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Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Low Activity Waste (Tank SX-105, Tank AN-103, and AZ-101/102) by Fluidized Bed Steam Reformation (FBSR)

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EXECUTIVE SUMMARY

The United States (U.S.) DOE ORP is responsible for the retrieval, treatment, immobilization, and disposal of Hanford's tank waste. A key aspect of the River Protection Project (RPP) cleanup mission is to construct and operate the Hanford Tank 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.

The projected throughput capacity of the WTP LAW Vitrification Facility is insufficient to complete the RPP mission in the time frame required by the Hanford Federal Facility Agreement and Consent Order, also known as the Tri-Party Agreement (TPA), i.e. December 31, 2047. Supplemental Treatment is likely to be required both to meet the TPA treatment requirements as well as to more cost effectively complete the tank waste treatment mission. The Supplemental Treatment chosen will immobilize that portion of the retrieved LAW that is not sent to the WTP's LAW Vitrification Facility into a solidified waste form. The solidified waste will then be disposed on the Hanford site in the Integrated Disposal Facility (IDF).

Fluidized Bed Steam Reforming (FBSR) offers a moderate temperature (700-750°C) continuous method by which LAW feeds can be processed irrespective of whether they contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form. The mineral waste form that is produced by co-processing waste with kaolin clay in an FBSR process has been shown to be comparable to LAW glass, i.e. leaches Tc-99, Re and Na at $<2 g/m^2$ during American Standards and Testing Materials (ASTM) C1285 (Product Consistency Test) durability testing. Monolithing of the granular FBSR product was investigated in previous studies to prevent dispersion during transport or burial/storage. Monolithing in an inorganic geopolymer binder, which is amorphous, macro-encapsulates the granules. The granular waste forms also pass the Environmental Protection Agency EPA TCLP test for all RCRA components at the Universal Treatment Standards (UTS).

Two identical Benchscale Steam Reformers (BSR) were designed and constructed at SRNL, one to treat simulants and the other to treat actual radioactive wastes. The results from the non-radioactive BSR were used to determine the parameters needed to operate the radioactive BSR in order to confirm the findings of non-radioactive FBSR pilot scale and engineering scale tests and to qualify an FBSR LAW waste form for applications at Hanford. Radioactive testing commenced using Savannah River Site (SRS) LAW from Tank 50 chemically trimmed to look like Hanford's blended LAW known as the Rassat simulant as this simulant composition had been tested in the non-radioactive BSR, the non-radioactive pilot scale FBSR at the Science Applications International Corporation-Science and Technology Applications Research (SAIC-STAR) facility in Idaho Falls, ID and in the TTT Engineering Scale Technology Demonstration (ESTD) at Hazen Research Inc. (HRI) in Denver, CO. This provided a "tie back" between radioactive BSR testing and non-radioactive BSR, pilot scale, and engineering scale testing. Approximately six hundred grams each of non-radioactive and radioactive BSR product were made for extensive testing and comparison to the non-radioactive pilot scale tests performed in 2004 at SAIC-STAR and the engineering scale test performed in 2008 at HRI with the Rassat simulant. The same mineral phases and off-gas species were found in the radioactive and non-radioactive testing.

This report contains the results of FBSR testing on simulated and radioactive Hanford LAW samples from tanks SX-105, AN-103, and AZ-101/AZ-102. Radioactive FBSR testing of Hanford-WTP secondary wastes had been designated Module A. Radioactive testing of SRS LAW shimmed to represent the Hanford Rassat 68 tank blend from SRS Tank 50 waste had been designated Module B. The BSR campaigns with Hanford Tank SX-105 were designated Module C and campaigns with Hanford

Tank AN-103 were designated Module D. Initial testing of a Hanford Tank Blend of AZ-101/AZ-102 was designated Module E.

The radioactive Hanford wastes received at SRNL were analyzed so that a surrogate recipe could be developed. During Module B radioactive testing, Re had been determined to be a good surrogate for Tc-99 in the off-gas mass balance and in durability testing. Thus, Module C and D non-radioactive and radioactive wastes were shimmed with Re as a surrogate for Tc-99 in order to provide additional supporting data. The radioactive samples already contained Tc-99 and no additional Tc-99 was shimmed into the wastes except for one sample made especially for Tc speciation by X-ray Absorption Spectroscopy (XAS). The tank waste simulant recipes' were made to perform tests in the SRNL non-radioactive BSR to determine the parameters for the radioactive BSR campaigns.

Due to funding constraints, the AZ-101/AZ-102 testing (Module E) only consisted of analyzing the radioactive waste when received after shimming it with Re in preparation for the radioactive BSR campaigns, developing a recipe for a simulant, shimming the simulant with Re, performing non-radioactive BSR campaigns, and sending the product for TCLP testing. Therefore, this report provides the data collected primarily from Module C and D BSR campaigns and testing. The data collected on Module C, D and E FBSR products are compared to the Module B testing and all of the other non-radioactive testing performed in pilot and engineering scale FBSR's with the Rassat simulant (68 tank Hanford blend) to provide the comparison between simulant and radioactive testing and the comparison between bench-scale, pilot-scale, and engineering scale testing.

Extensive testing and characterization of the granular product material from Modules C (SX-105) and Module D (AN-103) were made including the following (ASTM) tests:

- ASTM C1285 (Product Consistency Test) testing of granular waste forms
    - Comparison of granular BSR radioactive Module C product to Module B ESTD and pilot scale granular non-radioactive and radioactive waste forms made from the Rassat simulant
    - Comparison of granular radioactive to granular non-radioactive waste forms made from the Module C simulants using the SRNL BSR

- EPA Manual SW-846 Method 1311, TCLP
    - Comparison of granular BSR radioactive Module C and D to ESTD and pilot scale granular and monolithic non-radioactive waste forms made from the Rassat simulant
    - Comparison of granular radioactive to granular non-radioactive waste forms made from the Module C and D simulants made using the SRNL BSR
    - Comparison of the granular non-radioactive waste forms made from Modules C, D, and E to each other and to Module B as a function of REDOX

The following was determined from the extensive testing in this study:

- The mass balances of Tc-99, Re, Cs-137/Cs-133, and I-129/I-125/I-127 were determined in the BSR systems (non-radioactive and radioactive).
    - Good mass balance closure was achieved on Tc-99, Re, Cs, I and chloride in the Module C (SX-105) and Module D (AN-103) campaigns. The Module E (AZ-101/AZ-102) simulant consisted of only one run and a mass balance was not performed.
    - Module C- Hanford LAW Tank SX-105
        - 71-98% recovery of Re in the product streams for radioactive and simulant campaigns, respectively

    - 80-83% recovery of Tc-99 for once through processing which is ~2.5X greater retention than LAW glass for once through processing
    - ~75% recovery of I-127 (non-radioactive) and I-129 (radioactive)
    - 78-100% recovery of chloride, radioactive and non-radioactive, respectively
    - ~100% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns
  - Module D – Hanford LAW Tank AN-103
    - 90-95% recovery of Re in simulant runs, 88% recovery in radioactive campaign
    - 83-86% recovery of Tc-99 for once through processing which is ~2.6X greater retention than LAW glass for once through processing
    - 100% recovery of I-127 (non-radioactive) in two simulant campaign and 100% recovery of I-129 (radioactive) in the radioactive campaign
    - 86% recovery of Cl in the simulant campaigns
    - 87% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns

- The data indicates Tc-99, Re, Cs, and I (all isotopes) report preferentially to the mineral product

- Tc-99 and Re show similar behavior in partitioning between the product and off-gas: for mass balance Re is an acceptable simulant for Tc-99

- The FBSR minerals were found to retain Re in the cage structure (~100%) of the granular mineral products and varying percentages of Tc-99 depending on the REDOX conditions

- TCLP data are acceptable when REDOX is >0.30 $Fe^{2+}/\Sigma Fe$ or an iron oxide catalyst (IOC) is present as a spinel host for Cr
  - An IOC algorithm was derived to quantify how much IOC is needed to stabilize chromium in an iron chrome spinel if REDOX is <0.30 $Fe^{2+}/\Sigma Fe$

- The successful processing of AN-103, which contained large amounts of gibbsite ($Al(OH)_3$), demonstrated that precipitates do not have to be removed from LAW before FBSR processing.
  - excess Al is easily accomodated by adjustment of the composition of the clay additive

- ASTM C1285 (Product Consistency Test) testing is below 2 g/m^2 LAW glass leach rate limit for the constituents of concern (COC) by 2 orders of magnitude or 100-200X
  - Use of BET surface area to account for the surface roughness of the mineral granules demonstrates that the FBSR product is 2 orders of magnitude lower than the 2 g/m^2 LAW glass leach rate limit
  - Use of the geometric surface area, which ignores the surface roughness of the mineral granules and assumes the granules are hard spheres which is incorrect, gives an equivalent leach rate to LAW vitreous waste forms
  - All the durability results from SX-105 (Module C non-radioactive and radioactive) are in agreement with the data from the SRS LAW BSR testing (non-radioactive and radioactive) and the ESTD testing in 2008 and pilot scale testing from 2001 and 2004
  - Re is a good surrogate for Tc-99 during leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only
  - An aluminum buffering mechanism appears to control the leachate pH and all other element releases are released as function of solution pH for all radioactive and non-radioactive LAW wastes tested

  - The pH dependence is the same conclusions reached by SPFT and PUF testing of the Rassat FBSR ESTD and BSR products in other studies

- Long term testing (1, 3, 6 month and/or 1 year) at 90°C by ASTM C1285 of Module C (SX-105) non-radioactive and radioactive granular product has not shown any significant change in the mineral assemblages as analyzed by X-Ray Diffraction (XRD)
  - Silica concentrations in solution are decreasing with time indicating solution supersaturation: reaction products would have formed when the solution saturates or supersaturates if they were going to form.
  - Re is a good surrogate for Tc-99 during long term leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only

Coupling the results of this study with previous radioactive BSR studies demonstrates that when anions such as Cl, F, and I are present or oxyanions such as TcO_4^- or ReO_4^-, more sodalite forms. If more $SO_4^=$ is present the sodalite structured phase nosean forms. If anions, $SO_4^=$, Re and Tc are low, then less sodalite/nosean forms and more nepheline forms. Cs and K can be accommodated in either nepheline or sodalite where they substitute for Na.

Theoretically, a pure sodium chloride waste stream would make a chloride sodalite and could accommodate 12.06 wt.% NaCl or 7.32 wt.% Cl. A pure iodide waste stream in sodalite could accommodate 22.03 wt.% I and a pure fluoride sodalite could accommodate 4.06 wt.% F. A pure sodium sulfate waste stream could accommodate up to 9.90 wt.% SO_4 or 14.65 wt.% as Na_2SO_4 in nosean. Likewise the Re and Tc sodalites can accommodate 25.22 wt.% Re or 15.20 wt.% Tc-99, respectively. Note that in the Module A WTP-SW FBSR study that 0.89 wt.% F was accommodated in the fluoride sodalite of the theoretical 4.06 wt.% F meaning that ~22 w.t% of the waste form was a fluoride sodalite. In the simulant Module E studies, 2.18 wt.% $SO_4^=$ was accommodated in the nosean or ~22 wt.% of the theoretical $SO_4^=$ that could have been accommodated. The chemistry of the wastes that were tested, were relatively low in I, Cl, and Tc-99. Based on the mass balances reported in this study 85-100% of these species were retained in the FBSR minerals. The high mineral retentions mean that the following anion or oxyanion mineral incorporations were achieved which are well below the theoretical mineral retentions shown in the last column:

Anion or Oxyanion	**WTP-SW Radioactive**	**Hanford 68 Tank Blend Radioactive**	**LAW Tank SX-105 Radioactive**	**LAW Tank AN-103 Radioactive**	**LAW Tank AZ-101 /AZ-102 Simulant**	**Theoretical Pure Anion Stream**
	Wt.%	**Wt.%**	**Wt.%**	**Wt.%**	**Wt.%**	**Wt.%**
F^-	0.89	0.05	Below Detection Level	0.02	0.07	4.06
Cl^-	0.87	0.27	0.33	0.30	0.16	7.32
I^-	3.68E-03	0.25	5.61E-05	8.21E-05	0.21	22.03
$SO_4^=$	0.16	1.12	0.66	0.12	2.18	9.90
Tc^{+7}	2.13E-03	8.57E-05	5.33E-08	2.77E-04	non radioactive	15.20
Re^{+7}	0.05	0.04	0.05	0.04	0.04	25.22

