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September 2014
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REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

Bechtel National, Incorporated (BNI) asked that Savannah River National Laboratory (SRNL) survey past test programs that simulated plugging of process and transfer pipelines, particularly as these relate to Hanford applications. The objective of the survey is to provide recommendations for performance criteria for simulants used to emulate a plug in Hanford Tank Waste Treatment and Immobilization Plant (WTP) process piping containing waste process liquors. BNI will use the information in a procurement activity to support design and testing of remotely operated Plug Removal, Inspection, and Measurement Equipment (PRIME).

The author recommends use of the hydrostatic pressure needed to dislodge the simulated plug material (e.g., 300 psi) as the primary performance criteria for determining adequacy of candidate simulants. This report does not specify the physical configurations for study. BNI should define the different plugging scenarios from a review of the piping design and include such areas as piping dead-end lines, lines with constrictions, bends, or other geometries as deemed at risk for collecting solids. In addition, the author recommends using previously developed simulant recipes to the maximum extent practical.

In particular, the author recommends use of the Na-Al-Si simulant developed by Pacific Northwest National Laboratory (PNNL) and tested by FIU as the best available chemical simulant. Similarly, the author endorses the use of bentonite clay (or kaolin clay) simulants as tested by FIU as adequately representing physical properties of plugs from deposited sludge. Herting developed a recipe for phosphate solutions that precipitate as a solid mass when cooled below 50-55°C and this recipe is a credible initial formulation for chemically representative plugs from phosphate materials. Unfortunately, the hydraulic pressure required to purge such solids from prototypic size pipes has not been studied and, therefore, this formulation may require additional study or testing before fully assessing its adequacy for this application. The text of the report and an appendix provides details for the specific recipes with further information available in the cited source documents.

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1 The scope is limited to black cell and “hard to reach” areas of the design. There are no valves in these regions that will facilitate compaction of solids.
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# LIST OF ABBREVIATIONS

<table>
<thead>
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<th>Full Form</th>
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<tbody>
<tr>
<td>BC</td>
<td>black cell</td>
</tr>
<tr>
<td>BNI</td>
<td>Bechtel National Incorporated</td>
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<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>FIU</td>
<td>Florida International University</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>HTR</td>
<td>hard to reach</td>
</tr>
<tr>
<td>NDE</td>
<td>non-destructive equipment</td>
</tr>
<tr>
<td>PNNL</td>
<td>Pacific Northwest National Laboratory</td>
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<tr>
<td>PRIME</td>
<td>Plug Removal Inspection and Measurement Equipment</td>
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<tr>
<td>PT</td>
<td>Pretreatment</td>
</tr>
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<td>SRNL</td>
<td>Savannah River National Laboratory</td>
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<tr>
<td>SRS</td>
<td>Savannah River Site</td>
</tr>
<tr>
<td>SSC</td>
<td>systems, structures and components</td>
</tr>
<tr>
<td>WRPS</td>
<td>Washington River Protection Solutions</td>
</tr>
<tr>
<td>WTP</td>
<td>Waste Treatment and Immobilization Plant</td>
</tr>
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</table>
1.0 Review of Literature and Interviews with Knowledgeable Personnel

BNI requested that SRNL staff conduct a survey and recommend performance criteria for simulants that emulate pipeline plugging that may occur in the WTP process piping located in the PT and HLW Facilities, the bulk of which is located in the PT Facility. The information is to serve as input to a Request for Proposal to vendors for design and testing of remotely operated PRIME for use during process upsets relevant to the PT and HLW Facilities. The main function of PRIME is to obtain in-situ nondestructive examination (NDE) data as part of a Reliability and Integrity Management (RIM) Program for systems, structures and components (SSCs) in WTP black cell (BC) and hard-to-reach (HTR) areas. The equipment will also function to remove solids or chemical plugs in BC and HTR area process piping if they occur during operations. BNI asked that this survey include specific recommendations for solids and chemical plug composition / properties that would cover >95% of the plug types that could occur in WTP process piping. BNI further requested that SRNL recommend both a physical-property plug simulant and a chemical (i.e., representative of process chemistry) plug simulant, unless one will suffice for both.

