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**Report for Treating Hanford LAW and WTP SW Simulants:
Pilot Plant Mineralizing Flowsheet**

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by

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THOR ART PHASE 2 PILOT PLANT REPORT REVISION PAGE

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ABSTRACT

The U.S. Department of Energy, Office of River Protection (DOE-ORP), has responsibility for managing the safe storage, treatment, and disposal of radioactive liquid wastes in underground storage tanks at the Hanford Site in southeastern Washington State. There are 177 such tanks at the Hanford Site containing ~53 million gallons of highly radioactive wastes and ~190 million curies of radioactivity. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) will separate the wastes into a small-volume, high-level waste (HLW) fraction, containing most of the radioactive constituents, and a large-volume, low-activity waste (LAW) fraction, containing most of the non-radioactive chemical and hazardous constituents. The HLW and LAW will be converted into immobilized waste forms for ultimate disposal. The LAW fraction of the Hanford tank wastes will be disposed of at the Integrated Disposal Facility (IDF) on the Hanford Site. To be acceptable for land disposal, the characteristic and listed waste, as well as the underlying hazardous constituent, must be treated in accordance with federal and state treatment standards. Currently, there is inadequate LAW vitrification capacity planned at the Hanford Site to complete that mission within the required timeframe. Therefore, additional LAW capacity will be required, either as vitrification or as a supplemental treatment technology. One candidate supplemental treatment technology is the THOR[®] fluidized bed steam reforming (FBSR) process, offered by THOR Treatment Technologies, LLC (TTT).

In September of 2007, DOE's Office of Environmental Management (EM) awarded Phase II of the Advanced Remediation Technologies (ART) Project to TTT for demonstration testing of the THOR[®] FBSR process, using a mineralizing flowsheet for treating simulated Hanford LAW and secondary waste from the WTP (WTP SW). DOE-EM was seeking technologies that would provide high return on investment; could be deployed at the sites; would complement existing treatment plants and processing facilities with minimal disruption; and were mature enough so that when demonstration testing was completed, there would be sufficient processing data to enable initiation of a final design. The demonstration testing was conducted at the Hazen Research facility in Golden, Colorado, using the Engineering Scale Technology Demonstration (ESTD) pilot plant and at Savannah River National Laboratory with a Bench-scale Steam Reformer (BSR).

The ESTD testing program processed non-radioactive Hanford LAW and WTP SW simulants through a dual FBSR system and the BSR program processed non-radioactive and radioactive WTP SW simulants to produce leach-resistant, solid products and environmentally compliant gaseous effluents. The solid products incorporated normally soluble ions into an alkali alumino-silicate (NAS) mineral matrix that inhibits the leaching of those ions into the environment. An organic constituent was also added to the waste stream (for ESTD testing) in order to determine the organic destruction removal efficiency of the system. The solid products were used to prepare final monolithic waste forms representative of those suitable for disposal at the Hanford IDF. The purpose of the BSR testing program was to demonstrate processing with a radioactive simulant and provide test data comparable to the ESTD.

The ESTD test program was performed April 15 through May 6, 2008 and the BSR program was conducted intermittently late 2009 through 2011. The ESTD demonstrated the capability of the THOR[®] FBSR process to convert both the LAW and WTP SW simulants into a granular, mineralized solid product in a safe and efficient manner. Gaseous emissions were found to be within regulatory limits for both, with the minor exception of one case where the WTP SW emissions exceeded the low volatile metals standard by 1 µg/dscm. Based on ESTD data from manual off-gas sampling, cesium and rhenium were captured in the mineralized product with system removal efficiencies of 99.999% and 99.998%, respectively, for both simulants. The overall system removal efficiency for iodine from the LAW simulant ranged from 88% to 94%. The durability and leach performance of the ESTD and BSR FBSR granular

products, and subsequent monolithic waste forms, were superior to the Low-activity Reference Material (LRM) glass standards. Normalized Product Consistency Test (PCT) release rates for constituents of concern were about 2 orders of magnitude less than that of sodium in the Hanford glass standard (2 g/m^2), and the monolith waste form performed well in ASTM C1308 testing, such that the measured Leach Indexes for key components (Na, Re/ ^{99}Tc and I) were all below current Hanford Integrated Disposal Facility (IDF) target limits. Compressive strength of the geopolymer monoliths formed from ESTD and BSR granular products exceeded the >500 psi Hanford IDF criterion by 4 to 8 times for both simulants.

EXECUTIVE SUMMARY

The U.S. Department of Energy's Office of River Protection (ORP) is responsible for the retrieval, treatment, immobilization, and disposal of Hanford's tank waste. Currently there are approximately 53 million gallons of highly radioactive mixed wastes awaiting treatment. A key aspect of the River Protection Project (RPP) cleanup mission is to construct and operate the Waste Treatment and Immobilization Plant (WTP). The WTP will separate the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions, both of which will subsequently be vitrified in separate processing lines. Currently, there is inadequate LAW processing capacity planned at the Hanford Site to complete that mission within the required timeframe. Therefore, additional LAW processing capacity will be required, either as vitrification or as a supplemental treatment technology. One candidate supplemental treatment technology is the THOR[®] fluidized bed steam reforming (FBSR) process, offered by THOR Treatment Technologies, LLC (TTT).

In August 2005, the Department of Energy (DOE) issued a Request for Proposals (RFP) for the Advanced Remediation Technologies (ART) acquisition. This acquisition was based on the DOE's Office of Environmental Management's (EM) intent to evaluate various advanced technologies existing in the private sector, which would enable former weapons sites such as Hanford to accelerate their baseline clean-up schedules, reduce life cycle costs, reduce programmatic risk, and improve worker safety. In addition, DOE-EM was seeking technologies that would provide high return on investment; could be deployed at the sites; would complement existing treatment plants and processing facilities with minimal disruption; and were mature enough so that when demonstration was completed, there would be sufficient processing data to enable initiation of final design.

TTT responded to the RFP by proposing the THOR[®] FBSR technology for the LAW supplemental treatment mission at the Hanford Site. In August 2006, TTT was awarded Phase I of ART contract DE-AC09-06SR22521. Phase I, completed in late 2006, delivered a compilation of past FBSR pilot plant work relevant to the intended application and a plan to conduct new testing to demonstrate the capability to process the Hanford LAW into a final waste form that would meet the requirements for disposal at the Integrated Disposal Facility (IDF). This final waste form had to be at least as chemically durable (leach-resistant) as the projected WTP LAW glass product.

Phase II of the ART contract was awarded to TTT in September 2007. This phase demonstrated the processing of non-radioactive Hanford LAW and WTP secondary waste (WTP SW) simulants, using the Engineering Scale Technology Demonstration (ESTD) pilot plant at Hazen Research in Golden, Colorado. It also demonstrated the processing of a non-radioactive LAW and non-radioactive and radioactive WTP SW simulants using the Bench-Scale Steam Reformer (BSR) at the Savannah River National Laboratory (SRNL). In all cases the resulting granular products were formed into final monolithic waste forms and subjected to durability testing that showed the waste forms to meet the requirements for disposal at the IDF. Figure E-1 shows the basic TTT technical approach of Phases I and II.

Figure E-1 ART Project Approach

The THOR[®] technology combines two mature technologies, fluidized bed system technology and steam reforming chemical technology, into an integrated process to produce a robust thermal (700-750°C) treatment system capable of processing waste streams of widely varying compositions. Solids, liquids, gases, or slurries can be fed into the system and various output solid products are produced, depending on the additives utilized during the processing operations. LAW and/or WTP SW wastes can be processed irrespective of whether they contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components. The FBSR technology processes these wastes into a crystalline ceramic (mineral) waste form. The mineral waste form that is produced by co-processing waste with kaolin clay has been shown to be as durable as LAW glass, as detailed below. Monolithing of the granular FBSR product prevents dispersion during transport or burial/storage, which is a regulatory driver, but is not necessary for chemical durability.

ESTD Testing Summary

The ESTD is an engineering scale unit built and operated to demonstrate the integrated THOR[®] FBSR process and gather necessary technical data for the design and construction of full-scale processing systems. The ESTD includes all unit operations present in a full-scale unit except the final product packaging equipment. The process flow diagram and a detailed physical description are provided in Section 2 of the report.

The ESTD was designed, constructed, and functionally tested using rigorous engineering and quality control practices, as described in the THOR Treatment Technologies, LLC (TTT) Quality Assurance Plan, Project Quality Procedures, and Engineering Procedures. Rigor remained during testing operations with a robust system of operating documents and conduct of operations practices. A core team of technical professionals, the Joint Test Group (JTG), oversaw all testing activities and results. The JTG reviewed all test iterations and specified the details of each day's testing work, within the framework of the formal test plan and other controlling documents.

The main ESTD test objectives were:

- Verify steam reformer process chemistry and product quality consistent with that observed during previous mineralizing pilot plant and ESTD operations.
- Confirm that the final process off-gas complies with applicable environmental regulations. A key component is compliance with Maximum Achievable Control Technology (MACT) standards without the need for a wet scrubber. Another key component of this objective is the determination of iodine, cesium, and rhenium (a surrogate for radioactive ⁹⁹Tc) retention in the solid products and gaseous emissions from the process.
- Confirm scale-up parameters such as throughput, carbon usage optimization, feed nozzle and fluidizing gas parameter optimization, energy conservation, and optimal use of process additives.
- Confirm tandem operation of the two in-series steam reformers and that the second reformer effectively destroys residual organic gases and fully oxidizes carbon, organics, and carbon monoxide generated in the DMR.
- Demonstrate the safe, long-term, steady-state operation of the THOR[®] integrated FBSR process.
- Demonstrate, on a laboratory scale and then on a larger scale, the production of final monolith products from the mineralized ESTD LAW and WTP SW products that meet all IDF disposal

requirements. The retention and determination of leach resistance of cesium, iodine, and rhenium in the product are key elements of this objective.

- Generate an adequate quantity of monolith product for characterization, durability testing, and other analyses, as required.
- Maximize waste volume reduction.
- Confirm zero liquid secondary waste generated from process operations.

The ART ESTD tests were conducted in April and May 2008. The series of tests reflected a matrix of operating conditions that, for the most part, involved varying operating temperatures and mineralizing clay addition ratios. During the LAW simulant production tests (P-1A and P-1B), 1,193 gallons (~15,000 pounds) of LAW simulant were processed into ~7,395 pounds of granular solid product during 101.5 hours of “feed-on” operation, which was achieved during a total of 102.25 hours of operation, for an on-line factor of 99.3%. During the WTP SW simulant production tests (P-2A and P-2B), 1,223 gallons (~13,400 pounds) of WTP SW simulant were processed into ~5,127 pounds of granular solid product during 102 hours of “feed-on” operation, which was achieved during a total of 104.48 hours of operation, for an on-line factor of 97.6%.

The key results from the ESTD tests are as follows:

- The safe, long-term (>100hr) operation of the THOR[®] process and key components was demonstrated.
- The overall mass balances for the LAW and WTP SW tests were excellent, with differences of less than 1% between input and output masses. (See Section 9 of the report.)
- Based on data from manual off-gas sampling intervals, cesium and rhenium were captured in the mineralized product with system removal efficiencies of 99.999% and 99.998%, respectively, for both simulants (no HEPA filtration was used for engineering scale testing). (See Table 8-18)
- The overall system removal efficiency for iodine from the LAW simulant ranged from 89% to 94%, based on manual off-gas sampling. The system removal efficiency for the WTP SW simulant was lower at 19.1%. The difference in these system removal efficiencies for iodine can be partially attributed to the amounts of iodine added to the LAW simulant (0.13lb/hr) versus the amount iodine added to the WTP SW simulant (0.0090lb/hr), which affects the ability to detect iodine in the off-gas. (See Table 8-14)
- The HCl/Cl₂ off-gas concentration for the production tests averaged 8 ppm, or 37% of the Hazardous Waste Combustor (HWC) MACT standard of 21ppmv. During the production runs, Cl from NaCl in the feed was captured in the solid products, with an average removal efficiency of over 92%. In addition, fluoride was captured with 78% efficiency. (See Table 8-14)
- The stack gas particulate matter (PM) concentrations during the production tests averaged 18% of the HWC MACT standard of 3.4 mg/dscm. A full-scale production facility will include a HEPA filter, resulting in significantly lower PM releases. (See Table 8-14)
- System removal efficiencies for hazardous metals were calculated using the stack gas emission rates for hazardous metals and input feed rates of those metals. Concentrations of semi-volatile metals (SVM) and low volatility metals (LVM) measured during the LAW production tests were within the HWC MACT standards. However, a tube sheet seal in the Off-Gas Filter (OGF) failed, confirmed during post-production run inspections, most likely during the initial WTP SW

production tests. The failure likely allowed a small portion of non-filtered gas to be emitted to the stack. Off-gas sampling during the WTP SW production tests shows an increase in metals emission rates over that observed for LAW production tests. The LVM for the WTP SW test was equal to 24 µg/dscm, which is 1 µg/dscm above the MACT standard of 23 µg/dscm, and was apparently caused by the tube sheet seal failure. It could reasonably be expected that LVMs resulting from the WTP SW stream, based on observed data from LAW production tests, would be well below the MACT standard with a fully functional OGF (See Table 8-15). HEPA filtration that would be present in a full-scale facility, but not installed in the ESTD, would ensure that MACT standards would be met in the event of equipment failure.

- The system NO_x destruction from production test averages ranged from 91% to 94%. Production test-average stack NO_x concentrations ranged from 572 to 726 ppmv (dry basis), well below the desired performance level of <1,500ppmv (dry basis). (See Tables 8-7 and 8-8)
- Stack gas SO₂ levels measured during production testing ranged from 9 to 52 ppm (dry basis, corrected to 7% O₂), well below the desired performance level of <100 ppmv (dry basis). (See Table 8-7)
- The CO levels measured during production testing were essentially non-detectable (dry basis), well below the HWC MACT value of <100ppmv (dry basis). (See Table 8-7)
- The THC levels measured during production testing ranged from 0.0 to 0.61 ppmv (dry basis, corrected to 7% O₂), well below the HWC MACT level of <10ppmv (dry basis). (See Table 8-7)
- The Principal Organic Hazardous Constituent (POHC), benzene, was destroyed in the process at high efficiencies. The benzene destruction efficiency averaged five nines for all tests. These results are an order of magnitude better than the HWC MACT requirement of 99.99% DRE. (See Table 8-9, not performed for WTP SW simulant)
- No dioxins or furans were detected during any manual off-gas sampling intervals that were above the reporting limit. All dioxin and furan values, and the concentrations as percentages of the HWC MACT standard, were less than the reportable values. (See Table 8-12, not performed for WTP SW simulant)
- Virtually no PCBs were detectable for LAW simulant testing. PCBs totaled about 6.64 ng/dscm, corrected to 7% O₂. Most PCB congeners were not detected. Dioxin-like coplanar PCBs were not detected at detection limits of about 0.7 ng/dscm. (See Table 8-13; not performed for WTP SW simulant)
- VOCs were mostly non-detectable. The MACT standard of 99.99% DRE was achieved. (See Table 8-9; not performed for WTP SW simulant)
- No speciated SVOCs were detected except for di-n-butyl phthalate and diethyl phthalate, which were detected at low levels near the detection limit. (See Table 8-10; not performed for WTP SW simulant)
- Technical data and operational parameters applicable for the use of fluidized bed mineralizing technology in a full-scale process system were developed or confirmed.
- No liquid secondary waste streams were generated during operation of the ESTD pilot plant.
- Monoliths, representative of final waste forms, were generated using five binder types at a 2-inch cube scale with LAW ESTD granular product. Monoliths using both LAW and WTP SW

granular products were prepared from three of the best performing binder types by forming them into 3-inch diameter by 6-inch tall and 6-inch by 12-inch tall cylinders. Twenty-four 2-inch diameter by 4-inch tall monoliths were made from WTP SW granular product for independent testing. ESTD granular products and monoliths were subjected to Toxicity Characteristic Leaching Protocol (TCLP, EPA Method 1311), Product Consistency Testing (PCT, ASTM C1285), and compressive strength tests (ASTM C39 / C39M). Key results from these tests are:

- Evaluation of compressive strength and durability (PCT) data for the larger scale monoliths indicated that a geopolymer binder formulation, designated GEO-7, was the best overall performer when combined with ESTD LAW and WTP SW granular products. (See report Section 10.2.3)
- Analysis of ESTD granular product and GEO-7 monolith TCLP test data showed that the product materials passed for all hazardous constituents, with the exception of Sb, Cd, and Se. These constituents were added in higher concentrations to the simulants to determine their fate and performance in the process. An extrapolation of the TCLP results to the lower concentrations in which these elements would actually be present in the real LAW and WTP SW wastes showed that the granular solid and monolith products would pass the TCLP tests when formed with the actual wastes. (See report Section 10.2.3)
- The durability and leach performance of the ESTD granular products using the GEO-7 binder were found to be superior to the Low-Activity Reference Material (LRM) glass standard for sodium and silicon. Release rates for cesium and rhenium (used as a surrogate for radioactive ^{99}Tc) were much less ($\sim 0.04 \text{ g/m}^2$) than sodium for the LRM glass standard (0.27 g/m^2) when normalized with Brunauer-Emmett-Teller (BET) measured surface areas of the granular product and 2 orders of magnitude lower than the Hanford glass standard of 2 g/m^2 for Na. (See report Section 10.2)
- Compressive strengths of the GEO-7 monoliths formed from both LAW and WTP SW granular products at all scales averaged 1,960 psi, well above the Hanford disposal criteria of $>500 \text{ psi}$. (See report Section 10.2)

BSR Testing Summary

The BSR was designed and built at SRNL to demonstrate the FBSR technology with radioactive wastes. The BSR is a small, two-stage unit, the purpose of which is to reproduce the basic process parameters and chemical reactions of the ESTD, yielding the same solid products with a radioactive feed as the ESTD produces with a non-radioactive simulant feed (see Section 11). The BSR was built and operated under the rigorous Quality Assurance and operating practices of SRNL.

Radioactive BSR testing of Hanford's projected WTP SW was completed with secondary waste from the Defense Waste Processing Facility (DWPF) supplemented with a mixture of $^{125/129}\text{I}$ and ^{99}Tc to chemically resemble WTP SW. Prior to these radioactive feed tests, non-radioactive simulants were also processed. Ninety-six (96) grams of radioactive granular product were made for testing and comparison to the non-radioactive pilot scale test products.

Following the production of the granular products from the non-radioactive and radioactive simulants, monolithic solids were formed, representative of the projected final WTP SW waste form. A geopolymer binder using clay, rather than fly ash as was done for the ESTD product material, was used to form the final product monoliths. This represented an improvement on the GEO-7 binder

formulation used for the ESTD monolith tests. A description of the BSR system and the detailed results of the BSR testing are provided in Section 11 of the report.

The principal objectives of the BSR WTP SW test program were to:

- Demonstrate, with the BSR equipment, the production of a radioactive granular product and monolith final waste form comparable to those generated with non-radioactive simulant in ESTD testing.
- Generate monolith products from the mineralized WTP SW products and conduct characterization, durability testing, and other analyses as required. The retention and determination of leach resistance for cesium, iodine, and rhenium in the solid product material are key elements of this objective.
- Determine composition of the mineralized granular and monolith products via chemical analysis, x-ray diffraction (XRD), and scanning electron microscopy (SEM) analytical methods.

Key results from the monolith, BSR, and durability testing are as follows:

- Mineralogy of the radioactive and simulant products, as indicated from XRD and SEM patterns, from the BSR and ESTD tests are the same. (See report Tables 10-3 & 11-3)
- Good mass balance closures (>85%) were obtained for Tc, Re, Cs, and I in all BSR tests (radioactive and nonradioactive): 86-102% recovery of Re in the product streams for the simulant and radioactive campaigns; 109% recovery of ⁹⁹Tc in the product streams for the radioactive campaign; 91% recovery of I in the product streams for the simulant campaign; and 98% recovery of ¹²⁹I and ~93% recovery of ¹²⁵I in the product streams (¹²⁵I has highest analytic sensitivity) for the radioactive campaign. (See report Table 11-2)
- ⁹⁹Tc and Re show similar behavior in partitioning between product (major) and off-gas (trace), so Re is an acceptable process surrogate for ⁹⁹Tc. (See report Table 11-2)
- ⁹⁹Tc, Re, SO₄ and Cr behavior, with respect to their durability in the final granular product, are controlled by the oxygen fugacity in the ESTD/BSR process, i.e. control of the REDuction/OXidation (REDOX) equilibrium. (See report Section 14, reference 43)
- Data indicate that ⁹⁹Tc, Re, Cs, and I (all isotopes) report primarily to the mineral product and not significantly to the off-gas. (See report Table 11-2)
- A geopolymer binder using clay instead of fly ash produces a monolithic final waste form that is easier to form and has superior compressive strength. Fly ash compositions are variable, and have detrimental reactivity compared to clay. The monoliths made from non-radioactive and radioactive BSR granular products with the revised geopolymer recipe at 42% waste loading passed compressive strength testing at >4,000 psi, about 8 times greater than the >500 psi requirement. (See report Section 11.3 and Table 11-4)
- The BSR non-radioactive granular products, non-radioactive monolith products, and radioactive monolith products all passed TCLP testing. However, the BSR radioactive granular product failed TCLP testing for Cr and Zn. Failure to pass TCLP for these two elements was not observed for any other granular or monolith products. The failure for Cr is likely caused by the small quantity of sample tested (~3 g) and the BSR operating in a more oxidizing state. The radioactive granular product was produced at a much lower REDOX of ~ 0.26 (more oxidized) versus the earlier simulant granular product from the fall 2009 campaign that had a REDOX in the range of 0.87 to

0.98 (more reduced). The behavior of Cr on TCLP testing is known to be REDOX sensitive, with Cr in a higher oxidation state, e.g., +6, being more leachable. The failure for Zn was likely caused by excessive remote handling of the granular product in the SRNL shielded cell using brass (Cu/Zn containing) sieves; this has been previously observed by SRNL while preparing glass powders for PCT analyses. (See report Section 11.6)

- PCT testing, with the use of a BET measured surface area to account for the surface roughness of the product and monoliths, demonstrated that the normalized release rates from granular products and monoliths, for the constituents of concern, are 2 orders of magnitude lower than the Hanford glass standard of 2 g/m² for Na. (See report Figure 11-2)
- ASTM C1308 accelerated leach testing for a radioactive monolithic waste form showed that the measured Leach Indexes for key components (Na, Re/⁹⁹Tc and I) were >10, >11, and >12 respectively after 2-day leaching intervals. These are all above the current Hanford IDF target limit Leach Indices of 6, 9 and 11, respectively, which indicate acceptable performance. (See report Figure 11-3)

The ESTD testing demonstrated the capability of the integrated THOR[®] FBSR process to convert the LAW and WTP SW simulants into granular, mineralized solid products in a safe and efficient manner. BSR data confirmed this result. ESTD gaseous emissions were found to be within regulatory limits for LAW and within regulatory limits for WTP SW with the exception that the low volatile metals standard was exceeded by 1 µg/dscm. The solid products generated during the testing displayed durability characteristics that are similar to or better than environmental assessment and LRM glass.

There were no recordable injuries during the mineralizing ESTD or BSR operations programs.

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Many people contributed to the success of the ART pilot plant program.

The THOR® Treatment Technologies, LLC, team provided the management, technical expertise, and administrative support for the project. The TTT team consisted of Kevin Ryan, Brad Mason, Brad Eldredge, Brent Evans, Arlin Olson, Scott Roesener, Phil Staats, Don Dustin and Vishal Vora. Nick Soelberg, Battelle Energy Alliance, at the Idaho National Laboratory, also provided technical support to the TTT team.

The pilot plant facility was constructed and operated by Hazen Research, Inc., of Golden, Colorado. Larry May, Harry Mudgett, and Steve Will managed the operation of the pilot plant on a 24-hour per day, 7-day per week basis during test operations.

Manual sampling of off-gas emissions and operation of the continuous emissions monitoring system were performed by Air Pollution Testing, Inc., (APT) of Arvada, Colorado. Management and technical assistance were provided by Paul Ottenstein.

Bench scale Steam Reformer operations, monolith formation, analytical analyses, and durability testing were performed by individuals at the Savannah River National Laboratory. The major contributors include C.M. Jantzen, C.L. Crawford, P.R. Burket, A.D. Cozzi, W.E. Daniel, and D.M. Missimer.

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ACRONYMS

APT	Air Pollution Testing, Inc.
ATG	autothermal gas
CCB	continuous calibration blank
CCV	continuous calibration verification
CEM	Continuous Emissions Monitor
CEMS	Continuous Emissions Monitoring System
COT	cumulative operating time
CP	Carbonate Phase
CPMS	Continuous Process Monitoring System
CRR	Carbon Reduction Reformer
CWI	CH2M-WG Idaho, LLC
%Δ	percent difference
DACS	Data Acquisition and Control System
D/F	dioxin and furan
DMR	Denitration and Mineralization Reformer
DOE	U.S. Department of Energy
DOE-ID	U.S. Department of Energy Idaho Operations Office
DRE	destruction and removal efficiency
EPA	U.S. Environmental Protection Agency
ESS	Emergency Shutdown System
ESTD	Engineering-Scale Test Demonstration
FBSR	Fluidized Bed Steam Reforming
FG	fluidizing gas

GAC	granular activated carbon
GC-CRB	carbon (Term used by General Carbon Corporation.)
GDE	guide
GW	general work instruction
HE	heat exchanger
HEPA	high-efficiency particulate air
HM	heavy metal
HMI	human-machine interface
HMPD	harmonic mean particle diameter
HTF	High-temperature Filter
HWC	Hazardous Waste Combustor
I/O	input/output
ICB	initial calibration blank
ICP	Idaho Cleanup Project
ICV	initial calibration verification
ID	identification
IDL	instrument detection limit
ILAW	Immobilized Low Activity Waste
INL	Idaho National Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
IWTU	Integrated Waste Treatment Unit
JTG	Joint Test Group
K-T	Kentucky-Tennessee Clay Company
LCS	laboratory control sample
LAW	Low Activity Waste

LCSD	laboratory control sample duplicate
LQL	lower quantity limit
LRM	Low-activity Reference Material
LVM	low volatility metal
MACT	Maximum Achievable Control Technology
MEB	mass and energy balance
MMPD	mass mean particle diameter
MP	mineralization phase
MTEC	Maximum Theoretical Emissions Concentration
N/A	not analyzed
NAR	nozzle atomizing ratio
NAS	alkali aluminosilicate
NCR	nonconformance report
NGLW	newly-generated liquid waste
N/M	not measured
OGB	Off-gas Blower
OGC	Off-gas Cooler
OHM	Ontario Hydro Method
PAC	Programmable Automation Controller
PBF	Process Baghouse Filter
PC	personal computer
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofurans
PCT	Product Consistency Test

PGF	Process Gas Filter
PM	particulate matter
POHC	principal organic hazardous constituent
PR	Product Receiver
PSD	particle size distribution
PT	Pressure Transmitter
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RL	reporting limit
RRF	relative response factor
RSD	relative standard deviation
RT	real time
SAM	Sample and Analysis Management
SBW	sodium-bearing waste
SDS	serial dilution sample
SEM	scanning electron microscope
SOP	standard operating procedure
SRE	system removal efficiency
SRNL	Savannah River National Laboratory
SSV	superficial space velocity
STL	Severn Trent Laboratories
SVM	semi-volatile metal
SVOC	semi-volatile organic compound

TCLP	Toxicity Characteristic Leaching Procedure
TCO	total chromatographable organic
TCO/Grav	total organic emissions
TEQ	toxicity equivalent quotient
TGO	total gravimetric organic
THC	total hydrocarbon
THOR [®]	<u>T</u> hermal <u>O</u> rganic <u>R</u> eduction
TIC	tentatively identified compound
TOC	Total Organic Carbon
TRU	transuranic
TTT	THOR Treatment Technologies, LLC
UDS	undissolved solids
UTS	Universal Treatment Standard
VOC	volatile organic compound
WC	water column
WF	waste feed
WIPP	Waste Isolation Pilot Plant
WTP SW	Waste Treatment Plant Secondary Waste
XRD	x-ray diffraction

1. INTRODUCTION

The U.S. Department of Energy, Office of River Protection (DOE-ORP), has responsibility for managing the safe storage, treatment, and disposal of radioactive liquid wastes in underground storage tanks at the Hanford Site in southeastern Washington State. There are 177 such tanks at the Hanford Site containing 53 million gallons of highly radioactive wastes and 190 million curies of radioactivity. These wastes were generated primarily as a result of nuclear fuel reprocessing for defense production activities from 1943 to 1989. In 1996, DOE-ORP initiated a project to design, build, and commission a facility known as the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to treat the tank wastes and prepare them for disposal. The WTP will separate the wastes into a small-volume, high-level waste (HLW) fraction, containing most of the radioactive constituents, and a large-volume, low-activity waste (LAW) fraction. The HLW and LAW will be converted into immobilized waste forms for ultimate disposal.

The LAW fraction of the Hanford tank wastes are planned for disposal at the Integrated Disposal Facility (IDF) on the Hanford Site. However, the LAW wastes contain listed and characteristic hazardous waste constituents as well as underlying hazardous constituents that, under federal and state regulations, preclude the wastes from land disposal without treatment. The Hanford tank wastes carry the characteristic of corrosivity because of the high pH of the wastes and the characteristic of toxicity because of the presence of arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Also included in the wastes are organic constituents that have toxicity characteristics or are listed wastes. To be acceptable for land disposal, these characteristic and listed wastes, as well as the underlying hazardous constituent, must be treated in accordance with federal and state treatment standards. Currently, there is inadequate LAW processing capacity planned at the Hanford Site to complete that mission within the required timeframe. Therefore, additional LAW processing capacity will be required, either as vitrification or as a supplemental treatment technology. One candidate supplemental treatment technology is the THOR[®] fluidized bed steam reforming (FBSR) process, offered by THOR Treatment Technologies, LLC (TTT).

In August 2005, the Department of Energy (DOE) issued a Request for Proposals (RFP) for the Advanced Remediation Technologies (ART) acquisition. This acquisition was based on the DOE's Office of Environmental Management's (EM) intent to evaluate various advanced technologies existing in the private sector, which would enable former weapons sites such as Hanford to accelerate their baseline clean-up schedules, reduce life cycle costs, reduce programmatic risk, and improve worker safety. In addition, DOE-EM was seeking technologies that would provide high return on investment; could be deployed at the sites; would complement existing treatment plants and processing facilities with minimal disruption; and were mature enough so that when demonstration was completed, there would be sufficient processing data to enable initiation of final design.

TTT responded to the RFP by proposing the THOR[®] FBSR technology for the LAW supplemental treatment mission at the Hanford Site. In August 2006, TTT was awarded Phase I of ART contract DE-AC09-06SR22521. Phase I, completed in late 2006, delivered a compilation of past FBSR pilot plant work relevant to the intended application and a plan to conduct new testing to demonstrate the capability to process the Hanford LAW into a final waste form that would meet the requirements for disposal at the Integrated Disposal Facility (IDF). This final waste form had to be at least as chemically durable (leach-resistant) as the projected WTP LAW glass product.

Phase II of the ART contract was awarded to TTT in September 2007. This phase demonstrated the processing of non-radioactive Hanford LAW and WTP secondary waste (WTP SW) simulants, using the Engineering Scale Technology Demonstration (ESTD) pilot plant at Hazen Research in Golden, Colorado. It also demonstrated the processing of a non-radioactive LAW and non-radioactive and

radioactive WTP SW simulants using the Bench-Scale Steam Reformer (BSR) at the Savannah River National Laboratory (SRNL). In all cases the resulting granular products were formed into final monolithic waste forms and subjected to durability testing that showed the waste forms to meet the requirements for disposal at the IDF.

The THOR[®] fluidized bed steam reforming (FBSR) process has been shown in previous test programs to effectively convert similar types of liquid radioactive waste simulants into solid products. Those products may be water-soluble carbonate matrices or insoluble mineralized matrices, depending on the process additives used. An ESTD test of the mineralization process was completed in 2006 at the Hazen Research facility in Golden, CO, for Sodium Bearing Waste simulants for the DOE Idaho Cleanup Project. The products were shown to be chemically and physically compatible with existing and projected disposal requirements.

This document presents the results of the ART ESTD and BSR test programs.

1.1 Purpose and Overview of Test Program

An insoluble, mineralized product in which the radioactive and hazardous metal constituents are immobilized and hazardous organic constituents are destroyed are required for treated Hanford LAW and WTP SW wastes to be disposed of at the Hanford IDF. The primary purpose of the ART ESTD and BSR test programs was to demonstrate the effectiveness of the THOR[®] FBSR process to treat these wastes. ESTD and Bench scale Steam Reformer (BSR) test programs were conducted using non-radioactive (ESTD and BSR) and radioactive (BSR) simulants similar in chemical composition to actual Hanford LAW and WTP SW waste solutions, producing a mineralized product material in each case. A secondary objective was to continue building upon the knowledge base developed as a result of bench-scale, pilot-scale, and ESTD mineralization testing conducted previously.

The engineering scale testing program processed liquid waste simulants representative of the LAW and WTP SW at the Hanford Site through a dual FBSR system to produce leach-resistant, solid products and environmentally compliant gaseous effluents. The solid products incorporate normally soluble ions into an alkali alumino-silicate (NAS) mineral matrix that prevents the leaching of those ions into the environment. The simulants consisted of an alkaline aqueous solution whose principal constituents were sodium nitrate and sodium hydroxide. Minor constituent cations included aluminum, antimony, arsenic, barium, cadmium, calcium, cesium, chromium, lead, nickel, potassium, selenium, silver, and thallium. Rhenium was also added as a non-radioactive surrogate for radioactive ⁹⁹Tc. Minor anionic constituents included acetate, oxalate, carbonate, chloride, fluoride, iodide, nitrite, phosphate, and sulfate ions. A Principal Organic Hazardous Constituent (POHC) in the form of benzene was added to the feed stream in order to determine the Destruction Removal Efficiency (DRE) for organics in the process. The mineralizing agent was finely divided clay that has been demonstrated in past testing programs to immobilize the soluble components of the feed simulant into a leach-resistant matrix. The elemental constituents of the clay included aluminum, silicon, iron, magnesium, and oxygen.

ESTD testing was accomplished in two phases. The first phase was a series of parametric scoping tests in which optimum process temperatures and simulant-to-clay ratios were determined. The scoping tests were followed by two production run tests in which the process was operated for an extended period of time in order to demonstrate long-term system operability and to generate an adequate inventory of product for subsequent monolith testing. Each of the seven parametric scoping tests was up to 48 hours in duration. The production run tests operated for a minimum of 100 hours under the conditions determined by evaluation of the parametric scoping tests. Actual test durations and operating conditions were based on the success in achieving the test objectives, as evaluated by the Joint Test Group (JTG) [1]. The JTG was

a group of senior engineers, scientists, and managers who evaluated the progress of each test on a daily basis and made mid-course corrections, as needed, to address emergent technical issues in accordance with test plan objectives.

Following the ESTD tests, the mineralized products underwent bench-scale testing in which the NAS material was formed into monolith samples using various binders and a range of waste loading levels. Monolith performance testing included Toxicity Characteristic Leaching Procedure (TCLP), Product Consistency Testing (PCT), and compressibility testing. Monolith preparation and analytical work were performed by the Savannah River National Laboratory (SRNL).

Based on the results of the ESTD and monolith testing, Bench scale Steam Reforming (BSR) testing with actual radioactive waste derived from the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) was performed. Actual DWPF off-gas recycle material was chemically adjusted to mimic the expected composition of the WTP SW stream. The BSR testing was to provide reliable data and analysis on the behavior of radioactive technetium in the steam reforming system. Previous pilot-scale and ESTD testing used rhenium as a non-radioactive surrogate for technetium. Rhenium and technetium may have different volatilities when subjected to conditions in the steam reforming process or may have different solubility characteristics when incorporated into a NAS mineralized matrix. The BSR tests were to confirm that actual radioactive technetium in the form found in Hanford LAW is non-volatile in the steam reforming process and that technetium incorporated into the leach-resistant NAS mineralized structure passes the TCLP and PCT test evaluation criteria for disposal at the Hanford IDF.

1.2 Test Objectives

The principal objectives of the Hanford LAW/WTP SW mineralizing test program were to:

- Verify DMR process chemistry and product quality consistent with that observed during previous mineralizing pilot plant and ESTD operations.
- Confirm that the final process off-gas complies with applicable environmental regulations. A key component is compliance with the HWC Maximum Achievable Control Technology (MACT) standards without the need for a wet scrubber. Another key component of this objective is the determination of iodine, cesium, and rhenium emissions from the process.
- Confirm scale-up parameters such as throughput, carbon usage optimization, feed nozzle and fluidizing gas parameter optimization, energy conservation, and optimal use of process additives.
- Confirm tandem operation of the DMR and CRR and that the CRR effectively destroys residual organic gases and fully oxidizes carbon, organics, and carbon monoxide generated in the DMR.
- Demonstrate long-term steady-state operation of the integrated fluidized bed steam reforming process.
- Demonstrate, on a laboratory scale and then on a larger scale, the production of final monolith products from the mineralized ESTD LAW and WTP SW products that meet all IDF disposal requirements. The retention and determination of leach resistance of cesium, iodine, and rhenium in the product are key elements of this objective.
- Demonstrate, with the BSR equipment, the production of radioactive granular product and a monolith final waste form comparable to that generated via non-radioactive simulant in prior ESTD testing.

- Generate an adequate quantity of monolith product for characterization, durability testing, and other analyses, as required.
- Maximize waste volume reduction.
- Confirm zero liquid secondary waste generated from process operations.

Details concerning these overall objectives, along with quantifiable criteria (where appropriate) and the means of determining success in meeting those criteria, are summarized in Section 12. Also included in Section 12 are additional, more specific, quantifiable test objectives that were critical to the success of the Hanford LAW/WTP SW mineralizing test program.

2. STEAM REFORMING SYSTEM DESCRIPTION

2.1 Overview of Fluidized Bed Steam Reforming Mineralization Technology

Previous development work has shown that alkali aluminosilicate (NAS) minerals provide host phases to accommodate radionuclide species. Waste forms of aluminosilicate-based crystalline assemblages of mutually compatible, refractory, and leach-resistant solid solution phases have been proposed for the incorporation of radionuclide species of concern [2]. The NAS mineral phase assemblage(s) are anhydrous feldspathoid phases such as sodalite that are unique because they have cage-like structures formed of aluminosilicate tetrahedra. The remaining feldspathoid minerals, such as nepheline, have a silica “stuffed derivative” ring type structure. The cage structures are typical of sodalite and/or nosean phases where the cavities in the cage structure retain anions and/or radionuclides that are ionically bonded to the aluminosilicate tetrahedra and to sodium. The cage structured feldspathoid system of minerals have the basic structural framework formula $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]$ and an alumina:silica ratio of 1:1.

One of the feldspathoid cage structured minerals is nosean, $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{Na}_2\text{SO}_4)$, with Na_2SO_4 bonded in the sodalite cage-like structure. Since species such as Cl^- and SO_4^{2-} are bonded inside the sodalite cage structure, these species do not readily leach out of the respective waste form mineral phases. A second feldspathoid mineral is nepheline ($\text{NaAlSi}_3\text{O}_8$). Nepheline is a hexagonal structured feldspathoid mineral. The ring structured aluminosilicate framework of nepheline forms cavities within the framework. There are eight large (nine-fold oxygen) coordination sites and six smaller (8-fold oxygen) coordination sites. The larger nine-fold sites can hold large cations such as Cs, K, and Ca, while the smaller sites accommodate Na. The K analogue is known as leucite (KAlSi_2O_6). In nature, the nepheline structure is known to accommodate Fe, Ti and Mg as well.

The objective of this work has been to create the types of minerals that would provide leach resistant (durable) waste forms for the immobilization of LAW and WTP SW. This has been approached by selecting a clay type with the appropriate Al:Si mole ratio that would suitably react with the Na, K, other metals and anions in the LAW. The most favorable atomic ratios that would produce the desired nepheline and sodalite products are thought to be $\text{M}/\text{Si} = 1\text{--}1.33$, $\text{M}/\text{Al} = 1\text{--}1.33$, $\text{Al}/\text{Si} \geq 1$, and $\text{M}/(\text{Al}+\text{Si}) = 0.5\text{--}0.67$, where M represents an alkali metal, mostly Na in this case [3]. The atomic ratios provide guidelines because there may be significant substitution of different alkali and alkaline earths, and some Fe for Al, in these feldspathoid minerals.

It is important to select a clay type with a Si:Al mole ratio that is in a favorable range, when reacted with the liquid waste, for producing the desired durable mineral product phases. Previous bench scale activities led to identification of OptiKast and Sagger clays as the best candidate clays for mineralizing the LAW composition. These clays have a higher silica to alumina ratio. Particle size distribution is also important, with finely divided clays (high surface area) preferred such that as much of the clay mass as possible combines with and reacts with the liquid waste. K-T Sagger XX and OptiKast clay were successfully used for the previous bench scale experimental program as well as with previous ESTD activities. [4,5]

It was recommended, after team analysis of clay properties and laboratory and bench scale data, that as-received OptiKast clay should be added to simulated LAW in several different mix ratios for the mineralization scoping tests. A spreadsheet for calculating mineralization of the waste simulant [3] was used to calculate the theoretical OptiKastT clay addition ratio of 613.5g/L, based on typical clay composition data. Because some of the clay doesn't react (unreacted cores), this value was increased by 10% to give the high clay addition ratio of 675g/L. The theoretical value was reduced by 10 and 20% to get the medium and low clay addition ratios of 610g/L and 540g/L. A similar calculation was performed for the WTP SW stream, but for a mixture of OptiKastT and K-T Sagger XX clay. Figure 2-1 shows the

spreadsheet-calculated targeted production run mineralized product compositions for the LAW and WTP SW simulant compositions.

FIG. 501.—System Na₂O-Al₂O₃-SiO₂; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

Principal References

- G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, 28, 1187-79 (1924).
 F. C. Kracek, *J. Phys. Chem.*, 34, 1583-98 (1930).
 N. L. Bowen and J. W. Greig, *J. Am. Ceram. Soc.*, 7, 238-54 (1924); corrections, *ibid.*, 410.
 N. A. Toropov and F. Ya. Galakhov, *Voprosy Petrogr. i Mineralog., Akad. Nauk S.S.S.R.*, 2, 245-55 (1953).
 Shigeo Aramaki and Rustum Roy, *Nature*, 184, 631-32 (1959).
 J. F. Schairer and N. L. Bowen, *Am. J. Sci.*, 254, 129-95 (1956).
 Liberto De Pablo-Galan and Wilfred R. Foster, *J. Am. Ceram. Soc.*, 42, 491-98 (1959).

Figure 2-1 Phase Diagram Showing Clay Target Addition Quantities for LAW and WTP SW

The light purple star is for 640 g OptiKast clay per liter of LAW simulant. The dark purple star is for 675 g OptiKast clay per liter of LAW simulant. The bright green star is for 307 g of the 45% Sagger/55% OptiKast clay per liter of WTP SW simulant.

2.2 Process Flow Diagram

The process flow diagram for the LAW/WTP SW mineralizing testing program is shown in Figure 2-2, and it identifies each of the major THOR[®] system components and their configuration at the conclusion of the testing of the LAW/WTP SW simulant. The major components include the surrogate liquid waste preparation and feed system, the Fluidizing Gas (FG) Supply System, the Denitration and Mineralization Reformer (DMR), the Product Receiver (PR), the High-temperature Filter (HTF), the Carbon Reduction Reformer (CRR), and the off-gas treatment system. These components are discussed below in Section 2.4, but are described in much greater detail in the Design Basis Document [6].

During the LAW scoping tests the HTF was bypassed to provide data on the performance of the process system and the properties of the mineral product solids that elutriated out of the DMR and passed through the higher temperature CRR to further reduce the carbon content of the elutriated product fines. However, upon completion of the LAW scoping test runs, an evaluation was made of the process parameters and especially the process off-gas measurements collected during the variable conditions of the scoping runs. The data available indicated that the SO₄ in the nosean mineral was reduced to SO₂ in the CRR. In as much as data indicate that Re (and hence Tc) behavior follows that of S, it was postulated that Re retention would be adversely impacted without the HTF in service. Also, there was a significant build-up of solids in the OGC. Inasmuch as the analytical testing of the mineral products required a substantial period of time to perform the technical team decided that the HTF would be returned to service. Therefore, for the LAW and WTP SW production runs the HTF was placed on-line to remove elutriated product solids before they could pass through the CRR, as was performed in past test programs which all produced high leach-resistant products and minimum SO₂ in the off-gas.

The “LAW lite” (without heavy metals) surrogate was made-up in the Waste Holdup Tank and transferred to one of two Waste Feed Tanks. The mineralizing clay and heavy metals were mixed with the LAW lite surrogate in the feed tanks to form a slurry. This slurry was then fed continuously through a feed nozzle to the first steam reformer, the DMR. The DMR, operating in a chemically reducing mode, evaporated liquids, partially cracked and volatilized organics, converted nitrates to nitrogen gas, and converted nonvolatile constituents of the feed into an insoluble, alkali aluminosilicate granular product. The reducing condition in the DMR was created by the injection of fluidizing steam, carbon in the form of coal, and a small amount of oxygen to react with the carbon to produce energy in the bed.

The granular product was periodically removed from the bottom of the DMR using an auger. It was pneumatically transferred to the Product Receiver (PR) before being drained from the process. The process gas from the DMR, consisting mostly of steam, nitrogen, carbon dioxide, and hydrogen, with small amounts of carbon monoxide, NO_x, short-chained organics, and acidic gases, was then filtered through the High-Temperature Filter (HTF). This filter removed the finely divided product solids and carbon fines that elutriated out of the DMR with the process gas stream. The filtered gas stream was then introduced into the bottom of the second fluidized bed steam reformer, the CRR. A measured quantity of oxygen was also introduced into the CRR through two sets of distributors located above the fluidizing process gas distributors. The CRR, operating in a reducing mode in the bottom of the fluidized bed and in an oxidizing mode in the upper section and freeboard, oxidized the hydrogen, carbon monoxide, and organics in the gas stream to carbon dioxide and water. Supplemental energy sources in the form of granular carbon and liquid propylene glycol were added to maintain the CRR within the desired operating temperature range.

The CRR process gas stream, now almost entirely nitrogen, oxygen, water vapor, and carbon dioxide, was cooled in the Off-gas Cooler (OGC) and filtered in the Off-gas Filter (OGF). The presence of potential pollutants in the final off-gas was determined by a series of U.S. Environmental Protection Agency

(EPA)-compliant sampling devices, including grab sampling and a continuous emission monitoring system (CEMS). The final off-gas was discharged to the stack via the use of two Off-gas Blowers (OGBs).

More than half of the solid product produced in the DMR was elutriated to the HTF (during production runs) or the OGF (during the scoping runs) as finely divided solids. These solids were augured from the respective vessels into collection drums. Small quantities of solid materials were withdrawn from the bottom of the CRR and the OGF (during production runs) as separate, small volume streams in the form of samples.

2.3 Additive and Process Streams

In addition to showing the major components of the THOR[®] system, Figure 2-2 also shows the additive and process streams used to treat the LAW simulant during the pilot scale testing.

Table 2-1 contains calculated values for most of the active streams shown on the process flow diagram for a specific feed condition for the mineralizing test. The table is based on a calculational model of the mass and energy balance (MEB) for the system with the HTF on-line. It was calibrated to actual operating conditions and stream flow rates and is expected to be correct to within 10%. The model conditions are considered baseline and represent the most common feed stream for the actual plant; specifically, LAW slurry (with 675g/L clay) fed at 0.2 gallons per minute (gpm), the DMR operating at 725°C and the CRR operating at 950°C. A stream name, stream number, pressure, temperature, and various flows are shown for each stream. There are many unnumbered nitrogen streams on the process flow diagram. These streams are grouped together by unit operation. For example, most nitrogen flowing to the DMR, mostly line purges, is given the stream name “DMR Purge N₂”.

2.4 Subsystem Descriptions

2.4.1 Liquid Simulant Preparation and Feed System

The liquid surrogate waste preparation and feed system included the following major components:

- A 2,000-gallon (gal) stainless-steel surrogate, Waste Feed Makeup Tank (T-100) with mixer (MIX-100) and Heat Exchanger (HE-100)
- Surrogate Waste Feed Transfer Pump (P-100)
- Two parallel 500-gal plastic, surrogate Waste Feed Day Tanks (T-101 A&B) with mixers (MIX-101A/B)
- Four parallel surrogate waste feed tank recirculation pumps (P-101 A&B; C&D)
- Feed Solids Addition Mix Tank and Pump (T-102 and P-102)
- Principal Organic Hazardous Constituent (POHC) Tank and Pump (T-103 and P-205)
- Flow control pinch valve, 0.10 to 0.40gpm (FV-200-074)
- Feed Filters (F-200A & B)
- Surrogate waste feed (WF) injectors (2), one in operation at a time.

All of the equipment items listed above, as well as the interconnecting piping, valves, and instruments, were resistant to nitric acid corrosion.

**Table 2-1 Mass and Energy Balance at LAW Mineralizing Baseline Conditions:
0.20 gpm LAW Liquid Feed, 725°C in DMR, 950°C in CRR**

Stream Summary	Stream Number	P (psia)	T (°C)	Flow (ACFM)	Flow (SCFM)	Liquid (gpm)	Solids (lb/hr)	Total (lb/h)
Waste Feed	Stream 1	11.9	25	0.0	0.0	0.12	51	146
Carbon Reductant/Fuel	Stream 5	12.0	25	0.0	0.0	0.00	35	35
DMR Purge N ₂	Stream 51	62.1	21	4.7	20	0.00	0	87
DMR Outlet Gas and Fine Solids	Stream 15	14	616	278.0	93.6	0.00	55	405
DMR Solid Bed Product	Stream 14	16.1	725	0.0	0.0	0.00	18	18
HTF Purge N ₂	Stream 53	62.1	25	1.3	5.3	0.00	0	23
HTF Gas	Stream 17	14.2	420	240.7	98.8	0.00	0	373
HTF Solid	Stream 16	15.0	420	0.0	0.0	0.00	55	55
CRR Bed Media	Stream 21	14.2	25	0.0	0.0	0.00	1	1
CRR Propylene Glycol	Stream 22	14.2	25	0.0	0.0	0.10	52	52
CRR Purge N ₂	Stream 52	62.1	21	6.2	26.3	0.00	0	115
CRR Outlet Off-gas	Stream 27	11.4	854	988.9	199.3	0.00	1	837
OGC Quench Water/Atomizing Air	Stream 28/29	52.1	25	1.2	4.3	0.50	0	284
OGC Outlet Gas	Stream 30	11.3	203	626	298.4	0.00	1	1121
OGF gas	Stream 33	11.2	180	601.6	298.4	0.00	0	1120
OGF solid	Stream 31	11.2	180	0.0	0.0	0.00	1	1
Stack	Stream 34	11.2	180	601.6	298.4	0.00	0	1119

The Waste Feed Makeup Tank (T-100) was used to make up and mix the surrogate waste feed liquids prior to addition of heavy metals and mineralizing additives. The holdup tank was provided with a mixer capable of maintaining the liquids well-mixed and providing agitation required to mix and dissolve solid reagents. The transfer pump (P-100) was used to help mix the surrogate feed solution and transfer the waste surrogate solutions from the holdup tank to one of the two Waste Feed Day Tanks (T-101 A or B), as needed. The heat exchanger (HE-100) was provided to allow cooling of the feed solution during makeup, if required. If heavy metals or mineralizing additives were to be included in the feed solution for a particular test, they could be pre-mixed in the Feed Solids Addition Mix Tank (T-102) or added to the Waste Feed Day Tanks directly. The resulting slurry was then combined with the surrogate waste solution in the Waste Feed Day Tanks. Both Waste Feed Day Tanks were equipped with mixers and recirculation pumps to ensure that the UDS and mineralizing additives remained suspended in the solution.

The feed solution in each of the Waste Feed Tanks was continually recirculated to maintain the UDS and mineralizing additives in suspension. Two parallel pumps were provided for each Day Tank (P-101 A&B on T-101A and P-101 C&D on T-101B). Valves were provided to allow the parallel pumps to recirculate the feed solution even if one of the pumps required maintenance.

A small slip stream was drawn off of the day tank recirculation line to provide feed for the DMR. A pneumatically-controlled pinch valve was used to control the feed rate of the liquid surrogate into the DMR through one of two atomizing feed nozzles, only one of which was operated at a time. A magnetic flow meter was used to measure and record the volumetric injection rate of the surrogate feed into the DMR.

An auxiliary organic liquid metering pump (P-205) and tank (T-103) were used to meter the POHC into the process feed line at a rate of approximately 0.33 kilogram per hour (kg/hr) so that the Destruction and Removal Efficiency (DRE) of the POHC, chosen to be conservatively representative of the organics present in the actual LAW, could be determined during a portion of the test program.

2.4.2 Fluidizing Gas System

Steam was used to fluidize the DMR during normal operations. Steam reacted with carbon in the bed to produce a small quantity of carbon monoxide and hydrogen that reduced nitrates in the waste feed stream to nitrogen gas. Oxygen was also fed to the DMR via three dedicated oxygen injectors located above the fluidizing gas distributors. The oxygen that was fed to the bed through the injectors was diluted with nitrogen to prevent excessive temperature rise in front of the oxygen injectors. Oxygen reacted with the carbon and hydrogen to generate process heat and carbon dioxide and water vapor. During startup, the system was fluidized with nitrogen.

A steam generator (H-104) was used to provide the steam for the FG. The steam generator was capable of providing up to 500 pounds per hour (lb/hr) of low-pressure steam. The steam generator was equipped with an automatic temperature controller, an isolation ball valve, and a pressure regulator valve.

The FG flowed through two electric superheaters in series (H-105 A and B) to increase the fluidizing gas temperature to ~600°C before it was introduced into the FG distributor located at the bottom of the DMR. The superheaters also were used to heat nitrogen as the fluidizing gas during the DMR preheating (heat-up) operation. The major heat load for the superheater occurred during the initial heat-up of the reformers to the initial operating temperature because no external fluidized bed vessel heaters were provided. During initial startup and preheating of the DMR, the superheaters were capable of heating the fluidizing nitrogen to 700°C.

Automated control valves and flowmeters were used to control and monitor the amounts of steam and oxygen fed to the DMR during simulant treatment operations. The operator would set the desired fluidizing steam flow rate and the control system automatically maintained this flow rate. The amount of oxygen flow to the DMR bed was automatically controlled based on in-bed temperature, as indicated by one of eight thermocouples.

The FG flow rate was controlled within an operator-selected range that always exceeded the minimum fluidizing velocity for the bed average particle size. The minimum fluidizing velocity was determined using the Wen and Yu correlation [7] that accounted for the operating temperature and pressure, the FG composition, the bed particle density, and the average particle size.

2.4.3 Denitration and Mineralization Reformer

The DMR (T-200) was a fluidized bed vessel designed to operate in an autothermal steam reforming mode to evaporate water; reduce nitrates to nitrogen; volatilize and reform organics; convert alkali and alkaline earth metals into non-agglomerating solid products; and capture sulfur, fluoride, chloride, and phosphate compounds in the solid product. Non-volatile heavy metals, other metals, and the non-radioactive radionuclide surrogates (i.e., rhenium, and cesium) were also captured in the solid product.

The DMR was an existing 15-in. inside diameter carbon steel, refractory-lined vessel. The bottom section for the DMR contained ports for the fluidizing nozzles, solids removal auger, and auxiliary FG nozzle. Figure 2-3 is a photograph of the top of the DMR (viewed from the east).

Figure 2-3 Denitration and Mineralization Reformer (Top Section)

The DMR vessel was configured to provide continuous, metered, solid additive injection of particulate carbon reductant and recycled bed material or other solid additives (if desired). Solid additives were introduced into the DMR through two independent solid feeders. The feeders discharged into a small chamber bounded by two valves that operated sequentially to form a lock hopper or shotpot. A nitrogen gas purge on the hopper discharge pipe excluded atmospheric air from the process and provided some of the motive force needed to inject the lightweight carbon reductant into the DMR bed. An automatically controlled screw auger feeder with a weight scale was used to monitor and control the feed rate of carbon reductant into the DMR. The second solids feeder was a manually controlled auger that was used to add recycled bed material or other solid additives to the DMR.

As solid product was generated, it accumulated in the DMR bed and was periodically removed. The DMR vessel included a bottom solids removal auger for periodic batch draining of solid product materials to control the bed level within the desired bed depth range. A nitrogen jet below the auger transferred the hot bed solids pneumatically to the product receiver (PR) vessel. A manually operated, pneumatically actuated, full-port, rotating disk valve installed on the outlet of the auger assembly isolated the solids transfer system nitrogen jet eductor from the bottom of the DMR. Grab samples of the DMR bed material were acquired periodically through a sample line and valves located on the side of the vessel.

The DMR was connected to the Emergency Shutdown System (ESS) for the facility. The ESS provided an emergency shutdown capability upon loss of power or manual activation. Upon activation the ESS would isolate feeds to the DMR (steam oxygen, atomizing gas and liquid feed) and provides 100% nitrogen flow.

A pair of gas atomizing liquid feed nozzles was installed to introduce the LAW simulant liquid/slurry into the DMR fluidized bed reactor as an atomized droplet spray via a feed port on the side of the vessel. Only one feed nozzle was in use at any time. Valves were provided to allow easy switching from one nozzle to the other during operation. The feed nozzle that was not in use was purged to prevent bed solids from entering the nozzle orifices and plugging them. The atomizing gas flowed through an annulus to atomize the feed liquid into appropriately sized droplets for reaction in the DMR bed. The flow rate of the atomizing gas was set and automatically controlled with an integrated magnetic flow meter/controller.

The oxygen introduced via the atomizing nozzle and DMR oxygen injector nozzles generated heat within the DMR by reacting with the added carbon reductant and with the carbon monoxide and hydrogen produced in the bed by the steam reforming reactions. Oxygen flow was adjusted to maintain the DMR temperature within the desired range, 680°C to 800°C, for production of a mineralized product (680°C to 700°C for WTP SW, and 725°C to 800°C for LAW). Several thermocouples were used to monitor temperatures throughout the DMR. Generally, the DMR bed temperature was maintained within $\pm 15^\circ\text{C}$ of the desired setpoint by automatically controlling the DMR oxygen flow rate. The nominal residence time of the gas in the DMR was 2.0 to 2.5 seconds.

The water gas and water gas shift chemical reactions that occurred in the DMR bed were:

An additional important reaction in the bed was the reduction of alkali metal nitrates (NaNO_3 , KNO_3 or CsNO_3) with hydrogen and clay to give water, nitrogen and alkali metal aluminosilicates (e.g., nepheline). For example, the reaction of sodium nitrate with hydrogen and kaolin clay gives:

Other reactions with alkali metals, clay, and sulfate or chloride ions produced nosean and sodalite respectively:

The water gas and water gas shift reactions and evaporation of water were all endothermic processes. A small amount of oxygen was added to the bed to react with carbon, hydrogen and carbon monoxide to produce energy in the bed and maintain the bed temperature between 725°C and 775°C. The reactions were:

The DMR operated in a strongly reducing mode in order to ensure nearly complete conversion of nitrates directly to nitrogen gas, although a small oxidizing zone existed in the immediate vicinity of the point of oxygen injection into the vessel.

The DMR operated at a slight positive pressure (typically 2 to 4 pounds per square inch gauge [psig]) because of backpressure from the CRR FG distributors and the CRR fluidized bed pressure drop. The DMR flanges and nozzle connections incorporated qualified gaskets and flanges in order to prevent leakage of process gases to the building area. Prior to operation, and after any shutdown for system maintenance, the entire pilot plant system was pressure tested to verify leak tightness.

The DMR, its FG lines, and its process gas outlet line were well insulated to minimize heat losses. Multiple thermocouples and pressure differential transmitters were used to provide real-time operating data. The differential pressure transmitters (PTs) were equipped with nitrogen purge lines to prevent moisture condensation in the sensing lines and plugging of the sensing lines with bed solids. The Data Acquisition and Control System (DACS) provided remote readouts and trending for the thermocouples and differential pressure transmitters so that bed temperatures and pressure drops could be monitored continuously and employed for process control.

2.4.4 Product Receiver

The PR was used to collect high-temperature, granular bed product solids pneumatically transferred from the DMR. The PR (T-201) was a vertical, cylindrical filter vessel with a conical bottom. It was fitted with four sintered metal candlestick filters on a metal tube sheet. A manually actuated nitrogen gas pulse-back manifold was used to clean the filter elements when on-line or off-line. An automated pulse back system was not required because the PR filter was normally not on-line and was used only to receive occasional solids transfers from the DMR. When the fluidized bed height increased above ~48-in. in the DMR, operators would batch transfer a quantity of the bed media to the PR. A differential pressure gage, with sensing ports in the vessel and in the off-gas line downstream of the vessel, was used to determine the pressure drop across the filters and, in turn, alert the operator that the filters needed to be cleaned. External electrical heaters (H-201) were provided to maintain the filter elements and the vessel above ~120°C during operation to prevent condensation.

The outlet of the PR was vented to the freeboard of the DMR so that gases removed from the solid auger were reintroduced to the DMR. Hence, the PR operated at the same pressure as the freeboard of the DMR. The PR was provided with a product draining system incorporating a high-temperature, manually-operated, full-port ball valve and 5-gallon stainless-steel metal collection vessels for periodic batch draining of product material. The product collection vessels provided residence time for the product solids to cool before being bagged, labeled, and placed into standard carbon steel 55-gal drums for storage. The drain valve and collection vessels were designed to contain solids with temperatures of up to 400°C. The collection vessels were provided with a nitrogen purge to displace process gases from the filter to ensure that moisture did not condense in the collection vessel, drain port, or valve. Periodic grab samples were taken of the cooled solids in the collection vessel prior to the solids being placed into the carbon steel drums for storage.

During liquid feed processing operations, the inorganic components in the feed stream surrogates formed granular product solids that accumulated in the DMR. As described above, these accumulated solids were transferred periodically to the PR for collection and packaging into drums. The option to recycle some of the bed product particles back into the DMR to maintain the required particle size range in the DMR was incorporated into the operating philosophy of the test program. An off-line vibratory screen was provided for the separation of the larger particles from the smaller granules in the cooled solids. If required, the different size fractions of the bed product could be returned on a semi-continuous basis to the DMR bed through the solids additive auger feeder and airlock.

2.4.5 High-Temperature Filter

The HTF (T-202) was a filter vessel that received the process gases and entrained fines from the DMR. The purpose of the HTF was to remove and collect the finely divided solids—predominately mineralized product material and carbon reductant fines—elutriated from the DMR.

The HTF was a vertical, cylindrical filter vessel modified to accommodate eighteen 3 to 5-micron, sintered metal or silicon carbide, candlestick filters. An automated nitrogen gas pulse-back manifold with four nitrogen pulse-back valves was used to clean the filter elements while they were on-line. The pressure drop across the filter was measured with a differential pressure transmitter, with sensing ports in the vessel and in the gas outlet line downstream of the vessel, gave the pressure drop across the filters. When the pressure drop exceeded the setpoint, the DACS automatically actuated the pulse-back function. External electrical heaters (H-202) were provided to maintain the filter elements and filter vessel at least 400°C during operation.

During the scoping tests the HTF (bypassed) incorporated a product solids drain and collection system similar to that described for the PR. However, prior to using the HTF for the production runs an auger based collection system was installed to handle the expected collection rate of fines (~50lb/hr). The auger based system continuously conveyed the filtered solids into a 55 gallon drum located on a platform scale. The drum seal provided a pressure seal to the HTF since the pressure in the HTF was typically between 1 and 3 psig during normal operation. The drain valve and auger system were designed to contain solids with temperatures of up to 400°C. The collection system was provided with a nitrogen purge to displace process gases from the filter to ensure that moisture did not condense in the collection system.

2.4.6 Carbon Reduction Reformer

The CRR was a fluidized bed vessel operated in series with the DMR. The CRR (T-300) was an existing, vertical cylindrical, carbon steel, refractory-lined, fluidized bed vessel 24 inches in diameter. The pre-existing portion of the CRR was lined with Kasto-Lite-22 and Lo-Abraid refractory.

