



U.S. Department of Energy
Office of River Protection

P.O. Box 450, MSIN H6-60
Richland, Washington 99352

OCT 07 2005

05-WED-033

Mr. J. P. Henschel, Project Director
Bechtel National, Inc.
2435 Stevens Center
Richland, Washington 99352

Dear Mr. Henschel:

CONTRACT NO. DE-AC27-01RV14136 – TRANSMITTAL OF DESIGN OVERSIGHT
REPORT ON WASTE TREATMENT AND IMMOBILIZATION PLANT (WTP) OXIDATIVE
LEACHING

Reference: BNI letter from J. P. Henschel to R. J. Schepens, ORP, "Transmittal of Technical
Report on Oxidative Leaching (Deliverable 2.8) and Test Report on Oxidative
Leaching (Deliverable 2.9)," CCN: 123365, dated July 8, 2005.

The U.S. Department of Energy, Office of River Protection (ORP) conducted a design oversight of the Bechtel National, Inc. (BNI) oxidative leaching process design provided in the Reference. The WTP oxidative leaching process is intended to remove chromium from high-level waste (HLW) solids and reduce the quantity of HLW glass produced over the River Protection Project tank waste treatment mission. This letter transmits the subject Oversight Report which documents the conclusions, recommendations, and open items identified.

The Oversight Team concluded the following based on review of project information and discussions with BNI staff:

- The proposed use of sodium permanganate, as a reagent to conduct oxidative leaching of HLW tank sludge, for the dissolution of insoluble chromium, appears to provide a reference solution that can meet WTP project requirements. The chemistry of the proposed process has been shown to oxidize chromium to a soluble oxidation state but some optimization of the proposed process may still be realized by further testing.
- BNI work to test, evaluate, and design the oxidative leaching process was not completed and has not fulfilled all Contract requirements. Recommendations to improve the rationale for process selection and provide the technical basis to underpin the proposed process are included in the Oversight Report.

BNI will formally notify ORP of the plan and schedule for closure of the Open Items identified for BNI action in Section 5 of the Oversight Report by or within 45 days of receipt of this letter. These Open Items should be entered into the BNI Recommendation and Issue Report Tracking System.

Mr. J. P. Henschel
05-WED-033

-2-

OCT 07 2005

Work to complete testing, evaluation, and design of the oxidative leaching process is within Contract scope. If you have any questions, please contact me, or your staff may call William F. Hamel, Jr., Director, WTP Engineering Division, (509) 373-1569.

Sincerely,



Roy J. Schepens
Manager

WED:RAG

Attachment

cc w/attach:
L. Lamm, BNI
S. Piccolo, BNI

Attachment
05-WED-033

WTP Oxidative Leaching Design Oversight Report

D-05-DESIGN-013

WED:RAG
August 31, 2005

U.S. Department of Energy, Office of River Protection

WTP Oxidative Leaching
Design Oversight Report

D-05-DESIGN-013

August 2005

Prepared by:

R. A. Gilbert 9/1/05
R. A. Gilbert

L. K. Holton 9/1/05
L. K. Holton

J. E. Holland 9/1/05
J. E. Holland

D. H. Alexander 9/1/05
D. H. Alexander

C. K. Liu 9/1/05
C. K. Liu

Approved by:

William F. Hamel 9/1/2005
William F. Hamel, Director
WTP Engineering Division

Executive Summary

The U.S. Department of Energy (DOE), Office of River Protection (ORP) Waste Treatment and Immobilization Plant (WTP) Engineering Division (WED) performed a Design Oversight of the Bechtel National, Inc. (BNI) proposed oxidative leaching process design.

The objective of this Design Oversight was to assess the supporting technical basis and design for the BNI oxidative leaching process. Specific questions were evaluated with respect to Contract Compliance, Process Chemistry, Flowsheet Integration, Equipment Integration and Technical Risks.

The BNI proposed oxidative leaching process utilizes sodium permanganate to oxidize chromium in High-Level Waste (HLW) solids. This proposed treatment step would be conducted in the ultrafilter process system (UFP) and performed following caustic leaching and/or washing of HLW solids. This oxidative leaching process is shown by BNI to remove chromium from HLW solids, and reduce the number of HLW canisters required to be produced.

The Design Oversight Team concluded the following:

- The proposed use of sodium permanganate, as a reagent to conduct oxidative leaching of HLW tank sludge, for the dissolution of insoluble chromium, appears to provide a reference solution that can meet WTP project requirements. The chemistry of the proposed process has been shown to oxidize chromium to a soluble oxidation state but some optimization of the proposed process may still be realized by further testing.
- BNI has not provided information to indicate they have completed an evaluation of all available laboratory studies relating to oxidation of chromium in Hanford Tank waste. The Technical Report should be modified to clearly reflect the alternatives which were analyzed and the decision process for selection of candidate processes.
- BNI has not completed laboratory scale testing to demonstrate the proposed permanganate process in prototypical plant conditions. Therefore the performance of the process is uncertain.
- The use of a single value (e.g. 87%) for chromium removal efficiency from the proposed oxidative leaching process is not defensible considering the scatter in performance data from current testing and historical data.
- Other technologies for chromium oxidation; specifically ferrate, ozone, and high temperature extended contact caustic leaching with air appear to have the potential for reduced impact on processing in the River Protection Project compared to sodium permanganate. These other technologies may; be less corrosive to vessels and piping, minimize the dissolution of plutonium and other transuranic species during chromium dissolution, and have an acceptable impact on HLW glass production.

- BNI has not completed all WTP Contract requirements to support the proposal for the oxidative leaching technology. These include: an alternative technology evaluation and recommendation; a proof of process demonstration; demonstration that Cr will not be a limit in HLW glass production; and assessment of process impact on facility availability.

The Design Oversight Team made the following recommendations, that when completed by BNI, may support acceptance of the proposed oxidative leaching process:

- BNI should complete the following analyses, and present the results to ORP for further evaluation. These analyses include:
 - Completing a proof of process demonstration process test and assessing process impacts for all anticipated process systems,
 - Preparing Corrosion Evaluations on affected vessels and piping,
 - Updating the Criticality Safety Evaluation Report,
 - Assessing process impact on facility availability,
 - Identifying and costing WTP design changes to implement the process, and
 - Updating the Technical Report to document the final results of analyses and evaluations. The Technical Report should also be updated to address issues and comments identified in this design oversight on process control and sampling, Contract Specification 1 and Contract Specification 12.
- BNI should evaluate all existing data on oxidative leaching using permanganate to provide a defensible basis for the assumed oxidative leach factor(s), and addition rate of permanganate (e.g. mole permanganate to mole chromium) to be used in the modeling efforts. This factor should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs. The technical basis for the selection of the oxidative leaching factor should be presented to ORP for review and comment.
- BNI should replace the use of the TWINS/Feed Vector wash and leach factors for sulfate based upon their assessment provided in WTP-RPT-137. These wash and leach factor should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs and be used until updated sulfate wash and leach factors are incorporated into the TWINS data base/Feed Vector.

Additional Open Items for BNI action are summarized in Section 5.

The Design Oversight team recommends that ORP undertake the following actions to establish an optimized solution for the management of insoluble chromium in the River Protection Project.

- ORP should continue the evaluation of ozone, permanganate, ferrate, and high temperature caustic leaching with air in comparable conditions to support a balanced technical and cost comparison (including capital and operating costs) for final selection for implementation in the RPP.
- ORP should conduct HLW glass development testing to evaluate glass compositions that have higher concentrations of chromium, bismuth and sulfate compared to the WTP Contract

minimum specifications. These studies should be conducted to determine acceptable component waste loading considering: 1) avoidance of significant concentrations of crystal phases, and 2) production of crystal phases and evaluation of crystal settling and impact on the WTP HLW melter operations.

- ORP should work with the Tank Farm Contractor to capitalize on ongoing work to test samples of tank waste with high chromium content and limited data regarding oxidative leaching performance. Samples may become available from waste retrieval compatibility analysis or retrieval actions that could be tested with a small incremental cost.

The Design Oversight Team reviewed the results of this oversight report with BNI staff between August 23 and August 31, 2005.

Table of Contents

Executive Summary	i
1.0 Introduction.....	5
2.0 Evaluation of Proposed WTP Oxidative Leaching Process	5
2.1 BNI Deliverable Contract Compliance Questions	5
2.2 Proposed Process Chemistry Evaluation.....	8
2.2.1 Completion of Testing.....	8
2.2.2 Evaluation of Process Alternatives.....	9
2.2.3 Design Oversight Teams Evaluation of Process Alternatives.....	9
2.3 Process Flowsheet Integration.....	10
2.3.1 Basis for Chromium Removal Efficiency	10
2.3.2 Process Operating Concept.....	10
2.3.3 Process Modeling	12
2.4 Process Equipment Integration.....	14
2.5 Assessment of Risks	15
3.0 Conclusions.....	16
4.0 Recommendations.....	17
5.0 Open Items.....	18
6.0 References.....	20
Appendix A.....	22
Appendix B.....	46

List of Tables

Table 1 WTP Contract Requirements not met by the Technical Report and Supporting References	6
Table 2 List of Open Items from the ORP Oxidative Leaching Oversight.....	18

1.0 Introduction

The U.S. Department of Energy, Office of River Protection (ORP) will design, construct, commission, and operate a Waste Treatment and Immobilization Plant (WTP) to treat and immobilize waste contained in 149 single-shell tanks and 28 double-shell tanks (DST) at Hanford. These tanks contain approximately 54 Mgal waste with 190 MCi radioactivity. The WTP will receive waste in batches from the DSTs through transfer pipelines. This waste will be concentrated in an evaporator; strontium and transuranic will be precipitated from select waste streams; solids will be water washed, caustic leached, oxidative leached, and separated from the soluble fraction in an ultrafilter system; and cesium will be removed from the soluble fraction with an ion exchange system. The radionuclide rich solids and cesium ion exchange eluant will be combined and immobilized in High Level Waste (HLW) glass. The low-activity waste supernatant will be further concentrated and immobilized in Low Activity Waste (LAW) glass or immobilized in an alternative waste form currently being studied.

The WTP Contract requires Bechtel National, Inc. (BNI) to evaluate, recommend, and establish the capability to perform oxidative leaching to remove chromium from tank waste solids. This process is necessary to reduce the impact of chromium on HLW glass waste loading, and resulting volume of HLW glass. Without an oxidative leaching process, HLW glass volume projections exceed the capability of WTP HLW vitrification to complete the tank waste treatment mission by 2028, as required by the Tri-Party Agreement.

The *Pretreatment Oxidative Leaching Path Forward* (CCN: 089106), documented BNI's plan to evaluate, recommend, and establish the capability to perform oxidative leaching. BNI's *Technical Report on Oxidative Leaching* (24590-WTP-RPT-ENG-05-006) and associated references provide information to support completion of the WTP oxidative leaching Contract requirements.

This WTP Oxidative Leaching Design Oversight Report documents the ORP WTP Engineering Division (WED) evaluation of the BNI proposed oxidative leaching process design. ORP's Design Product Oversight Plan for WTP Oxidative Leaching is provided in Appendix B.

2.0 Evaluation of Proposed WTP Oxidative Leaching Process

Sections 2.1 through 2.5 of this report summarize design oversight conclusions pertaining to each line-of-inquiry grouping in the areas of: BNI Deliverable Contract Compliance, Proposed Process Chemistry Evaluation, Process Flowsheet Integration, Equipment Integration, and Assessment of Risks. Specific observations for each line-of-inquiry are documented in Appendix A.

2.1 BNI Deliverable Contract Compliance Questions

BNI provided to ORP for review and comment 24590-WTP-RPT-ENG-05-006 in support of the WTP Contract Standard 2 requirement as defined below.

Standard 2: Research, Technology, and Modeling, (a) Research and Technology Testing Program, (3) Required Research and Technology Testing, (ix) Oxidative Leaching:

The Contractor shall conduct a literature review and prepare a technical report (Table C.5-1.1, Deliverable 2.8 Technical Report on Oxidative Leaching) that evaluates the treatment processes for the oxidative leaching of chemical components (principally Cr and associated components, i.e. sulfate) that limit the loading of HLW solid oxides in the HLW glass waste form. The literature review shall summarize existing experimental results and data, and present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions. Based upon the study results, the Contractor shall provide a recommendation on the preferred process to conduct required separations.

The Contractor shall conduct technology testing work using simulants and actual waste testing to provide design and process operational information on the process used to remove Cr from the HLW waste stream. The process should have the capability to remove Cr from the pretreated HLW stream such that this chemical component, or reagents added to remove this component does not limit the HLW waste loading in the glass waste form. The Contractor shall test a minimum of (2) radioactive tank waste samples. (SY-102 and a second sample that must be provided so that analysis with sample SY-102 can be run concurrently) The test shall be conducted to provide proof of process demonstration (part of Deliverable 2.2 and 2.3) and to determine any impacts to the facility throughput and/or availability. The Contractor shall make recommendations to ORP for the modification of Specification 12, Number of High-Level Waste Canisters Per Batch of Waste Envelope D and Specification 1, Immobilized High-Level Waste, Table TS-1 limits for Cr₂O₃ and sulfate, based upon the results of this experimentation. (Table C.5-1.1 Deliverable 2.9 Test Report on Oxidative Leaching)

The 24590-WTP-RPT-ENG-05-006 (hereafter referred to as "Technical Report") summarized how the Contract requirements for the proposed oxidative leaching process were completed. The Technical Report provides a roadmap to supporting documentation to demonstrate completion of the Contract requirement.

The Design Oversight Team determined that the Technical Report and supporting deliverables met Contract requirements, except for those requirements described in Table 1 below.