The anion and oxyanion concentrations that can be accommodated in the sodalite/nosean mineral waste form are 10-20X what can be accommodated in LAW glass at equivalent Na_2O wt.% waste loadings. After monolithing the 10-20X factor decreases by ~33% (100%-67% FBSR loading per monolith) and that still provides a 6.6-13.2X higher solubility for anions and oxyanions in FBSR LAW at moderate temperatures that do not volatilize these anions and oxyanions or create the need for complex recycle loops during processing during LAW vitrification.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

ART	Advanced Remediation Technologies
AD	Analytic Development
ANS	American Nuclear Society
ANSI	American National Standard Institute, Inc.
ASTM	American Society for Testing and Materials
AR	Aqua Regia
BB	Berger Brothers
BDL	Below Detection Limit
BET-SA	Brunauer-Emmett-Teller – Surface Area
BSR	Benchscale Steam Reformer
CWF	Ceramic Waste Form
COC	Constituents of Concern
CRR	Carbon Reduction Reformer
CSEM	Contained Scanning Electron Microscopy
DWPF	Defense Waste Processing Facility
DMR	Denitration and Mineralization Reactor
DOE	Department of Energy
DOE-EM	Department of Energy-Environmental Managment
DQO	Data Quality Objectives
EA	Environmental Assessment
EBR	Experimental Breeder Reactor
EPA	Environmental Protection Agency
ESTD	Engineering Scale Technology Demonstration
FBSR	Fluidized Bed Steam Reformer
GEL	General Engineering Laboratory
HIC	High Integrity Container
HRI	Hazen Research Inc
HLW	High Level Waste
HTF	High Temperature Filter
HTWOS	Hanford Tank Waste Operations Simulator
IC	Ion Chromotography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
IDF	Integrated Disposal Facility
IEWO	Inter-Entity Work Order
INL	Idaho National Laboratory
IHLW	Immobilized HLW
ILAW	Immobilized LAW
IOC	Iron Oxide Catalyst
IC	Ion Chromatography
inwc	inches of water column
KAPL	Knolls Atomic Power Laboratory
LDR	Land Disposal Restrictions
LAW	Low-Activity Waste
LI	Leach Index
LLW	Low Level Waste
LOD	Loss on Drying
LOI	Loss on Ignition

MDL	Method Detection Limit
MFC	Materials and Fuels Complex
MS	Mass Spectrometer
NAS	Na-Al-Si
NQA	Nuclear Quality Assurance
NRC	Nuclear Regulatory Commission
OPC	Ordinary Portland Cement
ORNL	Oak Ridge National Laboratory
ORP	Office of River Protection
PA	Performance Assessment
PC	Personal Computer
PCT	Product Consistency Test
PDF	Powder Diffraction File
PF	Peroxide Fusion
PID	Pressure Indicating Device
PNNL	Pacific Northwest National Laboratory
PSD	Particle Size Distribution
PUF	Pressurized Unsaturated Flow
QAP	Quality Assurance Program
RA	Risk Assessment
REDOX	REDuction/OXidation
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
RPP	River Protection Project
SBW	Sodium Bearing Waste
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SEM	Scanning Electron Microscopy
SAIC	Science Applications International Corporation
STAR	Science and Technology Applications Research
sccm	standard cubic centimeters per minute
SCF	Shielded Cells Facility
SCO	Shielded Cells Operations
SPFT	Single Pass Flow Through
SST	Single Shell Tank
TCLP	Toxicity Characteristic Leaching Procedure
TDD	Technology Development & Deployment
TIC	Total Inorganic Carbon
TT&QAP	Technical Task & Quality Assurance Plan
TTT	THOR® Treatment Technologies
THOR®	THermal Organic Reduction
TPA	Tri-Party Agreement
US	United States
USGS	United States Geological Survey
UTS	Universal Treatment Standards
VHT	Vapor Hydration Tests
VSL	Vitreous State Laboratory
WFO	Work-for-Others
WAC	Waste Acceptance Criteria
WAPS	Waste Acceptance Product Specifications
WCP	Waste Compliance Plan

WIPP	Waste Isolation Pilot Plant
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WTP-SW	Waste Treatment Plant Secondary Waste
XAFS	X-ray Absorption Fine Structure
XAS	X-Ray Absorption Spectroscopy
XRD	X-Ray Diffraction

1.0 Introduction

The Hanford Site in southeast Washington State has 56 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks [1]. The U.S. DOE ORP, through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. The pretreated HLW mixture will be sent to the HLW Vitrification Facility, and the pretreated LAW stream will be sent to the LAW Vitrification Facility. The two WTP vitrification facilities will convert these process streams into glass, which is poured directly into stainless steel canisters. The immobilized HLW (IHLW) canisters will ultimately be disposed of at an offsite federal repository. The immobilized LAW (ILAW) canisters will be disposed of onsite in the Integrated Disposal Facility (IDF).

The projected throughput capacity of the WTP LAW Vitrification Facility is insufficient to complete the RPP mission in the time frame required by the Hanford Federal Facility Agreement and Consent Order, also known as the Tri-Party Agreement (TPA). The milestone date for the TPA is December 31, 2047 and without additional LAW treatment capacity, the mission would extend to 2070.[2] With additional treatment and acceleration the milestone will be met by 2047 and in 2002 the milstone was predicted to be met as early as 2028.[2] The life-cycle cost of tank waste cleanup is strongly influenced by the WTP operating duration. Each year the WTP operates beyond 2047 will cost billions of dollars more than disposition before 2047 due to inflation. Therefore, a significant life-cycle cost savings incentive exists to complete tank waste treatment processing at the earliest practical date.

Therefore, Supplemental Treatment is required both to meet the Tri-Party Agreement treatment requirements as well as to more cost effectively complete the tank waste treatment mission. The Supplemental Treatment Project will design, construct and operate the processes and facilities required to treat and immobilize into a solidified waste form that portion of the retrieved LAW that is not sent to the WTP's LAW Vitrification Facility. The solidified waste will then be disposed on-site in the IDF.

Four immobilization technologies are under consideration as part of the Supplemental Treatment Program including:

- second WTP LAW vitrification
- bulk vitrification
- cementitious solidification (cast stone)
- fluidized bed steam reforming (FBSR).

The DOE has made substantial past investments in evaluating each of the proposed vitrification processes (i.e., WTP LAW and bulk vitrification) and cementitious solidification processes at Hanford. Additionally, numerous other sites within the DOE complex have examined the performance of cementitious solidification of LAW for a number of years. DOE has made some but not sufficient investments to date in the FBSR process to produce a monolithic, mineralized waste form for Hanford LAW immobilization. This study is, therefore, focused on collecting the essential data required to objectively evaluate the FBSR waste form as a LAW immobilization alternative to the other technologies.

FBSR offers a moderate temperature (700-750°C) continuous method by which LAW and/or WTP Secondary Wastes (WTP-SW) can be processed. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form that is granular. The granular mineralized waste form that is produced by co-processing waste with kaolin clay in an FBSR process has been shown to be comparable to LAW glass (see multiple durability references given in Table 1-3). Monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage. Considerable durability testing has been performed by SRNL and the Pacific Northwest National Laboratory (PNNL): see Section 1.3 and Reference 3 for a summary of the work already performed and currently in progress including tests to demonstrate the waste form will meet preliminary waste acceptance criteria for the Hanford IDF.

1.1 Mineral Waste Forms

Crystalline (ceramic/mineral) waste forms made by moderate temperature (700-750°C) thermal treatment have not been as intensely investigated as those formed at high temperatures (1000-1500°C) by pressing and sintering (SYNROC, supercalcine ceramics, tailored ceramics, and Pu ceramics) [4]. However, crystalline waste forms made from clay have been studied almost continuously since 1953 [4,5]. Often the high temperatures used for sintering created sodalite-cancrinite mineral assemblages. In 1981, Roy [6] proposed "low-temperature", "hydrothermally processed", "low solubility" phase assemblages consisting of the micas, apatite, pollucite, sodalite-cancrinite, and nepheline, many of which could be made from reaction of various clays (kaolin, bentonite, illite) with waste.

Clay based crystalline (ceramic/mineral) waste forms were not pursued in the late 1970's and early 1980's because there was no continuous commercial technology available that could process the waste/clay mixtures in a hydrothermal environment [4]. A commercial facility to continuously process radioactive wastes at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee in 1999 [7,8]. The Erwin facility uses a steam reforming technology designated as the THermal Organic Reduction (THOR®) process to pyrolyze Cs-137 and Co-60 bearing organic ion-exchange resins from commercial nuclear facilities. The Erwin facility has the capability to process a wide variety of solid and liquid streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions and has treated these types of waste at radiation levels of up to 400R/hr.

If kaolin clay is added to an alkali-rich waste during FBSR processing, a "mineralized" waste form is produced that is composed of various Na-Al-Si (NAS) feldspathoid minerals discussed above, i.e. sodalites are the potential host minerals for the halides; nosean which has a larger cage structure is the host mineral for sulfate or sulfide species, Re and Tc-99; and nepheline sequesters the remaining alkali by nanoscale reaction of the clay and waste. Bench scale, pilot scale, and engineering scale tests have all formed this mineral assemblage with a variety of legacy U.S. DOE waste simulants. Illite type clay was tested at the bench scale and was shown to form dehyroxylated micas (potential host for nuclear fuel recycling wastes including lanthanides, Cs, Sr, Ba, Rb, Tl, etc.) by similar nanoscale reaction of clay and waste [9].

The fluidizing steam used in FBSR processing creates a hydrothermal environment which promotes mineral formation. Clays become amorphous at the nanoscale at the FBSR processing temperatures (700-750°C) because clays lose their hydroxyl groups between 550-750°C, which destabilizes the Al atoms in their structure. Once the Al cation is destabilized, the clay becomes amorphous and species in the waste "activate" the unstable Al cation to form new mineral structures. The hydrothermal environment created by the steam and the nanoscale reactivity of the clay catalyze mineralization allowing formation and templating at moderate temperatures. Kaolin clay has been found to template the feldspathoids and the illite clays have been found to template the dehydroxylated micas as radionuclide hosts [9]. Additional iron bearing co-reactants can be added during processing to stabilize any multivalent hazardous species present in a waste in durable spinel phases, i.e. Cr, Ni, Pb iron oxide minerals.

The NAS mineral waste forms are comprised of nepheline (hexagonal $Na_xAl_ySi_zO_4$ where x, y, and z nominally each are a value of 1) and other feldspathoid mineral phases that have large cages which trap anion constituents such as Na_2SO_4 (nosean), NaF, NaI, NaCl (sodalite nominally $Na_8[Al_6Si_6O_{24}](Cl_2)$ where Na_2MnO_4, Na_2MoO_4, Na_2TcO_4, Na_2ReO_4 can all substitute in the cage structure for 2NaCl or

$1Na_2SO_4$). The feldspathoid mineral nepheline has a ring type structure. A second nepheline phase that has been found is a sodium rich cubic derivative, $(Na_2O)_{0.33}NaAlSiO_4$,[f] with large twelve-fold oxygen cage like voids [10]. Nepheline also accommodates Cs, Sr, Ti, and Ca (Table 1-1).