Ports were provided in the CRR vessel for introduction of autothermal gas (ATG), continuous injection of propylene glycol fuel, supplement carbon fuel, or water and insertion of thermocouples and pressure probes in the bed. Two sets of nozzles were used to introduce a mixture of oxygen and nitrogen (the ATG) into the CRR. The oxygen/nitrogen mixtures and flow rates to the lower ATG nozzle set were automatically controlled by the DACS to maintain the desired CRR bed temperature in the range of 850 to 950°C. The oxygen/nitrogen mixture and flow to the upper nozzle set were controlled to achieve the desired level of oxygen in the CRR off-gas. Figures 2-4, 2-5, and 2-6 are photos of the top, middle and bottom of the CRR respectively.

During the production run, the hot process gas from the DMR was filtered through the HTF, which removed essentially all of the product solids and carbon fines elutriated from the DMR. The filtered DMR process gas then consisted mainly of water vapor, nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane and other short-chain organics, and small amounts of acidic gases such as hydrochloric acid and sulfur dioxide. This process gas mixture was introduced at the bottom of the CRR and fluidized the bed media. During operations, the bottom zone of the CRR fluidized bed (below the ATG nozzles) operated under reducing conditions to facilitate additional NO_x conversion. Above the ATG nozzles, the CRR operated in an oxidizing mode to convert carbon monoxide, hydrogen, and organics from the DMR to carbon dioxide and water vapor.

The CRR provided for initial and periodic batch injections of bed media and supplemental carbon. The initial bed media consisted of alumina particles. The only solids introduced into the CRR were bed media to replace bed media lost to attrition and elutriation and supplemental carbon that was converted in large part to carbon dioxide.

Figure 2-4 Carbon Reduction Reformer Vessel Top

Figure 2-5 Carbon Reduction Reformer Vessel Middle

Figure 2-6 Carbon Reduction Reformer Vessel Bottom

Carbon, used as a supplemental fuel, was introduced into the CRR through a loss-in-weight screw auger feeder, while makeup bed solids were added by a manual batch addition. The feeder discharged solids into a small airlock chamber bounded by two valves that operated sequentially to form a lock hopper or shot pot. A nitrogen gas purge on the hopper discharge pipe excluded atmospheric air from the process and provided some of the motive force needed to inject the solids into the CRR. The carbon feeder was calibrated for the specific carbon used, and the operator manually controlled the carbon feed rate at the desired value.

During start-up, the initial energy for heating up the CRR was provided by hot nitrogen from the FG superheaters without any bed material in the CRR. The DMR was bypassed during this heat-up. When the temperature in the CRR was above 125°C, the bed media was added to the CRR, and heat-up continued using the FG superheaters. In order to fully heat up the CRR in as short a time as possible, a natural gas-fired burner was inserted into the CRR near the top of the bed. This supplemental heating capability was not used during process operations. Once the CRR bed temperature was above about 350°C, a wood-based carbon was added to the bed to provide an energy source in the CRR and a small (~5 scfm) oxygen flow was initiated to the lower ATG nozzles. When the CRR bed temperature reached ~550°C, carbon or propylene glycol was used as the source of energy in the bed instead of the wood-based carbon, and the bed heat-up continued until the desired bed temperature was reached. As the CRR bed temperature increased, the amount of gas required to fluidize the bed decreased and the operators would reduce the flow manually as needed to maintain the desired SSV in the CRR. At any time after the CRR bed temperature was above ~850°C, the FG flow was reduced and the DMR bypass was closed. Once the DMR vessel temperature was above 125°C, bed material was added to the DMR and the FG flow was again increased. The heat-up of both reformers continued until the desired operating temperatures were reached in both.

To decrease the CRR temperature slowly over a period of time, the propylene glycol feed rate and oxygen injection rate to the CRR were reduced. To provide a faster temperature response in the CRR, water could be injected directly into the CRR bed through an automatically controlled service water injector in the bed.

The ESS provided an emergency shutdown capability that would isolate the oxygen, carbon, propylene glycol, and cooling water flow to the CRR upon activation of the emergency shutdown system or upon loss of power to the plant. The oxygen, propylene glycol, and cooling water supplies are provided with emergency isolation solenoid valves to provide positive isolation from the process. Nitrogen purges were provided to prevent plugging of the in-bed nozzles during these shutdowns.

2.4.7 Off-gas Cooler

The OGC (T-400) consisted of a direct contact, deionized water spray, air-atomizing nozzle inserted into a cylindrical vessel downstream of the CRR. The OGC was designed to cool the CRR process gas from 950°C to ~200°C in a fraction of a second. The water supply was provided with an automated flow control valve that could maintain the off-gas temperature within the 200°C range. The flow rate of cooling water was automatically controlled by the DACS, but the flow rate of atomizing air was controlled manually. Thermocouples, with readouts on the DACS, were placed upstream and downstream of the OGC. The downstream thermocouple indication automatically controlled the flow of water to the OGC via the DACS.

2.4.8 Off-gas Filter

The off-gases exiting the OGC contained particulate fines elutriated from the CRR. The OGF removed the particulates from the off-gas stream. The OGF was a square cross section vessel. It was fitted with ceramic filter elements rated for at least 250°C. An automated instrument air pulse-back manifold was provided to clean the filter elements with the filters on-line. A differential pressure instrument, with sensing ports in the vessel and in the off-gas line downstream of the vessel, was used to sense the pressure drop across the filters and automatically actuate the pulse-back function.

External electrical heaters were installed to maintain the filter elements and vessel above the gas dew point (minimum of 120°C) to prevent moisture condensation on the filter media during normal operations and during start-up and shutdown periods. A silicon-controlled rectifier (SCR) was used to control the heater power level to maintain the off-gas outlet temperature at the desired level and to prevent excessive temperatures of the heater elements. The OGF was provided with a product draining auger system during the scoping runs that cooled and purged the filtered solids and conveyed them into a drum located on a platform scale. A knife valve was used to regulate the flow of solids between the OGF and auger assembly. The drum lid provided a pressure seal to the OGF. However, when the HTF was utilized during the production tests, the accumulation of solids in the OGF was greatly reduced and the auger system was no longer needed, so it was replaced with a solids collection vessel similar to that used on the PR.

2.4.9 Off-gas Blowers

Two Off-gas Blowers (OGBs) (B-407 and B-409) provided airflow and process vacuum for the DMR, HTF, CRR, and the downstream off-gas handling equipment. The OGBs maintained all systems downstream of the CRR under negative pressure. The freeboard vacuum of the CRR was maintained at -10 to -30 in. water column (WC). A differential pressure instrument was provided to measure the system vacuum in the freeboard of the CRR. The OGBs were each capable of achieving a differential pressure of 20 inches of vacuum at a flow rate of 1000 acfm. The off-gas was discharged through a monitored exhaust stack in compliance with State of Colorado environmental regulations.

2.5 Process Data Acquisition and Control System

The test system DACS used National Instruments Programmable Automation Controllers (PACs) for control and data acquisition. The PAC architecture is a combination of LabView software and Fieldpoint controllers and I/O modules. LabView software was utilized to monitor and control operations of the process from two or more human-machine interfaces (HMIs) running on personal computers (PCs) located in a control room adjoining the process equipment. Additional PCs were available for monitoring only (no control allowed) from three remote locations. The Fieldpoint controllers contained real-time (RT) programs that ran independently of any PC. These RT programs ran the primary control algorithms for the process. The Fieldpoint I/O modules were the means of acquiring signals from and transmitting signals to field devices and sensors to be used in the DACS.

The process control functions included automatic and/or manual control for the following primary process loops:

- Superheater #2 Temperature Control
- DMR Fluidizing Temperature Control
- DMR Bed Fluidizing Flow
- DMR Temperature Control
- DMR Simulant Feed Control
- DMR Atomizing Control
- DMR H₂ Control
- DMR Carbon Feed rate Control
- DMR Shotpot Control
- HTF Temperature Control
- HTF Blowdown Timer Control
- CRR Temperature Control
- CRR O₂ Control
- CRR N₂ Control
- CRR Shotpot Control
- CRR Carbon Feed rate Control
- OGC Temperature Control
- OGF Temperature Control
- OGF Blowdown Timer Control
- Blower Control.

The HMIs for the system showed the status of components, provided a control interface for the operators and displayed readings from all the instrumentation in numerical and graphical trend form. In addition,

the HMI performed several process engineering calculations, e.g., NO_x destruction calculations, and displayed the calculated results on the HMI.

The data acquisition system utilized National Instrument's proprietary Citadel database for electronically archiving data as it is monitored. Each day, data were transferred from the Citadel database to an SQL database where it could be exported to an Excel spreadsheet for analysis. Each record in the database included the tag name for the data-point, the description, the value, the units, and a time-stamp.

3. MEASUREMENTS, SAMPLE COLLECTION, AND SAMPLE ANALYSIS

Operational information gathered during the test program included: (1) continuous process measurements (e.g., key flow rates, temperatures, and pressures); (2) continuous off-gas composition measurements at the outlet of the HTF and CRR for selected gas species and Continuous Emissions Monitoring System (CEMS) stack monitoring; (3) off-gas sampling and analysis in the discharge stack downstream of the last OGB and at the outlet of the HTF; and (4) periodic grab samples of process liquids and solids for analysis. More specifics regarding data to be gathered and the desired quality of the data can be found in the test plan and the quality assurance project plan. [8.9]

3.1 Process Measurements

Key process data were recorded during the production and scoping runs. Many other parameters and calculations, including the CEMS data, were automatically logged. Additional parameters, such as purge gas flow rates, measured using rotameters, were logged manually.

Process data were logged by the DACS database according to appropriate deadband settings. A deadband was the minimum percentage of a given range by which a measured value must vary in order for the DACS to register a change. For example, if a DACS channel reading pressure was ranged 0–100 PSI and the channel “update” deadband was set to 1%, then the pressure from the device must have varied by at least 1 PSI in order for the DACS to realize a change of value.

The two main deadbands that control logging resolution were as follows:

- Update deadband. This parameter dictated the threshold that a value must change by before a new value was registered in the tag engine for update on the HMI.
- Logging deadband. This parameter dictated the threshold that a value must change by before it was actually logged in the Citadel database.

The deadband setting that was of most concern was the logging deadband. In this DACS, the update deadbands were always set equal to or smaller than the logging deadbands. This allowed the DACS to update sensor/device values at least as frequently as it logged those values.

Process data that were not electronically logged by the DACS system were recorded manually on operator data sheets. Manual control of many process parameters was also done according to operator discretion and the test plan. The measured data are provided in subsequent sections of this report.

3.2 Continuous Process Monitoring System

Continuous monitoring of gaseous emissions provided real-time, off-gas composition for purposes of process control, safety, air emissions measurements, and a determination of the fate of feed constituents converted to gaseous compounds [10]. Continuous process gas measurements were made at the outlet of the HTF downstream of the DMR and immediately downstream of the CRR. The measurements at both locations were logged into the DACS.

At the outlet of the HTF, the Continuous Process Monitoring System (CPMS) monitored for O₂, CO₂, CO, NO, NO₂, NO_x, and H₂. Carbon dioxide, CO, and H₂ measurements provided an indication of the extent of reducing conditions that existed in the DMR. Measurements of NO_x indicated the extent of nitrate conversion to nitrogen gas in the DMR. Total hydrocarbon, CO, and H₂ measurements reflected the amount of oxidation that was required in the CRR to convert organic constituents completely to carbon dioxide and water. The amount of reductant added to the DMR to maintain adequate reducing conditions was controlled based on the hydrogen concentration in the DMR process outlet gas.

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At the second CPMS location, downstream of the CRR, O₂ was the only gaseous constituent measured. Output from the oxygen analyzer automatically controlled the amount of excess oxygen in the CRR to maintain an adequate oxidizing environment to ensure complete oxidation of all carbonaceous materials, CO, and H₂ from the DMR process gas.

Table 3-1 identifies the types of analyzers and their relevant analytical capabilities used at the two CPMS sampling locations. The analyzers listed in Table 3-1 [11] were used in conjunction with sample conditioning equipment that included sample probes, heated sample lines running from the sample point to the instrument location, filters, condensers, pumps, manifolds, and calibration gases. The analyzers were calibrated with calibration span gases and zero concentration gases (either air or nitrogen). The calibration frequency was determined considering calibration error and calibration drift that the CPMS instruments incurred during each test and considering the schedule for test activities when the analyzers needed to be online for key test periods. At a minimum, the entire suite of process gas analyzers was calibrated at least once per operating day.

3.3 Continuous Emissions Monitoring System

The CEMS was used to monitor the concentrations of gaseous species of environmental concern in the exhaust stack. Continuous sampling and analyses used instrumental analyzers and sample conditioning units in accordance with appropriate EPA methods. Calibrations were also conducted per the applicable EPA method. Stack gas analyses were performed by an independent subcontractor (Air Pollution Testing, Inc., of Arvada, Colorado) who has several years of experience in stack gas sampling and analysis. Specifications for the CEMS instruments are listed in Table 3-2 [11]. Data acquired by the CEMS were automatically logged by both the stack gas sampling subcontractor and the DACS for purposes of operational monitoring and control.

3.4 Periodic Manual Stack Gas Sampling

Manual stack gas sampling was performed periodically at multiple locations in the system to determine the concentrations of the various potential pollutants. The specified locations were at three points in the exhaust gas stack downstream of the last OGB. Multiple sample points in the exhaust gas stack were provided to allow for at least two isokinetic sample trains to run simultaneously. The sampling ports consisted of 2-in. diameter pipe couplings welded to the 6-in. diameter exhaust duct. The manual stack gas sampling ports were in addition to the instrumental sample ports identified for the CPMS and CEMS analyzers. Sampling events for each of the tests are shown in Table 3-3. In all cases, sampling took place after the system reached a stable operating condition.

Table 3-1 Analyzers Used in the Continuous Process Monitoring System

Gas Species	Instrument	Detection Principle	Range	Acceptance Limits (% of Full Scale)				Reference Method
				Calibration	Drift	Linearity	Bias	
HTF Outlet:								
CO (2 avail.)	CAI, ^a Models 200 / 100	Non-Dispersive Infrared	0–1%, 0-10%	5	10	2	—	40 CFR 60, App. A Method 10
CO ₂ (2 avail.)	Nova, Model 4230	Non-Dispersive Infrared	0–100%	2	3	4	5	40 CFR 60 App. A Method 3A
NO / NO _x (2 avail.)	CAI, ^a Model 400CLD	Chemiluminescence	0–3,000ppm	2	3	4	5	40 CFR 60 App. A Method 7E
H ₂ (2 avail.)	Nova, Model 4230	Thermal Conductivity	0–20%	—	—	—	—	—
THC	TECO, ^b Model 51	Flame Ionization Detection	0–10,000ppm	5	3	—	—	40 CFR 60 App. A Method 25A
O ₂ (2 avail.)	CAI, ^a Models 200 / 110	Paramagnetic	0–25%	2	3	4	5	40 CFR 60 App. A Method 3A
CRR Outlet:								
In situ O ₂	Teledyne 9060UH-HT	Zirconium Oxide	0–30%	2	3	4	5	40 CFR 60 App. A Method 3A
Notes: (a) California Analytical Instruments. (b) Thermo Electron Corporation								

Table 3-2 Analyzers Used in the Continuous Emissions Monitoring System

Gas Species	Instrument	Detection Principle	Range, Scale, Analyzer Max.	Acceptance Limits (% of Full Scale)				Reference Method
				Calibration	Drift	Linearity	Bias	
CO	Thermo Electron Model 48C	Gas Filter Correlation Infrared	0–396, 0-79.1 Scale 0-500, Max 10,000ppm	2	3	2	5	40 CFR 60 App. A Method 10
CO ₂	Servomex Series 1400	Non-Dispersive Infrared	0–19.3% Scale 0-20%, Max 20%	2	3	4	5	40 CFR 60 App. A Method 3A
NO, NO ₂ , NO _x	Thermo Electron Model 42C	Chemilumi-nescence	0–1099, Scale 0-5000, Max 5,000ppm	2	3	4	5	40 CFR 60 App. A Method 7E
SO ₂	Western Research Model 721M	Ultraviolet	0–468, Scale 0-500, Max 5,000ppm	2	3	—	5	40 CFR 60 App. A Method 6C
THC	JUM Model 3-300A	Flame Ionization Detection	0–57, Scale 0-100, Max 10,000ppm	5	3	—	—	40 CFR 60 App. A Method 25A
O ₂	Servomex Series 1400	Para-magnetic	0–21%, Scale 0-25%, Max 25%	2	3	4	5	40 CFR 60 App. A Method 3A

Table 3-3 Manual Stack Sampling Events for Hanford ART Tests

Test Number	Metals	PM/ (HX+X ₂)	D/F/PCBs	VOCs	SVOCs	Field GC	TCO/Grav	Total Sample Events	Test Purpose
EPA Method	29	5/26A	0023A	0031	0010	0040	0010		
ART-S-1	X	X						2	Baseline DMR temperature, High CRR temperature, Baseline clay stoichiometry
ART-S-2	X	X	X	X	X	X	X	7	High DMR temperature, High CRR temperature, Baseline clay stoichiometry
ART-S-4	X	X						2	High DMR temperature, Low CRR temperature, Baseline clay stoichiometry
ART-S-5	X	X	X	X	X	X	X	7	Low DMR temperature, Low CRR temperature Baseline clay stoichiometry
ART-S-6	X	X	X	X	X	X	X	7	Optimum DMR and CRR temperatures, -10% clay stoichiometry
ART-S-7	X	X	X	X	X	X	X	7	Optimum DMR and CRR temperatures, -20% clay stoichiometry
ART-P-1a	X	X	X	X	X	X	X	7	Optimum DMR and CRR temperatures, 675g/L CLAY
ART-P-1B	X	X	X	X	X	X	X	7	Optimum DMR and CRR temperatures, 640g/L CLAY
ART-P-2 (WTP SW)	X	X						2	Optimum DMR and CRR temperatures, Feed solution and clay stoichiometry to be determined by the JTG
Sampling Events	9	9	6	6	6	6	6	48	

Isokinetic and extractive samples taken at all locations were collected in impingers, filters, absorbents, and Tedlar® bags for subsequent laboratory analysis. Sample acquisition was performed in accordance with the appropriate EPA method [12]. Sample analyses were performed by a qualified laboratory (Test America Laboratories). All samples withdrawn from the process were carefully collected, individually packaged, recorded, and archived. Chain-of-custody documentation was prepared for all samples taken for environmental permitting purposes.

Analytes determined via extractive sampling in the exhaust stack included HCl, Cl₂, metals, dioxins/furans, polychlorinated biphenyls (PCB), POHCs, volatile organic compounds (VOC), semi-volatile organic compounds (SVOC), total organics, and particulate matter. All of these analyses were intended to demonstrate compliance with applicable environmental requirements.

3.5 Periodic Process Liquid and Solid Sampling

Throughout the test program, samples of the feed solutions to the DMR and the solid products from the PR, HTF, CRR, and OGF were collected for later analysis. The primary purpose of the solid product sampling and analysis was to determine the effectiveness of the THOR® FBSR Process system to accomplish some of the primary objectives of the test program as stated in Section 1.2. Specifically, sampling and analyses were intended to confirm that:

- Essentially all of the nitrates and nitrites in the simulant feed were destroyed, and conversion of these species to nitrogen gas was maximized
- Essentially all of the organics in the simulant feed were removed and converted to carbon dioxide and water
- Essentially all fluorides, chlorides, aluminum, and other elements in the simulant feed were retained in the solid waste products generated by the process.

The THOR® Process is intended to be operated in such a manner that no liquid waste streams are generated.

The analyses of the solid products were performed at an on-site laboratory at the pilot plant testing subcontractor's facility (Hazen Research, Inc. laboratory) and an independent laboratory (ACS Laboratories). Analyses of the leach and durability performance of the solid products were performed off-site at the Savannah River National Laboratory (SRNL).

Periodic process samples were obtained during the production run tests at the frequencies shown in Table 3-4. All liquid and solid materials withdrawn from the process were carefully collected, individually packaged, weighed, recorded, and archived. Chain-of-custody documentation was prepared for all samples taken for off-site analysis. Constituents analyzed for and measurement methods are listed in Table 3-5.

3.6 Metallurgical Analysis

The THOR® Process utilizes moderate temperature thermal treatment to convert liquid wastes into mineralized solid products. Operation of the treatment equipment subjects the materials of construction to potentially corrosive environments. To verify the most suitable materials of construction for a full-scale production plant, it is necessary to install coupons of selected metal alloys into the process equipment for the duration of the test. The metal coupons are subjected to thermal and chemical environments typical of process operating conditions. Upon completion of the test program, the exposed coupons were archived for performance of metallurgical evaluations to determine the extent of corrosion or wear as part of a

future contract. The coupons will not be metallurgically evaluated as part of the ART test activity, but will be archived for possible future use. In the future, metallurgical evaluation corrosion mechanisms may be identified and corrosion rates estimated.

Each corrosion coupon installed in the Hazen equipment was assigned a unique number that was stamped on the coupon. The manufacturer's data and individual coupon alloy heat number, CMTR number, and other unique identification information were recorded on datasheets. Following assembly of each set of coupons, a photograph was taken prior to insertion or placement of the coupons in the process equipment. This is important, as certain corrosive mechanisms can render scribing and surface identification numbers illegible.

The detailed "Metallurgical Evaluation Plan" [13] provides details on the metallurgical evaluation plan for the corrosion coupons for the mineralizing demonstration tests.

Table 3-4 Process Liquids and Solids Sampling and Analysis Matrix

Sample Location	Sample Frequency	Minimum Sample Volume (ml)	Number of Samples per Sampling Event (Original plus archive)	Analyses/Data Required
LAW or WTP SW Simulant Solution (TK-100, and 101-A/B)	Once every makeup batch or as requested	1,000	Two	Specific Gravity, concentration of each constituent in simulant, % UDS. (Constituents as noted in Tables 4-4 and 4-6 of Section 4.)
DMR Startup Alumina	Sample from each new container, for each new bed addition.	500	Two	Analyze composite for PSD, particle density, bulk density, Al, Na, K, Si, Ti, Fe, Ca, Mg. Archive 2nd one.
DMR Feed Reductant (carbon)	Daily composite	500	Two	Analyze first and last samples for heating value, elemental analysis of ash. Archive all others.
DMR Active Bed Sample	Every 4 hours or as requested	1,000	Two	Archive one, sample one. Each drain: total mass, particle size distribution (PSD), bulk density, and particle density. As Requested: wt% of each constituent in simulant, nitrates, nitrites.
PR Solids Product	Sample from each container of material removed from system	1,000	Two	Archive one, sample one. Each drain: total mass, particle size distribution (PSD), bulk density, and particle density. As Requested: wt% of each constituent in simulant, nitrates, nitrites.
HTF Solids Product	Sample from each container of material removed from system	1,000	Two	Archive one, sample one. Each drain: total mass, bulk density, As Requested: particle size distribution (PSD by Malvern), particle density, wt% of each constituent in simulant, nitrates, nitrites.
CRR Alumina	Sample from each new container, for each new bed addition.	500	Two	Analyze composite for PSD, particle density, bulk density, Al, Na, K, Si, Ti, Fe, Ca, Mg. Archive 2nd one.
CRR Carbon Additive	Daily composite	500	Two	Analyze first and last samples for heating value, elemental analysis of ash. Archive all others.
CRR Propylene Glycol Additive	Sample from each new container	500	Two	Analyze as requested. Archive all others.
CRR Active Bed Sample	Once every 8 hours or as requested.	1,000	Two	Archive one, sample one. Each drain: total mass, particle size distribution (PSD), bulk density, and. As Requested: particle density, wt% of each constituent in simulant.
OGF Solids Product	Sample from each container of material removed from system	1,000	Two	Archive one, sample one. Each drain: total mass, bulk density. As Requested: particle size distribution (PSD by Malvern), particle density, wt% of each constituent in simulant.
CPMS and CEMS Condensates	Daily or as requested	500	One each	pH, nitrate, nitrite, sulfate, NH_4^+ , CN^- , total inorganic carbon, TOC
Other	As directed	500	One plus an Archive.	As requested.

Table 3-5 Constituents Analyzed for and Measurement Methods

Analysis	Laboratory	Digestion	Measurement Method
Silver	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Aluminum	Hazen	Na ₂ O ₂ fusion	FAA
Aluminum	Hazen	Na ₂ O ₂ fusion	ICP-OES
Arsenic	Hazen	HNO ₃ /HClO ₄	HYAA
Barium	Hazen	HNO ₃ /HClO ₄	ICP-OES
Carbon, total	Hazen	Combustion	LECO CHN 1000
Carbon, inorganic	Hazen	Acid evolution of CO ₂	Coulometric titration
Carbon, organic	Hazen	By difference	---
Chloride	ACS	HNO ₃	Titration w/AgNO ₃
Chromium	Hazen	Na ₂ O ₂ fusion	FAA
Cesium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Fluoride	Hazen	Na ₂ O ₂ fusion	Specific Ion Electrode
Iron	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Iodide	ACS	HNO ₃	ICP-MS
Potassium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Sodium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Nickel	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Nitrite, as NO ₂	Hazen	Hot water soluble	Ion Chromatography
Nitrate, as NO ₃	Hazen	Hot water soluble	Ion Chromatography
Hydroxide	Hazen	Water leach	Titration w/std. Acid
Lead	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Phosphate, as PO ₄	Hazen	HNO ₃ /HCl/HF	Colorimetry
Rhenium	Hazen	NaClO ₃ /HNO ₃	ICP-OES
Total S (liquids)	Hazen	Oxidize w/Br	Gravimetry-BaSO ₄ ppt
Total S (solids)	Hazen	---	LECO
Antimony	Hazen	HNO ₃ /HClO ₄ /H ₂ SO ₄	ICP-OES
Selenium	Hazen	HNO ₃ /HClO ₄	XRF
Silicon	Hazen	Na ₂ O ₂ fusion	FAA
Silicon	Hazen	Na ₂ O ₂ fusion	ICP-OES
Sulfate, as SO ₄	Hazen	Hot 4.8N HCL	Gravimetry-BaSO ₄ ppt

Analysis	Laboratory	Digestion	Measurement Method
Thallium	Hazen	HNO ₃ /HCL/HF	ICP-OES
Zinc	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Boron	Hazen	Na ₂ CO ₃ fusion	ICP-OES
Calcium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Cadmium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Magnesium	Hazen	HNO ₃ /HCl/HClO ₄ /HF	FAA
Ammonium	Hazen	Distillation w/NaOH	Titration
Titanium	Hazen	Li ₂ B ₄ O ₇ fusion	ICP-OES
Other analyses, units as indicated:			
Bulk density, kg/L	Hazen	---	ASTM C29/29M or equivalent
Particle density, kg/L	Hazen	---	ASTM C128-04 or equivalent
PSD	Hazen	---	Bed solids: ASTM C92-95 or equivalent; Fines: Malvern Laser Diffraction or equivalent
UDS	Hazen	---	EPA 160.2, 5 mg/L detection limit
TCLP leachability	EPA Certified Lab	Method 1311	EPA Method 1311
XRD	SRNL		
PCT	SRNL		ASTM C1285-02
Surface area	SRNL		Method of Brunauer, Emmett, and Teller (BET)
Compressive strength	SRNL		ASTM C39/C39M, ASTM C1231
<p>Notes:</p> <p>CVAA = Cold Vapor Atomic Absorption</p> <p>FAA = Flame Atomic Absorption</p> <p>HYAA = Hydride Atomic Absorption</p> <p>ICP-OES = Inductively Coupled Plasma - Optical Emission Spectroscopy</p> <p>ppt = precipitation</p> <p>TBD = To be determined</p> <p>TCLP = Toxicity Characteristic Leachability Procedure</p> <p>XRD = X-ray diffraction</p>			

4. SIMULANT COMPOSITIONS

Aqueous solutions of various metal salts in combination with organic constituents were prepared for use as LAW and WTP SW waste feed simulants in the pilot plant test program. Non-radioactive constituents were utilized as surrogates for radiological components for the purpose of this test. The composition of the simulant used for the ESTD LAW testing program was derived from a recommended Hanford LAW composition, Table 3.1 of Reference 14. That composition is reproduced below as Table 4-1. A simulant solution of similar composition was used during previous pilot-scale testing of the THOR[®] Process at INL [4]. The INL composition differed from that recommended by PNNL with the addition of iodine and rhenium (as a surrogate for technetium) so that the retention of specific radionuclides in the mineralized product could be determined. The compositions of the various batch make-ups that are combined to form the process feed are discussed in the following sections.

Table 4-1 Cold Dissolved LAW Saltcake Solution Simulant Analyte Concentrations

Metals	Concentration (M)
Al	0.0637
Cs ^(a)	5.10E-08
Cr	0.0104
K	0.0124
Na	5.00
Anions/Other	Concentration (M)
Cl	0.0438
CO ₃ (or total inorganic carbon) ^(b)	0.475
F	0.0316
NO ₂	0.424
NO ₃	2.51
PO ₄	0.0492
SO ₄	0.0900
C ₂ O ₄ (oxalate)	0.0118
Other TOC (as carbon, from acetate)	0.263
TOC total ^(c)	0.287
OH Total	0.740
Free OH	0.485
<p>The concentration of cold Cs in the simulant is based on the estimated concentration of Cs in the actual waste solution prior to ion exchange and then reduced by a factor of 100, accounting for a conservatively low ion exchange decontamination factor. Because of the very low Cs chemical concentration in the simulant solution, its concentration in simulant batch preparations is estimated by formulation. Analysis of ¹³⁷Cs in the actual waste solution is possible because radiochemical methods (e.g., GEA) are highly sensitive.</p> <p>In the simulant solution preparations, ion chromatography or, alternatively, a total inorganic carbon analysis will be used to determine carbonate.</p> <p>For the simulant, TOC can be calculated from the analysis of TOC contributors oxalate and acetate, or it can be measured directly with a total inorganic carbon/TOC analysis.</p>	

Based on the literature data and information obtained from the site, the test team proposed compositions for the LAW and WTP SW simulants as shown in Table 4-2. The makeup reagents used, as well as the target LAW and WTP SW simulant compositions, are listed.

4.1 LAW Simulant Solution

The target composition of the LAW simulant solution is shown in Table 4-2. The simulant is an alkaline solution consisting primarily of sodium and potassium salts. The table presents each desired component as either the element or anion of interest. The purpose of adding RCRA and non-radioactive surrogate metals to the feed mixture is to establish whether or not a feed slurry with the composition of a fully-mixed waste tank can be accommodated by the feed system and whether the FBSR system can process the feed simulant into a durable, leach resistant waste form.

The ART ESTD test program utilized the following metals in the various test runs: Ag, Ba, Cd, Cs, Ni, Pb, Tl, As, Re, Se, Sb, and Cr. The determination of the appropriate metal concentrations was based on an evaluation of the anticipated feed composition (see Table 4-1); discussions with the DOE field office; discussions with the environmental regulators, and an evaluation of the Hanford Tank Waste Envelopes A, B, and C [15]. It was determined through the evaluation of the actual tank waste metals concentrations that some metal levels were not sufficient to achieve reliable detection in the off-gas sampling. Therefore, the identified metals concentrations were increased in the simulant feed to ensure detection and enable calculation of system removal efficiencies, product retention efficiencies, and mass balance closure without regard to potential results to those determinations. The primary goal of collecting reliable data would then produce data which could then be applied to the actual tank waste metal concentrations. The results of this strategy are discussed in detail in Sections 8, 9, and 10. The target concentration for the LAW was increased by a factor of 10 for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 254,902 for Cs.

Creation of the types of the NAS minerals that would provide leach resistant (durable) waste forms for the immobilization of LAW and WTP SW in the FBSR requires the addition of an appropriate clay to the simulant prior to introduction to the FBSR. OptiKasT clay was chosen for the addition to the LAW simulant. The OptiKasT composition is shown in Table 4-3.

The feed to the ESTD pilot plant was prepared by first mixing up a feed solution without heavy metals or clay (lite feed solution). Separately a feed solution of heavy metals was mixed up for use in the process. Specific quantities of both the lite solution and heavy metal solution were mixed in a third tank, where the required quantity of clay was also added. Procedurally, all batched are documented on make-up sheets and the steps involved are as follows:

- Mix the LAW lite feed solution (no heavy metals or clay) in tank T-100.
- Mix the LAW heavy metals solution (no lite solution or clay) in tank T-102.
- Transfer specific volumes of LAW lite solution and LAW heavy metal solution to tank T-101B.
- Add the required mass of clay to tank T-101B.
- Mix the tank until the overall batch is well mixed.
- Transfer batch to tank T-101A for use as feed for the specific test.

Table 4-2 Target Constituent Concentrations for LAW and WTP SW Simulants

Component	Component	LAW Target Component Concentration [mol/L]	WTP SW Target Component Concentration [mol/L]	Makeup Reagent
Oxalate	C ₂ O ₄	0.0118	--	Na ₂ (C ₂ O ₄)
Acetate	CH ₃ COO	0.132	--	Na(C ₂ H ₃ O ₂)
Hydroxide	OH	0.74	1.564	NaOH
Carbonate	CO ₃	0.475	0.200	Na ₂ CO ₃
Sulfate	SO ₄	0.09	0.005	Na ₂ SO ₄
Chloride	Cl	0.0438	0.106	NaCl
Fluoride	F	0.0316	0.219	NaF
Iodide	I	0.013	0.001	NaI
Nitrite	NO ₂	0.424	0.036	NaNO ₂
Phosphate	PO ₄	0.0492	0.007	Na ₃ PO ₄ •12H ₂ O
Aluminum	Al	0.0637	0.548	Al(NO ₃) ₃ •9H ₂ O, 60 wt% solution
Potassium	K	0.0124	0.010	KNO ₃
Sodium	Na	5.0161	2.668	NaNO ₃
Nitrate	NO ₃	2.58487	1.991	[from other components]
Silver	Ag	0.00161	0.00086	AgNO ₃
Arsenic	As	0.00137	0.00010	H ₃ AsO ₄ , 75 wt% solution
Barium	Ba	0.00751	0.00002	Ba(NO ₃) ₂
Cadmium	Cd	0.0042	0.00087	Cd(NO ₃) ₂ •4H ₂ O
Chromium	Cr	0.0104	0.00606	Na ₂ Cr ₂ O ₇ •2H ₂ O
Cesium	Cs	0.013	0.01469	CsNO ₃
Nickel	Ni	0.0106	0.00458	Ni(NO ₃) ₂ •6H ₂ O
Lead	Pb	0.00606	0.00131	Pb(NO ₃) ₂
Rhenium	Re	0.0017	0.00113	NaReO ₄
Antimony	Sb	0.00434	0.00160	Sb ₂ O ₃
Selenium	Se	0.00123	0.00247	SeO ₂
Thallium	Tl	0.00202	0.00096	TlNO ₃
Ammonium	NH ₄	--	0.292	NH ₄ NO ₃
Boron	B	--	0.132	Na ₂ B ₄ O ₇ •10H ₂ O
Silicon	Si	--	0.018	Na ₂ O•SiO ₂ , 37.6 wt% solution
Zinc	Zn	--	0.00729	Zn(NO ₃) ₂ •6H ₂ O

Table 4-3 Compositions of Clay Used for LAW and WTP SW Simulants

Oxide	Clay Type		
	OptiKasT	Sagger XX	55% OptiKasT / 45% Sagger XX Mixture
Al ₂ O ₃	37.76%	31.48%	34.94%
SiO ₂	44.67%	55.09%	49.35%
Fe ₂ O ₃	0.55%	0.84%	0.68%
TiO ₂	1.67%	0.63%	1.20%
CaO	0.04%	0.13%	0.08%
MgO	0.03%	0.15%	0.08%
Na ₂ O	0.02%	0.09%	0.06%
K ₂ O	0.11%	0.65%	0.36%
P ₂ O ₅	0.07%	0.00%	0.04%
H ₂ O	15.08%	10.94%	13.22%
Sum	100.0%	100.00%	100.00%

The batch solutions listed in the above outline utilized feed batches of LAW lite solution, heavy metal solution, and clay additive. The composition of these three components varied based on the scoping or production test being performed [8]. Generation of these batches was proceduralized and documented for use [16].

The target composition for the LAW simulant for the production tests is shown in Table 4-4. Two clay additive concentrations were used, 675 g clay per liter of simulant and 640 g clay per liter of simulant.

Table 4-4 Target Composition for LAW Simulant Mixed with Clay

Component	Component	Target Component Concentration with 675 g clay/L [g/L]	Target Component Concentration with 640 g clay/L [g/L]
Oxalate	C ₂ O ₄	0.829	0.838
Acetate	CH ₃ COO	6.221	6.287
Hydroxide	OH	10.046	10.152
Carbonate	CO ₃	22.752	22.993
Sulfate	SO ₄	6.901	6.974
Chloride	Cl	1.239	1.253
Fluoride	F	0.479	0.484
Iodide	I	1.317	1.331
Nitrite	NO ₂	15.570	15.735
Phosphate	PO ₄	4.216	4.235
Aluminum	Al	109.056	104.566
Potassium	K	0.888	0.871
Sodium	Na	91.957	92.924
Nitrate	NO ₃	127.932	129.285
Silver	Ag	0.139	0.140
Arsenic	As	1.042	1.003
Barium	Ba	1.419	1.403
Cadmium	Cd	0.377	0.381
Chromium	Cr	0.432	0.436
Cesium	Cs	1.379	1.394
Nickel	Ni	0.497	0.502
Lead	Pb	1.002	1.013
Rhenium	Re	0.253	0.255
Antimony	Sb	0.422	0.426
Selenium	Se	0.078	0.078
Thallium	Tl	0.330	0.333
Silicon	Si	112.496	107.791
Iron	Fe	2.070	1.983
Titanium	Ti	5.386	5.161
Calcium	Ca	0.141	0.135
Magnesium	Mg	0.086	0.083

Appendix C provides the as-analyzed chemical makeup of the feed solution surrogates used in the test program. Some of the sample results exceeded the target composition by >20%. Reasons for these discrepancies can be: (1) Weight and volume measurements during simulant make ups were in error; (2) Raw material certificates of analysis were in error; and (3) Laboratory measurement methods were not appropriate for the sample matrix. Item 3 is the more likely cause, as the analyses was performed using both SW-846 methods [12] and more aggressive digestion methods, both unable to meet objectives due to the matrix, interferences, etc.

There was little potential effect on the process chemistry due to the discrepancies with the target compositions. The composition was reasonably close to actual LAW and representative of how LAW would be processed and how elements would interact and flow through an actual production plant. The actual concentration of constituents in the feed was important in obtaining a process mass balance. Accordingly, the analytical results of the feed solutions were used for confirming the accuracy of the mass balance calculations.

4.2 WTP SW Simulant Solution

A second application of the THOR[®] Process would be to treat the Hanford WTP secondary waste—or WTP SW stream—to produce a solidified mineral product. The projected composition of this recycle stream was based on a prediction of the secondary waste stream resulting from operation of the WTP Low Activity Waste Facility.

Phased startup of WTP could potentially involve the operation of the LAW or HLW facilities prior to the availability of the Pretreatment Plant (PT). The implications of this, in the case of the LAW facilities, would be that the effluent streams generated during melter operations (and off-gas treatment) could not be recycled to the PT facility as designed based on predictions of the composition of three streams: the Submerged Bed Scrubber (SBS) condensate, the Wet Electrostatic Precipitator (WESP) drainage, and the Caustic Scrubber effluent. The composition of the combined LAW effluent prediction was based on an Excel spreadsheet mass balance that calculated the major operations of the LAW systems. The assumptions/basis used in this process included:

- The waste feed stream to the LAW receipt vessel was calculated using a ten year average of the Ion Exchange treated output obtained from the WTP's Dynamic Flowsheet (G2 model run, MRQ 07-0015 Scenario 4.1.53a).
- Water was removed from the waste feed stream to simulate concentration from a nominal 5 to 8 molar Na (this step may or may not be part of an early LAW flowsheet).
- Glass formers were added to the waste stream based on input from the WTP glass model.
- The amount of melter carryover and efficiency of the SBS and WESP (DFs) were based on the latest research and technology reports.
- WESP flow rate was based on steady state flows (includes misting and daily flushes) described in the WTP Steady State Flowsheet Model Design Description.
- Caustic scrubber composition (water, sodium, carbonate and hydroxide) and flow rate were based on WTP Aspen Tiered model 2006/2007 verification runs (average of three cases).
- Other Immobilized Low Activity Waste (ILAW) streams were not included, e.g. CRV demister flushes, decontamination activities, ventilation condensates, etc.

The components selected for inclusion in the simulant and their predicted concentrations are shown in Table 4-5. This table depicts the rationale for constituent selection. The first column lists the selected constituents, the next 5 columns identify the rationale used for the selection of each and the last column shows the component molar concentration. Components that make up either 99% of the weight percent and/or mole percent of the solutes were selected (selection bases “1” and “2”). Components of concern are identified in selection basis “3”; this includes the RCRA metals. The radioactive components are identified by selection basis “4”, and selection basis “5” picks the hydroxide anion. Rhenium was included as a surrogate for technetium.

Table 4-5 Selection Basis for Constituents WTP SW Simulant Solution

Components	Selection Basis					mol/L
	1	2	3	4	5	
Ag ⁺			X			5.75E-08
Al/Al ⁺³		X				4.34E-04
As ⁺⁵			X			7.01E-06
B ⁺³	X					8.91E-03
Cl ⁻	X					7.13E-03
CO ₃ ⁻²	X					1.35E-02
Cr/Cr ⁺³		X	X			4.07E-04
Total Cs ⁺ (bounds Cs-137)				X		9.88E-10
F ⁻	X					1.47E-02
Hg ⁺²			X			8.65E-07
K ⁺		X				7.04E-04
Na ⁺	X				X	6.17E-02
NH ₃ /NH ₄	X				X	1.97E-02
Ni ⁺²			X			3.08E-06
NO ₂ ⁻	X				X	2.45E-03
NO ₃ ⁻	X				X	3.99E-03
OH ⁻					X	5.40E-05
Pb ⁺²			X			8.84E-07
PO ₄ ⁻³		X				4.95E-04
Si ⁺⁴		X				1.21E-03
SO ₄ ⁻²		X				3.68E-04
Zn ⁺²		X				4.91E-04
Sb			X			2.26E-06
Ba			X			3.58E-08
Cd			X			4.51E-08
Se			X			1.03E-05
Tl			X			2.25E-06
Re (Tc-99)				X		7.63E-06
I (I-129)				X		5.30E-07
1 = Component included in 90% of the solute mass/moles						
2 = Component included in 99% of the solute mass/moles						
3 = Component in list for Constituents of Concern						
4 = Radionuclide of Interest						
5 = Added as characteristic of solution						

Since the anticipated WTP SW stream from the WTP is very dilute (~97% water), it is expected that the WTP SW stream will be concentrated up to a factor of ~20 times in an evaporator. The as-received waste stream would also require the addition of solid sodium hydroxide to complex halides and sulfate and prevent scaling and gel formation prior to the evaporation step, and aluminum nitrate addition to prevent formation of low-melting point glass during processing in the FBSR processing.

The target concentration was increased by a factor of 10 for Re, 100 for Ni and Pb, 1,000 for Ag, and 1,000,000 for Cs. The target concentrations for Ba, Cd, Sb, Se and Tl were set to provide a 1000X analytical detection limit in feed solution. This was performed to ensure the ability to detect and measure those constituents in the pilot plant off-gas and products, thus providing information for mass balance calculations and their fate/performance in the process and monolithic waste form as noted above in Section 4.1. It was also done without specific regard to a potential TCLP exceedance in the granular product or final monolithic waste form.

A mixture of Sagger XX and OptiKasT clay was chosen as the mineralizing additive for the WTP SW simulant. The clay mixture composition is shown in Table 4-3.

The WTP SW simulant was prepared in a manner similar to the LAW simulant; by first mixing up a lite solution without metals or clay, then adding the metal solution, and clay additive. Generation of these batches was also proceduralized and documented for use. [16]

The WTP SW simulant for the ESTD program had the targeted composition with clay added at 307 g per liter of simulant as shown in Table 4-6. Appendix C provides the as-analyzed chemical makeup of the feed solution surrogate batches used during the WTP SW portion of the test program.

Table 4-6 Composition of WTP SW Simulant Solution with Clay Added

Component	Component	Target Component Concentration with 307 g clay/L [g/L]
Hydroxide	OH	23.850
Carbonate	CO ₃	10.773
Sulfate	SO ₄	0.471
Chloride	Cl	3.370
Fluoride	F	3.727
Iodide	I	0.090
Nitrite	NO ₂	1.502
Phosphate	PO ₄	0.764
Aluminum	Al	64.171
Potassium	K	1.180
Sodium	Na	50.489
Nitrate	NO ₃	110.716
Silver	Ag	0.083
Arsenic	As	0.007
Barium	Ba	0.003
Cadmium	Cd	0.088
Chromium	Cr	0.282
Cesium	Cs	1.751
Nickel	Ni	0.241
Lead	Pb	0.244
Rhenium	Re	0.189
Antimony	Sb	0.175
Selenium	Se	0.175
Thallium	Tl	0.175
Ammonium	NH ₄	4.728
Boron	B	1.284
Silicon	Si	63.971
Zinc	Zn	0.428
Iron	Fe	1.311
Titanium	Ti	1.983
Calcium	Ca	0.151
Magnesium	Mg	0.138

4.3 Principal Organic Hazardous Constituent

Production tests incorporated the metered injection of a POHC into the feed line from the liquid waste feed tank (T-101-A or T-101-B) to the DMR. The POHC injection rate was at a higher concentration in the total simulant feed than the combined total of all potential organics in the actual LAW, in order to achieve detection limits needed to provide data on organic DRE in the steam reforming process. The POHC was metered into the feed stream rather than mixed with the remainder of the feed slurry so that a very accurate measurement could be made of the amount fed to the DMR for purposes of determining the DRE.

The POHC chosen for the DRE phase of the testing was benzene, a Class 1 POHC from the Dayton List, which is ranked higher than any other organic constituent either found or speculated to be in the INL liquid waste tanks. Monochlorobenzene, used as the POHC in previous testing, was not used in these tests due to the adverse impact of excess chloride on the mineralization process. Based on an assumed detection limit of 10 µg/dscm for benzene in the off-gas, the rate of addition of benzene to the DMR was maintained at a flow rate of at least 0.73lb/hr to report a DRE of at least 99.99%.

5. TEST PROGRAM DESCRIPTION

The overall mineralizing test program was conducted in the following multiple discreet phases:

(1) equipment checkout and functional testing, (2) parametric scoping tests in which optimum process temperatures and simulant-to-clay ratios were determined, (3) production tests for both LAW and WTP SW in which the process was operated for an extended period of time in order to demonstrate long-term system operability and to generate an adequate inventory of product for subsequent monolith testing, and (4) monolith bench-scale testing in which the NAS material was formed into monolith samples using various binders and a range of waste loading. Monolith performance testing includes TCLP, PCT, and compressibility testing. The equipment checkout, the scoping tests, and the production tests are discussed in the sections below. The monolith formation and analysis tests are discussed in Section 10.

5.1 Equipment Checkout and Functional Testing

The primary purpose of equipment checkout and functional testing was to verify that all hardware was correctly installed and that the individual components operated properly and safely. The checkout tests verified the readiness of all systems, equipment, safety shutdowns, interlocks, and instrument calibrations.

Checkout testing was conducted in accordance with a General Work Instruction [17] that included pre-developed checklists for the testing of each piece of equipment, as determined by the testing management team. Each piece of equipment was tested to a predetermined set of parameters that were listed on each testing checklist. In addition to the testing of each individual piece of equipment, the entire system was pressure tested to ensure that piping and vessels would perform per the design requirements and that the system would be free of leaks. All results were documented on the appropriate forms, reviewed, approved and filed for future reference.

In addition to functional testing, specific items of equipment, such as pressure gauges, feeders, flow meters, and thermocouples, were calibrated to verify input to-output performance. Some equipment was received with manufacturer's calibrations and others were calibrated on-site in accordance with a General Work Instruction. [18]

Functional tests, logic checks, and calibrations were used to verify the DACS functions, such as superheater operation, system flow capacities, valve timing and orientation, feeder speed control for solid additives, waste feed flow rates, cooling water control, blower performance, and DMR auger/grinder operation.

Emergency shutdown system tests were performed to assure the plant would shutdown in case operating conditions approached parameters that were determined to be possibly unsafe. Overall system performance was determined and operating limits were set for process temperatures, flows, and additive addition rates. Operating procedures were validated and updated as required. [19,20,16,21,22,10,23]

The implementation of the requirements of GWI 3.3 and GWI 3.2 [17,18] ensured the proper manual and automated operation of all equipment to achieve consistent and reproducible results. At the completion of the checkout and functional tests, the integrated DMR/CRR process system was ready for the next phase of testing.

5.2 Scoping Tests

The main purposes of the scoping tests were to establish the upper and lower bounding temperatures for both the DMR and the CRR and to define a range of clay stoichiometries that would generate an acceptable LAW product. The mineralizing clay stoichiometry is defined as that amount of clay needed to react with the alkali metals present in the liquid waste feed such that the alkali metals are converted to

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crystalline minerals that are insoluble in water. The POHC (benzene) was fed concurrently with the simulant only during those tests where manual sampling of organic species in the off-gas took place. Instrumental analyses using the CPMS and CEMS were sufficient to determine relevant process gas and off-gas compositions for all other tests.

The feed utilized during the scoping tests was the baseline LAW simulant solution with radionuclide surrogates, heavy metals, and the POHC during selected tests. The conditions and principal focus of the various scoping tests, broken down by test number, are summarized in Table 5-1. This includes the conditions, the purpose, and the parameters for each individual test. As in previous tests, the shift engineers had the responsibility and discretion to direct adjustments to the DMR and CRR operating conditions to accommodate the changes in the process and feed parameters. Changes to process operation were implemented via Communication Sheets as required by the Testing Plan. [8]

Each of the seven scoping tests lasted 25 ± 6 hours. The JTG reviewed the value of performing scoping test S-3. The technical team decided that test S-3 would be eliminated from the test schedule, as the data from the test would be a repeat of data produced from other scoping tests. In particular, test S-1 already demonstrated operation of the DMR at 750°C and tests S-4 and S-5 demonstrated operations of the CRR at 850°C . CRR operations at 850°C during tests S-4 and S-5 bounded the S-3 test so that it was not beneficial to perform test S-3 as the data would already be generated by other tests. The JTG chose the conditions for test S-6 and S-7, based on the results of the previous scoping tests in order to optimize the DMR temperature for particles size control and fines generation and to optimize CRR temperature for off-gas quality.

In addition to the scoping tests, a series of bench scale crucible tests were performed to determine the propensity for the formation of glassy phases with various combinations of clay and the respective LAW and WTP SW simulants. Such glassy phase formation would likely indicate a tendency toward agglomeration formation in the DMR bed, which is undesirable. The crucible tests were patterned after tests developed by SRNL [3]. Based on the findings from the scoping tests and the crucible tests the JTG reviewed, set, and approved the test conditions for the production tests.

Table 5-1 Operating Conditions from Parametric Scoping Tests

Test Number	Start /Stop	Duration (hrs)	Feed	Feed Rate (gpm)	DMR Temp (°C)	CRR Temp (°C)	Approximate Clay Conc. (g/L)	POHC	Off-gas Testing Methods	Test Purpose
Preheat/ cure refractory	9 Apr 08:00/ 13Apr 04:45	92.75 hours	None	0	Per curing schedule		0	No	None	Bring system up to temperature
Water feed	15 Apr 02:30/04:00	1.5 hours	Water	~0.1	750	950	0	No	None	Initiate water feed
Shakedown/ tuning	15Apr 04:00/16:15 16Apr 1:30/11:00	21.72	LAW w/o HM	0.2	750	950	675	No	None	Shakedown of system, tune control loops
ART-S-1	16Apr 11:00/ 17Apr 16:30	29.5	LAW	0.2	750	950	675	No	29, 5/26A	Baseline DMR T, High CRR T, High clay ratio
ART-S-2	17Apr16:30/ 18Apr 19:30	27	LAW	0.2	800	950	675	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	High DMR T, High CRR T, High clay ratio
ART-S-3	DELETED	0	LAW	0.2	750	850	675	No	29, 5/26A	Baseline DMR T, Low CRR T, High clay ratio
ART-S-4	18Apr 19:30/ 19Apr 16:00	19.7	LAW	0.2	800	850	675	No	29, 5/26A	High DMR T, Low CRR T, High clay ratio
ART-S-5 ^{*1}	19Apr 16:00/ 21Apr 00:45	31.2	LAW	0.2	680	850	675	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	Low DMR T, Low CRR T, High clay ratio
ART-S-6 ^{#2}	21Apr 00:45/21:45	21	LAW	0.2	725	900	610	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	Optimum DMR and CRR T, Medium clay ratio
ART-S-7	22Apr 00:00/18:45	18.75	LAW	0.2	725	925	540	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	Optimum DMR and CRR T, Low clay ratio
	Total COT ³	168.87								

- * H₂O on for 1.6 hours during feed tank transfer while COT remained on for 1 hour of the time (4/20/08 20:16 to 21:17)
- # H₂O on for 2.2 hours while COT remained running (4/21/08 21:50-24:00)
- This is the Cumulative operating time (COT), which accrued only while simulant feed was flowing to the DMR.

5.3 Mineralizing Production Tests

The optimum process conditions utilized during the production runs were based, in part, on the results obtained from the scoping tests. Once the scoping tests were complete, the JTG reviewed the results to agree upon the preferred operating conditions for the DMR and CRR. As expected, the higher DMR operating temperatures produced better overall system performance. Balancing this fact against the need to protect the bed material from fusing, the JTG selected a DMR operating temperature for the production tests of 725°C, with a DMR feed rate of 0.2gpm. A CRR operating temperature of 950°C was chosen, as this temperature produced an acceptable final off-gas stream, without having to run at a higher temperature. Table 5-2 summarizes the production test conditions.

The success rate for production testing was improved by performing the scoping tests first, which explored bounding process conditions, helped identify the best operating conditions, and thereby reduced the chances of major process and equipment failures during the production tests. The production tests for the LAW surrogate solution with heavy metals were run with two different concentrations of mineralizing clay. The POHC (benzene) was added to the DMR during the scheduled tests so that the DRE of the combined DMR/CRR steam reforming system, under varying conditions, could be determined.

The second set of production tests was run with the WTP SW at what was considered to be a safe operating temperature, with the last 25 hours of operation at a higher temperature to provide data for establishing a reasonable operating range. The CPMS and CEMS were operational during the entire sequence of production run tests.

As the quality of the product produced would be a function of the clay concentration, which could not be determined analytically until after the completion of the test, the test team incorporated two clay mix ratios as part of the LAW production tests (675g/L – nominal mid-range, 640g/L nominal low-range).

Additional bench scale tests were conducted to determine the potential for WTP SW product to agglomerate at higher temperatures. Loss on Ignition (LOI) testing was performed on HTF and PR samples from both LAW and WTP SW production runs. The testing was conducted at 600, 700, 750, 850, 950 and 1200°C. The results are presented in Section 7, Test Observations and Results.

5.4 Bench Scale Steam Reformer Tests

A Bench scale Steam Reformer (BSR) was designed and constructed at the SRNL to treat actual radioactive wastes to confirm the findings of the non-radioactive FBSR pilot scale tests and to qualify the waste form for applications at Hanford. BSR testing with WTP SW waste surrogates and associated analytical analyses and tests of granular products and monoliths began in the fall of 2009, and then was continued from the fall of 2010 through the fall of 2011.

Radioactive testing commenced in 2010 with a demonstration of Hanford's WTP-SW where Savannah River Site (SRS) High Level Waste (HLW) secondary waste from the Defense Waste Processing Facility (DWPF) was shimmed with a mixture of $^{125/129}\text{I}$ and ^{99}Tc to chemically resemble WTP-SW. Prior to these radioactive feed tests, non-radioactive simulants were also processed. Ninety six grams of radioactive granular product were made for testing and comparison to the non-radioactive pilot scale tests. Results of BSR testing are presented in Section 11.

Table 5-2 Operating Conditions for the Production Tests

Test Number	Start /Stop	Test Duration (hrs)	Feed	Feed Rate (gpm)	DMR Temp (°C)	CRR Temp (°C)	Approximate Clay Conc. (g/L)	POHC	Off-gas Testing Methods	Test Purpose
ART-P-1A	27Apr 04:00/ 29Apr 07:15	50.6	LAW	0.2	725	950	675	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	Optimum DMR and CRR temperatures, Nominal mid-range clay stoichiometry
ART-P-1B	29Apr08:00/ 01May 11:00	50.9	LAW	0.2	725	950	640	Yes	29, 5/26A, 0023A, 0031, 0010, 0040	Optimum DMR and CRR temperatures, Nominal low-range clay stoichiometry
ART-P-1 Total		101.5								
ART-P-2A	02May 02:00/ 05May 07:30	75	WTP SW	0.2	680	950	307	No	29, 5/26A	Safe DMR T, Optimum CRR T, Low clay ratio
ART-P-2B	05May 07:30/ 06May 10:29	27	WTP SW	0.2	700	950	307	No	None	High DMR T, Optimum CRR T, Low clay ratio
ART-P-2 Total		102								
	Total COT	203.5								

6. QUALITY ASSURANCE/QUALITY CONTROL

The Quality Assurance (QA) Program implemented for the ART ESTD demonstration program was in accordance with the THOR Treatment Technologies, LLC (TTT) Quality Assurance Plan, Project Quality Procedures, and the TTT Quality Assurance Project Plan [9]. These documents are based on ASME NQA-1-2000 [24], DOE Order 414.1C [25], and 10 CFR 830.120 [26]. Personnel performing work at the pilot plant were trained to these documents and the implementing procedures and instructions to ensure that work was performed safely and in a consistent manner. Records for each individual were documented and maintained in the project training file.

The design and fabrication of the treatment system were conducted in a prescribed and controlled manner. The design documents for the system were generated in accordance to the TTT engineering procedures and approved by the TTT Testing and Operations Manager, TTT Chief Engineer, and the TTT QA Manager. Numerous procedures and work instructions were generated for the project and were controlled through the TTT Document Program. Records resulting from the project activities were retained temporarily onsite at Hazen or in the TTT Document Control System. Upon completion of all records, they were turned over to TTT Records Management for storage and archival. The records will be submitted to the client, as defined in the records submittal schedule. Archived records shall be maintained by Washington Division of the URS Corporation as defined in the TTT Final Disposition of Project Documents and Files procedure.

Items procured for the project followed the TTT and Hazen procurement procedures and processes. Receipt and inspection of these items were conducted at Hazen and logged upon receipt.

Data generated for the program were documented on data sheets, in logbooks, and electronically by the DACS managed with LabVIEW 7.1 software. Logbooks were controlled through Document Control and were issued to technical personnel for the project. Personnel documented their observations and activities in the logbooks, and initialed and dated each entry. Various data sheets were also used throughout the project to capture operational information and results and were maintained in binders. These data sheets were turned over to Records Management for storage, archival, and submittal to the client as defined in the approved submittal schedule.

The majority of the data collected for the testing and operations of the pilot plant were collected through the use of the DACS utilizing LabVIEW 7.1. The data were automatically backed up daily to ensure no loss of information. The software was subjected to various tests to ensure that it functioned properly on the various computer systems. A General Work Instruction [27] provided the testing, verification and validation of the system software used for the operations. The data collected by the system has been copied to electronic media, stored, and archived. It will be submitted to the client as defined in the approved submittal schedule.

Off-gas and solids sampling conducted during pilot plant testing was performed by trained and qualified personnel to prescribed procedures and methods as defined in the ART Test Plan [8] and the QAPP [9]. Instrumentation used to capture data and perform measurements was calibrated in accordance with GWI 3.2 [18]. Functional tests of these instruments and systems were performed prior to startup to ensure that the data generated would be acceptable and usable to meet the objectives of the tests, as described in Section 5.1.

Air Pollution Testing, Inc. (APT), the contractor hired to acquire these samples, collected samples for air emissions testing from the stack. APT also performed off-gas monitoring using the CEMS. All samples were drawn and prepared in compliance with the applicable EPA methods [12] for each analyte by APT. TestAmerica, Inc. performed the analytical analyses for each of the analytes in accordance the QAPP [9].

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A validation of the off-gas sample analytical data was performed in accordance with applicable procedures. The results of the validation are summarized in Appendix A.

Management assessments conducted in preparation for the test program addressed test readiness and emergency preparedness. Issues identified and related corrective actions are presented Table 6-1.

Six non-conformances were identified for activities or items related to plant operations and two deficiency reports were generated during the demonstration. The non-conformances were related to material receipt, stack gas samples shipped for analyses, and instrument calibration. The deficiencies resulted from receipt of chemicals at Hazen.

A surveillance was conducted at SRNL during the BSR test phase resulting in the issuance of a deficiency report. The report documents the failure to properly complete logbook entries.

These non-conformances and deficiencies have been closed and are presented, with associated corrective actions, in tables in Appendix B.

Table 6-1 ART ESTD Management Surveillances

Management Assessment Subject	Management Areas Addressed	Period of Performance	Comments Requiring Action	Corrective Action
ART Test Readiness	Environment, Safety, and Health Material Condition Plans, Procedures, and Training Design Drawings Design Input Design Process Design Verification Design Change Control Document Control	April 2008	Three NCRs had been issued as a result of material receipt verification. The process for material receipt inspection was deemed inadequate by the TTT QA Manager. The extent of conditions was determined to be minimal.	The TTT QA Manager conducted a review and upgrade of the receiving process and retrained personnel on material receipt inspection procedures.
ESTD Operations	Review of Adequacy of and Compliance with Field Work Procedures and Other Work Documents Field work procedures and documents	April 2008	The Solid and Liquid Sample Collection Log was reviewed for conformance with OI 3.5. Several entry lines were incomplete in that gross weights were not entered and in other cases, the entry was not initialed per Sec. 4.2.3 of OI 3.5. The Feed Makeup Log was also reviewed and was found to be complete.	Re-inspected the Solid and Liquid Collection Log on 4/28/08, all entries had been completed and the log appeared to be accurate.
APT Operations	Review of Adequacy of and Compliance with Field Work Procedures and Other Work Documents Field work procedures and documents	April 2008	A review of the sample collection datasheets was performed. Stop time was not recorded on S-4 and leak check was not recorded on S-1, S-5, and S-7. The COCs were reviewed. The collector signature/date and relinquished to signature/date were blank on all forms. The sample ID number entry fields were blank on all forms.	Re-inspected the APT offices and found the completion of the data sheets was in progress. The COCs were completed during the return review.

7. TEST OBSERVATIONS AND RESULTS

Pilot plant testing activities were initiated on April 7, 2008. These initial activities were focused on refractory curing, equipment checkout and functional testing. Scoping and production tests were performed from April 15, 2008, through May 6, 2008, with scheduled shutdowns for data evaluation, equipment maintenance, and system modification.

The scoping tests, intended to provide and verify the baseline operating conditions for the production testing operations, started on April 16 and were completed at 6:45 pm on April 22. Mineralizing production testing operations were initiated at 4:00 am on April 27, 2008, and were successfully completed at 10:30 am on May 6, 2008.

7.1 Scoping Tests

The main purpose of the scoping tests was to explore the upper and lower bounding temperatures for both the DMR and the CRR, help identify the best system operating conditions, and define a range of mineralizing clay stoichiometries that would generate an acceptable product. The mineralizing clay stoichiometry is defined as that amount of clay needed to react with the alkali metals present in the liquid waste feed such that the alkali metals are converted to crystalline minerals that are insoluble in water. The feed was the LAW simulant solution with heavy metals, or POHCs, as described in detail in Section 4. In addition to instrumental analyses using the CPMS and CEMS, manual sampling of stack gas was conducted. Based on the results of the scoping tests, the JTG set the operating conditions for the production tests.

The actual scoping tests were performed at the conditions depicted in Table 5-1. Table 7-1 details the operating period and presents a summary of the feed used and product materials produced during the scoping tests.

