October 2, 2009

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

RE: CRESP Review Team Letter Report 5

Dear Ms. Olinger,

A CRESP review team1 was asked to review the status of progress by Office of River Protection and its contractors to achieve resolution and closure to the EFRT issues of M-3 Undemonstrated Mixing and M-12 Undemonstrated Leaching Process. The team reviewed the documents listed in Appendix A and met on-site with the appropriate technical teams on September 10-11. Below are the team’s assessment and comments for your consideration.

M-3 Undemonstrated Mixing

Evaluation of the effectiveness of mixing in vessels equipped with pulse jet mixers is an on-going task in support of process vessel design. Extensive evaluation of mixing requirements has been carried out for each of the vessels based on the mixing functions and operating conditions within each vessel.2 The most important questions to be answered are:

Will the mixing in the vessels be sufficient to adequately maintain dispersion of particulates?
  a) Will the mixing provide enough circulation (up-welling from the bottom of the vessel to provide the required mixing function (along the full depth of the vessel)), within the mixing time required under process design conditions?
  b) Will the mixing in the vessels be adequate to prevent undue settling during normal operations; and to re-suspend and clear particulates from the vessel bottom after complete settling (e.g., after process interruption due to upset conditions) to facilitate process recovery?

Mixing tests should employ simulants that adequately represent the particle size and rheological properties for a range of Hanford tank waste compositions. Testing to date has used simulants

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1 Richard V. Calabrese served as an advisor to the CRESP team.
that are comprised of: 1) water and inert primary particles and 2) water, rheological modifiers and inert primary particles.

The question above about recovery from upset conditions was considered beyond the scope of the current pulse jet mixer (PJM) mixing requirements. However, testing to demonstrate recovery from a settled solids condition using a complex simulant is planned and is an important requirement that should be part of the mixing design. The strategy for recovery from an off-normal event, resulting in a loss of PJM mixing, is planned to be addressed as part the facility restart strategy in the Waste Treatment Plant (WTP) Authorization Basis.

Full-scale testing of the vessels is not possible, so a combination of laboratory experiments using various testing approaches and scales (from bench to maximum practical scale), is being carried out in conjunction with computation fluid dynamics (CFD) simulation of mixing in the vessels. The objectives of the bench, intermediate sized vessel and flume experiments should be to demonstrate a physics-based understanding of the scale up of pulse jet mixing for the wastes to be processed and to verify the efficacy of using CFD simulations as an important component in the basis for extrapolating from experimental test conditions to the range of full-scale vessel configurations and operating conditions. Thus, the simulants used during testing need to be physically and rheologically analogous to the wastes to be mixed and provide for appropriate mixing visualization and measurements to use as a quantitative basis to assess mixing. Furthermore, the scale-up basis and associated ability to extrapolate beyond calibration conditions should be verified by calibration on a range of data sets reflecting the range of operating conditions and then used to independently predict system performance, with experimental verification, on a larger-scale over a sufficiently broad range of operating conditions.

At the time of our review, experimental testing on multiple PJM testing platforms and CFD modeling and analyses were still in progress. Considerable work remains. Therefore, we offer the following observations in support of completing the remaining effort and reaching closure of the M-3, Inadequate Mixing EFRT issue:

1. There should be a clear and succinct description of the logic that indicates the flow from the PJM mixing requirements as the WTP vessel design basis down to specific testing approaches (e.g., testing in scaled down vessels, full-scale single pulse-jet testing in a flume, use of simplified simulants such as glass beads vs. simulants representative of waste feeds). This description should provide a clear mapping of how each type of test provides required information to establish the mixing scale-up relationships along with the methodology, verification of the scale up methodology with independent calibration and verification data, and criteria to verify adequate mixing design in WTP PJM mixed vessels. Verification through testing with waste simulants that include representative

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3 See p. 19 (24590-WTP-ES-PET-08-022, rev 1): “Also, the definition of mixing criteria and requirements for process upset situations that result in “beyond bounding” or “beyond design basis” conditions in vessels is not within the scope of this study.”

