests for Task 4). This task will determine gas retention differences among:

(i) AZ-101 simulant prepared by hydroxide precipitation method with trace elements;
(ii) (ii) AZ-101 simulant prepared by hydroxide precipitation method without trace elements; and
(iii) AZ-101 simulant prepared using hydroxide reagents."

Similarly, development of a new set of “bounding” simulants (TP, Section 8) appears superfluous[9]. As mentioned earlier (and cited in the IRP and TP) considerable uncertainty exists about the properties of actual waste to be processed. Current operational plans for WTP include at least a one year window for actual waste evaluation after each batch is blended in a double-shell holding tank and prior to beginning processing. Thus, the focus should be on what testing should be carried out on each waste prior to processing, rather than developing additional simulants with uncertain relationships to actual waste.

Overall, testing is proposed using both clay mixtures and AZ-101 simulant. Prior testing reported by Stewart (2006) established that clay mixtures and the AZ-101 simulant exhibited different behavior. If the goal is to establish the basis for measurements and scaling relationships for WTP application, then it appears that the primary focus should be on AZ-101 simulant testing at different scales, instead of clay mixtures, with the AZ-101 simulant serving as the basis for evaluation of relevant phenomena and as a baseline for understanding data from waste testing. AZ-101 simulant is expected to behave much more like the actual waste to be processed than the clay mixtures. In the absence of a clearly stated rationale, testing with clay mixtures appears unnecessary.

System Rheology

Rheological (Bingham) Model: It is stated in the IRP that the non-Newtonian surrogates follow the Bingham model. This presumes that once the yield stress is exceeded the fluid behaves like a Newtonian fluid. That is, the η^{γ} of Eqn. (2-6) on page 8 of the IRP is constant and equivalent to a shear independent viscosity. Such an assumption may be based on the idea that the flow becomes everywhere turbulent. It is doubtful that this will be the case since the gas spargers and PJMs are not operated continuously. Throughout the cycle, there will also be regions of no flow, laminar flow and transitional flow. It is more likely that the clay and AZ-101 surrogates are also shear thinning and follow a more complex rheological model such as the Herschel Buckley model; that is, $\eta^{\gamma} = \eta_0 \left|\dot{\gamma}\right|^{n-1}$, where η_0 is the consistency index, n is the power law index, and $\left|\dot{\gamma}\right|$ is the absolute value of the shear rate. Even this rheological model may be too simplistic. While this idea is addressed in the Jain response documents, the Bingham model is chosen as a limiting case. Experimental evidence has not been provided that actual wastes and the simulants do not exhibit shear thinning behavior, or that such behavior is unimportant[10]. In the absence of such evidence we recommend that the actual rheology be evaluated and considered when interpreting bubble size and bubble rise velocity.

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[9] AZ-101 is also claimed to be a “bounding” simulant (Stewart, 2006), but not necessarily for bubble retention and release. The “bounding simulant” task is to investigate the effects of major waste components (including slurries of two forms of sodium aluminate and iron hydroxide slurry, pure liquid sodium hydroxide and sodium nitrate) on gas retention to determine if AZ-101 simulant is “bounding” or whether there may be others that tend to retain more gas. If so, new simulants may be developed at a future time. However, the relationships to actual waste characteristics that affect small bubble retention needs to be clear.

[10] A separate research effort currently is underway to evaluate the rheology of archived waste samples from the ORP tanks.

Let us assume for the moment, that the Bingham model is valid. In the IRP and the Jain presentation, the yield stress is considered to be the only important parameter, but no basis is given for this. It is not clear why the consistency (viscosity) does not play an important role in bubble rise. For a given simulant (e.g., AZ-101 or clay mixture), as the amount of solids loading increases, the consistency and yield stress should increase, significantly affecting bubble dynamics.