The NAS cage structures are typical of sodalite and/or nosean phases where the cavities in the cage structure bond oxyanions and/or radionuclides to the alumino-silicate tetrahedra and to sodium in the mineral structure. The sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn (Table 1-1). These cage-structured sodalites were minor phases in HLW supercalcine waste forms[i] and were found to retain Cs, Sr, and Mo into the cage-like structure as indicated in Table 1-1. In addition, sodalite structures are known to retain B [11,12] and Ge [13] in the cage like structures. Waste stabilization at the Materials and Fuels Complex (MFC) operated by Battelle Energy Alliance at Idaho National Laboratory (INL) currently uses a glass-bonded sodalite ceramic waste form (CWF) for containment of I from electrorefiner wastes from the Experimental Breeder Reactor (EBR) II fast breeder reactor [14,15]. Researchers' at Hanford had also researched and patented a process for stabilizing alkali metal iodides or aqueous solutions into alkali sodalites for applications at Hanford.[16]

Table 1-1. Substitutional Cations and Oxy-anions in Feldspathoid Mineral Structures

Nepheline – Kalsilite Structures*	Sodalite Structures**	Nosean Structures
$Na_xAl_ySi_zO_4$ [22] *where x=1-1.33, y and z = 0.55-1.1*	$[Na_6Al_6Si_6O_{24}](NaCl)_2$ [22]	$[Na_6Al_6Si_6O_{24}](Na_2SO_4)$ [18,22]
$KAlSiO_4$[22]	$[Na_6Al_6Si_6O_{24}](NaFl)_2$ [22]	$[Na_6Al_6Si_6O_{24}](Na_2MoO_4)$ [17,22]
$K_{0.25}Na_{0.75}AlSiO_4$[22]	$[Na_6Al_6Si_6O_{24}](NaI)_2$ [18]	$[Na_6Al_6Si_6O_{24}]((Ca,Na)SO_4)_{1-2}$ [19]
$(Na_2O)_{0.33}NaAlSiO_4$ [10]	$[Na_6Al_6Si_6O_{24}](NaBr)_2$ [18]	$[(Ca,Na)_6Al_6Si_6O_{24}]((Ca,Na)S,SO_{4,}Cl)_x$ [PDF[f] #17-749]
$CsAlSiO_4$ [22]	$[Na_6Al_6Si_6O_{24}](NaReO_4)_2$ [20]	
$RbAlSiO_4$ [22]	$[Na_6Al_6Si_6O_{24}](NaMnO_4)_2$ [21]	
$(Ca_{0.5},Sr_{0.5)}AlSiO_4$ [22]	$[NaAlSiO_4]_6(NaBO_4)_2$ [11,12]	
$(Sr,Ba)Al_2O_4$ [22]	$Mn_4[Be_3Si_3O_{12}]S$ [18]	
$KFeSiO_4$ [22]	$Fe_4[Be_3Si_3O_{12}]S$ [18]	
$(Na,Ca_{0.5})YSiO_4$ [21]	$Zn_4[Be_3Si_3O_{12}]S$ [18]	
$(Na,K)LaSiO_4$[21]		
$(Na,K,Ca_{0.5})NdSiO_4$[21]		

Iron, Ti^{3+}, Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in nepheline.[22]

** Higher valent anionic groups such as AsO_4^{3-} and CrO_4^{2-} form Na_2XO_4 groups in the cage structure where X= Cr, Se, W, P, V, and As [21]

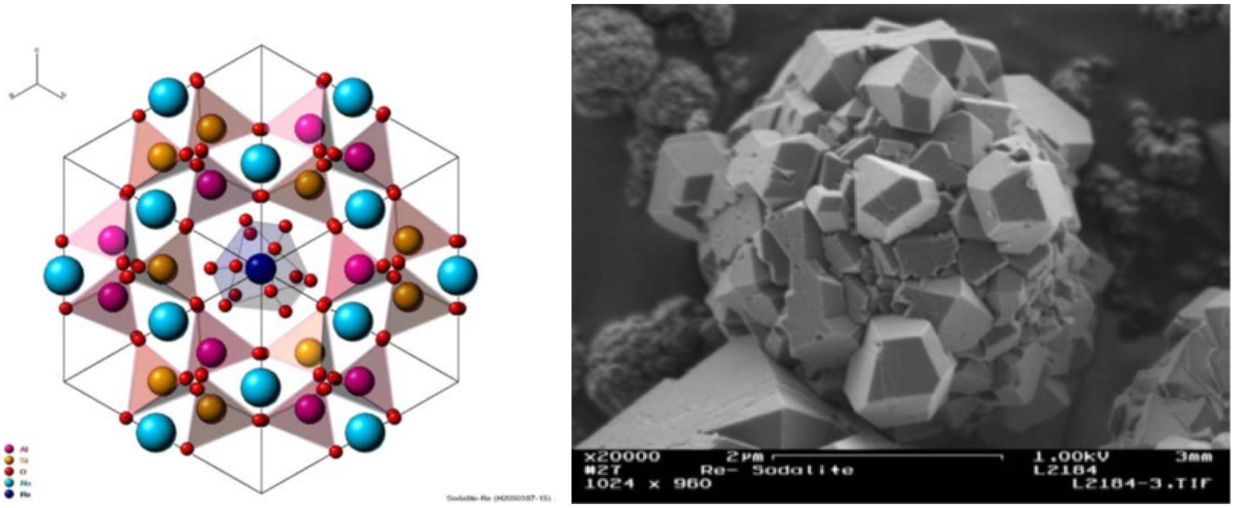
The sodalites are classified [23] as "clathrasils", which are structures with large polyhedral cavities where the "windows" in the cavity are too small atomically to allow the encaged polyatomic ions and/or molecules to pass through once the structure is formed - see the structure for the Re-sodalite from reference 20 for more detail. They differ from zeolites in that the zeolites have tunnels or larger polyhedral cavities interconnected by windows large enough to allow diffusion of the guest species

---

[f] Powder Diffraction File (PDF)

[i] Supercalcines were the high temperature silicate based "mineral" assemblages proposed for HLW waste stabilization in the United States (1973-1985).

through the crystal.[23] The sodalite cage structure usually has alternating Si and Al tetrahedra with equal numbers of each that bond to form the cage. If there are more Al tetrahedra and fewer Si tetrahedra or vice versa they are all treated as solid solutions with the same cavity structures.[23]



(a) (b)

Figure 1-1. Structure of a Re-sodalite (left) and a scanning electron microscope image of the same Re sodalite [20].

1.2 FBSR Technology

The commercialization of the FBSR technology at the Erwin, Tennessee facility has created interest in this technology for the immobilization of a wide variety of radioactive wastes across the US DOE complex. Of special relevance is the capability of the FBSR technology to destroy organics while converting alkali/alkaline earth/rare earth salts to aluminosilicate minerals that are suitable for direct geological disposal and/or to carbonate or silicate species for subsequent vitrification or disposal.

An FBSR facility has been designed and constructed at the INL for treatment of their Sodium Bearing Waste (SBW) for potential disposal in the Waste Isolation Pilot Plant (WIPP) (Table 1-3). Another facility was considered for use at the Savannah River Site (SRS) to convert a salt supernate waste (Tank 48) containing nitrates, nitrites, and insoluble cesium tetraphenyl borate (CsTPB), to carbonate or silicate minerals which are compatible with subsequent vitrification in the Defense Waste Processing Facility (DWPF) [24,25].

The FBSR technology uses reformers to pyrolyze organics in the presence of a fluidization media of steam. FBSR's can be externally heated or internally heated or a combination of the two heating methods. Externally heated FBSR's are normally limited to a diameter in the 6-8" range while coal or another reductant can be used to assist in the denitration reactions. Coal is also used to auto-thermally heat larger reformers (24" diameter) via the water-gas shift reaction which produced H_2. Then small amounts of O_2 are bled in to complex the excess H_2 and that reaction is exothermic and creates heat. FBSR flowsheets can be single reformer or dual reformer. A dual reformer is only necessary if high boiling organics are present in a waste as the second reformer usually runs at higher temperatures and is more oxidizing than the first reformer. In TTT's dual reformer flowsheet, the 1st reformer is called the "Denitration and Mineralizing Reactor" or DMR, while the second reformer is called the "Carbon Reduction Reformer" or

CRR. Reformers can be vertical or horizontal in design but all the FBSR's used for testing in this study and the related studies were vertical. Sometimes an iron oxide in the form of an Iron Oxide Catalyst (IOC) is used to facilitate the denitration and organic destruction and provide an iron spinel mineral host to stabilize the chrome as iron chrome spinel.

During 2001-2002, there was a pilot scale FBSR at HRI used for TTT's demonstrations of Hanford's AN-107 simulant. This pilot scale facility was an externally heated 6" diameter FBSR but coal was also used to auto-thermally heat the reformer (Table 1-2 and Table 1-3). An IOC was used during these pilot scale tests. References are given in Table 1-3.

During the 2003-2004 FBSR testing at the SAIC-STAR facility in Idaho, an externally heated 6" diameter FBSR pilot scale facility was used to test INL's SBW and the Hanford Rassat simulant. The Hanford non-radioactive LAW simulant known as the Rassat simulant represents a 68 tank blend of dissolved salt cake from Hanford single shell tanks (SSTs).[26] Berger Brothers (BB) charcoal was used as the reductant for denitration at the SAIC-STAR facility for these tests. No catalyst was used (Table 1-2 and Table 1-3). Both these 6" pilot-scale reformers were single DMR type reformers (Table 1-2 and Table 1-3). References are given in Table 1-3.

During the 2006-2008 FBSR engineering scale testing by TTT at HRI in the 15" dual reformer, auto-thermal heating was used and Bestac coal was the reductant of choice for heating and denitration (Table 1-2 and Table 1-3). The 15" dual flowsheet was used to test the WTP-SW and the Rassat 68 tank blend. [26] The WTP-SW simulant was based on melter off-gas condensate analyses from Vitreous State Laboratory (VSL) (Table 1-2 and Table 1-3). The IOC catalyst was used in the WTP-SW and Rassat simulant tests in the ESTD. References are given in Table 1-3

Since the SRNL BSR was built to duplicate the 15" TTT dual reformer flowsheet, a dual reformer was designed for both the non-radioactive and radioactive units but the CRR was not used unless a waste contained high organics. Testing was performed with and without a catalyst as noted in this report. The same coal, BB, was used in the BSR as in the SAIC-STAR pilot scale and the TTT/HRI engineering scale testing. The BSR tested radioactive and non-radioactive WTP-SW where the radioactive WTP-SW was made from radioactive melter off-gas condensates from the SRS DWPF.[27] Additional testing with the radioactive and non-radioactive Rassat 68 tank blend are reported elsewhere [28] and discussed in this report to complete comparisons across LAW waste types. The primary focus of this report is the demonstrations with Hanford radioactive and non-radioactive LAW compositions from Tank SX-105 and Tank AN-103 and the preparations made to process a blend of AZ-101/AZ-102 before funding issues precluded processing of this tank waste blend.

Table 1-2. Comparison of Pilot-scale, Engineering-scale, and Bench-scale FBSR's

Facility/ Reformer	Column Diameter	Externally or Internally Heated?	Dual or Single Reformer Flowsheet?	Reductant of Choice	Catalyst?	Waste
TTT 2001-2002	6"	External and with Coal	Single	BB charcoal	Yes	AN-107
SAIC-STAR 2003-2004	6"	External and with Coal	Single	BB charcoal	No	SBW
						Rassat
TTT ESTD 2006-2008	15"	Internal	Dual	Bestac coal	Yes	WTP-SW
						Rassat
SRNL BSR (non-radioactive and radioactive)	2.75"	External and with Coal	Dual	Bestac coal	Some tests	WTP-SW
						Rassat
						SX-105
						AN-103
						AZ-101/ AZ-102 (Simulant Only)

Table 1-3 provides a summary of the references to the various Hanford LAW and INL SBW FBSR tests and the subsequent studies which characterized the granular products and tested the granular waste form performance using various durability tests such as ASTM C1285 (Product Consistency Test) and ASTM C1662 (Single Pass Flow Through Test; SPFT). In addition, Table 1-3 provides similar references for Hanford's melter recycle WTP-SW wastes stabilized by FBSR and data on monoliths produced with WTP-SW and LAW. Table 1-3 also provides the references that compare the results of durability tests with and without the coal fraction of the FBSR product removed.

For the engineering tests with WTP-SW and the Rassat simulant, it should be noted that the target concentrations for the Resource Conservation and Recovery Act (RCRA) metals in the Rassat simulant and Cs were increased anywhere from 10X to 1297X to be detectable in the product durability testing and the off-gas analyses. Therefore, the identified metals concentrations were increased by TTT at HRI to ensure detection and enable calculation of system removal efficiencies, product retention efficiencies, and mass balance closure without regard to potential results of those determinations or impacts on product durability response such as the Toxicity Characteristic Leaching Procedure (TCLP).[29] This will be discussed in Section 2 in more detail.