Table 7-1 Summary of Mineralizing Scoping Test Operations

Test	Start	End	Operating Hours	Simulant Processed (gal)	Product: DMR + PR (lb) (lb/hr)		Fines: OGF (lb) (lb/hr)	
Shakedown	04/15/2008 04:00	04/16/2008 11:00	21.72	269.87	225.41	10.38	1874.3	86.29
ART-S-1	04/16/2008 11:00	4/17/2008 16:30	29.5	361.52	276.42	9.37	1773.7	60.13
ART-S-2	4/17/2008 16:30	4/18/2008 19:30	27	330.89	21.62	0.8	1756.2	65.04
ART-S-4	4/18/2008 19:30	4/19/2008 16:00	19.7	243.51	46.38	2.35	1365.3	69.31
ART-S-5	4/19/2008 16:00	4/21/2008 00:45	31.2	383.8	727.56	23.32	1683.7	53.97
ART-S-6	4/21/2008 00:45	4/21/2008 21:45	21	256.27	220.89	10.52	1233.1	58.72
ART-S-7	4/22/2008 00:00	4/22/2008 18:45	18.75	229.45	249.61	13.31	861.6	45.95
Totals (including Shakedown)			168.87	2075.31	1767.89	10.01	10547.9	62.77
Product:Fines Ratio								0.17

A system readiness assessment and pre-operational checks were completed by April 7th and a controlled heat-up of the equipment for curing the new refractory in the DMR was initiated. During the refractory cure, several pieces of refractory were observed in the DMR bed samples. Consequently, the technical team decided to cool the DMR and inspect the refractory. The inspection revealed that ~12lb of refractory had spalled away during heat-up. The largest piece was approximately 8" x 6" x 1.5" and came from the vicinity of the joint between the upper and lower section of the DMR. The failure of the refractory was likely due to stresses imposed while assembling the expanded upper section. The JTG decided that the missing refractory would not need to be repaired since it represented a very small section of the abrasion-resistant refractory and only about half of its thickness. Following the clean-out, heat-up for the scoping tests was resumed.

Other items of note that occurred during the heat-up/refractory soak prior to the scoping tests were a reconfiguration of the CPMS, some asymmetric fluidization of the DMR bed, and an upgrade of the glycol pump. The CPMS reconfiguration was due to anomalies in the N₂ feedrate to the analyzers. FTCV-700-016 and FTCV-700-012 had identical N₂ flow, yet read significantly different flow values. It was determined that FTCV-700-012 was likely damaged by high temperature and moisture from being located upstream of the cooler/condenser. Until a replacement control valve was obtained, FCTV-700-016 was relocated downstream of the condenser/cooler and a rotameter was installed at its previous location. FTCV-700-012 was removed from the system. Asymmetric flowrate between the two DMR fluidizing gas rails was corrected by briefly suspending DMR operations, collapsing the bed and removing a couple of teaspoons of bed materials from inside each rail. A new glycol pump was installed to increase the injection rate of glycol.

During heat-up, operating and technical personnel familiarized themselves with the tuning and balancing of carbon and oxygen inputs to maintain stable operation. Once the system was up to temperature, the feed system was switched on and water was injected into the DMR through the feed injection nozzle. Water feed was added to the DMR while maintaining the baseline DMR and CRR operating temperatures. Once the DMR and CRR were stabilized using water feed, the feed was switched from water to LAW simulant. During the various tests, operational upsets and changes in the operational conditions occasionally required the water feed to be temporarily reinstated.

Simulant feed makeup was completed and LAW/clay slurry feed (without heavy metals) at a target feed rate of 0.1 to 0.2gpm was started to the DMR at ~4:00 am on April 15 to initiate shakedown/tuning. This test utilized a high target clay concentration of 675g/L. This test was performed to allow shakedown of systems and to tune various process control loops.

The feed system and DMR functioned well. No feed interruptions were experienced during the shakedown period. Multiple bed drains were conducted without issue. Bed temperature spreads and differential pressures ran as intended. The new disengaging section appeared to be functioning well, returning an acceptable fraction of product and carbon fines to the DMR for processing. Initial operating parameters were stable.

Figure 7-1 provides a timeline graphic for the period of April 14 through April 22, 2008.

Some above-bed oxidation was experienced in the CRR. This was due to the process gas from the DMR depleting the oxygen level in the CRR to the point that the glycol would volatilize and react above the bed, along with the oxygen injected into the upper part of the CRR bed. Operation was improved by increasing the CRR bed height, maintaining manual control of glycol injection to the CRR to ensure that oxygen levels were not depleted, and using carbon as a supplement temperature fuel source in the CRR. Also, the flow orifice for the glycol atomizing N₂ was increased in size. It was learned that an improved automatic control scheme for the CRR temperature would be to control on fuel input rather than O₂ input to the bed.

It was observed during the shakedown run that the OGF was not pulsing correctly, as the pressure drop across the OGF filter elements increased to 40 inches of water. Investigation revealed plugs had been installed in the vent lines of the N₂ purge system that prevented the N₂ valves from actuating. Removal of the plugs resolved the issue. The OGC temperature setpoint was increased to 225°C and the OGF blowback setpoint was decreased to 15" of water to control the outlet temperature and increase the pulse frequency of the OGF filter elements.

At 16:10 on April 15, the DMR temperature rapidly decreased due to a failed oxygen controller. Troubleshooting discovered a loose wire in the junction box caused the oxygen flow controller to fail.

Figure 7-1 Pilot Plant Activities for Scoping Test Period April 14 to April 22, 2008

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The shakedown/tuning was completed and Test ART-S-1 was started at 11:00 on April 16 by starting LAW feed with heavy metals. This test was performed to evaluate the baseline DMR temperature (750°C) with a high CRR temperature (950°C) and a high clay loading (675g/L). Process operation was generally acceptable. Most of the product was elutriating out of the DMR as fines. The fluidizing gas flow rate and atomizing air flow were decreased to reduce DMR bed loss.

A low flow system trip occurred while tuning the steam control valve. Although the FG steam and feed were restored promptly, the DMR O₂ flow was not restored for ~15 minutes. As a result, the DMR bed temperature dropped to 590°C before the O₂ flow was restored.

APT began sampling at 11:00 on April 17. Sampling consisted of Method 29 (metals) and Method 5/26A (PM/Cl₂). The moisture content was estimated at 52%. APT confirmed the actual moisture content was 51% and that isokinetic sampling conditions were met. Off-gas was clean with typical levels as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
30-50ppm	< 1ppm	300-500ppm	~95%	150-250ppm

At 16:30 on April 17 the operating conditions were changed for ART-S-2 test conditions: high bounding temperature for the DMR at 800°C while CRR temperature continued at 950°C. The feed conditions remained as before, LAW with heavy metals at 0.2gpm with a clay loading of 675g/L.

The feed system and DMR continued to operate smoothly. No plugging of the feed nozzle was experienced. Bed temperature spreads and differential pressures were as intended. Bed particle size was stable within the desired size range, with the presence of a few larger product pieces the size of grape seeds up to ¼" size nuggets. The DMR bed consisted of a mix of alumina start-up bed particles from S-1 and product granules. No bed was drained and no seed particle additions were made during ART-S-2. Essentially all mineral product material was elutriating out of the DMR as fines and was efficiently removed by the OGF. Operation of the DMR at 800°C instead of 750°C resulted in moderate reduction in coal usage. No DMR bed agglomerations were formed.

CRR and OGC operation were acceptable. CRR bed depth was stable at ~42 inches with no media addition during S-2. OGC and OGF operations were acceptable.

At 05:50 on April 18, POHC (benzene) addition to the DMR feed line commenced in anticipation of stack gas sampling. APT arrived at 0700 to calibrate the CEMS and prepare the collection of stack gas samples. Manual stack gas sampling consisted of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was split into two efforts. The morning sample collection consisted of metals and PM/Cl₂ that began at 09:00 and was completed at 12:17. The afternoon sample collection, organics and D/F/PCB, began at 13:15 and was completed at 16:20. CEMS readings were: O₂ – 5.6%, CO₂ – 16.0%, NO_x – 393ppm, H₂ – 5.1%, THC – 5.2ppm, and SO₂ – 229ppm. The injection of the POHC was terminated at the completion of off-gas sampling. APT reported successful isokinetics, 95.9-100.5%, for the sample collection effort. Moisture content was 50.5 to 53.2%.

The JTG reviewed the potential value of performing scoping test S-3 and decided that test S-3 would be eliminated from the test schedule, as the data from the test would be a repeat of data produced from other scoping tests. In particular, test S-1 already demonstrated operation of the DMR at 750°C and tests S-4 and S-5 would demonstrate operations of the CRR at 850°C.

At 19:30 on April 18, a change to operating conditions for ART-S-4 was initiated: DMR temperature of 800°C and CRR temperature of 850°C. The feed, LAW with metals, continued to be fed at 0.2gpm.

Early on April 19, at 0420, the ‘A’ feed nozzle plugged and feed was switched to the ‘B’ nozzle to continue operations. At 06:00, it was observed the CO emission had increased from 45 to 100ppm after reducing the CRR bed temperature to 850°C. NO_x system destruction efficiency was at 98%. APT arrived at ~07:00 to calibrate the CEMS and prepare for the collection of manual stack gas samples. At 0830, the stack gas CO emission level was still at 90-100ppm with the NO_x level at ~550ppm. NO_x system destruction efficiency was at 93%. SO₂ was at 50ppm.

At 08:41 the CRR outlet O₂ control setpoint was increased from 4 to 6%. This resulted in a decrease of the stack CO from ~100ppm to 65-70ppm. The added O₂/N₂ feedrate was 10 scfm at ~4% dilution. The stack gas NO_x level increased from 550ppm to 590ppm.

APT began sampling at 10:02. Sampling consisted of Method 29 (metals) and Method 5/26A (PM/Cl₂). APT completed the collection of manual samples at 13:17 and reported successful isokinetics: 96.8-97.8%, for the sample collection effort. Moisture content was 46.9 to 47.5%. The OGF pulse logic was not pulsing all of the filters as the pressure drop across the OGF filter element dropped below 15”. This was corrected by manually pulsing the filters at ~1 hr intervals.

Overall operation during ART-S-4 conditions was acceptable. Bed temperature spreads and differential pressures were as intended. Average DMR bed particle size, as indicated by the harmonic mean particle diameter (HMPD), was stable within the desired size range, with the presence of a few larger product pieces up to 3/8” in size. Essentially all mineral product material was elutriating out of the DMR as fines. No bed agglomerations were formed. Removal of the fines by the OGF was a smooth and consistent operation. CRR operation was acceptable. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
30-50ppm (after increasing CRR freeboard O ₂ to 8%)	< 1ppm	500-700ppm (~200ppm higher than before due to lower CRR temp)	~93%	0-20ppm (Large reduction in SO ₂ emissions is likely due to retention of sulfur in nosean in the solid product fines due to more oxidizing CRR conditions)

At 16:00 on April 19, the change of operating conditions for ART-S-5 was initiated: DMR temperature of 680°C and CRR temperature of 850°C. The feed, LAW simulant with metals, continued to be fed to the DMR at 0.2gpm. At 16:45, it was observed that the OGF product flow had ceased. The drum tube was disassembled and a piece of tape was removed from the tube. The drum tube was re-assembled and functioned correctly.

Early in the morning of April 20, the CRR bed height was raised by adding more alumina bed media. By 03:30, a total of 320lb had been added to the CRR. At 02:15, it was noted that with the DMR bed temperature at 680°C bed production was increasing. Samples from the product receiver appeared significantly finer in particle size, possibly due to the auger/grinder. At a DMR bed temperature of 680°C, H₂ generation had decreased.

At 06:00, POHC feed was initiated to achieve scoping test ART-S-5 conditions for stack sampling.

APT arrived at 07:00 to calibrate the CEMS and prepare the collection of stack gas samples. Manual stack gas sampling consists of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was split into two efforts. The morning sample collection consisted of metals and PM/Cl₂ which began at 09:00 and was completed at 14:30. CEMS readings were: O₂ – 12.1%, CO₂ – 12.9%, NO_x – 692ppm, THC – 0.13ppm, CO – 102ppm, and SO₂ – 0ppm. A delay in completing the metals and PM/Cl₂ occurred just after the traverse. The CEMS system began giving erratic readings at ~10:30. The system was repaired with a new condenser/filter and an additional gas sample line.

The DMR bed HMPD had grown from 280 µm at the start of ART-S-5 to over 400 µm. To address this increase, the DMR atomizing air flow rate was increased and DMR bed product was screened at 50 mesh (~300µm) for later use as seed particle material. APT completed the metals and PM/Cl₂ manual sampling at 14:30. At 15:00, the CRR O₂ setpoint was increased to 10% to lower the stack CO levels. This change, however, did not appear to affect the stack CO levels.

The afternoon sample collection, organics and D/F/PCB, began at 15:30 and was completed at 18:45. CEMS readings were: O₂ – 11.4%, CO₂ – 13.6%, NO_x – 577ppm, THC – 0ppm, CO – 92.8ppm, and SO₂ – 26.9ppm. The injection of the POHC was terminated at the completion of off-gas sampling. APT reported successful isokinetics, 96.8-101.5%, for the sample collection effort. Moisture content was 44.6% to 46.5%.

Overall process operation during ART-S-5 was acceptable. Bed temperature spreads and differential pressures were as intended. Average bed particle size had steadily increased at the lower temperature condition of 680°C from ~280 µm to over 400 µm. However, it stabilized around 400 µm following the adjustment of the DMR atomizing air flow rate. DMR bed drains increased in frequency to every hour-and-a-half, with a greater percentage of the product coming off the bottom of the DMR. The lower temperature of ART-S-5 (680°C) clearly resulted in much more particle growth and less fines generation than the higher temperatures of ART-S-2 and -4. CRR operations were acceptable with a stable bed depth. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
70-100ppm	< 1ppm	600-800ppm	~88%	0-20ppm

The preparations for transitioning to the test conditions for ART-S-6 began at 20:00. The JTG chose the operating conditions of the DMR (725°C) and CRR (900°C) to optimize the DMR temperature for particle size control and fines generation and to optimize CRR temperature for off-gas quality. The feed, LAW with metals, continued at 0.2gpm; however, the clay concentration in the feed was reduced to 610g/L.

The CRR bed temperature of 900°C was reached at 00:45 on April 21 for the start of ART-S-6. NO_x destruction was above 90%, the CRR outlet O₂ setpoint was at 10%, and the stack SO₂ level had increased from 8 to ~20ppm. CO levels decreased from ~100 to ~65ppm.

APT arrived at 07:00 to calibrate the CEMS and prepare for the collection of stack gas samples. Manual stack gas sampling consisted of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was again split into two efforts. The morning sample collection, organics and D/F/PCB, began at 08:45 and was completed at 11:42. CEMS readings were: O₂ – 9.1%, CO₂ – 11.5%,

NO_x – 399ppm, THC – 0ppm, CO – 55ppm, and SO₂ – 50.7ppm. The injection of the POHC was terminated at the completion of the morning off-gas sampling.

The afternoon sample collection consisted of metals and PM/Cl₂ that began at 13:00 and was completed at 16:32. CEMS readings were: O₂ – 12.8%, CO₂ – 12.5%, NO_x – 584ppm, THC – 0.6ppm, CO – 34.6ppm, and SO₂ – 2.3ppm. APT reported successful isokinetics, 103.1-105%, for the sample collection effort. Moisture content was 47.5% to 50.8%.

At 17:10 a test for SO₂ generation in the CRR was commenced. The lower ATG flow was used to control bed temperature while running the glycol to keep TC-300-009 above the bed TCs. The lower ATG flow rate was decreased. The SO₂ concentration began increasing while the NO_x concentration decreased. There appeared to be a correlation between the lower ATG O₂ flow and the SO₂ and NO_x concentrations in the stack. Decreasing the ATG O₂ flow rate had a continued similar affect on the SO₂ and NO_x concentrations. At 18:05, the ATG flow rate was decreased while adjusting the glycol flow to keep TC-300-009 at 915 to 920°C. Keeping the glycol feed constant caused the opposite effect from turning the O₂ down; hence, the NO_x, SO₂, and CO remained about the same. When the ATG flow rate was decreased, the following readings were observed: NO_x – 384ppm, CO – 44ppm, SO₂ – 4.5ppm, and O₂ – 9%.

Overall process operation during ART-S-6 was acceptable. Bed temperature spreads and differential pressures run intended. Average DMR bed particle size decreased at the higher temperature condition from ~400 µm to ~300 µm. About half as much product was coming off the bottom of the DMR as compared to ART-S-5. The higher DMR temperature of ART-S-6 (725°C) clearly resulted in less particle growth and more fines generation than the lower temperature of ART-S-5. CRR operation was satisfactory with a steady bed depth. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
15-40ppm	< 1ppm	300-600ppm	~93%	0-60ppm

The preparations for transitioning to the test conditions for ART-S-7 began at 19:30 on April 21. The JTG chose the operating conditions of the DMR (725°C) and CRR (925°C) to optimize the DMR temperature for particle size control and fines generation and to optimize the CRR temperature for off-gas quality. The feed, LAW with metals, continued at 0.2gpm; however the clay concentration in the feed was reduced to 540g/L.

APT arrived at 07:00 on April 22 to calibrate the CEMS and prepare the collection of stack gas samples. Manual stack gas sampling consists of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was split into two efforts. The morning sample collection, organics and D/F/PCB, began at 09:00 and was completed at 12:48. CEMS readings were: O₂ – 11.8%, CO₂ – 12.9%, NO_x – 258ppm, THC – 0ppm, CO – 16.1ppm, and SO₂ – 0ppm.

The afternoon sample collection consisted of metals and PM/Cl₂ that began at 13:20 and was completed at 16:48. CEMS readings were: O₂ – 10.7%, CO₂ – 14.6%, NO_x – 334ppm, THC – 0ppm, CO – 24.7ppm, and SO₂ – 0ppm. The injection of the POHC was terminated at the completion of off-gas sampling. APT reported successful isokinetics, 104.0-105.3%, for the sample collection effort. Moisture content was 49.9% to 50.0%.

At 16:38 it was noted that the CRR bed height and average particle size had been increasing since 00:00 coinciding with the change to scoping test ART-S-7 conditions. The CRR bed sample collected at 10:23

indicated the particles were coated with a light grey material, probably due to partially mineralized product carryover from the DMR.

At 1800, another series of SO₂ production tests were conducted. The initial conditions were: CRR bed temperature of 923°C, lower ATG stable, glycol feed at 66%, CO at 12.9ppm, NO_x level of 378ppm and SO₂ at 2.2ppm. At 1801, the glycol was increased to 70% and the ATG was reduced. The CRR bed temperature remained stable at 923°C. At 1812, the conditions were: CO at 10.7ppm, NO_x level of 360ppm, THC at 0.03ppm, O₂ at 7%, and SO₂ at 2.2ppm. At 1813, the lower ATG was reduced further. At 1817, the conditions were: CO at 10.4ppm, NO_x level of 315ppm, THC at 0.02ppm, O₂ at 5.4%, and SO₂ at 1.1ppm. At 1818, the lower ATG flow rate was decreased to zero. At 1824, the conditions were: CO at 8.2ppm, NO_x level of 230ppm, THC at 0.03ppm, O₂ at 4.6%, and SO₂ at 1.1ppm.

At 1826, the upper ATG was reduced. At 1830, the conditions were: NO_x level of 151ppm, THC at 0.03ppm, O₂ at 2.1%, and SO₂ at 19.5ppm. At 1833, the upper ATG was reduced. At 1836, the conditions were: NO_x level of 125ppm, CO at 11.2ppm, THC at 0.04ppm, O₂ at 0.12%, and SO₂ at 135ppm. At 1842, the conditions were: NO_x level of 145ppm, CO at 6.7ppm, THC at 0.07ppm, O₂ at 0.12%, and SO₂ at 1.4ppm.

Overall process operation during ART-S-7 was acceptable. Bed temperature spreads and differential pressures ran as intended. Average bed particle size steadily increased from ~300 μm to ~425 μm. The product mass coming off the bottom of the DMR was approximately midway between that for ART-S-5 and ART-S-6. CRR operation was steady with a bed depth of ~45 inches. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
1-20ppm	< 1ppm	250-500ppm	~95%	0-250ppm

At 1845 a controlled shutdown of the process was initiated, thus concluding the scoping test portion of the project.

7.2 Production Tests

Production tests were performed from April 27 to May 1, 2008 for the LAW and from May 2 to May 6, 2008 for the WTP SW. The process operating conditions for the production run tests were established by the JTG, based on the results of the scoping tests. The LAW production tests utilized LAW simulant, including heavy metals, at two different concentrations of mineralizing clay. The POHC (benzene) was added to the DMR at appropriate times so that the organic DRE of the combined DMR/CRR steam reforming system under varying conditions could be determined. The WTP SW production run tests were run at two different DMR temperatures with a single mineralizing clay concentration. No POHC was added to the DMR during the WTP SW tests, as the WTP SW waste stream is not projected to contain organics.

The primary objective of the production runs was to operate the steam reforming system for significant periods of time so that the system and the DMR product composition could be evaluated. Section 5.3 of this report describes the planned scope of these tests and the general conditions under which the tests were performed.

Each test was performed in accordance with the approved test plan and operating procedures. Data were subjectively assessed based on CPMS and CEMS monitors being lined out, liquid feed continuing uninterrupted, all required liquid and solid samples being obtained, documentation of test conditions, and

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all scheduled manual stack gas sampling iterations being completed and determined acceptable by the sampling contractor.

Figure 7-2 provides a timeline graphic for the ART-P-1 test. Table 7-2 provides a summary of the operating period for ART-P-1 and the feed and products.

During the shutdown prior to the production tests a number of maintenance items were performed. The major items were:

- Putting the HTF in service and installing a product removal auger on the HTF outlet.
- Cleaning the feed nozzles
- Removing and replacing DMR and CRR bed material
- Replacing the OGC nozzle
- Cleaning out the OGC and OGF inlet pipe

At 07:52 on April 25, communication sheet P-1 was issued to initiate heat-up of the system. By 10:56, new alumina bed material had been added to the CRR to achieve a fluidized bed height of 36". By midnight the natural gas burner was switched off and the CRR heat-up was progressing well with glycol feed.

At 04:40 on April 26, the DMR was brought online and the CRR had reached its target temperature of 950°C. By 20:43 the DMR had reached 350°C and the heat-up was continuing with charcoal. The carbon source was switched to coal at 23:35.

Test P-1A operating conditions had been reached by 02:52 on April 27. Water feed was initiated followed by simulant feed to the DMR at 04:00. The operating parameters for production test ART-P-1A were: DMR temperature, 725°C and the CRR temperature: 950°C. The feed, LAW with metals and POHC, was being fed at 0.20gpm, with a mineralizing clay concentration of 675g/L.

Table 7-2 Summary of Feed and Products for ART-P-1

Test	Start	End	Operating Hours	Simulant Processed (gal)	Product: DMR + PR (lb) (lb/hr)		Fines: HTF (lb) (lb/hr)	
ART-P-1A	04/27/2008 04:00	4/29/2008 07:15	50.6	604.29	853.71	16.87	2843.4	56.19
ART-P-1B	4/29/2008 08:00	5/1/2008 11:00	50.9	588.92	749.95	14.73	2947.7	57.91
Totals			101.5	1193.21	1603.66	15.8	5791.1	57.06
Product:Fines Ratio								0.28

At 03:46 on April 27, a sample of the HTF was taken and observed to be black in color with high carbon content. Microscopic analysis indicated the sample to be separate particles of attrited coal and bed material. At 04:00 simulant feed was initiated to start ART-P-1A. At 07:20, steam flow to the DMR was lowered to reduce the SSV at the distributor. It was observed that a decrease in fluidization velocity had improved the HTF operating conditions. The differential pressure across the HTF filter elements dropped from 25" to 12" within ~10 minutes. At 11:00, APT calibrated the CEMS.

At 16:45 the carbon feed to the CRR was shut off to determine if CRR temperature could be maintained by glycol alone. By 18:00 the CRR temperatures had stabilized around 940°C without any DMR bed drains. It was felt that the next DMR bed transfer would reduce CRR temperatures to the point that glycol alone would not be able to recover the temperatures, so the carbon feed was placed back on line. After draining bed from the DMR at ~21:00 the CRR bed temperature dropped to about 935°C. With the carbon feeder set at 15% and the glycol at 100% the CRR bed temperature, was recovered to 950°C in ~15 minutes.

Between 20:11 and 21:42, samples were collected from the DMR, PR, and HTF. Samples of the DMR bed contained a few bare alumina particles, with some ~¼-inch nuggets. No bed agglomerations were formed. The PR sample contained smaller nuggets, with ~10-20% alumina particles. The HTF sample was mostly light colored product particles, with some small coal particles.

At 23:45, water feed was initiated during the transfer from feed tank 101B to tank 101A. Feed pressure with water was ~3 psig and 20 psig with simulant. At 24:28, simulant feed was resumed.

At 04:00 on April 28, carbon feed to the CRR was again shut off. The bed temperature barely held at 949°C with glycol feed in manual at maximum flow of 0.11gpm, the lower ATG O₂ setpoint was stable, and the upper ATG O₂ set at 6%. At 05:57 the carbon feed to the CRR was restored to ~3lb/hr. The lower ATG O₂ setpoint was stable with 6% excess O₂. APT arrived at 07:00 to calibrate the CEMS and prepare the collection of stack gas samples. Manual stack gas sampling consisted of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was split into two efforts. The morning sample collection, organics and D/F/PCB, began at 09:20 and was completed at 12:57. CEMS readings were: O₂ – 8.9%, CO₂ – 12.9%, NO_x – 628.8ppm, CO – 0ppm, and SO₂ – 20.4ppm.

The afternoon sample collection consisted of metals and PM/Cl₂ that began at 13:30 and was completed at 17:25. CEMS readings were: O₂ – 10.1%, CO₂ – 14.9%, NO_x – 727.1ppm, CO – 0ppm, and SO₂ – 30.6ppm. The injection of the POHC was terminated at the completion of the off-gas sampling. APT reported successful isokinetics, 93.0-94.7%, for the sample collection effort. Moisture content was 49.2% to 50.3%.

At 17:22, the CRR outlet O₂ concentration was reduced to 4% to decrease the NO_x levels at the stack. Samples of the HTF were obtained for LOI analysis. The result was 10.8% mass loss. At 20:30, the atomizing air was increased to control the DMR bed material PSD, as the last HMPD exceeded 400µm. The CEMS experienced a power failure at 19:39 and again at 20:07 due to a tripped breaker. The power supply was switched to a separate circuit to correct the problem. At 22:30, fresh media was added to the CRR bed. The DMR bed drain at 23:36, produced 32.3lb and lowered the bed height from 45” to 41”.

After ~35 hours of operation under ART-P-1A conditions, the feed system and DMR operations had been very satisfactory. Feed nozzle A was operating well; feed rate was constant and pressures on atomizing gas and liquid feed lines were well behaved. Bed temperature spreads and differential pressures were running as intended. Average bed particle size increased to ~360 microns from ~280 microns 24 hours previous. Product was being drained from the DMR approximately every four hours. About 25% of DMR product was going to the PR, with the remainder to the HTF. CRR operation was acceptable, although a small amount of carbon was still required to get adequate fuel into the unit. OGC, OGF, and balance of plant were operating well. Typical off-gas values were:

CO	THC	NO _x	NO _x Destruction	SO ₂
0-50ppm	< 1ppm	400-700ppm	~93%	20-80ppm

At 01:06 on April 29, the carbon feed to the CRR was stopped with the bed height at ~45". At 03:48 the CRR O₂ outlet was lowered from 4% to 3% and the atomizing air setpoint was decreased. It was observed over the previous 24 hours that the HTF fines grew lighter in color and the stack SO₂ decreased from 60-90ppm to 27-40ppm. However, stack NO_x levels increased from 420-460ppm to 750-800ppm. At 05:33, it was observed that lowering the CRR outlet O₂ concentration from 4% to 3% lowered the stack NO_x from 620-680ppm to 570-640ppm and CO levels decreased from 0-50ppm to mostly 0ppm.

After ~51 hours of operation under ART-P-1A conditions, the feed system and DMR operations had been very satisfactory. Feed nozzle A was operating well; feed rate was constant and pressures on atomizing gas and liquid feed lines were well behaved. Bed temperature spreads and differential pressures were running as intended. Average bed particle size was stable at ~400 microns. Product was being drained from the DMR approximately every five hours. About 15% of DMR product was going to the PR, with the remainder to the HTF. CRR operation was acceptable, although a small amount of carbon was still required to get adequate fuel into the unit. OGC, OGF, and balance of plant were operating well. Typical off-gas values were:

CO	THC	NO _x	NO _x Destruction	SO ₂
<1ppm	< 1ppm	300-700ppm	~91%	20-40ppm

At 08:00 feed was transferred from Tank 101B to Tank 101A. This initiated the start of production test ART-P-1B at a clay concentration of 640g/l LAW. Other test conditions for ART-P-1B were: DMR temperature - 725°C and the CRR temperature, 950°C. The feed was LAW with metals, mineralizing clay, and POHC, fed at 0.20gpm.

At 11:15 carbon addition resumed to the CRR. Above-bed temperatures were greater than 50°C higher than bed temperatures when controlling those temperatures with glycol rate only.

At ~15:00 the carbon rate to the DMR was increased (to increase H₂ concentration) and fresh media was added to the CRR (to increase bed height to 46 inches). At 18:00 the carbon feed rate was 43lb/hr with H₂ concentration in the DMR ~1.7-1.8%. NO_x drifted down to ~580ppm and SO₂ rose to about 56ppm.

APT arrived at 07:00 on April 30 to calibrate the CEMS and prepare the collection of stack gas samples. Manual stack gas sampling consisted of Method 29 (metals), Method 5/26A (PM/Cl₂), Method 0023A (D/F/PCB), Method 0031 (VOC), Method 0010 (SVOC), Method 0040 (Field GC), and Method 010 (TCO/Grav). The sampling effort was split into two efforts. The morning sample collection, organics and D/F/PCB, began at 09:20 and was completed at 12:57. CEMS readings were: O₂ – 8.9%, CO₂ – 12.9%, NO_x – 628.8ppm, CO – 0ppm, and SO₂ – 20.4ppm.

The afternoon sample collection consisted of metals and PM/Cl₂ that began at 13:30 and was completed at 17:25. CEMS readings were: O₂ – 10.1%, CO₂ – 14.9%, NO_x – 727.1ppm, CO – 0ppm, and SO₂ – 30.6ppm. The injection of the POHC was terminated at the completion of off-gas sampling. APT reported successful isokinetics, 93.0 - 94.7%, for the sample collection effort. Moisture content was 49.2% to 50.3%.

At 18:15 the atomizing gas rate was decreased to increase DMR bed particle size. Another LOI was performed at noon on an HTF sample. Loss was measured at 11.5%.

At 19:30 the fluidizing gas steam PCV setpoint was reduced. This was done to help eliminate the oscillation on the steam control valve. While making the change, the steam flow fell below the low flow

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trip point, which caused the feed and O₂ to the DMR to go off. Conditions were restored to pre-trip values after about 3 minutes.

During the 23:20 bed drain the stack NO_x on the CEMS increased substantially due to low DMR H₂ (0.8-1.0%), with the carbon feedrate at 18lb/hr.

At 01:58 on May 1 the DMR carbon feedrate was increased to 30lb/hr and 10lb of additional carbon were added to the DMR bed to recover from the low carbon inventory in the bed.

At ~ 05:45 the differential pressure across the DMR distributor jumped up and caused steam flow oscillations to increase. At 07:30 the atomizing gas rate was increased to control particle size (latest HMPD was 450 μm). Also, the simulant feed rate was reduced to 0.15gpm from 0.2gpm to ensure the feed lasted to the end of the 100 hour test.

ART-P-1 test concluded with the COT clock at 101.5 hours at 11:00, at which time a controlled process shutdown was initiated.

During the ART-P-1 test the feed system and DMR operated well. Feed nozzle A continued to operate properly and was flushed with water when simulant feed was terminated. Average bed particle size was controlled in the 250 to 450 micron range for the duration of the production test.

The CRR and balance of the process operated well. As expected, the higher CRR temperature, compared to the last scoping test, produced a better overall NO_x destruction efficiency. Figure 7-2 provides a timeline graphic for the ART-P-1 test period.

Figure 7-2 Pilot Plant Activities ART-P-1 Test Period: April 26 to May 2, 2008

Figure 7-3 Pilot Plant Activities for ART-P-2 Test Period: May 2 to May 6, 2008

Table 7-3 Product Summary for ART-P-2

Test	Start	End	Operating Hours	Simulant Processed (gal)	Product: DMR + PR (lb) (lb/hr)		Fines: HTF (lb) (lb/hr)	
ART-P-2A	5/2/2008 02:00	5/5/2008 07:30	75	899.56	1001.1	13.35	2766	36.88
ART-P-2B	5/5/2008 07:30	5/6/2008 10:29	27	323.49	334.34	12.38	1025.6	37.99
Totals			102	1223.05	1335.44	13.09	3791.6	37.17
Product:Fines Ratio								0.35

At 16:45 on May 1, 2008 bed was added to the DMR and heat-up for ART-P-2A was initiated. The heat-up progressed smoothly and by 01:25 on May 2, H₂O feed to the DMR was initiated.

At 02:00 ART-P-2A was officially started by beginning WTP SW simulant feed, with 307g/L mineralizing clay, @ 0.2gpm. The DMR was at 680°C and the CRR was at 950°C. DMR coal was being fed at 35lb/hr. Glycol, supplemented with carbon at ~4lb/hr, was being used to maintain temperature in the CRR. Typical CEMS readings were O₂ ~ 6.8%, CO₂ ~ 17.1%, NO_x ~ 493ppm, and SO₂ ~ 10%.

At 3:30 200lb of alumina bed media were added to the CRR. Shortly thereafter, at 04:05, the carbon feedrate to the DMR was increased to 40lb/hr. The H₂ concentration had been ~1.4% (dry basis).

At 08:35 the feed was switched to water while the repaired rotary lobe pump was put back on line. Simulant flow was restored after three minutes and fluctuations were reduced.

Due to nuggets in the bed samples that appeared to potentially contain some glassy phases, Communication Sheet P2-7 was executed at 12:30 to reduce the O₂:N₂ ratio and to reduce the steam fluidization rate. No bed agglomerations were formed.

At 15:45 the atomizing air was increased to improve nozzle performance.

At 21:30 feed was switched to nozzle "B" to decrease feed pressure variations and to get more operating time on nozzle "B".

At 23:34 the CRR upper ATG nozzle flow was set to a constant value to see if CRR bed temperature swings were related to changes in the upper ATG flow rate.

A general assessment of the first 14 hours of operation with the WTP SW feed was as follows:

The feed system and DMR operations were very satisfactory. Feed was stable, particularly after the switch to nozzle "B" was made. Average bed particle size was 260 µm with a slow upward trend. Bed temperature spreads and differential pressures were as intended. Some small nuggets in the bed samples were observed and measures were taken to reduce the potential for localized hot-spots. No bed agglomerations were formed. The CRR operation was acceptable with a combination of glycol and carbon. The balance of the plant was operating smoothly. Typical off-gas values were as shown below, although the NO_x destruction readings had not been adjusted for the new feed composition.

CO	THC	NO _x	NO _x Destruction	SO ₂
<1ppm	< 1ppm	300-650ppm	-	10-15ppm

At 00:02 on May 3, O₂ flow to the upper ATG was increased, as the CRR outlet O₂ concentration had dropped to 0.6% and the stack CO was >500ppm.

The NO_x analyzer malfunctioned at about 00:50 due to a bad ozonator. NO, NO₂, and NO_x readings were erroneous until 10:17.

At 10:40 the DMR coal feedrate was decreased to ~33lb/hr.

At 16:20 the DMR coal feedrate was increased from 26 to 28% (~32-35lb/hr).

At 19:45 the DMR FG flow rate was decreased and the DMR atomizing air flow rate was decreased to try to retain more solids in the DMR bed.

DMR carbon feedrate setpoint was reduced from 28 to 27% at 22:42, as the DMR H₂ was approaching 2%.

The general assessment of the ESTD plant operations after nearly 40 hours of WTP SW feed was that the feed and DMR operations were acceptable. Average particle size was about 280 μm, with a slow upward trend. Bed temperature spreads and differential pressures were as intended. Some small nuggets continued to appear in the bed samples but the number and size were not increasing. No bed agglomerations were formed. XRD analysis on the HTF and DMR products showed them to be the expected alkali aluminosilicate minerals. The CRR operation continued smooth with a combination of glycol and carbon. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
<1ppm	< 1ppm	600-750ppm	~89%	10-20ppm

At 04:07 on May 4, process conditions necessary to repair the DMR shot pot 3-way valve were established.

At 04:57 the DMR atomizing flow rate was increased. The average particle size had increased from ~295 to 350 μm over the previous 8 hours. This change was executed at COT 50.0 hours to allow the DMR to stabilize after the repairs to the shot pot valve and restoration of the feed.

Process operations continued at production test ART-P-2A conditions: DMR at 680°C, CRR at 950°C, WTP SW feed at 0.2gpm, DMR carbon feedrate at ~34lb/hr. CEMS readings were O₂ – 6.5%, CO₂ – 15.3%, NO_x – 592ppm, and SO₂ – 13.5ppm. DMR outlet H₂ was ~1.2%. HMPD-12 mesh at 08:00 was ~370 μm.

At 08:20 APT started sampling. Sampling consisted of Method 29 (metals) and Method 5/26A (PM/Cl₂). Sampling was completed by 11:35. APT data: M29 - 49.2% H₂O, 103% isokinetic; M26A – 50.1% H₂O, 104% isokinetic.

At 21:18 the atomizing air flow was increased and the fluidizing gas flow rate was reduced to help maintain the particle size distribution. The HMPD at 16:00 was ~395 μm.

General process operations remained very stable during the first 60 hours of operation at ART-P-2A conditions. Feed nozzle “B” continued to perform well, with a stable simulant feed rate and steady liquid and atomizing gas line pressures. Average DMR bed particle size was ~380 μm, with a slow upward trend. DMR bottoms product increased from about 12% earlier in the test to about 33%, due to recent reductions in fluidizing steam flow rate and fluidizing gas velocity at the bottom of the bed. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
<1ppm	< 1ppm	550-650ppm	~91%	10-15ppm

At 01:55 on May 5, the atomizing air flow was increased. During the early morning hours of May 5, various muffle furnace tests were conducted on the DMR product to investigate the possibility of increasing the DMR operating temperature for the latter part of the P-2 test.

At 07:26 the DMR operating temperature setpoint was raised to 700 °C. This ended test P-2A and started test P-2B.

At 10:20, in order to better control the DMR bed particle size, the atomizing air was increased; also the lower bed O₂:N₂ ratio was decreased.

As of 12:22 the quality of the CPMS readings started to degrade, because FTCV-700-016 was reading a flow rate of ~10 L/min, but only flowing ~6 L/min. Operation continued with a Brooks rotameter, calibrated using the O₂ analyzer to provide the 5X dilution.

At 15:20 a bridge was noted in the OGF and ~408.4lb of material were removed. CEMS reading were not valid from 15:20 to ~16:00, since air was drawn into the system during the removal of the bridged material in the OGF.

At 19:25 the DMR carbon addition setpoint was increased from 28 to 29% and 5lb of carbon were added to the DMR immediately. The stack NO_x had been increasing all day since the DMR bed temperature was increased.

At 22:27 the DMR carbon feedrate setpoint was again increased to 30% to continue trying to increase DMR H₂ and decrease stack NO_x.

Through nearly 90 hours of operation, the general process operation remained very stable. Average DMR bed particle size was ~430 μm with a continued slow upward trend. Atomizing airflow was increased to control particle size. Bed temperature spreads and differential pressures were as intended. A few nuggets (up to ~1/2" in size) were still being observed in the bed samples, but the number and size were not increasing. DMR bottoms products were running ~27% of total DMR product mass (little change from the previous 24 hours). No bed agglomerations were formed. The balance of the plant continued to operate smoothly. Typical off-gas values were as shown below:

CO	THC	NO _x	NO _x Destruction	SO ₂
<3ppm	< 1ppm	350-650ppm	~90%	5-15ppm

At 10:29 on May 6, 2008 ART P-2B was officially concluded and a shutdown per OI 3.9 at a COT of 102 was initiated. Figure 7-3 provides a timeline for the ART-P-2 test period and Table 7-3 provides a summary of the operating period for ART-P-2 and the feed and the products.

7.2.1 Production Test Operating Conditions

The production mineralizing tests included four sets of operating conditions, which varied simulant feed composition, clay concentration and DMR operating temperature. The desired process setpoints may be found in Section 5. The average operating conditions for each production test condition may be found in Table 7-4 through Table 7-6.

Table 7-4 Summary of DMR Production Test Operational Parameters

Condition		LAW			WTP SW		
		ART-P-1A	ART-P-1B	Entire P-1	ART-P-2A	ART-P-2B	Entire P-2
Start		4/27/2008 04:00	4/29/2008 08:00		5/2/2008 02:00	5/5/2008 07:30	
Finish		4/29/2008 07:15	5/1/2008 11:00		5/5/2008 07:30	5/6/2008 10:29	
Duration	Hours	50.6	50.9	101.5	75	27	102
Simulant	gpm	0.20	0.19	0.196	0.19	0.20	0.20
N ₂ purge	scfm	53.6	56.3	55.0	53.4	52.5	53.2
DMR coal	lb/hr	36.7	32.8	34.7	35.6	44.0	37.8
DMR Gas Additions	scfm	43.6	44.4	44.2	48.5	49.0	48.5
HTF	Δp (inches water)	21.0	22.1	21.6	25.6	27.1	26.2
DMR freeboard pressure	psig	4.1	4.1	4.1	4.2	4.3	4.2
DMR bed height	inches	45.8	45.3	45.6	44.5	45.5	44.8
DMR bed fluidized specific gravity	—	0.70	0.67	0.68	0.85	0.69	0.81
DMR - bed temp. (6" NNW)	°C	726	725	725	680	702	686
DMR - bed temperature (24" E)	°C	726	725	726	679	700	685
DMR - freeboard temperature (92" S)	°C	711	718	715	677	694	682
DMR - outlet gas temperature	°C	600	620	610	589	602	592
HTF outlet gas temperature	°C	451	464	457	448	454	449

Table 7-5 Summary of CRR and Off-gas Production Test Operational Parameters

Condition		LAW			WTP SW		
		ART-P-1A	ART-P-1B	Entire P-1	ART-P-2A	ART-P-2B	Entire P-2
CRR Gas Additions	scfm	78.6	61.5	70.0	66.0	67.1	66.3
CRR outlet O ₂ (%)	%	4.7	3.0	3.9	3.1	3.0	3.1
CRR carbon	lb/hr	6.46	2.97	5.07	6.59	4.94	6.29
CRR propylene glycol	lb/hr	42.8	42.7	42.7	37.9	38.0	37.9
OGC atomizing air	scfm	4.5	4.3	4.4	5.4	2.8	4.7
OGC cooling water	gpm	.53	.51	.52	.48	.51	.49
Mass flow rate to stack	lb/min	19.09	18.38	18.74	18.32	18.84	18.41
CRR bed height	inches	41.7	45.1	43.4	47.6	46.4	47.3
CRR bed specific gravity (fluidized)	—	1.98	2.06	2.02	2.11	2.13	2.11
CRR freeboard pressure	Pressure (psia)	11.7	11.5	11.6	11.6	11.6	11.6
OGF	Δp (inches water)	2.1	4.0	3.1	1.1	0.8	1.1
CRR bed T (8" W)	°C	943	941	942	945	948	946
CRR free-board T (54" SE)	°C	959	951	955	950	952	951
CRR free-board T (150" NE)	°C	933	944	939	916	926	919
CRR outlet gas T	°C	849	852	851	826	840	829
OGC outlet gas T	°C	202	201	202	205	200	203
OGF outlet gas T	°C	172	172	172	171	172	172
Stack T	°C	172	172	172	171	171	171

Table 7-6 Summary of Production Test Feeds and Products

Condition		LAW			WTP SW			
		ART-P-1A	ART-P-1B	Entire P-1	ART-P-2A	ART-P-2B	Entire P-2	Grand Totals
Simulant Processed	gal	604.3	588.9	1193.2	899.6	323.5	1223.1	2416.3 gal
DMR + PR product	lb/hr	16.9	14.7	15.8	13.4	12.4	13.1	2939.1 lb
HTF product	lb/hr	56.2	57.9	57.1	36.9	38.0	37.2	9582.7 lb
PR:HTF ratio	—	0.30	0.25	0.28	0.36	0.33	0.35	0.31

7.3 System Performance

The principal objectives of the Hanford LAW and WTP SW mineralizing test program were to:

- Verify DMR process chemistry and product quality consistent with that observed during previous mineralizing pilot plant and ESTD operations.
- Confirm that the final process off-gas complies with applicable environmental regulations.
- Confirm scale-up parameters such as throughput, carbon usage optimization, feed nozzle and fluidizing gas parameter optimization, energy conservation, and optimal use of process additives.
- Confirm tandem operation of the DMR and CRR and that the CRR effectively destroys residual organic gases and fully oxidizes carbon, organics, and carbon monoxide generated in the DMR.
- Demonstrate long-term steady-state operation of the integrated fluidized bed steam reforming process.
- Demonstrate, on a laboratory scale and then on a larger scale, the production of a final monolith product from the mineralized ESTD LAW product that meets all IDF disposal requirements.
- Generate an adequate quantity of monolith product for characterization, durability testing, and other analyses, as required.
- Maximize waste volume reduction.
- Confirm zero liquid secondary waste generated from process operations.

Many of these test objectives relate to the performance of the fluidized beds and auxiliary systems. The performance of these systems is described below.

7.3.1 Fluidized Bed Performance

The DMR and CRR work in tandem to produce a mineralized product and a regulatory-compliant off-gas stream for discharge. The important parameters for evaluating the performance of the DMR are the particle size distribution (PSD), the bed temperature and temperature spread, waste simulant feed rate, bed mass, fluidized bed density or turnover, superficial space velocities, atomizing air flow rate and nozzle atomizing ratio (NAR), and oxygen flow rate.

The fluidized bed performance for the production tests is discussed in detail below. The discussion applies to both the LAW and WTP SW tests unless broken out separately.

7.3.1.1 Production Tests – DMR.

One of the most important parameters in the operation of the DMR is the average particle size. If the particle size is not in control, the particles can become too large and defluidize the bed or too small and elutriate excessively from the bed. In either case, the average bed particle size can change with time and prevent proper operation of the bed. Two average particle sizes were used during the mineralizing test, the harmonic mean particle diameter (HMPD) and the mass mean particle diameter (MMPD). The HMPD is the surface-volume average particle size and represents the size of particle that has the same surface area-to-volume ratio as the entire bed. The HMPD is calculated as follows:

$$HMPD = \frac{1}{\sum_{i=1}^N \frac{x_i}{d_i}} \quad (7-1)$$

where

x_i = mass fraction of particles caught on sieve i (dimensionless)

d_i = average size of particles caught on sieve i (μm)

N = number of sieve screens.

Since the drag force on a particle in a fluidized bed is a function of the particle's surface area and the weight of the particle is a function of the particle's volume, the HMPD is the appropriate average particle size for calculating the minimum fluidizing velocity in a fluidized bed (the velocity where the drag force equals the weight of the bed particles and the particles are neutrally buoyant or fluidized).

The MMPD has no corresponding physical interpretation, but represents the particle size at the middle of the cumulative distribution curve. The MMPD is calculated as follows:

$$MMPD = \sum_{i=1}^N x_i d_i \quad (7-2)$$

The particle size distribution of the DMR bed material was measured using standard 8-in. diameter sieve trays in a Ro-Tap testing sieve shaker machine. The HMPD and MMPD for the DMR bed particles were calculated two ways – the first using all the data from all the sieve screens and the second mathematically

removing the mass of particles from the top two screens in the shaker machine (4 and 8 mesh). The carbon particles in the bed samples were generally much larger than the bed particles and were primarily collected on these top two sieve screens. Mathematical removal of the material on these two screens gave a more representative value for the DMR bed particles average particle size. The average particle sizes in the DMR bed during the respective production tests are shown in Figure 7-4 and Figure 7-5.

Figure 7-4 Average Particle Size of the DMR Fluidized Bed during the ART-P-1 Production Tests (P-1A to the Left of the Break and P-1B to the Right)

Figure 7-5 Average Particle Size of the DMR Fluidized Bed during ART-P-2 Production Tests

As can be seen in these figures, the average particle size in the DMR was well controlled without the addition of seed particles. The initial 100lb of starting bed for ART-P-1 was alumina. The remainder of the bed was screened product from scoping tests S-5 and S-6. The HMPD without carbon (HMPD-12 mesh), was controlled to less than 450 μm for the entire P-1 test. For the ART-P-2 test the entire starting bed was alumina. The average particle size, HMPD without carbon (HMPD-12 mesh), was controlled to less than 450 μm for the entire P-2 test.

The bed and product masses are important indicators of the amount of bed turnover that has taken place in the DMR. Figures 7-6 and 7-7 show the bed mass (fluidized) and cumulative mass of the bed product removed from the DMR and the cumulative mass of the bed additions for the respective production tests. The DMR was operated such that product solids were removed as necessary to maintain the desired bed height.

Figure 7-6 DMR Fluidized Bed Mass and Cumulative Bed Additions and Product Removals during the ART-P-1 Production Tests

Figure 7-7 DMR Fluidized Bed Mass and Cumulative Bed Additions and Product Removals during the ART-P-2 Production Tests

The total mass of DMR bed solids collected during the mineralizing production tests was 2939lb Of this, a small percentage was particles larger than $\frac{1}{4}$ in. Figure 7-8 is a close-up example of typical larger particles that formed. The particle on the left is similar in size to the tip of a little finger.

Figure 7-8 Example of Large (>1/4-in) Particles Removed from the DMR Bed during the Mineralizing Tests

An important parameter in determining of the performance of a fluidized bed process such as the DMR is the amount of bed turnover. Bed turnover may be broadly defined as the amount of original bed solids that are replaced with solids from the simulated waste feed solution. Mathematically, the bed turnover is calculated using the following equation:

$$\frac{P_{in} - P(t)}{P_{in} - P_0} = \exp \left[\frac{-M_p(t)}{M_0} \right] \quad (7-4)$$

where:

P_{in} = mass fraction of product in entering feed

P_0 = mass fraction of product in bed at time $t = 0$

$P(t)$ = mass fraction of product in bed at time t

$M_p(t)$ = cumulative mass of product removed from the bed at time t

M_0 = mass of bed solids at time $t = 0$.

The value of P_{in} was 1 except when seed particles are added to the bed. During seed particle addition, P_{in} is calculated based on the amount of net solid product produced during that time period divided by the total solid product. In performing these calculations, it is assumed that the seed particles elutriate at the same rate as the rest of the bed particles. However, no seed particle additions were required during the production tests. P_0 was assumed to be equal to zero at $t = 0$; however, when starting bed solids were added to the bed, the value of P_0 was adjusted to account for the solids addition to calculate the bed turnover during subsequent time intervals. For ART-P-1, all but 100lb of the starting bed was screened product from S-5 and S-6. As seen in Figure 7-9, that starting bed was 60-90% turned over.

Figure 7-9 DMR Bed Turnover for ART Scoping Tests

The bed turnover for the ART-P-2, which started with virgin bed material, is shown in Figure 7-10. At the end of the production test for WTP SW, the bed turnover had reached 95.0%. The fluidized bed density in the DMR also reflected the bed turnover as shown in Figures 7-11 and 7-12. Initially, the fluidized bed density was high, reflecting the high alumina content of the bed solids.

Figure 7-11 DMR Bed Specific Gravity (Fluidized) for ART-P-1 Production Tests

Figure 7-12 DMR Bed Specific Gravity (Fluidized) for ART-P-2 Production Tests

The controlled temperatures in the DMR bed during the production tests are shown in Figures 7-2 and 7-3. DMR bed temperatures were controlled by oxygen flow rate that successfully maintained the DMR bed at stable temperatures.

The temperature spreads in the DMR bed during the production tests are shown in Figures 7-13 and 7-14. The temperature spread was calculated by subtracting the minimum DMR bed temperature from the maximum (using TC's -001 through -008). The bed temperature spread was typically 2-4°C; indicating the bed was well fluidized. When the switch to feed nozzle "B" occurred during P-2, the typical spread increased several C.

Figure 7-13 Temperature Spreads in the DMR Bed during the P-1 Production Tests

Figure 7-14 Temperature Spreads in the DMR Bed during the P-2 Production Tests

The waste simulant feed rates to the DMR during the P-1 and P-2 production tests are shown in Figures 7-2 and 7-3, respectively. The test plan initially called for a feed rate of up to 0.25gpm. A feed rate of 0.20gpm was consistently maintained during the production tests with the exception of a short period at the end of test P-1B when there was a concern about running out of feed before the last few hours of the test were completed.

The superficial space velocities (SSV) in the DMR bed were found to be acceptable for the respective production tests. The SSV changes through the DMR bed due to the increased gas flow from addition of oxygen and nitrogen, waste simulant liquid feed, atomizing air, and purges.

The oxygen flow rate to the DMR is shown in Figure 7-15 for ART-P-1 and Figure 7-16 for P-2. Oxygen was added to the DMR to provide process energy to maintain the bed temperature. The oxygen reacted with the carbon, hydrogen and carbon monoxide in the DMR to provide this process heat. The oxygen injectors were located above the FG distributors and the oxygen was diluted with nitrogen to reduce localized temperatures at the nozzles. Additional nitrogen purge flow was also added to the oxygen injectors to prevent solids from entering the nozzles during low-flow conditions. This purge nitrogen further reduced the oxygen concentration in the oxygen/nitrogen injectors to approximately 40%.

Figure 7-15 Oxygen and Nitrogen Flow Rates and O₂/N₂ Ratio in the DMR during ART-P-1 Production Tests

Figure 7-16 Oxygen and Nitrogen Flow Rates and O₂/N₂ Ratio in the DMR during ART-P-2 Production Tests

The expanded upper section of the DMR functioned as designed. It achieved a far better fines recycle performance than had the recycle cyclone and downcomer of the previous DMR configuration.

7.3.1.2 Production Tests – CRR.

The important parameters in evaluating the operation of the CRR are the CRR bed average particle size, the bed temperatures, the ATG flow rate, and the carbon feed rate.

The CRR average particle size during the respective production tests are shown in Figures 7-17 and 7-18. Bed material was added twice to the CRR during April 29th to increase the CRR bed height, thus the two peaks. Other than that, the average particle size in the CRR was quite stable. Unlike the average particle size in the DMR, the top two sieve screens were used in calculating the CRR HMPD and MMPD. Thus, these average particle sizes include the contribution of the carbon added to the CRR in the particle size calculation. However, the average carbon concentration in the CRR solids was relatively low, so it had little effect on the calculated average particle sizes.

Figure 7-17 Average CRR Particle Sizes during the ART-P-1 Production Tests

Figure 7-18 Average CRR Particle Sizes during the ART-P-2 Production Tests

The temperatures in the CRR during the production tests were shown earlier in Figures 7-2 and 7-3. During the first part of ART-P-1, significant above bed oxidation was experienced while attempting to maintain temperature on glycol alone. Figure 7-19 shows that once the right combination of bed height, carbon: glycol ratio, and O₂ setpoints were achieved, the temperature spreads stabilized to less than 20°C. Figure 7-20 shows the temperature spread of the bed thermocouples experienced during ART-P-2. The spread was generally less than 10°C.

Figure 7-19 Temperature Profile in the CRR during the ART-P-1 Production Tests

Figure 7-20 Temperature Spread in the CRR during the ART-P-2 Production Tests

A mixture of oxygen and nitrogen (autothermal gas or ATG) was fed to the CRR to react with carbon in the bed and with the hydrogen and carbon monoxide in the process gas from the DMR to produce heat in the CRR.

The ATG was introduced in two locations in the CRR bed. The lower ATG nozzles (set of three nozzles) were located above the FG distributors; the upper nozzles (set of four nozzles) were located a few more inches above the lower ATG nozzles. The ATG flow rate to the lower nozzles was controlled by the CRR bed temperature; the flow rate to the upper nozzles was controlled by the CRR outlet oxygen concentration.

The CRR bed temperature was well controlled during the tests and the ATG flow rates were quite stable. Figures 7-21 and 7-22 show profiles for the CRR controlled bed temperature and the CRR outlet O₂%, for ART-P-1 and P-2 respectively. As shown in the figures, the temperatures were quite stable and the outlet O₂% cyclical as required to maintain low emissions goals with variable gas flows and compositions from the DMR.

Figure 7-21 CRR Temperature and Overbed O₂% during the ART-P-1 Production Tests

Figure 7-22 CRR Temperature and Overbed O₂% during the ART-P-2 Production Tests

Figure 7-23 shows the typical CRR carbon and glycol addition rates during the production tests. The carbon addition rate varied between 25 and 45lb/hr. The glycol addition rate was placed in manual in anticipation of each DMR bed drain in order to reduce temperature fluctuations.

Figure 7-23 Typical Carbon and Glycol Addition Rates to the CRR during the ART Production Tests

7.3.2 Auxiliary Systems Performance

The auxiliary systems included the fluidizing steam boiler, the fluidizing gas superheaters, the simulated waste feed pumps, the feed nozzles, the Off-gas Filter (OGF) and the Off-gas Cooler (OGC). The performance of each of these auxiliary systems during the production tests is described below.

7.3.2.1 Fluidizing-Steam Boiler Performance.

The fluidizing steam boiler (H-104) performed well. The low steam flow trip that occurred was due to a tuning effort, not an instrument malfunction with the boiler system.

7.3.2.2 Fluidizing Gas Superheaters Performance.

Both of the fluidizing gas superheaters (H-105 A and B) worked very well. There were no element or other failures during the ART tests.

7.3.2.3 Simulant Waste Feed Pumps Performance.

For the ART tests, a rotary lobe pump served as the main feed pump (P-101A). Three progressive cavity pumps served as spares. These feed pumps operated with a recycle system that maintained the feed solution continuously in suspension. A small slip-stream of feed solution was taken from the recirculation line to feed the DMR. A pneumatically-operated pinch valve was used to control the feed flow rate based on the signal from a magnetic mass flowmeter.

The main feed pump worked well for the entire test except during an ~13 hour period while a seal leak was repaired.

7.3.2.4 Feed Nozzle Performance.

As in previous tests, two different proprietary feed nozzle designs were used in the mineralizing tests. The feed nozzles, designated A and B were evolutions of the feed nozzle designs that had been used in previous tests. Both of the nozzles performed well during the tests, producing an atomized feed that was able to give reasonable particle growth and control in the DMR. Feed nozzle restrictions were minimal during the tests; however, the post test inspections revealed significant erosion on nozzle B. Table 7-7 shows the accumulated run time on each nozzle.

Table 7-7 Accumulated Runtime on Feed Nozzles

Test	Nozzle A COT time		Nozzle B COT time	
	Feed	Hours	Feed	Time
Shakedown	LAW	21.72	LAW	0
S-1	LAW	29.5	LAW	0
S-2	LAW	27	LAW	0
S-3	LAW	0	LAW	0
S-4	LAW	4.5	LAW	15.2
S-5	LAW	0	LAW	31.2
S-6	LAW	0	LAW	21
S-7	LAW	0	LAW	18.75
P-1A	LAW	50.6	LAW	0
P-1B	LAW	50.9	LAW	0
P-2A	WTP SW	18.5	WTP SW	56.5
P-2B	WTP SW	0	WTP SW	27
Nozzle A		Nozzle B		
LAW Total	184.22	LAW Total	86.15	
WTP SW Total	18.50	WTP SW Total	83.50	
Grand Total	202.72	Grand Total	169.65	

7.3.2.5 Off-gas Cooler Performance

The OGC worked well but additional cooling margin was desired so a larger atomizing nozzle was ordered and installed during the shutdown just before the start of the production tests.

7.3.3 Filter Performance

The HTF and OGF performed the essential task of removing fine particulates from the gas streams in the ESTD pilot plant. During the scoping tests the HTF was bypassed and the OGF was used to collect all the

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finer from the process. Due to the high collection rate (~37lb/hr) in the OGF the technical team decided to put the HTF on-line for the production tests. The HTF was modified to accept an auger-based collection system, which worked well with the OGF during the scoping tests. However, evidence of minor particulate leakage past the OGF developed during the production tests. Post-test inspections revealed a breach in the gasket. (See Figure 7-24).

Figure 7-24 OGF Tube Sheet Gasket Breach

The HTF solids represented the single largest product stream during the production tests. The average solids rate from the HTF during the ART-P-1 production tests (based on cumulative operating time [COT] time) was 57.06 lb/hr. The average solids rate during the ART-P-2 tests (based on COT time) was 37.17 lb/hr.

The collection rate of DMR/PR product during the ART-P-1 production tests was 15.8 lb/hr. During the ART-P-2 tests the rate was 13.11 b/hr. The product-to-fines ratio for the ART-P-1 production tests was 0.28, while it was 0.35 for the ART-P-2 tests.

7.3.4 Data Acquisition and Control System Performance

This section documents the performance of the DACS during the production test runs, summarizing the following key performance items:

- Automated control loops
- Modifying DACS configuration files and logic
- DACS maintenance activities.

7.3.4.1 Automated Control Loops

Control loops in the context of this test are defined as device-sensor process loops, where the device controls a process parameter, which is measured by a sensor, based on a desired set point entered at the HMI by an operator. A device is a mechanism for controlling process parameters, such as a valve or pump. A sensor is an instrument for measuring process parameters, such as a thermocouple or pressure transducer.

There were 26 control loops that could be automatically or manually controlled from the HMI. Nearly 20 of these control loops were typically set in automatic mode. Each of these loops required some amount of “tuning,” that is, setting the control parameters such that the device controlled the process parameter very near the set point, even when a minor upset in the process occurred. Control loop tuning was an ongoing process that was required as changes were made to the system.

As reflected in the previous discussion and figures, most control loops functioned well. The upper ATG nozzles flow rate control loop demonstrated the need for some additional refining. Similarly, the frequent need to place the glycol control in manual control indicated the need to improve the control scheme.

7.3.4.2 Modifying DACS Configuration Files and Logic

Every attempt was made to minimize changes to the DACS during test operations avoid control system upsets. For example:

- Frequent changing of the DACS configuration files and logic during a test was avoided as much as possible.
- Visiting any of the Fieldpoint controllers within the LabVIEW user interface was avoided.
- Attempts were made to minimize the number of hypertrend cursors in use simultaneously. It was found that the trend screens would freeze and not update properly if too many cursors were opened at one time.
- The Windows firewall was disabled so that the computers could communicate with the Fieldpoint controllers.
- The Windows time service was disabled on the computers. This is a background service that usually starts automatically on Windows boot. It was found that this would sometimes interrupt communication with the Citadel database.
- The system rails and controls computers were moved to a different subnet IP address resulting in less data collisions, better communication for Fieldpoint network writes, and better overall reliability.

These practices helped to make the DACS more stable than it had been in previous testing.

7.3.4.3 DACS Maintenance Activities.

During previous testing, it was noticed that the LabVIEW software could begin developing problems after running for very long periods of time. This was caused by database growth and memory leaks, and is quite common for virtually any program being run in a Microsoft Windows operating system. Routine maintenance activities on the DACS were performed on an as-needed basis. Such maintenance activities would consist of systematically archiving databases, rebooting computers, and rebooting rails and controllers to keep the DACS system stable. During operations, it was observed that maintenance activities would be required every 10 to 14 days.

When the Citadel Database grew above 500 MB, the control room computers would begin to slow down noticeably. This slowdown would start at about 450MB and became pronounced after 600 MB. This slowdown was especially evident when navigating between HMI trend screens or when switching between programs. In addition, the communication between computers would slow down or halt completely. The trends acquired their data from the database, so trend problems were typically a warning that the database was growing too large. The corrective action in this case was to archive all databases soon after they exceeded 600 MB. The database file size was routinely monitored and archived when necessary to avoid this issue.

8. PROCESS GAS AND STACK GAS MEASUREMENTS

Process gas and stack gas measurements were made at the outlet of the HTF, the outlet of the CRR, and at the stack. Measurements included:

- HTF outlet: DMR process gas composition and limited hydrocarbon speciation
- CRR outlet: CRR process gas oxygen concentration
- Stack: Continuous monitoring and manual sampling to determine destruction efficiencies and stack gas emissions.

These measurements were used for process control, to evaluate process effectiveness, and to:

- Determine the degree of NO_x and organic species destruction
- Determine process and stack gas concentrations for mass balance calculations
- Determine the fate of feed constituents
- Perform an inventory of emissions, including gaseous and aerosol-phase organic and inorganic species emissions.

The process gas and stack gas compositions were directly and continuously measured (except for the H_2O concentration in the DMR process gas and the N_2 concentrations in the process gas and stack gas, which were calculated). The stack gas flow rate was also directly and continuously measured, but the DMR process gas flow rate was calculated using the flow rates of all process inputs to the DMR. The gas species mass and volumetric flow rates, used in mass balance calculations to determine destruction efficiencies and emission rates, were calculated using the measured gas concentrations and the measured stack gas or calculated DMR process gas flow rates.