Changes in Simulant and Waste Slurry Rheology Resulting from Composition Changes: Rheological properties of the test simulants may potentially change during the course of planned experiments because of changes in the waste slurry compositions. Planned changes in rheology to achieve desired experimental conditions are focused on achieving a desired yield stress in the clay and AZ-101 simulants, primarily by dilution or increasing solids concentration in a baseline simulant recipe. However, additional changes in system rheology can be foreseen and are considered in the test plan[11], but are not accounted for in the IRP. These changes are as a consequence of (i) hydrogen peroxide addition and attendant system dilution[12], (ii) addition of AFA[12], and (iii) the presence of small in-situ bubbles from oxygen evolution. These changes in system composition may impact the consistency term in the Bingham model, in addition to the yield stress and the potential to exhibit shear thinning behavior.

During normal operations, the waste slurry rheology is expected to change in response to changes in composition and solids content during the pretreatment steps. During the evolution of a post-DBE event, the rheology (and hydrogen retention characteristics) of the waste slurry also are expected to change in response to composition changes, primarily from solids settling, accumulation of small in-situ bubbles generated by radiolysis, and radiolytic decomposition of AFA.

Measurement of Simulant Rheology: The methods to be used to measure the simulant rheology need to be described in more detail in the Test Plan. Rheology measurement techniques and confirmation of simulant rheology are not described in the report by Stewart (2006). Measurement of simulant rheology is not trivial. The description given in Section 7.6.3, pages 44 & 45 of Guzman-Leong (undated) is a good initial step, however there are some areas where care is needed. The protocol for measuring the rheogram is being standardized at the outset. This may lead to an overly simplified view that does not accurately reflect the physics. The results from these should be considered in the context of the actual analysis to be done. The techniques used to analyze the raw data should be discussed. Specifically how is the yield stress being calculated and how sensitive are these calculations to the measurement conditions?[13] For example, assume that the standard analysis is used to find the yield stress:

1. Plot the shear stress versus shear rate on a linear scale.
2. Find the intercept with zero shear rate.
3. This intercept is the yield stress.

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[11] The test plan indicates that rheology will be evaluated on simulant samples obtained at the beginning and end of each test sequence.

[12] We acknowledge that the addition of 40 L of peroxide to 3200 L of simulant is most likely unimportant. The same may be true for the amount of AFA to be added other than the effects of small bubble retention.

[13] The term “dynamic yield stress” is used (see Table 2-2, IRP) without reference or describing why this is appropriate as opposed to the “static yield stress”.

4. For non-zero shear rates, determine if the relationship between the shear stress and shear rate is linear.

It would be useful to examine the sensitivity of the calculated yield stress to the experiment duration, which is specified to be 5 minutes, as well as the range of shear rates to be accessed during that period. It also needs to be recognized that at lowest stresses it takes a long time for the sample to reach steady state in response to the applied stress. It is understood that the protocol for rheological testing needs to be standardized, but if results like the counterintuitive finding for AZ-101 simulant with AFA, indicating decreasing the yield stress increases the holdup are found, one cannot overlook the possibility that the rheology measurement protocol may need to be questioned. This is especially important if results are found such as those shown in Fig. 5.10 (Stewart, 2006) where this effect is weak.

As discussed above, it is also important to look carefully at item 4 in the analysis procedure. It is unusual that a linear relationship between shear stress and shear rate is found after the yield stress is exceeded. In this case an alternative means of finding the intercept should be used based on a more complex yield stress model.

We need to know not just what appears to be the standard deviation of the measurements (i.e. precision) but also their accuracy. The data that tend to point to the counterintuitive trend between yield stress and gas retention in Stewart (2006) are at the lower yield stresses. These are harder to measure accurately. Since many concepts used to describe bubble transport rely on the idea of the yield stress, the accuracy of its determination is important. It is also important to characterize the rheology during flow. Finally, as stated above, it would be expected that simulant rheology will change during the test experiments. This was not discussed by Stewart.