The engineering scale technology demonstration (ESTD) product characterization simulant testing is reported in Reference 30 and summarized in Table 1-3. Prior to the Reference 30 studies, the FBSR bed products and fines had been studied independently to determine the leaching mechanisms and appropriate leach tests to perform. In Reference 30, the FBSR bed products were studied separately and together: it was shown that the mineral phases observed in the high temperature filter (HTF) fines are the same as the mineral phases in the FBSR bed products and have comparable durability. The combined FBSR bed products and fines from the two ESTD campaigns were monolithed in a geopolymer formulation (GEO-7) made from fly ash, sodium silicate, and NaOH, which was chosen from a downselect of different matrices including cements (Portland and 3 high alumina types), Ceramicrete, hydroceramics, and various geopolymers made from kaolin clays.[31,32,33] The durability of the monolithed FBSR waste forms were then compared to the granular product responses.[33]

Table 1-3. Sources of FBSR Granular/Monolith Product Durability Testing

Pilot Scale Facility	Date	FBSR Diam.	Acidic and Basic Wastes	Gran. PCT Testing	TCLP of Gran. Form	Gran. SPFT Testing	Preliminary Risk Assessment	Product Tested	Coal	Particle Size Distribution (PSD)	Monolith	Mono. PCT Testing	Mono. SPFT Testing	Mono. ANSI/ANS 16.1/ ASTM C1308 Testing	TCLP of Mono. Form
Non-Radioactive Testing															
HRI/ TTT	12/01 Ref 34	6”	LAW Env. C	Ref. 35	Ref 34,35	Ref 36, 37 and PUF testing 38)	Ref. 39	Bed	Removed By Hand	Gaussian	No	N/A			
		6”	LAW Env. C	Ref 40,41,42		None	“Tie-back” Strategy	Fines	Removed by 525°C Roasting						
SAIC/ STAR	7/03 Ref 43	6”	SBW			None	None	Bed			Yes (Samples were combined; 20% LAW, 32 % SBW and 45% Startup Bed	Ref 31,32	N/A		
SAIC/ STAR	8/04 Ref. 44	6”	LAW Rassat			Ref 42,45,46 and PUF 47	Data from Ref 42,45,46 “Tie-back” Strategy	Bed and Fines Separate							
SAIC/ STAR	7/04 and 11/04 Ref. 48	6”	SBW			Ref 42,45	None								
HRI/ TTT	12/06	15”	SBW	Ref 49		None	None				No	N/A			
HRI/ TTT	2008 Ref. 29		LAW Rassat	Ref 30, 33,50, 51,52	Ref 33,50, 51,52	53	“Tie-back” Strategy	Bed and Fines Together	Not removed	Bi-Modal	Yes	Ref 33	PNNL	28	
			WTP-SW			None	None						None	Ref 27,54	33,50, 51,52
Radioactive Testing															
SRNL/ BSR	2010-2011	2.75”	LAW Rassat	28, 52,55		53	“Tie-back” Strategy	Bed and Fines Together	Not removed	Gaussian	Yes	28	PNNL	28	
			WTP-SW	27,52,55		None	None					27	None	27	27

PCT – product consistency test method (ASTM C1285-08); SPFT – single pass flow-through test method (ASTM C1662); ANSI/ANS16.1/ASTM C1308/EPA 1315 – monolith emersion tests all similar with different leachate replenishment intervals; Pressure Unsaturated Flow Test (PUF); -LAW Env. – low activity waste envelope A, B, and C; PSD - particle size distribution; FY11 – Joint program between SRNL, PNNL, ORNL; PNNL Test Results are complete and being documented; N/A – not applicable.

The Module B simulant and radioactive LAW BSR testing [28] and the ESTD simulant tests [29], including characterization, monolithing, and durability testing [29,30,33], formed the basis for performing the comparative studies on the SX-105, AN-107 and AZ-101/AZ-102 radioactive LAW waste streams (Table 1-7).

1.3 Performance Assessment Testing

1.3.1 *Durability Requirements*

For HLW, Waste Acceptance Product Specifications (WAPS) [56] and a Waste Compliance Plan (WCP) [57] were developed for the waste form to ensure the acceptance of the product to the federal geologic repository. Similar durability requirements were developed for LAW glass at Hanford which are delineated in Specification 2 of the WTP contract.[58] The WAPS and extensive characterization of the borosilicate glass both before and after production began was required. In order to satisfy the WAPS and WCP product consistency requirement, a leach test was needed which could reliably and easily provide rapid confirmation of the consistency of the glass being produced.

The WAPS specifications most relevant to public health and safety are those relating to release of radionuclides. WAPS Specification 1.3 relates to the ability of the vitrification process to consistently control the final waste form durability, i.e., the stability of the glass against attack by water:

> 1.3 Specification for Product Consistency
> “The producer shall demonstrate control of waste form production by comparing, either directly or indirectly, production samples to the Environmental Assessment (EA) benchmark glass [59].”
>
> 1.3.1 Acceptance Criteria
> “The consistency of the waste form shall be demonstrated using the Product Consistency Test (PCT).† For acceptance, the mean concentrations of lithium, sodium and boron in the leachate, after normalizing for the concentrations in the glass, shall each be less than those of the benchmark glass described in the Environmental Assessment for selection of the Defense Waste Processing Facility (DWPF) waste form [60]…One acceptable method of demonstrating that the acceptance criterion is met, would be to ensure that the mean PCT results for each waste type are at least two standard deviations below the mean PCT results of the [standard] EA glass.”

Lithium, sodium, and boron releases were monitored as nonradioactive indicator(s) that were similar or identical to the maximum radionuclide releases expected for HLW glass because many of the radionuclides were present at concentrations as low as 10^{-8} weight % and thus difficult to measure. For example, in high level borosilicate waste glass, Tc-99, present at ~4.1 x 10^{-4} wt. % in the waste form, has been shown to be released at the same maximum normalized concentration as boron, lithium, and sodium.[61,62,63,64,65,66,67,68,69] Tc-99 is the radionuclide released

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† C.M. Jantzen, N.E. Bibler, D.C. Beam, W.G. Ramsey, and B.J. Waters. “Nuclear Waste Product Consistency Test Method Version 5.0,” U.S. DOE Report WSRC-TR-90-539, Rev. 2 (January 1992).

from HLW at a rate higher than all the other radionuclides. Therefore, for borosilicate glass waste forms, the leachates are routinely analyzed for boron, lithium, and sodium if these elements are present at > 1 mass % in the glass as an indicator of the maximum radionuclide release, i.e., the Tc-99 release, which has been shown to leach congruently with B, Li, and Na.

While relating Tc-99 release to Na, Li, B release for a material that leaches congruently[‡] is an acceptable practice once the congruent relationship among these elements has been established, this has to be done for each phase present in a glass-ceramic or mineral waste form because each phase leaches at a different rate, i.e., the multiphase waste form leaches incongruently.[†] For multiphase materials like glass-ceramics and mineral waste forms, the most important elements to be analyzed in the leachate are those that represent the maximum dissolution of the radionuclides from the waste form. Elements that are not sequestered in precipitates that participate in surface alteration reactions, and elements that are not solubility limited are good indicators of waste form durability. In the case of a multi-phase glass or mineral waste form, it may be important to analyze for elements from each significant phase present as these waste forms leach incongruently. Extensive testing [61-69] of any glass or glass ceramic waste form must be performed in order to determine what these elements are unless the radionuclide release (or surrogate radionuclide release) is measured which is what has been done in this study, i.e. either Re or Tc-99 release has been measured.

The use of the PCT test protocol for HLW vitrified waste was applied at Hanford for testing the consistency of both the Hanford HLW vitrified waste and the immobilized LAW waste form.[70] The PCT is used to determine the waste form leaching and durability in conjunction with ANSI/ANS-16.1 [71] and the PCT is used for determining waste form stability.[70] The Hanford contract [72] and the ILAW Product Compliance Plan specify the following:

> “The normalized mass loss of sodium, silicon, and boron shall be measured using a seven day product consistency test run at 90°C as defined in ASTM C1285. The test shall be conducted with a glass to water ratio of 1 gram of glass (-100 +200 mesh) per 10 milliliters of water. The normalized mass loss shall be less than 2.0 grams/m^2. Qualification testing shall include glass samples subjected to representative waste form cooling curves. The product consistency test shall be conducted on waste form samples that are statistically representative of the production glass.”

In addition, the Hanford contract [72] requires durability testing for LAW glass by the Vapor Hydration Test (VHT) [73] as follows:

> “The glass corrosion rate shall be measured using at least a seven day vapor hydration test run at 200°C as defined in the DOE concurred upon ILAW Product Compliance Plan. The measured glass alteration rate shall be less than 50

[‡] Congruent dissolution of a waste form, like glass, is the dissolving of species in their stoichiometric amounts. For congruent dissolution, the rate of release of a radionuclide from the waste form is proportional to both the dissolution rate of the waste form and the relative abundance of the radionuclide in the waste form. Thus, for borosilicate glass, Tc-99 has been shown to be released at the same rate, congruently, as Na, Li and B.

[†] Incongruent dissolution of a waste form means that some of the dissolving species are released preferentially compared to others. Incongruent dissolution is often diffusion-controlled and can be either surface reaction-limited under conditions of near saturation or mass transport-controlled. Preferential phase dissolution, ion-exchange reactions, grain-boundary dissolution, and dissolution-reaction product formation (surface crystallization and recrystallization) are among the more likely mechanism of incongruent dissolution, which will prevail, in a complex polyphase ceramic waste form.

> grams/(m^2 day). Qualification testing shall include glass samples subjected to representative waste form cooling curves. The vapor hydration test shall be conducted on waste form samples that are representative of the production glass."

Because the VHT test interpretation for waste forms other than glass has not been investigated and the results of this test are used solely for engineering calculations of contaminant release, [70] the PCT durability test was used in this study as the screening test for the FBSR granular and monolith products.

1.3.2 *Durability Testing and Preliminary Risk Assessment*

All of the PCT testing on various FBSR LAW products is summarized in Table 1-3. The granular waste form must meet the Hanford performance standard of <2g/m^2 release during ASTM C1285 (PCT) testing. This performance standard is applied to Na in glass waste forms since Na has been shown to be released at similar rates as Tc-99 as discussed in Section 1.3.1. Since Re release, as a substitute for Tc-99, does not track Na release in the mineral product, it is the Re release that must meet the 2g/m^2 limit during PCT testing. The references cited in Table 1-3 confirm that the LAW FBSR releases are <2g/m^2 Re and radioactive testing in this report supports this conclusion for Tc-99 as well (see Section 5.5).

In addition, SPFT testing was conducted on several FBSR LAW products and the results were used to perform a preliminary Risk Assessment (RA). The NAS waste form is primarily composed of nepheline (ideally $NaAlSiO_4$) and the sodalite family of minerals (ideally $Na_8[AlSiO_4]_6(Cl)_2$, which includes nosean (ideally $Na_8[AlSiO_4]_6SO_4$). Oxyanions such as ReO_4^- and TcO_4^-, have been found to replace sulfate in the larger cage structured nosean.[20, 74] Halides such as I^- and F^- are known to replace chlorine in the nosean-sodalite mineral structures (see Table 1-1) – immobilizing them. The release of radionuclides Tc-99 and I-129 from granular NAS waste forms was hypothesized during the preliminary RA to be limited by nosean solubility as the rhenium releases during durability testing tracked the sulfate releases.[36,37,39] The predicted performance of the granular NAS waste form was found to be comparable to the glass waste form in the initial supplemental LAW treatment technology risk assessment (Figure 1-2) [39].

Wastes intended for disposal in Hanford's IDF must meet requirements of DOE Order 435.1 and permit requirements established by Washington State Ecology. The IDF waste acceptance criteria have not been established for wastes disposal in the facility although there have been several draft Waste Acceptance Criteria (WAC) proposed. Initial draft waste acceptance criteria for a secondary waste form are based on the draft IDF waste acceptance criteria [75] and criteria related to free liquids, compliance with land disposal restrictions, compressive strength, and leachability.

For an FBSR waste form the following requirements would likely apply [76]:

- Land Disposal Restrictions (LDR): The waste form will meet the land disposal requirements in 40 CFR Part 268 by meeting the universal treatment standards (UTS) in 40 CFR 268.48 via the TCLP test.
- Free Liquids: The waste form shall contain no detectable free liquids as defined in EPA SW-846 Method 9095 [77]
- Leachability Index (LI): The waste form shall have a sodium LI greater than 6.0 when tested in deionized water using the ANSI/ANS-16.1 method. The waste form shall have a rhenium or technetium LI greater than 9.0. These requirements are based on the 1991

Nuclear Regulatory Commission's (NRC) Technical Position on Waste Forms [78] and on early waste disposal RA and performance assessment (PA) analyses.

- Compressive Strength: The compressive strength of the waste form shall be at least 3.54 E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M (ASTM 2010c). This is based on the NRC's Technical Position on Waste Forms [78], which is more restrictive for cement-based waste forms.