4 It should be noted that the Eulerian-Granular 2-phase model used in the FLUENT CFD code was originally developed for gas-solid flows. Verification that the various model closures have been properly adjusted to accommodate liquid-solid systems should be made part of the record.
concentration, particle size and rheological properties. Consideration should be given using chemical simulants as part of the testing program.

2. The most important scaling bases appear to be (i) the particle dispersion achieved by the mixing system operating at constant power per unit mass of the fully mixed system\(^5\), (ii) the radius of influence of individual pulse jets under the anticipated operating conditions (e.g., solids properties and depth, tank fill height), and (iii) the degree of particle dispersion throughout the tank (cloud height) under anticipated operating conditions.

3. Useful scaling correlations can only be derived from formulations with an appropriate fluid physics basis. The system is too complex to rely on purely statistically derived correlations that cannot be extrapolated beyond the set of system results from which they have been derived, and therefore cannot form a sound basis for evaluating scale-up to WTP vessels. Furthermore, any reasonable correlation must be developed from data over a range of the considered parameters. For example, the mixing gap analysis identified 6 different PJM vessel geometries with liquid height \(H\), to tank diameter \(D\), ratios in the range \(0.34 < H/D < 1.39\), but all physical tests were performed at \(H/D = 2\). For developing correlations to be used at the plant scale, correlations based on bounding conditions for estimates of cloud height or critical jet velocity for particle suspension will not provide confidence in accurate prediction, although they may be used to indicate that more than sufficient mixing is occurring. Accurate prediction of cloud height is required to insure that the entire tank volume is being effectively mixed during leaching and other mass transfer operations.

4. Precise quantitative validation of the CFD models is not likely because of (i) the coarse simulation grid relative to the scale of particle-fluid phenomena, (ii) the lack of an adequate experimental data base (sampling was limited to one vertical axis at a fixed radius from the vessel centerline), and (iii) the uncertainty associated with the current state of the art in CFD simulations. However, an appropriate level of validation and verification can be achieved to render a useful CFD tool to aid in design and scale-up. At present, the rate limiting step is the availability of a sufficient data base, including testing with waste simulants in sodium hydroxide solution, to allow the natural progression from initial experiments to initial models to more insightful experiments and improved models that achieve necessary fidelity to actual system performance. The need for additional data is discussed in item 5 below. The appropriate use of CFD is to verify that it provides a reasonable representation of the system behavior at different scales, configurations and operating conditions, and then to use the resulting CFD model to (i) evaluate anticipated mixing in full-scale vessels under the range of configurations and operating conditions, considering the uncertainty in the model verification at smaller scales, and (ii) to evaluate alternative configurations and operating controls (see item 10 below). While the increased use of CFD since our last review is applauded, a few words of caution are in order. The state of the art and the extent of validation and verification have not yet reached a point where simulation can be indiscriminately substituted for experiment.

5. Additional sampling considering multiple radial and vertical sample locations (beyond a single vertical axis at a fixed radius from the tank centerline) should be used to provide

\(^5\) Often, the mixing energy input is defined as power per unit volume, but for this case, power per unit mass of fully dispersed slurry is the more appropriate scaling quantity due of variable solution density.
adequate quantification of mixing in test platforms. Sampling should be specific to the intake and discharge strokes of the PJMs. Instantaneous samples should be correlated to the cycle time while time averaged samples should be appropriately devised. It should be noted that in PJM mixed vessels, fluid velocities and particle concentrations exhibit steep gradients; that is, they can change significantly over small spatial displacements and times within the cycle. As a result, repetitive samples grabbed at a fixed location but at the same point in the time cycle can vary significantly. The same will be true for samples grabbed at the same time at two closely located sample positions. A means to bring the data into congruence is to perform area sampling, rather than point or line sampling, and look for reproducible trends over appropriately defined area (sampling) windows. These data are most appropriate to CFD validation and verification. Window averages can be compared; or CFD and data contours (within a window) can be overlaid to validate trends. For example, if CFD and data contours can be aligned by displacing the graphs by a few centimeters, then the agreement is excellent. Initial CFD simulations prior to validation can be exploited to define the data sampling windows.

6. The approach of using a pyramidal shaped momentum deflector, with and without gas sparging, at the bottom center of the PJM mixers is an appropriate approach to enhancing mixing and upward particle momentum. Scaled-testing and CFD simulation, to the extent practical, should be used to verify system effectiveness.