Table 1 WTP Contract Requirements not met by the Technical Report and Supporting References

Contract Requirement	Comment
<i>The literature review shall summarize existing experimental results and data, and present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions.</i>	The literature review provided in WTP-RPT-117 summarized experimental data on previously evaluated Cr oxidation leaching processes. These processes were not developed to "present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions"

Table 1 WTP Contract Requirements not met by the Technical Report and Supporting References

Contract Requirement	Comment
	for the alternatives considered. BNI did not conduct a formal evaluation of the alternatives to provide a technical basis for their recommendation. See Appendix A for additional discussion.
<i>The Contractor shall conduct technology testing work using simulants.</i>	The contractor did not conduct any simulant testing to test or provide further understanding of process performance. A rationale for not conducting simulant testing was provided in WTP-RPT-137. The Design Oversight Team believes that simulant testing can help resolve some of the technical issues associated with the process.
<i>The process should have the capability to remove Cr from the pretreated HLW stream such that this chemical component, or reagents added to remove this component does not limit the HLW waste loading in the glass waste form.</i>	The Dynamic Model results (model runs completed by BNI) demonstrated that when sulfate is washed/leached based upon more realistic wash and leach factors presented in WTP-RPT-137, that Cr is a glass loading constraint at 0.5 wt% Cr ₂ O ₃ in about 13% of the HLW melter feed batches. See Appendix A for additional discussion.
<i>The test shall be conducted to provide proof of process demonstration.</i>	The laboratory test procedure documented in WTP-RPT-117 and the proposed WTP Plant procedure have significant differences. The testing completed does not provide a proof of process demonstration. This is further confirmed by testing strategy in the Test Plan for the oxidative leaching process (TP-RPP-WTP-275).
<i>....determine any impacts to the facility throughput and/or availability.</i>	The contractor did not present an analysis on plant availability. The contractor indicated that this requirement is being met in a future Contract deliverable.

The Design Oversight Team concluded the Technical Report was an engineering study covered by 24590-WTP-3DP-G04B-00016. The Technical Report does not meet the requirements on content for an engineering study as defined in 24590-WTP-3DP-G04B-00016. The following additions are required in the revision of the Technical Report.

- Approval by the cognizant DEM (Section 2.1)
- Cost and schedule estimates/impacts from Project Controls (Section 3.1.2)
- Review and approval by the DEM/APEM or APE (Section 3.2.1)
- Formal Studies report format in attachment B (Section 3.3.1) including: Study

Basis criteria, assumptions, description of alternative solutions considered and selection of the recommended alternative.

Open Item 1: BNI should revise the Technical Report to comply with the requirements of the Engineering Department procedure on Engineering Studies (24590-WTP-3DP-G04B-00016).

2.2 Proposed Process Chemistry Evaluation

2.2.1 Completion of Testing

In review of the Test Plan for the Oxidative Leaching experiment (TP-RPP-WTP-275) it was determined that the testing presented in WTP-RPT-117 was not intended to provide a proof of process test demonstration. The testing reported was “advisory” and to be used to define the conditions for time, temperature and the oxidant addition rate. This information would be used to provide a recommendation for a larger scale testing of the oxidant leaching procedure in the Cells Unit Filter (CUF) device. Therefore the assertion in the Technical Report that the scoping tests provide a proof of process demonstration is incorrect. (See page 10 of the Technical Report, Section 4.7).

The proposed process recommends an addition rate of 1.1 mole permanganate to 1 mole Cr at a free hydroxide concentration of 0.25 molar. Comparison of the experimental results, shown in Table 3.6 of WTP-RPT-117, indicates variation from expected behavior in terms of the dose rate and Cr removal. Therefore the prescribed dose may only be indicative, and should be further verified in additional experiments.

The fate of chromium in the WTP process system was not completely evaluated in the proposed process. Chromium will be dissolved in the UFP system, and recycled through the PWD and FEP systems, before return to the UFP system for separation and transfer to the LAW melter feed stream. The proof of process demonstration should demonstrate that chromium does not precipitate (e.g. accumulate) in chemistry conditions expected in the PWD and FEP systems, and can be effectively transferred to the LAW melter feed system.

BNI has indicated (WTP-RPT-137) that the use of simulants may not be beneficial because the low concentration of Pu in the waste may make it difficult to prepare a useful simulant. However, because of the lack of clear understanding on the process, it could be useful to conduct further testing using simulants to determine the level to which organics and inorganics compete with chromium for the oxidant over a range of potential conditions.

Open Item 2: BNI should perform a proof of process demonstration test (s) following finalization of process parameters to demonstrate the oxidative leaching process at conditions which more closely represent the anticipated plant flowsheet conditions for all anticipated process systems. Based upon the results of this work, the Contractor should re-assess the benefits of the proposed process.

2.2.2 Evaluation of Process Alternatives

Preliminary experiments were conducted as part of previous studies to screen oxidants that could be suitable for oxidative leaching of insoluble chromium. These reagents which showed the most promise included: permanganate, ozone, ferrate, and high temperature extended contact caustic leaching with air. The proposal to use permanganate for the treatment of the tank wastes is made based upon a very limited set of experiments, when considering permanganate only, and when comparing the permanganate with other candidate technologies. This suggests that without a further evaluation, the basis for the proposed recommendation is weak. See Appendix A for additional discussion.

The literature review, presented in WTP-RPT-117, is the only documented evidence that alternative processes were evaluated before a recommendation on the final process was made. There is no objective evidence, that BNI engineering participated in any evaluation of the candidate processes or conducted any evaluation to examine the advantages and disadvantages of the candidate processes. This evaluation should have included definition of requirements, conceptual flowsheet development with material balances and identification of equipment requirements and an assessment of advantages and disadvantages prior to making a recommendation. This evaluation protocol is defined in the WTP Contract (...*present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions, Standard 2*) and the procedure for *Engineering Studies* (24590-WTP-3DP-G04B-00016, Rev 2).

2.2.3 Design Oversight Teams Evaluation of Process Alternatives

Comparison of results of oxidant screening experiments for several different oxidants is included in Table 1.3 of WTP-RPP-117. Inconsistencies in this comparison are summarized below.

- The oxidants were not tested under equivalent conditions and tank waste compositions. Permanganate, ozone, and air were compared across samples in tanks SY-103, B-111, BY-110, SX-108, and S-107, whereas persulfate and ferrate were compared in S-110 and peroxyntirite was compared in U-108. Ferrate has also been tested on S-107, results of which were not included in this report, but in a peer reviewed journal (Sylvester et al). High temperature caustic leaching with extended contact time and air was compared in S-110, S-104, S-101, and S-111.
- The composition and form of Cr and Pu, as well as the concentration of oxidant scavengers in these tank samples differ. Comparing the percent removal of Cr and percent removal of Pu for different oxidants in different tank samples may therefore lead to incorrect conclusions.

This variety of tank samples tested combined with the lack of a side by side comparison calls into question the recommendation to use permanganate.

Open Item 3: *ORP should continue the evaluation of ozone, permanganate, ferrate, and high temperature caustic leaching with air in comparable conditions to support a*

balanced technical and cost comparison (including capital and operating costs) for final selection for implementation in the RPP. Previous studies have evaluated these different technologies in different tank wastes; therefore a review of the existing literature should be completed to determine the major differences in conditions under which currently available data were collected. This literature review should be used to determine whether further experiments should be conducted and if so, what components should be included in the design of these experiments.

2.3 Process Flowsheet Integration

2.3.1 Basis for Chromium Removal Efficiency

The oxidative leaching process proposed by BNI was described at a conceptual level and was supported by limited research and technology data. The proposed process utilizes the ultrafilter feed vessels (UFP-VSL-00002A/2B) to conduct oxidative leaching. This process is performed sequential to, and following, caustic leaching and sludge washing. Washed HLW solids are oxidized at 25°C in 0.25 molar free hydroxide with sodium permanganate, added as a dose of 1.1 to 1 mole permanganate to chromium in the solids. The solids are reacted for six hours and then washed.

The testing results from two tank waste samples (SY-102/SX-101) provided the basis for the preliminary conceptual process design selection. One specific test with SX-101 (SX-101-3) was used as the single basis for performance modeling. In addition, the tank waste samples were washed, caustic leached, and oxidative leached in different sequences, and with different wash concentration ratios compared to those proposed in the oxidative leaching process design.

***Open Item 4:** BNI should evaluate all data, including that to be collected in the proof of process demonstration experiment, on oxidative leaching using permanganate to provide a defensible basis for the assumed oxidative leach factor(s), and addition rate of permanganate (e.g. mole permanganate to mole chromium) to be used in the modeling efforts. This factor should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs. The technical basis for the selection of the oxidative leaching factor should be presented to ORP for review and comment.*

2.3.2 Process Operating Concept

There were two basic alternatives for the potential implementation of the oxidative leaching process in the Pretreatment facility. These were:

- Completion of the oxidative leaching process concurrent with (e.g. combined with) the caustic leaching process, and
- Completion of the oxidative leaching process sequential to (e.g. following) the caustic leaching.

These process alternatives were evaluated in the radioactive scoping tests (WTP-RPT-117), initial evaluations of the proposed process (CCN: 110724) and initial criticality evaluations of

the proposed process (24590-WTP-RPT-NS-05-001). The conclusions from these evaluations indicated that the sequential process is preferred based primarily upon minimizing the dissolution of Pu. It was recognized that the concurrent process would remove more Cr due to operation at a higher temperature and caustic concentration. However, the dissolution of Pu could increase up to 13% at 3 M NaOH and 85°C as indicated in test SX-101-1 (Table 3.9, page 3.15, WTP-RPT-117).

As discussed in Appendix A based on the Dynamic Model results, the proposed sequential process does not remove sufficient Cr from the HLW batches to eliminate Cr as a waste loading constraint. It is also not clear if the dissolution of Pu will present an issue with respect to plant operations. This suggests that the specific conditions for process operation must be evaluated more carefully.

The proposed process for the oxidative leaching process is identified in Section 4.3 of the Technical Report and CCN: 110724. While the basic steps of the process are defined, the specific operational parameters are not identified. Missing are the following:

- Solids concentration for the slurry
- Identification of the mixing requirements (e.g. PJM and/or spargers) during the process
- Identification of UFP filter pump/ultrafilter loop status during process operations.
- Sampling and analysis requirements and decisions associated with the sample results.

Included in the Technical Report is a suggested test protocol (Appendix A, Proposed Revision to Specification 12) for deciding if the oxidative leaching should be used to treat a given feed batch. This test protocol is based upon the use of a "representative HLW sample".

The use of a tank farm waste sample, for process decision making, as required by Specification 12 will not adequately support the oxidative leaching process due to the quality of the sample and precise dosage rates suggested by the proposed procedure. This situation is different than water washing and caustic leaching for Specification 12 which can be accomplished by the use of a tank farm waste sample to provide supporting information. This water wash/caustic sample strategy works because the component of interest in the waste, namely aluminum, is present as a large fraction in the composition. Insoluble Cr by comparison, will be present in a much smaller concentration in the waste. In addition, the specific composition of the HLW solids in the UFP system will be impacted by processing of various waste streams in the WTP. The proposed oxidative leaching process relies on a precise dose of permanganate based upon the composition being processed (e.g., 1.1 mole permanganate/1 mole Cr suggested). A dose less than this level may not be effective in removal of Cr. A dose in excess of this level may dissolve excessive Pu, or react with the ion-exchanger as suggested in the Technical Report. In addition the behavior of Pu will be impacted based upon its relative concentration to Cr and the permanganate dose rate. Thus, it appears that a sample from the UFP system will be required to support operations.

Open Item 5: BNI should revise the description of the proposed oxidative leaching process to include the requirements for process control, including sampling and analysis, to allow a further determination on the viability of the process.

2.3.3 Process Modeling

Dynamic model runs were performed for a “No Oxidative Leach Case” and an “Oxidative Leach Case” for the tank waste treatment mission. These model runs summarized in CCN: 110731 assumed that the ultrafilter system would be operating in a “sequential” operating mode. The UFP system performs two major functions; dewatering of the sludge which is estimated to take 100 hours, and treatment of the sludge which is estimated to take 80 hours for caustic leaching and 90 hours for caustic leaching and oxidative leaching combined. In the parallel operating mode selected for the Dynamic model runs, the treatment in one UFP system is not initiated until the dewatering is completed in the other UFP system. This in effect sets the batch process time at 200 hours regardless of the sludge treatment method (e.g. water wash, caustic wash or caustic wash/oxidative leach.). This assumption is inconsistent with BNI’s identified “design” repair of the UFP system design capacity. Because of this, the Dynamic Model runs mask a determination of the potential impacts of the proposed process on WTP Plant throughput.

The Dynamic Model runs indicate a completion date of 12/31/2059 for the “No Oxidative Leach Case” and a completion date of 12/31/2043 for the “Oxidative Leach Case”. The reduction in the processing schedule for the Oxidative Leach Case is a direct result of the HLW glass mass reduction of 34%. These results are also impacted by key assumptions used in the model runs including the: parallel UFP operating mode, glass waste loading constraints and the feed vector. This long schedule for processing is not representative of the anticipated performance of the WTP facilities and the results are only considered indicative by the Oversight Team. Thus, the assertion of a 34% HLW glass mass reduction is speculative.

The availability of the Pretreatment facility is being evaluated in the Operational Research Assessment due in August 2005. Thus, this Design Oversight did not assess the availability of the Pretreatment facility. This assessment should consider the: reliability of the design features added to support the proposed process, impacts to sampling and analysis of the process streams to support process control, including Specification 12 testing, and criticality safety monitoring and verification.

The Technical Report did not provide a detailed assessment of the impact of the oxidative leaching process on the IHLW and ILAW waste forms. The Dynamic Models assumed that the waste loading constraints were those specified in the WTP Contract. Thus, the only impact to the waste forms was to the total volume and mass projected to be produced.

The literature review (WTP-RPT-137) provided an assessment of sulfate chemistry in the Hanford tank waste. Based upon this, BNI has determined that the estimated wash and leach factors for sulfate, as identified in the TWINS data base, and the Tank Farm Contractors provided feed vector are low compared to their results. The Dynamic Model runs provided as part of the Oxidative Leach deliverables assumed these lower values and show that SO_3 will be the limiting component for >20% of the HLW glass batches following the removal of chromium by oxidative leaching. Updating the assumptions on sulfate washing and leaching will provide a more realistic estimate of WTP performance.