Interestingly, in a 2010 NRC document, the NRC declares that the variance in sampling intervals in the ANS 16.1 method and the use of the average value from different intervals are not consistent with the diffusion-controlled mechanism that is used to calculate the leach index. Because of this, the leachability index does not provide a reliable measure of the effective diffusion coefficient that is needed for performance modeling or any other characteristic of the material that is used in the test.[79]

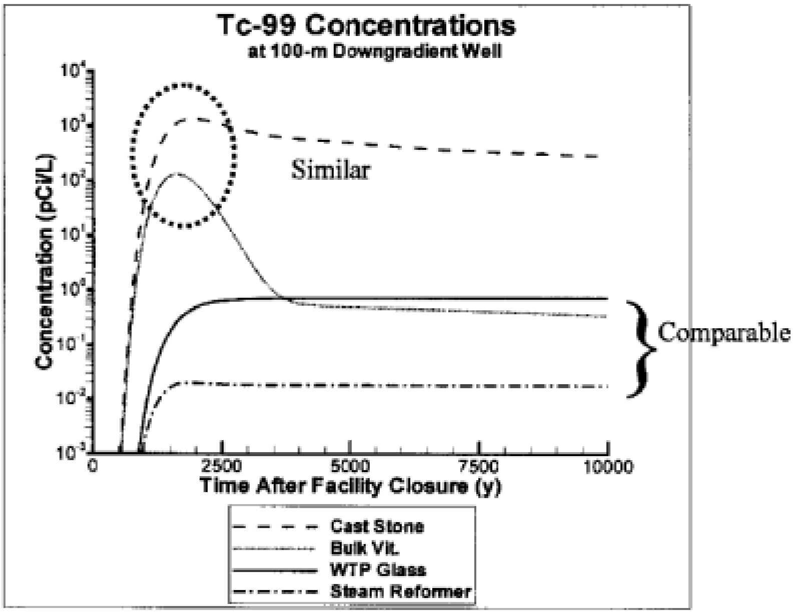

Figure 1-2. Comparison of Tc-99 concentration in a well 100 m downgradient of the IDF as a function of time from Mann et.al. (2003) RA.[39]

1.3.3 *Compressive Strength*

In the 1983 version (Revision 0) of 10 CFR 61.56(b)(1) regarding the stability of a waste form for shallow land burial, it is stated that "a structurally stable waste form will generally maintain its physical dimensions and form under expected disposal conditions (45 feet) such as weight of overburden and compaction equipment…". Assuming a cover material density of 120 lbs/ft^3, a minimum compressive strength criterion of 50 psi after curing for minimum of 28 days was established, although it was also stated that the waste forms should achieve the "maximum practical compressive strength" not just the "minimum acceptable compressive strength." Later, the burial depth was increased to 55 feet and the minimum compressive strength criterion was increased to 60 psi after curing for a minimum of 28 days.

In the early 1990's the compressive strength criterion was re-evaluated. Because Ordinary Portland Cement (OPC) mortars (cement, lime, silica sand and water) are capable of achieving compressive strengths of 5000-6000 psi, the minimum compressive strength for a waste form for shallow land burial was increased to 500 psi after curing for a minimum of 28 days. The rationale was that low-level radioactive waste material constituents are not capable of providing the physical and chemical functions of silica sand in a cement mortar and so a reasonable compressive strength was 1/10th that of a cement made with silica sand.[78]

Thus, to be accepted for near-surface disposal at Hanford, a waste form is required to meet this acceptance criterion for compressive strength of 500 psi. This requirement is derived from an NRC Branch Technical Position on Low Level Waste (LLW) forms discussed above which somewhat arbitrarily specifies 500 psi to preclude subsidence in the waste disposal. It is also noted that a monolithic waste form would reduce the impact to human health for the intruder scenario in the waste site PA. While a monolith is desirable there are other means by which this requirement can be met, e.g. waste stabilization in High Integrity Containers (HICs).

The Hanford contract [72] for LAW specifies the following:

> "The mean compressive strength of the waste form shall be determined by testing representative non-radioactive samples. The compressive strength shall be at least 3.45E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M-99 or an equivalent testing method"

No monoliths were made with the Hanford SX-105 or AN-103 non-radioactive or radioactive granular FBSR products produced in this study. The granular material was archived under the RCRA sample exclusion should funding become available for monolith formulation and testing.

1.3.4 *Waste Loading*

For disposal of FBSR wastes at Hanford in Richland, WA there is an additional specification that governs the waste loading for glass. Waste loading for Hanford LAW wastes are specified in terms of the amount of Na_2O from the waste that can be accommodated in the waste form. The most stringent of these criteria is for Envelope A waste. The specification (Section 2.2.2.2 of the Product Requirements) [72] states:

> "Waste Loading: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na_2O. The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na_2O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na_2O."

All of the Na_2O in the Hanford LAW granular FBSR products made during pilot scale testing in 2003-2004 [40,41] contained 20.87 wt% Na_2O. All of the Na_2O in the FBSR product is from the waste because the kaolin contains no sodium. If the FBSR granular product needs to be monolithed versus disposal in a HIC it should not dilute the product Na_2O concentration to less than ~14 wt.% Na_2O so that the Na_2O content will be comparable to LAW Envelope A glass. Therefore, the FBSR loading in a monolith should be ~67 wt.% for Envelope A type wastes to be comparable to LAW glass. Since monoliths were not made in this study with radioactive Hanford wastes one must rely on the demonstrations made with the non-radioactive ESTD FBSR products and the radioactive BSR Module B studies.[28, 33] Table 1-4 summarizes the requirements that an FBSR monolith would likely need to meet.

For a cementitious grout waste form, there is a PA requirement on nitrate/nitrite leaching that limits the grout waste loading.[76] There are also LDR limits for concentrations of hazardous organics from grout waste forms as well.[76 and 40 CFR 268] Nitrate/nitrite and solvents/organics get destroyed in the FBSR process so this requirement is always met for the FBSR waste form but the requirement is listed in Table 1-4 for completeness.

Table 1-4. Summary of Requirements for an FBSR LAW Waste Form

Test Criteria	Requirement for FBSR Product
Compressive Strength after 28 day cure (psi)	≥500
Crystalline Phases	Phase Identification
PCT Re (g/m^2)	< 2.0
PCT Tc (g/m^2)	< 2.0
ANSI/ANS 16.1 or ASTM C1308 (Leaching Index, LI after 90 days leaching)	Tc-99 and/or Re ≥ 9 Na ≥ 6
FBSR loading in a monolith with 21 wt.% Na_2O from waste that is equivalent to 14 wt.% Na_2O in LAW Envelope A glass (wt.%)	67
Toxicity Characteristic Leaching Procedure (TCLP)	< Universal Treatment Standards (UTS)
Nitrate/nitrite leaching requirement for grout PA	Not Applicable as nitrate/nitrite destroyed in processing
Solvent/organic leaching requirement for LDR	Not Applicable as solvents/organics destroyed in processing

1.4 DOE-EM Program Goals

The need for advanced waste forms and processes was discussed in the National Research Council report "Advice on the Department of Energy's Cleanup Technology Roadmap: Gaps and Bridges", Waste Processing gap number 5 (WP-5): "The baseline tank waste vitrification process significantly increases the volume of high-level waste to be disposed". This report comments that waste forms that include little or no additives compared to glass should be investigated for Hanford and INL.

The current DOE site baseline technologies include: 1) vitrification of the HLW fractions of tank wastes at Hanford and Savannah River for disposal at a Federal repository; 2) vitrification of the LAW fraction at Hanford for disposal at the IDF; 3) cementation of the LAW fraction at Savannah River; 4) FBSR of the tank waste at INL for disposal at the WIPP; 5) hot isostatic pressing of the calcined HLW at INL; and, 6) treatment and disposal of various secondary LLW at each site. These treatment options are reasonably proven technologies and those remaining technological gaps are being filled by site contracts. However, some of the disposal options are currently risky and may not be ideal. In addition there are likely more cost effective treatment/disposal options that should be considered to reduce risk and cost of tank cleanup in the U.S. This task explores one such option, FBSR, and develops the necessary technology to implement a promising waste form.

Fluidized Bed Steam Reforming is one of four immobilization technologies under consideration as part of the Supplemental Treatment Program for WTP Hanford LAW as discussed above. It is anticipated that the FBSR product would reduce the treatment costs and waste volumes at increased waste throughput for Hanford LAW compared to LAW vitrification or cementation. FBSR granular and monolithic waste forms have already been developed for several Hanford LAW waste streams (the Rassat 68 tank blend and AN-107) [5,6,9,28,33] and data has been generated on the granular waste form to demonstrate preliminary acceptance in the IDF [1,2,3,4,5,6,8,15,17,20].

1.4.1 *Defining the Hanford Radioactive Wastes for FBSR Demonstrations*

As part of the current DOE-EM enhanced tank waste strategy at Hanford this multi-laboratory FBSR work scope was initiated under the DOE EM-31 Technology Development & Deployment (TDD) Program Task Plan WP-5.2.1-2010-001.[80] Treatability studies were performed in this study in the SRNL BSR using three actual Hanford tank waste samples to demonstrate the range of Hanford LAW to be treated by FBSR (representing the middle 80% of the total LAW feeds based on anion content).

Prior to performing tests with actual Hanford LAW, a test with a radioactive SRS LAW that was compositionally adjusted to reflect the expected composition of a Hanford 68 tank blend, known as the Rassat simulant, was performed.[27] The Rassat 68 tank blend waste simulant was also tested in 2008 at TTT's ESTD Facility in Golden, CO and tested in 2004 at INL's SAIC-STAR's Facility in Idaho Falls. Testing in the SRNL BSR with the Rassat formulation (non-radioactive and radioactive) was designated as Module B testing and provided the tie-back strategy discussed in the next section and the earliest scientific data regarding the FBSR waste form leachability and the fate of Tc-99 in the mineral waste form.

Based on direction from DOE/ORP, three Hanford LAW samples were selected for steam reformer treatability testing in the SRNL BSR. A Data Quality Objectives (DQO) process was undertaken to ensure appropriate samples were selected.[81] The BSR campaigns with Hanford Tank SX-105 were designated Module C, campaigns with Hanford Tank AN-103 were designated Module D, and campaigns with a blend of AZ-101/AZ-102 were designated Module E.

The following considerations guided the development of Hanford LAW sample selection criteria:

- Because schedule considerations to obtain data from the treatability studies were critical, LAW samples would be selected from the existing sample archives in Hanford's 222-S Laboratory.
- SRNL advised that two of the tests (Modules C & D) required approximately one liter of LAW solution at the target 5M sodium concentration. For the third sample, 1.5 to 2 liters would be required to facilitate inter-laboratory comparison of the diffusion (ASTM C1308 run at the same temperature and time intervals as ANSI/ANS 16.1 so the data are comparable) and PCT (ASTM C1285) test results.
- The sample should be representative of full-scale feed in respect to sodium (Na) molarity (4-7 M Na, i.e., ≥100g Na).

Washington River Protection Solutions (WRPS) identified thirty nine tank waste samples (supernatant or salt cake) as having sufficient sample material. Past experience suggested that sample handling in the hot cell environment and the amount of undissolvable solids in salt cake samples could result in losses on the order of 30%. This more conservative approach yielded a set of 25 samples (9 saltcakes and 15 supernates) as potential candidates for treatability testing.

Additional criteria were used in conjunction with the DQO process to select samples for treatability testing. The chosen criteria were as follows:

- Scientists at SRNL and PNNL noted that certain anions (sulfate (SO_4^{-2}) chloride (Cl^-), fluoride (F^-), and phosphate (PO_4^{-3})) play an important role in determining which NAS mineral phases are formed. For example, sulfate and chloride are known to be bound in the sodalite cage structure and consequently do not readily leach out of the NAS matrix.[34] Therefore, variations in the relative abundance of these anions and their impact on the quality of the NAS product formed needed to be examined.
- If possible, samples would be chosen from tanks that have been evaluated for treatment by LAW vitrification, including radioactive, crucible-scale melts. This would allow direct performance comparisons for Tc retention, durability, and leach resistance. Data from these samples would help to address regulatory/stakeholder concerns of glass-versus mineral waste forms.
- If possible, select samples that have been used in previous demonstrations of the FBSR process using simulants of that tank composition. This would allow a comparison of products made from the bench-scale reformer and the pilot or engineering-scale FBSR and provide data to validate the use of simulants instead of real waste.
- If possible, both supernate and saltcake samples should be represented to replicate the likely feed to any Supplemental Treatment technology.

To support the qualification of the FBSR process and waste form, the samples should be representative of the majority of the LAW to be treated; the project determined the extreme ends of the compositional ranges do not need to be tested at this time. To evaluate samples relative to the 1st criterion above, anion concentrations in waste feed batches were taken from the Hanford Tank Waste Operations Simulator (HTWOS) output for the proposed ORP-11242, River Protection Project System Plan (System Plan 6) modeling case [82]. The LAW feed batches were sorted from low to high anion content for each of the four anions of interest with the lower 10th and upper 90th percentiles selected as the bounding limits. Conceptually, this target range represents the middle 80% of total LAW feed and eliminates the compositional outliers. Table 1-5 provides a summary of the target anion concentrations at the 10th and 90th percentiles.