Mass Transfer Coefficients (Task 4)

According to the IRP, tests will be conducted with oxygen gas to determine mass transfer coefficients for stripping of dissolved gases by the sparge air bubbles. It is stated on page 20 and in Eqn. (3-2) that mass transfer coefficients for other gases can be calculated from these data by simply taking the ratio of diffusion coefficients. This is most likely based on the assumption that the Sherwood number, defined below, is constant. It is unlikely that this procedure will yield accurate estimates. As inferred in the IRP, it is not possible to independently measure the sparge air bubble interfacial area per unit volume, a, and the mass transfer coefficient k_L (subscript L indicates that the major resistance is in the liquid phase). As a result their product k_La (referred to as $\beta_g A/V_\lambda$ in the IRP), often called a capacity coefficient, is measured instead.

There are numerous correlations for k_La in sparged, stirred tanks (see, for instance Tatterson, 1991; Middleton & Smith, 2004) and bubble columns (see, for instance Kantarci el al., 2005). These geometries are referenced here since they bound the behavior that might occur in the WTP tanks. Many of the correlations have been developed exclusively for oxygen. The more mechanistic correlations, that apply to all dissolved gases, are presented in dimensionless form and relate the Sherwood number, $Sh = k_La L^2/D_g$, (L is the impeller or bubble column diameter and D_g is the liquid phase diffusion coefficient) to Reynolds number, Schmidt number and other relevant dimensionless parameters. There is a power law dependency on the Schmidt number Sc

= (ν/D_g), where ν is the kinematic viscosity. That is, Sh ~ Sc^N, where N is empirically determined. Typically N = 0.5 (for both stirred tanks and bubble columns). This implies that a square root ratio of diffusivities should be used to scale capacity coefficients. As shown in Table 6.3-1 of Geankoplis (2003), the diffusivity of hydrogen in water (not simulant) is about twice that of oxygen. As substantially different estimates of the hydrogen mass transfer coefficient are obtained from linear and square root scaling, this should be examined. Also, N may not be equal to 0.5 for the geometry and flow conditions of the gas release tests. Therefore, N needs to be determined experimentally, which may require the use of at least two dissolved gases with different diffusion coefficients. More importantly, a correlation should be developed for k_La, since it is needed to scale the capacity coefficient, to full-scale for the large sparge air bubbles. Furthermore, this experimentally determined empirical correlation is needed for preliminary calculations to design the experiments in Task 3, as discussed above.

It is reasonable to assume that for a given geometry, liquid medium, and flow conditions, the interfacial area per volume a will be the same for all dissolved gases. However, it could vary in different surrogates and could be a strong function of AFA concentration. It is important that the bases for correlating mass transfer data for sparged air bubbles be well understood prior to specifying the pilot-scale experiments.

The small in-situ bubbles, particularly in the presence of AFA, will behave as rigid spheres (see comments above on hydrogen release mechanisms). Then, k_L and a (interfacial area per volume) are not coupled and a classical Froessling equation applies. That is, for example,

$$\mathrm{Sh} = k_L d / D_g = 2 + 0.60\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$$

where d is the sphere diameter. Small bubbles rise according to Stokes Law so the Reynolds number Re, based upon the relative velocity between the sphere and fluid, is extremely small. For typical values of Sc, the Froessling equation yields Sh = k_L d/ D_g = 2, so $k_L = 2\,D_g/d$. Since d is also small, very small bubbles can have a large mass transfer coefficient under all process conditions. As a result, they may dissolve rapidly if the liquid phase becomes depleted in dissolved hydrogen. Ostwald ripening may further promote small bubble dissolution. Therefore, if stripping of hydrogen from the liquid phase by large sparge air bubbles is a viable mechanism for hydrogen release, the dissolution of hydrogen from small in-situ bubbles back into the liquid phase will serve to feed the stripping mechanism. If coalescence and drafting are ruled out as viable release mechanisms, then this newly proposed mechanism should be investigated. This requires carefully specified experiments, based on mechanistically motivated arguments, which are designed to discriminate among the various mechanisms that have been proposed. Such systematic discrimination trials are not currently in the IRP. Indeed, the current draft of the Test Plan does not contain an in depth discussion of Task 4