***Open Item 6:** BNI should replace the use of the TWINS/Feed Vector wash and leach factors for sulfate, based upon their assessment provided in WTP-RPT-137, and use these sulfate wash and leach factors in future Aspen Custom Modeler and Dynamic Modeling Runs. These wash and leach factors should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs and be used until updated sulfate wash and leach factors are incorporated into the TWINS data base/Feed Vector.*

An evaluation of the Dynamic Flowsheet modeling results was completed to determine which chemical components limited the effective HLW loading. Five cases were compared:

- Case 1-WTP Baseline
- Case 2-WTP Baseline with oxidative leaching
- Case 3-WTP Baseline with oxidative leaching with the sulfate wash/leach factors to be at least 0.75, and the Cr₂O₃ concentration in the glass at 0.5 wt%
- Case 4-WTP Baseline with oxidative leaching with the sulfate wash/leach factors to be at least 0.75, and the Cr₂O₃ concentration in the glass at 1.0 wt%
- Case 5 WTP Baseline with oxidative leaching with the sulfate wash/leach factors to be at least 0.75, and the Cr₂O₃ concentration in the glass at 1.5 wt%

These cases illustrate the following:

- The proposed process, Case 2, will remove a significant fraction of the Cr from the tank wastes, and allow the HLW canister mass to be reduced. An estimated 34% reduction in HLW canisters (35,076 to 23,165) is projected. However, even with oxidative leaching, the Cr₂O₃ is still limiting as a glass component for 3580 HLW canisters of HLW glass.
- Case 3 removes the constraint on HLW glass waste loading caused by sulfate. This results in an increased number of MFPV glass batches limited by Cr₂O₃, potentially up to 70% of the batches if other waste loading constraints are removed. Increasing the allowable Cr₂O₃ to 1.0 wt% (Case 4), and 1.5 wt% (Case 5), will reduce the number of MFPV glass batches that are limited by Cr₂O₃. However even at these increased concentrations, chromium will still be a glass loading limit.
- Increasing the Cr₂O₃ concentration in the glass by up to 1.5 wt% (Case 5) will not result in further reduction in HLW glass mass due to other components in the HLW glass that limit waste loading. An inspection of the Dynamic Model runs reveals that other components, primarily Bi and Al will limit glass waste loading. In the case of Bi it is likely that the loading constraint is understated. However, little data is available on Bi. In the case of Al the waste loading assumption is also low and the assumption on when to complete caustic leaching may be too conservative. The model assumes that caustic washing is used when there is at least a 10% reduction in the HLW canister projection from a treated batch. This assumption however results in an additional 20% of more glass being produced. This decision variable in the Dynamic Model should be reassessed.

The canister production estimates from the Dynamic Model, and those estimated by the Tank Farm Contractor (RPP-20003) are significantly different. The primary difference is due to the

assumptions used on glass waste loading. BNI has used the WTP Contract Table TS-1 limits as the basis for glass loading. The Tank Farm Contractor has used a glass properties model as the basis for glass loading. The glass property model will project a lower number of canisters to be produced. This in turn will impact an assessment of the efficiency created by the oxidative leaching process.

These results indicate the need to continue glass development studies to reduce the HLW canister production requirement. These studies should focus on; increasing the allowable concentration of Cr, Al and Bi in the glass formulation, and demonstration of the capability of the HLW melter to remove crystalline phases from the melter. This is needed because a significant number of melter feed batches will have a Cr_2O_3 concentration of greater than 1.5 wt% in the glass.

***Open Item 7:** ORP should conduct HLW glass development testing to evaluate glass compositions that have higher concentrations of chromium, bismuth and sulfate compared to the WTP Contract minimum specifications. These studies should be conducted to determine acceptable component waste loading considering: 1) avoidance of significant concentrations of crystal phases, and 2) production of crystal phases and evaluation of crystal settling and impact on the WTP HLW melter operations.*

2.4 Process Equipment Integration

The Technical Report states the only required modification to the facility to perform oxidative leaching is to connect two spare lines to the ultrafilter feed vessels (UFP-VSL-00002A/2B) to the reagent source in the C3 area. The reagent is provided from the pretreatment distribution header for 1.0M NaMnO_4 . The Technical Report stated all other required equipment is included in the WTP baseline design. The Design Oversight Team agrees with this assessment based on the current conceptual level of oxidative leaching design completion. However, additional design impacts may be defined through:

- Completing the proof of process demonstration and development of a complete description of the process operating requirements.
- Completing required integrated safety management (ISM) safety analysis of the oxidative leaching process.
- Updating the Preliminary Safety Analysis Report (PSAR) to include oxidative leaching.
- Preparing and obtaining approval of a revised Criticality Safety Evaluation Report (CSER) to include the oxidative leaching process.
- Completing environmental permit modifications to include the oxidative leaching process.

BNI has not updated the Corrosion Evaluations (CE) for the UFL-VSL-00002A/2B vessels (24590-PTF-N1D-UFP-00003, Rev 4) for the proposed oxidative leaching process, where the primary selective oxidation reaction will occur. In addition, proposed permanganate oxidation process will generate secondary waste streams, such as the Cr rich stream that is recycled back through the Plant Wash and Drain System (PWD). The impact of these process streams, and other secondary waste streams, on the Pretreatment Facility CEs was not completed. Other vessels that should be reviewed include the: Acidic/Alkaline Effluent Vessels (PWD-VSL-00015/00016) and the Waste Feed Evaporator Feed Vessels (FEP-VSL-00017A/00017B).

Open Item 8: BNI should complete an evaluation of the impacts of the proposed oxidation process on the materials of construction for the affected vessels and piping, and identify any operating limitations. The Corrosion Evaluations for the affected vessels and piping should be updated consistent with the procedures identified in Preparation of Corrosion Evaluations (24590-WTP-GPG-M-047).

2.5 Assessment of Risks

BNI updated their risk assessment based on the proposed conceptual design of the oxidative leaching process. Risks identified relate to Pu separation by ion-exchangers and Pu accumulation at points down stream of the ultrafilter system, impact to the quantity of glass produced as a result of manganese added as a reagent, and degradation of the ion exchange resin due to exposure to permanganate.

Several other risks were identified by the Design Oversight Team including:

- The tank waste samples tested, and the data in literature, may not represent the spectrum of waste requiring oxidative leaching over the mission. Actual data may not be available until waste is staged for treatment and samples taken and tested. ORP and the Tank Farm Contractor should evaluate opportunities to test samples projected to require oxidative leaching when they are being tested for waste compatibility or other process testing.
- Competing species in the waste stream (insoluble metals and organics) will compete for the permanganate. Therefore, the quantity of permanganate will be difficult to estimate without direct sampling and testing of each new waste composition after washing and caustic leaching.
- Available data from samples tested was generated using procedures different and likely not representative of the proposed oxidative leaching process. Integrated testing should be performed demonstrating the caustic leaching, washing, and oxidative leaching processes including recycle streams perform as predicted.
- Impacts of the process on plant throughput and availability could be considerable if process stream sampling (e.g. for criticality criteria) and line/vessel flushing requirements become substantial.
- Uncertainties associated with pitting corrosion and stress-corrosion cracking induced by permanganate (especially at welds) need to be evaluated.
- Integrated Safety Management (ISMS) and criticality safety evaluations (CSER) have not been completed and need to be completed before an adequate assessment of the risks associated with the recommended process can be fully evaluated.

Based upon the preceding the Design Oversight team has identified the following Open Item

Open Item 9: BNI should reassess the technical and programmatic risks associated with the oxidative leaching process following the completion of the BNI assigned Open Items identified in this Design Oversight Report.

Open Item 10: ORP should work with the Tank Farm Contractor to capitalize on ongoing work to test samples of tank waste with high chromium content and limited data regarding oxidative leaching performance. Samples may become available from waste retrieval compatibility analysis or retrieval actions that could be tested with a small incremental cost.

Other risks associated with implementing oxidative leaching are operational and can be deferred to the future WTP operating contractor. The waste currently planned to be treated by BNI during hot commissioning does not require oxidative leaching.

3.0 Conclusions

The Design Oversight Team has concluded the following:

- The proposed use of sodium permanganate, as a reagent to conduct oxidative leaching of HLW tank sludge, for the dissolution of insoluble chromium, appears to provide a reference solution that can meet WTP project requirements. The chemistry of the proposed process is not clearly understood and appears to have a significant potential for optimization.
- BNI did not complete a comprehensive evaluation of alternative process approaches for the dissolution of chromium from Hanford tank wastes. This comprehensive evaluation would have characterized the performance, and impact, of candidate processes on baseline WTP performance and waste form volume estimates. The BNI evaluation focused on the characterization of a single process approach. As a result, it is not clear that the proposed process is optimum for implementation in the WTP in terms of technical performance, treatment benefits, and life cycle cost compared to alternative technologies identified.
- BNI has not completed laboratory scale testing to demonstrate the proposed permanganate process in prototypical plant conditions. Therefore the performance of the process is uncertain.
- The use of a single value (e.g. 87%) for chromium removal efficiency from the proposed oxidative leaching process is not defensible considering the scatter in performance data from current testing and historical data.
- Other technologies for chromium oxidation; specifically ferrate, ozone, and high temperature extended contact caustic leaching with air appear to have the potential for reduced impact on processing in the River Protection Project compared to sodium permanganate. These other technologies may; be less corrosive to vessels and piping, minimize the dissolution of plutonium and other transuranic species during chromium dissolution, and have an acceptable impact on HLW glass production.

- BNI has not completed all WTP Contract requirements to support the proposal for the oxidative leaching technology. These include: an alternative technology evaluation and recommendation; a proof of process demonstration; demonstration that Cr will not be a limit in HLW glass production; and assessment of process impact on facility availability.

4.0 Recommendations

The Design Oversight Team makes the following recommendations, that when completed by BNI, may support acceptance of the proposed oxidative leaching process:

- BNI should complete the following analyses, and present the results to ORP for further evaluation. These analyses include:
 - Completing a proof of process demonstration process test and assessing process impacts,
 - Preparing Corrosion Evaluations on affected vessels and piping,
 - Updating the Criticality Safety Evaluation Report,
 - Assessing process impact on facility availability,
 - Identifying and costing WTP design changes to implement the process, and
 - Updating the Technical Report to document the final results of analyses and evaluations. The Technical Report should also be updated to address issues and comments identified in this design oversight on process control and sampling, Contract Specification 1 and Contract Specification 12.
- BNI should evaluate all existing data on oxidative leaching using permanganate to provide a defensible basis for the assumed oxidative leach factor(s), and addition rate of permanganate (e.g. mole permanganate to mole chromium) to be used in the modeling efforts. This factor should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs. The technical basis for the selection of the oxidative leaching factor should be presented to ORP for review and comment.
- BNI should replace the use of the TWINS/Feed Vector wash and leach factors for sulfate based upon their assessment provided in WTP-RPT-137. These wash and leach factors should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs and be used until updated sulfate wash and leach factors are incorporated into the TWINS data base/Feed Vector.

The Design Oversight team recommends that ORP undertake the following actions to establish an optimized solution for the management of insoluble chromium in the River Protection Project.

- ORP should continue the evaluation of ozone, permanganate, ferrate, and high temperature caustic leaching with air in comparable conditions to support a balanced technical and cost comparison (including capital and operating costs) for final selection for implementation in the RPP.
- ORP should conduct HLW glass development testing to evaluate glass compositions that have higher concentrations of chromium, bismuth and sulfate compared to the WTP Contract minimum specifications. These studies should be conducted to determine acceptable component waste loading considering: 1) avoidance of significant concentrations of crystal

phases, and 2) production of crystal phases with evaluation of crystal settling rates and potential impacts on WTP HLW melter operations.

- ORP should work with the Tank Farm Contractor to capitalize on ongoing work to test samples of tank waste with high chromium content and limited data regarding oxidative leaching performance. Samples may become available from waste retrieval compatibility analysis or retrieval actions that could be tested with a small incremental cost.

5.0 Open Items

The following Open Items have been identified by the Design Oversight team for BNI and ORP action.

Table 2 List of Open Items from the ORP Oxidative Leaching Oversight

Open Item Number	Open Item
1	BNI should revise the Technical Report to comply with the requirements of the Engineering Department procedure on Engineering Studies (24590-WTP-3DP-G04B-00016).
2	BNI should perform a proof of process demonstration test (s) following finalization of process parameters to demonstrate the oxidative leaching process at conditions which more closely represent the anticipated plant flowsheet conditions for all anticipated process systems. Based upon the results of this work, the Contractor should re-assess the benefits of the proposed process.
3	ORP should continue the evaluation of ozone, permanganate, ferrate, and high temperature caustic leaching with air in comparable conditions to support a balanced technical and cost comparison (including capital and operating costs) for final selection for implementation in the RPP. Previous studies have evaluated these different technologies in different tank wastes; therefore a review of the existing literature should be completed to determine the major differences in conditions under which currently available data were collected. This literature review should be used to determine whether further experiments should be conducted and if so, what components should be included in the design of these experiments.
4	BNI should evaluate all data, including that to be collected in the proof of process demonstration experiment, on oxidative leaching using permanganate to provide a defensible basis for the assumed oxidative leach factor(s), and addition rate of permanganate (e.g. mole permanganate to mole chromium) to be used in the modeling efforts. This factor should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs. The technical basis for the selection of the oxidative leaching factor should be presented to ORP for review and comment.