Table 1-5. Molar Anion to Sodium Ratios in WTP Feed Batches

	SO_4/Na Ratio [mol/mol]	**Cl/Na Ratio [mol/mol]**	**F/Na ratio [mol/mol]**	**PO_4/Na Ratio [mol/mol]**
High = 90th percentile	0.032	0.016	0.060	0.040
Low = 10th percentile	0.008	0.007	0.013	0.008

In reality, the waste samples available for FBSR mineralization and product testing are not likely to contain all of the anions of interest at high or low concentration ranges simultaneously. Further, SO_4^{-2} and Cl^- are considered more important since they are associated with specific mineral phases. Therefore, first it was identified which criteria were met for each sample, and then the sample selection was narrowed down for high or low anion content through a process of elimination with greater weight given to SO_4^{-2} and Cl^- ratios compared to F- and PO_4^{-3} ratios.

The results of the sample selection relative to this criterion are shown in Table 1-6.

Table 1-6. Molar Anion-to-Sodium Ratios for Hanford LAW Samples

	SO_4/Na ratio [mol/mol]	**Cl/Na Ratio [mol/mol]**	**F/Na Ratio [mol/mol]**	**PO_4/Na ratio [mol/mol]**
SX-105	0.011	0.013	0.0007	0.016
AN-103	0.002	0.011	0.003	0.002
AZ-101/AZ-102 composite	0.033	0.006	0.015	0.005

Based on archive sample analysis data, the SX-105 sample (Module C) was initially selected as a high anion case. However, due to the heterogeneity of this salt cake sample, the final SO_4^{-2} concentration was much lower than anticipated and this sample only scored near the high end with respect to Cl^- concentration. The AN-103 sample (Module D) was selected to represent the low anion case particularly for SO_4^{-2} concentration. The third sample, a composite of AZ-101 and AZ-102 (Module E), was selected after the first two had been shipped to SRNL and to fulfill the criterion for high SO_4^{-2} concentration.

With respect to the 2nd criterion, prior vitrification tests with actual waste samples, only six tank waste samples have been tested with LAW vitrification: AW-101, AN-103, AN-102, AN-107, AZ-101, and AZ-102. Thus, results from the AN-103 and AZ-101/AZ-102 samples selected for FBSR treatability testing will be available for comparison to results for vitrified waste forms. The waste feed that is not represented is Envelope C, high organic complexant concentrate, but this Envelope represents less than 5% of the Hanford LAW to be treated on a metric tons of sodium (MT Na) basis.

The 3rd criterion was selection of samples that matched the composition of previous FBSR tests with simulants. Two Hanford LAW compositions have been used to produce a mineralized NAS waste form:

- Simulated AN-107 (complexant tank)
  - in a 6-inch reformer (2001, reference 34)
- Simulated Rassat 68-tank LAW composite
  - in a 6-inch reformer (2004, reference 44), and
  - in a 15-inch reformer (2009, reference 29).

By far the most material produced and tested is from the latter, which is represented by the SRS LAW chemically adjusted to match the Rassat 68 tank blend (Module B). No compelling reason existed to attempt to replicate this composition with a sample of actual Hanford LAW and the SRS sample was used instead (see reference 28 for complete details).

Three Hanford Tank Samples were successfully identified that in conjunction with the two chemically adjusted SRS samples provided test samples for the FBSR program that largely span the target compositional ranges for the anions of interest.[83] The resulting data will expand the body of knowledge on the FBSR product as a waste form for the immobilization of Hanford LAW.

1.4.2 *Defining the Testing Program for Hanford FBSR Waste Forms*

Table 1-**7** gives a description of the testing planned for the three Hanford wastes in the SRNL BSR. The data resulting from the demonstration test programs and data in previous publications, as summarized in Table 1-3, will be used to support the IDF performance assessment and decisions regarding deployment of a non-vitrification technology to immobilize LAW. A review was also produced [84] summarizing all previous and current leaching results and their impact on acceptance of the granular FBSR waste form in the IDF.

The SRS LAW tests provided the earliest scientific data regarding waste form leachability and the fate of Tc-99 in the mineral phase waste form. The granular products from the treatability studies were subjected to the same regulatory and performance testing protocols as the non-radioactive tests as shown in Table 1-3 and Table 1-**7**. The additional data from this study on the Hanford radioactive tank wastes (Modules C, D, and E) will provide support to the previous testing with simulants and SRS Hanford LAW (Module B). All the data and resulting analyses from all the non-radioactive and radioactive testing will be used to minimize technical risk regarding waste form performance and to support critical decisions associated with enhanced tank waste strategy at Hanford for the deployment of the FBSR transformational technology.

In contrast to most waste form development programs where bench-scale research precedes pilot scale testing, the FBSR process has been run at the pilot and engineering scale (Table 1-3) with simulants but not at the bench-scale with either simulants or radioactive wastes. SRNL has successfully operated a BSR in the SRNL Shielded Cells Facility (SCF).[85,86] The BSR is a unique SRNL design and this radioactive capability does not exist elsewhere. SRNL also has unique expertise, analytical chemistry skills, and equipment for monolithing the granular FBSR product and measuring durability of waste forms (granular and monolithic). SRNL used two BSR's – one for non-radioactive testing and one for radioactive testing on the Hanford tank wastes.

Non-radioactive Re was added to the radioactive feed to determine the effectiveness of Re as a surrogate for Tc-99 during BSR processing. Data from Module B had demonstrated that Re and Tc-99 track each other in the off-gas and during durability measurement indicating that they substitute for each other in the solid mineral products. Additional information regarding the mineral partitioning and how Re and Tc-99 respond to the reduction/oxidation (REDOX) in the BSR was needed from the Hanford tank waste radioactive testing.

During the Hanford radioactive BSR Module C campaign, ~93% of the waste was processed with the Tc, Re, and I levels equivalent to the Rassat ESTD simulant processed by TTT, while the remaining ~7% of the waste (see Table 1-8 for exact amounts) was doped with Tc-99, Re, and I-125/I-129 at a minimum of 150 μg/g as this is the level needed to detect these species during follow on X-ray Absorption Fine Structure (XAFS) analyses to determine the oxidation state and local bonding of the Tc-99 and I-125/I-129 in the mineral waste form. The remaining ~7% of the feed was processed at the end of the BSR campaigns, after the off-gas condensate was sampled and lines were flushed. This was done to ensure that the mass balance and leaching tests were not compromised by the elevated concentrations required by the XAFS.

Table 1-7. Module C, D, and E BSR Scale Tests

Task	Module C (SX-105)		Module D (AN-103)		Module E (AZ-101/102)	
	BSR Simulant	BSR Radioactive	BSR Simulant	BSR Radioactive	BSR Simulant	BSR Radioactive
Mass Balance	●	●	●	●	○	○
Prepare Monolith	○	○	○	○	○	○
REDOX vs Tc, Re, Cr	●	●	●	●	●	○
TCLP (Granular)	●	▲	●	●	●	○
TCLP (Monolith)	○	○	○	○	○	○
Mineral Characterization (Gran/Mono)	●/○	●/○	●/○	●/○	●/○	○/○
SPFT (ASTM 1662)		▲		○		○
Diffusion (Mono only) (ASTM C1308)	○	○	○	○	○	○
PUF Testing						
Short Term PCT (Gran/Mono) ASTM C1285	●/○	●/○	○/○	○/○	○/○	○/○
Long Term PCT (Gran/Mono) ASTM C1285	●/○	●/○		○/○		○/○
Tc & Re Speciation		■				○
Pure Phase Mineral Testing	■					

Key [●] Completed at SRNL, [▲] Completed at PNNL, [■] Completed at ORNL, [○] Not Funded

1.4.3 *Defining the "Tie-Back" Strategy*

The importance of the BSR radioactive modules C, D, and E are how well they do or do not compare to the radioactive BSR Module B made with radioactive SRS LAW because the radioactive Module B campaigns were intended provide a tie back to the 2008 ESTD simulant FBSR tests at HRI by TTT and the 2004 pilot-scale simulant FBSR tests at SAIC-STAR (see Figure 1-3).

Building correlations between work with radioactive samples and simulants is critical to being able to conduct future relevant simulant tests, which are more cost effective and environmentally protective than tests with radioactive wastes. Specifically, the following correlations can be derived between the Module B simulant and radioactive tests and the Module C and D simulant and radioactive tests:

- Radioactive bench scale reformer with Module C and D to Module B tests
- Radioactive bench scale reformer to non-radioactive bench scale reformer tests for Modules C and D
- Correlate non-radioactive bench scale reformer with Module C and D to Module B tests

For this reason, over 600 grams of non-radioactive and over 600 grams of radioactive Module B material was needed from the SRNL non-radioactive and radioactive BSR's (Table 1-8) but less is needed for the non-radioactive and radioactive testing of Modules C and D.

Table 1-8. Bench-Scale Reformer (BSR) Tests Performed at SRNL for Hanford Wastes

BSR Module	Reference	Test	Source of Radioactive Waste	Amount of Radioactive Product (g)	Amount of Non-Radioactive Product (g)
A	27	SRS WTP-SW	Shim of SRS DWPF melter recycle to resemble Hanford WTP- Secondary Waste	96	188
B	28	SRS-LAW	Shim of SRS LAW (Tank 50) to resemble Hanford LAW based upon Hanford 68 tank blend	640*	645
C	This Study	Hanford LAW Sample #1 (medium S, Cl, F, and P)	Hanford Tank SX-105	317[f]	189
D		Hanford LAW Sample #2 (low S, Cl, F, and P)	Hanford Tank AN-103	224	192
E		Hanford LAW Sample #3 (high Cr and high S)	Hanford Tank Blend AZ-101/AZ-102	N/A	N/A

N/A – Testing not completed

* an additional 23.45g (~3.66%) was made at the desired REDOX with the enhanced Tc-99 spike and sent for XAS analyses and an additional 25.45g (3.98%) was made under more reducing conditions with the enhanced Tc-99 and sent for XAS analyses for comparison

[f] an additional 24.37 g (7.69%) was made at the desired REDOX with the enhanced Tc-99 spike and sent for XAS analyses.

Figure 1-3. Tie-back strategy between engineering scale non-radioactive pilot testing (top row) and BSR non-radioactive and radioactive testing (bottom row).

Notes: In order of importance, tie-back #1 is between the radioactive BSR run with the Tank 50 waste shimmed to be like the Rassat Blend (this study) and the non-radioactive engineering scale Rassat Blend tested in 2008. Tie-back #2 is between the non-radioactive BSR testing with Rassat Blend simulant and the radioactive BSR testing with the Tank 50 waste shimmed to be like the Rassat Blend. Tie-back #3 is between the non-radioactive BSR and the non-radioactive pilot testing with the Rassat Blend simulant. Tie-back #4 is between the pilot scale testing performed at SAIC-STAR in 2004 and the pilot scale testing performed at HRI in 2008 with the Rassat Blend simulant. Note that the radioactive BSR controllers and data acquisition are in a radioactive hood and not in the shielded cells (bottom right photo).

2.0 Quality Assurance

The overarching Task Plan for the FBSR studies supported by SRNL, PNNL, and ORNL is the DOE EM-31 TDD Program Task Plan WP-5.2.1-2010-001.[80] A summary of the multi-laboratory success criteria outlined in the TDD program task plan is given in Section 3.0. The list is annotated with references to different documents which contain the results of the testing.

The task was performed in accordance with a Quality Assurance Program (QAP) that meets the Quality Assurance criteria specified in DOE O. 414.1, *Quality Assurance*, 10 CFR 830, *Nuclear Safety Management*, Subpart A, "*Quality Assurance Requirements*", paragraph 830.122 and also meets the requirements of ASME Nuclear Quality Assurance (NQA)-1-2004, *Quality Assurance Requirements for Nuclear Facility Applications* including NQA-1a-2005 and NQA-1b-2007 Addenda, or later version. The SRNL Quality Assurance Program and implementing procedures were evaluated by the Hanford Mission Support Alliance Acquisition Verification Services and placed on the Evaluated Supplier List (MSA-1201714, April 25, 2012).