The term “pipeline plugging” can represent a variety of degrees of obstruction for flow, from partial constriction of the pipe to full restriction that is impervious for flow. In this survey, attention focuses on the nearly full restriction to flow. Numerous relevant reports exist that cover less restrictive blockage using various simulants. These simulants consisted of simple mixtures of particulates such as glass beads, alumina, 316 stainless steel particles, zirconium hydroxide, aluminum hydroxide, or sand. The carrier fluid varied from water to water plus glycerin. Limited testing used a water and kaolin mixture. In some instances, the simulant contained sodium thiosulfate to modify the viscosity and density. The simulant design attempted to match targeted particle size distributions in selected cases. The reader may refer to the cited reports for details.

A wealth of prior studies exists funded by the Department of Energy (DOE) that provides a wide exploration of this topic. The program at Florida International University (FIU) is noteworthy in that the organization still maintains an active program in this subject area dating back more than a decade. FIU customers to date include Pacific Northwest National Laboratory (PNNL), Washington River Protection Solutions (WRPS) and most recently AEM Consulting, LLC. In addition, PNNL conducted relevant studies aimed explicitly at WTP needs. WRPS is actively investigating plug removal and recently

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6 For current status, see for example “QUARTERLY PROGRESS REPORT: October 1 to December 31, 2013 Florida International University’s Continued Research Support for the Department of Energy’s Office of Environmental Management”, Leonel E. Lagos, Ph.D., PMP, and David Roelant, Ph.D.
issued a report on the status of efforts since 2000. This report includes a brief history of pipeline plugging at Hanford and is an excellent primer on this subject. (Additional details on prior plugging events at Hanford are available in one of the cited reports.) In addition to reviewing various reports, the author conducted limited interviews with Dennis Washenfelder (WRPS), Dwayne McDaniel (FIU), and Mario Servin (WRPS). Cursory discussions occurred with staff at PNNL – especially helpful was Beric Wells – who provided a number of background documents (including some unpublished studies).

The author also surveyed numerous SRNL colleagues – including Erich Hansen, Dan Lambert, Michael Poirier, Mike Stone, and Bill Wilmarth – for insights and any relevant Savannah River Site (SRS) information. There have been fewer plugging incidents at SRS than at Hanford – largely due to the efforts to mitigate risk of plugging by controlling minimum transfer velocity (i.e., pump discharge pressure), rheology of the slurry (e.g., limiting solids content and maximum yield stress), and duration between transfers or flushes (e.g., restricting settling and “hardening” time). To further reduce risk of plugging and adverse behavior (e.g., foaming, solids adhering to vessel internals, exceeding pump limits), the SRS practice includes simulating process operations with streams containing high solids content with both simulated and actual waste samples to qualify the waste in advance of processing. Even with all these efforts, full chemical simulants can exhibit rheology that is markedly different – and less challenging – than the actual waste, as occurred with the second major sludge processing batch at SRS.

These gaps between laboratory studies and actual facility operations can lead to equipment fouling concerns and flow restrictions as observed in the second and fifth major sludge campaigns, or “batches”, in DWPF. A comprehensive review of these operational issues and near plugging experiences are beyond the scope of this report; these examples are provided as illustrative of the fact that even with extensive laboratory studies and qualification program, facility experience can prove problematic.

The bulk of the SRS experience involves two types of plugging. The first is precipitation of aluminum or aluminum-silicate materials such as fouling of gravity drain lines from High Level Waste evaporators. In these events, personnel detect the obstruction of the gravity drain lines and clear the lines before full blockage occurs. Recovery efforts originally depended on acid cleaning of the lines although some cleaning involves only use of periodic hydraulic (elevated pressure) scrubbing or simple caustic flushing. More recent plugging of the gravity drain line in a second evaporator resulted from nitrate and carbonate salts, similar to other line plugging events observed historically at Hanford.

The second type of fouling is the recent line plugging in the Modular Caustic-Side Solvent Extraction Unit in which aluminum-silicate and oxalate materials plugged a ~27-30 inch length of nominal 2 inch
diameter line leading to a valve that is normally closed except during cleaning evolutions. The exact mechanism of this fouling is still under investigation. The event appears to involve at least two mechanisms: deposition of aluminosilicate solids as well as capture of oxalate solids precipitated from the process stream. The adjoining centrifugal contactor enhances solids capture and compaction in the line and prior work shows the contactor facilitates plating out of aluminosilicates. The discovery of the fouling occurred in a period that included more frequent chemical cleaning of the upstream ultrafilter and included chemical cleaning of the contactors after an outage period.