Table 2 List of Open Items from the ORP Oxidative Leaching Oversight

Open Item Number	Open Item
5	BNI should revise the description of the proposed oxidative leaching process to include the requirements for process control, including sampling and analysis, to allow a further determination on the viability of the process.
6	BNI should replace the use of the TWINS/Feed Vector wash and leach factors for sulfate, based upon their assessment provided in WTP-RPT-137, and use these sulfate wash and leach factors in future Aspen Custom Modeler and Dynamic Modeling Runs. These wash and leach factors should be applied in future Aspen Custom Modeler and Dynamic Modeling Runs and be used until updated sulfate wash and leach factors are incorporated into the TWINS data base/Feed Vector.
7	ORP should conduct HLW glass development testing to evaluate glass compositions that have higher concentrations of chromium, bismuth and sulfate compared to the WTP Contract minimum specifications. These studies should be conducted to determine acceptable component waste loading considering: 1) avoidance of significant concentrations of crystal phases, and 2) production of crystal phases and evaluation of crystal settling and impact on the WTP HLW melter operations.
8	BNI should complete an evaluation of the impacts of the proposed oxidation process on the materials of construction for the affected vessels and piping, and identify any operating limitations. The Corrosion Evaluations for the affected vessels and piping should be updated consistent with the procedures identified in Preparation of Corrosion Evaluations (24590-WTP-GPG-M-047).
9	BNI should reassess the technical and programmatic risks associated with the oxidative leaching process following the completion of the BNI assigned Open Items identified in this Design Oversight Report.
10	ORP should work with the Tank Farm Contractor to capitalize on ongoing work to test samples of tank waste with high chromium content and limited data regarding oxidative leaching performance. Samples may become available from waste retrieval compatibility analysis or retrieval actions that could be tested with a small incremental cost.

6.0 References

1. 24590-PTF-N1D-UFP-00003, Corrosion Evaluation for UFP-VSL-00002A/B (PTF) Ultrafiltration Feed Vessels, Rev. 4, Bechtel National, Inc., March 10, 2005.
2. 24590-WTP-3DP-G00B-00001, Rev 56, Master Index of Engineering Department Procedures, July 5, 2005.
3. 24590-WTP-3DP-G04B-00016, Rev 2, *Engineering Studies*, August 4, 2003.
4. 24590-WTP-GPG-M-047, Rev 1.0, *Preparation of Corrosion Evaluations*, March 8, 2004.
5. 24590-WTP-M0E-50-00003, Rev C. "Engineering Calculation Change Notice, Wear Allowances for WTP Waste Slurry Systems" dated September 3, 2004.
6. 24590-WTP-RPT-M-04-0008, Rev 2, Krafft, HM, "Evaluation of Stainless Steel Wear Rates in WTP Waste Streams at Low Velocities". January 24, 2005. Bechtel National Inc., Richland, Washington.
7. 24590-WTP-M0C-50-00004, Rev C. "Wear Allowances for WTP Waste Slurry Systems" dated June 14, 2004.
8. 24590-PTF-N1D-UFP-00003, Corrosion Evaluation for Vessel UFP-VSL-00002A/2B
9. 24590-WTP-RPT-ENG-05-006, *Technical Report on Oxidative Leaching*, Rev. 0, Bechtel National, Inc., June 30, 2005.
10. 24590-WTP-RPT-NS-05-001, *Criticality Safety Aspects of Oxidative Leach*, Rev. A, Bechtel National, Inc., May 9, 2005.
11. 24590-WTP-RPT-PR-04-0001
12. Brown, B.E., Lu, H.H., Duquette, D.J.1992. "Effect of Flow-Rates on Localized Corrosion Behavior of 304 Stainless-Steel in Ozona Ted 0.5 N NaCl." *Corrosion* 48(12): 970-975
13. CCN 110724, Design Process Baseline Process Description for Oxidative Leaching, Eric Slaathaug to Dale Obenauer, April 29, 2005.
14. CCN 110731, *Oxidative Leaching Flowsheet Evaluation*, Jacob Reynolds to Eric Slaathaug, June 22, 2005.
15. Damerow, F. "Oxidative Leaching R&T Scope alternatives" email to W. Hamel 5/13/05
16. DE-AC27-01RV14136, Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant and Immobilization Plant, Section C, Modification M041, Richland, Washington
17. draft RPP-25903, Review of Phosphate and Sulfate Wash and Leach Factors
18. Kovach, C.W. 1999. "Types 304 and 316 stainless steels can experience permanganate fitting in water-handling systems." *Materials Performance* 38(9): 70 - 75
19. Lu , H.H., Duquette, D.J.1990. "The Effect of Dissolved Ozone on the Corrosion Behavior of CU-30NI and Type-304L Stainless-Steel in 0.5 N NaCl Solutions." *Corrosion* 46(24-25): 3783-3790
20. Lumetta, G. J., K. J. Carson, L. P. Darnell, L. R. Greenwood, F. V. Hoopes, R. L. Sell, S. I. Sinkov, C. Z. Soderquist, M. W. Urie, J. J. Wagner. 2001. *Caustic Leaching of Hanford Tank S-110 Sludge* Pacific Northwest National Laboratory PNNL-13702
21. RPP-25903, Review of Phosphate and Sulfate Wash and Leach Factors (Draft), CH2M Hill, Richland Washington
22. RPP-20003, Sensitivity of Hanford High Level Waste Glass Mass to Chromium and Aluminum Partitioning Assumptions, March 2005, CH2M Hill, Richland Washington.

23. Sylvester, P., Rutherford, L.A. Jr., Gonzalez-Martin, A., Kim, J., Rapko, B.M., Lumetta, G.J. 2001. "Ferrate Treatment for Removing Chromium from High-Level Radioactive Tank Waste." *Environmental Science & Technology* 35(1): 216-221
24. Tatarchenko, G.O. and Cherkas, K.V. 2005. "Corrosion resistance of Hastelloy-B in the ozonized medium." *Protection of Metals* 41(3): 259 – 262
25. TP-RPP-WTP-275, Bench Scale Oxidative Leaching of SY-102 and SX-101 Tank Sludges, Bechtel National, Inc., September 2003
26. Tank Waste Information System (TWINS) <http://twins.pnl.gov/twins.htm>
27. Ultrafiltration and Washing/Leaching of Hanford Tank 241-SY-102 Waste, Rev. 0, Bechtel National, Inc., April 16, 2003.
28. Varga, K., Baradlai, P., Hirschberg, G., Nemeth, Z., Oravetz, D., Schunk, J., Tilky, P. 2001. "Corrosion behaviour of stainless steel surfaces formed upon chemical decontamination." *Electrochimica Acta* 46(24-25): 3783 - 3790
29. Viera, M.R., de Mele, F.L., Videla, H.A. 2001. "Comparative study of the effect of oxygen and oxygen/ozone mixtures on the electrochemical behaviour of different metals." *Journal of Applied Electrochemistry* 31(5): 591-598
30. WTP-RPT-117, *Oxidative-Alkaline Leaching of Washed 241-SY-102 and 241-SX-101 Tanks Sludges*, Rev. 0, Battelle - Pacific Northwest Division, Richland, Washington, October, 2004.
31. WTP-RPT-137, *Oxidative-Alkaline Leaching of SX-101 and SY-102 and Its Impact on Immobilized High-Level Waste*, Rev. 0, Battelle - Pacific Northwest Division, Richland, Washington, June 23, 2005.
32. Wylie, W.E. and Duquette, D.J. 1998. "Effect of dissolved ozone on corrosion behavior of stainless steels in artificial seawater." *Corrosion* 54(10): 781 - 799

Appendix A

**Oxidative Leaching Design Oversight
Line-of-Inquiry****Contract Compliance Questions**

1. Has the Contractor conducted a literature review and prepared a technical report (Table C.5-1.1, Deliverable 2.8 Technical Report on Oxidative Leaching) that evaluates the treatment processes for the oxidative leaching of chemical components (principally Cr and associated components, i.e. sulfate) that limit the loading of HLW solid oxides in the HLW glass waste form?

Assessment: The contractor completed this requirement by submitting technical report 24590-WTP-RPT-ENG-05-006, Rev. 0 to ORP; this report is a review of BNI documents and reports as well as subcontracted PNNL reports. The Technical Report breaks down the contract requirements into 10 sub-tasks required to complete contract deliverables 2.8 and 2.9. The contractor has included the literature review as Sub-Task 1 of the Technical Report; it is a summary of the literature reviews included in references PNNL reports, WTP-RPP-117 and WTP-RPP-137.

2. Does the literature review summarize existing experimental results and data?

This requirement has been met; the literature review summarizes existing experimental results and data. The results of all experiments previous to those reported in WTP-RPP-117 and WTP-RPP-137 are summarized in Tables 1.3 – 1.5 in the literature review of WTP-RPP-117. A detailed summary of the experimental results from reports WTP-RPP-117 and WTP-RPP-137 is also included as Subtask 2 in the technical report, 24590-WTP-RPT-ENG-05-006, Rev. 0.

3. Does the literature review identify the “*chemical components (principally Cr and associated components, i.e. sulfate) that limit the loading of HLW solid oxides in the HLW glass waste form*”?

This requirement has been met by the contractor. Chemical components which are likely to limit HLW loading are identified in Table 2.10 of WTP-RPP-137. This table is directly referenced from the WTP Contract (DE-AC27-01RV14136). However, this table does not indicate the order of which components are limiting, and no discussion of how limiting components will change after oxidative leaching is provided by the contractor.

The contractor further identifies manganese (Mn) itself as a possible limiting factor in glass production (24590-WTP-RPT-ENG-05-006, Rev. 0, Sub-Task 5) when permanganate is used as the oxidant.

4. Does the literature study present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions?

The contractor has not met this requirement. The Technical Report includes descriptions of the preliminary process flow sheets in memos CCN: 110724 and CCN: 110731 in Sub-Task 4. Further R&T work must be completed before detailed realistic process flowsheets can be provided.

This contract requirement refers to the preparation of process flowsheets for candidate processes that could be used to remove Cr from tank waste sludge in the WTP. The contractor did not develop pre-conceptual flowsheets for the candidate processes considered in the process evaluation and recommendation phase of the work. Candidate technologies were identified in WTP-RPT-117 and included ferrite, ozone, air, caustic, and permanganate oxidation. These processes were not evaluated for potential implementation in the WTP and were not characterized by the use of a systematic engineering evaluation that included a material balance, equipment identification, and process operating concept. This is necessary to evaluate the candidate processes and to select and recommend a preferred process for the WTP.

5. Does the literature review provide a recommendation on the preferred process to conduct the required separations?

This requirement has been only partially met by the contractor. The recommendation of permanganate (MnO_4^-) as the preferred oxidative leaching process is presented in Sub-Task 3 of the Technical Report. This recommendation is not technically defensible because it is not clear that this technology is the best choice to complete the required task. The recommendation was not developed based upon a clear technical comparison of the alternatives.

6. Has the contractor conducted technology testing activities using simulants and actual waste testing to provide design and process operational information on the process used to remove Cr from the HLW waste stream?

This requirement has been only partially met by the contractor. The contractor has conducted testing activities with actual waste, but not with simulants. Further testing is in the process of being conceptualized by the Contractor and this testing may include simulants. BNI has indicated (WTP-RPT-137) that the use of simulants may not be beneficial because the low concentration of Pu in the waste may make it difficult to prepare a useful simulant. However, because of the lack of clear understanding on the process, it could be useful to conduct further testing using simulants to determine the level to which organics and inorganics compete with chromium for the oxidant over a range of potential conditions.

7. Does the proposed process have the capability to remove Cr from the pretreated HLW stream such that this chemical component, or reagents added to remove this component does not limit the HLW waste loading in the glass waste form?

The proposed process for oxidative leaching (permanganate [$NaMnO_4$] oxidation) of Cr does have the capability to remove insoluble Cr from tank waste compositions and thereby reduce the total mass of HLW to be produced. However, as discussed further below, the process will not reduce the Cr content in all HLW melter feed batches to a level that will eliminate Cr as a HLW loading constraint. Further improvements in the performance of the HLW System in terms of

reducing the mass of HLW glass will also require glass development studies aimed at increasing the allowable concentration in the HLW glass (compared to the current limit of 0.5 wt% that is specified in the WTP Contract) and developing a vitrification system that can accommodate crystalline phases.

The proposed process for oxidative leaching uses sodium permanganate (NaMnO_4) oxidation of Cr which has the capability to remove insoluble Cr from tank waste compositions. This is demonstrated by a review of the technical information presented in WTP-RPT-117. This report summarized previous experimental work on permanganate oxidation, and recent work completed for the current project to evaluate this process and provide a basis for projection of the Cr removal efficiency. Based upon the results of the recently completed BNI studies, a composite water wash/caustic leach/oxidative leach removal factor of 87% for Cr was selected for subsequent flowsheet modeling (see Table S.2, Test SX-101-3 on page xx).

An evaluation of the Dynamic Flowsheet modeling results presented in Table 1 below. Table 1 presents five scenarios for comparison; the WTP Baseline and four Cases assuming Oxidative Leaching. Case 1 is the WTP Baseline, Case 2 is the WTP Baseline with Oxidative Leaching, Case 3 assumes oxidative leaching with the sulfate wash/leach factors assumed to be at least 0.75 and the Cr_2O_3 concentration limited to 0.5 wt%, and Case 4 oxidative leaching with the sulfate wash/leach factors assumed to be at least 0.75 and the Cr_2O_3 concentration limited to 1.0 wt% and Case 5 assumes oxidative leaching with the sulfate wash/leach factors assumed to be at least 0.75 and the Cr_2O_3 concentration limited to 1.5 wt%. These scenarios and cases illustrate the following:

- The proposed process, Case 2, will remove a significant fraction of the Cr from the tank wastes and allow the HLW canister mass to be reduced. An estimated 34% reduction in HLW canisters (35,076 to 23,165) is projected based upon the Dynamic Model Runs. However, even with oxidative leaching, the Cr_2O_3 is still limiting as a glass component for 11,125 MT of HLW glass.
- Case 3 removes the constraint on HLW glass waste loading caused by sulfate. This results in an increased number of MFPV glass batches limited by Cr_2O_3 , potentially up to 70% of the batches if other waste loading constraints are removed. Increasing the allowable Cr_2O_3 1.0 wt%, and 1.5 wt%, will reduce the number of MFPV glass batches that are limited by Cr_2O_3 . However even at these increased concentrations, Chromium will still be a glass loading limit.