The SRNL work scope was performed in accordance with 1Q, QAP 2-3 (Control of Research and Development Activities). Under this procedure, research and development work was classified as either a Task Activity or Scoping Activity based upon the work initiating documentation and customer requirements. The WP-5 Project Team for the Fluidized Bed Steam Reformer Low-level Waste Form Qualification task (WP-5.2.1) determined that a graded approach would be utilized for this scope. Some of the testing to identify processing parameters was performed as "scoping" and was controlled using SRNL L1 Manual, 7.10 (Identification of Technical Work Requirements) and other appropriate SRNL QA protocols. Most of the testing was performed to a Task Technical & Quality Assurance Plan (TT&QAP).

SRNL wrote and worked to individual TT&QAP's for each module. For Modules C, D, and E, three different TT&QAPs were written and followed.[87,88,89] The TT&QAP's are attached to this report as Appendices A, B, and C.

The SRNL results are summarized in the current document. The original non-radioactive BSR run data can be found in notebooks SRNL-NB-2009-00115 and SRNL-NB-2011-00004. The radioactive BSR run data can be found in SRNL-NB-2010-00160. The data produced from the Module C runs can be found in notebooks SRNL-NB-2010-00144 and SRNL-NB-2011-00112. The data produced from the Module D runs can be found in notebooks SRNL-NB-2010-00145, SRNL-NB-2011-00070, and SRNL-NB-2011-00076. The data produced from the Module E runs can be found in notebook SRNL-NB-2011-00037.

3.0 Success Criteria for the TDD Program

The success criteria for the LAW FBSR Modules B, C, D, and E were to develop data and models necessary to provide data on the FBSR product necessary to support the Decision Point to Proceed with Supplemental Treatment. The activities described in this section were carried out to support this objective. These following activities were performed at SRNL and reported in this document and Reference 52. These activities were designed to:

1. Characterize the Module B FBSR products from the HRI/ESTD/TTT P1-B runs blended bed and fines products made from the Hanford Rassat (68 tank blend) simulant (see Reference 28).

2. Make a similar Hanford Rassat (68 tank blend) radioactive LAW from SRS LAW with Tc-99, I-129/I-125, Cs-137, and Re to determine how well Re tracks Tc-99 in the off-gas vs. the mineral product and the fate of I-129/I-125 and Cs in the off-gas vs. the mineral product (see Reference 28).

3. Receive three Hanford LAW samples (Modules C, D, and E): one with low anion content, one with high anion content, and potentially one with complexants. These will not be doped with additional Tc-99, I-129/I-125, Cs-137 but will have Re added.

4. Determine the mass balance of Tc-99, Re, Cs-137/Cs-133, and I-129/I-125/I-127 in the BSR system for all modules.

5. Subject the FBSR granular and monolith products to the TCLP – non-radioactive and radioactive (see Reference 28).

6. Use process control calculations and qualitative X-ray Diffraction (XRD) to determine the fractions and compositions of the minerals formed by FBSR. This will be performed on multiple different samples – primarily simulated waste samples but with confirmatory tests with actual LAW samples.

7. Prepare monolithic waste forms containing mineralized FBSR product (see Reference 28).

8. Perform XRD analysis on monolithic waste forms (see Reference 28).

9. Determine the transport properties of the monolithed waste form. This will be performed by diffusion tests such as ASTM C1308. These tests need to be performed for a number of samples including Re-loaded simulants and actual waste samples containing Tc-99 (see Reference 28).

10. Demonstrate that the binder used for monolithic waste form does not significantly impact the release/dissolution behavior based on ASTM C1285 and ASTM C1308 (see Reference 28).

11. Synthesize phase pure minerals (nepheline and sodalites) [74] for testing at other laboratories for activities #12 to #16 below.

The following activities were performed at ORNL, PNNL, and University of California at Davis and are reported in Reference 52 and the other references cited below:

12. Develop dissolution rate law parameters for each significant phase in the waste form. Using SPFT testing to isolate individual rate law parameters along with selected tests for multi-phase waste forms (primarily Re containing, with selected Tc-99 containing measurements to

demonstrate Tc-99 release is equivalent to Re-release). Additional tests were performed to determine the phases formed during reaction with water and this is documented elsewhere.[90]

13. Measure thermodynamic parameters of the phase pure minerals at University of California, Davis.[90]

14. Determine the distribution of Tc-99 and I-129 in the FBSR product and the distribution of Tc-99 and I-129 amongst the different mineral phases. The speciation refers to oxidation state and nearest neighbor which requires the use of X-ray absorption spectroscopy (XAS). Selected area X-ray diffraction XRD/micro-XRD and electron microscopy of the Tc-99 and I-129/I-125 loaded material are also required. When combined with other data, these results will determine where Tc-99 and I-129/I-125 is located in the waste form. Contained Scanning Electron Microscopy (CSEM) will also be performed. This will be documented elsewhere [52,90]

15. Determine the effect of Al, Si, and nepheline saturated solutions on Re and Tc-99 release from the FBSR product. This will be used to quantify the impact of the Al buffering effect seen in preliminary tests. This is mostly associated with the common ion effect and must be quantified so it can be accounted for in the source term model.

16. Develop and validate a modified waste form release/radionuclide source term model for inclusion in the IDF performance assessment code. This source-term model will start with that developed by McGrail et al. [36,37], but, include: a) the release rates for each phase, b) updated thermodynamic data for solid solution phases, c) common ion effect seen in preliminary experiments, d) transport properties measured in monolith samples, and e) Tc-99 and I-125/I-129 partitioning between phases in the waste form.

4.0 Experimental

The scope of work addressed in this report consists of tests in the SRNL non-radioactive BSR of simulants of Hanford's Tank SX-105 (Module C), Tank AN-103 (Module D), and Tank Blend AZ-101/AZ-102 (Module E) and tests in the SRNL radioactive BSR with actual LAW tank waste from Hanford from the same tanks. Non-radioactive testing provides (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the non-radioactive BSR product for comparison between waste streams and to the TTT engineering scale product, and (3) non-radioactive granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared during an SRNL Work for Others (WFO) [91,92] with TTT and to Module B results [28]. The radioactive testing provides (1) granular samples for testing the durability response of the radioactive BSR product for comparison between waste streams and between processing scales, and radioactive granular products to monolith and compare (durability and compressive strength) to other radioactive and non-radioactive monolithic waste forms described in References 28, 91, and 92. These demonstrations also provided needed tie backs to previous durability testing of the Rassat simulant FBSR granular and monolithic products as described in Section 1.4.3.

The BSR is not completely fluidized due to height limitations of the SCF but the gases, including the fluidizing steam, pass freely through the particles which form a porous biscuit and reactions between the gases, waste, and clay are the same as if they were actively colliding. Because of the lack of complete fluidization and collision, particle size growth is minimized. Also, due to the small fluidizing chamber the particles are harvested from the BSR chamber more frequently so there is less residence time of an individual particle in the BSR than in the ESTD pilot. This affects only the particle size and not the chemistry as the longer residence times and intense fluidization in the ESTD creates collisions which encourages particle size growth. Therefore, the BSR particles will be mostly of a smaller size than the engineering ESTD particles. Thus, the durability test responses were expected to be comparable when scaled to surface area and this comparison was demonstrated during the FBSR program in this study and Reference 28.

The work flow discussed in the TDD Task Plan [80] and the SRNL TT&QAP's [87,88,89] is given below. Note that requirements pertinent to monoliths and monolith testing have been removed since no monoliths were made with the granular BSR products produced from Modules C, D or E. Also test elements that were unique to Module B such as making phase pure standard nepheline and sodalites have been removed.

1. Prepare Non-Radioactive Simulant
    a. Module C
    b. Module D
    c. Module E
2. Prepare Radioactive Waste
    a. Module C
    b. Module D
    c. Module E (only shimmed with Re and analyzed)
3. Prepare Feed for BSR
    a. Module C
    b. Module D
    c. Module E (non-radioactive only)
4. Prepare Granular Waste Forms for Analyses
    a. Module C
    b. Module D

   c. Module E (non-radioactive only)
5. Prepare Sample Characterization Methods
   a. Module C
   b. Module D
   c. Module E (non-radioactive only)
6. Perform Regulatory Testing
   a. TCLP [93]
      i. Module C
      ii. Module D
      iii. Module E
7. Perform Waste Form Performance Testing
   a. PCT (ASTM C 1285-02) [94]
      - Short Term Testing (7 day)
        Module C only
      - Long Term Testing (up to 1 year)
        Module C only

4.1 Prepare Non-Radioactive Simulant and Radioactive Feed

For the BSR testing, both a non-radioactive simulant and an actual radioactive waste sample were used. Non-radioactive simulants of each of the modules were tested in the SRNL non-radioactive BSR in order to provide (1) optimization of processing parameters for radioactive testing and (2) granular samples for testing the durability response of the BSR product in comparison between waste streams and to the TTT engineering scale ESTD and the INL pilot scale products.

A description of the simulant make-up and characterization for each Hanford simulant and the characterization results for each radioactive sample by SRNL and WRPS is provided in Sections 4.1.1 through 4.1.3. Section 4.1.1 discusses Module C – Hanford Tank SX-105, Section 4.1.2 describes Module D – Hanford Tank AN-103, and Section 4.1.3 provides the information for Hanford Tank Blend AZ-101/AZ-102 (Module E).

Analyses of the simulants and radioactive samples included elemental composition as determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) measurements on either supernate or digested slurry samples; Ion Chromatography (IC) anion measurements on filtered, weighted dilutions of slurry or supernate; total base, free OH^-, and other base excluding CO_3^{2-} titration of unfiltered, weighted dilutions of slurry or supernate; Total Inorganic Carbon (TIC) measurement for carbonate; and solids measurements where insoluble solids were present. For the radioactive samples, the supernate was also measured by separation and counting techniques for Cs-137, Tc-99, I-125 (where applicable), and I-129.

4.1.1 *Hanford Tank SX-105 (Module C)*

The Hanford Tank SX-105 samples, which had been through cesium removal, were received in two separate bottles that were eventually composited for the SRNL BSR testing. Figure 4-1 provides a picture of the samples after they were unloaded in the Shielded Cells. Table 4-1 provides the SRNL analysis of the Hanford SX-105 Tank sample used in Module C, the WRPS analysis of SX-105 [95], and the SRNL simulant analysis that was prepared based upon the WRPS analysis of this sample prior to its shipment to SRNL. During simulant preparation any components that were below detection limit (<) in the WRPS analyses were omitted from the simulant as their impact on durability, i.e. TCLP, would be detected in the radioactive sample if it were a significant impact.

Both the simulant, though to an immeasurable degree, and the LAW samples had visible solids of gibbsite (as identified by XRD analysis, see Figure 4-2) that were not removed prior to processing. The SX-105 sample solids did appear to increase between the visible receipt inspection and the start of BSR processing. The estimation of solids in the table below was made after the sample had been at SRNL for a number of months and prior to the addition of clay, coal, or REDOX tracer Fe nitrate. The significant difference in the Re level between the SRNL and WRPS analyses reflects the addition of Re to the sample prior to characterization in SRNL. The characterization in Table 4-1 does not reflect the additional Tc-99 spike of the Hanford LAW sample done for the last two BSR runs in order to provide material for XAS analyses by ORNL personnel aimed at determining the Tc-99 bonding and crystallographic location.