7. Testing and CFD simulations should include particle size and particle density distributions and solids loadings reflective of the entire anticipated range of process conditions. If testing on single or a limited set of particle types is used as justification for meeting full-scale mixing requirements, the performance observed using limited particle types should be validated against particle distributions and loading reflective of both typical and limiting process conditions. Similarly, at least one set of tests should include both chemical and physical interactions that impact particle dispersion. The PEP should be considered as a platform for this testing. The link to rheological behavior is discussed below under Future Testing and PEP Demonstrations.

8. Testing should include evaluation of the capabilities of the planned mixing systems to recover from upset conditions that include completely settled solids in tanks containing the upper bound quantities of anticipated solids.

9. For vessels where accumulation of particles over time is an important concern, provisions should be included for determining the extent of particle accumulation and wash out methods. Provision should be made for adding chemicals needed to remove accumulated particles.

10. Some studies of mixing phenomena in stirred vessels have observed that non-periodic fluid motions tend to achieve better mixing than time periodic mixing approaches. While simultaneous operation of all PJMs may be desired to provide a temporal maximum in the energy (power) input into the system, alternative PJM operating strategies should be evaluated to determine if they can provide overall increased mixing and particle clearing from the bottom of vessels. CFD should provide an attractive means for evaluating the effectiveness of alternative PJM mixing strategies prior to experimental confirmation, though larger than “¼ unit simulations” will have to be used because of the loss of system symmetry.
M-12 Undemonstrated Leaching Process

Design evaluations and modifications, along with bench-scale and engineering scale (i.e., Pretreatment Engineering-scale Platform (PEP)) studies completed to-date, have been appropriate for meeting the closure criteria for the M-12 Undemonstrated Leaching Process. A single very important issue remains: post-filtration precipitation, which will likely have a significant impact on the process design and operations. This issue is commented on below, but is being addressed as a separate issue from M-12. The comments on other topics below reflect observations that will be important for process operations and optimization.

Post-filtration Precipitation

A system design critical issue that remains unresolved is the avoidance of the formation of solids in the ultrafilter permeate solutions prior to introduction to and during cesium ion exchange. This issue has been identified and is being resolved as a separate issue from EFRT M-12 but should be recognized as being intimately coupled to the leaching processes. Two primary resolution pathways are being explored: (i) dilution of permeates with water and sodium hydroxide coupled with improved segregation of different permeates (operational controls), and (ii) operation at elevated temperature (i.e., 45°C). Both resolution pathways would include a guard filter prior to the cesium ion exchange system. Alternatively, two of the primary post-filtration precipitates, phosphate and oxalate compounds, could be removed by addition of calcium ion followed by precipitate removal. This approach would reduce the likelihood of a precipitate forming in the Cs IX column due to slow kinetics of precipitation, a system upset, or mis-operation. Full flow sheet implications of this option should be evaluated. An objection to this approach has been voiced based on the amount of water that might be needed to wash these precipitates free of cesium to an acceptable level for LAW. However, this objection appears to be speculation unsupported by experiment. Regardless of the resolution approach selected, the objective should be that the permeate solutions are thermodynamically stable with adequate margins for variations of process conditions (e.g., temperature and composition) as feed to and during processing in the cesium ion exchange system. The review team was pleased to see use of thermodynamic modeling (OLI ESP thermodynamic simulations) coupled with the dynamic systems model (G2 model) to evaluate anticipated processing conditions that could result in unacceptable solids formation. However, experimental verification of proposed resolution approaches, including coupling with the cesium ion exchange columns, is essential because of the chemical complexity of the process streams and operations involved. Experimental verification over the full range of expected waste compositions should be initiated at the bench-scale and the need for engineering-scale testing should be evaluated.

In addition, the formation of solids in the cesium ion exchange feed vessel (i.e., CXP-VSL-00001) is a highly plausible upset condition that should be considered in the design process, including contingency clean out strategies.