Recovery from this event is in progress and involves replacement of the line section as well as extensive cleaning of the upstream vessels. The mitigating actions will also likely include process changes, especially a modification of the oxalic acid based cleaning protocols for the ultrafilters. BNI and WTP personnel should keep apprised of the final changes selected and the future processing history, as the filter cleaning operations are directly applicable for the PT Facility operations.

**Simulant Options**

Simulants developed include those intended to match the chemistry as well as simplified physical matrices that are easier to prepare and handle. The work at PNNL included, for example three chemical matrices that were aged over 6 months: Gibbsite from sodium aluminate solution, sodium phosphate, and sodium aluminosilicate from sodium aluminate and sodium metasilicate solutions.

FIU has examined a range of simulated plugs including:

- kaolin clay,
- bentonite clay,
- K-Mg saltcake,
- sodium aluminosilicate saltcake, or Na-Al-Si, and
- kaolin/plaster of Paris (currently using and received recipe from AEM).

The pressure required to move these plugs can exceed ~300 psig. The recipes for preparing several of these simulants are included in Appendix B of the report by Garfield et al.

These recipes reflect the classes or types of pipeline plugging solids historically observed at Hanford that concentrated from:

1. phosphate-containing supernatant,
2. alumininate-containing supernatant
3. concentrated, dissolved sodium nitrate and nitrite supernatant, and
4. solids-containing slurry.

The recipes used in FIU and other testing do not provide exact replication of material identified in the historical plugging events. Rather, the recipes broadly represent the major chemical elements present from the different groupings of plugging events and provide semi-realistic simulants for testing. Although the FIU recipes do not provide process chemistry equivalence, these materials do exhibit non-Newtonian rheological behavior and chemical interactions that lead to particle agglomeration (and even

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18 Double salts are known to form from Hanford wastes. In this report, the authors do not delineate this category, or class, of material separately. Many of the double salts may form from the phosphate bearing waste.
chemical bonding or adhesion to pipe walls – as observed in prior DWPF operations\textsuperscript{12,13,14}) thereby posing reasonable challenges.

A chemical recipe for plugs from phosphate containing supernatant appears lacking in the prior test program. Boomer et al.\textsuperscript{19} examined the solubility behavior of phosphate in the Hanford wastes and phosphate compounds contributed to a number of prior plugging incidents.\textsuperscript{8} In these cases, sodium phosphate formed needle-shaped crystals that resulted in very high slurry viscosity, causing what is commonly referred to as gel formation, though the slurry is not a gel in the true chemical sense of the word. Dan Herting, WTP Chief Chemist, provided the author with the following simplified recipe to prepare a phosphate solution that will form a “pseudo gel” when cooled below 50-55 °C without agitation or flow.

\begin{align*}
2.7\text{ M NaOH} \\
2.7\text{ M NaNO}_3 \\
2.7\text{ M NaNO}_2 \\
0.22\text{ M Na}_3\text{PO}_4
\end{align*}

Complete gel formation is reported by ~30 °C. A vial containing this solution will dissolve when immersed in hot water (e.g., dissolution begins near 50-60 °C). Herting indicates this recipe is a simplification of the following more representative solution.

\begin{align*}
1.3\text{ M NaAl(OH)}_4 \\
1.7\text{ M NaOH} \\
2.3\text{ M NaNO}_3 \\
2.2\text{ M NaNO}_2 \\
0.13\text{ M Na}_2\text{CO}_3 \\
0.25\text{ M Na}_3\text{PO}_4
\end{align*}

Reportedly, when the total sodium concentration exceeds ~8 M and the phosphate concentration exceeds 0.2 M, gel formation occurs. (Crystallization of solids begins at ~0.05 M phosphate.) Unfortunately, these formulations have not been prepared in prototypic pipe sections and hence the tenacity against removal or the applied hydraulic pressure required to remove the solids is not known.

Missing from this list but relevant to the PT Facility is the potential for solids formation and line plugging from chemical cleaning of the ultrafilters, such as observed recently at SRS from cleaning operations involving oxalic acid. (NOTE: Although the SRS example given is a plug from cleaning evolutions with oxalic acid, any acid cleaning operation that involves a shift in ionic strength and pH of the process streams is vulnerable to post-precipitation of solids and risks of plugging pipelines or equipment.)