The emissions inventory included measuring for essentially all organic and inorganic species that are typically of interest in evaluating the performance of thermal waste treatment processes, but only a limited number of measurements—typically one to three—were made for those species that were not continuously monitored. Larger numbers of sampling replicates were outside the scope of this test. The off-gas data provided by this test adds to the existing database of off-gas data provided by prior steam reformer demonstrations. The primary focus of the test was on the steam reformer system operability and capability to treat Hanford LAW and WTP SW waste simulants and produce a suitable mineralized product, rather than generation of off-gas data replicates under a variety of different test conditions.

The DMR process gas flow rate was calculated using the flow rates of all process inputs to the DMR. Table 8-1 shows DMR feed input conditions during the manual sampling timeframes. The manual sampling time periods covered the periods of manual gas sample collection for process and stack gas species such as particulate matter, metals, and organics that were not continuously monitored. The manual sampling time periods only represent a portion of the total operating time for each test condition, although they represent the time periods when the process was generally operating under the most stable process conditions, simultaneous with the continuous process gas and stack gas measurements. The average concentration and flow rate data for these time periods is the most representative of steady-state operation for each test condition. These feed input conditions were used to calculate DMR process gas mass balances, the total DMR process gas flow rate, and the concentrations of gaseous water and maximum theoretical emission concentration values for NO_x and benzene in the DMR process gas, as shown in Table 8-2.

These tables show that the largest single DMR process gas constituent was water (mostly from the simulant feed and fluidizing steam, with smaller contributions from water formed when hydrogen-bearing organics in the feed are oxidized in the DMR, less a small amount of water that is converted to H_2). The DMR outlet water concentration averaged ~50% of the total process gas flow at this point.

Nitrogen gas was the second largest DMR process gas constituent, ranging up to almost 40% of the process gas flow. The proportion of N_2 in a larger-sized DMR would likely be lower because in a larger DMR, the flow rates of other gases would be higher, but the total purge N_2 gas flow rate might not need to be appreciably higher. Most of this nitrogen is from various instrument and port purges. Only about 2% of this total N_2 is from chemical reduction of nitrates and nitrites in the feed to N_2 . The remainder of the process gas is mostly CO_2 , with smaller amounts of various gas species (H_2 , NO_x , benzene, THC [total hydrocarbon species measured by flame ionization detection continuous monitor], and CO) not included (for simplicity) in the total gas flow rate calculations, but quantified by the measurements made at the HTF outlet.

Table 8-3 shows key operating conditions for the CRR. The CRR temperature ranged between 850°C and 950°C for most test conditions. The temperature and excess O_2 control were well maintained, with little variation in the continuous automatic control of the CRR bed temperature. The propylene glycol feed rate was controlled automatically for the test operations. The lower ATG O_2 flow rate was generally automatically controlled based on CRR bed temperature, while the upper O_2 flow rate was controlled to maintain the outlet gas excess O_2 at the operator-entered set control point. A post-test calibration indicated that the lower ATG O_2 flow meter read two times the actual value. The DACS recorded value for this flow meter was divided by two before use in this report.

Table 8-4 shows the measurements and calculations that determine the average oxygen concentration in the input gas streams (on a dry basis) that is used to adjust stack gas concentration measurements to a 7% O_2 basis [28]. This input gas oxygen concentration typically ranged between 24–28%. These calculations also provide an estimate of the stack gas flow rate based on the cumulative input gas flow rates and the calculation of the process gas produced by the evaporation of the simulant feed and oxidation of the reductant.

Table 8-1 DMR Input Flow Rates Used in the DMR Process Gas Calculations for the Off-gas Sampling Periods

Date	Test period	Test	Test conditions	Process/ off-gas manual sampling	Simulant feed rate, gpm	Gas Flow to the DMR, scfm	POHC flow rate, lb/hr	Purge N ₂ flow rate, scfm	Coal feed rate, lb/hr	Total DMR O ₂ input flow rate, scfm	DMR Bed Temp, °C
17-Apr-08	11:00- 14:21	S-1	Baseline DMR temperature, High CRR temperature, Baseline clay stoichiometry	26A, 29	0.21	42.6	0.0	57.3	39.5	10.3	751
18-Apr-08	9:00-12:19	S-2	High DMR temperature, High CRR temperature, Baseline clay stoichiometry	26A, 29	0.21	43.8	0.78	60.6	40.1	10.9	799
18-Apr-08	13:15- 16:14			0023A, 0010 SVOC, TCO, 0031	0.19	42.4	0.94	58.4	34.9	10.2	799
19-Apr-08	10:07- 13:06	S-4	High DMR temperature, Low CRR temperature, Baseline clay stoichiometry	26A, 29	0.21	44.1	0.0	53.3	35.5	10.6	795
20-Apr-08	9:05-14:38	S-5	Low DMR temperature, Low CRR temperature Baseline clay stoichiometry	26A, 29	0.20	45.6	1.1	57.5	40.2	9.0	676
20-Apr-08	15:35- 18:34			0023A, 0010 SVOC, TCO, 0031	0.20	45.8	1.1	56.1	38.1	9.0	676
21-Apr-08	8:45-11:44	S-6	Optimum DMR and CRR temperatures, -10% clay stoichiometry	0023A, 0010 SVOC, TCO, 0031	0.19	42.0	1.2	61.0	35.7	9.1	724
21-Apr-08	13:00- 16:28			26A, 29	0.21	42.2	1.1	54.2	34.5	9.2	724
22-Apr-08	9:00-12:18	S-7	Optimum DMR and CRR temperatures, -20% clay stoichiometry	0023A, 0010 SVOC, TCO, 0031	0.20	42.1	1.2	54.6	31.1	9.1	724

Date	Test period	Test	Test conditions	Process/ off-gas manual sampling	Simulant feed rate, gpm	Gas Flow to the DMR, scfm	POHC flow rate, lb/hr	Purge N ₂ flow rate, scfm	Coal feed rate, lb/hr	Total DMR O ₂ input flow rate, scfm	DMR Bed Temp, °C
22-Apr-08	13:20-16:19			26A, 29	0.21	42.0	1.1	52.4	31.1	9.1	724
28-Apr-08	9:20-13:00	P-1A	Optimum DMR and CRR temperatures, 675g/L clay	0023A, 0010 SVOC, TCO, 0031	0.20	42.5	1.1	52.1	33.9	9.2	725
28-Apr-08	14:00-16:59			26A, 29	0.20	42.6	1.1	50.5	35.6	9.3	725
30-Apr-08	9:15-12:24	P-1B	Optimum DMR and CRR temperatures, 640g/L clay	0023A, 0010 SVOC, TCO, 0031	0.20	43.3	1.1	54.9	37.4	9.1	726
30-Apr-08	13:15-17:43			26A, 29	0.19	42.6	1.1	53.5	38.1	8.7	726
4-May-08	8:20-11:35	P-2A	Optimum DMR and CRR temps, WTP SW with 307g/L clay	26A, 29	0.20	47.5	0.0	53.6	34.9	9.5	677
5-May-08 to 6-May-08	5/5 7:30 to 5/6 10:29	P-2B	DMR Temp set equal to 700°C, Optimal CRR temp, WTP SW with 307g/L clay	None	0.20	49.0	0.0	52.5	37.8	9.7	698
Averages					0.2	43.8	0.8	55.2	36.2	9.5	729
Notes: 1. Standard pressure is 1 atm; standard temperature is 70°F. 2. The data for each test period was calculated using linear averaging over the test period stated.											

Table 8-2 DMR Process Gas Calculations for the Off-gas Sampling Periods

Date	Test period	Test	Total H ₂ O, scfm	Total N ₂ , scfm	CO ₂ Produced, scfm	Total DMR process gas flow rate, scfm	%H ₂ O in DMR process gas	NO _x MTEC, ppmv wet	Benzene MTEC, ppmv wet
17-Apr-08	11:00-14:21	S-1	52	44.2	12.0	109	48.2%	15,185	0
18-Apr-08	9:00-12:19	S-2	52	46.4	12.6	111	46.8%	14,508	581
18-Apr-08	13:15-16:14		49	44.6	11.8	106	46.7%	14,198	734
19-Apr-08	10:07-13:06	S-4	51	43.3	12.2	107	48.1%	15,121	0
20-Apr-08	9:05-14:38	S-5	55	44.5	10.7	110	50.0%	14,137	841
20-Apr-08	15:35-18:34		55	44.0	10.7	110	50.3%	14,357	815
21-Apr-08	8:45-11:44	S-6	50	46.5	10.7	107	46.6%	14,352	930
21-Apr-08	13:00-16:28		52	43.3	10.8	106	48.8%	15,435	832
22-Apr-08	9:00-12:18	S-7	51	43.4	10.7	105	48.5%	15,597	905
22-Apr-08	13:20-16:19		51	42.3	10.7	104	49.2%	15,888	896
28-Apr-08	9:20-13:00	P-1A	52	40.5	10.8	103	50.4%	14,954	887
28-Apr-08	14:00-16:59		52	39.8	10.9	103	50.8%	15,016	870
30-Apr-08	9:15-12:24	P-1B	53	42.8	10.7	106	49.7%	14,692	885
30-Apr-08	13:15-17:43		52	41.8	10.2	104	49.8%	14,419	839
4-May-08	8:20-11:35	P-2A	54	45.9	10.3	110	49.0%	12,184	0
5-May-08	5/5 7:30 to 5/6 10:29	P-2B	53	47.7	10.5	112	47.8%	12,038	0
Averages			52	43.8	11.0	107	48.8%	14,505	---

<p>1. Standard pressure is 1 atm; standard temperature is 70°F.</p> <p>2. Assume 50% of the total N₂ purge is assumed to enter upstream of the HTF; the remainder enters downstream of the HTF.</p> <p>3. Assume that the un-logged shot-pot N₂ is estimated = 0.1 scfm.</p> <p>4. The feed H₂O concentration was obtained from material balance results in Section 9.0.</p> <p>5. Assume that all H₂O from feed evaporates as H₂O. The total H₂O in the DMR process gas = actual H₂O + actual H₂.</p> <p>6. Assume that the O₂ is quantitatively converted to CO₂, with comparatively negligible CO and THC levels in the process gas.</p>	<p>7. Assume that all S, P, F, and Cl species, and other species in the feed, do not contribute significantly to the DMR process gas volumetric flow rate.</p> <p>8. Assume that all nitrate converts to N₂ for calculating the DMR process gas flow rate.</p> <p>9. Assume that the DMR process gas = sum of N₂ purges into DMR and HTF, shotpot and HTF pulse N₂, fluidizing H₂O, H₂O from water in feed, N₂ from nitrates and nitrites in feed, CO₂ from total O₂ input.</p> <p>10. MTEC = Maximum Theoretical Emission Concentration. The NO_x MTEC was calculated assuming that all feed nitrate converts to gaseous NO₂.</p> <p>11. The data for each test period was calculated using linear averaging over the test period stated.</p>
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Table 8-3 CRR Operating Conditions for the Off-gas Sampling Periods

Date	Test period	Test	CRR outlet gas %O ₂	CRR bed height, inches	CRR Gas Addition rate	PG feed rate	Petroleum coke feed rate	CO ₂ from PG	O ₂ used, H ₂ O made from PG	CRR bed T, °C (8" S)	CRR free-board T, °C (54" SE)	CRR free-board T, °C (150" NE)	CRR outlet gas T, °C	DMR process gas flow rate, scfm	Total CRR outlet gas flow rate, scfm
					scfm	gpm	lb/hr	scfm	scfm						
17-Apr-08	11:00-14:21	S-1	3.0	43	53.9	0.051	0.0	6.7	8.9	943	946	932	834	109	198
18-Apr-08	9:00-12:19	S-2	3.0	41	59.9	0.066	0.0	8.6	11.5	945	951	953	862	111	210
18-Apr-08	13:15-16:14		3.0	40	57.3	0.065	0.0	8.5	11.4	946	952	948	850	106	201
19-Apr-08	10:07-13:06	S-4	8.0	41	73.6	0.058	0.0	7.7	10.3	850	855	837	755	107	215
20-Apr-08	9:05-14:38	S-5	7.9	47	78.6	0.067	0.0	8.8	11.7	855	859	833	756	110	226
20-Apr-08	15:35-18:34		9.8	46	86.3	0.065	0.0	8.5	11.4	850	853	827	751	110	233
21-Apr-08	8:45-11:44	S-6	5.9	45	59.9	0.060	0.0	7.9	10.5	901	905	887	802	107	205
21-Apr-08	13:00-16:28		8.7	45	89.3	0.075	0.0	9.9	13.2	899	902	874	795	106	232
22-Apr-08	9:00-12:18	S-7	7.0	48	80.8	0.074	0.0	9.8	13.0	922	925	888	806	105	223

22-Apr-08	13:20-16:19		7.0	49	80.2	0.080	0.0	10.5	14.1	921	924	889	807	104	221
28-Apr-08	9:20-13:00	P-1A	6.0	41	78.6	0.093	3.0	12.3	16.4	944	962	936	848	103	220
28-Apr-08	14:00-16:59		6.0	40	78.5	0.091	3.1	12.0	16.0	945	962	938	850	103	219
30-Apr-08	9:15-12:24	P-1B	3.0	46	61.5	0.083	3.3	10.9	14.5	944	953	940	847	106	206
30-Apr-08	13:15-17:43		3.2	45	61.5	0.070	3.3	9.3	12.3	938	947	935	842	104	201
4-May-08	8:20-11:35	P-2A	3.0	49	66.0	0.001	6.1	0.10	0.13	944	951	918	827	110	203
5-May-08	5/5 7:30 to 5/6 10:29	P-2B	3.0	46	67.1	0.001	6.1	0.10	0.14	945	952	926	840	112	205
Averages			5.5	44	70.8	0.062	1.6	8.23	10.97	918	925	904	817	107	214
<p>1. Standard pressure is 1 atm; standard temperature is 70°F.</p> <p>2. The total CRR outlet gas flow rate is calculated by totaling the DMR process gas flow rate with all CRR gas flow inputs.</p> <p>3. The remaining purge N₂ not included in the DMR process gas flow rate calculation is included in the CRR outlet gas flow rate calculation.</p> <p>4. The data for each test period was calculated using linear averaging over the test period stated.</p> <p>5. The CRR Gas Addition rate was adjusted to reflect the finding that the lower ATG oxygen indicated a factor of 2 higher than actual based on a post-test calibration check.</p>															

Table 8-4 Process Gas Flow Rate Measurements and Calculations for the Off-gas Sampling Periods

Date	Test period	Test	DMR process gas flow rate, scfm	Total CRR outlet gas flow rate, scfm	OGC atomizing air flow rate	OGC cooling water flow rate		Total N ₂ and O ₂ input flow rates to the system, scfm	%O ₂ in total N ₂ , O ₂ , and air inputs, %	Total calculated stack gas flow rate, scfm
					scfm	gpm	scfm			
17-Apr-08	11:00-14:21	S-1	109	198	2.8	0.48	85	139	23.6%	286
18-Apr-08	9:00-12:19	S-2	111	210	2.6	0.52	93	150	23.7%	306
18-Apr-08	13:15-16:14		106	201	2.7	0.49	88	144	23.5%	291
19-Apr-08	10:07-13:06	S-4	107	215	2.5	0.44	80	156	27.1%	297
20-Apr-08	9:05-14:38	S-5	110	226	2.4	0.46	83	163	26.4%	312
20-Apr-08	15:35-18:34		110	233	2.5	0.47	84	170	28.0%	320
21-Apr-08	8:45-11:44	S-6	107	205	2.5	0.48	86	148	25.4%	294
21-Apr-08	13:00-16:28		106	232	2.5	0.53	95	171	28.1%	329
22-Apr-08	9:00-12:18	S-7	105	223	2.5	0.51	92	163	26.6%	317
22-Apr-08	13:20-16:19		104	221	2.3	0.51	92	160	26.9%	316
28-Apr-08	9:20-13:00	P-1A	103	220	4.4	0.53	95	158	27.6%	320
28-Apr-08	14:00-16:59		103	219	4.3	0.54	97	157	28.1%	320
30-Apr-08	9:15-12:24	P-1B	106	206	4.2	0.50	90	145	24.4%	300
30-Apr-08	13:15-17:43		104	201	4.1	0.49	88	142	24.6%	294
4-May-08	8:20-11:35	P-2A	110	203	5.5	0.49	87	153	23.7%	296
5-May-08	5/5 7:30 to 5/6 10:29	P-2B	112	205	2.8	0.50	90	153	23.8%	298
Averages			107	214	3.2	0.50	89	155	25.7%	306
1. Standard pressure is 1 atm; standard temperature is 70°F.						5. The total CRR input N ₂ flow rate is the sum of the upper and lower ATG N ₂ flow rates and the remaining purge N ₂ not accounted for in the DMR.				

Date	Test period	Test	DMR process gas flow rate, scfm	Total CRR outlet gas flow rate, scfm	OGC atomizing air flow rate	OGC cooling water flow rate		Total N ₂ and O ₂ input flow rates to the system, scfm	%O ₂ in total N ₂ , O ₂ , and air inputs, %	Total calculated stack gas flow rate, scfm
					scfm	gpm	scfm			
2. The total DMR input N ₂ flow rate is the sum of the N ₂ from the atomizing air, N ₂ from NO ₃ to N ₂ conversion, and DMR purge N ₂ .					6. The total system N ₂ input flow rate is the sum of N ₂ input to the DMR, the CRR, and the OGC.					
3. The total DMR input O ₂ input flow rate is the sum of the fluidizing O ₂ and O ₂ in the atomizing air.										
4. The total CRR input O ₂ flow rate is the sum of the upper and lower ATG O ₂ flow rates.					7. The total system O ₂ input flow rate is the sum of O ₂ input to the DMR, the CRR, and the OGC.					

The stack gas flow rate measurements and calculations are compared in Table 8-5. The stack gas flow rate was continuously monitored using the FE-500 flowmeter. The stack gas flow rate was independently determined during each off-gas manual sample train period using an S-type pitot tube according to EPA Methods 1 and 2A. The stack gas flow rate was also calculated from the input streams by mass balance. These three methods of determining the stack gas flow rate agreed reasonably well. The flow rate from the sample trains averaged about 13% higher than the coriolis flowmeter, and about 9.2% higher than the flow rate calculated by mass balance.

8.1 Process Gas and Stack Gas Continuous Monitoring

The CPMS monitored the process gas composition downstream of the DMR during the scoping tests and downstream of the HTF during the production tests. The HTF was bypassed during the scoping tests, but was valved into the flow path for the production tests. The oxygen concentration of the gas leaving the CRR was also continuously monitored. The CEMS monitored the stack gas composition discharging from the pilot plant to the atmosphere. These data were available for the operators to use in setting and maintaining DMR operating conditions. These data were also recorded using the DACS and are included in the electronically logged data for the tests.

The CPMS and CEMS were operated, calibrated, and maintained according to the test plan, QA plan, and operating procedures. The CPMS and CEMS data were provided and logged on a dry, moisture-free basis (except for the CRR outlet O₂ concentration and the stack gas THC concentration, which were measured on a wet basis), because the sample conditioning systems condensed and removed the moisture in the gas (along with filtering any particulate matter and condensed aerosols). This provided the sample gas conditioning necessary to protect the gas analyzers from fouling and damage. The CRR outlet O₂ measurement did not require this sample conditioning because the analyzer used an in-line sensor that did not require any sample extraction and operated at the process moisture and temperature conditions.

The CPMS sample gas was diluted with N₂ (at a nominal dilution factor of 5:1) to reduce fouling and instrument damage from condensable species. This dilution has improved CPMS operation compared to prior pilot plant runs when the sample gas was not diluted. The CPMS sample gas analyzed for NO_x concentration was further diluted with air (at a nominal dilution factor of 4:1) to provide excess O₂ during analysis to prevent passivation of the catalytic NO_x converter. The total dilution factor for the CPMS NO_x analysis was nominally 20:1. The CPMS was calibrated with these same dilution factors to ensure consistency between sampling and calibration periods. These dilution factors were continuously logged for normalizing the measured values for the instantaneous dilution. CPMS data in this report have been normalized for the respective N₂ and total N₂ plus air dilution. The dry-basis CPMS and CEMS data were normalized to a wet basis to perform calculations (e.g., NO_x destruction and mass balance closure calculations).

The CPMS and CEMS instruments were typically calibrated at least once daily to document and adjust the analyzers for calibration error and drift. The CPMS data have also been corrected for calibration error, if the average calibration error determined for each CPMS sample period exceeded acceptance limits. All of the stack gas CEMS data were adjusted for calibration error and drift.

Table 8-5 Stack Gas Flow Rate Measurements for Off-gas Sampling Periods

Date	Test period	Test	Stack gas mole weight	From sample trains	From stack gas flowmeter, FE-500		Flowmeter vs. Sample Train $\Delta\%$	Calculated from input flow rates	Calc'd vs. sample train flow $\Delta\%$
				wscfm	lb/min	wscfm	%	wscfm	%
17-Apr-08	11:00-14:21	S-1	24.3	313	17.1	273	12.9	286	8.6%
18-Apr-08	9:00-12:19	S-2	24.3	325	16.9	270	16.9	306	6.0%
18-Apr-08	13:15-16:14		24.4	338	17.0	269	20.4	291	13.9%
19-Apr-08	10:07-13:06	S-4	24.7	320	17.4	274	14.5	297	7.1%
20-Apr-08	9:05-14:38	S-5	24.6	343	19.9	313	8.9	312	9.1%
20-Apr-08	15:35-18:34		24.7	311	20.3	317	-1.9	320	-2.8%
21-Apr-08	8:45-11:44	S-6	24.5	343	18.5	292	14.8	294	14.4%
21-Apr-08	13:00-16:28		24.5	348	20.0	317	8.9	329	5.4%
22-Apr-08	9:00-12:18	S-7	24.2	339	19.8	316	6.8	317	6.4%
22-Apr-08	13:20-16:19		24.4	349	19.3	307	12.1	316	9.5%
28-Apr-08	9:20-13:00	P-1A	24.5	341	19.3	305	10.6	320	6.1%
28-Apr-08	14:00-16:59		24.4	376	18.8	298	20.8	320	14.9%
30-Apr-08	9:15-12:24	P-1B	24.3	332	18.0	288	13.4	300	9.6%

30-Apr-08	13:15-17:43		24.2	349	17.6	280	19.6	294	15.9%
4-May-08	8:20-11:35	P-2A	24.4	342	17.8	283	17.3	296	13.4%
5-May-08	5/5 7:25 to 5/6 10:29	P-2B	24.4	---	18.8	299	---	298	---
Averages			24.4	338	18.5	294	13.1	306	9.2%
<p>Notes:</p> <ol style="list-style-type: none"> 1. Standard temperature is 70°F. Standard pressure is 1 atm. 2. The stack gas mole weight is calculated using the wet basis composition. 3. The data for each test period was calculated using linear averaging over the test period stated. 4. The stack gas mole weight for test P-2B was not calculated because corrected CEMS data was not available. The assumed mole weight for test P-2B is equal to the mole weight for test P-2A. 									

8.2 DMR Process Gas Concentration and NO_x Destruction Efficiency Results

The DMR process gas compositions are shown in Table 8-6 converted to a wet basis. These values represent the actual concentrations within the process gas. The H₂ levels (ranging from about 0.6–2% wet) are reduced to about one-half of the dry-basis values, because the DMR process gas moisture content averaged about 49%. The DMR NO_x destruction efficiency ranged between 71–93%, depending on process test conditions.

Figure 8-1 shows average coal feedrate and DMR H₂ levels at different DMR bed temperatures for the scoping and production tests. While higher energy inputs were needed to heat the process input streams to higher temperatures, coal utilization was more efficient. On average, higher DMR temperatures did not require significantly higher coal feed rates. Even without increasing (on average) coal feed rates for higher DMR temperatures, more efficient steam reforming reactions resulted in higher average DMR H₂ levels.

8.3 Stack Gas Concentration and Destruction Efficiency Results

The DMR process gas was fully oxidized in the CRR to destroy residual CO, H₂, and THC, then cooled and filtered to remove particulate matter prior to exiting the stack. The stack gas dry- and wet-basis compositions are shown in Table 8-7 and Table 8-8. The stack gas contained mainly H₂O (averaging about 50% wet basis) and N₂, with smaller amounts of CO₂ and O₂, and trace amounts of other gas species, including smaller amounts of NO_x, CO, THC, and SO₂.

8.3.1 Stack Gas O₂, CO, and THC Levels

Figure 8-2 shows how the stack gas O₂, CO, and THC concentrations varied for different steam reformer system operating conditions during the scoping and production tests. Very low stack THC levels were observed during these tests, consistent with previous steam reformer tests. The highest stack THC levels occurred during the scoping tests that included lower CRR bed temperatures and carryover of product and coal fines from the DMR into the CRR. Even these higher THC levels ranged only about 30% of the HWC MACT standard of 10ppm THC (normalized as propane on a dry, 7% O₂ basis).

Stack CO levels during the scoping tests averaged between about 21-107ppmv (dry @ 7% O₂). The higher CO levels occurred during the tests with the lowest CRR bed temperatures that ranged around 850°C. The CRR excess O₂ concentrations were increased to as high as 10% (wet basis) to control stack CO levels below the HWC MACT limit of 100ppm (dry @ 7%O₂). Higher CRR temperatures enabled lower stack CO levels (as shown in Figure 8-3), even considering variations in stack CO levels due to variations in CRR excess O₂ levels and variations in coal fines and carbon in the CRR.

The lowest stack CO levels (as low as 0ppm) were achieved when the HTF was on-line during the production tests. The HTF filtered the DMR product and coal fines out of the DMR process gas upstream of the CRR, preventing the coal fines from passing into the CRR. Continued reaction of coal fines as they passed through and out of the CRR could have contributed to the higher stack CO and THC levels that occurred during the scoping tests, especially during low CRR bed temperature tests.

**Table 8-6 DMR Process Gas Composition, Wet Basis,
Dilution-Corrected, for Off-gas Sampling Periods**

Date	Test period	Test	CPMS Measurements						H ₂ O, wet %	DMR NO _x destruction efficiency, %
			O ₂ , wet %	CO ₂ , wet %	H ₂ , wet %	CO, wet %	NO _x , wet ppmv	THC, wet ppmv		
			AT- 700- 001- O ₂	Avg of 2 analyzers	Avg of 2 analyzers	AT- 700- 003- CO	Avg of 2 analyzers	AT- 700- 005- THC		
17-Apr-08	11:00-14:21	S-1	0.13	10.5	1.4	2.1	3,942	2,204	48.2%	74.0%
18-Apr-08	9:00-12:19	S-2	0.03	11.2	2.0	1.7	2,502	2,474	46.8%	82.8%
18-Apr-08	13:15-16:14	S-2	0.03	10.0	1.9	1.5	2,344	2,487	46.7%	83.5%
19-Apr-08	10:07-13:06	S-4	0.07	5.0	0.7	0.8	1,560	2,920	48.1%	89.7%
20-Apr-08	9:05-14:38	S-5	0.39	6.8	0.6	0.9	2,337	1,543	50.0%	83.5%
20-Apr-08	15:35-18:34	S-5	0.30	6.7	0.6	0.9	2,525	NM	50.3%	82.4%
21-Apr-08	8:45-11:44	S-6	0.26	15.0	1.7	0.9	1,806	3,438	46.6%	87.4%
21-Apr-08	13:00-16:28	S-6	0.21	12.9	1.1	0.7	1,889	3,751	48.8%	87.8%
22-Apr-08	9:00-12:18	S-7	0.13	8.4	1.8	0.4	1,088	NM	48.5%	93.0%
22-Apr-08	13:20-16:19	S-7	0.13	8.1	1.6	0.4	1,235	NM	49.2%	92.2%
28-Apr-08	9:20-13:00	P-1A	0.29	7.3	0.7	1.1	4,017	NM	50.4%	73.1%
28-Apr-08	14:00-16:59	P-1A	0.35	7.9	0.9	1.1	4,326	NM	50.8%	71.2%
30-Apr-08	9:15-12:24	P-1B	0.22	7.0	0.8	0.8	6,097	NM	49.7%	58.5%

30-Apr-08	13:15-17:43	P-1B	0.19	7.1	0.9	0.7	6,176	NM	49.8%	57.2%
4-May-08	8:20-11:35	P-2A	0.26	8.7	0.7	1.5	2,455	NM	49.0%	79.8%
5-May-08	5/5 7:25 to 5/6 10:29	P-2B	0.21	6.0	0.7	1.2	2,031	NM	47.8%	83.1%

Notes:

1. The valid results of two analyzers monitoring the same parameter (CO₂, and H₂) are averaged to provide a single result.
2. The CPMS results are corrected for both N₂ dilution (all CPMS analyzers) and air dilution (the NO_x analyzers).
3. The CPMS NO_x measurements are corrected for air dilution using the correction factor determined from NO_x analyzer calibrations.
4. The CPMS THC analyzer detects C-H compounds and reports them as C1 (methane). C_nH_m compounds are detected based the species-specific response factor for Flame Ionization Detection (FID) measurements, which is known for many species.
5. The averages were calculated using linear averaging and not accounting for overlap of some sample periods.
6. These data have not been adjusted to eliminate variations in process gas composition and flow rate caused by DMR bed removals, when the bed removal eductor N₂ dilutes the process gas and increases the process gas flow rate.
7. MTEC = Maximum Theoretical Emissions Concentration.
8. The DMR NO_x destruction = (1 - NO_x concentration / NO_x MTEC) x 100%, all on a wet basis.
9. The average O₂ wet % for 18 Dec was -0.02%. A zero has been substituted for this negative value.
10. NM = Not measured. The THC analyzer periodically malfunctioned, and was taken off-line after Test S-6.
11. The data for each test period was calculated using linear averaging over the test period stated.

Figure 8-1 DMR Coal Feedrate and H₂ Levels

8.3.2 System NO_x Destruction

The DMR destroyed nitrites and nitrates in the feed simulant, converting these species to N₂ and H₂O under stoichiometrically reducing conditions. NO_x destruction is the degree to which the nitrites and nitrates in the simulant feed are destroyed in the both the DMR and the CRR, as determined by mass balance using the feedrates of nitrates and nitrites in the simulant feed, and the stack gas flow rate and NO_x concentrations. Figure 8-4 shows NO_x levels and NO_x destruction results for this test. The system NO_x destruction increased from ~91% to ~97% as the DMR H₂ levels increased from ~0.6% to ~2% (wet basis). Test-average stack NO_x concentrations ranged from below 200ppmv to over 400ppmv (wet basis).

The NO_x destruction in the DMR, upstream of the CRR, was determined using the feed rates of nitrates and nitrites in the simulant feed, and the DMR process gas flow rate and NO_x concentrations. DMR NO_x destruction was more scattered than was the total system NO_x destruction, because other factors such as DMR bed temperature and bed height can also affect DMR NO_x destruction, and because, when higher NO_x levels persist in the DMR process gas, then increased NO_x destruction in the CRR is possible to reduce those higher levels. Even considering the data scatter, DMR NO_x destruction also trended higher, from under 60% to about 93%, with increasing DMR H₂ levels. Test-average DMR NO_x concentrations ranged from about 1,100ppm to over 6,000ppm (wet basis).

The degree of NO_x destruction in the CRR, downstream of the DMR, was determined using the respective DMR NO_x destruction and the total system (CRR + DMR) NO_x destruction. As in prior tests, NO_x remaining in the DMR process gas was further destroyed in the CRR. CRR NO_x destruction data are also scattered, in part because of the varying levels of NO_x in the DMR process gas. Test-average CRR NO_x destruction increased with increasing DMR H₂ levels, ranging from about 39% to 86%. This result is consistent with prior steam reformer tests that showed that the CRR will further reduce NO_x, when the process gas entering the CRR contains NO_x at levels higher than chemical equilibrium levels in the CRR.

Table 8-7 Stack Gas Composition, Dry Basis, for Off-gas Sampling Periods

Date	Test period	Test	O ₂ dry % AT-500-001	CO ₂ dry % AT-500-002	NO _x dry ppmv AT-500-005	CO dry ppmv AT-500-006	THC dry ppmv C ₃ AT-500-007	SO ₂ dry ppmv AT-500-008	Avg O ₂ % in input gas (dry %)	7% O ₂ correction factor	CO dry ppmv @ 7% O ₂	SO ₂ dry ppmv @ 7% O ₂	THC dry ppmv @ 7% O ₂
17-Apr-08	11:00-14:21	S-1	6.1	16.5	605	70	0.2	249	23.6%	0.80	56	200	0.28
18-Apr-08	9:00-12:19	S-2	5.6	16.4	417	49	0.8	254	23.7%	0.77	38	196	1.31
18-Apr-08	13:15-16:14		5.6	16.3	408	42	0.5	221	23.5%	0.78	33	173	0.77
19-Apr-08	10:07-13:06	S-4	11.4	14.2	604	52	0.2	0	27.1%	0.89	46	0.09	0.29
20-Apr-08	9:05-14:38	S-5	12.0	11.4	768	104	1.9	2	26.4%	0.97	101	1.7	3.70
20-Apr-08	15:35-18:34		13.8	12.6	786	108	0.9	5	28.0%	0.99	107	4.8	1.87
21-Apr-08	8:45-11:44	S-6	9.5	15.7	431	61	0.4	40	25.4%	0.88	53	35	0.76
21-Apr-08	13:00-16:28		12.5	14.4	581	38	5.0	2	28.1%	0.90	34	1.4	9.08
22-Apr-08	9:00-12:18	S-7	12.1	12.4	296	22	1.7	<u>0</u>	26.6%	0.97	21	0	3.26
22-Apr-08	13:20-16:19		10.6	14.7	381	31	0.2	<u>0</u>	26.9%	0.86	27	0	0.27
28-Apr-08	9:20-13:00	P-1A	9.9	15.4	681	<u>0</u>	0.0	26	27.6%	0.79	0	21	0.05
28-Apr-08	14:00-16:59		10.0	15.7	726	<u>0</u>	0.4	29	28.1%	0.77	0	23	0.61
30-Apr-08	9:15-12:24	P-1B	6.4	16.6	572	<u>0</u>	<u>0.0</u>	67	24.4%	0.78	0	52	<u>0.00</u>
30-Apr-08	13:15-17:43		6.4	16.5	604	1	<u>0.0</u>	66	24.6%	0.77	1	51	<u>0.00</u>
4-May-08	8:20-11:35	P-2A	6.4	15.6	618	<u>0</u>	0.1	11	23.7%	0.81	0	8.7	0.24
5-May-08	5/5 7:25 to 5/6 10:29	P-2B	6.9	14.3	675	3	0.0	15	23.8%	0.83	3	13	0.00

1. The stack gas THC measurement was made on a wet basis, without removing H₂O from the sample gas stream, and reported as ppmv propane.

4. The 7% O₂ correction factor is $14/(E - Y)$, where E is the average O₂ content of all input air, O₂, and N₂, and Y = measured O₂ concentration in the off-gas, on a dry basis [28,29]. The oxygen contents of the simulant feed and of the coal are not included in this calculation,

<p>2. The data for each test period was calculated using linear averaging over the test period stated</p> <p>3. These data have not been adjusted to eliminate variations in process gas composition and flow rate caused by DMR bed removals, when the bed removal eductor N₂ dilutes the process gas and increases the process gas flow rate.</p>	<p>making the calculation of E conservatively low.</p> <p>5. Italicized and underlined zero values are values for which the measurements were slightly negative, resulting from typical ranges in analytical precision or zero drift when measuring values that are near zero compared to the analyzer full scale measuring range. These slightly negative values are reported here to be zero..</p> <p>6. Corrected CEMS data was not available for test P-2B from 7:30 May 5th to 10:29 May 6th. CEMS data was used without calibration corrections. Since the CEMS corrections are minor for all the prior test conditions, the calibration corrections are not expected to affect the data significantly during this time period.</p>
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Table 8-8 Stack Gas Composition, Wet Basis, for Off-gas Sampling Periods

Date	Test period	Test	O ₂ , wet %	CO ₂ , wet %	NO _x , wet ppmv	CO, wet ppmv	THC, wet ppmv	SO ₂ , wet ppmv	H ₂ O, wet %	N ₂ , wet %	Stack gas flow rate from sample trains		Stack NO _x MTEC, ppmv wet	System NO _x destruction, %	NO _x destruction in CRR, %
											dscfm, 68°F	wscfm, 70°F			
17-Apr-08	11:00-14:21	S-1	3.0	8.0	294	34	0.2	121	51.3	37.7	152	313	5,268	94.4%	78.5%
18-Apr-08	9:00-12:19	S-2	2.7	8.0	203	24	0.8	124	51.2	38.0	158	325	4,954	95.9%	76.2%
18-Apr-08	13:15-16:14		2.8	8.1	203	21	0.5	110	50.3	38.8	167	338	4,444	95.4%	72.3%
19-Apr-08	10:07-13:06	S-4	6.0	7.4	316	27	0.2	0	47.6	39.0	167	320	5,058	93.7%	39.4%
20-Apr-08	9:05-14:38	S-5	6.4	6.1	411	56	2.0	1	46.5	41.0	183	343	4,545	91.0%	45.3%
20-Apr-08	15:35-18:34		7.4	6.8	421	58	1.0	3	46.4	39.4	166	311	5,073	91.7%	52.8%
21-Apr-08	8:45-11:44	S-6	4.7	7.9	216	30	0.4	20	49.9	37.5	171	343	4,485	95.2%	61.7%
21-Apr-08	13:00-16:28		6.3	7.3	294	19	5.1	1	49.5	36.9	175	348	4,686	93.7%	48.8%
22-Apr-08	9:00-12:18	S-7	6.0	6.2	148	11	1.7	0	50.0	37.7	168	339	4,841	96.9%	56.1%

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22-Apr-08	13:20-16:19		5.3	7.3	191	16	0.2	0	49.9	37.5	174	349	4,750	96.0%	48.3%
28-Apr-08	9:20-13:00	P-1A	5.0	7.8	346	0	0.0	13	49.2	38.0	173	341	4,537	92.4%	71.6%
28-Apr-08	14:00-16:59		4.9	7.7	358	0	0.4	14	50.7	36.7	185	376	4,116	91.3%	69.8%
30-Apr-08	9:15-12:24	P-1B	3.1	8.1	277	0	0.0	33	51.5	37.3	160	332	4,705	94.1%	85.8%
30-Apr-08	13:15-17:43		3.1	7.9	292	0	0.0	32	51.7	37.2	168	349	4,279	93.2%	84.1%
4-May-08	8:20-11:35	P-2A	3.2	7.8	308	0	0.1	5	50.1	38.9	170	342	3,926	92.1%	61.0%
5-May-08	5/5 7:25 to 5/6 10:29	P-2B	3.4	7.1	337	2	0.1	8	50.1	39.3	24	306	4,388	92.3%	54.5%
<p>Notes:</p> <ol style="list-style-type: none"> 1. MTEC = Maximum Theoretical Emissions Concentration, based on the simulant feedrate, the simulant composition, and the off-gas flow rate. 2. The data for each test period was calculated using linear averaging over the test period stated. 3. No moisture content was measured for test P-2B because manual stack gas sampling was not performed during that time period. The moisture content is assumed to be equal to the moisture content that was measured during test P-2A.

Figure 8-2 Stack Gas O₂ and CO Levels Compared to CRR Outlet O₂ Levels

Figure 8-3 Stack Gas CO Levels Dependence on the CRR Bed Temperature

Figure 8-4 NO_x levels and NO_x DRE vs. DMR H₂ Levels

The CRR can either create or destroy NO_x, depending on NO_x levels in input gas streams and depending on the CRR temperature, stoichiometry, and residence time conditions, and within kinetic limits. NO_x-forming or reducing reactions in the CRR will tend to approach equilibrium concentrations for O₂, N₂, NO, and NO₂, for the CRR operating conditions. Whether or not equilibrium conditions are actually reached depends on kinetic limitations. When the DMR process gas contained no NO_x, such as at startup, prior to the start of simulant feed, then the CRR produces some “thermal NO_x” when O₂ and N₂ react to form NO and NO_x. For example, during this test series on April 27, between 0001 and 0400, prior to starting the P-1A test, the stack gas NO_x concentration ranged between 100-150ppm (wet basis) as a result of thermal NO_x formation in the CRR. When the DMR process gas contained residual NO_x from the simulant feed, then the some of that NO_x was destroyed in the CRR, as the NO_x reaction stoichiometry shifted due to CRR outlet NO_x levels that were higher than would be expected to result from thermal NO_x formation. The NO_x reactions in the CRR shift between NO_x formation and destruction, depending on if the average NO_x concentrations from the input gas streams are less than or higher than the equilibrium NO_x concentration for the specific CRR operating conditions at that time.

8.3.3 Stack Gas SO₂ Emissions

Figure 8-5 shows stack gas SO₂ concentrations during the scoping and production tests. Higher SO₂ levels occurred early in the scoping tests, when product fines in the DMR process gas entered the higher-temperature CRR, especially when the CRR outlet O₂ concentrations were moderately low at about 3% (wet basis). Stack gas SO₂ concentrations decreased when (a) the CRR excess O₂ concentrations were increased to up to 10% (wet basis), and (b) the CRR temperature was decreased from about 950°C to

about 850°C. Stack SO₂ were higher during Test S-6, when the CRR bed temperature was increased again to 900°C and the CRR outlet O₂ level was reduced to 6% (wet basis). Increasing the CRR excess O₂ levels in Test S-7 again lowered stack gas SO₂ levels, even though the CRR bed temperature was increased. This suggests that, at the range of CRR temperatures that were tested, sulfur species can be thermally decomposed from product fines in the CRR, especially under less oxidizing conditions.

This theory is supported by results from the production tests, when higher stack SO₂ levels again occurred simultaneously with decreased CRR outlet O₂ levels. Even though the HTF captured DMR product fines during the production tests, the small amount of product fines that could have passed through the HTF, combined with residual product fines in the CRR remaining from the scoping tests, could have evolved some SO₂. The higher CRR bed temperature (nominally 950°C) during Test P-1 may have contributed to higher SO₂ evolution during that time.

Figure 8-5 Stack SO₂ Concentrations during the Scoping and Production Tests

8.3.4 Organic Species Emissions and Destruction

A limited number of measurements were performed to determine stack emissions of organic species during the production tests. Typically, one to three measurements were made for determining:

- Speciated VOC emissions
- Destruction efficiencies of benzene, which was the POHC injected into the feed line
- Speciated SVOCs
- Unspeciated total organics

- Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (dioxins and furans [D/Fs])
- PCBs.

These measurements were performed to determine the organic stack gas emissions for mineralizing steam reforming and to compare them to the earlier steam reforming tests that produced a carbonate product.

8.3.4.1 VOC Emissions.

VOC emissions were measured at the stack to determine what species, if any, remained in the off-gas downstream of the CRR and to measure benzene destruction efficiency. Table 8-9 shows the results of the Method 0031 VOC measurements. These VOCs are normally analyzed in routine Method 0031 off-gas analyses. These particular species are those of greatest common interest in off-gas measurements because they are either common products of incomplete combustion, or represent a variety of higher-risk species in risk assessments. Most of the VOCs speciated by this measurement were consistently not detected above the method detection limits.

VOCs that were detected at low concentrations in one or more of the sampling periods, typically near the detection limits, were:

- Acetone
- Acrylonitrile
- Benzene (the spiked POHC)
- Bromobenzene
- Bromodichloromethane
- Bromomethane
- N-Butylbenzene
- Carbon disulfide
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- Chloromethane
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- Dichlorodifluoromethane (Freon 12)
- 1,1-Dichloroethene
- 1,1-Dichloropropene
- Ethylbenzene
- Methylene chloride

- Styrene
- Toluene
- 1,2,4-Trichlorobenzene
- 1,1,1-Trichlorethane
- Trichloroethene
- Trichlorofluoromethane
- 1,2,4-Trimethylbenzene
- 1,3,5-Triemethylbenzene
- meta- para-, and ortho- xylene

Some of these VOCs are likely contaminants that are typically detected at low levels in most GC-MS VOC analyses. Typical lab contaminants include acetone and methylene chloride. Compounds like bromomethane were detected, although no bromide compounds were knowingly fed into the system.

Benzene was detected in all of these tests. This is because benzene, as the POHC, was spiked into the system at a target feedrate of 1 lb/minute as shown in Table 8-1. This allowed for a calculation of benzene destruction efficiencies as shown in Table 8-9 for the scoping tests and for production tests P-1A and P-1B. No benzene was injected into the WTP SW feed (production test P-2).

VOCs that were included in the GC-MS analyses but that were not detected in any of the sampling periods were:

- Bromochloromethane
- Bromoform
- 2-Butanone
- sec-Butylbenzene
- tert-Butylbenzene
- Chlorodibromomethane
- Chloroethane
- 2-Chlorotoluene
- 4-Chlorotoluene
- 1,2-Dibromo-3-chloropropane
- 1,2-Dibromoethane
- Dibromomethane
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- cis-1,2-Dichloroethene

- trans-1,2-Dichloroethene
- 1,2-Dichloropropane
- 1,3-Dichloropropane
- 2,2-Dichloropropane
- cis-1,3-Dichloropropene
- trans-1,3-Dichloropropene
- Hexachlorobutadiene
- 2-Hexanone
- Isopropylbenzene
- P-Isopropyltoluene
- 4-Methyle-2-pentanone
- Naphthalene
- N-Propylbenzene
- 1,1,1,2-Tetrachloroethane
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethene
- 1,2,3-Trichlorobenzene
- 1,1,2-Trichloroethane
- 1,2,3-Trichloropropane
- Vinyl chloride

Table 8-9 Stack Gas Volatile Organic Compound Concentrations, Mass Emission Rates, and Benzene Destruction Efficiencies

Test	ART-S2		ART-S5		ART-S6		ART-S7		ART-PIA		ART-PIB	
Date	4/18/2008		4/20/2008		4/21/2008		4/22/2008		4/20/2008		4/20/2008	
Test Period	13:15 - 16:05		15:30-18:35		8:45-11:30		9:00-11:28		9:20-12:07		9:15-11:41	
Total Sample Duration, Min	110		120.0		120.0		120.0		120.0		120.0	
Total Sample Volume, dry standard liters	32.00		64.44		78.39		99.83		93.56		86.91	
VOC Species Concentration	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr
Acetone	< 0.032	<2.0E-05	< 0.019	< 1.2E-05	< 0.015	< 9.8E-06	< 0.010	< 6.8E-06	< 0.011	< 7.5E-06	< 0.012	< 7.1E-06
Acrylonitrile	< 0.121	<7.6E-05	< 0.060	< 3.7E-05	< 0.049	< 3.2E-05	< 0.039	< 2.5E-05	< 0.041	< 2.8E-05	< 0.044	< 2.7E-05
Benzene	< 0.007	<4.6E-06	0.008	4.7E-06	0.009	5.8E-06	< 0.005	< 3.6E-06	< 0.005	< 3.5E-06	< 0.003	< 1.6E-06
Bromobenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Bromochloromethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Bromodichloromethane	< 0.006	<3.8E-06	0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.003	< 2.3E-06	< 0.002	< 1.3E-06
Bromoform	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Bromomethane	< 0.016	<1.0E-05	0.046	2.9E-05	< 0.017	< 1.1E-05	< 0.004	< 2.8E-06	< 0.021	< 1.4E-05	< 0.011	< 6.7E-06
2-Butanone	< 0.025	<1.6E-05	< 0.013	< 7.9E-06	< 0.010	< 6.7E-06	< 0.008	< 5.3E-06	< 0.009	< 5.9E-06	< 0.009	< 5.6E-06
n-Butylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
sec-Butylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
tert-Butylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Carbon disulfide	< 0.023	<1.4E-05	0.005	< 3.4E-06	< 0.013	< 8.3E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.004	< 2.5E-06
Carbon tetrachloride	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Chlorobenzene	< 0.006	<3.8E-06	0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Chlorodibromomethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Chloroethane	< 0.011	<6.7E-06	< 0.005	< 3.3E-06	< 0.004	< 2.8E-06	< 0.003	< 2.2E-06	< 0.004	< 2.5E-06	< 0.004	< 2.4E-06
Chloroform	< 0.009	<5.6E-06	0.015	< 9.4E-06	< 0.008	< 5.0E-06	< 0.008	< 5.0E-06	< 0.006	< 4.3E-06	< 0.006	< 3.7E-06
Chloromethane	0.076	4.8E-05	< 0.022	< 1.4E-05	< 0.018	< 1.1E-05	< 0.009	< 6.1E-06	< 0.015	< 1.0E-05	0.130	7.8E-05

Test	ART-S2		ART-S5		ART-S6		ART-S7		ART-P1A		ART-P1B	
Date	4/18/2008		4/20/2008		4/21/2008		4/22/2008		4/20/2008		4/20/2008	
Test Period	13:15 - 16:05		15:30-18:35		8:45-11:30		9:00-11:28		9:20-12:07		9:15-11:41	
Total Sample Duration, Min	110		120.0		120.0		120.0		120.0		120.0	
Total Sample Volume, dry standard liters	32.00		64.44		78.39		99.83		93.56		86.91	
VOC Species Concentration	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr
2-Chlorotoluene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
4-Chlorotoluene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2-Dibromo-3-chloropropane	< 0.012	<7.6E-06	< 0.006	< 3.7E-06	< 0.005	< 3.2E-06	< 0.004	< 2.5E-06	< 0.004	< 2.8E-06	< 0.004	< 2.7E-06
1,2-Dibromoethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Dibromomethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2-Dichlorobenzene	< 0.006	< 3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,3-Dichlorobenzene	< 0.006	< 3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,4-Dichlorobenzene	< 0.006	< 3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.5E-06	< 0.002	< 1.3E-06
Dichlorodifluoromethane	< 0.007	<4.6E-06	< 0.006	< 3.7E-06	< 0.005	< 3.4E-06	< 0.003	< 2.0E-06	0.013	8.7E-06	0.003	1.6E-06
1,1-Dichloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2-Dichloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
cis-1,2-Dichloroethene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
trans-1,2-Dichloroethene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1-Dichloroethene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2-Dichloropropane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,3-Dichloropropane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
2,2-Dichloropropane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
cis-1,3-Dichloropropene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
trans-1,3-Dichloropropene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1-Dichloropropene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06

Test	ART-S2		ART-S5		ART-S6		ART-S7		ART-P1A		ART-P1B	
Date	4/18/2008		4/20/2008		4/21/2008		4/22/2008		4/20/2008		4/20/2008	
Test Period	13:15 - 16:05		15:30-18:35		8:45-11:30		9:00-11:28		9:20-12:07		9:15-11:41	
Total Sample Duration, Min	110		120.0		120.0		120.0		120.0		120.0	
Total Sample Volume, dry standard liters	32.00		64.44		78.39		99.83		93.56		86.91	
VOC Species Concentration	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr
Ethylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Hexachlorobutadiene	< 0.007	<4.6E-06	< 0.004	< 2.3E-06	< 0.003	< 1.9E-06	< 0.002	< 1.5E-06	< 0.003	< 1.7E-06	< 0.003	< 1.6E-06
2-Hexanone	< 0.025	<1.6E-05	< 0.013	< 7.9E-06	< 0.010	< 6.7E-06	< 0.008	< 5.3E-06	< 0.009	< 5.9E-06	< 0.009	< 5.6E-06
Isopropylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
p-Isopropyltoluene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Methylene Chloride	0.033	2.1E-05	0.052	3.2E-05	0.015	9.6E-06	0.015	9.9E-06	0.060	4.1E-05	0.145	8.7E-05
4-Methyl-2-pentanone	< 0.025	<1.6E-05	< 0.013	< 7.9E-06	< 0.010	< 6.7E-06	< 0.008	< 5.3E-06	< 0.009	< 5.9E-06	< 0.009	< 5.6E-06
Naphthalene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
n-Propylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Styrene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1,1,2-Tetrachloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1,2,2-Tetrachloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Tetrachloroethene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Toluene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2,3-Trichlorobenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2,4-Trichlorobenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1,1-Trichloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,1,2-Trichloroethane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Trichloroethene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Trichlorofluoromethane	< 0.012	<7.6E-06	< 0.006	< 3.7E-06	< 0.005	< 3.2E-06	< 0.004	< 2.5E-06	< 0.004	< 2.8E-06	< 0.004	< 2.7E-06

Test	ART-S2		ART-S5		ART-S6		ART-S7		ART-P1A		ART-P1B	
Date	4/18/2008		4/20/2008		4/21/2008		4/22/2008		4/20/2008		4/20/2008	
Test Period	13:15 - 16:05		15:30-18:35		8:45-11:30		9:00-11:28		9:20-12:07		9:15-11:41	
Total Sample Duration, Min	110		120.0		120.0		120.0		120.0		120.0	
Total Sample Volume, dry standard liters	32.00		64.44		78.39		99.83		93.56		86.91	
VOC Species Concentration	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr
1,2,3-Trichloropropane	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,2,4-Trimethylbenzene	< 0.006	< 3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
1,3,5-Trimethylbenzene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Vinyl chloride	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
m-Xylene & p-Xylene	< 0.011	<6.7E-06	< 0.005	< 3.3E-06	< 0.004	< 2.8E-06	< 0.003	< 2.2E-06	< 0.004	< 2.5E-06	< 0.004	< 2.4E-06
o-Xylene	< 0.006	<3.8E-06	< 0.003	< 1.9E-06	< 0.002	< 1.6E-06	< 0.002	< 1.3E-06	< 0.002	< 1.4E-06	< 0.002	< 1.3E-06
Results Summary												
Benzene (µg/dscm)	0.23		0.12		0.12		0.05		0.06		0.03	
Benzene (lb/hr)	4.57E-06		4.68E-06		5.78E-06		3.57E-06		3.51E-06		1.57E-06	
Detected Constituents (µg/dscm)	40.1		30.3		37.3		13.2		62.8		23.1	
Detected Constituents (lb/hr)	1.21E-04		2.22E-04		1.30E-04		1.07E-04		2.09E-04		3.19E-04	
Sum of DL values for all Non-detected Constituents (µg/dscm)	226.4		104.4		79.4		72.6		71.4		93.7	
Sum of DL values for all Non-detected Constituents (lb/hr)	3.92E-04		3.17E-04		3.19E-04		3.16E-04		3.37E-04		2.77E-04	
Benzene Feed Rate (lb/hr)	0.94		1.09		1.21		1.15		1.11		1.14	
Benzene Destruction Efficiency (%)	99.99951%		99.99957%		99.99952%		99.99969%		99.99968%		99.99986%	

Notes:

- Each 0031 test consisted of triplicate runs. Each run include 3 sorbent tubes per EPA 0031. The two TENAX tubes from each run were analyzed together; the Anasorb tube was analyzed separately. A single composite condensate sample, representing the total condensate collected for all 3 runs, was analyzed. The reported value for each analyte is the sum of the mass of the analyte detected

Test	ART-S2		ART-S5		ART-S6		ART-S7		ART-P1A		ART-P1B	
Date	4/18/2008		4/20/2008		4/21/2008		4/22/2008		4/20/2008		4/20/2008	
Test Period	13:15 - 16:05		15:30-18:35		8:45-11:30		9:00-11:28		9:20-12:07		9:15-11:41	
Total Sample Duration, Min	110		120.0		120.0		120.0		120.0		120.0	
Total Sample Volume, dry standard liters	32.00		64.44		78.39		99.83		93.56		86.91	
VOC Species Concentration	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr	µg/m ³ x10 ³	lbm/hr

in 6 tube analyses, 2 per run, and 1 condensate analysis.

- Each 0031 run was performed for nominally 40 minutes, and collected ~20 L at a sample rate of ~0.5 L/min, per the "Slow-VOST" method of extending the sample time without increasing the sample volume.
- If there were no detects in any analyses of a 3-run test, then the reported value is the sum of the analytical reporting limits with a "<" sign. If there was a detect in any of the analyses in a 3-run test, then the reporting protocol depends on the amount of the detected value compared to nondetect detection limits. If the sum of detected amounts is at least 10x greater than the sum of nondetects, then the total sum is **bolded**; but if less than 10x greater than the sum of nondetects, then the value is **bolded with a < sign**. Destruction efficiency results reported using "<" emissions data are greater than (">") the reported value.
- The total concentration and emission rate for all analytes is shown as **bolded** and without a "<" sign, even though a significant portion of the total reported values is the sum of non-detect values. Total Detected Constituent values may not equal the sum of the values of individual detected species, because detection limit values have been included in the total values of detected species, but excluded from the Total Detected Constituent values.
- Bold-faced and underlined** values indicate detected levels that are above the calibration range and so were estimated by extrapolation.
- *The Tenax 1 & 2 tube set from sampling set ART-S2 were broken during shipment to the laboratory; the reporting limits (RL) for each analyte were substituted in the data.
- No blank values, even if detected, have been subtracted from the stack sample values.

8.3.4.2 Benzene Destruction Efficiency.

Even though benzene was detected in the stack gas, it was destroyed in the process at high efficiencies. The benzene destruction efficiency using the Method 0031 results averaged 99.99989% for all tests. For production tests P1A and P1B the benzene destruction efficiencies were 99.99968% and 99.99986% respectively, averaging out to 99.99977% for both tests that were limited by the detection limits compared with the amount of benzene added.

8.3.4.3 SVOC Emissions.

The stack gas SVOC emissions are shown in Table 8-10. These SVOCs are normally analyzed in routine Method 0010 off-gas analyses. These particular species are those of greatest common interest in off-gas measurements because they are either common products of incomplete combustion, or represent a variety of higher-risk species in risk assessments. No speciated SVOCs were detected except for di-n-butyl phthalate and diethyl phthalate, which were detected at low levels near the detection limit. These same compounds were detected in prior steam reformer tests and may be due to low-level contamination.

Table 8-10 Stack Gas SVOC Concentrations and Emission Rates

Field Reference Method Data						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Date	4/18/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008
Results (lb/hr)						
Disulfoton	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
4-bromophenyl phenyl ether	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
4-chloro-3-methylphenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
2-chloronaphthalene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2-chlorophenol	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
4-chlorophenyl phenyl ether	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
dibenz(a,h)anthracene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
di-n-butyl phthalate	<u>2.77E-06</u>	<u>4.47E-06</u>	<u>2.62E-06</u>	<u>2.68E-06</u>	<u>3.06E-06</u>	<u>2.83E-06</u>
3,3'-dichlorobenzidine	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2,4-dichlorophenol	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Diethyl phthalate	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	<u>3.06E-06</u>	< 2.83E-06
2,4-Dimethylphenol	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Dimethyl phthalate	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
1,3-Dinitrobenzene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2,4-Dinitrophenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
2,4-Dinitrotoluene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2,6-Dinitrotoluene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Di-n-octyl phthalate	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Fluoranthene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Fluorene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Hexachlorobenzene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Hexachlorocyclopentadiene	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
Hexachloroethane	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Indeno (1,2,3-cd) pyrene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06

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Field Reference Method Data						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Date	4/18/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008
Results (lb/hr)						
Isophorone	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2-Methylphenol	< 5.55E-06	< 5.58E-06	< 5.24E-06	< 5.37E-06	< 6.11E-06	< 5.65E-06
3-Methylphenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
4-Methylphenol	< 5.55E-06	< 5.58E-06	< 5.24E-06	< 5.37E-06	< 6.11E-06	< 5.65E-06
2-Nitroaniline	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
3-Nitroaniline	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Nitrobenzene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2-Nitrophenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
N-Nitrosodi-n-butylamine	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
N-Nitrosodimethylamine	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
N-Nitrosodiphenylamine	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
N-Nitrosodi-n-propylamine	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Pentachlorobenzene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Pentachloronitrobenzene	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
Pentachlorophenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
Phenanthrene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
Phenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
1,2,4,5-Tetrachlorobenzene	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2,3,4,6-Tetrachlorophenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
o-Toluidine	< 5.55E-06	< 5.58E-06	< 5.24E-06	< 5.37E-06	< 6.11E-06	< 5.65E-06
2,4,5-Trichlorophenol	< 2.77E-06	< 2.79E-06	< 2.62E-06	< 2.68E-06	< 3.06E-06	< 2.83E-06
2,4,6-Trichlorophenol	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
1,3,5-Trinitrobenzene	< 1.39E-05	< 1.40E-05	< 1.31E-05	< 1.34E-05	< 1.53E-05	< 1.41E-05
Summary:						
di-n-butyl phthalate (lb/hr)	2.77E-06	4.47E-06	2.62E-06	2.68E-06	3.06E-06	2.83E-06
Diethyl phthalate (lb/hr)	< 06	< 06	< 06	< 06	3.06E-06	< 2.83E-06
Sum of DL values for the Non-detected SVOCs (lb/hr)	2.69E-04	2.71E-04	2.54E-04	2.60E-04	< 2.93E-04	< 2.74E-04
All SVOC Emission Rate	2.72E-04	2.75E-04	2.57E-04	2.63E-04	< 3.00E-04	< 2.77E-04
Notes:						
1. Bold-face results are detected and quantifiable, Bold and Underlined results are estimated; Result is less the reporting limit (reporting limit is substituted).						
2. Bold and italicized values are detected; the associated method blanks contain the target analyte at a reportable level.						

Field Reference Method Data						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Date	4/18/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008
Results (lb/hr)						
<p>3. All other values are non-detected with the detection limit being substituted.</p> <p>4. Sample ART-P1B arrived at the laboratory at 14°C. EPA specified temperature is 4°C.</p> <p>5. Samples ART-S2, S5, S6, S7, and P1 were received at 14°C, which is slightly above the 10°C EPA requirement.</p> <p>6. One pair of tenax tubes for ART-S2 arrived at the lab broken.</p>						

8.3.4.4 Total Organic Emissions.

The total organic emission measurements are shown in Table 8-11. Hydrocarbons in the C1 to C7 range were determined using EPA Method 0040. Larger hydrocarbons were determined using chromatographic methods (TCO/Grav analyses of sample obtained using EPA Method 0010). These organic emissions were measured, but not speciated, using these methods (except for benzene, which was speciated in the Method 0040 GC analysis).

The Method 0040 field GC results for benzene were 162 μ g/dscm for ART-P-1A and 292 μ g/dscm for ART-P-1B. During the scoping runs, the Method 0040 field GC results for benzene averaged 155 μ g/dscm.

The TCO/Grav results showed detectable total gravimetric organics emissions ranging between 0.3g/dscm to 10.5g/dscm. For the production tests ART P-1A and P-1B, the detectable total gravimetric organics emissions were 0.8 and 0.4g/dscm respectively.

The measured ranges of the C1 to C7 compounds and the TCO/Grav compounds are generally consistent with levels measured in prior steam reformer tests.

Table 8-11 Stack Gas Total Organic Emission Measurements

Field Data - 0040 Train						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Laboratory Data						
Tedlar Bag (ppmv)						
C ₁ compounds	1.23	1.17	1.00	1.49	1.18	1.25
C ₂ compounds	0.12	0.19	0.63	0.04	0.04	0.04
C ₃ compounds	0.05	0.08	0.14	0.12	0.17	0.13
C ₄ compounds	0.12	0.22	0.19	0.02	0.03	0.04
C ₅ compounds	0.02	0.02	0.05	0.02	0.06	0.05
C ₆ compounds	0.02	0.02	0.06	0.02	0.02	0.02
C ₇ compounds	0.02	0.02	0.02	0.02	0.02	0.02
Benzene	0.05	0.06	0.04	0.04	0.05	0.09
Condensate (µg/L)*						
C ₄ compoundsµ	---*	---*	2.0	2.0	---*	2.0
C ₅ compounds	---*	---*	1.0	2.0	---*	1.0
C ₆ compounds	---*	---*	1.0	1.0	---*	1.0

Field Data - 0040 Train																		
Run #	ART-S-2			ART-S-5			ART-S-6			ART-S-7			ART-P-1A			ART-P-1B		
C ₇ compounds	---*			---*			1.0			1.0			---*			1.0		
Surrogate Recovery																		
C ₈ compounds (% recovery)	N/A			N/A			101			103			N/A			102		
Calculations																		
tedlar bag volume (dscf)	0.30			0.30			0.30			0.30			0.30			0.29		
Organic Results (µg/dscm)	Volatile	Con _d	Tot _{al}	Volatile	Con _d	Tot _{al}	Volatile	Con _d	Tot _{al}	Volatile	Con _d	Tot _{al}	Volatile	Con _d	Tot _{al}	Volatile	Con _d	Tot _{al}
C ₁ compounds (BP < 0°C)	820	--	--	780	--	--	667	--	--	994	--	--	787	--	--	834	--	--
C ₂ compounds (BP < 0°C)	150	--	--	238	--	--	788	--	--	50	--	--	50	--	--	50	--	--
C ₃ compounds (BP < 0°C)	92	--	--	147	--	--	257	--	--	220	--	--	312	--	--	238	--	--
C ₄ compounds (BP 0°C - 30°C)	290	--	290	532	--	532	459	10.1	469	48	10.1	58	73	--	73	97	10.5	107
C ₅ compounds (BP 30°C - 60°C)	60	--	60	60	--	60	150	5.1	155	60	10.1	70	180	--	180	150	5.2	155
C ₆ compounds (BP 60°C - 90°C)	72	--	72	72	--	72	215	5.1	220	72	5.1	77	72	--	72	72	5.2	77
C ₇ compounds (BP 90°C - 98°C)	83	--	83	83	--	83	83	5.1	88	83	5.1	88	83	--	83	83	5.2	89
Benzene	162	--	162	195	--	195	130	--	130	130	--	130	162	--	162	292	--	292
Total Chromatographable Organics Emissions																		

Field Data - 0040 Train						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
total chromatographable organics (µg/dscm)	1.1E+03	9.9E+02	1.7E+03	3.5E+04	2.6E+03	1.6E+03
total chromatographable organics (g/hr)	0.30	0.28	0.48	10.45	0.79	0.44
total chromatographable organics (lb/hr)	6.7E-04	6.2E-04	1.1E-03	2.3E-02	1.7E-03	9.6E-04
Total Gravimetric Organics Emissions						
total gravimetric organics (µg/dscm)	2.2E+03	1.4E+03	1.8E+03	7.4E+03	2.0E+03	8.0E+02
total gravimetric organics (g/hr)	0.62	0.40	0.51	2.21	0.62	0.22
total gravimetric organics (lb/hr)	1.4E-03	8.7E-04	1.1E-03	4.9E-03	1.4E-03	4.8E-04
Notes:						
1. *ART-S-2, 5 and ART-P-1 condensate samples were lost during shipping; no analysis was conducted for those samples. Samples ART-S6 and ART-S7 were received by the laboratory at 20°C.						
2. Bold-face results are detected and quantifiable, <i>Bold and italic-face results</i> are estimated results that are less than the reporting limit (RL substituted).						
3. Bold and underlined values are detected; the associated method blanks contain the target analyte at a reportable level. All other values are non-detected with the reporting limit being substituted.						