The canister production estimates from the WTP Dynamic Model, and those estimated by the Tank Farm Contractor (RPP-20003) are significantly different. The primary difference is due to the assumptions used on glass waste loading. The WTP Contractor has used the WTP Contract Table TS-1 limits as the basis for glass loading. The Tank Farm Contractor has used a glass properties model as the basis for glass loading. The glass property model will project a low number of canisters to be produced. This in turn will impact an assessment of the efficiency created by the oxidative leaching process.

The results presented in Table 1 indicate the need to continue glass development studies to reduce the HLW canister production requirement. These studies should focus on the following:

- Increasing the allowable concentration of Cr, Al and Bi in the glass formulation, and
- Demonstration of the capability of the HLW melter to remove crystalline phases from the melter. This is needed because a significant number of melter feed batches will have a Cr_2O_3 concentration of greater than 1.5 wt% in the glass.

August 2005

Table 1 Comparison of HLW Production Requirements for No Oxidative Leaching and Oxidative Leaching in WTP

	Case 1 No Oxidative Leaching	Case 2 Proposed Oxidative Leaching Process	Case 3 Proposed Oxidative Leaching Process with Sulfate Removed as Glass Loading Constraint	Case 4 Proposed Oxidative Leaching Process with Cr2O3 limit at 1.0 wt% and Sulfate Removed as Glass Loading Constraint	Case 5 Proposed Oxidative Leaching Process with Cr2O3 limit at 1.5 wt% and Sulfate Removed as Glass Loading Constraint
MFPV Batches Limited by Cr2O3	4,253	353	3,810	1,787	817
Percent of MFPV batches Limited by Cr2O3	64%	6%	70%	33%	15%
Total Number of MFPV Batches	6,678	5,688	5,458	5,458	5,458
Mass of HLW Glass Limited by Cr2O3, MTG	75305	11,125	42,940	20,085	9,216
Key Assumptions					
SO4 Concentration in HLW Glass, wt%	0.5	0.5	None, SO4 removal at least 75% in Washing and Leaching	None, SO4 removal at least 75% in Washing and Leaching	None, SO4 removal at least 75% in Washing and Leaching
Cr2O3 Concentration in HLW Glass, wt%	0.5	0.5	0.5	1	1.5

8. Has the Contractor tested a minimum of two radioactive tank waste samples? (SY-102 and a second sample that must be provided so that analysis with sample SY-102 can be run concurrently)

The contractor has met the minimum of this requirement. Two composite samples, SY-102 and SX-101 were tested. The testing protocol and the proposed process differ greatly. These two tank compositions contain the two most bounding concentrations of Cr and Pu in the Hanford tank farm based upon the TWINS database. No recommendation of other tanks which would be useful to test was presented to ORP.

9. Does the radioactive sample test provide a proof of process demonstration (part of Deliverable 2.2 and 2.3) and determine any impacts to the facility throughput and/or availability?

Summarized in Table 2 is a comparison of the laboratory procedure used to conduct the SX-101 and SY-102 experiments and the proposed Oxidative Leaching procedure for Pretreatment facility implementation. The laboratory procedure and proposed WTP Plant procedure differ primarily by the degree of washing between each process step and the efficiency of the solids liquids separation process. In each case the laboratory procedure was more efficient. Therefore it is anticipated that the laboratory procedure would over predict the performance of the plant flowsheet and correspondingly the benefits of the proposed process.

In review of the Test Plan for the Oxidative Leaching experiment (TP-RPP-WTP-275) it was determined that the testing presented in WTP-RPT-117 was not intended to provide a proof of process test demonstration. The testing reported was "advisory" and to be used to define the conditions for time, temperature and oxidant. This information would be used to provide a recommendation for a larger scale testing of the oxidant leaching procedure in the Cells Unit Filter (CUF) device. Therefore the assertion in the Technical Report that the scoping tests provide a proof of process demonstration is incorrect. (See page 10 of the Technical Report, Section 4.7).

Facility throughput impacts cannot be determined until proof of process has been demonstrated.

August 2005

Table 2 Comparison of Test Procedure and Plant Procedure for Sludge Processing

Process Function	Test Procedure described in WTP-RPT-117	Proposed process procedure described in Technical Report, 24590-WTP-RPT-ENG-05-006	Comments
Retrieval Wash/Initial separation	<p>Contents of tank waste samples were combined in a jar and blended into one composite. Aliquots of each waste sample composite were transferred into a centrifugation cone. The aliquots were washed twice with 0.01 M NaOH. (Ratio of liquid/solids varied from 1:1 to 5:1). Solids were separated from liquids by centrifugation after each wash.</p> <p>Washings were repeated until the liquid was clear, typically 5 washes. Yellow tint of hot-cell window made visual determination of solution color very speculative.</p> <p>NaOH (0.01 M) was added to the washed slurry.</p> <p>Washed solids were separated into two weighed and dried to a constant weight at 105 °C.</p>	<p>Not addressed. However, a portion of this procedure would represent the initial dewatering of the sludge in the WTP.</p> <p>Process is not currently designed to include centrifugation.</p> <p>Number of washings in proposed process will be less than in experimental procedure.</p>	<p>Solids are contacted up to 5 times with wash solution. No data was presented on the mass and composition of material removed in the experimental procedure.</p> <p>Centrifuged solids will be concentrated to ~40 to 50 wt% which is higher than the WTP's assumption of ~20 wt%.</p> <p>The initial "washing of the sludge" as conducted in the lab procedure is more efficient than the WTP facility procedure.</p>
Caustic Leaching	<p>A NaOH solution was added at a rate of 3 parts NaOH to one part sludge. 4.8 mLs of 10 M NaOH and 8.2 mLs of DI</p>	<p>Caustic leach as currently designed (concentrate solids, add caustic [≥ 3M], elevate temperature [80-90 °C]).</p>	<p>Samples were potentially allowed to sit longer during the cooling process in the</p>

Table 2 Comparison of Test Procedure and Plant Procedure for Sludge Processing

Process Function	Test Procedure described in WTP-RPT-117	Proposed process procedure described in Technical Report, 24590-WTP-RPT-ENG-05-006	Comments
	<p>water were added to each 4 mL sample. It appears that NaOH and DI water were added separately.</p> <p>Mixture heated at 85 degree C for 8 hours. Sample mixture allowed to cool overnight.</p> <p>Samples were centrifuged and subsequently washed with 0.1 M NaOH added at a 3:1 solution to solids ratio and centrifuged again. This process was repeated until the supernatant was colorless.</p> <p>Sludge mixture filtered through a 0.2 micron syringe filter.</p>	<p>digest for 8 hours)</p> <ul style="list-style-type: none"> • Cool resulting slurry to 25 °C • Re-concentrate slurry to original volume or original solids weight percent and route the permeate produced forward to ion exchange • Wash slurry with process condensate (at least 3x re-concentrated slurry volume¹) as currently designed and route the wash permeate produced to the Plant Wash and Disposal (PWD) system 	<p>experimental method than in the proposed process. Some reprecipitation may have occurred in experiments.</p> <p>Centrifugation and excess washing in experimental method will not be included in proposed process. Data collected is biased toward greater removal of dissolved constituents.</p>
Oxidative Leach	<p>Centrifuge the slurry for 5 minutes. Decant the residual supernatant from the solids. Wash the solids, 3 to 4 times with 0.1 M NaOH to remove components in the interstitial liquid. Final wash solution appeared colorless.</p> <p>For Test SX-101-3 Add to 4 ml of sludge:</p>	<ul style="list-style-type: none"> • Add 19M caustic to adjust the slurry to 0.1M free hydroxide² (the free hydroxide molarity will be determined mathematically and not by sampling) • Add 1M NaMnO₄ at 1:1:1 molar ratio with Cr in solids³ • Allow 6 hours for reaction • Re-concentrate slurry to original re- 	<p>Centrifugation of experimental samples not included in proposed process. Will lead to excess dissolution that is attributed to oxidation so the dose added may be greater than what is needed.</p> <p>Excess washing in</p>

Table 2 Comparison of Test Procedure and Plant Procedure for Sludge Processing

Process Function	Test Procedure described in WTP-RPT-117	Proposed process procedure described in Technical Report, 24590-WTP-RPT-ENG-05-006	Comments
<ul style="list-style-type: none"> • 2.85 ml of 0.5 M NaMnO₄ • 0.4 ml of 10 M NaOH • 8.75 ml of DI water • Total reaction time is 24 hours. Samples taken 2, 6, and 24 hours. • Reaction complete in 6 hours • Centrifuge and decant <p>Wash 3 to 4 times until solution appears colorless</p>	<ul style="list-style-type: none"> • concentrated slurry volume and route the permeate produced to the PWD system • Wash slurry with process condensate (at least 2x re-concentrated slurry volume) as currently designed and route the wash permeate produced to the PWD system <p>¹The 3x volume is required to remove the interstitial hydroxide from the caustic leached slurry down below 0.2M.</p> <p>²The 0.1M target value does not include the hydroxide present in the original slurry. The 0.1M target plus the residual hydroxide in the slurry will result in a slurry that is 0.1M-0.25M free hydroxide.</p> <p>³The Cr in the solids will be determined via the Specification 12 procedure and will account for the removal of Cr by water washing/caustic leaching.</p>	<p>experimental method not included in proposed processed. Results may be biased towards greater dissolved constituent removal than what will be actualized during plant operation.</p>	

10. Has the contractor provided recommendations to ORP for the modification of *Specification 12, Number of High-Level Waste Canisters Per Batch of Waste Envelope D* and *Specification 1, Immobilized High-Level Waste*, Table TS-1 limits for Cr₂O₃ and sulfate, based upon the results of this experimentation?

This requirement has been met. Proposed modifications to Contract Specification 12 were included in Appendix A of the Technical Report (24590-WTP-RPT-ENG-05-006). Revised Contract Table TS-1 limits for Cr₂O₃ and sulfate were not proposed. The proposed revision to Specification 12 is discussed in Other Technical Questions – Chemistry, number 6 below. Revisions to Contract Table TS-1 are discussed in Other Technical Questions – Chemistry, number 7 below.

The potential HLW sludge treatment resulting from the revised specification include:

- Water Washing
- Caustic leaching and water washing
- Caustic leaching, water washing, and oxidative leaching
- Water Washing and oxidative leaching

11. Has the contractor prepared a test report that summarizes the results of the oxidative leaching? (Table C.5-1.1 Deliverable 2.9 Test Report on Oxidative Leaching)” Standard 2(a),(3),(ix).

This requirement has been met. The contractor subcontracted PNNL to prepare reports WTP-RPP-117 and WTP-RPP-137 which describe permanganate experiments conducted at the bench scale.

Other Technical Questions – Chemistry

1. Does the testing/literature review provide a clear technical basis for the selection of the oxidative leaching reagents?

A summary of the oxidants tested, tank waste compositions evaluated and number of testes completed is summarized in Table 3. This summary indicates that a limited amount of testing has been completed on the oxidation leaching process. This summary includes the current testing completed and reported in WTP-RPT-117. Comparison of results of oxidant screening experiments for several different oxidants is included in Table 1.3 of WTP-RPP-117.

Inconsistencies in this comparison are summarized below.

- The oxidants were not tested under equivalent conditions and tank waste compositions. Permanganate, ozone, and air were compared across samples in tanks SY-103, B-111, BY-110, SX-108, and S-107, whereas persulfate and ferrate were compared in S-110 and peroxyxynitrite was compared in U-108. Ferrate has also been tested on S-107, results of which were not included in this report, but in a peer reviewed journal (Sylvester et al). High temperature caustic leaching with air with extended contact time was compared in S-110, S-104, S-101, and S-111.

- The composition and form of Cr and Pu, as well as the concentration of oxidant scavengers in these tank samples differ. Comparing the percent removal of Cr and percent removal of Pu for different oxidants in different tank samples may therefore lead to incorrect conclusions.

This variety of tank samples tested combined with the lack of a side by side comparison calls into question the recommendation to use permanganate.

Table 3 Summary of Experiments Conducted to Evaluate Oxidative Leaching of Hanford Tank Wastes

Technology	Tank Waste Samples Tested	Number of Tests
Permanganate (MnO_4^-)	SY-103	1
	B-111	1
	BY-110	2
	SX-108	4
	S-107	2
	U-108	4
	U-109	2
	S-110	4
	SY-102 (WPT-RPT-117)	6
	SX-101(WPT-RPT-117)	6
	TOTAL	32
Ozone (O_3)	SY-103	1
	B-111	1
	BY-110	2
	SX-108	2
	S-107	2
	TOTAL	8
Air	SY-103	1
	B-111	1
	S-110	4
	U-108	2
	TOTAL	8
Oxygen (O_2)	BY-110	2
	S-107	2
	U-108	2
	U-109	2
	SX-108	2
	TOTAL	10
Persulfate (S_2O_8)	S-110	4
Ferrate (FeO_4^{2-})	S-110	4
Peroxyntirite	U-108	2

Table 3 Summary of Experiments Conducted to Evaluate Oxidative Leaching of Hanford Tank Wastes

High Temperature Extended Contact Alkaline Leaching with Air	S-110	9
	S-104	2
	S-101	2
	S-111	2
	TOTAL	15

Furthermore, the BNI's basis for the rejection of ozone, ferrate, and high temperature caustic leaching with air is reviewed below.

Ozone

Ozone was rejected in the Technical Report for four reasons:

- There is some evidence for significantly enhanced and concomitant dissolution of transuranic elements,
- Ozone is toxic,
- Ozone is highly corrosive, and
- The reduced form of ozone, oxygen gas, may introduce flammability concerns in the off-gas system

Taking a closer look at the data and chemistry, and considering the limits for glass production, along with current ozone application processes, one can make the argument that ozone may be an equally attractive choice for oxidative leaching. This is based on the following:

- Results of studies which compared ozone to permanganate for treatment *of samples collected from the same tank* in Table 1.3 of WTP-RPP-117 indicate that ozone solubilizes less Pu than permanganate while achieving an equal or even greater removal of Cr.
- Ozone is toxic when exposure occurs at levels greater than 0.1 ppm, but the treatment vessel in the pretreatment facility will be contained in a C5 area where exposure risk is negligible. If ozone is generated from air and applied in a manner such that it is completely consumed, only oxygen (at the normal partial pressure found in air) will be found in the vessel vent system.
- Current literature suggests that under quiescent conditions, ozone is not more corrosive, but in fact increases the passivity of stainless steel over its passivity gained by exposure to oxygen.