Since filter cleaning operations proposed for the ultrafilters in the PT Facility represent new processing scenarios, simulants derived from historical classes of plugs observed in tank farm operations do not emulate solids that may results from those cleaning operations. The author did not find evidence that the previous programs assessed this risk from PT Facility operations. Oxalate plugs that result from chemical cleaning operations should dissolve relatively easily, although it is possible that severe packing of such solids – or concurrent precipitation of these solids with other materials such as sodium aluminosilicates –

will render simple flushing protocols ineffective. While no testing has occurred with plugs derived from cleaning solutions, the subjective opinion of the author is that the Na-Al-Si simulant likely will bracket these cases.

Properties and Performance Metrics

The work at PNNL measured various properties of the simulated plugs including free water content, bulk density, yield stress, and unconfined compressive stress (upon extrusion). No specific guidance is provided in the report for performance metrics for the simulant; work terminated prior to testing of the plug removal from pipelines.

The work at FIU uses a “blow out” pressure (of 300 psi) as the primary means of qualifying plugging behavior for simulants. The “blow out” pressure is the maximum hydrostatic load the simulant can withstand within the nominal 3-inch diameter pipeline without breaking free. Customers provided this criterion to FIU as the maximum pressure allowable for portions of the inter-area transfer lines at Hanford. The intent is that the simulated plug represents a material that resisted removal simply by high pressure flushing of the pipeline.

2.0 Conclusions and Recommendations

BNI requested that SRNL recommend simulants to “cover >95% of the plug types that could occur in WTP process piping” including both a chemical and a physical simulant, if deemed appropriate.

Covering the full range of expected plugs is not possible. As noted in the “Simulant Options” section, there are at least five classes of plugs that could occur in WTP process piping. The four classes of plugs derived from historical Hanford data are:

1. phosphate-containing supernatant,
2. aluminat-containing supernatant
3. concentrated, dissolved sodium nitrate and nitrite supernatant, and
4. solids-containing slurry.

The fifth class identified in this report is

5. solids from chemical cleaning operations (for example, of the ultrafilters in the PT Facility).

The test program to date has not developed chemical simulants for all five classes, relying primarily on physical simulants. In addition, testing has not yet explored the potential for plugs from sodium (or mixed metal) oxalates formed during filter cleaning operations as recently identified in analogous SRS operations.

The author recommends use of the Na-Al-Si simulant developed by PNNL and tested by FIU as the best available chemical simulant. Similarly, the author endorses the use of bentonite clay (or kaolin clay) simulants as tested by FIU as adequately representing physical properties of plugs from deposited sludge. Herting developed a recipe for phosphate solutions that precipitate as a solid mass when cooled below 50-55°C and this recipe is credible initial formulation for chemically representative plugs from phosphate materials. Unfortunately, the hydraulic pressure required to purge such solids from prototypic size pipes

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20 Communications from Dwayne McDaniel, Ph.D., P.E., to S.D. Fink, 24 June 2014.
has not been studied and, therefore, this formulation may require additional study or testing before fully assessing its adequacy for this application.

Consistent with the approach used in FIU testing, the author recommends use of the hydrostatic pressure needed to dislodge the simulated plug material (e.g., 300 psi) as the primary performance criteria for determining adequacy of candidate simulants.
Appendix A. Simulant Recipes

Na-Al-Si Simulant

PNNL personnel developed the recipe for the Na-Al-Si simulant and transferred it to FIU for use in testing. The following table and instructions come directly from the FIU report. PNNL tested several compositional variations from that shown here and the interested reader should review the source report for more detail.

Table 1. Chemicals Used to Manufacture 4 ft Na-Al-Si Plug

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(N0₃)₃·9H₂O</td>
<td>28136.27</td>
</tr>
<tr>
<td>NaOH</td>
<td>6000</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>2287.5</td>
</tr>
<tr>
<td>Na₂S0₄</td>
<td>133.1</td>
</tr>
<tr>
<td>NaF</td>
<td>15</td>
</tr>
<tr>
<td>NaH₂P0₄</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The procedure to prepare a 4 ft Na-Al-Si plug is given as:

NOTE: These instructions are quoted verbatim from the report and do not imply SRNL endorsement of the safety nor the efficacy for the operations as listed. The mention of white fumes (Step 5) implies a health hazard and the use of ventilation or worker protection needs assessed prior to start of work. In addition, the efficacy of the mixing tools and configuration in Step 5 may be non-optimal; the final instructions by a contractor need assessed (e.g., by BNI and appropriate experts) to ensure the mixing is sufficient to disperse the chemicals. SRNL recommends that any recipe or simulant preparation instructions used by the vendor receive a review by BNI – and any appropriate experts – prior to release of the work scope to the vendor.