Field Data - 0040 Train

Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
4. Samples ART-S2, S5, and P1 arrived broken at the laboratory. Samples ART-S6 and S7 arrived at the laboratory at 10°C. EPA specified temperature is 4°C.						
5. M0010-TCO samples for ART S2, S5, S6, S7, and P1 were received by the lab at 20°C. EPA specified temperature is 10°C. The back-half solvent rinse for the ART-P1 sample was lost and therefore not included in the measurements.						

8.3.4.5 Dioxin and Furan Emissions.

Stack gas dioxin and furan emission measurements are summarized in Table 8-12. No dioxins or furans were detected in any samples above the reporting limit. All dioxin and furan values, and the concentrations as percentages of the HWC MACT standard, were less than the reportable values.

Table 8-12 Stack Gas Dioxin and Furan Emission Measurements

Field Reference Method Data							
Run #		ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
date		4/18/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008
start time		13:15	15:30	8:45	9:00	9:20	9:15
stop time		16:30	18:45	12:00	12:18	12:56	12:25
sampling time (minutes)		180.0	180.0	180.0	180.0	180.0	180.0
sample volume (dscf)		78.837	78.973	88.037	83.274	78.009	74.965
sample volume (dscm)		2.232	2.236	2.493	2.358	2.209	2.123
moisture volume (dscf)		89.744	67.428	85.404	82.387	76.762	79.322
O ₂ Correction Factor		0.558	0.708	0.798	0.703	0.584	0.558
Concentration in Toxicity Equivalents (ng/dscm)							
	Relative Toxicity						
2,3,7,8-Cl4-Dibenzofuran	0.1	2.9E-04	3.0E-04	2.6E-04	2.8E-04	2.6E-04	3.7E-04
2,3,7,8-Cl4-Dibenzo-p-dioxin	1	5.4E-03	3.2E-03	2.8E-03	3.4E-03	2.9E-03	4.2E-03
1,2,3,7,8-Cl5-Dibenzofuran	0.05	1.9E-04	1.8E-04	1.8E-04	2.1E-04	1.9E-04	2.6E-04
2,3,4,7,8-Cl5-Dibenzofuran	0.500	1.9E-03	1.7E-03	1.8E-03	2.1E-03	1.9E-03	2.6E-03
1,2,3,7,8-Cl5-Dibenzo-p-dioxin	0.500	3.1E-03	2.9E-03	3.2E-03	4.0E-03	2.7E-03	4.5E-03
1,2,3,4,7,8-Cl6-Dibenzofuran	0.100	4.9E-04	3.4E-04	5.6E-04	4.7E-04	4.1E-04	6.1E-04
1,2,3,6,7,8-Cl6-Dibenzofuran	0.1	4.2E-04	2.9E-04	4.8E-04	3.9E-04	3.5E-04	5.2E-04
2,3,4,6,7,8-Cl6-Dibenzofuran	0.1	5.4E-04	3.7E-04	6.0E-04	5.1E-04	4.4E-04	6.6E-04
1,2,3,7,8,9-Cl6-Dibenzofuran	0.1	6.3E-04	4.2E-04	7.2E-04	5.5E-04	5.0E-04	7.5E-04
1,2,3,4,7,8-Cl6-Dibenzo-p-dioxin	0.1	5.4E-04	4.4E-04	6.4E-04	6.8E-04	4.5E-04	8.0E-04
1,2,3,6,7,8-Cl6-Dibenzo-p-dioxin	0.1	5.4E-04	4.3E-04	6.4E-04	6.8E-04	4.5E-04	8.0E-04
1,2,3,7,8,9-Cl6-Dibenzo-p-dioxin	0.1	4.5E-04	3.7E-04	5.6E-04	5.5E-04	4.0E-04	7.1E-04
1,2,3,4,6,7,8-Cl7-Dibenzofuran	0.01	1.1E-04	8.0E-05	6.4E-05	9.3E-05	5.4E-05	8.0E-05
1,2,3,4,7,8,9-Cl7-Dibenzofuran	0.01	1.3E-04	9.8E-05	8.0E-05	1.1E-04	6.8E-05	9.9E-05
1,2,3,4,6,7,8-Cl7-Dibenzo-p-dioxin	0.01	4.9E-05	5.4E-05	6.4E-05	8.5E-05	5.4E-05	1.3E-04
1,2,3,4,6,7,8,9-Cl8-Dibenzofuran	0.001	9.0E-06	8.9E-06	1.1E-05	1.7E-05	1.0E-05	2.4E-05
1,2,3,4,6,7,8,9-Cl8-dibenzo-p-dioxin	0.001	6.7E-06	6.7E-06	1.0E-05	1.4E-05	9.1E-06	2.0E-05
Total		1.5E-02	1.1E-02	1.3E-02	1.4E-02	1.1E-02	1.7E-02

Field Reference Method Data						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Concentrations in Toxicity Equivalents (ng/dscm, at 7% O ₂)						
2,3,7,8-Cl4-Dibenzofuran	1.6E-04	2.2E-04	2.1E-04	2.0E-04	1.5E-04	2.1E-04
2,3,7,8-Cl4-Dibenzo-p-dioxin	3.0E-03	2.3E-03	2.2E-03	2.4E-03	1.7E-03	2.4E-03
1,2,3,7,8-Cl5-Dibenzofuran	1.0E-04	1.2E-04	1.4E-04	1.5E-04	1.1E-04	1.4E-04
2,3,4,7,8-Cl5-Dibenzofuran	1.0E-03	1.2E-03	1.4E-03	1.5E-03	1.1E-03	1.4E-03
1,2,3,7,8-Cl5-Dibenzo-p-dioxin	1.7E-03	2.1E-03	2.6E-03	2.8E-03	1.6E-03	2.5E-03
1,2,3,4,7,8-Cl6-Dibenzofuran	2.7E-04	2.4E-04	4.5E-04	3.3E-04	2.4E-04	3.4E-04
1,2,3,6,7,8-Cl6-Dibenzofuran	2.3E-04	2.0E-04	3.8E-04	2.7E-04	2.0E-04	2.9E-04
2,3,4,6,7,8-Cl6-Dibenzofuran	3.0E-04	2.6E-04	4.8E-04	3.6E-04	2.6E-04	3.7E-04
1,2,3,7,8,9-Cl6-Dibenzofuran	3.5E-04	3.0E-04	5.8E-04	3.9E-04	2.9E-04	4.2E-04
1,2,3,4,7,8-Cl6-Dibenzo-p-dioxin	3.0E-04	3.1E-04	5.1E-04	4.8E-04	2.6E-04	4.5E-04
1,2,3,6,7,8-Cl6-Dibenzo-p-dioxin	3.0E-04	3.1E-04	5.1E-04	4.8E-04	2.6E-04	4.5E-04
1,2,3,7,8,9-Cl6-Dibenzo-p-dioxin	2.5E-04	2.6E-04	4.5E-04	3.9E-04	2.3E-04	3.9E-04
1,2,3,4,6,7,8-Cl7-Dibenzofuran	6.0E-05	5.7E-05	5.1E-05	6.6E-05	3.2E-05	4.5E-05
1,2,3,4,7,8,9-Cl7-Dibenzofuran	7.2E-05	7.0E-05	6.4E-05	8.0E-05	4.0E-05	5.5E-05
1,2,3,4,6,7,8-Cl7-Dibenzo-p-dioxin	2.7E-05	3.8E-05	5.1E-05	6.0E-05	3.2E-05	7.1E-05
1,2,3,4,6,7,8,9-Cl8-Dibenzofuran	5.0E-06	6.3E-06	8.6E-06	1.2E-05	5.8E-06	1.3E-05
1,2,3,4,6,7,8,9-Cl8-dibenzo-p-dioxin	3.7E-06	4.7E-06	8.3E-06	9.8E-06	5.3E-06	1.1E-05
Total	8.2E-03	8.0E-03	1.0E-02	9.9E-03	6.5E-03	9.6E-03
% of the HWC MACT Standard (0.11 ng/dscm)	7.5%	7.2%	9.2%	9.0%	5.9%	8.7%
Notes:						
1. No dioxins or furans were detected in any samples above the reporting limit. All dioxin and furan levels, and the concentrations as percentages of the HWC MACT standard, are less than the reported values.						

8.3.4.6 PCB Emissions.

The sample train used to determine stack gas dioxin and furan emissions was also used to determine stack gas PCB emissions. These results are shown in Table 8-13. PCBs totaled about 6.64 ng/dscm, corrected to 7% O₂. Most PCB congeners were not detected. Dioxin-like coplanar PCBs were not detected at detection limits of about 0.7 ng/dscm.

Table 8-13 Stack Gas PCB Measurements

STACK GAS PCB MEASUREMENTS						
Run #	ART-S-2	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B
Date	4/18/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008
start time	13:15	15:30	8:45	9:00	9:20	9:15
stop time	16:30	18:45	12:00	12:18	12:56	12:25
sampling time (minutes)	180.0	180.0	180.0	180.0	180.0	180.0
sample volume (dscf)	78.837	78.973	88.037	83.274	78.009	74.965
sample volume (dscm)	2.232	2.236	2.493	2.358	2.209	2.123
Total PCB Congener Concentrations (ng/dscm)						
Monochlorobiphenyl (total)	1.34	0.67	0.60	0.64	0.77	0.71
Dichlorobiphenyl (total)	5.82	3.44	2.21	0.64	4.12	2.31
Trichlorobiphenyl (total)	6.72	1.79	4.41	0.64	1.90	0.71
Tetrachlorobiphenyl (total)	1.57	0.67	0.60	0.64	0.68	0.71
Pentachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Hexachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Heptachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Octachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Nonachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Decachlorobiphenyl (total)	0.67	0.67	0.60	0.64	0.68	0.71
Total	19.49	10.60	11.43	6.36	11.54	8.67
Dioxin-like Coplaner PCB Concentrations (ng/dscm)						
3,4,4',5'-Tetrachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
3,3',4,4'-Tetrachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2',3,4,4',5'-Pentachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3',4,4',5'-Pentachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3,4,4',5'-Pentachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3,3',4,4'-Pentachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
3,3',4,4',5'-Pentachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3',4,4',5'-Hexachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3,3',4,4',5'-Hexachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3,3',4,4',5'-Hexachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
3,3',4,4',5,5'-Hexachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,2',3,3',4,4',5'-Heptachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
2,3,3',4,4',5,5'-Heptachlorobiphenyl	0.67	0.67	0.60	0.64	0.68	0.71
Total	9.41	9.39	8.42	8.91	9.51	9.89
Notes:						
1 Bold-face results are detected and quantifiable. Bold and Underlined results are were positively identified, but the quantization is an estimate.						

2 *Bold and italicized values* are detected; the associated method blanks contain the target analyte at a reportable level.

3 All other values are non-detected with the detection limit being substituted.

8.3.5 Particulate Matter and Halide Emissions

A limited number of manual sample trains were performed to determine stack gas concentrations and emission rates of particulate matter and total HCl/Cl₂, HI/I₂, and HF/F₂ emissions. The total HCl/Cl₂, HI/I₂, and HF/F₂ emissions are normalized as total HCl, HI, and HF. Table 8-14 shows these results.

Figure 8-7 shows that the behavior of these halides was similar to that of SO₂ during the scoping and production tests. Elevated levels of these halides were detected in the stack gas during the scoping tests, S-1 and S-2. These likely occurred because halide-laden product fines that elutriated from the DMR passed into the higher-temperature, oxidizing CRR. A portion of the halides in the product were probably roasted from the product, forming halide gases. During these tests, the product retained about 70-90% of the halides in the feed.

Halide roasting was apparently reduced during S-3 through S-7, when the average CRR bed temperature was reduced from ~950°C to ~850°C. The product during these tests retained about 88-99% of the halides for all but iodine during S-3. When the HTF was in-line and filtering product fines from the process gas stream during the P-1 tests, the product retained about 83-95% of the halides, even when the CRR was operated at higher temperatures. Halide concentrations varied during the P-2 test when the WTP SW simulant was fed. While Cl was retained with a relatively high efficiency (95%), the F and I retentions were lower at 66% and 19%, respectively. The difference in these system removal efficiencies for iodine can be partially attributed to the amounts of iodine added to the LAW simulant (0.13lb/hr) versus the amount iodine added to the WTP SW simulant (0.0090lb/hr), which therefore affects the ability to detect iodine in the off-gas.

The HCl/Cl₂ off-gas concentration for the three production tests averaged 7.8 ppmv, or 37% of the HWC MACT standard of 21ppmv. During the production runs, Cl from NaCl in the feed was captured in the solid products, with an average removal efficiency of over 92%. In addition, fluoride and iodide were captured with 78% and 68% efficiencies averaged over the production tests.

While emissions of iodine species are not regulated under the HWC MACT standards, emissions of radioactive iodine are restricted by other EPA regulations. Control of non-radioactive iodine in the LAW and WTP SW simulants indicates how radioactive iodine would be controlled in a radioactive waste treatment process. Off-gas concentrations of non-radioactive iodine species HI and I₂, normalized to an HI basis, ranged between 2-11ppmv (dry basis at 7% O₂) while the HTF was bypassed, and between 1-5ppmv (dry basis at 7% O₂) after the DMR process gas was filtered through the HTF. The system removal efficiency for iodine in LAW simulant ranged from 59-95% when the HTF was bypassed. The system removal efficiency for iodine in the LAW simulant ranged from 89-94% when the DMR process gas was filtered through the HTF. The system removal efficiency for iodine in the WTP SW simulant was lower at about 19%, because the input feed rate of iodine in the WTP SW simulant was less than one tenth of the iodine feed rate for the LAW tests, and the stack gas iodine concentration for the WTP SW test was in the same range as the iodine concentrations in the LAW tests.

Figure 8-8 shows that particulate emissions during the scoping tests exceeded the HWC MACT limit. During the scoping tests the process gas from the DMR bypassed the HTF. DMR product and coal fines passed into the CRR, and product fines were captured in the OGF. After the scoping tests, it was found that OGF tube sheet seal had been damaged or incorrectly installed such that it did not seal. This allowed some of the dirty gas to flow straight from the dirty side of the filter housing to the clean side, bypassing the filter elements.

After the HTF was valved back in for the scoping tests, most of the product filtration occurred in the HTF and not the OGF. The gas filtered in the OGF was already relatively clean containing only small amounts

of particulate matter that either passed through the HTF or elutriated from the CRR bed. The stack gas particulate matter concentrations during the production tests were much lower than during the scoping tests, and averaged only 18% of the MACT standard for the production runs. High-efficiency particulate air (HEPA) filtration, typically used in nuclear facilities for radionuclide control, will result in even lower stack gas PM levels than were measured in the Hazen test system, which was not HEPA filtered.

Table 8-14 Stack Gas Particulate Matter and HX/X₂ Concentrations

Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Date	4/17/2008	4/18/2008	4/19/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008	5/4/2008
Start time	11:00	9:00	10:02	9:00	13:00	13:20	14:00	13:15	8:20
Stop time	14:20	12:17	13:17	14:30	16:32	16:48	17:20	17:45	11:35
SO₄ Impingers (Reported as HX)									
1 (ppmvd)	32.7	30.4	6.0	1.6	2.3	0.7	13.4	3.2	16.9
1 (lb/hr)	2.82E-02	2.72E-02	5.64E-03	1.57E-03	2.31E-03	6.49E-04	1.37E-02	3.02E-03	1.64E-02
1 (tpy)	1.23E-01	1.19E-01	2.47E-02	6.88E-03	1.01E-02	2.84E-03	6.02E-02	1.32E-02	7.20E-02
1 (ppmvd)	5.7	7.6	2.8	1.5	3.3	2.3	6.9	6.2	121.6
1 (lb/hr)	5.23E-03	7.31E-03	2.86E-03	1.59E-03	3.48E-03	2.38E-03	7.52E-03	6.27E-03	0.13
1 (tpy)	2.29E-02	3.20E-02	1.25E-02	6.96E-03	1.53E-02	1.04E-02	3.29E-02	2.75E-02	0.55
1 (ppmvd as HI)	9.3	12.8	16.5	2.5	1.7	1.9	3.6	1.9	2.0
1 (lb/hr as HI)	2.81E-02	4.01E-02	5.48E-02	8.73E-03	5.78E-03	6.36E-03	1.29E-02	6.32E-03	6.69E-03
1 (tpy as HI)	1.23E-01	1.76E-01	2.40E-01	3.83E-02	2.53E-02	2.78E-02	5.64E-02	2.77E-02	2.93E-02
OH Impingers (Reported as X₂)									
1 (ppmvd)	0.84	0.32	0.28	0.57	0.85	0.26	1.55	1.58	0.32
1 (lb/hr)	1.41E-03	5.56E-04	5.11E-04	1.10E-03	1.64E-03	4.92E-04	3.10E-03	2.89E-03	6.12E-04
1 (tpy)	6.17E-03	2.43E-03	2.24E-03	4.82E-03	7.20E-03	2.15E-03	1.36E-02	1.26E-02	2.68E-03
1 (ppmvd)	0.19	0.16	0.15	0.13	0.24	0.99	0.38	0.30	0.22
1 (lb/hr)	1.71E-04	1.53E-04	1.51E-04	1.34E-04	2.56E-04	1.01E-03	4.17E-04	3.03E-04	2.34E-04
1 (tpy)	7.48E-04	6.72E-04	6.61E-04	5.87E-04	1.12E-03	4.43E-03	1.83E-03	1.33E-03	1.02E-03
1 (ppmvd)	0.28	0.24	0.55	0.24	0.18	3.20	0.28	0.22	0.17
1 (lb/hr)	8.38E-04	7.53E-04	1.82E-03	8.42E-04	6.28E-04	1.08E-02	1.02E-03	7.41E-04	5.73E-04
1 (tpy)	3.67E-03	3.30E-03	7.97E-03	3.69E-03	2.75E-03	4.71E-02	4.47E-03	3.25E-03	2.51E-03
1 (ppmvd as HCl equivalents)	1.68	0.64	0.56	1.14	1.69	0.53	3.11	3.15	0.65
1 (ppmvd as HF equivalents)	0.37	0.32	0.30	0.25	0.48	1.97	0.76	0.60	0.45
1 (ppmvd as HI equivalents)	0.55	0.48	1.10	0.48	0.36	6.40	0.57	0.45	0.34

Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Date	4/17/2008	4/18/2008	4/19/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008	5/4/2008
HF/ HI Equivalent Emission Rates (dry basis, as measured)									
H ₂ + Cl ₂ (ppmvd as HCl equivalents)	34.4	31.1	6.51	2.71	4.00	1.20	16.5	6.36	17.5
H ₂ + F ₂ (ppmvd as HF equivalents)	6.04	7.96	3.13	1.74	3.74	4.29	7.62	6.83	122
H ₂ + I (ppmvd as HI equivalents)	9.85	13.25	17.59	2.98	2.01	8.29	4.15	2.36	2.29
Stack Gas Particulate Matter Concentration and Emission Rate (dry basis, as measured)									
Sample volume (dscf)	75	74	75	85	86	84	85	79	84
Moisture volume (dscf)	79	78	68	74	84	84	87	85	84
Sample volume (dscm)	2.24	2.20	1.93	2.10	2.38	2.36	2.46	2.39	2.38
PM ₁₀ (lb/hr)	0.0689	0.0616	0.1300	0.0683	0.0431	0.0185	6.50E-04	1.01E-03	5.24E-04
PM ₁₀ (mg/dscm)	115	99	229	115	67	29	0.91	1.5	0.82
PM ₁₀ (gr/dscf)	0.0529	0.0455	0.0909	0.044	0.029	0.013	4.10E-04	7.02E-04	3.59E-04
Concentrations and Emission Rates Corrected to 7% O₂ Basis (dry)									
O ₂ Correction Factor	0.57	0.56	0.64	0.70	0.67	0.64	0.57	0.55	0.59
H ₂ + Cl ₂ (ppmvd as HCl equivalents)	19.6	17.5	4.1	1.9	2.7	0.8	9.5	3.5	10.4
H ₂ + F ₂ (ppmvd as HF equivalents)	3.4	4.5	2.0	1.2	2.5	2.8	4.4	3.8	72.1
H ₂ + I (ppmvd as HI equivalents)	5.6	7.4	11.2	2.1	1.3	5.3	2.4	1.3	1.4
PM ₁₀ (lb/hr)	2.96E-02	2.78E-02	6.15E-03	2.67E-03	3.95E-03	1.14E-03	1.68E-02	5.91E-03	1.70E-02
PM ₁₀ (lb/hr)	5.40E-03	7.46E-03	3.01E-03	1.72E-03	3.74E-03	3.39E-03	7.94E-03	6.58E-03	1.27E-01
PM ₁₀ (lb/hr)	2.90E-02	4.08E-02	5.66E-02	9.58E-03	6.41E-03	1.71E-02	1.39E-02	7.06E-03	7.26E-03
PM ₁₀ (lb/hr)	3.92E-02	3.46E-02	8.26E-02	4.75E-02	2.89E-02	1.19E-02	3.73E-04	5.61E-04	3.10E-04
PM ₁₀ (mg/dscm)	65.38	55.73	145.33	79.88	45.08	18.80	0.52	0.83	0.48
PM ₁₀ (gr/dscf)	3.01E-02	2.56E-02	5.78E-02	3.03E-02	1.93E-02	8.21E-03	2.35E-04	3.89E-04	2.12E-04
PM ₁₀ as % of MACT Std (3.4 mg/dscm)	1923%	1639%	4274%	2349%	1326%	553%	15%	24%	14%
PM₁₀ and F Mass Feed Rates (lb/hr)									
PM ₁₀ (lb/hr)	0.13	0.13	0.13	0.12	0.13	0.13	0.12	0.12	0.34
F (lb/hr)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.37
I (lb/hr)	0.14	0.14	0.14	0.13	0.14	0.14	0.13	0.13	0.0090
Mass Removal Efficiencies (%)									
PM ₁₀ Removal Efficiency (%)	77.6%	78.4%	95.3%	97.9%	97.0%	99.1%	86.4%	95.1%	94.9%
F Removal Efficiency (%)	89.4%	85.0%	94.0%	96.4%	92.6%	93.4%	83.4%	85.8%	66.0%
I Removal Efficiency (%)	79.3%	70.2%	58.9%	92.8%	95.4%	87.9%	89.4%	94.4%	19.1%

Figure 8-6 Halide Species Emissions during the Scoping and Production Tests

Figure 8-7 Particulate Matter Concentrations during ART Tests

8.3.6 Metals Emissions Including Radionuclide Surrogates

Stack gas metals emissions were determined using EPA Method 29 at the stack sample location. Stack gas concentrations for the low volatility and semi-volatile metals (LVMs and SVMs) as defined by the HWC MACT standards are shown in Table 8-15. The only LVMs that were present in the feed were Cr and As. Both SVMs (Pb and Cd) were in the feed. Aluminum and sodium were the most detected in the off-gas at higher concentrations than other metals, which is consistent with their proportionately higher levels in the liquid feed.

Figure 8-9 shows that, like the total particulate emissions, emissions of these metals were several times higher during the scoping tests than for the production tests, because a failure of the OGF tubesheet seal allowed some unfiltered gas to pass from the dirty side of the OGF to the clean side. Concentrations of SVM and LVM during the scoping tests exceeded the HWC MACT standards. When the process gas was filtered through the HTF during the LAW production test, both the SVM and LVM were within the HWC MACT standard. The LVM for the WTP SW test was equal to 24 µg/dscm, which is slightly above the MACT standard of 23 µg/dscm.

Table 8-15 Low Volatility and Semi-Volatile Metals Stack Gas Concentrations

Field Reference Method Data									
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Date	4/17/2008	4/18/2008	4/19/2008	4/20/2008	4/21/2008	4/22/2008	4/28/2008	4/30/2008	5/4/2008
start time	11:00	9:00	10:02	9:00	13:00	13:20	14:00	13:15	8:20
stop time	14:20	12:17	13:17	14:29	16:32	16:48	17:20	17:45	11:35
sampling time (minutes)	180	180	180	180	180	180	180	180	180
sample volume (dscf)	74.354	75.673	76.798	86.272	88.101	83.507	86.491	80.580	82.190
sample volume (dscm)	2.105	2.143	2.175	2.443	2.495	2.365	2.449	2.282	2.327
moisture volume (dscf)	75.383	77.463	69.452	70.384	79.850	82.871	87.734	83.846	80.904
Metals Concentrations in the Stack Gas Corrected to 7% O ₂ Basis- µg/dscm									
7% O ₂ Factor	0.57	0.56	0.64	0.70	0.67	0.64	0.57	0.55	0.59
silver	3.25	2.95	1.74	1.47	1.12	1.57	0.07	0.08	0.13
Aluminum	4,925	2,364	4,338	3,479	4,081	3,084	121	141	599
arsenic	10.3	9.5	19.0	12.3	7.8	3.4	0.23	0.93	20.7
barium	23.6	18.2	24.2	22.1	35.8	28.1	2.65	2.55	8.0

Field Reference Method Data									
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
cadmium	21.3	22.7	38.7	20.4	19.9	15.0	0.83	0.59	1.2
Chromium	50.9	43.3	97.1	82.9	39.5	11.0	2.47	5.00	3.5
Cesium	60	51	111	97	62	69	2	1	1
iron	448	531	1,072	496	251	126	44	46	230
Potassium	98	83	106	98	79	58	18	19	99
Magnesium	16.2	9.6	11.1	9.2	16.1	15.3	9.7	9.2	49.2
Sodium	5,631	3,817	7,273	5,601	2,962	2,745	374	368	3,430
Nickel	46	43	103	76	35	17	3	6	3
Lead	61	57	105	76	48	37	2	1	1
Rhenium	22.9	21.0	45.8	20.0	13.4	9.41	0.36	0.37	0.39
Antimony	33.4	32.1	76.1	62.5	34.3	11.7	0.3	0.3	0.3
Selenium	17.5	47.1	51.6	28.8	32.0	20.7	7.8	46.1	2,154
Thallium	22.5	25.0	48.2	42.2	23.8	20.9	25.9	30.4	12.3
Low and Semi-Volatile Metals Stack Gas Concentrations at 7% O ₂ - µg/dscm									
Low Volatility Metals	61	53	116	95	47	14	3	6	24
arsenic	10.3	9.5	19.0	12.3	7.8	3.4	0.23	0.93	20.7

Field Reference Method Data									
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Chromium	50.9	43.3	97.1	82.9	39.5	11.0	2.47	5.00	3.5
MACT Standard (µg/dscm)	23	23	23	23	23	23	23	23	23
LVM as % MACT Std	266%	230%	505%	414%	206%	63%	12%	26%	105%
Semi-Volatile Metals	82	80	144	97	68	52	2	2	2
cadmium	21.3	22.7	38.7	20.4	19.9	15.0	0.83	0.59	1.2
Lead	60.9	56.9	105.5	76.2	48.3	37.46	1.55	1.00	1.22
MACT Standard (µg/dscm)	10	10	10	10	10	10	10	10	10
SVM as % MACT Std	822%	797%	1441%	967%	682%	524%	24%	16%	24%
<p>1. Bold-face results are detected and quantifiable.</p> <p>2. All other values are non-detected with the reporting limit being substituted.</p> <p>3. Se detected during the ART-P-2 test was 40-300x higher than Se detected during other tests, even though Se in the WTP SW feed was only about 2x higher. This data point appears to be an outlier; while reported here, it is not included in trending with the other Se data.</p>

Figure 8-8 LVM and SVM Emissions for ART Tests

LVM emissions during the WTP SW production test, ART-P-2, slightly exceeded the HWC MACT standard. The Hazen facility is not HEPA filtered like a full-scale radioactive processing facility. With more effective filtration such as would be seen in a full-scale radioactive processing facility, it could reasonably be expected that LVMs resulting from the WTP SW stream would be well below the MACT standard for LVMs

Total emission rates in pounds of metal per hour emitted from the stack were calculated and are shown in Table 8-16. These emission rates were compared against the metal feed rates shown in Table 8-17 to calculate system removal efficiencies for these metals as shown in Table 8-18. The difference represents the amounts of those metals retained by the process and removed from the off-gas. Figure 8-10 shows that, during the scoping tests when the HTF was bypassed, metal SREs ranged between about 99.9 and 99.99%, even with the elevated PM emissions that bypassed the OGF. After the HTF was valved into the process, metal SREs increased. SREs for most of the metals during P-1 averaged about a factor of 10 higher than for the scoping tests. The metal SREs for the WTP SW test trended lower than for the other production tests.

The SREs for those metals known to be more volatile (Cs, Pb, K, Na, and Cd) are seen to trend in the same ranges as the SREs for the other metals. The steam reforming process retains these more volatile metals in the solid products with the same general efficiencies as for less volatile metals, because of the

relatively low operating temperatures and the high filtration efficiencies (even though the test facility was not HEPA filtered).

Table 8-16 Stack Gas Metals Emissions Rates

Metals Emissions - lb/hr									
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Silver	3.3E-06	3.1E-06	1.7E-06	1.5E-06	1.1E-06	1.5E-06	8.8E-08	8.7E-08	1.4E-07
Aluminum	5.0E-03	2.5E-03	4.3E-03	3.5E-03	4.1E-03	3.0E-03	1.5E-04	1.6E-04	6.5E-04
Arsenic	1.0E-05	1.0E-05	1.9E-05	1.2E-05	7.9E-06	3.4E-06	2.8E-07	1.1E-06	2.2E-05
Barium	2.4E-05	1.9E-05	2.4E-05	2.2E-05	3.6E-05	2.8E-05	3.2E-06	2.9E-06	8.7E-06
Cadmium	2.2E-05	2.4E-05	3.8E-05	2.0E-05	2.0E-05	1.5E-05	1.0E-06	6.8E-07	1.3E-06
Chromium	5.2E-05	4.6E-05	9.6E-05	8.3E-05	4.0E-05	1.1E-05	3.0E-06	5.8E-06	3.8E-06
Cesium	6.1E-05	5.5E-05	1.1E-04	9.7E-05	6.3E-05	6.8E-05	2.8E-06	1.6E-06	1.6E-06
Iron	4.6E-04	5.6E-04	1.1E-03	5.0E-04	2.5E-04	1.2E-04	5.4E-05	5.3E-05	2.5E-04
Potassium	9.9E-05	8.8E-05	1.0E-04	9.8E-05	8.0E-05	5.7E-05	2.2E-05	2.2E-05	1.1E-04
Magnesium	1.6E-05	1.0E-05	1.1E-05	9.2E-06	1.6E-05	1.5E-05	1.2E-05	1.1E-05	5.3E-05
Sodium	5.7E-03	4.1E-03	7.2E-03	5.6E-03	3.0E-03	2.7E-03	4.5E-04	4.2E-04	3.7E-03
Nickel	4.7E-05	4.5E-05	1.0E-04	7.6E-05	3.5E-05	1.7E-05	3.1E-06	6.6E-06	3.3E-06
Lead	6.2E-05	6.1E-05	1.0E-04	7.6E-05	4.9E-05	3.7E-05	1.9E-06	1.2E-06	1.3E-06
Rhenium	2.3E-05	2.2E-05	4.5E-05	2.0E-05	1.4E-05	9.3E-06	4.4E-07	4.3E-07	4.3E-07
Antimony	3.4E-05	3.4E-05	7.5E-05	6.3E-05	3.5E-05	1.2E-05	4.0E-07	2.9E-07	3.2E-07
Selenium	1.8E-05	5.0E-05	5.1E-05	2.9E-05	3.2E-05	2.0E-05	9.4E-06	5.3E-05	2.3E-03
Thallium	2.3E-05	2.7E-05	4.8E-05	4.2E-05	2.4E-05	2.1E-05	3.1E-05	3.5E-05	1.3E-05
Total Metals (lb/hr)	1.2E-02	7.6E-03	1.3E-02	1.0E-02	7.8E-03	6.2E-03	7.4E-04	7.8E-04	7.2E-03
1 Bold-face results are detected and quantifiable.									
2 All other values are non-detected with the reporting limit being substituted.									

Of special interest are the SREs for the radionuclide surrogates Cs and Re. Cs was added to the simulant feed as a surrogate for radioactive Cs and Re was added as a surrogate for ⁹⁹Tc. The SREs for these species were 99.999% and 99.998%, respectively, for the production tests, indicating near complete capture of these species in the solid product. The reported SRE values for these radionuclide surrogates are conservatively low estimates of the actual SREs that might be achievable in a HEPA-filtered steam reformer system.

Table 8-17 Simulant Metal Feed Rates

Average Metals Feedrates - lb/hr									
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7	ART-P-1A	ART-P-1B	ART-P-2A
Silver	0.015	0.014	0.014	0.014	0.015	0.015	0.014	0.013	0.008
Aluminum	10.936	10.680	10.737	10.339	9.789	8.827	10.266	9.399	6.307
Arsenic	0.105	0.103	0.103	0.099	0.095	0.086	0.099	0.091	0.001
Barium	0.147	0.144	0.145	0.139	0.140	0.136	0.138	0.131	0.000
Cadmium	0.040	0.039	0.039	0.038	0.040	0.040	0.038	0.036	0.009
Chromium	0.046	0.045	0.045	0.043	0.045	0.046	0.043	0.042	0.028
Cesium	0.147	0.143	0.144	0.139	0.145	0.148	0.138	0.133	0.175
Iron	0.207	0.203	0.204	0.196	0.185	0.167	0.195	0.178	0.122
Potassium	0.041	0.040	0.040	0.039	0.041	0.041	0.039	0.037	0.163
Magnesium	0.0086	0.0084	0.0085	0.0082	0.0077	0.0070	0.0081	0.0074	0.013
Sodium	9.798	9.568	9.619	9.263	9.691	9.852	9.197	8.874	5.700
Nickel	0.0529	0.0516	0.0519	0.0500	0.0523	0.0532	0.0496	0.0479	0.0241
Lead	0.107	0.104	0.105	0.101	0.106	0.107	0.100	0.0966	0.0244
Rhenium	0.0269	0.0263	0.0264	0.0254	0.0266	0.0270	0.0252	0.0244	0.0190
Antimony	0.0449	0.0438	0.0441	0.0424	0.0444	0.0451	0.0421	0.0407	0.0175
Selenium	0.0083	0.0081	0.0081	0.0078	0.0082	0.0083	0.0077	0.0075	0.0175
Thallium	0.207	0.203	0.204	0.196	0.185	0.167	0.195	0.178	0.018
Total Metals (lb/hr)	21.9	21.4	21.5	20.7	20.6	19.8	20.6	19.3	12.6

Table 8-18 Simulant Metal System Removal Efficiencies

Sampling Train Parameters												
Run #	ART-S-1	ART-S-2	ART-S-4	ART-S-5	ART-S-6	ART-S-7		ART-P-1A	ART-P-1B		ART-P-2A	
date	4/17/2008	4/18/2008	4/19/2008	4/20/2008	4/21/2008	4/22/2008		4/28/2008	4/30/2008		5/4/2008	
start time	11:00	9:00	10:02	9:00	13:00	13:20		14:00	13:15		8:20	
stop time	14:20	12:17	13:17	14:29	16:32	16:48		17:20	17:45		11:35	
System Removal Efficiencies (SRE) for Scoping Tests, %							Average	Production Run SRE, %		Average		Average
silver	99.98%	99.98%	99.99%	99.99%	99.99%	99.99%	99.99%	99.999%	99.999%	99.999%	99.998%	99.999%
aluminum	99.95%	99.98%	99.96%	99.97%	99.96%	99.97%	99.96%	99.999%	99.998%	99.998%	99.990%	99.996%
arsenic	99.99%	99.99%	99.98%	99.99%	99.99%	99.996%	99.99%	99.9997%	99.999%	99.999%	96.794%	98.931%
barium	99.98%	99.99%	99.98%	99.98%	99.97%	99.98%	99.98%	99.998%	99.998%	99.998%	96.819%	98.938%
cadmium	99.95%	99.94%	99.90%	99.95%	99.95%	99.96%	99.94%	99.997%	99.998%	99.998%	99.986%	99.994%
chromium	99.89%	99.90%	99.79%	99.81%	99.91%	99.98%	99.88%	99.993%	99.986%	99.990%	99.986%	99.989%

cesium	99.96%	99.96%	99.92%	99.93%	99.96%	99.95%	99.95%	99.998%	99.999%	99.998%	99.999%	99.999%
iron	99.78%	99.72%	99.48%	99.75%	99.86%	99.93%	99.75%	99.972%	99.970%	99.971%	99.796%	99.913%
potassium	99.76%	99.78%	99.74%	99.75%	99.80%	99.86%	99.78%	99.943%	99.942%	99.943%	99.934%	99.940%
magnesium	99.81%	99.88%	99.87%	99.89%	99.79%	99.78%	99.84%	99.855%	99.858%	99.856%	99.601%	99.771%
sodium	99.94%	99.96%	99.93%	99.94%	99.97%	99.97%	99.95%	99.995%	99.995%	99.995%	99.935%	99.975%
nickel	99.91%	99.91%	99.81%	99.85%	99.93%	99.97%	99.90%	99.994%	99.986%	99.990%	99.986%	99.989%
lead	99.94%	99.94%	99.90%	99.92%	99.95%	99.97%	99.94%	99.998%	99.999%	99.998%	99.995%	99.997%
rhenium	99.91%	99.92%	99.83%	99.92%	99.95%	99.97%	99.92%	99.998%	99.998%	99.998%	99.998%	99.998%
antimony	99.92%	99.92%	99.83%	99.85%	99.92%	99.97%	99.90%	99.999%	99.999%	99.999%	99.998%	99.999%
selenium	99.79%	99.38%	99.37%	99.63%	99.60%	99.75%	99.59%	99.878%	99.290%	99.584%	86.621%	95.263%
thallium	99.99%	99.99%	99.98%	99.98%	99.99%	99.99%	99.98%	99.984%	99.980%	99.982%	99.924%	99.963%

Figure 8-9 Metals System Removal Efficiencies Measured during the ART Test

9. MASS BALANCE

An important objective of the test program is to close the mass balance around the ESTD system. The mass balance measures and calculates the mass of material fed to the system and the amount removed and compares those values to determine closure. The mass balance is performed on both an overall and an elemental (or component) basis. Overall and component mass balances have been measured and calculated for the both the LAW and WTP SW production tests (4:00 am April 27, 2008, to 11:30 am May 1 for LAW and 10:00 pm May 1, 2008, to 11:15 am May 6, 2008, for WTP SW).

Various inaccuracies can be introduced to the determination of mass balance closure. These include:

Solids samples may not be entirely representative of the streams from which they were taken.

Laboratory measurement methods may not have been entirely appropriate for the sample matrix. The analyses were performed using both SW-846 methods and more aggressive digestion methods, but these methods may not have been completely appropriate due to the difficulty in digesting the sample matrix or analytical interferences from other components.

Because of these potential influences, an overall balance showing a difference (or “closure”) of less than 10% is considered acceptable for major components and less than 5% is considered excellent. The test plan calls for a mass balance closure of $\pm 10\%$ for major components (C, N₂, O₂, Al, Na, Si, B, Ti and H₂O) and a mass balance closure of $\pm 30\%$ for minor components (S, Cl, F, I, PO₄, K, Cs, Fe). The mass balance closure for trace components (Ag, As, Ba, Ca, Cd, Cr, Mg, Ni, Pb, Re, Sb, Se, Tl, Zn) depends on the analytical detection limits for these compounds and hence is difficult to be specified *a priori*. In general, components present at greater than 0.1 molar in the feed are considered major; components less than 0.1 molar, but greater than 0.01 molar are minor; and all other components are trace.

9.1 Methodology

The methodology for calculating the overall and component mass balance closures, the component flows of each inlet and outlet stream, as well as any assumptions made, are described in this section. ESTD feed logs, product logs, operator logs, data logs, DACS data, chemical supplier data, and analytical data were used to determine the flow and composition of each stream. The mass balance for each component was performed using the following equation:

$$\frac{(\sum_i \text{Output mass}_i * \text{Weight \% of component} - \sum_i \text{Input Mass}_i * \text{Weight \% of component})}{\sum_i \text{Input Mass}_i * \text{Weight \% of component}} = 0 \quad (9-1)$$

where the sum indicates summing over all the various input or output streams.

The total mass balance was calculated using the sum of all the individual components:

$$\frac{(\sum_e \sum_i \text{Output mass}_i * \text{Weight \% of component} - \sum_e \sum_i \text{Input Mass}_i * \text{Weight \% of component})}{\sum_e \sum_i \text{Input Mass}_i * \text{Weight \% of component}} = 0 \quad (9-2)$$

where the sums indicates summing over all the various input or output streams and over all the components.

The mass balance for the LAW production test covers the time from the addition of feed (4:00 am April 27, 2008) until oxygen feed to the DMR was stopped (11:30 am May 1, 2008). The mass balance for the WTP SW production test covers the time from the placement of the new starting bed in the DMR (10:00 pm May 1, 2008) until oxygen feed to the DMR was stopped (11:15 am May 6, 2008). These time frames were chosen in order to account for the consumption of all carbon fed to the process during the production tests. During shutdown, once the oxygen is shut off and the process is switched to nitrogen fluidization, the carbon oxidation reactions are stopped and only nitrogen is sent out through the stack. Thus, the time when oxygen is not fed has no impact on the solid mass balance and, since all gas inputs go directly to the stack, this time may be discounted from the gaseous mass balance without affecting the overall mass balance closure.

Determining the component mass balance involved tracking several gaseous, liquid, and solid inputs and solid and gaseous outputs (there were no liquid outputs). All the inputs and outputs are shown in Figure 9-1 and summarized in Table 9-1. The total masses of all solid and liquid flows were measured by weight or flow instrumentation and the composition of each stream was based on supplier data and/or analytical results. The total masses of all gaseous streams were measured and the compositions of all input gaseous streams were known. While the flow rate of the output gas was continuously measured, the composition of the major components was only partially characterized; specifically, the oxygen, carbon dioxide, carbon monoxide, nitrogen oxide, sulfur dioxide, and total hydrocarbons were continuously measured, but the nitrogen and water were not. These major outlet gas components had to be estimated based on inputs and process chemistry (see detailed explanation below). Detailed gas emissions analyses for short time periods during the tests were performed as described in Sections 8.3.6 and 8.3.7. These gas analyses included measurement of moisture and estimation of nitrogen as well as measurement of trace chemical components.

All significant gaseous inputs were continuously measured by flowmeters and the measurements were recorded by the DACS. The compositions of all the input gaseous streams were known. Most of the streams were pure components – e.g., nitrogen, oxygen, or water (steam). Some of the streams consisted of air, which were estimated to be 21% oxygen and 79% nitrogen. There were no other input gaseous stream compositions. Some of the gaseous nitrogen input streams were not directly measured; however, their total flow was insignificant compared to monitored nitrogen streams and were not included in the mass balance calculation (see Table 9-1 for specific streams).

All of the solid input flows were measured either by loss of weight metering devices (coal) or by measurement on a scale before manual addition to the process. The manual weights were recorded in logs. The compositions of all the solids were known from supplier specifications or in the case of the coal composition, by direct analytical measurements.

Figure 9-1 Diagram of Inputs and Outputs for the ESTD

Table 9-1 Summary of Feed and Discharge Streams - Method of Flow Rate Composition Quantification

Process Unit and Stream (see Figure 9-1)	Flow Measured (Yes or No)	Composition and Comments
DMR – inputs		
Fluidizing gas steam	Yes - DACS	Pure water
Fluidizing gas nitrogen	Yes - DACS	Pure nitrogen
Heat source gas oxygen and dilution nitrogen	Yes - DACS	Pure oxygen and nitrogen gas species are individually measured
Atomizing air	Yes - DACS	Pure air
Nitrogen purges	Yes - DACS	Pure nitrogen
Carbon addition nitrogen transfer gas (shotpot nitrogen)	No	Pure nitrogen - Contributes a negligible amount of nitrogen to the system and was therefore not calculated for the mass balance
Product transfer nitrogen	No	Pure nitrogen - Contributes a negligible amount of nitrogen to the system and was therefore not calculated for the mass balance
Initial bed	Yes – scale, logged	Supplier data
Coal	Yes – loss of weight - DACS	Analytical measurement
Seed particles	Yes – scale, logged	Supplier data
Iron oxide	Yes – scale, logged	Supplier data
Simulated Waste Feed	Yes - DACS	Based on feed recipe combining feed chemicals, water, and mineralizing additive used recipe (logged) and supplier data (see Tables 4-4 and 4-6)
HTF – inputs		
Nitrogen purges	Yes - DACS	Pure nitrogen
Filter back-pulse nitrogen	No	Pure nitrogen - Contributes a negligible amount of nitrogen to the system and was therefore not calculated for the mass balance
CRR – inputs		
Auto-thermal gas oxygen	Yes - DACS	Pure oxygen – readings on two meters added for total flow (Note that a calibration check of the lower flowmeter indicated it was reading a factor of two high – the DACS recorded value was divided by two to obtain the proper flow)
Auto-thermal gas nitrogen	Yes - DACS	Pure nitrogen – readings on two meters added for total flow
Nitrogen purges	Yes - DACS	Pure nitrogen
Propylene Glycol (liquid feed)	Yes - DACS	Pure propylene glycol
Carbon addition nitrogen transfer gas	No	Pure nitrogen - Contributes a negligible amount of nitrogen to the system and was therefore not calculated for the mass balance
Initial bed	Yes – scale, logged	Supplier data
Carbon	Yes – scale, logged	Supplier data
Bed makeup (alumina additive)	Yes – scale, logged	Supplier data
OGC – inputs		
Atomizing air	Yes	Pure air
Cooling water (liquid feed)	Yes	Pure water
OGF – inputs		
Nitrogen purges	Yes	Pure nitrogen
Filter back-pulse nitrogen	No	Pure nitrogen - Contributes a negligible amount of nitrogen to the system and was therefore not calculated for the mass balance.

Process Unit and Stream (see Figure 9-1)	Flow Measured (Yes or No)	Composition and Comments
DMR – outputs Samples Final Bed	Yes – scale, logged Yes – scale, logged	Selected samples were analyzed for composition (see table 9-2) Sample of final bed was analyzed for composition (see table 9-2)
PR – outputs Periodic bed drains from DMR HTF – outputs Continuously collected fines	Yes – scale, logged Yes – scale, logged	Selected samples were analyzed for composition (see table 9-3) Selected samples were analyzed for composition (see table 9-4)
CRR – outputs Samples Final Bed	Yes – scale, logged Yes – scale, logged	Selected samples were analyzed for composition (see table 9-2) Sample of final bed was analyzed for composition (see table 9-2)
OGF – outputs Periodic collected fines	Yes – scale, logged	Selected samples were analyzed for composition (see table 9-5)
Stack – outputs Stack gas	Yes - DACS	Output gas was continuously monitored for oxygen, carbon dioxide, carbon monoxide, nitrogen oxide, sulfur dioxide, and total hydrocarbons using calibrated online instruments Extensive emissions monitoring (as described in Section 8) was performed for about 3% of the operating time for the LAW production test and about 1.5% of the operating time for the WTP SW production test

All of the solid output flows were measured on a scale and the weights were recorded in logs. The solid outputs included samples (small mass overall), DMR bed drains (PR product) while operating (each bed drain was individually weighed), continuous collection of solids from the HTF using an auger and a 55-gallon drum (each drum was weighed individually and sampled when removed from the process), and collection and weighing of the final DMR and CRR beds at the end of processing. The composition of each stream was determined by analysis of representative samples (one or more per day). The analytical results were applied to each stream using time interpolation of the analytical data. For example, if a DMR drain (PR product) was performed at 12 noon on 5/1/08, and a sample of drained material from 8 am that morning and 8 am the following day was analyzed, then the composition of the sample at 12 noon on 5/1/08 would be estimated to consist of 20/24 parts of the 5/1/08 sample and 4/24 parts of the 5/2/08 sample. More detail on the treatment of the analytical data to develop elemental compositions is presented below. The sample results are shown in Tables 9-2 through 9-5.

There were four liquid inputs and no liquid outputs. The flows of all the liquid inputs were measured by flowmeters and recorded by the DACS. The composition of the OGC cooling stream was pure water, the POHC stream was pure benzene, and the CRR heat source liquid was pure propylene glycol. The composition of the simulant feed stream was calculated based on the target composition for the make-up, which in turn was based on the certified compositions of the constituent chemicals supplied by the vendors and the measured masses or volumes of these chemicals added to the feed make-up. Compositions are shown in Tables 4-4 and 4-6. Occasionally, water was fed to the DMR instead of feed. This was done when performing waste transfers and when flushing lines. The amount of water fed was measured by the waste feed flowmeter. Periods of water feed were recorded in the operator logs and were accounted for in the mass balance.

Table 9-2 Solids Sample Results for the DMR and CRR

Date/Time	4/28/08	4/29/08	5/1/08	5/2/08	5/6/08	4/27/2008	5/1/2008	5/2/2008	5/6/2008
	4:08	9:05	5:00	9:04	8:00	12:00	9:10	1:50	8:10
Test	DMR-P1	DMR-P1	DMR-P1	DMR-P2	DMR-P2	CRR-P1	CRR-P1	CRR-P2	CRR-P2
Sample Log ID#	5288	5320	5369	5393	5515	5272	5374	5386	5516
Constituent wt%									
Al	11.7	12.9	12.6	39.9	10.4	52.5	52.6	52.5	47.7
Ag	0.025	0.03	0.042	0.007	0.02	Not Detected			
As	0.00794	0.00971	0.0143	0.00057	0.001	0.00005	0.00007	0.00007	0.00008
B	Not in Simulant			0.0433	0.172			0.0503	0.0998
Ba	0.0738	0.0866	0.121	0.00951	0.0131	0.00122	0.00329	0.0108	0.00111
Ca	0.043	0.051	0.048	0.059	0.055	0.024	0.017	0.022	0.019
Cd	0.072	0.083	0.1	0.014	0.027	Not Detected			
Fe	2.54	1.42	2.06	1.68	1.07	0.179	0.151	0.205	0.126
Mg	0.012	0.01	0.014	0.024	0.03	0.002	0.004	0.004	0.002
I	0.0345	0.0512	0.0791	0.0141	0.0213	0.0087	0.0109	0.0162	0.0189
Na	6.95	10.8	14.1	2.48	8.25	0.162	0.14	0.153	0.132
K	0.063	0.086	0.117	0.059	0.169	0.005	0.003	0.004	0.003

Date/Time	4/28/08	4/29/08	5/1/08	5/2/08	5/6/08	4/27/2008	5/1/2008	5/2/2008	5/6/2008
	4:08	9:05	5:00	9:04	8:00	12:00	9:10	1:50	8:10
Test	DMR-P1	DMR-P1	DMR-P1	DMR-P2	DMR-P2	CRR-P1	CRR-P1	CRR-P2	CRR-P2
Sample Log ID#	5288	5320	5369	5393	5515	5272	5374	5386	5516
Constituent wt%									
Si	10.9	14.4	16.2	3.16	11	Not Detected			0.01
Sb	0.0406	0.0522	0.0749	0.0082	0.0227	Not Detected			
Se	0.0025	0.0034	0.0074	0.0032	0.0083	Not Detected		0.0002	ND
Ti	0.47	0.573	0.679	0.136	0.487	Not Detected			
Tl	0.0094	0.01	0.0115	0.0035	0.0096	ND	0.0042	0.0029	ND
Cs	0.11	0.097	0.115	0.057	0.209	Not Detected			
Cr	0.03	0.039	0.055	0.006	0.032	Not Detected			
Pb	0.079	0.089	0.119	0.024	0.033	ND	0.001	Not Detected	
Ni	0.058	0.07	0.092	0.014	0.043	ND	0.002	0.002	ND
Zn	Not in Simulant			0.015	0.048	Not Detected			
Re	0.0419	0.0437	0.0673	0.0176	0.0469	Not Detected			
Cl	0.0727	0.0428	0.0214	0.0342	0.0599	Not Detected			

Date/Time	4/28/08	4/29/08	5/1/08	5/2/08	5/6/08	4/27/2008	5/1/2008	5/2/2008	5/6/2008
	4:08	9:05	5:00	9:04	8:00	12:00	9:10	1:50	8:10
Test	DMR-P1	DMR-P1	DMR-P1	DMR-P2	DMR-P2	CRR-P1	CRR-P1	CRR-P2	CRR-P2
Sample Log ID#	5288	5320	5369	5393	5515	5272	5374	5386	5516
Constituent wt%									
F	0.01	Not Detected		0.02	0.08	0.01	Not Detected		
NO ₃	Not Detected		0.003	Not Detected					0.002
NO ₂	Not Detected								
PO ₄	0.609	0.703	0.829	0.113	0.196	0.012	0.018	0.017	0.007
SO ₄	0.13	0.37	0.72	0.17	0.08	0.04	Not Detected		
CO ₃	Not Detected								
Total Carbon	29.8	23.6	5.58	11.4	34.1	0.11	Not Detected		8.97
O (calc)	26.2	32.3	35.5	40.6	25.7	46.8	46.9	46.9	42.8
Mass Balance Component Sum %	90.1	97.9	89.3	100.1	92.4	99.9	99.8	99.9	99.8

Table 9-3 Solids Sample Results for the PR

Date/ Time	4/27/2008 7:45	4/28/2008 12:36	4/28/2008 13:19	4/29/2008 5:29	4/30/2008 9:10	5/1/2008 7:00	5/1/2008 11:30	5/2/2008 1:32	5/2/2008 9:30	5/2/2008 23:20	5/3/2008 17:00	5/4/2008 16:00	5/5/2008 16:45
Test	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2
Sample Log ID#	5268	5270	5295	5318	5348	5372	5378	5387	5394	5407	5430	5460	5494
Constituent wt%													
Al	23.8	26.9	18.6	21.4	13.8	18.1	17.5	49	44	40	29.1	18.9	16.5
Ag	0.024	0.023	0.034	0.032	0.029	0.044	0.048	0.004	0.009	0.011	0.019	0.028	0.029
As	0.00671	0.00601	0.00992	0.00865	0.00936	0.0135	0.0133	0.000945	0.000573	0.00041	0.000704	0.000949	0.000949
B	Not in Simulant							0.0309	0.0098	0.01	0.0811	0.192	0.167
Ba	0.0707	0.0668	0.0959	0.0875	0.0983	0.127	0.121	0.0121	0.0106	0.0077	0.0109	0.0132	0.0132
Ca	0.07	0.082	0.064	0.051	0.091	0.049	0.093	0.035	0.029	0.045	0.053	0.062	0.067
Cd	0.062	0.069	0.097	0.093	0.067	0.101	0.108	0.011	0.017	0.022	0.037	0.041	0.041
Fe	4.55	6.53	4.67	5.08	8.61	2.79	4.05	1.39	1.95	4.63	5.74	4.88	4.08
Mg	0.02	0.025	0.019	0.017	0.026	0.016	0.018	0.01	0.012	0.023	0.034	0.039	0.044
I	0.025	0.0219	0.057	0.0474	0.0698	0.083	0.0757	0.0165	0.013	0.0122	0.016	0.0206	0.022
Na	7.66	7.32	12	11.6	10.5	14.8	14.7	1.46	2.79	3.78	7.32	11.1	11.7
K	0.08	0.071	0.114	0.103	0.11	0.118	0.116	0.016	0.057	0.082	0.155	0.279	0.254

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No. DE-AC09-06SR22521.