Sparger Scaling and Gas Retention in the Simulant During Experiments

Bubble Rise Explanation: Section 2 of the IRP does not provide a clear explanation of bubble rise phenomena and appears to have several errors. If Eqns. (2-3) and (2-4) on pages 6 & 7 are intended to follow the Stokes derivation then a factor of 2 is missing. Perhaps the factor of ½ in Eqn. (2-3) represents a virtual or added mass effect that is not explained. We could not find this equation in the referenced book by Batchelor (1967). Virtual mass effects are transient phenomena and Eqn. (2-4) with the factor of 2 only applies to the steady rise velocity of a bubble or the terminal velocity of a sphere. Furthermore, Stokes law only applies to small rigid spheres in creeping flow conditions, such as the small hydrogen containing bubbles in the presence of AFA. There is no discussion of theory or correlations for the rise velocity of the large, momentum dominated sparge air bubbles.

Eq. (2-5) on page 8 also does not make sense. It seems that $\Delta\rho$ should be the difference between the liquid and gas densities as defined in Kulkarni & Joshi (2005) and not due to surfactant density.

<u>Bubble Volume Calculation:</u> On page 30 of Guzman-Leong (undated) it is stated that...*Based on data and several models for bubble formation, Chhabra (1993) recommends the following equation for the bubble volume, v_b, for inviscid flowing non-Newtonian fluids at sparger-tip conditions*

$$v_b = 0.25Q^{1.2}.$$

There is a footnote that *"Bubbles are sufficiently large to satisfy inviscid criteria"* (for the equation above). In this equation *Q* is the gas volumetric flow rate.

In Chhabra (2007), the basis for this (and the following) equation are discussed on pages 205-207. Equation 6.2a there is

$$v_b = 1.378Q^{6/5}g^{-3/5}$$

which, on earth, reduces to

$$v_b = 0.35Q^{1.2}$$

so the leading coefficient is 0.35, not 0.25. However, the more serious criticism is that these equations apply to surrounding fluids of low viscosity. For highly viscous liquids, the appropriate equation for bubble rise is

$$v_b = \left(\frac{4\pi}{3}\right)^{1/4}\left(\frac{15\mu Q}{2g\rho_L}\right)^{3/4}$$

The important difference is that the volume of a bubble would depend on the ¾ power of the gas flow rate, rather than the 1.2 power. Consequently, the bubble size will be quite different than that used by the authors of the Test Plan. An implication is that the bubble volume will increase much more slowly with gas sparger flow rate than the volumetric increase presented in the Test Plan, and the authors then conclude in eqn. 7.7 on page 31 of the document, that the bubble frequency will <u>decrease</u> with the 0.2 power of the increasing gas flow rate. When using the correct equation above it will actually <u>increase</u> with the 0.25 power of the increasing gas flow rate. The information on predicted volume of a bubble and bubble frequency is then used to develop the scaling relation for the gas sparger in the scale tests. Consequently, the entire sparger scaling calculation must be questioned.

<u>Determining Gas Volume Fraction from Simulant Level Change (Test Plan, p.39):</u> The accuracy of the level measurements is unclear. The level will be measured by four laser triangulation devices (see page 43)…in quiescent areas between the spargers…… The Test Plan proposes to measure liquid levels in what may well be a frothy mixture, so the accuracy may be uncertain, especially since level changes are quite small for gas volume fractions from 0.005 to 0.05.

Increasing Gas Retention with Decreasing Yield Stress: Stewart (2006, p. 5.8) reported greater gas holdup at AZ simulant yield stress of 13 Pa than at AZ simulant yield stress of 30 Pa when AFA was used in both tests. The AZ simulant with yield stress of 13 Pa is a diluted variant of the AZ simulant with yield stress of 30 Pa. It is unfortunate that these stirred tank tests with the latter simulant were run at higher agitation rates (impeller speed) to avoid dead zones, thereby making data interpretation more difficult. However, this would not explain this anomalous behavior. The unexpected result of increased gas retention with lower yield stress[14] possibly may be a consequence of (i) greater particle-bubble/AFA interaction at lower particle loadings, whereas particle-particle interactions are more dominant at the higher particle loadings that produce a higher yield stress, (ii) reaction of AFA with particles[15] at the bubble interface (AFA and hydrogen peroxide loading relative to particles is greater in the lower yield stress AZ simulant)[16], (iii) change in simulant solution ionic strength, or (iv) another, yet to be postulated, AFA-simulant-gas bubble interaction. Determining the cause of this unexpected result is important to providing a basis for selecting alternative anti-foam agents and insuring that the observed result is not an artifact of the simulant and test conditions used.