The passivity of a 0.320 cm² coupon of AISI 304 stainless steel in an electrolyte balanced solution (containing among other ions, 105 ppm Cl⁻) of pH = 8.0 - 8.5 was not affected by exposure to up to 0.8 ppm of ozone. The open circuit potential (OCP) initially decreased, and then increased, demonstrating that there is only an initial competition between dissolution of the metal, and build up of passivity (Viera et al) before passivity takes over. Exposure to a 4.8 mg/L (reported as 0.1 mol/m³) solution of ozone (O₃), as compared to aeration, resulted in only an increase in corrosion potential (E_{corr}) from 0.2 to 0.3 V of a

coupon of Hastelloy-B in a 70% sulfuric acid solution (Tatarchenko and Cherkas). Other publications which could not be obtained but whose abstracts were reviewed also support the finding that stainless steels are resistant to ozone corrosion (in the presence of 0.5 M NaCl) during no flow and laminar flow. In no-flow conditions, the shift in anodic potential indicates that passivation layers formed during ozonation are more resistant to pitting formation than those formed during oxygenation. However, surface pitting was observed during turbulent flow conditions with high ozone concentration (Lu and Duquette; Brown et al). When crevices pre-exist in the surface treated, crevice-corrosion is more severe in stainless steels immersed for time periods extending over weeks in ozonated simulated seawater than in non-ozonated water (Wyllie and Duquette).

The corrosion of stainless steel by permanganate is not as well studied as ozone. However, results included in two publications found indicate similar phenomena occur as those observed in previously discussed ozone studies: in non-flow conditions, oxidation by permanganate increases the stability of the passivation layer, but induces pitting when flowing through pipes (Varga et al; Kovach).

These studies indicate that during turbulent pulse jet mixing, permanganate as well as ozone will cause corrosion of stainless steel and this corrosion must be accounted for in the design of the treatment vessel.

- Ozone can be produced from oxygen or air feed gas. If ozone is produced from air, the partial pressure of oxygen in the steady-state flow of air through the vessel will not vary from normal atmospheric conditions and flammability will not be a concern.
- Washing and caustic leaching will remove nitrite and organics from waste samples so ozone will not be scavenged by these compounds during a sequential oxidative leach.
- Efficient application of ozone to waste can be accomplished by routing it through fine bubble diffusers which can be attached to spargers.

Ferrate, (FeO₄²⁻)

Ferrate was rejected in the Technical Report for two reasons:

- Mass is added to the HLW waste stream
- The thermal stability is less than that of permanganate solutions and so it must be kept at 5 °C to remain stable

Although ferrate adds mass to the waste stream, this mass is in the form of iron oxide, Fe(OH)₃, which adsorbs Pu. Results of ferrate testing of samples from tank S-107 indicated that less than 0.3% of transuranic components (TRU) were solubilized while up to 65% of the Cr was removed at 50 and 70 °C over varying caustic leach concentrations. These results indicate ferrate can be used to remove a substantial amount of Cr from the waste feed while simultaneously immobilizing Pu (Sylvester et al). The amount of iron added to the waste would be 1:1 with Cr and would not increase glass production.

It is possible to generate ferrate at the point-of-use, so it would not be necessary to store ferrate solutions at decreased temperatures. No literature concerning the corrosion of stainless steel by ferrate has been found.

Ferrate, instead of peroxide (Damerow) can also be used as a reagent to precipitate plutonium after the main oxidative leaching process.

High Temperature Extended Contact Caustic Leaching with Air

An alternate solution for removing aluminum and chromium from the high level waste melter feed is high temperature caustic leaching with air. Greater than 90% of the Cr and 90% of the Al were removed from tank S-110 sludge when treated with 3 M NaOH at 80 °C as demonstrated by Lumetta et al. Radionuclide dissolution was insignificant. The reaction requires approximately 1 week in order to reach 90% dissolution of both Al and Cr and would therefore need to be implemented in a holding tank (or Hanford tank farm) which would not affect processing schedule.

2. Does the testing/literature review address the leaching of sulfate from the HLW sludge?

Yes, this issue is addressed in WTP-RPT-137. The argument is presented that it could be reasonably assumed that sulfur in the tank waste is largely present as the sulfate ion. Because this is the most oxidized form of sulfur, the effectiveness of permanganate is not expected to be limited by sulfate. It is further argued based on TWINS data on sulfur forms in the tank waste, and the sulfate dissolution thermodynamics that all sulfate will be completely dissolved and therefore will not be a limiting component in HLW glass. However there is up to 50% uncertainty in the TWINS data which identifies the form of sulfur, and because there is no data on the behavior of sulfur during oxidative or caustic leaching, it is uncertain whether sulfate will be completely dissolved during this process.

3. Have the selected reagents been evaluated over a range of chemistry conditions that are anticipated in actual plant scale operations? Do these conditions define the limits of application of the process?

Oxidants have been evaluated at different caustic concentrations and temperatures at the bench scale only. The behavior of oxidative leaching on downstream processes has not been experimentally evaluated so the limits of the application of this process cannot yet be defined.

4. Does the testing/literature review provide a clear technical basis for the usage rate for the oxidative leaching reagents, e.g. mass or moles of reagent per moles of insoluble Cr (and sulfate)?

No, the basis for the usage rate of permanganate in the recommended process is not clear. The literature recommends a dose rate of permanganate of 1.1:1 moles of sodium per mole of Cr. This ratio is that which was used in bench testing and has been recommended to maximize Cr dissolution while minimizing Pu dissolution. The experimental conditions of

bench tests are not comparable to that which is recommended for the in-plant process because solids as discussed above. The performance of permanganate was also observed to be inconsistent over the range of samples tested; the reason for this unexpected variation in oxidation rate across samples is unknown. It is also not clear whether the proposed Mn/Cr addition rate of 1.1 to 1, will be acceptable for tank batches other than those tested because of differing Cr:Pu mass ratios.

5. Do the selected oxidative leaching reagents lead to any adverse process impacts, such as: excessive corrosion, dissolution of radioactive components (e.g. Am, Pu, Np) or impact subsequent processing of the tank waste sludge?
 - Corrosion: BNI has not evaluated the corrosion or erosion potential associated with the potential implementation of the permanganate leaching process. The updated Corrosion Evaluation (24590-PTF-NID-UFP-00003) submitted for review as part of the "Oxidative Leach" package was updated to account for refinements in the erosion wear and margin calculations (24590-WTP-MOE-50-00003, 24590-WTP-M-04-0008). This update did not include a re-assessment of the WTP process flowsheet for the proposed oxidative leaching process. The protocol for completion of materials evaluation requires a revision to the affected Process Control Data Sheets (24590-WTP-RPT-PR-04-0001, *WTP Process Control Data*). This occurs through information developed in a WEBBPPS Mass Balance Assessment which was not completed.
 - Dissolution of Radioactive Components: The experimental testing data on the proposed oxidative leaching process (WTP-RPT-117) assumes a free hydroxide concentration of ~0.25 M NaOH and a permanganate to chromium mole ratio of 1.1 to 1. Based upon the results of testing of a tank waste sample from SX-101 this process would result in the dissolution of Pu less than 0.1%, Am less than 0.01% and Cm less than 0.01%. In subsequent criticality scoping analyses completed (24590-WTP-RPT-NS-05-001) it was assumed that the Pu concentration would be less than 1%. The data presented in the technical report on the oxidative leaching process (WTP-RPT-117) is presented in a format that combines the removal of radioactive components from alkaline leaching and oxidative leaching. Thus the reader is not able to determine the relative mass of the radioactive components that are removed in each of these process steps. It is also noted that these test results are very specific to the tank waste sample tested and cannot be extrapolated to other compositions or conditions. Of particular concern is the impact associated with the presence of other waste components (organics and aluminum) than could interfere with the selective oxidation reaction.

Criticality safety aspects of the proposed process have been introduced in a preliminary evaluation (24590-WTP-RPT-NS-05-001). This assessment suggests controls on process operations including potential increased sampling to ensure the proposed process is acceptable. A double contingency analysis is required to be performed for the process to ensure that criticality will not occur. A criticality safety review of the proposed process has not been completed. BNI has indicated in the Technical Report (24590-WTP-RPT-ENG-05-006) that the oxidative leaching process has not been evaluated in a formal ISM process along with updates to the appropriate Authorization Basis (AB) documentation (CSER,

PSAR, SRD).

An update to the AB based upon a single tank waste sample test, without understanding the behavior of the process may be a fruitless effort because the behavior of the actual process may be much different the limited experiment conducted. BNI and ORP need to ensure that the suggested changes to the AB are sufficiently robust to ensure that plant operations are possible. It is not clear that sufficient data exists to proceed with the ISM process at this time.

- Secondary Impacts to WTP Process Flowsheet: Based upon a review of the technical information compiled as a result of the Oxidative Leaching work there does not appear to be any secondary unfavorable impacts associated with the processing of the treated waste sludge. There are however potential secondary impacts associated with the processing of permeates generated from the oxidative leaching solution. These involve the management of Pu chemistry and potential impacts to criticality safety in the WTP Pretreatment facility.

6. Does the testing provide a basis for a potential modification to Specification 12?
 - Can the proposed change be used as a performance standard for determining if oxidative leaching should be deployed in the WTP flowsheet?
 - Can the proposed change be conveniently implemented in the WTP flowsheet?

Assessment: The proposed modification of Specification 12, Section 12.1, deletes the function of Specification 12 as a performance specification from the scope. The current Contract Specification 12 determines the number of HLW canisters that would be accepted by DOE for each batch of HLW feed. After performing the procedure, DOE determines the sludge treatment method and the Contractor's treatment performance must meet the performance specification. The revised specification eliminated the performance specification limiting the number of HLW canisters that would be accepted and now functions to simply determine the treatment scheme for each batch of HLW feed. Current planned HLW feed for hot commissioning is not projected to require caustic or oxidative leaching. Elimination of this performance specification should not impact BNI. However, a performance specification on HLW feed treatment effectiveness will be needed for the WTP operating Contract.

The revised specification could be used as a procedure to determine if oxidative leaching should be employed. However, its value is limited if implemented on a sample taken from the tank farms for a HLW feed batch (double shell tank). HLW slurry is blended with LAW feed and recycle streams in WTP. The content of the LAW feed and recycles can influence the need to perform oxidative leaching. A more meaningful test would be to perform the Specification 12 procedure for each batch of feed prepared in UFP system vessels. Alternatively, testing of waste feed from the source tanks in tank farms coupled with modeling of recycles to predict the composition of the ultrafiltration feed preparation vessels may provide a meaningful measure of the benefit with oxidative leaching. BNI should assess the WTP capability to sample and test material in the ultrafiltration feed preparation vessels considering available turnaround time and assess the capability to use process models to predict the optimum treatment considering waste leaching data from the tank farm source tanks and WTP recycle streams. This information is needed to develop an appropriate procedure to determine HLW treatment schemes.

The proposed Specification 12 procedure has not been tested on either actual tank waste samples or simulants. It is not clear if the procedure accurately represents the proposed WTP oxidative leaching process, under-predicts facility performance, or over-predicts facility performance. If the procedure is included in a revised Specification 12, its performance relative to the WTP oxidative leaching process should be determined.

Section 12.2.6 states "DOE will determine the sludge treatment method (aqueous-washing or caustic-washing) and will determine whether oxidative leaching testing is warranted." The specification should be modified to perform the oxidative leaching procedure if the projected HLW glass waste loading is limited by chromium without the DOE determination.

7. Does the testing and evaluation provide a defensible basis for the revision to Specification 1, Table TS-1 limits for chromium oxide and sulfate?

Assessment: Revised Contract Table TS-1 limits for Cr_2O_3 and sulfate were not proposed by BNI. BNI stated the test results did not provide a basis for increasing the limits.

While the tests provided no data to increase the Contract Specification 1, Table TS-1 limits, the results of BNI's study of oxidative leaching may provide a basis to eliminate Contract Table TS-1 limits for Cr_2O_3 . CCN: 110731, Oxidative Leaching Flowsheet Performance Runs to Support Deliverable 2.8, concluded "Oxidative leaching effectively removed chromium as the limiting component for waste loading in the IHLW." If WTP implements oxidative leaching when Cr_2O_3 limits HLW glass waste loading and no HLW batches are limited by Cr_2O_3 after implementation of oxidative leaching, then the Specification 1, Table TS-1 Cr_2O_3 limit does not serve a purpose and can be eliminated.

BNI report *Oxidative-Alkaline Leaching of SX-101 and SY-102 and Its Impact on Immobilized High-Level Waste* (WTP-RPT-137) stated that it could be reasonably assumed that sulfur in the tank waste is largely present as the sulfate ion. Because this is the most oxidized form of sulfur, the addition of permanganate is not expected to remove the sulfur by oxidation. WTP-RPT-137 recommended assuming 70 – 80% of sulfate could be removed from tank solids through caustic leaching and washing. It was also recommended that this value be verified by caustic leach testing on selected high-sulfate sludges. The tank farm contractor is performing a review of sulfate wash and leach factors (draft RPP-25903, *Review of Phosphate and Sulfate Wash and Leach Factors*) that, when complete, may provide insight to the impact of sulfate on HLW canister waste loading. No revision to the Specification 1 Table TS-1 limits for sulfate should be made at this time.

8. Do the testing results with simulants and actual wastes produce comparable results?

Testing with simulants was not performed so a comparison cannot be made.

Other Technical Questions - Flowsheet Integration

1. Has the technical work considered and evaluated flowsheet alternatives for the implementation of the oxidative leaching process? Has the optimum flowsheet condition been evaluated and identified?