Date/ Time	4/27/2008 7:45	4/28/2008 12:36	4/28/2008 13:19	4/29/2008 5:29	4/30/2008 9:10	5/1/2008 7:00	5/1/2008 11:30	5/2/2008 1:32	5/2/2008 9:30	5/2/2008 23:20	5/3/2008 17:00	5/4/2008 16:00	5/5/2008 16:45
Test	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2
Sample Log ID#	5268	5270	5295	5318	5348	5372	5378	5387	5394	5407	5430	5460	5494
Constituent wt%													
Si	9.4	9.17	16.2	14.8	14	18.4	17.8	1.44	3.4	4.62	8.76	14.7	15.7
Sb	0.0397	0.0368	0.058	0.0555	0.0636	0.0775	0.0774	0.0076	0.0091	0.0113	0.0201	0.0292	0.03
Se	0.0022	0.0014	0.0017	0.0022	0.0026	0.0063	0.0059	0.0008	0.0019	0.0019	0.0037	0.0061	0.006
Ti	0.383	0.369	0.624	0.535	0.525	0.711	0.717	0.063	0.143	0.196	0.379	0.6	0.667
Tl	Not Detected							0.0012	Not Detected				
Cs	0.062	0.044	0.078	0.069	0.114	0.116	0.109	0.005	0.049	0.055	0.113	0.176	0.214
Cr	0.033	0.031	0.048	0.045	0.044	0.062	0.063	0.004	0.012	0.016	0.029	0.045	0.048
Pb	0.099	0.077	0.068	0.084	0.088	0.075	0.13	0.012	0.029	0.041	0.074	0.098	0.097
Ni	0.053	0.054	0.082	0.074	0.075	0.094	0.097	0.008	0.019	0.023	0.038	0.056	0.059
Zn	Not in Simulant							0.001	0.016	0.031	0.076	0.093	0.093
Re	0.0394	0.0354	0.049	0.0486	0.0566	0.0643	0.0695	0.0078	0.0169	0.025	0.0456	0.0633	0.058
Cl	0.0342	0.0299	0.0428	0.047	0.0556	0.047	0.0214	0.0171	0.0235	0.0342	0.0513	0.0556	0.064

Date/ Time	4/27/2008 7:45	4/28/2008 12:36	4/28/2008 13:19	4/29/2008 5:29	4/30/2008 9:10	5/1/2008 7:00	5/1/2008 11:30	5/2/2008 1:32	5/2/2008 9:30	5/2/2008 23:20	5/3/2008 17:00	5/4/2008 16:00	5/5/2008 16:45
Test	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P1	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2	PR-P2
Sample Log ID#	5268	5270	5295	5318	5348	5372	5378	5387	5394	5407	5430	5460	5494
Constituent wt%													
F	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.03	0.04	0.08	0.13	0.13
NO ₃	Not Measured					0.006	0.005	Not Measured					
NO ₂	Not Detected												
PO ₄	0.539	0.56	0.833	0.785	0.869	0.879	0.919	0.086	0.101	0.157	0.246	0.293	0.292
SO ₄	0.38	0.36	0.39	0.62	0.19	0.84	0.88	0.14	0.17	0.34	0.52	0.47	0.18
CO ₃	Not Detected						0.48	Not Detected					
Total Carbon	11.3	5.46	6.92	3.83	15.7	2.87	1.47	1.05	2.6	2.48	4.4	8.41	13.2
O (calc)	36	39	40.8	41.6	34.6	43.3	42.3	46.2	44.6	43.6	40.3	39.2	38.3
Mass Balance Component Sum %	94.7	96.3	101.9	101.1	99.8	107.5	102	101.1	100.2	100.3	97.8	100.4	102.4

Table 9-4 Solids Sample Results for the HTF

Date/ Time	4/27/20 08	4/27/2 008	4/28/2 008	4/29/2 008	4/30/2 008	5/1/20 08	5/1/20 08	5/2/20 08	5/2/20 08	5/2/20 08	5/3/20 08	5/4/20 08	5/5/20 08	5/6/20 08	5/6/2 008
	9:14	21:42	13:30	8:35	8:15	4:30	16:40	2:00	8:15	20:08	17:05	18:00	16:15	6:45	10:00
Test	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2
Sample Log ID#	5265	5280	5294	5319	5346	5368	5379	5384	5396	5405	5429	5459	5492	5514	5520
Constituent wt%															
Al	18.6	17.2	17	16.3	16	18.1	19.1	27.4	17.6	13.3	15	13	14	31.2	12.8
Ag	0.013	0.015	0.013	0.015	0.017	0.01	0.014	0.016	0.014	0.015	0.014	0.015	0.015	0.012	0.02
As	0.00997	0.0104	0.0108	0.0106	0.0106	0.010 9	0.011 6	0.007 63	0.003 18	0.002 5	0.002 48	0.001 95	0.002 79	0.007 83	0.001 26
B	Not in Simulant							0.008 4	0.341	0.298	0.384	0.275	0.35	0.016 6	0.248
Ba	0.123	0.121	0.117	0.115	0.116	0.118	0.118	0.054	0.012	0.011	0.007	0.009	0.007	0.064	0.009
Ca	0.082	0.046	0.066	0.061	0.159	0.057	0.063	0.382	0.087	0.094	0.091	0.106	0.079	0.183	0.058
Cd	0.035	0.037	0.035	0.04	0.043	0.042	0.049	0.051	0.015	0.014	0.013	0.014	0.013	0.06	0.022
Fe	0.789	0.692	0.677	0.468	0.421	0.618	0.581	0.76	0.593	0.489	0.605	0.703	0.584	0.586	0.44

Date/ Time	4/27/20 08	4/27/2 008	4/28/2 008	4/29/2 008	4/30/2 008	5/1/20 08	5/1/20 08	5/2/20 08	5/2/20 08	5/2/20 08	5/3/20 08	5/4/20 08	5/5/20 08	5/6/20 08	5/6/2 008
	9:14	21:42	13:30	8:35	8:15	4:30	16:40	2:00	8:15	20:08	17:05	18:00	16:15	6:45	10:00
Test	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2
Sample Log ID#	5265	5280	5294	5319	5346	5368	5379	5384	5396	5405	5429	5459	5492	5514	5520
Constituent wt%															
Mg	0.016	0.009	0.012	0.01	0.014	0.011	0.012	0.02	0.028	0.039	0.031	0.035	0.037	0.017	0.038
I	0.105	0.0899	0.0933	0.0938	0.113	0.105	0.080 2	0.031 2	0.029 7	0.021	0.024 2	0.025 8	0.022 5	0.030 1	0.022
Na	11.3	11.8	11.6	11.6	12.5	13	13	7.57	10.1	11.5	10.1	9.88	10.4	8.25	10.2
K	0.148	0.136	0.136	0.129	0.126	0.141	0.177	0.11	0.2	0.247	0.226	0.209	0.227	0.101	0.236
Si	18.6	19.8	19.6	18.6	19.1	21	21.1	11.2	17.8	17	17.7	17	17.2	10.1	15.3
Sb	0.057	0.059	0.0609	0.0559	0.0578	0.063 4	0.069	0.044	0.042 9	0.043	0.040 6	0.037	0.043	0.035 2	0.034
Se	0.0049	0.003	0.0036	0.0004	0.0058	0.005 2	0.004 5	0.006 7	0.006 9	0.014 7	0.016 3	0.021 6	0.000 4	0.066	0.000 3
Ti	0.727	0.711	0.678	0.679	0.668	0.674	0.667	0.329	0.575	0.752	0.644	0.692	0.711	0.348	0.727
Tl	0.0267	0.0283	0.0268	0.0219	0.0341	0.038	0.035	0.015	0.021	0.025	0.024	0.019	0.022	0.565	0.013

Date/ Time	4/27/20 08	4/27/2 008	4/28/2 008	4/29/2 008	4/30/2 008	5/1/20 08	5/1/20 08	5/2/20 08	5/2/20 08	5/2/20 08	5/3/20 08	5/4/20 08	5/5/20 08	5/6/20 08	5/6/2 008
	9:14	21:42	13:30	8:35	8:15	4:30	16:40	2:00	8:15	20:08	17:05	18:00	16:15	6:45	10:00
Test	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2
Sample Log ID#	5265	5280	5294	5319	5346	5368	5379	5384	5396	5405	5429	5459	5492	5514	5520
Constituent wt%															
						9	2	7	4		3				
Cs	0.204	0.201	0.234	0.195	0.204	0.25	0.227	0.137	0.42	0.442	0.455	0.458	0.448	0.172	0.378
Cr	0.041	0.041	0.04	0.043	0.043	0.039	0.044	0.027	0.04	0.038	0.042	0.036	0.038	0.025	0.038
Pb	0.139	0.142	0.139	0.062	0.1	0.199	0.119	0.106	0.037	0.02	0.037	0.024	0.022	0.136	0.039
Ni	0.067	0.07	0.068	0.067	0.067	0.073	0.073	0.047	0.055	0.055	0.057	0.054	0.059	0.068	0.059
Zn	Not in Simulant							0.003	0.061	0.057	0.061	0.055	0.068	0.004	0.066
Re	0.0203	0.0198	0.0191	0.0183	0.0171	0.014 3	0.021 1	0.020 3	0.020 2	0.024 7	0.021 6	0.025 6	0.021 9	0.014 9	0.035 5
Cl	0.148	0.133	0.115	0.0631	0.0983	0.051 3	0.038 5	0.017 1	0.167	0.171	0.154	0.122	0.128	0.359	0.079 1
F	0.08	0.08	0.09	0.08	0.09	0.1	0.09	0.1	0.58	0.67	0.65	0.47	0.66	0.37	0.25
NO ₃	Not Measured					0.003	0.003	Not Measured			0.004	Not Measured			0.004

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Date/ Time	4/27/20 08	4/27/2 008	4/28/2 008	4/29/2 008	4/30/2 008	5/1/20 08	5/1/20 08	5/2/20 08	5/2/20 08	5/2/20 08	5/3/20 08	5/4/20 08	5/5/20 08	5/6/20 08	5/6/2 008
	9:14	21:42	13:30	8:35	8:15	4:30	16:40	2:00	8:15	20:08	17:05	18:00	16:15	6:45	10:00
Test	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P1	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2	HTF-P2
Sample Log ID#	5265	5280	5294	5319	5346	5368	5379	5384	5396	5405	5429	5459	5492	5514	5520
Constituent wt%															
NO ₂	Not Detected														
PO ₄	0.702	0.681	0.68	0.766	0.79	0.809	0.773	0.51	0.367	0.301	0.314	0.323	0.317	0.488	0.271
SO ₄	0.46	0.36	0.41	0.6	0.43	0.68	0.57	0.67	0.37	0.25	0.23	0.23	0.25	1.32	0.19
	0.46	0.36	0.41	0.60	0.43	0.68	0.57	0.67	0.37	0.25	0.23	0.23	0.25	1.32	0.19
CO ₃	Not Detected														
Total Carbon	8.8	9.17	8.94	8.9	11.1	1.24	1.26	8.03	13.7	18	16.2	20.7	14.9	3.43	23.4
O (calc)	42.3	42.5	42	40.2	40.8	45	46	40.2	40.5	36.3	38.3	35.5	36.9	42.2	33.5
Mass Balanc e Comp.	103.5	104.2	102.9	99.1	103.1	102.4	104.3	97.9	103.8	100.2	101.4	100	97.5	100.2	94.8

Date/ Time	4/27/20 08	4/27/2 008	4/28/2 008	4/29/2 008	4/30/2 008	5/1/20 08	5/1/20 08	5/2/20 08	5/2/20 08	5/2/20 08	5/3/20 08	5/4/20 08	5/5/20 08	5/6/20 08	5/6/2 008
	9:14	21:42	13:30	8:35	8:15	4:30	16:40	2:00	8:15	20:08	17:05	18:00	16:15	6:45	10:00
Test	HTF-P1	HTF- P1	HTF- P1	HTF- P1	HTF- P1	HTF- P1	HTF- P1	HTF- P2	HTF- P2	HTF- P2	HTF- P2	HTF- P2	HTF- P2	HTF- P2	HTF- P2
Sample Log ID#	5265	5280	5294	5319	5346	5368	5379	5384	5396	5405	5429	5459	5492	5514	5520
Constituent wt%															
Sum %															

Table 9-5 Solids Sample Results for the OGF

Date/Time	4/28/2008	5/1/2008	5/5/2008	5/5/2008	5/5/2008	5/6/2008	5/6/2008
	20:30	16:15	15:45	19:50	23:50	3:20	10:00
Test	OGF-P1	OGF-P1	OGF-P2	OGF-P2	OGF-P2	OGF-P2	OGF-P2
Sample Log ID#	5307	5380	5493	5497	5501	5510	5521
Constituent wt%							
Al	16.5	17.1	25.5	19.4	23.3	32.1	33.2
Ag	0.018	0.017	0.012	0.016	0.009	0.007	0.003
As	0.0116	0.0103	0.00755	0.0115	0.00663	0.00471	0.00253
B	Not in Simulant		0.0225	0.0205	0.0196	0.0208	0.0284
Ba	1.42E-05	1.41E-05	8.30E-06	0.000013	6.20E-06	4.50E-06	1.70E-06
Ca	0.049	0.071	0.167	0.073	0.151	0.146	0.106
Cd	0.065	0.061	0.056	0.067	0.042	0.036	0.03
Fe	0.543	0.47	0.593	0.439	0.44	0.463	0.241
Mg	0.011	0.013	0.018	0.018	0.015	0.015	0.013
I	0.0997	0.0839	0.0601	0.103	0.0482	0.0263	0.0169
Na	15.2	13.9	9.31	13.6	7.49	5.1	2.39
K	0.137	0.128	0.101	0.125	0.081	0.065	0.046

Date/Time	4/28/2008	5/1/2008	5/5/2008	5/5/2008	5/5/2008	5/6/2008	5/6/2008
	20:30	16:15	15:45	19:50	23:50	3:20	10:00
Test	OGF-P1	OGF-P1	OGF-P2	OGF-P2	OGF-P2	OGF-P2	OGF-P2
Sample Log ID#	5307	5380	5493	5497	5501	5510	5521
Constituent wt%							
Si	19.8	18.2	11.5	16.7	9.47	6.4	3.19
Sb	0.093	0.056	0.039	0.05	0.031	0.023	0.013
Se	0.0026	0.0008	0.0142	0.0144	0.0141	0.0507	0.063
Ti	0.694	0.691	0.428	0.623	0.356	0.257	0.132
Tl	0.079	0.071	0.0233	0.0122	0.0119	0.0314	0.0697
Cs	0.225	0.211	0.168	0.212	0.134	0.102	0.069
Cr	0.032	0.033	0.022	0.026	0.017	0.014	0.011
Pb	0.14	0.098	0.135	0.138	0.102	0.074	0.042
Ni	0.085	0.085	0.068	0.08	0.054	0.051	0.053
Zn	Not in Simulant		0.003	0.002	0.002	0.003	0.004
Re	0.0235	0.0218	0.0186	0.0229	0.0144	0.0108	0.0062
Cl	0.184	0.15	0.175	0.197	0.128	0.197	0.222

Date/Time	4/28/2008	5/1/2008	5/5/2008	5/5/2008	5/5/2008	5/6/2008	5/6/2008
	20:30	16:15	15:45	19:50	23:50	3:20	10:00
Test	OGF-P1	OGF-P1	OGF-P2	OGF-P2	OGF-P2	OGF-P2	OGF-P2
Sample Log ID#	5307	5380	5493	5497	5501	5510	5521
Constituent wt%							
F	0.1	0.1	0.15	0.11	0.13	0.22	0.16
NO ₃	Not Detected						
NO ₂	Not Detected						
PO ₄	0.744	0.683	0.525	0.672	0.41	0.288	0.179
SO ₄	0.83	0.9	0.89	0.82	0.68	0.75	0.61
CO ₃	Not Detected						
Total Carbon	0.15	1.2	2.09	1.03	1.73	2.52	3.75
O (calc)	42.9	41.2	39.3	41.4	34.4	37.8	34.1
Mass Balance Component Sum %	98.7	95.5	91.4	96	79.3	86.8	78.7

9.1.1 Calculation of Stack Gas Composition

The stack gas consisted primarily of four components – water, nitrogen, carbon dioxide and oxygen. The dry percentage composition of carbon dioxide was continuously measured (as were the trace components carbon monoxide, nitrogen oxide, sulfur dioxide and total hydrocarbons) by the on-line gas analyzers (CEMS). The water and nitrogen are estimated based on the composition of all the feeds and on the process chemistry. The basic approach was to calculate, on a minute-by-minute basis, the expected output flow rate of all four of the major species and then to calculate the associated percentage in the gas flow rate. The results were then compared to the measured total flow rate and the measured percentage dry concentration of oxygen and carbon dioxide to check for consistency.

Nitrogen was calculated by converting all feed nitrogen to nitrogen gas and then adjusting this value for the ppm levels of measured nitrogen oxide. Most of the nitrogen was fed as nitrogen gas and the flow rates were continuously recorded on the DACS. There was also a significant amount of nitrogen associated with the simulant feed (mostly in the form of nitrates), which was accounted for by multiplying the feed concentration by the feed flow rate. There was a minor amount of nitrogen in the coal fed to the DMR, which was accounted for by multiplying the concentration in the coal by the measured coal feed rate.

Most of the water component was fed as water, e.g., steam, cooling water, and water associated with the feed. Hydrogen in the feed, coal, coke, and glycol was accounted for by multiplying the feed concentrations by the feed flow rates and converting it to water by oxidation.

CO₂ and O₂ were calculated by summing all oxygen fed (not associated with feed water) and then adjusting this value to reflect the loss of oxygen to the hydrogen that was converted to water. Most of the oxygen fed was fed as oxygen gas or air and the flow rates were continuously measured. There was also a significant amount of oxygen associated with the simulant feed (mostly in the form of nitrates), which was accounted for by multiplying the feed concentration by the feed flow rate and adjusting this value by the stoichiometric amount of oxygen needed to form product solids. There was a minor amount of oxygen in the coal fed to the DMR, which was accounted for by multiplying the concentration in the coal by the measured coal feed rate. The oxygen associated with the CRR and DMR alumina bed was expected to come out as alumina solids and was not included in the O₂ calculation. Once the total oxygen expected at the stack was calculated, a portion was converted to CO₂, such that the remaining O₂ to CO₂ ratio is the same as that measured by the analyzers.

Using this approach, the following stack gas distributions (% by volume) were determined for the LAW and WTP SW production tests:

- LAW: 51.8% water, 36.9% nitrogen, 7.6% carbon dioxide, and 3.6% oxygen
- WTP SW: 50.2% water, 38.8% nitrogen, 7.5% carbon dioxide, and 3.4% oxygen

The total moisture compares well to the moisture values measured during emissions gas manual sampling, which averaged 50.8% for LAW and 50.1% for WTP SW. The moisture adjusted analyzer (CEMS) readings for the LAW test for carbon dioxide and oxygen were 7.3% and 3.5%, respectively, and are in excellent agreement with the values estimated from the input gases and process chemistry. The moisture adjusted analyzer (CEMS) readings for the WTP SW test for carbon dioxide and oxygen were 7.5% and 3.4%, respectively, and are in excellent agreement with the values estimated from the input gases and process chemistry.

The values above for water, nitrogen, carbon dioxide, and oxygen were used in the mass balance discussed below. The wet percentages were multiplied by the total mass flow rate of stack gas flow that

was the sum of the major components as calculated above. The total stack gas flow for LAW was 4,940 lb-moles and for WTP SW was 5,070 lb-moles. The resulting molar flow rate of gas for each of the two tests was then converted to mass (pounds) using the appropriate molecular weights. These are the values reported for stack water, nitrogen, oxygen and carbon dioxide in the mass balance below. Sulfur dioxide out of the stack was estimated by multiplying the average measured sulfur concentration (as measured dry by the on-line gas analyzer (CEMS) and adjusted for moisture) by the total stack mass flows.

The values for iodine, chlorine, and fluorine release were estimated from the gas emissions data (See Section 8). The average emissions rates measured were multiplied by the feed-on time to obtain estimates of the total component gas releases.

9.1.2 Calculation of Feed Composition

The simulant waste feed compositions used were the targets as recorded in Section 4 above. A review of the Hazen make-up logs showed that the actual make-ups followed the planned recipes to within a few tenths of a percent (the measured weights and intended weights were very close). The component form of the final feed, including the added water and mineralizing agent (clay), were needed for input to the mass balance. The component feed values calculated from the target recipes are shown in Tables 4-4 and 4-6.

9.1.3 Calculation of Output Solids Compositions

The compositions of the PR, DMR, HTF, CRR, and OGF solids were analytically determined by the Hazen analytical laboratory (except for iodine and chlorine which were measured by ACS labs). The analytical methods that were used are listed in Table 3-5. The results were then charge balanced assuming that any cation not associated with a sulfate, phosphate, carbonate, nitrate, or halogen would be associated with an oxide anion. This mass of oxide was summed with the masses of species specifically analyzed for, to determine if the total mass of material in each sample summed to 100 wt%. With the oxide addition, the total mass of analytically determined species in almost all samples summed to between 90 and 110%, and often to between 95 and 105%. This was considered to be an acceptable range, considering reasonable sample representativeness and analytical error. The exception to this is for samples that contained significant alumina starting bed (CRR for the entire test and the DMR at the start of WTP SW). The alumina bed media was sintered alumina, which was very difficult to digest for analytical measurement resulting in an Al concentration that was under-represented in the analytical values due to the incomplete digestion. Analytical results from previous test programs have shown the same difficulty with alumina digestion. Since the composition of the alumina feed material was known, the Al was adjusted to an appropriate value, while leaving other components alone. The adjustment resulted in sample balance sums, as explained above, of 99-101%. The Al adjusted values were used for the mass balance. See Section 9.2 for solids analytical results. The analytical results, including the calculated oxygen values, are shown in Tables 9-2 through 9-5. Additional data analysis of the solids compositions is presented in Section 9-2.

9.2 Product Solids Compositional Data

Samples from the DMR bed, PR solids, HTF solids, CRR bed, and OGF solids were submitted for chemical analysis. The oxygen content of the solids was estimated from a charge balance on the individual samples as described above.

The results of these analyses for the DMR and PR solids are shown in Tables 9-2 and 9-3 and are displayed graphically Figure 9-2 for the LAW and WTP SW production tests. The sums of the component mass fractions for the individual samples ranged between 89 and 103 wt% when the oxygen charge

balance is included. The original analyses included total carbon in the samples. The values shown in Figure 9-2 have been normalized to a carbon-free basis. The average carbon content of the unscreened solids removed from the PR was 7 wt%, while the average carbon content in unscreened solids from the DMR was 20 wt%.

The aluminum concentration of the product solids was higher at the beginning of the LAW (P1) and WTP SW (P2) tests. This was to be expected, since the starting bed for the LAW test was the final bed for the last scoping test run just prior to starting of the LAW P1 tests, combined with 100 pounds of alumina, while the starting bed for the WTP SW test was pure alumina. With the exception of iron, the solid component concentrations throughout the LAW test were constant. The iron varies more than is expected and is likely due to variability in feed materials and inadequate digestion of samples prior to component measurement. The first sample shown for the WTP SW test was drawn on the first day of operation and shows almost pure alumina (Al_2O_3). As the test progressed, the aluminum concentration approached that of the LAW test and the other elemental concentrations show the expected buildup. Once again, the iron concentration shows unexpected variability.

Nitrates for both the LAW and WTP SW production tests were at or below detection levels in the DMR and PR solids (<0.002 wt%).

The results of the analyses for HTF solids samples are shown in Figure 9-3 for the LAW and WTP SW production tests. The sums of the component mass fractions of the individual samples ranged between 97 and 105 wt% when the oxygen charge balance is included. The original analyses included total carbon in the samples. The values shown in Figure 9-3 have been normalized to a carbon-free basis. The average carbon content of the solids removed from the HTF was 7 wt% for the LAW test and 15 wt% for the WTP SW test.

The aluminum concentration in the HTF solids at the beginning of the WTP SW test is higher, reflecting the alumina starting bed. Otherwise, the concentrations are basically constant throughout the tests with the exception of the alumina in the next to the last WTP SW (P2) sample. Analytical inaccuracy is the likely cause and this particular sample was considered anomalous and was not included in the general mass balance.

The analyses for the CRR bed throughout the tests were almost completely aluminum oxide, as expected. The carbon concentration in the CRR ranged from <0.01 to 9 wt%. Alumina and carbon accounted for ~99 wt% of the CRR bed material. The analytical results of the CRR composition accounted for only 56–62% of the total mass of the samples. Analytical results during previously performed pilot plant testing [30] also accounted for a minor percentage of the total samples. It is believed that a portion of the alumina bed material remained undigested in the samples and was therefore not detected in the analyses.

A total of 517 lb of solid product was collected from the OGF during the production tests. The OGF solids did not drain well during the first part of the test due to a solid bridge in the bottom of the filter vessel. The samples obtained reflected the concentration of the CRR alumina bed and of the Na-Al-Si product from the scoping test runs. On 5-5-08, near the end of the testing, the solid bridge was removed and 408 pounds of solids were collected (only 9 pounds had been collected in the prior eight days of testing). The 408 pounds of solids were more concentrated in Al and less concentrated in Na and Si. As the tests progressed, another 100 lb were collected and the concentration of the alumina in the OGF product fines increased from less than 50 wt% to greater than 90 wt%, while the remainder of the elements decreased in concentration. Thus, it is expected that the OGF solids contained some of the product from the scoping tests, when the HTF was not in service. As the total OGF solids were less than 3% of the total solids collected, their effect on the overall mass balance was minor. For purposes of the mass balance, the total

OGF solids collected were divided equally between the two test runs, and the average elemental concentrations for all the solids were used. Note that all the solids in the OGF were collected once the bridge was removed.

Figure 9-2 Solids Analysis for DMR and PR Samples for LAW and WTP SW Production Tests

The minor constituent series in this figure included the metals: Ag, B, Ba, Ca, Cs, K, Mg, Ni, Re, Sb, Se, Ti, Tl, and Zn. The HM series included the RCRA metals: As, Cd, Cr, and Pb. The Halides series includes the Cl, F, and I.

Figure 9-3 Solids Analysis for HTF Solids for LAW and WTP SW Production Tests

The minor constituent series in this figure included the metals: Ag, B, Ba, Ca, Cs, K, Mg, Ni, Re, Sb, Se, Ti, Tl, and Zn. The HM series included the RCRA metals: As, Cd, Cr, and Pb. The Halides series includes the Cl, F, and I.

9.3 Overall and Component Mass Balance Results

The total mass balance closure for both tests is excellent, with a difference of 0.7 and 0.2% respectively for the LAW and WTP SW tests between feeds and discharges. Table 9-6 summarizes the findings. The component distributions and mass balances for the LAW and WTP SW production tests are shown in Tables 9-7 and 9-8, respectively.

Table 9-6 Components Exceeding Mass Balance Closure Objectives

Test	Major Components (Test Objective <10%)	Minor Components (Test Objective <30%)	Trace Components of Interest (Closure >30%, Although No Specific Test Objective Established)
LAW	Si (+17.3%)	Cl (-36.3%), S (-42.2%), I (-38.6%)	Ca, Se
WTP SW	Si (+25.5%), Ti (72.2%)	Fe (-34.7%), Cl (-74.9%), S (-60.6%) I (+130.6%), PO ₄ (+49.5%)	As, Ba, Cd, Se, Tl

For the LAW test, the component mass balances for the major components Al, Na, C, Ti, N₂, O₂ and H₂O met the test objectives. The component mass balance for the major component Si did not meet the objectives; silicon had a mass closure of +17.3% (+209lb). The component balance for the minor components met the test objective of ±30% except for Cl, S, and I which showed balances of -36.3%, -42.2%, and -38.6% respectively. Although there was no specified mass balance closure requirement in the test plan for trace components, the closure for trace components was ±30% for all components except for selenium and calcium, which had mass balance closures of -65.1% and 41%, respectively.

For the WTP SW test, the component mass balances for the major components Al, Na, C, N₂, O₂ and H₂O met the test objectives. The component mass balance for the major components Si and Ti, did not meet the objectives. Silicon had a mass closure of +25.5% (+181lb); and Ti had a mass balance closure of +72.2% (15.1lb). The component balance for the minor components met the test objective of ±30% except for Cl, S, I, Fe, and PO₄ which showed balances of -74.9%, -60.6%, 130.6%, -34.7% and 49.5% respectively. Although there was no specified mass balance closure requirement in the test plan for trace components, the closure for trace components was ±30% for all components except for arsenic, barium, cadmium, selenium and thallium, which had mass balance closures of 69.2%, 615%, 41.5%, -53.8% and 31.5%, respectively.

For silicon in both the LAW and WTP SW tests, the mass out exceeded the mass in. The analytical data shows normal variability and the reason for the mass balance difference is unknown, but is likely due to a combination of weight measurements, analytical inaccuracies, and varying Si concentrations in the clay and coal additives, both of which are natural products.

For the LAW and WTP SW tests, 42.2% (20.0lb) and 60.6% (12.7lb) respectively, of the sulfur in the feed was not accounted for in the products/off-gas. Sulfur is difficult to analyze for in the mineralized product, as the mineral form of sulfur is not water soluble. This difficulty was seen in previous pilot plant test results [5, 31, 32]. In addition, 40% to 90% of the sulfur in the feed was introduced as an impurity in

the coal fed to the DMR. Variability of a factor of 2 in the sulfur content of the coal is expected. The observed difference in mass balance is within a 50% variation for the sulfur concentration.

For the LAW and WTP SW tests, 36.3% (4.5lb) and 74.9% (26lb) respectively, of the chlorine in the feed was not accounted for in the products/off-gas. There is considerable variability in the measured concentration of chlorine in both the HTF and PR solids streams. This variability is not seen in most of the other measured component concentrations. It is concluded that the LAW PR solid analytical results are low for Cl due to analytical inaccuracies.

A mass imbalance of -38.6% and +130.6% was observed respectively for I in the LAW and WTP SW tests. The imbalance values are not consistent, indicating a shortfall for the LAW test and an over recovery for the WTP SW test. This discrepancy is likely due to variability in the output solids analytical results, as noted for chloride above. Iodine emissions from the stack were even less for the WTP SW test than for the LAW test (see Section 8.3.7). The analytical inaccuracy is likely due to an inappropriate sample preparation (digestion) method.

For the LAW test, 41% (1.9lb) more calcium was found in the product than was present in the feed. 80% of the calcium in the feed was introduced as an impurity in the coal and clay fed to the DMR. Variability of a factor of 2 in the calcium content of the coal and clay is expected. The observed difference in mass balance is well within this expected variation.

More titanium (72.2%, 15.1lb) was recovered in the solid products for the WTP SW test than was fed. Titanium is a trace element in the mineralizing clay additive and is subject to concentration variability from the supplier. Additionally, the mineralizing clay was a mixture of two clay types for the WTP SW test. It is concluded that the titanium content variability in the supplied, raw clay materials is the likely cause for this imbalance.

The iron mass out was less than the mass in for the WTP SW test, resulting in a mass balance closure error of -34.7% (-46lb). Normal variability was observed in the WTP SW solids sample analytical data and the reason for the iron mass balance difference in the WTP SW test is unknown other than weight measurement and analytical inaccuracies.

Additional phosphate (49%, 5.9lb) was found in the products for the WTP SW test. Variability in analytical results was not seen. Forty percent of the phosphate in the feed was introduced as an impurity in the coal fed to the DMR. Variability of a factor of 2 in the phosphate content of the coal is expected. The observed difference in mass balance is within a 50% variation of the phosphate concentration.

Although there was no specified mass balance closure requirement in the test plan for trace components, the closure for the trace components was $\pm 30\%$ for all components except for arsenic, barium, cadmium, calcium, selenium and thallium. The majority of the variability in the minor and trace components in both the LAW and WTP SW tests can be explained by the relatively sizeable variability in the analytical results. As these elements are present in quantities very near the detection limit, the observed variability is expected, and the relatively poor mass balance closure is to be expected for some of the minor and trace components. For example, the chloride concentrations ranged from about 1.5g/kg down to below the detection limit of 0.15 grams per kg. In other words, the values were all within a factor of 10 or less of the detection limits. The expected uncertainty at a factor of 10X the detection limit is about 6%, while the expected uncertainty at just 3X the detection limit is greater than 15%. Quality control replicate values at 10 times the detection limit (3 of them) show an average relative percent deviation (RPD) of 3%, consistent with the expected 6%. A replicate for a measurement at 3 times the detection limit showed an RPD of 18%, also consistent with expectations. With only four analytical measurements of chlorine in a solid stream, a single undetectable value can introduce enough error to result in a considerable uncertainty

in the calculated values – plus or minus 50% (or greater) at the 95% confidence level is expected. This means that a mass balance closure that is within 50% is not significantly different from a 0% (perfect) mass balance closure and does not represent a failure to balance. There are inaccuracies in the measurements, but it does not represent a statistical failure for mass balance closure failure. This is why a priori limits are not set for trace components, as they frequently cannot be balanced to better than $\pm 30\%$.

Note that the high fidelity off-gas measurements have a much lower detection limit and can be used with confidence to describe the component releases from the process. It is possible that some of the components that show a negative mass balance indicate that mass was deposited somewhere in the system. This is possible, but not likely, as the internals of the process components were viewed post-test and appeared to be reasonably free of deposits in the quantity required to account for the mass imbalances.

Table 9-7 Component Distribution and Mass Balance Closure for LAW Production Tests

LAW Test (target)		Total	Al	Ag	As	Ba	Ca	Cd	Fe	Mg	I	Na	K	Si	Sb	Se	Ti	Tl	C2O4	Cs	Cr
4/27/08 4:00 to 5/1/08 11:30		lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb
Feeds	DMR Starting Bed	418	112	0.140	0.035	0.000041	0.021	0.30	4.76	0	0	45	1	64	0	0	0			0	0
	CRR Starting Bed	1650	866		0.00	0.02	0.40		2.95	0.03	0.14	2.67	0.08								
	Simulant Feed	15107	1062	1.38	0.82	8.22	1.37	3.77	20.1	0.84	13.2	919	8.74	1095	4.21	0.77	52.5	3.29	8.28	13.8	4.31
	DMR Coal BSTAC	3400	23.5				2.74		8.80	0.15		6.43	0.29	51.43			0.63				
	DMR Alumina	32	17				0.0069		0.0090	0.0039		0.036	0.040	0.007			0.0019				
	SphereOx	144							105						0.40						
	CRR Coke	318			0.0027																
	CRR Glycol	4829																			
	CRR Alumina	300	158						0.084	0.036		0.33	0.37	0.070			0.018				
	DMR Gas	17367																			
	CRR Gas	32423																			
	OGC Cooling Adds	28938																			
	Purge N2	24839																			
Total		129765	2239	1.52	0.86	8	4.60	4.1	142	1	13.3	973	10	1211	4.21	0.8	53.2	3	8.28	14	4.5
Outlets	DMR Solids	1604	318	0.52	0.150	1.49	1.09	1.35	83.18	0.32	0.84	177	1.6	226	0.91	0.05	8.62	0.35		1.34	0.73
	HTF Solids	5905	1007	0.84	0.63	7.0	4.92	2.33	34.39	0.70	5.88	710	8.0	1148	3.49	0.22	40.46	1.7		13	2.45
	CRR Solids	1715	902		0.0012	0.056	0.294		2.60	0.068	0.19	2.41	0.05				0.071				
	OGF Solids	259	44	0.044	0.027		0.18	0.16	1.22	0.034	0.22	36.0	0.33	47.08	0.14	0.0021	1.8	0.18		0.55	0.09
	Stack	119401	0								1.04										
Total		128884	2271	1.40	0.80	8	6.49	3.8	121.4	1	8.2	925.1	10	1420	5	0.3	50.9	2	0.0	14	3.3
Produced																					
Reacted																			8.28		
Mass Balance		-881	32.5	-0.12	-0.052	0.25	1.89	-0.23	-20.6	-0.01	-5.13	-48.1	-0.03	209	0.33	-0.51	-2.29	-1.0	0.00	0.55	-1.22

LAW Test (target)		Pb	Ni	CH3COO	Re	OH	Cl	F	NO2	PO4	H+	H2O	Nitrogen		Sulfur		Carbon			O2
		lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	NO3	N2	SO4	SO2	Carbon	CO3	CO2	lb
4/27/08 4:00 to 5/1/08 11:30																				
Feeds	DMR Starting Bed	0.57	0.30		0.00002			0.12		2.89			0.0064		3.15		5.79	0.79		189
	CRR Starting Bed							0.17		0.20					0.66		1.82			772
	Simulant Feed	10.0	4.96	62.2	2.5	100	12	5	156	42	0.03	7685	1278		69			227		2232
	DMR Coal BSTAC									3.46	104.1	138		25.8	47.6		2792			205
	DMR Alumina																			15
	SphereOx									0.040					0.043		0.13			37
	CRR Coke										0.92	0.10		0.11	0.24		308			8
	CRR Glycol										512						2286			2031
	CRR Alumina																			141
	DMR Gas											5854		6685						4829
	CRR Gas													17880						14543
	OGC Cooling Adds											26881		1578						479
	Purge N2													24839						
	Total	10.6	5.26	62.2	2.52	100	12.4	5.1	156	48.6	617	40557	1278	51008	121	0.00	5394	228	0.00	25481
Outlets	DMR Solids	1.41	1.19		0.81		0.66	0.26		12.23			0.019		8.10		121	0.69		629
	HTF Solids	7.23	4.05		1.07		5.70	5.12		43.90			0.028		28.93		484			2480
	CRR Solids	0.017	0.034					0.00		0.31					0.012		0.033			804
	OGF Solids	0.25	0.22		0.056		0.39	0.26		1.77					2.33		3.10			106
	Stack						1.13	0.72				46081		51085	14.2				16490	5725
	Total	8.91	5.49		1.94		7.89	6.37		58.2		46081	0.047	51085	39.4	14.2	608	0.69	16490	9745
Produced												5647		289		14.2			16490	1305
Reacted				62.2		100			156		617		1278		21.33		4786	227		17005
Mass Balance		-1.68	0.23	0.00	-0.582	0.00	-4.50	1.29	0.00	9.61	0.00	-124	-211		-20.0		-331.5			-36.6

Table 9-8 Component Distribution and Mass Balance Closure for WTP SW Production Tests

WTP SW Test (target)		Total	Al	Ag	As	B	Ba	Ca	Cd	Fe	Mg	I	Na	K	Si	Sb	Se	Ti	Tl	Cs	Cr
5/1/08 22:00 to 5/5/08 11:15		lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb
Feeds	DMR Starting Bed																				
	CRR Starting Bed	1650	868		0.00	0.00	0.05	0.28	0.00	2.49	0.07	0.18	2.31	0.05					0.07		
	Simulant Feed	13337	653	0.84	0.07	13	0.03	1.54	0.89	13.35	1.40	0.91	514	12	651	1.78	1.78	20	1.78	18	2.88
	DMR Coal BSTAC	3838	26.6					3.09		9.93	0.17		7.25	0.33	58.1			0.71			
	DMR Alumina (start bed)	500	263					0.11		0.14	0.06		0.56	0.62	0.12			0.030			
	SphereOx	147								107					0.41						
	CRR Coke	609			0.0052																
	CRR Glycol	4191																			
	CRR Alumina	300	158					0.06		0.08	0.04		0.33	0.37	0.070			0.018			
	DMR Gas	20139																			
	CRR Gas	32622																			
	OGC Cooling Addis	28562																			
	Purge N2	25389																			
Total		131284	1969	0.84	0.08	13	0.08	5.1	0.9	133	1.7	1.1	524	13	710	1.8	1.8	21	1.9	18	2.9
Outlets	DMR Solids	1655	393	0.33	0.014	2.16	0.20	0.89	0.52	60	0.52	0.31	132	2.92	171	0.36	0.09	7.33	0.31	2.43	0.52
	HTF Solids	4044	578	0.62	0.10	13	0.37	3.52	0.60	23	1.40	0.98	419	9.06	690	1.63	0.70	28	0.85	18	1.57
	CRR Solids	1795	858		0.0015	1.77	0.023	0.34	0.00	2.29	0.04	0.34	2.38	0.05	0.18		0.0035		0.051		
	OGF Solids	259	66	0.031	0.020	0.058	0.00002	0.43	0.14	1.53	0.05	0.16	24.08	0.26	30	0.10	0.037	1.11	0.060	0.43	0.06
	Stack	123245	0									0.74									
	Total	130998	1894	0.98	0.13	17	0.59	5.2	1.3	87	2.0	2.5	577	12	891	2.1	0.8	36	1.3	21	2.1
Produced																					
Reacted																					
Mass Balance		-286	-75	0.14	0.054	3.8	0.51	0.10	0.37	-46	0.3	1.43	52.3	-1.1	181	0.30	-1.0	15.1	-0.58	2.7	-0.73

		Pb	Ni	Zn	NH3	Re	OH	Cl	F	NO2	PO4	H+	H2O	Nitrogen		Sulfur		Carbon			O2
WTP SW Test (target)														NO3	N2	SO4	SO2	Carbon	CO3	CO2	
5/1/08 22:00 to 5/5/08 11:15		lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb
Feeds	DMR Starting Bed																				
	CRR Starting Bed	0.017	0.033								0.30										774
	Simulant Feed	2.49	2.46	4.36	48.1	1.93	243	34.3	37.9	15.3	7.77	0.0029	8524	1127		4.79			110		1265.2
	DMR Coal BSTAC										3.91	118	156		29.1	53.8		3151			231
	DMR Alumina (start bed)																				235
	SphereOx										0.041					0.044		0.13			38
	CRR Coke											1.8	0.18		0.213	0.456		591			15.3
	CRR Glycol											444						1984			1762
	CRR Alumina																				141
	DMR Gas												6227		8933						4979
	CRR Gas														18549						14072
	Total	2.50	2.49	4.36	48.1	1.93	243	34.3	37.9	15.3	12.0	563	41170	1127	54665	59.1	0.00	5727	110		24048
Outlets	DMR Solids	0.98	0.68	1.01		0.74		0.83	1.43		3.70			0.0046		4.48		220	0.18		617
	HTF Solids	1.20	2.28	2.47		0.99		5.60	23		12.8			0.054		10.20		715			1492
	CRR Solids		0.04								0.13			0.035				158			769
	OGF Solids	0.35	0.18	0.0078		0.048		0.45	0.39		1.36					2.30		5.41			102
	Stack							1.73	12.9				45805		55152	2.58				16717	5568
	Total	2.5	3.2	3.5		1.8		8.6	37.3		18.0		45805	0.094	55152	17.0	2.6	1099	0.18	16717	8548
Produced													5369		299		2.6			16717	971
Reacted					48.1		243			15.3		563		1127		4.0		4628	109		16923
Mass Balance		0.027	0.69	-0.86		-0.15		-26	-0.65		6.0		-734	188		-12.7			-88		452

Figure 9-8 and Figure 9-9 show the component mass distributions for all component discharges for the production tests, including gases for LAW and WTP SW, respectively. The gases, at 96% of discharges, tend to dominate these figures, which is why only the solids are shown in Figure 9-6 to Figure 9-9. Figures 9-6 and 9-8 are for the LAW test and Figures 9-7 and 9-9 are for the WTP SW test.

The non-volatile components, including RCRA metals and radionuclide surrogates in the LAW and WTP SW simulants, were incorporated into the solid product and were either transferred out the bottom of the DMR to the PR as product or elutriated to the HTF as fines. A small portion of the fines passed through the HTF filters and into the CRR. These fines either built up in the CRR or elutriated out to be collected in the OGF.

The majority of non-volatile components in the simulant feed tended to split, with approximately 70% to 85% percent being elutriated to the HTF and 15% to 30% remaining in the DMR product. There was little difference between the overall solids split and the individual component splits. A higher fraction of some components was elutriated to the HTF (>85%). In the LAW test this occurred for iodine, fluorine, chlorine and cesium. In the WTP SW test this occurred for arsenic, boron (present only in the WTP SW test), selenium, fluorine, chlorine and cesium. A lower fraction of some components elutriated to the HTF (<60%). In the LAW test this occurs for iron and rhenium. In the WTP SW test this occurs for iron, rhenium, cadmium and lead.

As mentioned previously, it is expected that significant solids from the scoping runs were present in the OGF at the start of the production tests. The presence of these solids did not significantly affect the overall solids mass balance (the total weight in the OGF is only 5% of the solids); however, it is not possible to draw firm conclusions on how much solid material passed through the HTF filters to be collected in the CRR and OGF. Past testing has indicated about 0.3% of the sodium (only present in the feed constituents) was found in and downstream of the CRR, indicating that about 0.3% of feed solids passed through the HTF filter.

Overall mass balance closures for constituents of interest were:

Cs: +3.9% for LAW and +15.1% for WTP SW

I: -38.6% for LAW and +130.6% for WTP SW

Re: -23.1% for LAW and -7.6% for WTP SW.

Only the I is not within $\pm 30\%$. However, based on the extent of these data, and the low values measured in the high fidelity off-gas emission sample results, it is reasonable to conclude that the mineralizing THOR[®] FBSR process system retained these constituents of interest in the mineralized product, as expected.

The total mass balance closure for both tests is considered excellent, with a difference between feeds and discharges of 0.7 and 0.2% respectively for the LAW and WTP SW tests. The major gaseous components, including water, oxygen, nitrogen, and carbon dioxide, account for 94% of the total mass. All the major gaseous components show good to excellent balance (0% to 3% difference).

Figure 9-4 Component Distribution of All Discharges – LAW Production Test

Figure 9-5 Component Distribution of All Discharges - WTP SW Production Test

Figure 9-6 Component Distribution of Solids Discharges From DMR And HTF – LAW Production Test

Figure 9-7 Component Distribution of Solids Discharges From DMR and HTF – WTP SW Production Test

Figure 9-8 Component Distribution of All Solids Discharges – LAW Production Test

Figure 9-9 Component Distribution of All Solids Discharges – WTP SW Production Test

10. EVALUATION OF SOLID PRODUCT PERFORMANCE

The THOR[®] FBSR technology evaporates water, converts organic compounds to CO₂ and H₂O, converts nitrate/nitrite species to N₂, and produces a granular solid product. A “mineralized” solid product is produced that retains the hazardous and radioactive species in the atomic structure of the solid mineral phases formed by reaction of the waste with clay and iron that are added to the process as co-reactants. The formation of optimal mineralized species is important to maximizing the durability of the mineralized product as a final radioactive waste form. The characteristics of the mineral waste forms produced during the ART ESTD production tests and the formation of final product monolithic waste forms are discussed below.

10.1 Physical Properties

A sample of the DMR bed material is depicted in Figure 10-1. A 5-mm scale is visible in the lower right portion of this photograph. Individual product particles are more spherical in form and some have a nodular appearance when compared to the alumina starting bed material. The particle size, composition, and other properties of this material can be found in Sections 7 and 9. The large dark particles are carbon used as an energy source and reductant in the DMR. Figure 10-2 is a photograph similar to Figure 10-1, except that it shows material recovered from the PR vessel. This is product material that has been drained from the bottom of the DMR.

Figure 10-1 Typical DMR Bed Material Sample

Figure 10-2 Typical PR Material Sample

Fine solids elutriated from the DMR bed were collected in the HTF vessel and were periodically removed from the system. Individual HTF particles tended to clump together, but were relatively easy to collect. Figure 10-3 shows two micrographs of the morphology of the HTF product. The particles appear to be loose clumps of smaller particles. The two photos show the HTF material magnified at 100X and 400X. A 300 μ m scale is shown on the bottom left corner of the 100X micrograph and a 90 μ m scale is shown in a similar location for the 400X micrograph.

100x

400x

Figure 10-3 Microprobe Photographs of Product Fines Collected from the HTF

Figure 10-4 is a photograph of material from the CRR. The material is alumina and the photo indicates little or no buildup of product material on the bed particles. The photo shows that the HTF is performing

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efficiently, not allowing significant amounts of product fines to flow to the CRR, and that the CRR is converting constituents in the process gas to the desired H₂O, CO₂ and N₂ components.

Figure 10-4 Typical CRR Material Sample

Fines elutriated from the CRR and passing through the off-gas cooler were collected in the OGF, and periodically removed from the system. These filter fines are very similar to HTF material in physical properties, but are different compositionally. Figure 10-5 is a photograph of the morphology of the OGF material. The two photos show the OGF material magnified at 100X and 400X. A 300µm scale is shown on the bottom left corner of the 100X micrograph and a 90µm scale is shown in a similar location for the 400X micrograph.

Compositions for the HTF and OGF materials can be found in Section 9.

5493 OGF No. 2

100x

5493 OGF No. 1

400x

Figure 10-5 Microprobe Photographs of the Alumina Fines Collected from the OGF

Particle size distributions for the HTF fines are shown in Figure 10-6. The filter fines present a generally bi-modal size distribution, with modes at ~0.25 microns and ~30 microns. The first mode is likely due to a spray drying effect in the DMR and the second is likely due to attrition in the DMR. The majority of the clay additive particles are ~8 microns, which is between the two size distribution modes. One sample

(5514) shows a tri-modal distribution. This is attributed to a change in operational parameters, which would be expected to revert, to the bi-modal distribution soon thereafter.

Figure 10-6 Particle Size Distribution of HTF Materials

The OGF product presented a tri-modal size distribution as shown in Figure 10-7. The modes are ~0.25, 2 and 35 microns. The larger particles are likely attrited alumina material from the CRR bed. Some of the smaller particles likely passed through the HTF filters and were caught in the OGF. Some variability is observed in one sample (5521), which likely represents a transition due to an extended holdup of solids between drains.

Figure 10-7 Particle Size Distribution of OGF Materials

The bulk density and particle density of HTF and OGF samples were measured from samples obtained during the production tests. Those values are shown in Table 10-1. This material, after collection, could be further densified via tapping (bulk density, packed column in Table 10-1). The increased densification is indicated by the percent compaction value (packed bulk density divided by the loose bulk density). The weight percent total carbon is also listed in the table. The carbon weight percentage affects the bulk density by decreasing it as the weight percent carbon increases. The carbon originates in the carbon used to supplement the energy needed in the CRR. A more efficient propylene glycol addition method would likely eliminate the carbon in the OGF product and a more dense material would result. A more dense material is seen in sample 5521. This material is nearly all alumina.

Table 10-1 Bulk and Particle Densities of HTF and OGF Collected Solids

Run	Material	Sample ID	Date/Time	Bulk Density		% Compaction	Particle Density g / cc	Total C wt%
				Loose	Packed			
				g / cc				
P1	HTF	5319	4/29/2008 8:35	0.472	0.585	24.0%	2.04	8.90
P1	HTF	5379	5/1/2008 16:40	0.492	0.673	36.8%	2.13	1.26
P2	HTF	5459	5/4/2008 18:00	0.485	0.576	18.9%	1.68	20.7
P2	HTF	5514	5/6/2008 6:45	0.722	0.898	24.4%	2.92	3.43
P2	OGF	5493	5/5/2008 15:45	0.764	0.906	18.6%	2.69	2.09
P2	OGF	5501	5/5/2008 23:50	0.756	0.964	27.5%	2.66	1.73
P2	OGF	5521	5/6/2008 10:00	1.019	1.290	26.6%	3.48	3.75

10.2 Final Waste Form and Durability Results

The purpose of the final waste form (monolith) testing is to determine the suitability of a number of candidate binder materials for the production of monolithic solid waste forms from the NAS mineralized products generated by the treatment of Hanford LAW and WTP SW simulants. The Hanford IDF has requirements that apply to all waste forms to be disposed of at the facility. These requirements include minimum acceptable limits on leach resistance, compressive strength, free liquids, dispersible fines, and waste loading. Risk scenario pathways must also be considered. The NAS mineralized product will easily meet all of the known IDF disposal requirements except for compressive strength and dispersibility. Therefore, the binding of the NAS product solids into a final monolithic waste form will be required prior to disposal at the IDF to eliminate dispersibility and to provide a waste form that has compressive strength greater than 500 psi.

The NAS product, as a granular solid, has been shown to be as durable as low activity reference material (LRM) glasses. This is partially due to the high aluminosilicate content of the mineral product, which provides an aluminum buffering mechanism that inhibits leaching and is known to occur in aluminosilicate minerals in nature [33].

The term “near-surface disposal” indicates disposal in the uppermost portion, or approximately the top 30 meters of the earth's surface. For burial at the Hanford Site in the State of Washington, the Hanford contract [34] and the Immobilized Low Activity Waste (ILAW) Product Compliance Plan specify the following:

- The mean compressive strength of the waste form shall be at least 3.45E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M [35] or an equivalent testing method.
- The normalized mass loss of elements of concern shall be less than 2.0 grams/m² when tested by ASTM C1285 [36] or equivalent. This is the Product Consistency Test (PCT) A, which uses a glass-to-water ratio of 1 gram of -100 to +200 mesh glass (149 micron to 74 micron mesh opening size) to 10 milliliters of ASTM Type I water for 7 days at 90°C.
- The waste form shall pass the Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311. The test is used to determine if a waste meets the definition of EP Toxicity, that is, carrying

a hazardous waste code under RCRA (40 CFR Part 261.24), or meeting the Universal Treatment Standards (40 CFR 268.48).

To that end, the objectives of the monolith testing phase of this program were as follows:

- Determine acceptable binder material(s)
- Determine acceptable waste loadings of the NAS product in the monolith matrix
- Analyze monolith properties to ensure adherence to regulatory requirements

The operation of the ESTD facility during both the LAW and WTP SW production runs, described in this report, generated the NAS product used for the monolith tests. SRNL performed the granular and monolith testing phase of this program[37] and implemented the SRNL Quality Assurance Program.

10.2.1 Selection of FBSR Materials for Monolith Preparation

Representative FBSR product materials from processing the LAW and WTP SW simulants, respectively, were selected for further monolith experiments, based on chemical durability analyses of the granular products and desired operating conditions. The reason for performing an initial set of durability analyses on the granular NAS product was to establish a baseline set of data to which the chemical and physical properties of the final monolith products could be compared. Twelve NAS product samples generated from the production runs at Hazen were delivered to SRNL for analysis.

At SRNL, the 12 granular solid product samples underwent elemental analysis (for both cations and anions), Brunauer Emmett Teller (BET) surface area analysis, X-ray diffraction (XRD), Product Consistency Testing (PCT, ASTM C1285), Toxicity Characteristic Leaching Procedure (TCLP), and REDuction/Oxidation (REDOX) analysis to determine the $\text{Fe}^{+2}/\Sigma\text{Fe}$ value of the material, which is used to determine the oxidation state of other transition metals and hazardous species in the product. These data provided the basis for choosing the material with the best durability for generating monolith products. The samples which were analyzed are listed in Table 10-2.

Table 10-2 Samples Analyzed for Durability Performance

Sample Description	Sample Log #	Date Sample Obtained	Test	Hours of Operation at Test Conditions Before Sample Obtained	DMR Temperature	Simulant
HTF	5280	4/27/2008 21:42	P-1A	17.7	725°C	LAW
PR	5274	4/28/2008 5:15	P-1A	25.3	725°C	LAW
HTF	5297	4/28/2008 17:28	P-1A	37.5	725°C	LAW
PR	5316	4/29/2008 3:54	P-1A	47.9	725°C	LAW
HTF	5351	4/30/2008 12:00	P-1B	28.0	725°C	LAW
HTF	5357	4/30/2008 19:44	P-1B	35.7	725°C	LAW
PR	5359	4/30/2008 22:55	P-1B	38.9	725°C	LAW
PR	5372	5/1/2008 7:00	P-1B	47.0	725°C	LAW
HTF	5471	5/5/2008 0:20	P-2A	70.3	680°C	WTP SW
PR	5475	5/5/2008 4:00	P-2A	74.0	680°C	WTP SW
HTF	5520	5/6/2008 10:00	P-2B	26.5	700°C	WTP SW

PR	5522	5/6/2008 10:00	P-2B	26.5	700°C	WTP SW
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The compositional data for the samples listed in Table 10-2 have been plotted on the $\text{SiO}_2\text{—Na}_2\text{O—Al}_2\text{O}_3$ phase diagram shown in Figure 2-1. These compositional data are shown in Figure 10-8. The data indicate that target mineralized product composition was achieved within experimental error and that the DMR fluidized bed composition was uniform.

FIG. 501.—System $\text{Na}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

Principal References

- G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, 28, 1167-79 (1924).
 F. C. Kracek, *J. Phys. Chem.*, 34, 1583-98 (1930).
 N. L. Bowen and J. W. Greig, *J. Am. Ceram. Soc.*, 7, 238-54 (1924); corrections, *ibid.*, 410.
 N. A. Toropov and F. Ya. Galakhov, *Voprosy Petrogr. i Mineralog., Akad. Nauk S.S.S.R.*, 2, 245-55 (1953).
 Shigeo Aramaki and Rustum Roy, *Nature*, 184, 631-32 (1959).
 J. F. Schairer and N. L. Bowen, *Am. J. Sci.*, 254, 129-95 (1956).
 Liberto De Pablo-Galan and Wilfred R. Foster, *J. Am. Ceram. Soc.*, 42, 491-98 (1959).

Figure 10-8 Plot of Product Compositions on $\text{Na}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$ Phase Diagram

Table 10-3 shows the results of XRD analyses performed on the granular FBSR product. For ease of comparison, the results of XRD analyses performed on products generated from previous FBSR testing demonstrations for Hanford and INL simulated wastes are included in Table 10-3. The crystalline phases observed were those expected.

Table 10-3 XRD Crystalline Phases Observed in FBSR Granular Product

Sample	Low-Carnegieite ^f Nominally NaAlSiO ₄	Nepheline Nominally NaAlSiO ₄ or K _{0.25} Na _{0.75} AlSiO ₄	Nosean Na ₆ [Al ₆ Si ₆ O ₂₄](Na ₂ SO ₄) and/or Sodalite Na ₆ [Al ₆ Si ₆ O ₂₄](2NaX where X=Cl,F,I)	Other Minor Components
HANFORD ENVELOPE “C” LAW WASTES (2002) Fe ⁺² /ΣFe of Bed = 0.15				
SCT02-098-FM		X	Y	Al ₂ O ₃ , Fe ₂ O ₃ , Fe ₃ O ₄
Fines PR-01	X	X	Y	Al ₂ O ₃ , Fe ₂ O ₃ , Fe ₃ O ₄
HANFORD ENVELOPE “A” LAW WASTES (2004) Fe ⁺² /ΣFe of Bed = 0.28-0.81				
Bed 1103	X	X	Y	TiO ₂
Bed 1104	X	X	Y	TiO ₂
Fines 1125	X	Y		TiO ₂
INL SBW WASTES (2003-4) Fe ⁺² /ΣFe of Bed = 0.51-0.61				
Bed 260	Y	X	TR	Al ₂ O ₃ and TiO ₂
Bed 272	Y	X	TR	TiO ₂
Bed 277	Y	X	TR	TiO ₂
Bed 1173		X	TR	Al ₂ O ₃ , SiO ₂ , NaAl ₁₁ O ₁₇ , (Ca,Na)SiO ₃
HANFORD LAW WASTES Fe ⁺² /ΣFe of Bed = 0.41-0.90				

PR 5274 (P-1A)	Y	X	X	Al ₂ O ₃
PR 5316 (P-1A)	Y	X	X	Pyrophyllite*
HTF 5280 (P-1A)	X	Y		NaAl ₁₁ O ₁₇ (Diaoyudaoite), TiO ₂
HTF 5297(P-1A)	X	Y	X	SiO ₂
PR 5359(P-1B)	Y	X	X	Pyrophyllite*
PR 5372(P-1B)	Y	X	Y	Pyrophyllite*
HTF 5351(P-1B)	X	Y	Y	SiO ₂
HTF 5357(P-1B)	X	Y	Y	TiO ₂
Composite (P-1A)	X	Y	Y	SiO ₂ and TiO ₂
Composite (P-1B)	X	Y	Y	SiO ₂ and TiO ₂
HANFORD WTP SW WASTES Fe ⁺² /ΣFe of Bed = 0.41-0.90				
PR 5475 (P-2A)	Y	Y	X	Pyrophyllite*
HTF 5471 (P-2A)	X	X	X	SiO ₂
PR 5522 (P-2B)	Y	Y	X	Pyrophyllite*·TiO ₂
HTF 5520 (P-2B)	X	X	X	SiO ₂ and TiO ₂
Composite (P-2B)	Y	X	X	SiO ₂

X = Major constituent ; Y = Minor constituent ; TR = trace constituent

f = the PDF for this phase states it is orthorhombic nepheline and possibly low-carnegeite (PDF 052-1342). Note low-carnegeite also has ring structures that are oval for sequestration of K, Cs, etc.

*Al_{1.333}Si_{2.667}O_{6.667}(OH)_{1.333}

** The XRD method gives information on the specific crystalline phases present by comparison to reference library spectra. Although this method is not used with any internal standards to allow for quantitative measurement of the various crystalline phases, it does provide information as to the ‘major’ and ‘minor’ and ‘trace’ phases present by intercomparison of the main peaks of each crystalline pattern within a given sample.

The PR and HTF minerals were sieved through an 18-mesh sieve to screen out any particles at ~ 1 mm diameter. The REDuction/OXidation (REDOX) measurements are shown in Table 10-4. The REDOX value is defined as $\text{Fe}^{+2}/\Sigma\text{Fe}$ and provides a method of estimating the oxidation state of the other multivalent elements [38]. The oxidation state of the constituents affects the release rate of the constituent from the waste form. The higher the REDOX value, the more reduced the FBSR granular product is, i.e., more Cr^{+3} than Cr^{+6} . The HTF products are more reduced than the PR products, which is expected since they remain exposed to the reducing gases in the DMR freeboard, which includes small amounts of hydrogen and carbon monoxide, longer than the PR products. Table 10-4 also shows the mass losses from LOI treatment (coal content).

The REDOX data for the PR samples indicate that total iron is about 40 to 60% reduced in the LAW tests and about 40 – 45% reduced in the WTP-SW tests. Similar comparisons for the HTF REDOX data indicate that total iron is about 75 – 90% reduced for the LAW, and about 86 – 90% reduced in the WTP-SW. The LOI data indicate that the HTF samples contain between 9 and 13% residual carbon, and it is possible that the residual carbon in these samples could alter the REDOX measurements by serving to reduce the iron during the dissolution and absorption measurements. This high bias or ‘increase’ in measured Fe-II has been observed in scope tests that added trace amounts of fresh ground coal to the standard Environmental Assessment (EA) glass that is used in the REDOX procedure. [37]

Table 10-4 REDOX Values for the FBSR Granular Product Samples

Sample	Fe^{+2}	Fe^{+3}	Fe(total)	$\text{Fe}^{+2}/\text{Fe}(\text{total})$	Coal Content (wt%)
5280 HTF, LAW	0.024	0.009	0.032	0.735	9.96
5297 HTF, LAW	0.023	0.004	0.027	0.869	10.01
5351 HTF, LAW	0.027	0.003	0.030	0.899	9.52
5357 HTF, LAW	0.027	0.003	0.030	0.899	8.62
5471 HTF, WTP SW	0.027	0.004	0.031	0.869	12.81
5520 HTF, WTP SW	0.023	0.003	0.026	0.903	13.00
5274 PR, LAW	0.171	0.246	0.416	0.410	2.14
5316 PR, LAW	0.066	0.048	0.114	0.582	0.96
5359 PR, LAW	0.242	0.234	0.476	0.508	0.95
5372 PR, LAW	0.061	0.061	0.121	0.500	0.37
5475 PR, WTP SW	0.065	0.094	0.159	0.410	0.82
5522 PR, WTP SW	0.112	0.130	0.241	0.463	1.10

The chemical durability of the granular product solids was determined using the PCT. Prior to sizing and washing, carbon was removed from the material. The product carbon was removed by heating to 525°C overnight in an air atmosphere. Heating to remove the carbon was chosen because it was a more thorough

removal method and adaptable for the filter fines, i.e., hand removal of the carbon in the filter fines would not be feasible. This temperature was chosen because it is high enough to oxidize (remove) the carbon, but not high enough to change the composition or the phase assemblages. This is the temperature specified in a United States Geological Survey procedure [39] for carbon removal in preparation for the analysis of coal combustion by-products.

The PR samples were sized between -100 and +200 mesh (74 μm to 149 μm), the same size fraction used to express glass waste form performance. The HTF samples were sieved to <200 mesh size. To remove the electrostatic fines, the sized material was washed six times with 100% ethanol. Water was not used for washing to insure that any water soluble phases were not removed prior to leaching, as cautioned by the ASTM C1285 procedure.

Figure 10-9 lists PCT normalized release data (average of duplicate PCTs) for the 12 granular samples as determined by SRNL. [37] Normalization of the measured PCT leachate concentrations involves dividing the leachate responses by both the elemental fraction and the BET surface areas. Various researchers have suggested that BET is a more appropriate surface area characterization for mineral and ceramic waste forms, which have much different porosities than glass waste forms. Geometric surface areas, as defined by ASTM C1285, are used for the less porous glass waste forms [40]. A discussion of the use of BET by various researchers for mineral and ceramic waste form durability via PCT and Single Pass Flow Through Testing (including bulk vitrified foam glass) is summarized in Reference 40. The measured BET surface areas for the HTF and PR samples, with coal roasted out, ranged from 3.8 m^2/g to 5.5 m^2/g .

Figure 10-9 PCT Results for the FBSR Granular Product Samples

The data in Figure 10-9 indicate that the normalized PCT release rates are all well below the desired value of 2.0 g/m² for all elements tested (Al, Cs, Na, Re, S, Si, and I). Normalized release (NL) for sulfur is highest for all samples. NL(Re) is higher for the HTF fines versus NL(Re) in the PR bed products. The NL(Cs) is higher for PR bed products versus the HTF fines. NL(Na) is about the same across all bed products and fines and NL(Al) and NL(Si) are less than 0.005 and 0.001 g/m², respectively. The higher release rates for some constituents, such as S and Re, are attributed to the fact that the DMR process conditions could have been somewhat more oxidizing. The Re release rate is, however, about an order of magnitude less than that measured for the SBW mineralized product [5]. After all data were gathered for this report, it was discovered that the peroxide fusion method performed at lower temperature than the lithium tetraborate fusion method gives better recovery for Re. Accordingly, all data shown in this report give Re on a peroxide fusion analysis basis. Also, it has been determined in more recent BSR mineral dissolution testing that a sealed vessel aqua regia dissolution method provides better recovery of sulfur versus the open vessel digestion methods used in this study. [41] Accordingly, it is expected that the measured sulfur content for solid products is likely biased low. This would result in normalized release values for sulfur, when calculated per ASTM C1285 methods, that are biased high.

Normalized release rates for HTF vs. PR product material seem to be consistently higher, but this might be attributed to the higher measured REDOX values for the HTF (more reduced) vs. the PR material from

Table 10-4. Even for the worst case Re and HTF release rates, the values are still much lower than the 2.0 g/m² specification for Na and the LRM glass standard (0.27 g/m²).

The results show that, over the entire REDOX range of conditions shown in Table 10-4, all FBSR mineral product solids showed high leach resistance, with release rates for the measured constituents well below the acceptance values.

The technical team decided, based on examination of the operating conditions and PCT data, to choose product from test P1-B (LAW), at a product to fines ratio of 0.25, for continuing the monolith activity. The lowest Re release and lower clay mass (640 g/L) resulting in lower total waste mass were the reasons for this choice. It was also decided to use product from test P2-B (WTP SW), at a product to fines ratio of 0.33. Table 10-5 lists the test conditions for the products used to prepare monoliths. Although the durability data are quite close in comparison, it was judged that the materials under these test conditions were represented and would likely perform best in a monolith.

Table 10-5 Test Conditions for Product Used in Monolith Preparation

Test	Main bed (DMR) Temperature	Simulant	Grams Clay per Liter Simulant
P-1B	725°C	LAW	640
P-2B	700°C	WTP SW	307

10.2.2 Preparation and Analysis of Preliminary Small Cube Monolith Specimens

Quantities of the selected FBSR product (PR) materials were screened to remove the greater than ~1.0 mm particle size solids, mainly large carbon particles. Carbon is an additive and reductant in the THOR[®] process. These carbon particles would be removed and sent back to the process in an actual processing plant, and thus their removal is representative of material formed from actual processing. The PR materials from the main bed of the DMR were combined with a representative amount of product fines from the HTF, as observed via the operational product to fines ratio and noted above, and then sent to SRNL. The following measurements were performed on the P-1B and P-2B materials. However, since this material needs to be representative of that produced in a production facility and then incorporated into the final waste form with the binder, the carbon was not roasted out of the NAS product material that were incorporated into the monolithic waste forms. A small quantity of carbon less than 900 µm in size, perhaps 2 to 5 wt%, is not removed from the granular product and returned to the FBSR process. These two sets of mixed material (LAW and WTP SW) were used to perform monolith experiments.

The following measurements were performed on the P-1B (LAW) and P-2B (WTP SW) product materials. The carbon was not roasted out of the material, except for the BET surface area measurement. SRNL data shows BET surface areas for roasted samples give nominally 20% lower surface areas when the residual coal is roasted out. The lower roasted BET surface areas then increase the calculated normalized release data, since the surface area is in the denominator for calculating normalized releases.[37] The TCLP was performed on the as received P1-B and P-2B products. The elemental analyses, BET surface area and particle size distribution were performed on a portion of the sized, washed and dried -100 to +200 mesh powders that were prepared for leaching in the PCT.

- Elemental analyses

- BET Surface Area (with coal roasted out)
- Particle Size Distribution
- PCT (ASTM 1285)
- TCLP

These results provide a basis for comparison to results from monoliths prepared by mixing the material with binders. Five different binder types were selected to prepare monoliths; the following binders were the candidates:

Ordinary Portland Cement (OPC), a very common binder consisting mainly of calcium silicates, calcium aluminates, and calcium aluminoferrate.

High Alumina Cements, composed mainly of calcium aluminates rather than calcium silicates; these cements usually have less basic pore water than OPC.

Geopolymers, which are amorphous to semi-crystalline, three-dimensional silicoaluminate polymers.

Ceramicrete (ceramic cement), which is composed of magnesium phosphate.

NuCap™ material, an advanced silicone geopolymer composite material developed by Global Matrechs, Inc.

Small 1.875-inch diameter monolithic cylinders were prepared initially, with material from P-1A tests because of its faster availability, to determine optimum waste loading [granular product weight/(granular product weight + binder dry weight)] and water additions. Several dozen formulations were generated and tested for compressive strength before selecting and preparing 17 different formulations to form 2x2x2-inch cubic monoliths with the P-1B (LAW) material for more extensive analyses (see Figure 10-10) [37].

Table 10-6 shows the binder types and waste loadings selected for more extensive analysis using the P-1B (LAW) product solids. More extensive details regarding the monolith formulation recipes can be found in Reference 37. The selections were made based on compressive strength and waste loading information gained during the exploratory efforts with the smaller diameter monolithic cylinders. The OPC and High Al cements in Table 10-6 were all made as three-component mixes (FBSR, dry binder, water). The various geopolymers were all made with FBSR and heat-treated clay, mixed in with concentrated, caustic sodium hydroxide solution and liquid sodium silicate solution. Soluble solids in the sodium hydroxide and silicate solution were factored into the waste loading calculations.