Evaluation of Alternative Anti-Foam Agents (Task 5)

Clear criteria should be established for the selection and demonstration of success of alternative anti-foam agents, if they are considered necessary after review of the DBE. Establishment of the criteria should include review of the basis used for selection of the current AFA, as well as impacts on the overall WTP flow sheet (e.g., feed evaporator), and should be linked to performance objectives needed to mitigate the DBE. Specific criteria should include definition of the level of small bubble retention and minimal release rate that would provide acceptable performance under the current WTP design conditions. Improved performance relative to the current AFA using small scale testing with AZ-101 simulant should be demonstrated prior to proceeding with testing to verify the applicability of the gas holdup and hydrogen release model.

Model Development and Validation (Task 7)

Development of an improved model for gas holdup and gas release should reflect consideration of distinguishing among the controlling mechanisms and mathematical representations of phenomena discussed above. In addition, the model should be validated using data from a prototype test system at a different scale (larger) than that used to develop and calibrate the model. Model uncertainty also should be quantified by comparing independently predicted behavior to observed behavior at conditions other than those used for model calibration.

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[14] Increased gas retention with lower yield stress was not observed when clay simulants were tested with AFA.

[15] The AZ simulant composition (Stewart, 2006) suggests that the precipitated particulates contain a large fraction of iron surfaces which may be reactive, especially in the presence of hydrogen peroxide.

[16] The antifoam agent Dow Corning Q2-3183A is comprised primarily of polydimethylsiloxane (PDMS) and polypropylene glycol (PPG).

Recommendations

The overarching recommendations based on this review are

1. Before refining and carrying out a testing program, review the DBE, its underlying assumptions, the fraction of the WTP processing potentially impacted and carry out a trade-off analysis of alternative mitigation strategies. Results of this evaluation should then be used to focus the testing program.
2. The goals of the planned experimental program should be to (i) reduce uncertainty in the evaluation of the DBE, and (ii) provide guidance on waste characterization, to be carried out as part of WTP operations, and (iii) to identify when and what operating conditions or operational constraints should be imposed to meet necessary safety requirements. The refined experimental program should provide a basis for a validated mathematical formulation that allows for predicting, within understood uncertainty bounds, the hydrogen retention and release during normal operating and upset conditions based on measurable waste and processing characteristics. Testing should focus on measuring gas holdup and oxygen (as a surrogate for in-situ generated gases) release at different prototypical test scales and operating conditions. The tests should be designed to provide improved system understanding and for model validation and uncertainty estimation based on data independent of the test data used for model development and calibration. For example, results obtained using AZ-101 simulant and AFA on a ¼ scale prototype system can be used to calibrate the gas release model and then the model can be used to predict results obtained for the same experiments on a ½ scale prototype system.   Emphasis should be placed on testing with the current AZ-101 simulant, with and without the current AFA.
3. Development of new simulants, if necessary, should be based on a clear rationale from results of on-going characterization being carried out on archived actual waste samples. The objective for new simulants should be to provide a basis for testing actual waste prior to processing to the extent necessary to verify that planned operations will be within established safety limits.
4. Selection and testing of alternative AFAs, if necessary, should be based on success criteria clearly linked to the recommended DBE evaluation and quantitative performance necessary to achieve desired mitigation strategies.

The CRESP Review Team looks forward to further discussion regarding these topics and future review meetings.

Sincerely,

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APPENDIX

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