1) Take a clean plastic bucket.

2) Add the required quantities of Sodium sulphate, sodium silicate, sodium fluoride and sodium phosphate in order. Mix the chemicals by manually shaking the bucket for 30 seconds.

3) Add sodium hydroxide to the above mixture. Make sure that the NaOH is weighed just before addition, so that the amount of water it gains from the atmosphere is minimal. Also all the chemical must be covered with air tight lids.

4) Once again manually shake the bucket so that NaOH gets mixed thoroughly and coated with other chemicals.

5) Add Na-Al-Si to the mix. Use an automatic drill with a long mixer extension to mix aluminum nitrate with the earlier chemicals mixture. Keep on stirring the entire mixture for about 2 minutes until you see the white fumes coming out. At this point you will not be able to see the bottom of the bucket clearly due to the fumes. Also the mixture should have turned into a gel like solution. It is recommended that this step is done in a walk-in fume hood.
6) Let the white fumes clear. This should take about 15-20 seconds. Once cleared, you can resume stirring for about 1 minute. The gel-like mixture turns into liquid. You also see the white fumes coming out again.

7) Stop mixing and let the white fumes clear out. Keep the bucket still for 1 minute. The solution is very hot, so make sure you have the rubber gloves on top of the latex gloves.

8) Tilt the bucket sideways and scoop the gel-like mixture into the pipes and leave the solution in the pipe overnight to solidify.

Since the extrusion pressure of the plug is low, engineers from PNNL suggested an alternative procedure for developing a plug that has stronger mechanical properties and is more likely to occur. The alternative approach is to keep mixing at the point (in line 7) where the recipe indicates to stop. This creates a semi-solid precipitate, and the liquid mixture and the solid can be removed and placed into the 4 ft pipe. After a short period of time the semi-solid precipitate settles and forms a hard crystallized material and the remaining liquid is decanted off.

**K-Mg Simulant**

FIU personnel selected potassium-magnesium sulfate (K-Mag®) to represent a crystallized salt plug due to its high mechanical strength. The material is a commercial fertilizer available from the Mosaic company composed of 22 wt % potash (K₂O), 10.8 wt % magnesium (as magnesia, MgO), (22%) as sulfur from sulfate (SO₄), with trace impurities and moisture. Per the FIU report: “The product comes in a granular form and had to be pulverized using a grinding machine before mixing with water. For a 4 ft plug containing 90% of K-Mag® and 10% water mixture, 1.5 liters of water was mixed with 13.5 kg of K-Mag® in a bucket using a drill mixer for about 30 minutes. The mixture was then poured into a 4 ft steel pipe that was closed on one side using a Victaulic cap and a Victaulic 77 coupling. The material is packed using a plunger during filling. When the pipe was full the open end is sealed using parafilm and the pipe is left to cure overnight.”

FIU tested the K-Mag® both as pulverized and unpulverized material. Pulverized material gave higher “blow out” pressures; presumably due to better packing in the pipeline.

**Kaolin or Bentonite Simulant**

FIU used kaolin (66-67 wt % in water) or bentonite (66-68 wt % in water) as simulants for deposited sludge slurry plugs. They expressed a preference for bentonite as it exhibited a higher yield stress and higher “blow out” pressure in testing. The preparation method as stated in the report is: “The bentonite-water mixture was prepared in a large bucket and mixed using a drill attachment until uniformity was achieved. Four-foot steel pipes that are closed on one side were then completely filled with the mixture by dropping small pieces in and compressing with a long plunger rod. In order to remove air gaps that can get entrapped inside the blockage during filling, the blockages were compressed using a torque wrench.”

NOTE: The concentrations specified by FIU are subject to variation as the supply of the clay materials varies. The subcontractor may need to optimize the concentration during testing.
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