Leaching Kinetics and Scale Up Factors

The leaching rate scale up factor of importance is the one for the constituent that defines the leaching interval duration in full-scale processing. For aluminum leaching, it is the scale up
factor for boehmite. We believe that the scale up factor for gibbsite is not important because its dissolution will be more rapid than the process cycle time defined by other factors (e.g., process heat up). For well-mixed processing (i.e., in UFP-01 or UFP-02) there is no reason or experimental evidence for the scale up factor from bench-scale tests to full-scale tests to be less than one (i.e., the same leaching rates at the same temperature and solution conditions at bench- and full-scale). The possibility of a localized region of higher temperature than the bulk temperature at the point of steam injection and shear within the recirculation pump during mixing within the PEP and full-scale system presents the possibility that boehmite dissolution rates may be faster during actual processing than observed in bench-scale experiments. Experimental results from bench-scale testing and PEP testing support this assertion, however, the bench-scale testing was carried out with insufficient precision to resolve differences between a scale up factor of 1.0 +/- approximately 30 percent. The limited precision in the bench-scale testing is a consequence of (i) only two replicates per case, (ii) inherent difficulties in obtaining representative samples of solids in slurries to establish the initial conditions for the experiments and subsequent grab samples for analysis, and (iii) analytical quality control tolerances (+/- 25% for matrix spike recoveries and +/- 10% on calibration precision). Statistical analysis of actual experimental results (e.g., evaluation of obtained analytical quality control results; analysis of variance from overall results with hypothesis testing) were not reported or available for our review. In addition, the basis for Monte Carlo estimates of uncertainty was reported with insufficient methodological detail to be validated by independent peer review. Future experimental designs for determining leaching rates should carefully consider these limitations and the needed precision in dissolution rate determinations as inputs to future test plans. This will be especially important as part of waste batch prequalification for full-scale pretreatment operations.

The scale up factor for oxidative chromium leaching is not important for fast leaching chromium solids, and has not been determined for slow leaching chromium species because of the absence of a suitable simulant. However, as discussed for aluminum leaching, the risk of the scale up factor being significantly less than one is small.

**Ultrafilter Flux**

Scale up of ultrafilter flux from the bench-scale (CUF) testing to the prototypic filter assembly configuration and operation in the PEP was demonstrated. Effective strategies have been demonstrated for recovering from degradation in filter flux due to fouling, including back-pulsing, nitric acid cleaning and oxalic acid cleaning. However, strategies for maintaining necessary filter flux have not been optimized and will require testing over a broader range of simulant compositions reflecting the different waste categories to be processed. These later results will impact operations but will not impede completion of the current system design.6

**Future Testing and PEP Demonstrations**

The greatest benefit of the engineering scale PEP demonstrations was to discover design and operational issues that could not be anticipated from laboratory testing. These include mechanical and hydrodynamic interferences as well as chemical process operating constraints. Thus, the important findings are those which are unexpected, beyond the necessary

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6 It should be noted that the back-pulsing procedure to clean the ultra-filters as practiced in PEP will need to be optimized for WTP.
demonstration of process integration. It has been documented that the limited PEP testing to-date has resulted in approximately $1 billion in avoided costs, had instead the needed process modifications been discovered during systemization. In the future, PEP should be cost effective for optimization of process operations and testing previously undemonstrated operating regimes.

The waste simulant used during bench-scale (e.g., CUF) and PEP testing was designed to be analogous to waste for chemical, but not rheological, properties. Thus, interactions between rheological effects and chemical processes, such as may occur for mixing, particle suspension and mass transfer, and filtration, would not have been observed. Therefore, we recommend that future testing include simulants that represent both the chemical and rheological properties for the major tank waste groups. Integrated testing should include a range of simulant formulations that are representative of each of the anticipated waste groups to be processed. High priority should be given to understanding the behavior of ultrafiltration for waste groups anticipated to exhibit difficult-to-filter behavior, such as those that contain high phosphate content.

Integration of a prototypic cesium ion exchange process should be evaluated for inclusion in future PEP demonstrations. PEP testing completed to date has indicated that chemical interactions between streams blended as feeds for cesium ion exchange exhibit unexpected solids precipitation. Additional unexpected behavior may occur during introduction to the ion exchange columns.

We hope you find these comments helpful in your evaluation and are available to discuss any questions you may have regarding this review.

Sincerely,

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