Table 10-6 Monolith Binders, Formulation Designators and Waste Loadings

Binder Type	Test Designator	Calculated Waste Loading
OPC	OPC-1	80%
OPC	OPC-2	85.1%
High Al Cement	FON-1	68.6%
High Al Cement	FON-2	74.2%
High Al Cement	S41-1	68.6%

High Al Cement	S41-2	74.2%
High Al Cement	S71-1	68.6%
High Al Cement	S71-2	74.2%
Geopolymer	GEO-1	67.5%
Geopolymer	GEO-2	72.1%
Geopolymer	GEO-3	67.5%
Geopolymer	GEO-4	71.2%
Geopolymer	GEO-5	62.9%
Geopolymer	GEO-6	66.8%
Ceramicrete	CER-1	66.7/64.5%
Ceramicrete	CER-2	72.7/69.3%
NuCap	NUCAP-1	>45.5% ¹
1) Note: Since the NuCap™ binder paste is an insoluble solids-containing liquid, i.e., a 'slurry', then wt% FBSR loading on dry basis is $> 45.5\text{wt}\% (1 / (1 + (<)1.2) = > 0.45$

Figure 10-10 Preparation of 2-inch cube monoliths

The following measurements were performed on the 2-inch cube monoliths made with the LAW P-1B product solids at the waste loadings listed in Table 10-6. Bulk densities of the cubes were determined from weighing the cubes immediately before compression testing. After compression testing of the cubes, portions of the cubes were crushed to pass through 9.5 mm (0.375 inch) sieves for submission to the TCLP. Other pieces of the cubes were mechanically ground with a tungsten blade grinder to prepare the -100 to +200 mesh powders for the PCT. These powders were sized and washed with ethanol, dried and a portion was sampled for BET surface area and elemental analyses.

- Compressive strength test (ASTM-C39/C39M)
- BET Surface Area (coal not roasted out)
- PCT (ASTM 1285)
- Elemental analyses
- Density
- TCLP

A summary of the physical and TCLP data is listed in Table 10-7 below.

Table 10-7 2-inch Monolith Cubes With P-1B Product Solids - Measured Data

Monolith	Compressive Strength (psi)	Cure Time (days)	Density (g/cc)	BET Surface Area (m ² /g) w/coal included	TCLP Result
OPC-1	1,630	12	1.64	31.5	Pass
OPC-2	573	28	1.61	21.3	Pass
FON-1	770	7	1.77	20.0	Pass
FON-2	490	7	1.75	15.5	Pass
S41-1	672	7	1.75	12.2	Pass
S41-2	340	15	1.70	10.7	Pass
S71-1	1,120	7	1.70	13.1	Pass
S71-2	550	15	1.65	9.2	Pass
GEO-1	1,510	11	1.87	15.2	Note 2
GEO-2	860	14 (11)	1.87	17.3	Note 2
GEO-3	1,270	11	1.81	10.9	Note 3
GEO-4	410	11	1.84	6.2	Note 1
GEO-5	950	7	1.88	10.6	Note 1
GEO-6	1,080	7	1.82	10.0	Note 1

CER-1	520	8	1.81	32.2	Note 1
CER-2	550	28	1.81	27.7	Pass
NUCAP-1	1,250	34	1.44	0.09	Note 2
LAW (P-1B)				4.17 (Note 4)	Note 3
WTP-SW (P-2B)				4.10 (Note 4)	Note 1
Notes: Did not pass Universal Treatment Standard (UTS) for Sb. Did not pass UTS for Cd Did not pass UTS for Cd and Sb These values had coal roasted out.					

Several metals, including cadmium, antimony, and selenium were added to the LAW and WTP SW simulants at significantly higher levels than those expected in the actual waste streams so that they could be successfully measured and their fate/performance determined in the process and final waste form (See Section 4). They were increased by the factors shown in Table 10-8.

Table 10-8 Factors That Sb, Cd, And Se Were Increased in the ESTD Simulants.

Element	Factor increased in WTP SW simulant.	Factor increased in LAW simulant.
Sb	47.7	10
Cd	1296.9	10
Se	16.1	None

Several of the 2-inch cube formulations did not pass the TCLP limit for antimony and cadmium by factors ranging from 1.2 to 2.9 as prescribed by the Universal Treatment Standards (40 CFR 268.48). The LAW material used in formulating the monoliths also did not pass the TCLP (40 CFR 261.24) for Cd and Sb; the WTP SW granular material did not pass for Sb. With the exception of these two metals, all monoliths and product material passed TCLP. More discussion follows below regarding TCLP results.

PCT data, based on duplicate tests, are shown in Figure 10-11 below. Normalized PCT release was calculated using the elemental fraction of the crushed monoliths adjusted for moisture loss at 250°C (i.e., on an anhydrous basis), carbon content and the BET surface for better comparison to previous aggregate and blend data. The normalized PCT release values for the 7-day test, with the exception of the NUCAP

material, are all well below the desired mass loss value for Na of 2.0 g/m². The NUCAP values have been divided by 100 to be comparable on the figure with the other monoliths. Sulfur has the highest release and this is thought to be a function of the measured REDOX [Fe⁺²/Fe_(total)] of the product material used in preparing the monoliths and analytical measurement methods (see discussion above regarding the granular starting waste material). The measured values listed in Table 10-4 indicate a “reduced” material that would likely have higher release rates for some constituents such as S and Re than if the DMR were operated under more oxidizing conditions, which is a potential area for further investigation.

Figure 10-11 PCT Results for the 2-in Cube Monoliths using LAW P-1B Product Solids

The data shown in Table 10-7 and Figure 10-11 were examined by the technical team with regard to several criteria. The criteria included:

- Waste Loading
- Compressive strength (>500 psi)
- TCLP results
- PCT release rates for Re

The technical team decided to move forward and up in scale with the following binders to generate 3-in diameter by 6-in and 6-in diameter by 12-in cylinder monolith specimens:

- FON-2 – This binder and formulation had a high waste loading, but failed the compressive strength test. It was believed that a longer cure time could bring it into compliance with the compressive strength criterion.
- S71-2 – This binder and formulation appeared to meet all of the criteria.
- GEO-1 – This binder and formulation failed the TCLP test for Cd; however, it was believed that repeats of the TCLP test could show compliance because the results were very close to the limit.

The team also decided to carry forward a new geopolymer formulation, designated GEO-7. This binder and formulation was of additional interest since it used fly ash in place of the heat-treated meta-kaolin clay, and additional time was needed to work out the binder formula for that material. Information from the other geopolymers, as well as preliminary tests using the original small 1.875-inch diameter monolithic cylinders, provided indications that GEO-7 would pass compressive strength criteria and perform satisfactorily with regard to PCT and TCLP releases. The waste loading was 65.2%.

10.2.3 Preparation and Analysis of Larger Scale Cylinder Monolith Specimens

All of the scoping work (2-inch cubes) was done and optimized with the P-1B material (LAW). Monolith recipes were not optimized for P-2B (WTP SW) granular material; the focus was on the LAW material. Larger scale monolith cylinders, 3-in diameter by 6-in high and 6-in diameter by 12-in high, were prepared using each of the four binder formulations (FON-2, S71-2, GEO-1, GEO-7) for each of the two simulant products (LAW, WTP SW). These cylinders were formed using the same recipes and waste loadings as the corresponding 2-in cubes. The following measurements were performed on these larger scale monoliths with the exception of the BET surface area on the 6-in diameter by 12-in cylinders. It was judged that the measurements performed on the 3-in diameter by 6-in cylinders would be acceptable for the larger cylinders because of the similarity of that measurement between the 2-in cubes and the 3-in diameter by 6-in cylinders. As with the previous cube monoliths, bulk densities of the cylinders were determined from weighing the cylinders immediately before compression testing. After compression testing of the cylinders, portions of the cylinders were crushed to pass through 9.5 mm (0.375 inch) sieves for submission to the TCLP. Other pieces of the cylinders were mechanically ground with a tungsten blade grinder to prepare the -100 to +200 mesh powders for the PCT. These powders were sized and washed with ethanol, dried and a portion was sampled for BET surface area and elemental analyses. Analyses performed were:

- Compressive strength test (ASTM-C39/C39M)
- BET Surface Area (coal not roasted out)
- PCT (ASTM 1285)
- Elemental analyses
- Density
- TCLP

Figure 10-12 shows typical monoliths which were formed.

3-in diameter by 6-in cylinders

6-in diameter by 12-in cylinders

Figure 10-12 Typical 3-in Diameter by 6-in and 6-in Diameter by 12-in monoliths

Table 10-9 shows the measured physical data for the larger scale cylinders, as well as the 2-in cubes for comparison purposes. BET surface areas were not measured for the 6-in diameter by 12-in cylinders; it was judged that previous data and the consistency of preparation and test performance would allow the use of the 3-in diameter by 6-in cylinder measurements without biasing PCT data.

One of the 6-in diameter by 12-in GEO-7 WTP SW cylinders experienced a mold deformation during the cure period and became badly deformed. The mold split was caused by a combination of 'pre-splitting' the mold with a vertical cut from top to bottom (allows easier 'demolding' of the sample after curing) and the fact that the geopolymers tended to exhibit noticeable volume expansion on curing. It is postulated that the expansion and deformation phenomena, and subsequent failure of the form were factors in the lower compressive strength measured for that cylinder.

There is variability in the compressive strength data for the individual recipes, a general trend of decreasing with increased scale, although not for every formulation. An explanation for the phenomena is not available at present and further testing to determine the cause is recommended for any future investigations, in particular, a measure of the efficiency of mixing for the larger monoliths should be evaluated.

Table 10-9 Data Measured for the Larger Scale Cylinders

Binder & Size	Compressive Strength (psi)	Cure Time (days)	Density (g/cc)	BET Surface Area (m ² /g) w/coal included
LAW (P-1B Product Solids)				
FON-2	74.2% waste loading			
2" Cube	490	7	1.75	15.50
3" dia x 6" cylinder	580	28	1.69	15.50*
6" dia x 12" cylinder	370	28	1.69	15.50*
S71-2	74.2% waste loading			
2" Cube	550	15	1.65	9.20
3" dia x 6" cylinder	660	17	1.68	9.20*
6" dia x 12" cylinder	550	19	1.70	9.20*
GEO-1	67.5% waste loading			
2" Cube	1,510	11	1.87	15.20
3" dia x 6" cylinder	1,690	14	1.85	15.20*
6" dia x 12" cylinder	1,530	14	1.82	15.20*
GEO-7	65.2% waste loading			
3" dia x 6" cylinder	2,500	14	1.90	11.70
6" dia x 12" cylinder	1,920	18	NM	11.70**
WTP SW (P-2B Product Solids)				
FON-2	74.2% waste loading			
3" dia x 6" cylinder	570	18	1.68	30.83
6" dia x 12" cylinder	420	28	1.67	30.83***
S71-2	74.2% waste loading			
3" dia x 6" cylinder	820	17	1.67	8.99
6" dia x 12" cylinder	660	19	1.66	8.99***
GEO-1	67% waste loading			

3" dia x 6" cylinder	890	14	1.83	12.55
6" dia x 12" cylinder	1,710	19	1.83	12.55***
GEO-7	65.2% waste loading			
3" dia x 6" cylinder	1,980	14	1.83	26.86
6" dia x 12" cylinder	520	28	NM	26.86***

*These BET surface areas were obtained from the 2-inch cube PCT prepared powders.

** These BET surface areas used an average of the GEO-1 to GEO-6 2-inch cube data.

*** These BET surface areas were obtained from the 3-inch x 6-inch cylinder PCT prepared powders.

Table 10-10 summarizes the TCLP data for the cylinders and 2-in cubes. All of the binder formulations passed the TCLP test, with the noted exceptions for Sb, Cd, and Se. However, the FON-2 binder formulation passed the TCLP test for all constituents. The results are not consistent between the monolith sizes as can be seen from Table 10-10. The mean relative standard deviation, for all measurements, ranges between ~50 and 92%, indicating that the analytical results for the TCLP measurements are not very repeatable at these low concentration levels, but do provide data for further analysis as discussed below.

Table 10-10 Monolith TCLP Data Summary

Binder & Size	Pass TCLP		
	Sb	Cd	Se
LAW			
S71-2			
2" Cube	YES	YES	YES
3" dia x 6" cylinder	YES	YES	YES
6" dia x 12" cylinder	YES	NO	YES
GEO-1			
2" Cube	YES	NO	YES
3" dia x 6" cylinder	NO	YES	YES
6" dia x 12" cylinder	YES	YES	YES
GEO-7			
3" dia x 6" cylinder	NO	NO	YES
6" dia x 12" cylinder	YES	YES	NO

WTP SW			
S71-2			
3" dia x 6" cylinder	YES	NO	NO
6" dia x 12" cylinder	YES	NO	YES
GEO-1			
3" dia x 6" cylinder	NO	YES	YES
6" dia x 12" cylinder	NO	YES	YES
GEO-7			
3" dia x 6" cylinder	YES	YES	YES
6" dia x 12" cylinder	YES	YES	NO

As previously noted, Sb, Cd, and Se were constituents added in higher concentrations to the simulant to determine their fate and performance. This allows the data, when applied to the expected concentrations in the actual waste, to be used to project performance for a waste form generated from the actual waste. This was done with the data as follows:

- Assumed that the total amount of the element fed to the process is contained in the FBSR solids (PR+HTF), calculated a maximum mg element/kg value in the solids, and then adjusted it for the waste loading in the monoliths.
- Averaged the actual TCLP data for each of the formulations and sizes to get a mg element/L value in the TCLP leachate.
- Performed a mass balance to calculate the concentration of each element (mg/kg) in the solids that have been leached via TCLP.
- Calculated a product retention efficiency for each formulation: $E = (1 - ((\text{max mg element per kg waste form} - \text{mg element per kg of leached solids}) / \text{max mg element per kg waste form})) * 100$

The results are shown in Table 10-11. The analysis was also extended to the FBSR granular products used to prepare the monolithic waste forms, and those data are also included in Table 10-11.

Table 10-11 Waste Form Product Retention Efficiencies

Waste Form	Product Retention Efficiency					
	LAW			WTP SW		
	Sb	Cd	Se	Sb	Cd	Se
FON-2	98.52%	99.96%	96.86%	97.63%	99.89%	96.58%
S71-2	97.63%	99.09%	97.54%	92.14%	96.59%	92.26%

GEO-1	93.97%	99.32%	87.29%	82.89%	99.39%	92.12%
GEO-7	91.60%	95.03%	75.74%	94.47%	99.69%	93.58%
LAW Granular Product	92.69%	96.09%	---	---	---	---
WTP SW Granular Product	---	---	---	89.60%	99.84%	---

Next the maximum mg element/kg waste form is adjusted downward by the concentration factors shown in Table 10-8 to the levels expected in the projected waste compositions. Then, using the retention efficiency and a mass balance, calculate a TCLP leachate concentration. Those results are shown in Table 10-12 along with the regulatory limits.

Table 10-12 Projected Waste Form TCLP Results

Waste Form / Regulatory Limit	After Adjustment to Actual Waste Concentration					
	mg/L in LAW Leachate			mg/L in WTP SW Leachate		
	Sb	Cd	Se	Sb	Cd	Se
FON-2	0.0321	0.0008	0.1242	0.0057	5.00E-06	0.0244
S71-2	0.0512	0.0176	0.0975	0.0189	1.52E-04	0.0551
GEO-1	0.1178	0.0118	0.4547	0.0372	2.45E-05	0.0507
GEO-7	0.1685	0.0891	0.8910	0.0123	1.29E-05	0.0424
LAW Granular Product	0.213	0.102	---	---	---	---
WTP SW Granular Product	---	---	---	0.0337	9.41E-06	---
RCRA Limit	---	1.0	1.0	---	---	---
UTS Limit	1.15	0.11	5.7	---	---	---

Examination of the data in Table 10-12 shows that all of the formulations, including the FBSR granular products, would pass TCLP quite readily, for waste forms generated from the projected, actual waste streams.

Figure 10-13 shows the PCT results for the monoliths, with the available 2-in cube results included for comparison. Normalized PCT release was calculated using the elemental fraction of the crushed monoliths adjusted for moisture loss at 250°C, carbon (i.e., on an anhydrous, coal free basis) and the BET (coal included) surface areas. [37] Again, all of the PCT release rates are all well below the desired mass loss value of 2.0 g/m² for Na. The S71-2 binder formulation appears to be the lowest performer with

regard to durability, especially with respect to Re and I release rates. It is worth noting that the S71-2 formulation has the lowest BET surface area of the monoliths. This value appears in the denominator of the formula to calculate release rates, and a lower value increases the calculated release rate. The technical team judged the GEO-7 formulation to be the most durable monolith with regard to the PCT data, although this GEO-7 monolith recipe was not optimized for WTP SW granular material; the focus was on the LAW material.

Figure 10-13 Summary PCT Results for the Monoliths

Heat of hydration isotherms were measured over the cure time for the 6-in diameter by 12-in monoliths. These monoliths were all cured in a controlled temperature/humidity curing room at nominally 23°C. The isotherms are shown in Figure 10-14. There was a less than 25°C temperature rise for all of the monoliths and then a return to ambient temperature over a period of about 10 hours. Immediate reactions can be seen for the geopolymer formulations. The high Al cement formulations have reactions, but the rate of temperature rise is more gradual before peaking in 7-8 hours. These are not unexpected results and provide data regarding the potential temperature increase during curing for monoliths prepared from actual waste.

Figure 10-14 Cure time Isotherms for the 6-inch Diameter by 12-inch Monoliths

Limited testing was also performed with one other geopolymer binder. It is designated as L-TEM and was provided by Columbia Energy and Environmental Services (CEES). Three 3-inch diameter by 6-inch monolith cylinders at waste loadings of 76%, 80%, and 82.5% were formed with granular product from the LAW production test (P-1A) at CEES. These particular monoliths were sent to and tested by SRNL for compressive strength, TCLP, and PCT. Compressive strengths were above 900 psi for all monoliths, all monoliths passed the TCLP test, and PCT results were similar (about an order of magnitude less than the LRM glass standard) to the other binder formulations described above. [37] However, the starting FBSR granular material was different from that used for the other binder formulations described above,

and a consistent performance comparison is not possible. However, this binder is recommended for further testing if resources become available and a need is identified.

The technical team evaluated all of the data presented above and concluded that the GEO-7 formulation performed the best with respect to compressive strength and durability (TCLP and PCT) for both the LAW and WTP SW simulant products. A batch of 24 replicate 2-inch diameter by 4-inch cylinders formed with the GEO-7 recipe and WTP SW granular product (P-2B) were produced that could be tested by an independent laboratory. The 2-inch diameter by 4-inch cylinders were batched using the same recipe as applied to the previous cylinders. The batching was done to produce four replicate cylinders per mixing-batch in the mixer. These cylinders were allowed to cure in the plastic molds for ~ 30 days.

Four cylinders were randomly chosen for physical property and durability testing. Table 10-13 lists the measured physical property data for those cylinders. [37] It should be noted that the surface area of the PCT-prepared powders were measured to be about 10 times lower than previous BET surface area measurements on the 3-inch diameter by 6-inch GEO-7 WTP-SW cylinder.

Cylinder No.'s 5, 9, and 17 were subjected to TCLP testing. The data showed all TCLP leachate levels below the UTS limits, with the exception of Se. The Se value is below the UTS limit (5.7 mg/L), but above the toxicity characteristic value (1.0 mg/L). These data are in agreement with previous TCLP data shown for the GEO-7 recipe used for WTP-SW monolithing.

Results of the 7-day PCT performed on the 2-inch diameter by 4-inch cylinders (No.'s 5, 9, and 17) are shown in Figure 10-15 along with the WTP SW granular product data (which is coal free). [37] All normalized release data were calculated similarly to the 2-inch cube data, i.e., anhydrous, coal-free basis, for better comparison to the previous data. The 10 times lower measured BET surface areas for the 2-inch diameter by 4-inch cylinders monoliths are responsible for what appears to be slightly higher normalized release values as compared to the previous monoliths. As has been previously mentioned, the GEO-7 geopolymer formulation was developed out of the LAW initial studies and was not optimized for the WTP-SW aggregate blend. One concern for the WTP-SW blend and subsequent monolith durability is the relatively higher F and Cl present versus the LAW. Release of these anion constituents into solution during leaching could produce strong conjugate acid species (HF and HCl) that could attack the leached monolith surface.

Table 10-13 Data Measured for the 2-inch by 4-inch Cylinders

Cylinder ID	Compressive Strength (psi)	Density (g/cc)	BET Surface Area (m ² /g) w/coal
Batch #2, No. 5	2,230	1.78	3.23
Batch #3, No. 9	2,320	1.76	2.89
Batch #5, No. 17	2,440	1.78	2.79

Figure 10-15 PCT Results for 2-inch by 4-inch WTP SW Monoliths and Granular Product

It is recommended that further test work be performed to investigate formulation compressive strength versus waste loading, increased mixing efficiency versus monolith size, scale of monolith versus cure time, and preparation of larger-scale monoliths to further develop this technology. It is also recommended that a more detailed investigation of the behavior of Sb and Cd in the binder be performed as well as additional studies related to the REDOX effects on the product.

11. SMALL SCALE RADIOACTIVE DEMONSTRATION

A Bench scale Steam Reformer (BSR) was designed and constructed at the SRNL to treat actual radioactive wastes to confirm the findings of the non-radioactive FBSR pilot scale tests. BSR testing with WTP SW waste surrogates and associated analytical analyses and tests of granular products (GP) and monoliths began in the fall of 2009, and then was continued from the fall of 2010 through the spring of 2011. Radioactive testing commenced in 2010 with a demonstration relevant to Hanford's WTP-SW where Savannah River Site (SRS) High Level Waste (HLW) secondary waste from the Defense Waste Processing Facility (DWPF) was shimmed with a mixture of $^{125/129}\text{I}$ and ^{99}Tc to chemically resemble the projected WTP-SW composition as shown in Section 4. Prior to these radioactive feed tests, non-radioactive simulants were also processed through the BSR.

The principle objective of this activity was to demonstrate, with the BSR equipment, the production of radioactive granular product and a monolith final waste form comparable to those generated using non-radioactive simulant in prior ESTD testing. Simulant was tested in the non-radioactive BSR in order to provide: (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the BSR product in comparison with the ESTD product, and (3) granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from the ESTD products as described in Section 10.

The granular, mineralized waste form products were characterized and tested. A portion of the granular product was made into a monolith. The monolith was then subjected to a compression test. Crushed pieces of the radioactive monolith resulting from the compression testing were then re-characterized and subjected to PCT analyses. A radioactive monolith was leach tested according to ASTM C1308. Both the granular product and the monolith product were leach tested using the EPA TCLP procedure performed by a certified offsite laboratory.

All information and data provided in this section can be found, along with greater technical detail, in Reference 42.

11.1 Preparation of WTP SW Simulants

The non-radioactive WTP SW simulant was prepared as described in Section 4. However, it should be noted that SRNL did not add the simulant chemicals for the RCRA/UTS metals Ba, Cd, Tl, Se and Sb. The technical team determined that addition of these metals would not provide any further beneficial information and that it is unlikely that these constituents would actually be present in measurable quantities in the actual WTP SW stream.

SRNL obtained a recycle stream sample from the Defense Waste Processing Facility (DWPF). The DWPF radioactive sample was evaporated by a factor of 20 and then supplemented with radioactive ^{99}Tc and mixtures of ^{129}I (radioactive) and ^{125}I (radioactive) to make the DWPF sample mimic the anticipated WTP SW composition at Hanford. Re, at the same concentration as the non-radioactive simulant, was also added to provide a comparison of performance with Tc. This information would confirm the use of Re as an acceptable Tc surrogate during non-radioactive testing.

During the BSR processing, 307 grams of a 55% OptiKasT / 45% Sagger XX kaolin clay mixture was added to both the non-radioactive simulant and the modified DWPF melter recycle waste to form the mineralized granular product.

11.2 BSR Operation

The BSR designed at SRNL is a two-stage unit used to produce the same mineralized products and gases as the ESTD FBSR (see Figure 11-1). Unlike the FBSR, the BSR is not fluidized since it had to fit in the SRNL shielded cells, and there is not enough height in the cells to allow for product disengagement. Steam does flow through the product freely, which is in the form of a biscuit, and Scanning Electron Microscopy (SEM) analysis showed well-reacted particles in the BSR are similar to those formed in the FBSR.

Figure 11-1 Schematic of Bench Scale Steam Reformer

The BSR system used a mass spectrometer and personal computer for real time off-gas analysis and process control. The process parameters measured were: slurry feed rate, DMR outer pressure, DMR inner pressure, DMR bed temperature, DMR control temperature, DMR H₂, DMR O₂, DMR N₂, DMR CO₂, DMR argon, filter pressure inlet, filter pressure outlet, and chiller bath temperature. The process parameters controlled were: slurry feed rate, DMR control temperature, DMR outer pressure, and the DMR air flow-rate coupled to the N₂ and Ar flowrates. [42]

The WTP-SW campaigns were performed at three different times sufficiently spaced apart such that it was possible to improve the technique used to control the operation of the BSR, particularly the control of the REDOX level of the granular product. Campaigns were performed in the fall of 2009 using non-radioactive simulant and relatively high coal levels. Non-radioactive simulant campaigns were again

performed in August of 2010 at reduced coal levels to target lower residual coal levels in the BSR granular product. Two radioactive simulant BSR runs were then performed in September of 2010, shortly after the August 2010 runs. All of the 2009 and 2010 BSR campaigns used measured H₂ gas concentrations as the critical process control. A final set of non-radioactive simulant BSR runs were performed in the spring of 2011 that used an improved REDOX control strategy. This technique controlled the air flow and the cumulative value of CO₂ per mL of simulant feed to the DMR and operated the DMR in post feed operation until a predetermined endpoint was achieved. This ensured the product did not have excessive unreacted coal in it. The purpose of the latter 2011 BSR runs was to produce more granular product for the monolith tasks (non-radioactive BSR granular product from the previous fall 2009 and fall 2010 tests had been consumed in the failed monolith formulation attempts). Another goal of these latter spring 2011 BSR runs was to investigate further the mass balance of the BSR runs under the improved REDOX control operational strategy.

Table 11-1 shows the parameters used in the BSR as compared to typical FBSR parameters. The first two data columns in Table 13 simply show the parameters in different units. The feed rate of ~1 mL/min for the DMR was established based on the equipment's ability to pump the clay/coal/waste slurries and the DMR's ability to convert the waste slurries to mineral product without the presence of unreacted product. Coal was fed at a rate of 0.20 g/min, which is less than the 0.35 g/min scaled equivalent because the BSR does not use coal to auto-catalytically heat the DMR, and excess unreacted coal in the product is undesirable because it adds unnecessary volume to the product and causes REDOX measurement problems. Total gas flow was as high as reasonable, but limited based on observed solids carry over. Using nitrogen from a cylinder, the total gas flow was controlled to allow for inert conditions (no air leakage with 100% N₂) all the way up to 100% air. The measured H₂ gas concentration was the critical control parameter for the 2008 HRI ESTD FBSR and initial 2009 and 2010 campaigns performed with the SRNL BSR. The H₂ concentration was maintained at the nominal range of 1 to 3% (dry basis) by the amount of air leakage allowed into the BSR system. The DMR temperatures were the same as in the ESTD FBSR. The BSR ran at a slightly negative pressure; whereas, the ESTD FBSR ran at a slightly positive pressure.

Table 11-1 Relative Scaling of Process Operating Parameters, FBSR vs BSR

Parameter	FBSR	FBSR	Scaled BSR	Actual BSR
Feed Rate	0.2 gpm	757 mL/min	1 mL/min	1 mL/min
Coal Rate	35 lbs/hr	265 g/min	0.35 g/min	0.2 g/min
Gas Rate	101.9 scfm	2,885 SLM	3.8 SLM	0.7 SLM
Steam Rate	--	--	--	36 mL/hr
H ₂ Conc.	1% - 2%	--	--	1% - 3%
DMR Temp.	700 °C	--	--	720 °C
Pressure	+2 to +3 psig	--	--	-3 in wc

The DMR had two thermocouples for measuring the reaction zone temperature. The placement of these thermocouples changed and the choice of the controlling thermocouple changed over the course of the runs performed. Originally, the controlling thermocouple was 1 inch into the beads, and the upper thermocouple was positioned 4 inches above the beads. This configuration was uncontrollable due to the

water and steam from the slurry making contact with the controlling thermocouple. Later, the controlling thermocouple was positioned 2-½ inches above the beads, and the lower thermocouple was at the bead surface. This configuration worked best.

11.3 Monolith Fabrication

Monolith formation for the granular products produced from the BSR was initially started using the GEO-7 fly ash geopolymer formulation described in Section 10. That work optimized monolith formation based on LAW FBSR products (not WTP-SW FBSR products). However, in that work, several different monolith sizes were also fabricated with the WTP-SW ESTD FBSR granular products. These WTP-SW GEO-7 monoliths gave satisfactory PCT durability, TCLP and compressive strength results, so this GEO-7 formulation was specified as the monolith recipe to use in this Module A BSR work. Initial attempts to monolith the fall 2009 granular product using the GEO-7 formulation with 65% dry basis waste loading resulted in 1-inch diameter x 2-inch cylinder monoliths made using properly sized plastic syringe tube molds with compressive strengths of only 53 to 132 psi, which did not pass the 500 psi compressive strength criterion. This result was likely due to extra water that had to be added to get the monoliths to form in the curing molds.

After these initial unsuccessful monolith attempts, follow-on scope testing using some granular product from earlier BSR runs indicated that longer stirring times were needed to make the GEO-7 formulation using the granular product. These latter tests produced monoliths with compressive strengths above 500 psi (590 to 1570 psi). It should be noted that the crystalline phases produced in the monolith formation were similar to the starting crystalline phases of the initial BSR granular products. However, follow-on monolith activities in the fall of 2010 using BSR WTP SW granular products again indicated that even with prolonged stirring/mixing, the mixture did not form a monolithic form using the prescribed water amounts for the GEO-7 formulation.

A detailed investigation was performed [43], and the technical team determined that formulations should be made with the reactive clay rather than fly ash. Two reasons for preferring kaolin over fly ash are: (1) the unreactive nature of some of the components found in fly ash, e.g. the minerals mullite and quartz, and (2) the variable nature of fly ash compositions from various coal production facilities. Accordingly, the technical team decided to switch geopolymer binder components from the fly ash to the heat-treated clay and to use less sodium hydroxide solution to attain an acceptable binder composition.

After successful monolith fabrication with the simulant WTP SW granular product using the clay geopolymer at 42 wt% dry basis waste loading, several scoping runs were performed in preparation for forming the radioactive WTP SW monolith with granular product using remote handling and mixing.

Triplicate BSR WTP SW 1-inch diameter x 2-inch monolith cylinders made with the clay formulation and the WTP SW granular product from spring 2011 were prepared, and one was compression tested. The crushed monolith was then used for all subsequent testing including chemical composition, PCT and TCLP. A single 1-inch diameter x 2-inch cylinder was made with the radioactive BSR WTP SW granular product along with a smaller 0.5-inch diameter x 1-inch 'button.' The radioactive 1-inch diameter x 2-inch monolith was compression tested, and the crushed monolith was then used for subsequent testing including chemical composition, PCT and TCLP. The radioactive button was used for monolith accelerated leach testing (ASTM C1308).

11.4 Mass Balance Results

The total mass balance recoveries of the key species were calculated for three of the WTP SW campaigns. No mass balance was performed on the original fall 2009 WTP SW BSR processing campaign. Percent recovery data for measured and calculated constituents are presented in Table 11-2.[42]

The non-radioactive ¹³³Cesium recovery was 99% for the original fall 2010 simulant campaign and 77% for the spring 2011 simulant campaign. The lower recovery in the spring 2011 simulant campaign compared to the fall 2010 was due to the low concentration of ¹³³Cs in the feed for the spring 2011 run (about 200,000 µg/L) versus that in the fall 2010 campaign (about 2,000,000 µg/L) . For any mass balance, it is more difficult to track a lower amount through a system, and any errors are amplified which impacts the overall recovery. It is expected that had the spring 2011 campaign ¹³³Cs feed levels been similar to the fall 2010 levels that the recovery would have been similar.

The mass balances for Cr, Cl, and Re are also impacted by taking the difference (feed input vs. feed output) of two very small numbers.

Table 11-2 Mass Balance Recoveries for BSR WTP SW Tests

Element	WTP SW Simulant (Fall 2010) (%)	WTP SW Simulant (Spring 2011) (%)	WTP SW Radioactive Campaign (%)	Radioactive Product Retention (Normalized %)
¹³³ Cs	99	77	Not Added	Not Added
¹³⁷ Cs	Not Added	Not Added	94	99.3
¹²⁷ I	91	106	151	94
¹²⁵ I	Not Added	Not Added	93	98.2
¹²⁹ I	Not Added	Not Added	98	98
⁹⁹ Tc	Not Added	Not Added	109	99.8
Re	86	95	102	99.45
Al	101	107	100	99.9
Cr	137	125	181	99.9
Na	107	111	151 [#]	99.7
Si	114	117	110	99.9
Cl ⁻	78	99.5	129	100
SO ₄ ⁻²	Indeterminate due to low concentration in feed and large contribution from coal.			

High recovery due to as-batched feed value versus measured product value and small amount added in feed

The radiometric analysis for I was done on each stream by Beta counting which did not involve any sample preparation like KOH digestion followed by the specific analytical method like ICP-MS. Therefore, the radiometric concentration analyses have less error than the simulant analytical methods that involve a dissolution preparation.

The SO_4^{-2} recovery was indeterminate for all WTP SW runs due to the relatively low amount of sulfate in the feed versus the coal-derived sulfur species. The SO_4^{-2} recovery is very dependent on the SO_4^{-2} coming in via the coal in the feed mix and how much of the coal in the feed is ashed.

All total recoveries for the radionuclides in the WTP SW radioactive campaign were in the range of 93% to 109%. The body of mass balance data suggests that all analytes remained predominately with the granular product in processing the feed slurries in the BSR. This observation is supported by the data in the last column of Table 11-2 which indicate, after the radioactive mass balance data are normalized, almost total retention of the analytes in the solid product.

11.5 Granular Product and Monolith Characteristics

Table 11-3 summarizes the mineralogy as determined by XRD for all the WTP SW BSR campaigns and the monoliths made from the non-radioactive and radioactive granular products. The mineralogy of the WTP SW products is about the same for all three different BSR campaigns. Sodalite (from the halides) is a major phase, and the sulfate sodalite, known as nosean, is a minor phase since there is less sulfate than halides in this waste simulant. Nepheline is a major phase and low-carnegieite is a minor phase in the fall 2009 WTP SW BSR product, and the spring 2011 WTP SW BSR product. Low-carnegieite is not observed in BSR product samples from the fall 2010 simulant campaign, the radioactive campaign or in the radioactive monolith.

Two different BSR simulant products were analyzed. Simulant 1 is a combination of the three separate runs performed on 8/26/09, 9/2/09, 9/8/09, and Simulant 2 is a combination of the three separate runs performed on 9/10/09, 9/15/09, 9/17/09. Chemical composition measurements on the fall 2009 Simulant A Batch 1 and Simulant A Batch 2 BSR granular products indicated excellent recovery of all species as the sum of oxides was very close to 100%. Chemical composition measurements on the fall 2010 radioactive granular product indicated excellent recovery of all species, as the sum of oxides was also very close to 100%.

Chemical composition of the simulant and radioactive monoliths showed similar behavior as the sum of analyzed oxides was 9 to 12 wt% low. These data suggest that the LOI measurements were biased low, i.e., not all the moisture and/or residual carbon was removed from heat treatment of the crushed monolith pieces during successive drying from 105 °C up through 525 °C. Consequently, the 100% normalized oxide chemical compositions were used in normalizing both the PCT and the ASTM C1308 durability data discussed below.

Table 11-3 Mineral Phases Analyzed in FBSR Products

Sample	Low-Carnegieite Nominally NaAlSiO_4	Nepheline Nominally NaAlSiO_4 or $\text{K}_{0.25}\text{Na}_{0.75}\text{AlSi}$	Nosean $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_2_4](\text{Na}_2\text{SO}_4)$ and/or Sodalite $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_2_2]$	Other Minor Components
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		O ₄	₄](2NaX where X=Cl,F,I)	
Fall 2009 (REDOX 0.87 - 0.98)	Y	X	X	SiO ₂ and TiO ₂
Fall 2010 (REDOX 0.65 - 0.78)	Not Observed	X	X	SiO ₂ and TiO ₂
Spring 2011 (REDOX 0.15 - 0.23)	Y	X	X	SiO ₂ and TiO ₂
Radioactive (REDOX 0.25 - 0.26)	Not Observed	X	X	SiO ₂
Simulant Monolith	Y	Y	X	SiO ₂ and TiO ₂
Radioactive Monolith	Not Observed	X	X	SiO ₂ and TiO ₂

X = Major Constituent; Y = Minor Constituent

Table 11-4 shows BET surface area measurements for granular products and monoliths and compressive strength measurements for the monoliths.

Table 11-4 Data Measured for Granular Products and Monoliths

Monolith	Compressive Strength (psi)	BET Surface Area w/o Coal (m ² /g)
Sim BSR Granular Product 1	NA	3.87
Sim BSR Granular Product 2	NA	3.87
Rad BSR Granular Product	NA	1.1*
Sim Monolith	4,350	21.1
Rad Monolith	4,161	12.6

- * A value of 3.87 m²/g was used to normalize the PCT release.

- In the September 2009 tests, the BET surface area was determined on the PCT 100/200 mesh powders without pre-roasting of the samples to remove any residual carbon. The presence of residual coal could explain the relatively high measured BET surface areas for these materials in the range of 78 to 123 m²/g. Accordingly, an average BSR granular product roasted BET surface area of 3.87 m²/g was used. The observed 1.1 m²/g BET surface area value for the roasted radioactive granular product is suspect low, perhaps from the difficulty of remote preparation and handling leading to the powder preparation for the BET surface area measurement. Accordingly, as was done with the simulant PCT surface area, an average of BSR granular product roasted BET surface area of 3.87 m²/g was used.

11.6 Durability Results

Due to the limited quantity of available BSR material, only 10 gram duplicate samples of the simulant granular product and a ~3 gram single sample of the radioactive granular product were sent to GEL Laboratories, LLC of Charleston, SC, an EPA-certified laboratory, for TCLP testing. The metals Sb, Ba, Cd, Se and Tl were not requested for testing as they were not added into the BSR simulant feed. The Zn analysis was inadvertently not requested. All other metals shown for the simulant granular product passed the UTS limits. The radioactive granular product passed TCLP for all elements except for Cr and Zn.

The radioactive granular product was produced at a much lower REDOX of ~ 0.26 (more oxidized) versus the earlier simulant granular product from the fall 2009 campaign that had a REDOX in the range of 0.87 to 0.98 (more reduced). The behavior of Cr on TCLP testing is known to be REDOX sensitive, with Cr in a higher oxidation state, e.g., +6, being more leachable. The use of a mixed oxide iron compound catalyst as an insoluble spinel host for Cr was not used as it was for the ESTD testing. A potential explanation for the failure on Zn could be the excessive remote handling of the granular product in the SRNL shielded cell using brass (Cu/Zn containing) sieves. For instance, nodules of Cu and Zn from the brass sieves have been observed previously in unpublished SEM scans of glass powders prepared for PCT.

Due to the limited quantity of the available BSR material, a single 25 gram sample of the simulant monolith and a single ~6 gram sample of the radioactive monolith were TCLP tested. The simulant and radioactive monoliths passed TCLP for all elements analyzed.

Triplicate PCT testing was performed on the WTP SW BSR granular products and monoliths formed from the granular products. PCT test results were adjusted for elemental composition (i.e. anhydrous, coal free), and then adjusted for the BET surface area to obtain normalized release values in units of g/m². Figure 11-2 shows the results. In general, these data indicate that the monolith normalized releases are comparable to the granular product normalized releases, specifically for the non-monolith binder elements such as Cs, I, Re and S. This suggests that the monolith process is not detrimental to the overall waste form performance. Figure 11-2 shows that the BSR products and monoliths gave similar overall average normalized release of most elements when compared to Figures 10-13 and 10-15. The granular FBSR waste form that is produced is as durable as glass based on comparison of normalized releases for glass and FBSR granular product using BET measured surface areas.

The radioactive 0.5-inch diameter x 1-inch cylinder monolith was subjected to ASTM C1308 accelerated leach testing at ambient room temperature for the specified intervals. Leachate data were used to calculate the constituent diffusivities. The degree of leaching in these tests is reflected in the diffusivity calculations – the lower the diffusivity, the lower the cumulative fraction leached. The Leach Index (LI) is a negative log of the diffusivity; therefore, the higher LI values indicate a lower leaching (more durable) monolith. Figure 11-3 shows the calculated leach indexes for the measured constituents. This figure shows that the

Leach Indexes for Na, Re/⁹⁹Tc and I are above 6, 9 and 11, respectively, after at least the 2-day leaching intervals. These are minimum LI target levels associated with the IDF at Hanford, which indicates that this matrix should be acceptable for disposal at the IDF.

Figure 11-2 PCT Results for BSR Granular Products and Monoliths

Figure 11-3 Calculated Leach Indices for Radioactive Monolith

12. TEST RESULTS COMPARED TO TEST OBJECTIVES

Briefly stated, the general objectives of the ART testing program were to:

- Establish target steady-state system operating conditions for the processing of LAW and WTP SW via an FBSR process
- Confirm extended, i.e., several days, FBSR system operability with respect to process chemistry, material flows, mass and energy balance, and particle size control
- Establish system operating parameters for the ESTD, BSR, and a full-scale facility
- Gather off-gas emissions data
- Generate granular, solid products that incorporate the alkali metals, halides, sulfur, radionuclide surrogates, and hazardous metals into alkali aluminosilicate mineral forms using both the ESTD and the BSR
- Demonstrate, with the BSR equipment, the production of radioactive granular product and a monolith final waste form comparable to that generated via non-radioactive simulant in prior ESTD testing.
- Generate acceptable monolith final waste forms from FBSR and BSR granular products
- Determine leach resistance and durability of granular and monolith product generated with the ESTD and BSR and the fate of radionuclide surrogates and hazardous metal components.

The test conditions as specified in the ESTD and BSR test plans were completed. Details concerning the overall objectives, along with quantifiable criteria where appropriate, and an evaluation of the success in meeting the criteria are provided in Table 12-1.

Table 12-1 ART Testing Program Objectives, Measurable Parameters, and Performance Summary

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
Verify DMR process chemistry and product quality consistent with that observed during previous mineralizing pilot plant and ESTD operations		
1. Verify initial charcoal/carbon selections for DMR and CRR (steady autothermal process operation is maintained).	<ul style="list-style-type: none"> Monitoring of charcoal/carbon types and addition rates CPMS process gas monitoring at high-temperature filter outlet CEMS off-gas monitoring at stack 	<p>Objective was achieved</p> <p>Coal was successfully used in the DMR, based on reactivity and H₂ generation. Propylene glycol was used successfully in CRR for bed temperature control. Carbon was successfully used to supplement the propylene glycol. See Sections 7 and 9.</p>
2. Verify adequacy of DMR startup bed media (bed does not agglomerate and sustainable DMR operation is maintained).	<ul style="list-style-type: none"> Monitoring of thermocouples in DMR Monitoring of DMR bed particle appearance and size distribution 	<p>Objective was achieved</p> <p>Alumina was selected as the starting bed for the test program. DMR bed TCs showed acceptable spread and bed PSD was under control using alumina bed. See Section 7.</p>
3. Demonstrate controlled, steady, carbon and O ₂ addition to DMR to maintain stable autothermal process operation within a $\pm 20^{\circ}\text{C}$ operating range.	<ul style="list-style-type: none"> Flow controllers for gas and oxygen injection Monitoring of thermocouples in DMR 	<p>Objective was achieved</p> <p>Both carbon and O₂ addition rates were automatically controlled and provided acceptable control of DMR bed temperatures. The temperature spread in the DMR was 15°C or less. See Section 7.</p>
4. Determine sustainable simulant feed rate to the DMR in gallons per minute and accompanying nozzle air ratios (NAR).	<ul style="list-style-type: none"> Monitoring of waste simulant feed rate and NAR 	<p>Objective was achieved</p> <p>The initial feed rate of 0.20gpm was selected to give the same mass flow rate of simulated liquid feed that was used during previous testing. Feed rates >0.20gpm were successfully demonstrated during the production tests. Atomizing air flow rates were successful in maintaining the DMR PSD. See Section 7.</p>
5. Demonstrate that BSR products (granular products and monoliths) were similar in composition and durability testing when compared to ESTD granular products and monoliths formed from that material.	<ul style="list-style-type: none"> Chemical composition analysis and XRD patterns. 	<p>Objective was achieved</p> <p>Similar aluminosilicate minerals were observed by XRD. See Tables 10-3 and 11-3.</p>
Gather process off-gas emissions data		

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
<p>6. Gather off-gas data from the process stack using an on-line Continuous Emissions Monitoring System (CEMS) and grab samples in accordance with EPA protocols. Species to be analyzed and desirable performance levels:</p> <ul style="list-style-type: none"> • HCl + Cl₂ <21ppm (by volume, HCl equivalents, dry basis, corrected to 7% O₂) • Particulate matter <3.4 mg/dscm, corrected to 7% O₂ • Cd + Pb <10 micrograms/dscm, corrected to 7% O₂ • As+Cr <23 micrograms/dscm, corrected to 7% O₂ • NO_x <1,500ppm (by volume, dry basis, corrected to 7% O₂) • SO₂ <100ppm (by volume, dry basis, corrected to 7% O₂) • CO <100ppm over an hour rolling average (by volume, dry basis, corrected to 7% O₂) • Total Hydrocarbons (THC) <10ppm (by volume, dry basis, corrected to 7% O₂) • Organic Destruction Removal Efficiency (DRE) >99.99% for the POHC • Dioxins/furans <0.11 ng TEQ/dscm, corrected to 7% O₂, where "TEQ" is the toxicity equivalent quotient that relates the total toxicity of all the dioxin/furan constituents to that for 2,3,7,8-TCDD. 	<ul style="list-style-type: none"> • Measurement of emissions in stack gas via EPA designated methods using both CEMS and/or grab samples 	<p><i>All objectives achieved with one exception</i></p> <p>All the indicated species were analyzed by CEMS and/or manual samples. The desired performance levels were met except for:</p> <p>Low-Volatility metals (As and Cr) averaged 4.32 µg/dscm for the LAW tests (ART-P1A and P1B). This equals 19% of the MACT standard. Low-Volatility metals (As and Cr) averaged 24 µg/dscm for the WTP SW test (ART-P2). This is almost at the MACT standard level of 23 µg/dscm. This performance was below the objective due to a failed section of the tubesheet gasket seal in the off-gas filter downstream of the CRR that allowed bypass of a small quantity of solids directly to the stack. See Section 7.3 and Section 8.3.7.</p>
<p><i>Establish system operating parameters for the pilot scale and a full-scale facility</i></p>		
<p>7. Determine acceptable sustainable liquid feed rate as a function of DMR cross-sectional area (DMR</p>	<ul style="list-style-type: none"> • DMR global temperature and axial temperature spread 	<p><i>Objective was achieved</i></p> <p>A simulated liquid waste feed rates of 0.2gpm was used during the production</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
operating temperature and bed fluidization are maintained).	<ul style="list-style-type: none"> DMR liquid feed rate Monitoring of general process operating parameters, observed presence or absence of nozzle accretions, and bed particle parameter analyses 	tests. The bed temperatures showed that the bed was well fluidized. There were no agglomerations in the bed. The waste feed nozzle experienced normal, acceptable, small accretion formations. See Section 7.
8. Determine acceptable range of fluidizing velocities for DMR.	<ul style="list-style-type: none"> DMR particle size distribution and bed product general appearance as a function of fluidizing velocities Monitoring of general process operating parameters, observed presence or absence of nozzle accretions, and bed particle parameter analyses 	<p>Objective was achieved</p> <p>The SSV's during the production tests were acceptable. The DMR bed average particle size was well controlled with these SSVs. There were no agglomerate formation in the DMR bed and the nozzle accretion size and quantity were as expected. See Section 7.</p>
9. Verify fluidizing gas distributor designs and configurations (DMR bed is well fluidized as indicated by bed temperatures and product inspection and analysis).	<ul style="list-style-type: none"> DMR global temperature and axial temperature spread DMR particle size distribution and bed product general appearance as a function of fluidizing velocities Post-test examination of distributors for plugging and erosion, and visual examination of bed solids 	<p>Objective was achieved</p> <p>The same distributors that have been used successfully for previous tests were used for this demonstration. The DMR bed temperature was well controlled and the axial temperature spread was small. The DMR average particle size was well controlled. Visual observations indicated that the FG distributors in the DMR had experienced minimal erosion. See Section 7.</p>
10. Determine if seed particle addition or product recycle are needed to maintain DMR bed particle size control.	<ul style="list-style-type: none"> DMR particle size distribution 	<p>Objective was achieved</p> <p>Seed particle addition was not required to control the bed particle size during the production tests. The DMR average bed particle size was well controlled without seed particle addition. See Section 7.</p>
<i>Confirm tandem operation of the DMR and CRR and that the CRR effectively destroys any residual organic gases and fully oxidizes carbon, organics, and carbon monoxide generated in the DMR</i>		
11. Perform continuous operation of the integrated dual fluidized bed steam reforming process during both the parametric scoping tests and extended duration production run tests	<ul style="list-style-type: none"> Monitoring and recording of process parameters both manually and utilizing the Data Acquisition and Control System (DACS) 	<p>Objective was achieved</p> <p>The DMR and CRR operated in tandem during the testing period. No modifications were required to achieve satisfactory operations.</p>
12. Gather organics, carbon monoxide, and oxygen off-gas data from the process stack using an on-	<ul style="list-style-type: none"> Measurement of emissions in stack gas via EPA 	<p>Objective was achieved</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
line CEMS. Gather organics and particulate off-gas data with grab samples	designated methods using both CEMS and grab samples	See item 5 above.
<i>Demonstrate long-term steady-state operation of the integrated fluidized bed steam reforming process</i>		
13. Achieve >100 hrs continuous operation (DMR>700°C, off-gas systems on line, feed rate up to 0.20gpm 90% of elapsed process operating time)	<ul style="list-style-type: none"> System flow meters, temperature indicators and pressure transducers 	<p>Objective was achieved</p> <p>A total of 101.5 hours of continuous operation “feed-on” was achieved for Test P1 (LAW) and 102 hours for Test P2 (WTP SW). The DMR operated at 725°C during Test P1 and at two temperatures, 680°C and 700°C, for Test P2. On line (feed-on) efficiency was 98.4%. See Section 7.</p>
14. Confirm basic process chemistry and material flows as established in previous pilot-scale and ESTD tests	<ul style="list-style-type: none"> Sampling and analysis of process solids and gaseous product streams Process material balances 	<p>Objective was achieved</p> <p>Analysis of solid products and gaseous streams from the mineralizing test confirmed that the process chemistry is similar previous FBSR tests and that the mineralizing test solids pass PCT for product durability. See Sections 9 and 10.</p>
15. Achieve uniform temperature distribution in DMR bed with no greater than ±15°C axial temperature variation	<ul style="list-style-type: none"> Monitoring of DMR bed temperatures 	<p>Objective was achieved</p> <p>DMR axial bed temperature spreads were well within the required ±15°C during the testing period. See Section 7.</p>
16. Achieve sustainable steady-state bed particle size distributions for the DMR (<5% bed agglomeration)	<ul style="list-style-type: none"> Analysis of bed and fines samples for particle size distribution, bulk density, etc. 	<p>Objective was achieved</p> <p>The average particle size during the productions tests was well controlled. The mass of oversize bed solids was well below the 5% requirement. See Section 7.</p>
<i>Demonstrate, on a laboratory scale and then on a larger scale, the production of final monolith products from the mineralized ESTD LAW and WTP SW products that meet all IDF disposal requirements</i>		
17. Determine mineralized product composition and performance by analysis of the product solids.	<ul style="list-style-type: none"> Chemical analysis of product samples XRD, SEM, or other product analyses, as appropriate 	<p>Objective was achieved</p> <p>The mineralized product composition is given in Section 9. Analysis of the DMR product solids shows that they have normalized release rates that are less for Na than the LRM reference glass standard, as measured by PCT. See Sections 10 and 11.</p>
18. Prepare monolith product samples using various	<ul style="list-style-type: none"> Number of monoliths prepared with various binders 	<p>Objective was achieved</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
binding agents and waste loading levels on a 100-cc, 0.18 -gallon, and 1.47-gallon scale	at different waste loading levels	Five binder types were used to prepare seventeen 2-inch cube monoliths. Three binder types were selected to prepare eight 0.18-gallon monoliths and eight 1.47 gallon monoliths. See Section 10.2.
19. Analyze monolith properties with respect to chemical characteristics and product durability	<ul style="list-style-type: none"> Chemical analysis of product samples TCLP, PCT, and compressibility analyses 	<p>Objective was achieved</p> <p>All monoliths were analyzed for chemical composition and subjected to TCLP, PCT, and compressibility analyses. See Section 10.2 and Section 11.</p>
20. Determine leachability characteristics of Cs, Re, and I	<ul style="list-style-type: none"> TCLP and PCT analyses 	<p>Objective was achieved</p> <p>Leachability characteristics of Cs, Re, and I from granular FBSR products and all monoliths were determined. Data is presented in Section 10.2 and Section 11.</p>
<i>Generate an adequate quantity of monolith product for characterization, durability testing, and other analyses, as required</i>		
21. Collect ESTD product from the LAW and WTP SW tests	<ul style="list-style-type: none"> Collect, document, archive, and safeguard ESTD product samples 	<p>Objective was achieved</p> <p>ESTD solid products have been collected, documented, and archived at appropriate Hazen facilities.</p>
22. Prepare monolith samples for testing as described above	<ul style="list-style-type: none"> Prepare, document, archive, and safeguard monolith samples 	<p>Objective was achieved</p> <p>Monoliths were prepared, subjected to testing and analyses, and documented as appropriate. See Section 10.2 and Section 11.</p>
23. Archive ESTD and monolith product for potential future testing	<ul style="list-style-type: none"> Prepare, document, archive, and safeguard monolith samples 	<p>Objective was achieved</p> <p>Granular FBSR product samples have been archived and documented at Hazen Research, Inc., monolith samples have been archived and documented at SRNL.</p>
<i>Maximize waste volume reduction</i>		
24. Minimize carbon content of DMR products	<ul style="list-style-type: none"> Carbon analysis of DMR and OGF products 	<p>Objective was achieved</p> <p>The average carbon content of the unscreened solids removed from the PR was 7 wt%, while the average carbon content in unscreened solid content from the DMR was 20 wt%. The average carbon content of the solids removed from the HTF was 7 wt%. The OGF carbon content ranged from 0.1 to 0.5%. See Section</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
		9.2.
25. Measure product-to-fines ratio for the DMR and CRR products	<ul style="list-style-type: none"> Measure the mass (weight) of PR, HTF, and OGF Products 	<p>Objective was achieved</p> <p>The measured product to fines ratio ranged from 0.2 to 0.35 dependent on operating conditions. The value tended to be higher when processing WTP SW simulant. See Section 7.</p>
26. Maximize waste loading in monolith products	<ul style="list-style-type: none"> Waste loadings on a dry basis of monolith product forms 	<p>Objective was achieved</p> <p>Monolith waste loadings were maximized to achieve monolith compressive strength criteria. Data is presented in Section 10.2.</p>
<i>Confirm zero liquid secondary waste generated from process operations</i>		
27. Visual observation of DMR, PR, CRR, and OGF products	<ul style="list-style-type: none"> Visual examination of ESTD solids products collected 	<p>Objective was achieved</p> <p>No free water was ever observed when collecting ESTD solid products.</p>
28. Moisture content analyses of DMR, PR, CRR, and OGF products	<ul style="list-style-type: none"> Chemical analyses of product streams for moisture content 	<p>Objective was achieved</p> <p>LOI analyses were performed on the ESTD solid products. The loss observed was consistent with carbon and volatile content. Free water was not observed. See Sections 7 & 9.</p>
29. Visual observation of OGC bottom drain	<ul style="list-style-type: none"> Visual examination of area near bottom of OGC 	<p>Objective was achieved</p> <p>No free water was ever observed during production operations around the OGC. See Section 7.</p>
<i>Determine degree of retention of inorganic feed constituents in the mineralized product and demonstrate acceptable material balance closure for feed constituents</i>		
30. Measure elemental concentrations in the feed and product streams	<ul style="list-style-type: none"> Chemical analysis of feed streams, product solids, and off-gas stream 	<p>Objective was achieved</p> <p>All simulant feed slurries, selected solid product samples, and manual off-gas samples have been analyzed for chemical composition. See Sections 8, 9, and Appendix D.</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
31. Achieve material balance closure of $\pm 10\%$ for major constituents	<ul style="list-style-type: none"> Calculate overall mass and elemental balance based on target values, measured inputs, and measured outputs 	<p>Objective was achieved</p> <p>An overall material balance closure of less than 1% was achieved. See Section 9.</p>
32. Report any elemental mass balance closures that exceed $\pm 10\%$ and estimate the fate of any major constituents for which a mass balance closure of $\pm 10\%$ is not met	<ul style="list-style-type: none"> Calculate overall mass and elemental balance based on target values, measured inputs, and measured outputs 	<p>Objective was achieved</p> <p>Two major components (Si, and Ti) exceeded the mass balance closure objective of $\pm 10\%$. See Section 9.3 and Table 9-6.</p>
33. Achieve material balance closure of $\pm 30\%$ for minor constituents (e.g., Re, Al, Mg, Cs, K, P, Cl, F, I, SO_4^{2-} , NO_2^- , NO_3^-)	<ul style="list-style-type: none"> Calculate overall mass and elemental balance based on target values, measured inputs, and measured outputs 	<p>Objective was achieved with exceptions</p> <p>All components were with the $\pm 30\%$ objective with some component exceptions for the LAW and WTP SW tests. The component exceptions varied between the two tests. See Section 9.3 and Table 9-6.</p>
34. Determine retention of Cs, Re (Tc surrogate), and I in the product	<ul style="list-style-type: none"> Chemical analysis of feed streams, product solids, and off-gas stream 	<p>Objective was achieved</p> <p>System removal efficiencies for Cs and Re exceeded 99.99% indicating those constituents are nearly totally contained in the solid product. The overall system removal efficiency for iodine from the LAW simulant was 94.4%. Although the system removal efficiency for the WTP SW simulant was lower at 19.1%, the stack concentration for iodine during WTP SW operations was lower than that during LAW operations (1.4ppm vs. 1.85ppm)</p>
35. Report any elemental mass balance closures that exceed $\pm 30\%$ and estimate the fate of any minor constituents for which a mass balance closure of $\pm 30\%$ is not met	<ul style="list-style-type: none"> Calculate overall mass and elemental balance based on target values, measured inputs, and measured outputs 	<p>Objective was achieved</p> <p>See Item 32.</p> <p>The discussion in Section 9.3 details the variability observed in the component mass balance closures.</p>

Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods	Performance Achieved Against Objectives
<i>Process simulant solution with at least two mineralizing clay ratios for LAW simulant and one clay ratio for WTP SW simulant</i>		
36. Process operation continues without plugging or process upset at varying mineralizing clay addition ratios	<p>Feed system pressure measurements and feed flow rates</p> <p>General process operation, including bed temperatures and differential pressures</p> <ul style="list-style-type: none"> Leach resistance of product solids and monolith product forms (TCLP, and PCT analyses) 	<p>Objective was achieved</p> <p>Production tests included three mineralizing clay ratios, two for the LAW simulant and one for the WTP SW simulant. Operations were smooth and the feed nozzles performed well, producing an atomized feed that was able to give reasonable particle size control in the DMR. Feed nozzle restrictions were minimal during the tests. Only minor nozzle accretions were observed in DMR bed products. Fluidized bed operation was acceptable as observed by narrow bed temperature spans and acceptable particle size control. No bed agglomerations were observed. See Section 7.</p>
<i>Monitor metal corrosion in process systems</i>		
37. Coupons of various metal alloys inserted into key pieces of process equipment	<ul style="list-style-type: none"> No post-test metallurgical analyses will be performed, but corrosion coupons will be archived for future evaluation 	<p>Objective was achieved</p> <p>Corrosion coupons were inserted into various key pieces of ESTD process equipment. See Section 3.6.</p>
38. Alloy test coupons will be archived for future analysis, if desired	<ul style="list-style-type: none"> No post-test metallurgical analyses will be performed, but corrosion coupons will be archived for future evaluation 	<p>Objective was achieved</p> <p>Corrosion coupons were removed from their respective process equipment locations. They have been appropriately documented and archived at the Hazen facility for future analyses.</p>

13. SUMMARY AND CONCLUSIONS

13.1 ESTD Testing

The Hanford LAW and the WTP SW waste simulant testing program was performed using the ESTD pilot plant at the Hazen Research facility in Golden, Colorado, during the period April 15, 2008 through May 6, 2008. The ESTD is a fully integrated engineering scale process system that utilizes the THOR[®] FBSR technology. The demonstration successfully produced leach-resistant, mineralized solid products, environmentally compliant gaseous effluents from the LAW and WTP SW simulants, and monolith final waste forms compliant with compressive strength and durability (PCT). The testing program also generated data that could be used to support full-scale process system design and operation of a facility to treat expected LAW and WTP SW waste streams at the Hanford Site.

Prior to operations, the ESTD was functionally tested with regard to components and systems. Scoping tests were performed to determine appropriate process additives and operating parameters. Production tests were performed at a variety of process conditions (e.g., reformer temperatures, waste/clay addition ratios, and liquid simulant feed rates), during which numerous process gas, off-gas, and product solids samples were obtained to confirm compliance with HWC MACT and other emissions regulations and general suitability of the product materials for preparing a final waste form for disposal at the Hanford Integrated Disposal Facility. Process samples also supported mass balance determination and closure.

The operational data were collated, evaluated, and integrated with the analytical data. The documented performance and analytical data verify that the testing activities were successful and met the test objectives. Specific achievements of the mineralizing test program include:

- Approximately 372.4 hours of ESTD operation with simulant feed were logged during the scoping and production runs, processing ~4,492 gallons (~56,100 pounds) of liquid simulant into ~24,838 pounds of solid product.
- The LAW and WTP SW production tests were operated for a total of 203.5 hours of “feed on” time with a “feed-on” availability of 98.4%, demonstrating sustained and successful steady process operation.
- Four different clay addition ratio mixtures with liquid simulant were demonstrated, producing DMR process chemistry and product quality consistent with that observed during previous mineralizing pilot plant and ESTD operations.
- The operational parameters of throughput, carbon usage optimization, feed nozzle and fluidizing gas parameter optimization, energy conservation, and optimal use of process additives were demonstrated.
- The DMR production test average particle size was well controlled within desired values.
- The total mass balance closure for the LAW and WTP SW production tests was excellent, with a difference of less than 1% between feeds and discharges. The major gaseous components, including water, oxygen, nitrogen, and carbon dioxide, accounted for 94% of the total mass. All the major gaseous components showed good to excellent balance (0% to 3% difference).
- The component distribution and mass balance for the LAW and WTP SW production tests are shown in Tables 9-7 and 9-8, respectively. The average system removal efficiencies for cesium and rhenium were found to be greater than 99%, indicating that the THOR[®] mineralizing process retains these constituents of interest in the solid products, as desired.