Discussion:

Evaluation of Alternative Flowsheets

There are two basic alternatives for the potential implementation of the oxidative leaching process in the Pretreatment facility. These are:

- Completion of the oxidative leaching process concurrent with (e.g. combined with) the caustic leaching process, and
- Completion of the oxidative leaching process sequential to (e.g. following) the caustic leaching.

These processes alternatives were evaluated in the radioactive scoping tests (WTP-RPT-117), initial evaluations of the proposed process (CCN: 110724) and initial criticality evaluations of the proposed process (24590-WTP-RPT-NS-05-001). The conclusions from these evaluations indicated that the sequential process is preferred based upon primarily upon minimizing the dissolution of Pu. It was recognized that the concurrent process would remove more Cr due to operation at a higher temperature and caustic concentration. However, the dissolution of Pu could increase up to 13% at 3 M NaOH and 85°C as indicated in test SX-101-1 (Table 3.9, page 3.15, WTP-RPT-117). As discussed above, the proposed baseline process which uses sequential oxidative leaching does not remove sufficient Cr from the HLW batches to eliminate Cr as a waste loading constraint. It is also not clear that the dissolution of Pu will present an issue with respect to plant operations. This suggests that the specific conditions for process operation be evaluated more carefully.

Proposed Process Approach

The proposed process for the oxidative leaching process is identified in Section 4.3 of the Technical Report (24590-WTP-RPT-ENG-05-006) and CCN: 100724. While the basis steps of the process are defined the specific operational parameters are not identified. Missing are the following:

- Solids concentration for the slurry in step 3 and 8
- Identification of the mixing requirements (e.g. PJM and/or spargers) during the process
- Identification of UFP filter pump/ultrafilter loop status during process operations
- Sampling and analysis requirements, and decisions associated with the sample results
- Requirements for the process condensate as identified in Step 9

Process Control

The proposed oxidative leaching process is summarized in CCN: 110724. Also included in the Technical Report (24590-WTP-RPT-ENG-05-006) is a suggested test protocol (Appendix A, Proposed Revision to Specification 12) for deciding if the oxidative leaching should be used to treat a given feed batch.

The process and decisions for water washing and caustic leaching are straightforward and can be accomplished by the use of a tank farm waste sample and subsequent tests to provide supporting information. This strategy works because the component of interest in the waste, namely aluminum, is present as a large fraction in the tank composition. Insoluble Cr by comparison, will be present in a much smaller fraction. The specific composition of the slurry in the UFP system will be impacted by processing of various waste streams in the WTP. The proposed oxidative leaching process relies on a precise addition rate of permanganate (e.g., 1.1 mole permanganate/1 mole Cr). Addition rates below this level will not be effective in removal of Cr. Addition rates in excess of these levels could dissolve excessive Pu. Thus the proposed process approach needs to be augmented with a definition of the process control, including sampling and analysis, to ensure an effective oxidative leaching process. This also suggests that the specific decision on oxidative leaching be based upon better quality information, compared to the caustic leaching decision and would need come from sampling of the HLW solids in the UFP System.

Completeness of the Technical Report

BNI has specified a set of Engineering Department Project Instructions to define requirements for the engineering work (24590-WTP-3DP-G00B-00001). A procedure on Engineering Studies (24590-WTP-3DP-G04B-00016) is included within the set of engineering procedures *"To outline the requirements for the initiation, development, and approval of engineering studies and reports developed by the Engineering Department"*. An engineering study *"is an analytic process used to evaluate alternative solution to an engineering problem..."* Furthermore, the engineering study format is required because, *"All client requested studies shall be treated as formal studies"*.

The deliverable "Technical Report on Oxidative Leaching" (24590-WTP-RPT-ENG-05-006) does not meet the requirements on content for an engineering study as defined in 24590-WTP-3DP-G04B-00016. The following additions appear to be needed in the revision of the Technical Report.

- Approval by the cognizant DEM (Section 2.1)
- Cost and schedule estimates/impacts from Project Controls (Section 3.1.2)
- Review and approval by the DEM/APEM or APE (Section 3.2.1)
- Formal Studies report format in attachment B (Section 3.3.1) including: Study Basis criteria, assumptions, description of alternative solutions considered and selection of the recommended alternative.

Will the oxidative leaching process reduce the production rate (e.g. capacity or availability) of the Pretreatment Facility?---3

Discussion:

Pretreatment Facility Capacity

Dynamic model runs were performed for a "No Oxidative Leach Case" and an "Oxidative Leach Case" for the tank waste treatment mission. These model runs summarized in CCN: 110731 assumed that the ultrafilter system would be operating in a "Parallel" operating mode. The UFP system performs two major functions; dewatering of the sludge which is estimated to take 100 hours, and treatment of the sludge which is assumed to 80 hours for caustic leaching and 90 hours for caustic leaching and oxidative leaching combined. In the parallel operating mode selected for the Dynamic model runs, the treatment in one UFP system is not initiated until the dewatering is completed in the other UFP system. This is effect sets the batch process time at 200 hours regardless of the sludge treatment method (e.g. water wash, caustic wash or caustic wash/oxidative leach.).

The Dynamic Model runs indicate a completion date of 12/31/2059 for the "No Oxidative Leach Case" and a completion date of 12/31/2043 for the "Oxidative Leach Case". The reduction in the processing schedule for the Oxidative Leach Case is a direct result of the HLW glass mass reduction of 34%. These results are also impacted by key assumptions used in the model runs including the: parallel UFP operating mode, glass waste loading constraints and the feed vector. This long schedule for processing is not representative of the anticipated performance of the WTP facilities.

Pretreatment Facility Availability

The availability of the Pretreatment facility is being evaluated in the Operational Research Assessment due in August 2005. Thus, this Design Oversight did not assess the availability of the Pretreatment facility.

What impacts will result to the ILAW and IHLW waste form (and waste form production rates) from the implementation of the oxidative leaching process?---4

Discussion:

The Technical Report (24590-WTP-RPT-ENG-05-006) did not provide a detailed assessment of the impact of the oxidative leaching process on the IHLW and ILAW waste forms. The Dynamic Models assumed that the waste loading constraints were those specified in the WTP Contract. Thus, the only impact to the waste forms was to the total volume and mass projected to be produced. The results are summarized below. The IHLW glass mass is reduced by about 34% as a result of oxidative leaching. However, there is a slight decrease in the amount of Na for the Oxidative Leaching scenario because of the shorter operations time for the WTP. This shorter operations time reduces the amount of Na needed for neutralization of process streams

Waste Form	WTP Baseline	WTP Baseline with Oxidative Leaching
IHLW, MT Glass (Canisters)	108,734 (35,076)	71,812(23,165)
ILAW (as MT Na Treated in WTP), MT Na	45,054	45,033

2. What differences exist in the flowsheet for the removal of Cr and sulfate?

Assessment: Cr is removed from the HLW slurries by combinations of caustic leaching, washing, and oxidative leaching. Sulfate is removed from HLW slurries through caustic leaching and washing. BNI concluded in the Technical Report on Oxidative Leaching (24590-WTP-RPT-ENG-05-006) that the addition of permanganate is not expected to remove sulfur by oxidation because sulfate is the most oxidized form of sulfur and the sulfur in tank waste is largely present as the sulfate ion.

Other Technical Questions – Equipment Integration

1. Are the equipment components required to implement the oxidative leaching process part of the current WTP design? If not, what additional equipment (and cost) will be required?, has it been specified?, and can this equipment be installed in the WTP facility?

Assessment: The Technical Report on Oxidative Leaching (24590-WTP-RPT-ENG-05-006) states the only required modification is to connect two spare lines to the ultrafilter feed vessels to the reagent source in the C3 area. The reagent is provided from the pretreatment distribution header for 1.0M NaMnO₄. 24590-WTP-RPT-ENG-05-006 stated all other required equipment is part of the WTP design.

The reviewers agree with this assessment based on the current conceptual level of oxidative leaching design completion. Further design impacts may be defined through:

- Completing required integrated safety management (ISM) safety analysis of the oxidative leaching process.
- Updating the Preliminary Safety Analysis Report (PSAR) to include oxidative leaching.
- Preparing and obtaining approval of a revised Criticality Safety Evaluation Report (CSER) to include the oxidative leaching process.
- Completing environmental permit modifications to include the oxidative leaching process.
- Revising WTP design to include equipment to perform oxidative leaching and implement new safety requirements derived from safety analysis.

BNI has not provided cost estimates for the additional equipment and other costs to implement oxidative leaching as required by BNI procedure Engineering Studies (24590-WTP-3DP-G04B-00016, Revision 2, August 4, 2003), Section 3.1.2. Section 3.1.2 states

“The responsible Area Discipline Supervisor or assignee must obtain any cost or schedule estimates/impacts from Project Controls.”

2. Have the corrosion and erosion issues for the vessels and other equipment been evaluated and have they been determined to be acceptable?

Discussion:

BNI has not updates the Corrosion Evaluation (CE) for the UFL-VSL-00002A/2B vessels (24590-PTF-N1D-UFP-00003, Rev 4) where the primary selective oxidation reaction will occur, and other associated vessels. The proposed permanganate oxidation process will generate secondary waste streams, such as the Cr rich stream that is recycled back through the Plant Wash and Drain System (PWD). The impact of this process stream, and other secondary waste streams, on the Pretreatment Facility CEs was not completed. Other vessels that should have been reviewed include the: Acidic/Alkaline Effluent Vessels (PWD-VSL-00015/00016) and the Waste Feed Evaporator Feed Vessels (FEP-VSL-00017A/00017B).

Other Technical Questions – Technical Risks

1. Has a risk assessment been completed to identify technical risks from the proposed implementation of the process?

Assessment: BNI has added 3 new risk sheets to their internal risk register as a result of the proposed implementation of the process:

- WTP-PT-091, Oxidative Leaching, Plutonium Accumulation
- WTP-PT-093, Oxidative Leaching, Glass Production
- WTP-PT-094, Oxidative Leaching, Resin Degradation

2. What new technical risks are anticipated from the proposed implementation of the process?

Assessment: Plutonium mobilization due to permanganate oxidation and subsequent accumulation due to reduction/recovery on the Cs IX resin will raise criticality concerns and will need to be evaluated through the CSER process. As noted by the BNI, controls for criticality may require sample hold-points, premature resin disposal, premature eluate (nitric acid) disposal, and higher resin disposal cost.

The addition of manganese could reduce HLW glass loading leading to an increased project cost. The savings from chromium oxidation will need to offset any cost increases associated with manganese loading of the HLW glass.

Excessive permanganate could carry over to the Cs IX columns and lead to their early degradation.

3. Has the proposed implementation of the oxidative leaching process changed any of the significant technical risks associated with WTP operations?

Assessment: Potential solubilization and subsequent precipitation of plutonium by permanganate will add to the risk of nuclear criticality.

Excessive permanganate could carry over to the Cs IX columns and lead to their early degradation.

The nature of the wastes to be treated by BNI will not require oxidative leaching. Therefore, the 3 new risks identified by BNI will be deferred to the operating contractor.

Several other risks were identified by the reviewers including:

- Samples tested and data in literature may not represent the spectrum of waste requiring oxidative leaching over the mission. Actual data may not be available until waste is staged for treatment and samples taken and tested. ORP and the Tank Farm Contractor should evaluate opportunities to test samples projected to require oxidative leaching when they are being tested for waste compatibility or other process testing.
- Competing species in the waste stream (metals and organics) will compete for the permanganate. Therefore, the quantity of permanganate will be difficult to estimate without direct sampling and testing of each new waste coupon arriving at the Pretreatment facility from the Tank Farms.
- Available data from samples tested was generated using procedures different and likely not representative of the proposed oxidative leaching process. Integrated testing should be performed demonstrating the caustic leaching, washing, and oxidative leaching processes including recycle streams performs as predicted.
- Impacts of the process on plant throughput and availability could be considerable if process stream sampling (e.g. for criticality criteria) and line/vessel flushing requirements become substantial.
- Uncertainties associated with pitting corrosion and stress-corrosion cracking induced by permanganate (especially at welds) need to be evaluated.
- Integrated Safety Management (ISMS) and criticality safety evaluations (CSER) have not been completed and need to be completed before an adequate assessment of the risks associated with the recommended process can be fully evaluated.

Assessment of BNI Oxidative Leaching Risk Evaluation:

BNI provides an insufficient summary evaluation of the risks associated with oxidative leaching. Two of the three primary risks identified (plutonium species accumulation and resin degradation) are deemed by BNI to fall within the scope of the operations contractor. The third risk identified by BNI (impact of manganese on glass production) was recommended to be dealt with as a "traceability risk." The resolution of the "traceability

risk" will depend on the development of experiments that will increase manganese glass loading. The overall recommendation is that these primary risks be deferred to operations.

There is no question that permanganate will oxidize Cr III to Cr VI when added in sufficient quantities. However, a number of risks (not evaluated by BNI) warrant further evaluation before the proposed process is accepted by ORP.

The six process related risks identified above should be evaluated, based on available data and information or through laboratory measurements. Process uncertainties associated with the quantity of permanganate to be added are unacceptable because of the potential for downstream deleterious impacts such as resin degradation, accelerated corrosion, and actinide dissolution.

Physical-chemical predictions of the quantity of permanganate to be added for any waste batch will be highly uncertain because of the high variability of the waste feed composition. Therefore, the resolution for these issues is likely to require an expensive batch-by-batch characterization of each waste batch received by the WTP.

Costs associated with line flushes, sample characterization, and impacts to plant life need to be weighed versus other oxidative leach options available to ORP. These options include oxidative leaching using the other processes identified by the contractor that minimize impact on WTP degradation. In addition, ORP should compare the net risk cost benefit of oxidative leaching recommended in the WTP versus oxidative leaching in the tank farms prior to treatment in the WTP.

In any event, the decision to endorse the proposed process should be deferred pending completion of the CSER and ISMS reviews.