- The overall system removal efficiency for iodine from the LAW simulant ranged from 89% to 94%, based on manual off-gas sampling. The system removal efficiency for the WTP SW simulant was lower at 19.1%. The difference in these system removal efficiencies for iodine can be partially attributed to the amounts of iodine added to the LAW simulant (0.13lb/hr) versus the amount iodine added to the WTP SW simulant (0.0090lb/hr), which affects the ability to detect iodine in the off-gas.
- The off-gas system operated well over the course of the test program. System removal efficiencies for hazardous metals were calculated using the stack gas emission rates for hazardous metals and input feed rates of those metals. Concentrations of semi-volatile metals (SVM) and low volatility metals (LVM) measured during the LAW production tests were within the HWC MACT standards. However, a tube sheet seal in the Off-Gas Filter (OGF) failed, confirmed during post-production run inspections, most likely during the initial WTP SW production tests. The failure likely allowed a small portion of non-filtered gas to be emitted to the stack. Off-gas sampling during the WTP SW production tests shows an increase in metals emission rates over that observed for LAW production tests. The LVM for the WTP SW test was equal to 24 $\mu\text{g/dscm}$, which is 1 $\mu\text{g/dscm}$ above the MACT standard of 23 $\mu\text{g/dscm}$, and was apparently caused by the tube sheet seal failure. It could reasonably be expected that LVMs resulting from the WTP SW stream, based on observed data from LAW production tests, would be well below the MACT standard with a fully functional OGF (See Table 8-15). HEPA filtration that would be present in a full-scale facility, but not installed in the ESTD, would ensure that MACT standards would be met in the event of equipment failure. A key component is compliance with HWC MACT standards without the need for a wet scrubber. No off-gas system scrubber was needed and no secondary process liquid waste streams were generated. The process demonstrated zero liquid release during operations. All water that entered the process was converted to benign water vapor that was monitored and discharged out the stack as a vapor.
- The HCl/Cl₂ concentration for the production tests averaged 8 ppmv (dry basis), or 37% of the HWC MACT standard of 21ppmv (dry basis). During the production runs, Cl from NaCl in the feed was captured in the solid products, with an average removal efficiency of over 92%. In addition, fluoride was captured with an average 78% efficiency.
- Stack gas SO₂ levels during the production tests ranged from 9 to 52 ppmv (dry basis), similar to levels observed in previous steam reforming tests, which was well below the desired performance level of 100 ppmv SO₂ on a dry basis. Therefore, no wet scrubber system is required for SO₂ removal.
- The system NO_x destruction from production test averages ranged from 91% to 94%. Test-average stack NO_x concentrations ranged from 572 to 726 ppmv (dry basis). The projected Hanford NO_x limits can be expected to be from 1000 to 2000 ppmv NO_x on a dry basis. Therefore, no off-gas NO_x destruction system and no wet scrubber system are required.
- The CO levels measured during production testing were essentially non-detectable (dry basis), well below the HWC MACT value of <100 ppmv (dry basis).
- The THC levels measured during production testing ranged from 0.0 to 0.4 ppmv (dry basis), well below the HWC MACT level of <10 ppmv (dry basis).
- The successful tandem operation of the DMR and CRR was demonstrated and the CRR effectively destroyed residual organic gases and fully oxidized carbon, organics, and carbon monoxide generated in the DMR. The Principal Organic Hazardous Constituent (POHC),

benzene, was destroyed in the process at high efficiencies. The benzene destruction efficiency averaged 99.99989% for all tests. For production tests P-1A and P-1B the benzene destruction and removal efficiencies (DRE) were 99.99968% and 99.99986% respectively, averaging out to 99.99977% for both tests. This DRE result is well above the HWC MACT requirement of 99.99% DRE.

- Granular product was produced for the production and testing of final monolith products from the mineralized ESTD LAW and WTP SW simulants.
- Evaluation of compressive strength and durability (PCT) data for the larger scale monoliths indicated that a geopolymer binder formulation, designated GEO-7, was the best overall performer when combined with ESTD LAW and WTP SW granular products.
- Analysis of ESTD granular product and GEO-7 monolith TCLP test data showed that the product materials passed for all hazardous constituents, with the exception of Sb, Cd, and Se. These constituents were added in higher concentrations to the simulants to determine their fate and performance in the process. An extrapolation of the TCLP results to the lower concentrations in which these elements would actually be present in the real LAW and WTP SW wastes showed that the granular solid and monolith products would pass the TCLP tests when formed with the actual wastes.
- The durability and leach performance of the ESTD granular products using the GEO-7 binder were found to be superior to the Low-Activity Reference Material (LRM) glass standard for sodium and silicon. Release rates for cesium and rhenium (used as a surrogate for radioactive ^{99}Tc) were much less ($\sim 0.04 \text{ g/m}^2$) than sodium for the LRM glass standard (0.27 g/m^2) when normalized with Brunauer-Emmett-Teller (BET) measured surface areas of the granular product and 2 orders of magnitude lower than the Hanford glass standard of 2 g/m^2 for Na.
- Compressive strengths of the GEO-7 monoliths formed from both LAW and WTP SW granular products at all scales averaged 1,960 psi, well above the Hanford disposal criteria of $>500 \text{ psi}$. (See report Section 10.2)
- All test objectives, as discussed in Section 11, were achieved successfully.
- Corrosion coupons were placed in strategic locations throughout the process system. These coupons were removed and archived for future metallurgical analysis.

13.2 BSR Testing

WTP SW simulant and radioactive testing was performed with the BSR at SRNL in the fall of 2009, and then was continued from the fall of 2010 through the fall of 2011. A key objective for the BSR activities was to demonstrate that both the simulant and radioactive WTP SW BSR products (granular products and monoliths) were similar in composition and durability testing when compared to ESTD granular products and monoliths formed from that material. The BSR test activities successfully produced leach-resistant, mineralized solid products and monoliths,

- Mineralogy features related to the XRD and SEM patterns associated with the identified crystalline species and their relative amounts in radioactive and simulant products from the BSR and ESTD were the same.
- Good mass balance closures ($>85\%$) were obtained on Tc, Re, Cs, and I in all BSR tests (radioactive and nonradioactive): 86-102% recovery of Re in the product streams for simulant

and radioactive campaigns; 109% recovery of ^{99}Tc in the product streams for radioactive campaign; 91% recovery of I in the product streams for the simulant campaign; and 98% recovery of ^{129}I and ~93% recovery of ^{125}I in the product streams (^{125}I has highest analytic sensitivity) for the radioactive campaign.

- ^{99}Tc and Re showed similar behavior in partitioning between product (major) and off-gas (trace) so Re is an acceptable process surrogate for ^{99}Tc .
- ^{99}Tc , Re, SO_4 and Cr behavior, with respect to their durability in the final granular product, were controlled by the oxygen fugacity in the FBSR/BSR process, i.e. control of the REDuction/OXidation (REDOX) equilibrium.
- Data indicate ^{99}Tc , Re, Cs, and I (all isotopes) reported primarily to the mineral product and not significantly to the off-gas.
- A geopolymer binder using clay instead of fly ash produces a monolithic final waste form that is easier to form and has superior compressive strength. Fly ash compositions are variable, and have detrimental reactivity compared to clay. The monoliths made from non-radioactive and radioactive BSR granular products with the revised geopolymer recipe at 42% waste loading passed compressive strength testing at >4,000 psi, about 8 times greater than the >500 psi requirement.
- The BSR non-radioactive granular products, non-radioactive monolith products, and radioactive monolith products all passed TCLP testing. However, the BSR radioactive granular product failed TCLP testing for Cr and Zn. Failure to pass TCLP for these two elements was not observed for any other granular or monolith products. The failure for Cr is likely caused by the small quantity of sample tested (~3 g) and the BSR operating in a more oxidizing state. The radioactive granular product was produced at a much lower REDOX of ~0.26 (more oxidized) versus the earlier simulant granular product from the fall 2009 campaign that had a REDOX in the range of 0.87 to 0.98 (more reduced). The behavior of Cr on TCLP testing is known to be REDOX sensitive, with Cr in higher oxidation state, e.g., +6, being more leachable. The failure for Zn was likely caused by excessive remote handling of the granular product in the SRNL shielded cell using brass (Cu/Zn containing) sieves; this has been previously observed by SRNL while preparing glass powders for PCT analyses.
- ASTM C1285 (Product Consistency Test) testing, with the use of a BET measured surface area to account for the surface roughness of the product and monoliths, demonstrated that the normalized releases from granular products and monoliths, for the constituents of concern, were 2 orders of magnitude lower than the Hanford glass standard of 2 g/m² for Na.
- ASTM C1308 accelerated leach testing for a radioactive monolith showed that the measured Leach Indexes for key components (Na, Re/ ^{99}Tc and I) were >10, >11, and >12 respectively after at least the 2-day leaching intervals. These results were all above the current Hanford IDF target limit Leach Indices of 6, 9 and 11, respectively, which indicated acceptable performance.
- All test objectives, as discussed in Section 11, were achieved successfully.

In general, it was shown that the mineralizing THOR[®] FBSR process system can provide safe, reliable, and predictable operation for the processing of LAW and WTP SW simulants over a range of waste feed rates and within a set of well-defined and robust operating parameters. It was also shown that a monolithic waste form of acceptable compressive strength and durability can be formed from the FBSR products for disposal at the Hanford IDF.

14. REFERENCES

GW1 3.7, "Joint Test Group for Engineering Scale Test Demonstration for the Advanced Remediation Technology (ART) Project," Rev. 0, THOR Treatment Technologiessm, December 17, 2007.

Jantzen, C. M., Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process (U), WSRC-TR-2002-00317, Rev. 0, July 12, 2002.

Burkett, P. R., J. C. Marra, J. M. Pariezs, and C. M. Jantzen, Evaluation of Fluidized Bed Steam Reforming (FBSR) Technology for Sodium-Bearing Wastes from Idaho and Hanford Using the Bench-Top Steam Reformer (BSR) (U), WSRC-TR-2004-00560, Rev. 0, February 2005.

Olson, A. L., N. R. Soelberg, D. W. Marshall, and G. L. Anderson, *Fluidized Bed Steam Reforming of Hanford LAW Using THORsm Mineralizing Technology*, INEEL/EXT-04-02492, December 2004.

28266-RT-001, "Pilot Plant Report for Treating SBW Simulants: Mineralizing Flowsheet," Rev 0, THOR Treatment Technologies, June 29, 2007

00-PP-002, "Design Basis Document for Engineering Scale Test Demonstration Testing for Treating Hanford Low Activity Waste," Rev. 1, THOR Treatment Technologies, April 3, 2008.

Kunii, D., and O. Levenspiel, *Fluidization Engineering*, 2nd Edition, Butterworth-Heinemann, Newton, MA, 1991.

00-PP-001, "Engineering Scale Technology Demonstration Testing Plan for Treating Hanford Low Activity Waste Simulant Using the THOR[®] Mineralizing Steam Reforming Process", Rev. 1, THOR Treatment Technologies, April 3, 2008.

00-PP-003, "Quality Assurance Project Plan for Treating Hanford LAW Waste Simulants Using the THOR[®] Mineralizing Steam Reforming Process," Rev. 0, THOR Treatment Technologies, November 12, 2007.

OI 3.8, "Advanced Remediation Technology Engineering Scale Technology Demonstration Unit CPMS Operation," Rev. 1, April 3, 2008.

40 CFR 60, "Standards of Performance for New Stationary Sources," *Code of Federal Regulations*, Office of the Federal Register, April 4, 2007.

EPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd Edition, Revised, U.S. Environmental Protection Agency, Washington, DC, November 1986.
(Available with updates at: <http://www.epa.gov/epaoswer/hazwaste/test/under.htm>.)

GW1 3.5, "Hanford LAW Mineralizing ESTD Test Metallurgical Evaluation Plan," Rev. 1, THOR Treatment Technologiessm, April 2, 2008.

Rassat, S. D., et al., "Cold Dissolved Saltcake Simulant Development, Preparation, and Analysis," PNNL-14194, Rev. 1, May 2003.

Flowsheet Basis and Assumptions Requirements Document, 24590-WTP-RPT-PT-02-005, Rev. 3, June 30, 2005

OI 3.3, "Advanced Remediation Technology Engineering Scale Technology Demonstration Unit Normal Operations," Rev. 1, THOR Treatment Technologies, April 3, 2008.

GW1 3.3, "Pre-Start and Checkout of ESTD Testing Facility Equipment," Rev. 0, THOR Treatment Technologies, December 11, 2007

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- GW1 3.2, "Calibration and Control of In-Process Instrumentation," Rev. 0, THOR Treatment Technologies, December 11, 2007.
- OI 3.1, "ART Demonstration Unit Preparation for Startup," Rev. 1, THOR Treatment Technologies, April 3, 2008.
- OI 3.2, "Advanced Remediation Technology Engineering Scale Technology Demonstration Unit Startup of Operations," Rev. 1, THOR Treatment Technologies, April 3, 2008.
- OI 3.4, "Advanced Remediation Technology Engineering Scale Technology Demonstration Unit Alarm Response," Rev 0, THOR Treatment Technologies, December 17, 2007.
- OI 3.5, "Hanford LAW Mineralizing ESTD Unit Solids and Liquid Sampling," Rev. 1, THOR Treatment Technologies, April 3, 2008.
- OI 3.9, "Advanced Remediation Technology Engineering Scale Technology Demonstration Unit Shutdown," Rev. 1, THOR Treatment Technologies, April 3, 2008.
- ASME NQA-1-2000, "Quality Assurance Requirements for Nuclear Facility Operations," American Society of Mechanical Engineers, January 1, 2000.
- DOE O 414.1C, "Quality Assurance," U.S. Department of Energy, June 17, 2005.
- 10 CFR 830, 2003, "Nuclear Safety Management," *Code of Federal Regulations*, Office of the Federal Register, January 1, 2003
- GW1 3.4, 2007, "DACS Configuration Control," Rev 0, THOR Treatment Technologiessm, December 11, 2007
- 55 FR 82, 1990, "Correction Factor for Oxygen," *Federal Register*, U.S. Environmental Protection Agency, p. 17918, April 27, 1990.
- 40 CFR 264, 2006, "Standard for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities," *Code of Federal Regulations*, Office of the Federal Register, July 18, 2006.
- Pilot Plant Report for Treating Sodium-Bearing Waste Surrogates-Carbonate Flowsheet, RT-ESTD-PMR-001, Rev. 0, THOR Treatment Technologiessm, October 2006.
- Soelberg, N. R., D. W. Marshall, S. O. Bates, and D. D. Taylor, *Phase 2 THOR[®] Steam Reforming Tests for Sodium Bearing Waste Treatment*, INEEL/EXT-04-01493, Rev. 0, January 2004.
- Olson, A. L., N. R. Soelberg, D. W. Marshall, and G. L. Anderson, *Fluidized Bed Steam Reforming of INEEL SBW Using THORsm Mineralizing Technology*, INEEL/EXT-04-02564, November 2004.
- Jantzen, C. M., *Characterization and Performance of Fluidized Bed Steam Reforming (FBSR) Product as a Final Waste Form*, WSRC-MS-2003-00595, Rev. 0, Environmental Issues and Waste Management Technologies IX, J. D. Vienna and D. R. Spearing (Eds); Ceramic Transactions 155, 319-329, 2004.
- DOE/ORP Contract with Bechtel, National, Inc., "Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant," Contract Number DE-AC27-01RV14136, U.S. Department of Energy, Office of River Protection, Richland, WA (Dec 2000).
- ASTM C39 / C39M - 05e1 "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens," ASTM International, 2005.
- ASTM C1285-02, "The Product Consistency Test," ASTM International, 2002.

Crawford, C. L., Jantzen, C. M., Evaluation of THORTM Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project, WSRC-STI-2009-00505, Rev. 0, October 2011.

H. D., Redox State of Model Fluidized Bed Steam Reforming Systems Final Report Subcontract AC59529T, VMI Research Laboratories, VMI, Lexington, VA 24450 (December 2007).

Bullock, Jr., J. H., J. D. Cathcart, W. J. Betterton, Analytical methods utilized by the United States Geological Survey for the analysis of coal and coal combustion by-products, U.S. Geological Survey, Denver, CO, 2002.

Jantzen, C. M., Mineralization Of Radioactive Wastes By Fluidized Bed Steam Reforming (FBSR): Comparisons To Vitreous Waste Forms, And Pertinent Durability Testing, WSRC-STI-2008-00268, Rev. 0, January 2009.

Crawford, C. L., Bannochie, C. J., Dissolution Methods and Chemical/Radiochemical Analyses Used to Support Research and Development Testing of FBSR for Hanford LAW, 242nd ACS National Meeting, Denver, CO, SRNL-STI-2011-00213, September 1, 2011

Crawford, C. L., et. al., Radioactive Demonstration of Final Mineralized Waste Forms for Hanford Waste Treatment Plant Secondary Waste (WTP-SW) by Fluidized Bed Steam Reforming (FBSR) using the Bench Scale Reformer Platform, WSRC-STI-2011-00331, Rev. 0, November 2011.

Jantzen, C.M., et. al., Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Low Activity Waste (Tank Farm Blend) by Fluidized Bed Steam Reformation (FBSR), SRNL-STI-2011-00383 (in draft).

APPENDIX A

SUMMARY OF DATA VALIDATION PACKAGES

A level “A” validation, as defined by Sample and Analysis Management (SAM) guide document (GDE)-7003¹, was performed on off-gas sample analysis data generated by TestAmerica Laboratories, Inc. (TAL). SAM implements the applicable criteria mandated by the U.S. Environmental Protection Agency’s Contract Laboratory Program at INL. The data were validated in accordance with the applicable procedures instituted by SAM for performing analytical method data validation as outlined in the following guides (GDEs): GDE-201, “Inorganic Analyses Data Validation for Sample and Analysis Management,”² for data packages pertaining to inorganic analyses; GDE-239, “Validation of Volatile Organic Compounds Data Analyzed Using Gas Chromatography/Mass Spectrometry,”³ GDE-240, “Validation of Gas and Liquid Chromatographic Organic Data,”⁴ and GDE-241, “Validation of Semivolatile Organic Compounds Data Analyzed Using Gas Chromatography/Mass Spectrometry,”⁵ for organic data packages, the “Engineering Scale Technology Demonstration Testing Plan for Treating Hanford Low Activity Waste Simulant Using the THOR[®] Mineralizing Steam Reforming Process”⁶ (Document #00-PP-001), and “Quality Assurance Project Plan for Treating Hanford Low Activity Waste Simulants Using the THOR[®] Mineralizing Steam Reforming Process”⁷ (Document #00-PP-003). This section provides a summary of the Limitations and Validation reports for these data.

A total of twelve (12) 0.1N H₂SO₄ samples, 12 5N NaOH samples, and one (1) water sample analyzed for hydrogen chloride, chlorine, hydrogen fluoride, and iodide using laboratory Standard Operating Procedures (SOPs) equivalent to specified test methods, i.e., SW-846 Method 9056A and Method 9057. The validation results were reported in file *idvoff-gasdnt08239.pdf*. All initial calibration verification standards (ICV) and continuing calibration verification standards (CCVs) percent recoveries were within the control limits of 90-110%. All initial calibration blanks (ICBs) and continuing calibration blanks (CCBs) were non-detects. All reported sample results for hydrochloric acid and chlorine were verified and confirmed from the raw data. The relative percent differences were all within the 20% control limit.

Hydrogen fluoride in samples 4.16-TB-M26A-C4 (H8E080240-002), 4.17-S1-M26AC4A, B (H8E080240-004), 4.18-S2-M26A-C4 (H8E080240-006), 4.19-S4-M26A-C4 (H8E080240-008), 4.20-S5-M26A-C4 (H8E080240-010), 4.21-S6-M26A-C4 (H8E080240-012), 4.28-P1-M26A-C4 (H8E080240-016), 4.30-P1B-M26A-C4 (H8E080240-018), 5.4-P2-M26A-C4 (H8E080240-020), 5.5-PTB-M26A-C4 (H8E080240-022), and 5.2-RB-M26A-C4 (H8E080240-024) was qualified with a “UJ” validation flag to denote that the data is non-detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data. Hydrogen fluoride in sample 4.22-S7-M26A-C4 (H8E080240-014) was qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

Chlorine in samples 4.21-S6-M26A-C4 (H8E080240-012), 4.22-S7-M26A-C4 (H8E080240-014), 4.28-P1-M26A-C4 (H8E080240-016), 4.30-P1B-M26A-C4 (H8E080240-018), and 5.4-P2-M26A-C4 (H8E080240-020) was qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data. Chlorine in samples 5.5-PTB-M26A-C4 (H8E080240-022) and 5.2-RB-M26A-C4 (H8E080240-024) was qualified with a “UJ” validation flag to denote that the data is non-detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

There were 75 field sample data points associated with the Sample Delivery Group (SDG) #H8E080240. Of these field sample data points: (a) 56 were assessed and left unqualified, (b) 13 were assessed and qualified with a “UJ” validation flag, and (c) 6 were assessed and qualified with a “J” validation flag. Using the criteria outlined in EPA540-R-93-071, “Data Quality Objectives Process for Superfund: Interim Final Guidance,” (Reference 8): (1) the 56 field sample data points (74.7% of the total) that were assessed

and left unqualified can be categorized as definitive data with no associated quality control deficiencies, (2) the 13 field sample data points (17.3% of the total) that were assessed and qualified with a “UJ” validation flag can be categorized as definitive data with a non-detectable analyte concentration that is only an estimate due to quality control deficiencies, and (3) the 6 field sample data points (8.0% of the total) that were assessed and qualified with a “J” validation flag can be categorized as definitive data with a positively identified analyte concentration that is only an estimate due to quality control deficiencies.

Two (2) condensate XAD/solvent/filter samples, SDG G8E080385, were collected and analyzed for semivolatile organic compounds (SVOC) by SW-846 8270C. The validation results were reported in file *TSO120_G8E080385.pdf*. The target compound analyses of these samples showed compliance with the QC requirements of SW- 846 Method 8270C, and all data are valid and acceptable, with the following exceptions:

The laboratory case narrative indicated that the XAD samples were received at 14°C. No action was taken because XAD resin has been documented to preserve sample integrity even at room temperature (20°C) for up to thirty days.

Several tentatively identified compounds (TICS) were detected in the method blank at various retention times. TICS with similar retention times were lined out of the samples because of laboratory contamination. Di-n-butyl phthalate was detected in the XAD method blank at 3.1 µg. Sample aliquot and dilution factors were used to establish blank action levels. The positive result for di-n-butyl phthalate was qualified as non-detected “U” in sample 4.30-P1B-M0010SVOC. The laboratory control sample duplicate (LCSD) associated with the soxhlet extraction had a percent recovery for indeno(1,2,3-cd)pyrene that exceeded quality control limit. No action was taken on this basis because only one LCS compound did not meet the recovery limit.

The LCS associated with the separatory funnel extraction had a low percent recoveries for diethyl phthalate, dimethyl phthalate, di-n-octyl phthalate, 1,3-dinitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, fluoranthene, fluorene, hexachlorobenzene, hexachloroethane, isophorone, 2-nitroaniline, nitrobenzene, N-nitrosodi-n-propylamine, N-nitrosodiphenylamine, phenanthrene, 4-bromophenyl phenyl ether, 2-chloronaphthalene, 4-chlorophenyl phenyl ether, and dibenz(a,h)anthracene. Non-detected results for the aforementioned compounds in environmental samples were qualified as estimated. The initial calibration performed on April 28, 2008 and the continuing calibration on May 23, 2008 contained average Relative Response Factors (RRFs) for 1,3,5-trinitrobenzene and pentachloronitrobenzene below the minimum criterion of 0.05. Non-detected results for the aforementioned compounds were qualified as rejected “R” in all samples. The surrogates 2-fluorobiphenyl and terphenyl-d14 had percent recoveries below the quality control limit for the LCS associated with the separatory funnel extraction. No action was taken on this basis because QC samples are not qualified. The result calculation for di-n-butylphthalate in sample 4.30-P1B-M0010SVOC was checked and verified.

The “UJ”, “U”, and “R” qualifier were applied to SDG G8E080385 by the reviewer. The “NJ” qualifier was added to TIC Form Is. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-241.

Seven (7) condensate XAD/solvent/filter samples, SDG G8D300305, were collected and analyzed for semi-volatile organic compounds (SVOC) by SW-846 8270C. The validation results were reported in file *TSO121_G8D300305.pdf*. The target compound analyses of these samples showed compliance with the QC requirements of SW- 846 Method 8270C, and all data are valid and acceptable, with the following exceptions:

The initial calibration performed on May 9, 2008 and the continuing calibration on May 13, 2008 contained average Relative Response Factors (RRFs) for 1,3,5-trinitrobenzene and pentachloronitrobenzene below the minimum criterion of 0.05. Non-detected results for the aforementioned compounds were qualified as rejected “R” in all samples. Several tentatively identified compounds (TICS) were detected in the method blank at various retention times. TICS with similar retention times were lined out of the samples because of laboratory contamination.

The surrogate 1,2-dichlorobenzene-d4 was not pre-spiked into the trap used for sample 4.28-P1-M0010SVOC. No action was taken on this basis as all other surrogate recoveries were acceptable. The surrogate 2-fluorophenol had a percent recovery less than the quality control limit for sample 4.22-S7-M0010SVOC. No action was taken on this basis because the recovery was greater than 10% and only one surrogate per fraction was outside of control limits. The surrogate 2-fluorophenol had a percent recovery greater than the quality control limit for laboratory control sample duplicate (LCSD). No action was taken on this basis because QC samples are not qualified. The result calculation for di-n-butylphthalate in sample 4.28-P1-M0010SVOC was checked and verified.

The “R” qualifier was applied to SDG G8D300305 by the reviewer. The “NJ” qualifier was added to TIC Form Is. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-241.

Four (4) samples, SDG 300384, were collected and analyzed for Polychlorinated Dibenzodioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF) by SW-846 Method 8290 and four (4) samples for Dioxin-like Polychlorinated Biphenyl (PCB) congeners using EPA Method 1668 were collected and analyzed. The validation results were reported in file *TSO130_G8D300384.pdf*. The target compound analyses of the samples showed compliance with the QC requirements of SW-846 Method 8290 and EPA Method 1668. No qualification of the data was necessary.

The target compound analyses of these samples showed compliance with the QC requirements of SW 846 Method 8290 and EPA Method 1668. All data are valid and acceptable, with the following exceptions:

The surrogate 13C-1,2,3,4,7,8-HxCDD had a percent recovery less than the quality control limit for sample 5.2-RB-M0023A. The non-detected results for 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD, and total HxCDD were qualified as estimated “UJ” for sample 5.2-RB-M0023A.

The laboratory control sample (LCS) had internal standard recoveries less than the quality control limit for 13C-1,2,3,6,7,8-HxCDD and 13C-1,2,3,6,7,8-HxCDF. The signal to noise ratio was greater than 10:1. No action was taken on this basis because QC samples are not qualified. The LCS had percent recoveries for 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF greater than the quality control limit. No action was taken on this basis because 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF were not detected in any associated samples. The PFK tune was not analyzed every twelve hours for the PCDD / PCDF and PCB congener analysis but was analyzed at the beginning and end of each PCDD / PCDF and PCB congener analytical sequence. Because the analytical sequence is continuous and the beginning and ending PFK are provided, no action was taken.

The “UJ” qualifier was applied by the reviewer to sample ID #5.2-RB-M0023A. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in ER-SOW-394.

Twelve (12) liquid samples from the front half and 12 liquid samples from the back half were collected and analyzed. The samples were analyzed for total metals for aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), cesium (Cs), chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), nickel (Ni), potassium (K), rhenium (Re), selenium (Se), silver (Ag), sodium (Na), and thallium (Tl) by

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TAL using SOPs equivalent to specified test methods, i.e., SW-846 Method 6020. Results of the validation effort were reported in file *idvoff-gasdnt08264.pdf*.

All applicable ICV and CCV percent recoveries were within their control limits. All applicable ICB and CCB results were below the reporting limit.

All samples received validation qualifying flags: Results for silver in samples 4.28-P1-M29-BH (G8E010188-002), 4.17-S1-M29-BH (G8E010188-004), 4.18-S2-M29-BH (G8E010188-006), 4.19-S4-M29-BH (G8E010188-008), 4.20-S5-M29-BH (G8E010188-010), 4.21-S6-M29-BH (G8E010188-012), 4.22-S7-M29-BH (G8E010188-014), 4.16-TB-M29-BH (G8E010188-016), 4.30-P1B-M29-BH (G8E010188-018), and 5.4-P2-M29-BH (G8E010188-020) were qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

Results for silver in samples 5.2-RB-M29-BH (G8E010188-022) and 5.5-PTB-M29-BH (G8E010188-024) were qualified with a “UJ” validation flag to denote that the data is non-detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data. Results for magnesium in all associated front half samples were qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

Results for antimony in all associated front half results, except in sample 5.2-RB-M29-FH (G8E010188-021), were qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data. Antimony in sample 5.2-RB-M29-FH (G8E010188-021) was qualified with a “UJ” validation flag to denote that the data is non-detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

Results for sodium in all associated back half samples were qualified with a “J” validation flag to denote that the data is detectable at the reported value, but the reported value is only an estimate due to anomalies in the quality control data.

There were 408 field sample data points associated with the SDG #G8E010188 IDP. Of these field sample data points: (a) 360 were assessed and left unqualified, (b) 3 were assessed and qualified with a “UJ” validation flag, and (c) 45 were assessed and qualified with a “J” validation flag. Using the criteria outlined in EPA540-R-93-071, “Data Quality Objectives Process for Superfund: Interim Final Guidance,” (Reference 7): (1) the 360 field sample data points (88.2% of the total) that were assessed and left unqualified can be categorized as definitive data with no associated quality control deficiencies, (2) the 3 field sample data points (0.7% of the total) that were assessed and qualified with a “UJ” validation flag can be categorized as definitive data with a non-detectable analyte concentration that is only an estimate due to quality control deficiencies and (3) the 45 field sample data points (11.0% of the total) that were assessed and qualified with a “J” validation flag can be categorized as definitive data with a positively identified analyte concentration that is only an estimate due to quality control deficiencies.

Two (2) samples, SDG H8E080225, were collected and analyzed for total chromatographable organics (TCO) and total gravimetric organics (TGO) by EPA Method 018. The validation results were reported in file *TS0122_H8E080225rev1.pdf*. The target compound analyses of the samples showed compliance with the QC requirements of EPA Method 018 and all data are valid and acceptable with the following exceptions:

The laboratory combined the filter, XAD, solvent, and condensate media together in one extract, which was then analyzed. It should be noted for data completeness that the data package deliverable did not

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contain a summary of sample surrogate recoveries as presented in CLP-like Form II. Surrogate recoveries were validated using the surrogate recoveries reported on the Form Is. The method blank associated with QC batch 8133063 contained TCO at a concentration of 0.056 mg. The TCO results were corrected for the amount in the method blank. The result calculation for TCO in sample 4.30-P1B-M0010TCO-C1,2,3,4+B,5 was checked and verified.

No qualifiers were applied to SDG H8E080225 by the reviewer. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-240.

Eight (8) samples, SDG H8D300271, were collected and analyzed for total chromatographable organics (TCO) and total gravimetric organics (TGO) by EPA Method 018. The validation results were reported in file *TS0123_H8D300271_SAM.pdf*. The target compound analyses of the samples showed compliance with the QC requirements of EPA Method 018 and all data are valid and acceptable with the following exceptions:

The laboratory combined the filter, XAD, and condensate media together in one extract, which was then analyzed. It should be noted for data completeness that the data package deliverable did not contain a summary of sample surrogate recoveries as presented in CLP-like Form II. Surrogate recoveries were validated using the surrogate recoveries reported on the Form Is. The result calculation for TCO in sample 4.17-TB-M0010 TCO;C1,2,3,4,5 was checked and verified.

No qualifiers were applied to SDG H8D300271 by the reviewer. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-240.

Three (3) condensate samples and eleven (11) tenax samples, SDG H8E080214, were collected and analyzed for Volatile Organic Compounds by SW-846 8260B. The validation results were reported in file *TS0127_H8E080214rev1.pdf*. The target compound analyses of the samples showed compliance with the QC requirements of EPA 0031/SW-846 8260B, and all data are valid and acceptable, with the following exceptions:

According to laboratory documentation, no custody seals were present on the coolers. No action was taken on this basis.

Sample 4.30-P1B-M0031-1C broke during the sample analysis. The laboratory could not analyze the sample and the entire sample volume was compromised. No action was taken on this basis. Methylene chloride and chloromethane were detected in the method blank associated with batch 8129369. Sample aliquot and dilution factors were used to establish the blank action level. The methylene chloride and chloromethane results, less than the blank action limit, for the samples associated with batch 8129369 have been qualified as non-detected "U". Hexachlorobutadiene, 4-chlorotoluene, methylene chloride, naphthalene, 1,2,3-trichlorobenzene, and 1,2,4-trichlorobenzene were detected in the method blank associated with batch 8130175. Sample aliquots and dilution factors were used to establish blank action levels. Methylene chloride results for samples 4.30-P1B-M0031-C1, 4.30-P1B-M0031-C2, and 5.7-RB-M0031-C1 have been qualified as non-detected "U". No action was taken on the other compounds because they were not detected in the associated samples.

The chloromethane result for sample 4.30-P1B-M0031-2C was greater than the linear calibration range of the instrument. The sample was not analyzed at a dilution because the entire sample was consumed for the initial analysis. The chloromethane result for sample 4.30-P1B-M0031-2C was qualified as estimated "J". All surrogates and had percent recoveries less than 10 percent recovery for samples 4.30-P1BM0031-2C and 4.30-P1B-M0031-3C. No re-analyses was preformed because the entire volume was consumed in the initial analysis. The laboratory stated that sample 4.20-P1B-M0031-3C was incorrectly spiked by the bench analyst. The positive results have been qualified as estimated "J" and the non-detected results have

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been rejected “R”, for samples 4.30-P1B-M0031-2C and 4.30-PaB-M0031-3C. All internal standards had low area counts for sample 4.30-P1B-M0031-2C. The internal standards fluorobenzene and Chlorobenzene-d5 had area counts less than 10 percent of the associated continuing calibration. The positive results have been qualified as estimated “J” and the non-detected results have been rejected “R”, for sample 4.30-P1B-M0031-2C.

The initial calibration performed on 11/28/07 contained an RRF below the 0.05 relative response factor (RRF) quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8129369. The continuing calibration performed on 05/09/08 at 07:53 was below the 0.05 RRF quality control limit for acetone, acrylonitrile, 2-butanone, dibromomethane, 4-methyl-2-pentanone, and 1,2-dibromo-3-chloropropane. Non-detected results for the aforementioned compounds were rejected, “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8129369.

The continuing calibration performed on 05/09/08 at 07:53 contained percent differences (%Ds) that exceeded the 20% quality control criterion for dichlorodifluoromethane, acetone, bromochloromethane, 1,1,1-trichloroethane, carbon tetrachloride, 1,2-dichloroethane, bromodichloromethane, 4-methyl-2-pentanone, trans-1,3-dichloropropene, 2-hexanone, chlorodibromomethane, 1,2-dibromo-3-chloropropane, naphthalene, and 1,2,3-trichlorobenzene. No action was taken for acrylonitrile, 2-butanone, dibromomethane, 4-methyl-2-pentanone, and 1,2-dibromo-3-chloropropane because these compounds were qualified for a more severe RRF noncompliance. Positive results for carbon tetrachloride, dichlorodifluoromethane, and bromodichloromethane were qualified as estimated “J”, in samples associated with preparation batch 8129369. Positive results for acetone were qualified as estimated “J” and non-detected results were rejected “R”, in samples associated with preparation batch 8129369. No action was taken for the remaining compounds because the associated results were non-detected.

The initial calibration performed on 04/09/08 contained RRFs below the 0.05 relative response factor (RRF) quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8130175. The continuing calibration performed on 05/09/08 at 12:48 was below the 0.05 RRF quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8130175.

The continuing calibration performed on 05/09/08 at 12:48 contained a %D that exceeded the 20% quality control criterion for n-butylbenzene. No action was required because all associated sample results with preparation batch 8130175 were non-detected. The tentatively identified compounds (TIC) identified with CAS numbers were qualified as presumptively present “NJ”. The result calculation for toluene in sample 4.30-P1B-M0031-1A,B was checked and verified.

The “J”, “UJ”, and “R” qualifiers were applied to SDG No. H8E080214 by the reviewer. All other qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in ER-SOW-394.

Eight (8) condensate samples, twenty (20) tenax, and twenty-one (21) anasorb samples, SDG H8D300235, were collected and analyzed for Volatile Organic Compounds by SW-846 8260B. The validation results were reported in file *TS0124_H8D300235REV2_SAM.pdf*. All data are valid and acceptable, with the following exceptions:

According to laboratory documentation, the cooler temperature for the samples was 14 degrees Celsius, which exceeded the quality control limit of 4 degrees Celsius. The positive and non-detected results for all compounds in all samples were qualified as estimated "J" and "UJ", respectively. In addition, the laboratory noted that no custody seals were present on the coolers. No action was taken on this basis. Hexachlorobutadiene, methylene chloride, naphthalene, 1,2,3-trichlorobenzene, and 1,2,4-trichlorobenzene were detected in the condensate method blank (8121443). Sample aliquot and dilution factors were used to establish the blank action level. The methylene chloride results for condensate samples 4.21-S6-0031-C-2, 4.22-S7-0031-C-2, 4.28-P-1-0031-C-1, and 4.28-P-1-0031-C-2 have been qualified as non-detected "U". Chloromethane, 1,4-dichlorobenzene, methylene chloride, and 1,2,4-trichlorobenzene were detected in the method blank analyzed on 05/01/08 (8121382). Sample aliquots and dilution factors were used to establish blank action levels.

Methylene chloride result for sample 4.18-S2-0031-T1-3 and chloromethane results for 4.18-S2-0031-TB-1,2, 4.18-S2-0031-TB-3, 4.20-S5-0031-TB-1,2, 4.20-S5-0031-TB-3, 4.21-S6-0031-TB-1,2, 4.21-S6-0031-TB-3, 4.22-S7-0031-TB-1,2, 4.22-S7-0031-TB-3, 4.28-P-1-0031-TB-1,2, and 4.28-P-1-0031-TB-3 have been qualified as non-detected "U". Chloromethane, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobutadiene, methylene chloride, and 1,2,4-trichlorobenzene were detected in the method blank analyzed on 05/02/08 (8122345). Sample aliquots and dilution factors were used to establish blank action levels. Methylene chloride results for samples 4.20-S5-0031-T2-1,2 and 4.22-S7-0031-T3-3; chloromethane, 1,3-dichlorobenzene, and 1,4-dichlorobenzene results for samples 4.18-S2-0031-T2-1,2 and 4.18-S2-0031-T3-1,2; chloromethane and methylene chloride results for samples 4.20-S5-0031-T1-1,2, 4.21-S6-0031-T3-1,2, A-5861 Media Check Tenax, and A-5862 Media Check Tenax / Anasorb; chloromethane and 1,4-dichlorobenzene results for sample 4.21-S6-0031-T2-1,2; chloromethane result for sample 4.20-S5-0031-T3-1,2; 1,4-dichlorobenzene result for sample 4.21-S6-0031-T1-1,2; 1,2,4-trichlorobenzene results for samples 4.22-S7-0031-T2-3, 4.28-P-1-0031-T1-3, 4.28-P-1-0031-T3-3 have been qualified as non-detected "U".

Hexachlorobutadiene, 1,4-dichlorobenzene, methylene chloride, and 1,2,4-trichlorobenzene were detected in the method blank analyzed on 05/05/08 (8123439). Sample aliquot and dilution factors were used to establish the blank action level. The 1,4-dichlorobenzene and 1,2,4-trichlorobenzene results for sample 4.22-S7-0031-T2-1,2 and 1,4-dichlorobenzene results for samples 4.22-S7-0031-T3-1,2 and 4.28-P-1-0031-T1-1,2 have been qualified as non-detected "U".

The bromomethane and methylene chloride results for sample 4.20-S5-0031-T1-3 were greater than the linear calibration range of the instrument. The sample was not analyzed at a dilution because the entire sample was consumed for the initial analysis. The bromomethane and methylene chloride results for sample 4.20-S5-0031-T1-3 were qualified as estimated "J". The methylene chloride results for samples 4.28-P-1-0031-T1-3 and 4.28-P-1-0031-T3-3 were greater than the linear calibration range of the instrument. The samples were not analyzed at a dilution because the entire sample was consumed for the initial analysis. The methylene chloride results for samples 4.28-P-1-0031-T1-3 and 4.28-P-1-0031-T3-3 were qualified as estimated "J". The surrogates toluene-d8, and bromofluorobenzene had percent recoveries less than the quality control limit and dibromofluorobenzene had a percent recovery greater than the quality control limit for sample 4.28-P-1-0031-T1-3. No re-analyses was performed because the entire volume was consumed in the initial analysis. The positive and non-detected results for sample 4.28-P-1-0031-T1-3 have been qualified as estimated "J" and "UJ", respectively.

The surrogates toluene-d8 and bromofluorobenzene had percent recoveries less than the quality control limit for samples 4.18-S2-0031-T2-3, 4.20-S5-0031-T1-3, 4.20-S5-0031-T3-3, 4.21-S6-0031-T1-3, 4.21-S6-0031-T2-3, 4.21-S6-0031-T3-3, 4.22-S7-0031-T2-3, and 4.28-P-1-0031-T2-3. No re-analyses were

performed because the entire volume was consumed in the initial analysis. The positive and non-detected results for the aforementioned samples have been qualified as estimated “J” and “UJ”, respectively.

The surrogate bromofluorbenzene had percent recoveries less than the quality control limit for samples 4.22-S7-0031-T1-3 and 4.28-P-1-0031-T3-3. No re-analyses were performed because the entire volume was consumed in the initial analysis. No action was taken on this basis because only one of four surrogates was outside control limits. The internal standards fluorobenzene and chlorobenzene-d5 had low area counts for samples 4.18-S2-0031-T1-3, 4.18-S2-0031-T3-3, 4.20-S5-0031-T2-3, and 4.22-S7-0031-T3-3. The positive and non-detected results quantitated using fluorobenzene have been quantified as estimated “J” and “UJ”, respectively, in the aforementioned samples. The internal standards fluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenene-d5 had low area counts for samples 4.18-S2-0031-T2-3, 4.20-S5-0031-T1-3, 4.20-S5-0031-T3-3, 4.21-S6-0031-T1-3, 4.21-S6-0031-T2-3, 4.21-S6-0031-T3-3, 4.22-S7-0031-T1-3, 4.22-S7-0031-T2-3, 4.28-P-1-0031-T1-3, 4.28-P-1-0031-T2-3, and 4.28-P-1-0031-T3-3. The positive and non-detected results quantified using fluorobenzene and chlorobenzene-d5 have been qualified as estimated “J” and “UJ”, respectively, in the aforementioned samples.

The initial calibration performed on 04/09/08 contained RRFs below the 0.05 relative response factor (RRF) quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8121443. The continuing calibration performed on 05/01/08 at 08:29 was below the 0.05 RRF quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8121443. The continuing calibration performed on 05/01/08 at 08:29 contained percent differences (%Ds) that exceeded the 20% quality control criterion for 1,2,4-trichlorobenzene and naphthalene. No action was required because all associated sample results with preparation batch 8121443 were non-detected. The initial calibration performed on 11/28/07 contained an RRF below the 0.05 relative response factor (RRF) quality control limit for acetone, acrylonitrile and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batches 8121382.

The continuing calibration performed on 05/01/08 at 07:20 was below the 0.05 RRF quality control limit for acetone, acrylonitrile, and 2-butanone. Non-detected results for the aforementioned compounds were rejected; “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8121382. The continuing calibration performed on 05/01/08 at 07:20 contained %Ds that exceeded the 20% quality control criterion for dichlorodifluoromethane, bromomethane, trichlorofluoromethane, acrylonitrile, carbon tetrachloride, 1,2-dichloroethane, 1,2,4-trichlorobenzene, hexachlorobutadiene, naphthalene, and 1,2,3-trichlorobenzene. No action was taken for acrylonitrile because these compounds were qualified for a more severe RRF noncompliance. Positive results for bromomethane, dichlorodifluoromethane, and trichlorofluoromethane were qualified as estimated “J”, in samples associated with preparation batch 8121382. No action was taken for the remaining compounds because the associated results were non-detected. The continuing calibration performed on 05/02/08 at 09:34 was below the 0.05 RRF quality control limit for acetone, acrylonitrile, 2-butanone, 4-methyl-2-pentanone and 1,2-dibromo-3-chloropropane. Non-detected results for the aforementioned compounds were rejected, “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8122345. The continuing calibration performed on 05/02/08 at 09:34 contained %Ds that exceeded the 20% quality control criterion for dichlorodifluoromethane, chloromethane, trichlorofluoromethane, acetone, carbon disulfide, 2-butanone, 1,2-dichloroethane, 4-methyl-2-pentanone, 2-hexanone, 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, hexachlorobutadiene, naphthalene, and 1,2,3-

trichlorobenzene. No action was taken for acrylonitrile, 2-butanone, 4-methyl-2-pentanone, and 1,2-dibromo-3-chloropropane because these compounds were qualified for a more severe RRF noncompliance. Positive results for acetone, carbon disulfide, trichlorofluoromethane, dichlorodifluoromethane, and chloromethane were qualified as estimated “J”, in samples associated with preparation batch 8122345. No action was taken for the remaining compounds because the associated results were non-detected.

The continuing calibration performed on 05/05/08 at 09:00 was below the 0.05 RRF quality control limit for acetone, acrylonitrile, 2-butanone, 4-methyl-2-pentanone and 1,2-dibromo-3-chloropropane. Non-detected results for the aforementioned compounds were rejected, “R” and positive results were qualified as estimated “J”, in samples associated with preparation batch 8123439. The continuing calibration performed on 05/05/08 at 09:00 contained %Ds that exceeded the 20% quality control criterion for dichlorodifluoromethane, trichlorofluoromethane, acetone, carbon disulfide, 2-butanone, 1,2-dichloroethane, 4-methyl-2-pentanone, trans-1,3-dichloropropene, 2-hexanone, 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, naphthalene, and 1,2,3-trichlorobenzene. No action was taken for acrylonitrile, 2-butanone, 4-methyl-2-pentanone, and 1,2-dibromo-3-chloropropane because these compounds were qualified for a more severe RRF noncompliance. Positive results for acetone, dichlorodifluoromethane, carbon disulfide, and trichlorofluoromethane were qualified as estimated “J”, in samples associated with preparation batch 8123439. No action was taken for the remaining compounds because the associated results were non-detected.

The tentatively identified compounds (TIC) identified with CAS numbers were qualified as presumptively present “NJ”. The result calculation for benzene in sample MAINSTACK P-4 RUN 1A TENAX was checked and verified. The “J”, “UJ”, and “R” qualifiers were applied to SDG H8D300235 by the reviewer. All other qualifiers in the data package were reported by TestAmerica personnel according to the format described in ER-SOW-394.

Two (2) condensate samples, SDG H8D300252, were collected and analyzed for Unspecified Volatile Organic Compounds by EPA 0040/SW-846 5030B/8015B. The validation results were reported in file *Organic in Condensate TS0125_HD300252.pdf*. The target compound analyses of the aqueous samples showed compliance with the QC requirements of EPA 0040 / SW-846 3050B/8015B, and all data are valid and acceptable, with the following exceptions:

It should be noted for data completeness that the data package deliverable did not contain a summary of sample surrogate recoveries as presented in CLP-like Form II. Surrogate recoveries were validated using the surrogate recoveries reported on the Form Is. According to laboratory documentation, the cooler temperature was 10 degrees Celsius, which exceeded the quality control limit of 4 degrees Celsius. The positive and non-detected results for all compounds were qualified as estimated “J” and “UJ”, respectively. In addition, the laboratory noted that no custody seals were present on the cooler. No action was taken on this basis. The laboratory reported that samples 4.18-S2-0040-COND, 4.20-S5-0040-COND, and 4.28-P1-0040-COND were received broken. No action was taken on this basis. The method blank associated with QC batch 8122064 contained C6 at a concentration of 0.16µg/L. The blank action level for C7 is 0.80µg/L. Sample aliquots and dilution factors were used to establish blank action levels. The result for C6 was qualified as non-detected “U” in sample 4.21-S6-0040-COND. The result calculation for C5 in sample 4.22-S7-0040-COND was checked and verified.

The “J” and “UJ” qualifiers were applied to SDG H8D300252 by the reviewer. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-240.

One (1) condensate sample, SDG H8E08221, was collected and analyzed for Unspeciated Volatile Organic Compounds by EPA 0040/SW-846 5030B/8015B. The validation results were reported in file *TS0126_HE080221_SAM.pdf*. The target compound analyses of the aqueous samples showed compliance with the QC requirements of EPA 0040 / SW-846 3050B/8015B, and all data are valid and acceptable, with the following exceptions:

For data completeness that the data package deliverable did not contain a summary of sample surrogate recoveries as presented in CLP-like Form II. Surrogate recoveries were validated using the surrogate recoveries reported on the Form Is. According to laboratory documentation, no custody seals were present on the cooler. No action was taken on this basis. The method blank associated with QC batch 8130051 contained C6 at a concentration of 0.18µg/L. The blank action level for C6 is 0.90µg/L. Sample aliquots and dilution factors were used to establish blank action levels. The result for C6 was qualified as non-detected "U" in sample 4.30-P1B-M0040-C1. The result calculation for C6 in sample 4.30-P1B-M0040-C1 was checked and verified.

The "U" qualifier was applied to SDG H8E080221 by the reviewer. All qualifiers in the data package were reported by TestAmerica Laboratories personnel according to the format described in GDE-240.

Table B-1 provides a listing of the data validation files with corresponding sample data package information.

Table A-1 Data Packages

Data Validation File	TAL Project Code (Sample Delivery Group)	Production Condition	Method Description	Date Sampled
idvoff-gasdnt08239.pdf	H8E080240	S-4	M 26A	4/16/2008
TSO120 G8E080385.pdf	G8E080385	S-7	M 0010 - Spec. VOCs	5/2/2008
TSO121 G8D300305.pdf	G8D300305	S-1, S-2, S-5, S-6, S-7, and P-1A	M 0010 - Spec. VOCs	4/17, 18, 20, 21, 22 and 28/2008
idvoff-gasdnt08264.pdf	G8E010188	P-2	M 29	4/28/2008
TSO130 G8D300384.pdf	G8D300384	S-1, S-5, P-1A and P-2	M 0023	4/17, 20, 28 and 5/2/2008
TSO122 H8E080225rev1.pdf	H8E080225	P-1B and P-2	M 0010 - TCO-Grav.	4/30/ and 5/2/2008
TSO123 H8D300271 SAM.pdf	H8D300271	S-1, S-2, S-5, S-6, S-7, and P-1A	M 0010 - TCO-Grav.	4/17, 18, 20, 21, 22 and 28/2008
TSO125 HD300252.pdf	H8D300252	S-6 and S-7	M 0040 Condensate	4/21,22/2008
TSO126 HE080221 SAM.pdf	HE080221	P-1B	M 0040 Condensate	4/30/2008
TSO124 H8D300235REV2 SAM.pdf	H8D300235	S-2, S-5, S6, S-7, and P-1A	M 0031	4/18, 20, 21, 22, and 28/2008
TSO127 H8E080214rev1.pdf	H8E080214	P-1B and P-2	M 0031	4/30 and 5/7/2008

APPENDIX A-1 REFERENCES

Bechtel BWXT Idaho, LLC (BBWI) Environmental Operations Division Sample Management Office, *Levels of Analytical Method Data Validation*, Guide Document No. GDE-7003, Revision 3, March 2005.

GDE-201, "Inorganic Analyses Data Validation for Sample and Analysis Management," current revision.

GDE-239, "Validation of Volatile Organic Compounds Data Analyzed Using Gas Chromatography/Mass Spectrometry," Sample and Analysis Management, current revision.

GDE-240, "Validation of Gas and Liquid Chromatographic Organic Data," Sample and Analysis Management, current revision.

GDE-241, "Validation of Semivolatile Organic Compounds Data Analyzed Using Gas Chromatography/Mass Spectrometry," Sample and Analysis Management, current revision.

00-PP-001, "Engineering Scale Technology Demonstration Testing Plan for Treating Hanford Low Activity Waste Simulant Using the THOR[®] Mineralizing Steam Reforming Process"

00-PP-003, "Quality Assurance Project Plan for Treating Hanford Low Activity Waste Simulants Using the THOR[®] Mineralizing Steam Reforming Process"

APPENDIX B

IDENTIFIED NONCONFORMANCES AND DEFICIENCY REPORTS

Table B-14-1 Nonconformances Identified During the ART ESTD.

NCR Number	Date	Nonconformance	Corrective Action	Status
NCR-THOR-001	2/11/08	1000lbs of Spherox Coarse was ordered and originally shipped in a mini-supersack. 850lbs of Spherox Coarse was received in a drum.	The vendor was contacted and the material was returned. A new shipment was received without incident.	Closed
NCR-THOR-002	4/3/08	Sodium chromate was ordered as a feed make-up constituent. On 3/25/08, sodium di-chromate was received at Hazen.	GW1 3.10 was generated to provide specific receiving/inspection procedures for material receipt. Personnel training was accomplished on 4/11/08 on GW1 3.10.	Closed
NCR-THOR-003	4/3/08	Selenium oxide was received at Hazen 3/26/08. The material arrived with a Certificate of Analysis, including a lot number that did not match the lot number on the material container or packing sheet.	GW1 3.10 was generated to provide specific receiving/inspection procedures for material receipt. Personnel training was accomplished on 4/11/08 on GW1 3.10.	Closed
NCR-THOR-004	4/14/08	A shipment of chemicals was received from Rocky Mountain Reagents. The Lot numbers for tri-sodium phosphate matched the packing lists but did not match the COA. Five of eight containers of sodium nitrite matched the packing list, COA and packing list. Three containers of sodium nitrite did not match the lot number and/or the associated COA.	Rocky Mountain Reagents was contacted and resolved the non-conformances by 1) correcting the COA lot number for the containers of tri-sodium phosphate and 2) exchanged 3 new containers of sodium nitrite with matching lot number, packing list and container labels and returned the three non-matching containers.	Closed
NCR-THOR-005	6/9/08	Stack gas samples shipped for analysis from various scoping and production run tests arrived at the laboratory above method required temperature or damaged.	1) A written procedure was developed and implemented describing proper sample packaging and shipping protocols. Personnel responsible for packaging and shipping were trained on the procedure. 2) Subcontractor personnel responsible for packaging and shipping will be trained on the QAPP and SW-846 requirements associated with the applicable EPA method and chain of custody requirements. Documentation of the training was provided to TTT. 3) The subcontractor's SOW was to be amended to include a requirement to provide verbal notification within 24hrs and written notification to TTT of any sample incidents within 3 days. The subcontractor is to flow down this requirement in writing to any/all of its contractors performing work on behalf of TTT. 4) The subcontractor provided a technical justification explaining the effect of the temperature exceedances and why the data from these samples remains useable. 5) The subcontractor provided a full explanation of how the samples were packaged resulting in the breakage, temperature exceedances, and missing sample with appropriate recommendations for corrective actions.	Closed
NCR-HRI-001*	2/11/09	During recertification of the Fox Thermal Instrument O ₂ flowmeter, 10A-10P-D1, S/N 3152 (FE300-001) the "As found" readings indicated an error of 100%. The vendor subsequently admitted the previous calibration to be faulty.	The instrument has been removed from further use and tagged "out of service". Fox Thermal Instrument has been removed as a viable vendor. A re-evaluation of the mass and energy balance was conducted to determine the impact of the instrument error. Using correction factors, the overall mass balance closure was improved.	Closed

*NCR generated by Hazen Research, Inc. as a result of post demonstration instrument calibration.

Table B-14-2 Deficiency Reports Identified During the ART ESTD.

Deficiency Number	Date	Issue	Corrective Action	Status
28915-08-01	4/11/08	The Lead TTT engineer, along with the URS-WGD procurement officer contacted the vendor for the proposed sodium chromate shipment on March 20th or 21st. Discussions with the vendor indicated that they did not have the material requested at the time but they did have sodium di-chromate at a significant cost reduction (\$90/kg vs. \$4/kg). The vendor was told to provide this material instead of the original sodium chromate and the engineer began the change order paperwork. Due to the need for support on another project, the MR did not get completed until the 25th of March and the material was received at the Hazen facility on March 25th. During the Receipt/inspection, the original PO was utilized by the inspector to verify the material per the procedure, instead of the revised PO with the change order. The inspector noted the difference in the name of the material and volume, but he did not contact the Project Manager and the material was accepted. In addition, the following events occurred that contributed to the issue: 1. The Hazen personnel did not receive the revised change Order until March 31st, well after the receipt of the material. 2. The attached table to the PO still reflected the same name of the material, sodium chromate, instead of sodium di-chromate even though the chemical formula was properly changed	Revise the Receipt and Inspection procedure. Train personnel on the procedure and notification of nonconforming conditions. Work with Procurement and engineering to properly process POs and issue to the field in a timely fashion for use during the receipt and inspection process.	Closed
28915-08-02	4/18/08	The ART Testing QA Manager was notified of a potential non-conformance issue the afternoon of 4/14/08, involving the receipt of chemicals at Hazen. Hazen was asked to verify the discrepancy with the vendor and identify resolutions. This was accomplished the morning of 4/15/08. The TTT Testing QA Manager notified the TTT QA Manager of the circumstances of the receipt and the team decided to generate an NCR (#NCR-THOR-004) to document the nonconformance. The new NCR and updated NCR Log were sent via email on 4/16/08, to the TTT QA Manager and the ART ESH&Q Manager. The President of TTT was notified of the NCR on 4/17/08. This notification did not occur in a timely manner as prescribed by <i>Quality Assurance Project Plan for Treating Hanford Low Activity Waste Simulants Using the THOR® Mineralizing Steam Reforming Process</i> , 00-PP-003, Rev.1, Section 14.0, "The president of TTT will be notified immediately of any nonconforming situations."	The president of TTT will receive all NCR/Deficiency Reports via distribution. The ART Testing QA Manager will inform the TTT QA Manager and ART Project Manager of all potential NCR/Deficiencies and the TTT QA Manager will immediately notify the president of TTT. The TTT QA Manager will review the NCR/Deficiency reporting requirements with the ART ESH&Q Manager and the ART Testing QA Manager. The ART Project Manager will discuss with the ART Test Personnel in the JTG the requirement in PQP 15.1 to initiate an NCR upon identification of a non-conformance and the requirement in the QAPP to immediately notify the TTT President.	Closed

Deficiency Number	Date	Issue	Corrective Action	Status
29387-DR-11-01	1/13/11	<p>Condition Description: Notebook WSRC-NB-2008-00070 was reviewed and found to be noncompliant with requirements found in SRNL Procedure 7.16, Rev. 3, <i>Laboratory Notebooks and Logbooks</i>, Sections 5.1.3, 5.1.8, and 5.1.14. Entries were made in the notebook from July 2008 thru October 2010.</p> <p>5.1.3 Each person entering information of any type (including reviewers/witnesses) shall print, sign, and initial under Contributing Entries on the Controlled Laboratory Notebook/Logbook Inside Front Cover form.</p> <p>Contrary to the requirement, the notebook did not contain the signature or initials of all individuals who had contributed to the notebook.</p> <p>5.1.8 Entries shall be signed/initialed and dated on the date the information is entered.</p> <p>Contrary to the requirement, the notebook did not contain signatures/initials on the date the information was entered.</p> <p>5.1.14 To close a page, sign and date at the bottom and draw a diagonal line through any unused portion of the page. If a page is inadvertently left blank, note accordingly (e.g., No information on this page) and draw a diagonal line through the page, sign/initial and date.</p> <p>Contrary to the requirement, the notebook did not contain a signature, date, and diagonal line on any page of the notebook.</p> <p>Further, a previous surveillance performed by SRNL 5/7/10, 2010-SUR-11-0012, documented failure to properly complete notebooks. A STAR report, 2010-CTS-005814, was issued a result of the surveillance and closed 9/29/10, with a closure action indicating the requirements of Procedure 7.16 would be discussed with staff.</p>	SRNL STAR No. 2011-CTS-000547 was issued to address the identified deficiencies, track their completion, and prevent recurrence. The logbook entries were made as required and a copy of the STAR report was placed in the logbook for future reference.	Closed

APPENDIX C

SUMMARY OF ANALYTICAL MEASUREMENTS ON SIMULANT FEED BATCHES

Table C-1 Measured Constituent Concentrations in ESTD ART LAW Feed Batches.

Component	Component	Target Component Concentration with 675 g clay/L [g/L]	P-1 #1 ID#5247	P-1 #2 ID#5291	Target Component Concentration with 640 g clay/L [g/L]	P-1 #3 ID#5321	P-1 #4 ID#5347
Oxalate	C ₂ O ₄	0.829	NM	NM	0.838	NM	NM
Acetate	CH ₃ COO	6.221	NM	NM	6.287	NM	NM
Hydroxide	OH	10.046	5.92	5.98	10.152	5.31	5.12
Carbonate	CO ₃	22.752	32.71	30.21	22.993	30.70	30.13
Sulfate	SO ₄	6.901	6.51	7.59	6.974	7.12	6.82
Chloride	Cl	1.239	0.99	1.04	1.253	1.02	1.25
Fluoride	F	0.479	0.512	0.542	0.484	0.489	0.469
Iodide	I	1.317	2.06	1.96	1.331	1.66	1.69
Nitrite	NO ₂	15.570	16.66	16.42	15.735	15.79	15.76
Phosphate	PO ₄	4.216	4.90	4.95	4.235	4.61	2.35
Aluminum	Al	109.056	164.30	134.76	104.566	134.36	131.06
Potassium	K	0.387	0.984	0.968	0.391	0.853	0.872
Sodium	Na	92.048	84.94	87.673	93.022	84.75	83.12
Nitrate	NO ₃	127.932	145.00	140.417	129.285	134.06	134.65
Silver	Ag	0.139	0.124	0.132	0.140	0.133	0.132
Arsenic	As	1.042	0.069	0.069	1.003	0.064	0.070
Barium	Ba	1.419	0.814	0.782	1.403	0.734	0.711
Cadmium	Cd	0.377	0.364	0.372	0.381	0.356	0.352
Chromium	Cr	0.432	0.295	0.294	0.436	0.297	0.286
Cesium	Cs	1.379	0.899	0.891	1.394	0.860	0.821
Nickel	Ni	0.497	0.512	0.519	0.502	0.526	0.476
Lead	Pb	1.002	0.775	0.844	1.013	0.786	0.755
Rhenium	Re	0.253	0.217	0.201	0.255	0.208	0.213

Antimony	Sb	0.422	0.434	0.449	0.426	0.423	0.418
Selenium	Se	0.078	0.088	0.084	0.078	0.082	0.088
Thallium	Tl	0.330	0.211	0.208	0.333	0.217	0.226
Silicon	Si	112.496	138.57	128.64	107.791	119.23	117.79
Iron	Fe	2.070	1.17	1.29	1.983	1.08	1.03
Titanium	Ti	5.386	4.75	4.89	5.161	4.61	4.30
Calcium	Ca	0.141	0.062	0.093	0.135	0.089	0.095
Magnesium	Mg	0.086	0.078	0.077	0.083	0.089	0.081

Reacted with ANN, decreasing target value

Greater than $\pm 20\%$ of target value.

Greater than $\pm 50\%$ of target value.

NM – Not Measured.

Table C-2 Measured Constituent Concentrations in ESTD ART WTP SW Feed Batches

Component	Component	Target Component Concentration with 307 g clay/L [g/L]	P-2 #1 ID#5392	P-2 #2 ID#5422	P-2 #3 ID#5450	P-2 #4 ID#5477
Hydroxide	OH	23.850	0.078	0.079	0.079	0.079
Carbonate	CO ₃	10.773	16.48	13.18	13.94	15.80
Sulfate	SO ₄	0.471	0.261	0.198	0.132	0.132
Chloride	Cl	3.370	3.73	4.28	4.0	4.32
Fluoride	F	3.727	4.17	4.22	4.21	4.35
Iodide	I	0.090	0.056	0.040	0.032	0.035
Nitrite	NO ₂	1.502	2.28	1.98	1.97	1.98
Nitrate	NO ₃	110.716	116.94	121.52	120.98	122.15
Ammonium	NH ₄	4.728	2.61	2.90	2.367	0.198
Phosphate	PO ₄	0.764	1.16	0.989	1.118	1.093

Aluminum	Al	64.171	59.35	62.87	59.31	60.12
Boron	B	1.284	1.49	1.47	1.46	1.46
Potassium	K	1.180	1.06	1.14	1.14	1.17
Silicon	Si	63.971	70.04	73.28	72.98	67.17
Sodium	Na	50.489	47.89	49.03	49.18	49.78
Silver	Ag	0.083	0.078	0.079	0.079	0.079
Arsenic	As	0.007	0.006	0.005	0.004	0.006
Barium	Ba	0.003	0.056	0.053	0.055	0.054
Cadmium	Cd	0.088	0.091	0.105	0.092	0.092
Chromium	Cr	0.282	0.248	0.244	0.237	0.244
Cesium	Cs	1.751	1.09	1.07	1.08	1.11
Nickel	Ni	0.241	0.241	0.231	0.250	0.250
Lead	Pb	0.244	0.215	0.145	0.171	0.171
Rhenium	Re	0.189	0.156	0.158	0.171	0.158
Antimony	Sb	0.175	0.189	0.198	0.197	0.184
Selenium	Se	0.175	0.193	0.179	0.185	0.198
Thallium	Tl	0.175	0.110	0.114	0.096	0.112
Zinc	Zn	0.428	0.339	0.303	0.329	0.290
Iron	Fe	1.311	0.769	0.699	0.789	0.705
Titanium	Ti	1.983	3.09	3.35	3.31	2.44
Calcium	Ca	0.151	0.143	0.158	0.145	0.125
Magnesium	Mg	0.138	0.208	0.224	0.171	0.211
	Completely reacted with ANN					
	Greater than $\pm 20\%$ of target value.					
	Greater than $\pm 50\%$ of target value.					