**U.S. Department of Energy
Office of River Protection**

August 2005

**Technical Design Oversight
WTP Oxidative Leaching**

Appendix B

**Design Product Oversight Plan
WTP Oxidative Leaching**

July 2005

U.S. Department of Energy, Office of River Protection

DESIGN PRODUCT OVERSIGHT PLAN

WTP OXIDATIVE LEACHING

July 2005

Design Oversight: D-05-DESIGN-013

Team Lead: Rob Gilbert

Reviewer(s): Langdon Holton
Jennifer Holland
Don Alexander
Chung-King Liu

Submitted by:

Team Lead: Robert a Gilbert Date 6/6/05
Rob Gilbert

Concurrence:

WTP Engineering Division Director: Bill Hamel Date 6/4/05
Bill Hamel

WTP Project Manager: John Eschenberg Date June 6, 2005
John Eschenberg

1.0 BACKGROUND, PURPOSE AND OBJECTIVES

1.1 Background

The U.S. Department of Energy, Office of River Protection (ORP) will design, construct, commission, and operate a Waste Treatment and Immobilization Plant (WTP) to treat and immobilize waste contained in 149 single-shell tanks and 28 double-shell tanks (DST) at Hanford. These tanks contain approximately 54 Mgal waste with 190 MCi radioactivity. The WTP will receive waste in batches from the DSTs through transfer pipelines. This waste will be concentrated in an evaporator; strontium and transuranic will be precipitated from select waste streams; solids will be water washed, caustic leached, oxidative leached, and separated from the soluble fraction in an ultrafilter system; and cesium will be removed from the soluble fraction with an ion exchange system. The radionuclide rich solids and cesium ion exchange eluant will be combined and immobilized in High Level Waste (HLW) glass. The low-activity waste supernatant will be further concentrated and immobilized in Low Activity Waste (LAW) glass or immobilized in an alternative waste form currently being studied.

The WTP Contract requires the contractor to develop and implement an oxidative leaching process to remove chromium from tank waste solids. This process is necessary to reduce the impact chromium has on HLW glass waste loading. Without an oxidative leaching process HLW glass projections to complete immobilization of tank waste slurries far exceed the capability of WTP HLW vitrification to complete the mission by 2028, as required by the Tri-Party Agreement.

Pretreatment Oxidative Leaching Path Forward, CCN: 089106, dated February 28, 2005, documented Bechtel National, Inc.'s (BNI) plan to develop and implement an oxidative leaching process.

1.2 Purpose

This design oversight will assess the supporting technical basis and design for the BNI oxidative leaching process. The review team should address the specific objectives defined below.

1.3 Specific Objectives

The contractor oxidative leaching process should be evaluated considering the following lines of inquiry:

Contract Compliance Questions

1. Has the Contractor conducted a literature review and prepared a technical report (Table C.5-1.1, Deliverable 2.8 Technical Report on Oxidative Leaching) that evaluates the treatment processes for the oxidative leaching of chemical components (principally Cr

- and associated components, i.e. sulfate) that limit the loading of HLW solid oxides in the HLW glass waste form?
2. Does the literature review summarize existing experimental results and data?
 3. Does the literature review identify the “*chemical components (principally Cr and associated components, i.e. sulfate) that limit the loading of HLW solid oxides in the HLW glass waste form*”?
 4. Does the literature study present conceptual and realistic process flowsheets including the identification of process equipment and operating conditions?
 5. Does the literature review provide a recommendation on the preferred process to conduct the required separations?
 6. Has the contractor conducted technology testing activities using simulants and actual waste testing to provide design and process operational information on the process used to remove Cr from the HLW waste stream?
 7. Does the proposed process have the capability to remove Cr from the pretreated HLW stream such that this chemical component or reagents added to remove this component does not limit the HLW waste loading in the glass waste form?
 8. Has the Contractor tested a minimum of two radioactive tank waste samples? (SY-102 and a second sample that must be provided so that analysis with sample SY-102 can be run concurrently)
 9. Does the radioactive sample test provide a proof of process demonstration (part of Deliverable 2.2 and 2.3) and determine any impacts to the facility throughput and/or availability?
 10. Has the contractor provided recommendations to ORP for the modification of *Specification 12, Number of High-Level Waste Canisters Per Batch of Waste Envelope D* and *Specification 1, Immobilized High-Level Waste*, Table TS-1 limits for Cr₂O₃ and sulfate, based upon the results of this experimentation.
 11. Has the contractor prepared a test report that summarizes the results of the oxidative leaching? (Table C.5-1.1 Deliverable 2.9 Test Report on Oxidative Leaching)” Standard 2(a),(3),(ix).

Other Technical Questions

Chemistry

1. Does the testing/literature review provide a clear technical basis for the selection of the oxidative leaching reagents?

2. Does the testing/literature review address the leaching of sulfate from the HLW sludge?
3. Have the selected reagents been evaluated over a range of chemistry conditions that are anticipated in actual plant scale operations? Do these conditions define the limits of application of the process?
4. Does the testing/literature review provide a clear technical basis for the usage rate for the oxidative leaching reagents, e.g. mass or moles of reagent per moles of insoluble Cr (and sulfate)?
5. Do the selected oxidative leaching reagents lead to any adverse process impacts, such as: excessive corrosion, dissolution of radioactive components (e.g. Am, Pu, Np) or impact subsequent processing of the tank waste sludge?
6. Does the testing provide a basis for a potential modification to Specification 12?
 - Can the proposed change be used as a performance standard for determining if oxidative leaching should be deployed in the WTP flowsheet?
 - Can the proposed change be conveniently implemented in the WTP flowsheet?
7. Does the testing and evaluation provide a defensible basis for the revision to Specification 1, Table TS-1 limits for chromium oxide and sulfate?
8. Do the testing results with simulants and actual wastes produce comparable results?

Flowsheet Integration

1. Has the technical work considered and evaluated flowsheet alternatives for the implementation of the oxidative leaching process? Has the optimum flowsheet condition been evaluated and identified?
2. What differences exist in the flowsheet for the removal of Cr and sulfate?
3. Will the oxidative leaching process reduce the production rate (e.g. capacity or availability) of the Pretreatment Facility?
4. What impacts will result to the Immobilized LAW and Immobilized HLW waste form (and waste form production rates) from the implementation of the oxidative leaching process?

Equipment Integration

1. Are the equipment components required to implement the oxidative leaching process part of the current WTP design? If not, what additional equipment (and cost) will be required? Has it been specified? And can this equipment be installed in the WTP facility?

2. Have the corrosion and erosion issues for the vessels and other equipment been evaluated and have they been determined to be acceptable?

Technical Risks

1. Has a risk assessment been completed to identify technical risks from the proposed implementation of the process?
2. What new technical risks are anticipated from the proposed implementation of the process?
3. Has the proposed implementation of the oxidative leaching process changed any of the significant technical risks associated with WTP operations?

2.0 PROCESS

This oversight shall be conducted within the guidelines of ORP PD 220.1-12, "Conduct of Design Oversight."

2.1 Scope

This oversight shall include reports, data, models, safety analysis, and design documentation for the oxidative leaching process.

2.2 Preparation

1. Identify the BNI and ORP Points of Contact for this review. Transmit this plan to the points of contact and meet with appropriate personnel to review the plan and establish a working relationship to complete the review.
2. Identify the pretreatment process and facility structures, systems, and components and other factors associated with oxidative leaching in WTP.
3. Collect documentation, e.g., test reports, flow sheets, process flow diagrams, calculations, system descriptions, and models that characterize the approach and capabilities for oxidative leaching solids in WTP.
4. Review current BNI open issues with oxidative leaching solids in WTP.

2.3 Review and identify, resolve, or document issues

Review the collected documentation, evaluate the selected attributes, and discuss with appropriate contractor personnel.

2.4 Reporting

De-brief ORP and BNI management as required and prepare a draft report that summarizes the activities, results, conclusions and recommendations of the review. The

draft report will be issued for review and comment. The final report will resolve comments received on the draft report.

3.0 SCHEDULE OF ACTIVITIES

Activity Description	Responsibility	Complete By
Develop Oversight Plan	Gilbert	6/2/05
Advise BNI of planned oversight and provide oversight plan to BNI	Gilbert	6/7/05
Collect preliminary information to prepare for the review	Team/BNI	7/11/05
Review documents and meet with BNI and ORP personnel as required	Team	7/18/05
Prepare Draft Design Oversight Report	Team	7/25/05
ORP and BNI review draft report	ORP and BNI	8/1/05
Resolve comments and issue final report	Team	8/8/05

4.0 DOCUMENTATION

The final report of this design oversight will be issued addressing the lines or inquiry and identify open issues requiring further action.

5.0 CLOSURE

The Team Leader with concurrence of the Director shall confirm that the open items from this oversight are adequately resolved.

6.0 REFERENCES

1. Contract No. DE-AC27-01RV14136.
2. CCN: 089106, "Pretreatment Oxidative Leaching Path Forward," February 2005.
3. Deliverable 2.8 Technical Report on Oxidative Leaching (TBD).
4. Deliverable 2.9 Test Report on Oxidative Leaching
 - a. WTP-RPT-117, Revision 0, "Oxidative-Alkaline Leaching of Washed 241-SY-102 and 241-SX-101 Tank Sludges," October 2004.

-
- b. WTP-RPT-137, Revision A, "Alkaline Leaching of SX-101 and SY-102 and its Impact on Immobilized High-Level Waste," May 2005.
 5. 24590-WTP-RPT-NS-05-001, DRAFT, "Criticality Safety Aspects of Oxidative Leach," April 2005.
 6. RPP-20003, Revision 1, "Sensitivity of Hanford Immobilized High-Level Waste Glass Mass to Chromium and Aluminum Partitioning Assumptions," March 2005.
 7. 24590-WTP-RPT-PT-02-012, "Material Balance and Process Flowsheet Assessment," (TBD).
 8. 24590-WTP-RPT-PT-02-010, "WTP Tank Utilization Assessment," (TBD).
 9. RPP-15552, Revision 0, "Hanford Tank Waste Oxidative Leach Behavior Analysis," April 2003.
 10. CCN: 110724, "Design Process Baseline Process Description for Oxidative Leaching," April 29, 2005.
 11. CCN: 110718, "Summary of Research and Technology Results on Oxidative Leaching and Discussions of Potential Downstream Impacts," April 15, 2005.

Task# ORP-WTP-2005-0209

E-STARS™ Report
 Task Detail Report
 10/11/2005 0759

TASK INFORMATION

Task# ORP-WTP-2005-0209

Subject CONCUR: (05-WED-033) TRANSMITTAL OF DESIGN OVERSIGHT REPORT ON WASTE TREATMENT AND IMMOBILIZATION PLANT (WTP) OXIDATIVE LEACHING

Parent Task# **Status** CLOSED

Reference 05-WED-033 **Due**

Originator Almaraz, Angela **Priority** High

Originator Phone (509) 376-9025 **Category** None

Origination Date 09/01/2005 0744 **Generic1**

Remote Task# **Generic2**

Deliverable None **Generic3**

Class None **View Permissions** Normal

Instructions Hard copy of the correspondence is being routed for concurrence. Once you have reviewed the correspondence, please approve or disapprove via E-STARS and route to the next person on the list. Thank you.

bcc:
 MGR RDG File
 WTP OFF File
 S. J. Ollinger, DEP
 J. J. Short, OPA
 R. A. Gilbert, WED
 W. F. Hamel, WED
 J. R. Eschenberg, WTP

ROUTING LISTS

1 Route List Inactive

- Gilbert, Rob A - Review - Concur - 09/01/2005 0853
Instructions:
- Short, Jeff J - Review - Concur - 09/27/2005 0918
Instructions:
- Hamel, William F - Review - Concur with comments - 10/11/2005 0758
Instructions:
- Eschenberg, John R - Review - Concur - 10/11/2005 0759
Instructions:
- Schepens, Roy J - Approve - Approved - 10/07/2005 1624
Instructions:

ATTACHMENTS

No Attachments

COLLABORATION

COMMENTS

RECEIVED

OCT 11 2005

DOE-ORP/ORPCC

Task# ORP-WTP-2005-0209

Poster Short, Jeff J (Short, Jeff J) - 09/01/2005 0909

There is no letter attachment to review.

Poster Hamel, William F (Almaraz, Angela) - 10/11/2005 0710

Concur

Rob Gilbert signed for Bill Hamel on 9/7/05

TASK DUE DATE HISTORY

No Due Date History

SUB TASK HISTORY

No Subtasks

-- end of report --

Task# ORP-WTP-2005-0209

E-STARS™ Report
Task Detail Report
09/01/2005 0753

TASK INFORMATION

Task#	ORP-WTP-2005-0209	Status	Open
Subject	CONCUR: (05-WED-033) ULTRAFILTRATION SYSTEM CAPACITY IMPROVEMENT STUDY RESULTS AND DIRECTION <i>Transmittal of Design oversight Report on WTP Oxidative Leaching</i>		
Parent Task#		Due	
Reference	05-WED-033	Priority	High
Originator	Almaraz, Angela	Category	None
Originator Phone	(509) 376-9025	Generic1	
Origination Date	09/01/2005 0744	Generic2	
Remote Task#		Generic3	
Deliverable	None	View Permissions	Normal
Class	None		

Instructions Hard copy of the correspondence is being routed for concurrence. Once you have reviewed the correspondence, please approve or disapprove via E-STARS and route to the next person on the list. Thank you.

bcc:
MGR RDG File
WTP OFF File
J. J. Short, OPA
R. A. Gilbert, WED
W. F. Hamel, WED
J. R. Eschenberg, WTP
S. J. Olinger, Dop

ROUTING LISTS

1 Route List Active

- Gilbert, Rob A - Review - Awaiting Response
Instructions:
- Short, Jeff J - Review - Awaiting Response
Instructions:
- Hamel, William F - Review - Awaiting Response
Instructions:
- Eschenberg, John R - Review - Awaiting Response
Instructions:
- Schepens, Roy J - Approve - Awaiting Response
Instructions:

RAJ 9/1/05
JJ 9/2/05
WFH 9/7/05
JE 10/2/05
RS 10/1

ATTACHMENTS

No Attachments

Reviewed - OK GJB

COLLABORATION

COMMENTS