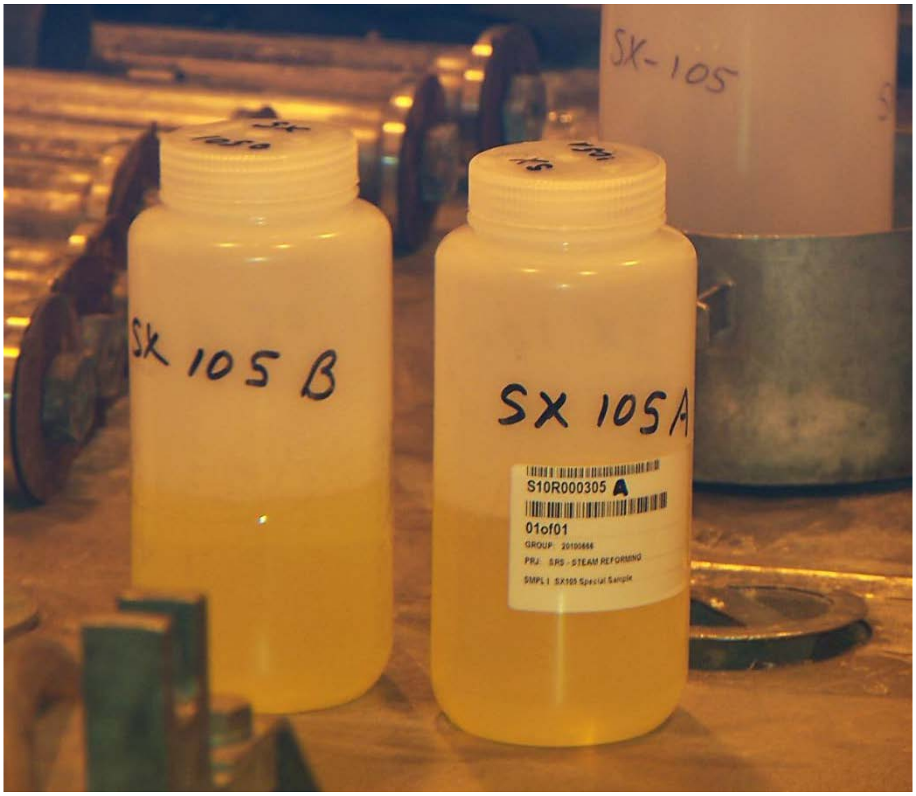

Figure 4-1. As-Received Hanford Tank SX-105 (Module C) Samples

Table 4-1. Feed Composition for Module C Simulant and Hanford Tank SX-105 after Re Addition but Prior to Clay, Coal, or Fe Addition

Species	SRNL Analysis SX-105	WRPS Analysis SX-105 [95]	SRNL Analysis Simulant C
	Molar	**Molar**	**Molar**
Al	3.74E-01	3.74E-01	3.78E-01
B	2.45E-03	2.95E-03	2.53E-03
Ba	1.40E-04	<2.18E-05	<5.08E-06
Be	<1.86E-05	<1.11E-04	NA
Ca	1.60E-03	<1.25E-03	<2.06E-04
Cd	<5.91E-06	<4.45E-05	<6.83E-06
Ce	<7.20E-05	<2.14E-04	<8.78E-05
Co	<3.08E-05	<1.70E-04	<4.27E-05
Cr	1.99E-02	1.79E-02	1.71E-02
Cs	NA	NA	4.01E-05
Fe	8.41E-04	<8.95E-05	1.75E-04
K	2.21E-02	1.42E-02	1.34E-02
La	<1.10E-05	<2.16E-05	<2.41E-05
Li	<1.66E-03	<4.32E-04	<4.08E-04
Mg	2.97E-04	<2.06E-03	<3.67E-05
Mn	9.54E-06	<5.46E-05	<1.72E-05
Mo	3.57E-04	<2.08E-04	<4.20E-05
Na	5.34E+00	5.13E+00	5.19E+00
Nb	NA	NA	<3.19E-05
Ni	8.56E-04	<3.41E-04	<3.65E-05
P	5.28E-02	8.81E-02	7.75E-02
Pb	2.30E-06	<2.41E-04	<2.76E-05
Re	1.67E-03	2.28E-05	2.20E-03
S	6.61E-02	5.74E-02	5.58E-02
Sb	<8.63E-05	<4.11E-04	NA
Si	4.96E-03	NA	<3.65E-04
Sn	<8.84E-04	NA	<4.94E-05
Sr	4.52E-06	<3.42E-05	<6.62E-06
Th	<3.29E-07	4.44E-09	NA
Ti	1.12E-04	<1.04E-04	<2.46E-05
U	1.18E-06	1.53E-06	NA
Zn	1.58E-04	1.07E-04	1.14E-04
Zr	1.90E-05	<5.48E-05	<1.17E-05
	Molar	**Molar**	**Molar**
Cs-137	6.49E-11	3.26E-11	NA
Tc-99	4.11E-05	4.28E-05	NA
I-129	2.91E-06	3.57E-06	NA

NA is Not Analyzed.

Table 4-1. Feed Composition for Module C Simulant and Hanford Tank SX-105 after Re Addition but Prior to Clay, Coal, or Fe Addition (Continued)

Species	SRNL Analysis SX-105	WRPS Analysis SX-105 [95]	SRNL Analysis Simulant C
	Molar	**Molar**	**Molar**
$C_2H_3O_2^-$	NA	6.61E-03	NA
CO_3^{2-}	4.26E-01	8.20E-02	3.15E-01
Cl^-	7.21E-02	6.63E-02	5.11E-02
Br^-	<1.56E-03	<1.54E-03	<1.25E-02
F^-	<6.57E-03	3.70E-03	<5.26E-03
HCO_2^-	1.70E-02	1.12E-02	5.77E-03
$C_2H_3O_3^-$	NA	<2.65E-03	
OH^-	4.99E-01	5.41E-01	7.13E-01
I^-	NA	NA	2.98E-03
NO_3^-	2.30E+00	2.24E+00	2.47E+00
NO_2^-	8.15E-01	7.87E-01	8.07E-01
$C_2O_4^{2-}$	<1.42E-03	6.44E-03	4.36E-03
PO_4^{3-}	3.48E-02	8.37E-02	7.24E-02
SO_4^{2-}	5.31E-02	5.49E-02	5.51E-02
	Molar	**Molar**	**Molar**
Total Base	1.27E+00	NA	1.59E+00
Other Base Excluding CO_3^{2-}	2.74E-01	NA	4.61E-01
	Wt%	**Wt%**	**Wt%**
Total Solids	30.38	NA	30.16
Dissolved Solids	29.92	NA	NA
Soluble Solids	29.72	NA	NA
Insoluble Solids	0.67	NA	~0
	g/mL	**g/mL**	**g/mL**
Density	NA	1.28	1.25

NA is Not Analyzed.

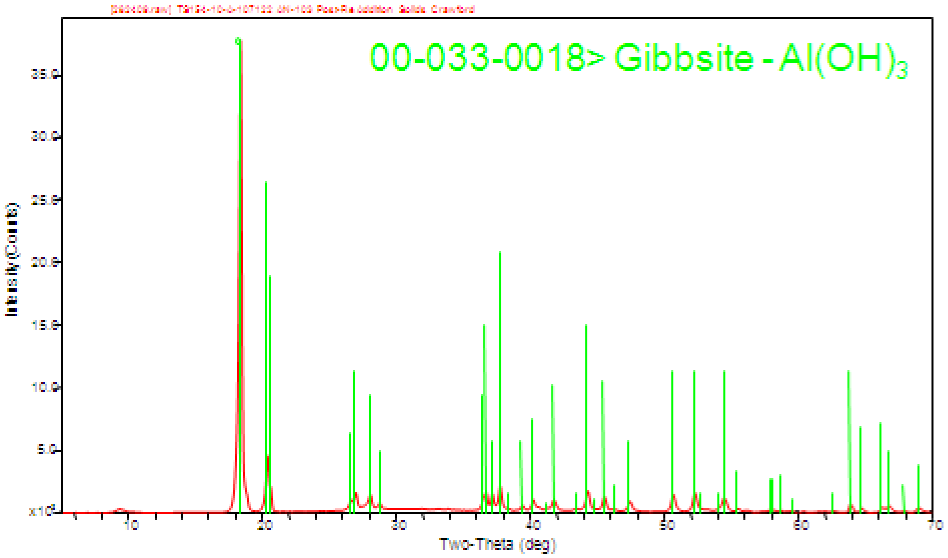

Figure 4-2. XRD of Precipitated Solids in Tank SX-105 Sample.

Gibbsite, $Al(OH)_3$, (PDF 00-033-0018)
Original XRD Spectra are in Appendix N

4.1.2 *Hanford Tank AN-103 (Module D)*

The Hanford Tank AN-103 samples were also received in two separate bottles that were composited for the SRNL BSR testing. Figure 4-3 provides a picture of the samples after they were unloaded in the Shielded Cells. Table 4-2 provides the analysis of the Hanford AN-103 Tank sample used in Module D testing. The SRNL simulant was prepared based upon the SRNL analysis of this tank sample as the WRPS analysis had been performed on a filtered sample and SRNL was processing an unfiltered sample with the gibbsite precipitates. Both the actual waste sample, which contained approximately 3 wt.% insoluble solids when measured several months after receipt at SRNL, and the Module D simulant had gibbsite, $Al(OH)_3$, solids as determined by XRD analysis. A programmatic decision was made to process the material through the BSR unit without removing the solids prior to addition of clay, coal, or REDOX tracer Fe nitrate. Again, the significant difference in the Re level between the SRNL and WRPS analyses (Table 4-2 and Figure 4-5) reflects the addition of Re to the sample prior to characterization in SRNL. The concentration of Al^{3+} as determined by SRNL was higher by a factor of 3.5X as SRNL analyzed the sample with the precipitates suspended while WRPS measured the supernate without the gibbsite solids.

Since the BSR demonstration was intended to demonstrate that this technology can process precipitated solids, the analysis and the Module D campaigns were performed with the gibbsite solids present. The rationale is that the solids are expected to behave like the clay additive in the FBSR process, i.e. at the processing temperature the hydroxides from the $Al(OH)_3$ will be stripped and the activated Al^{3+} will react and become part of the mineral product in an identical fashion to how the hydroxides are stripped from the clay additives and become reactive (see Figure 4-4). The additional Al was accounted for in the MINCALC™ process control spreadsheet as demonstrated in Figure 4-5.

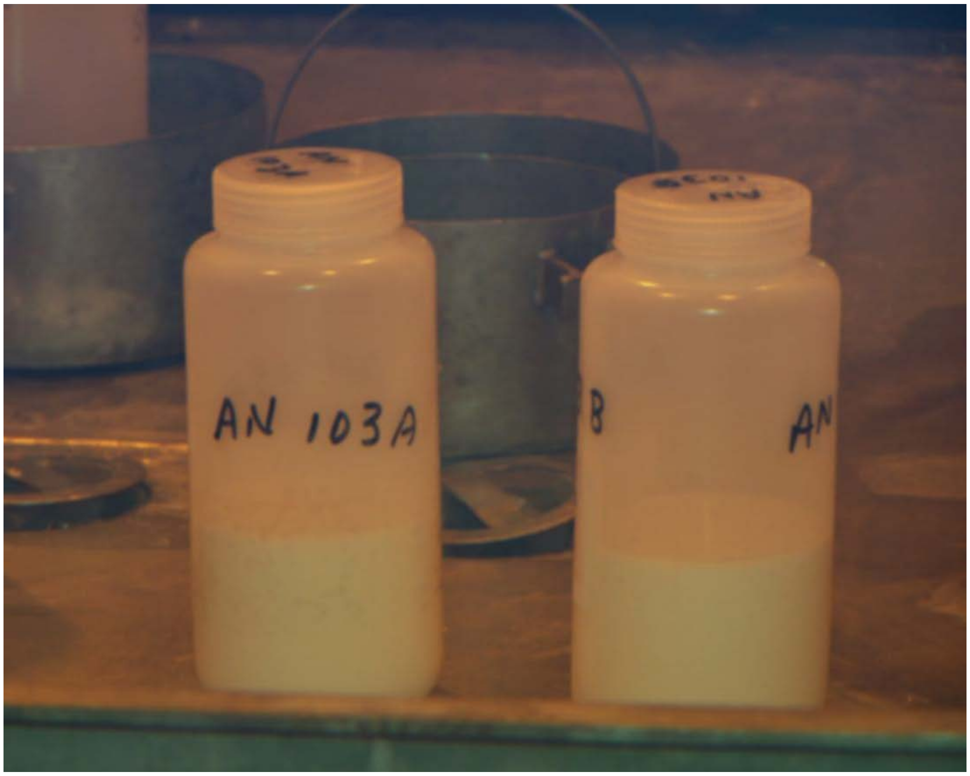

Figure 4-3. As-Received Hanford Tank AN-103 Samples

Table 4-2. Feed Composition for Module D Simulant and Hanford Tank AN-103 after Re Addition but Prior to Clay, Coal, or Fe Addition

Species	SRNL Analysis AN-103	WRPS Analysis AN-103 [95]	SRNL Analysis Simulant D
	Molar	**Molar**	**Molar**
Al	1.53E+00	4.41E-01	1.50E+00
B	8.27E-04	<2.77E-03	<7.43E-04
Ba	<4.73E-06	<2.18E-05	<4.77E-06
Be	1.73E-05	<1.11E-04	NA
Ca	3.64E-04	<1.25E-03	7.61E-04
Cd	3.97E-06	<4.45E-05	<6.46E-06
Ce	<5.18E-05	<2.14E-04	<9.90E-05
Co	<2.22E-05	<1.70E-04	<5.12E-05
Cr	3.96E-04	3.69E-04	3.25E-04
Cs	NA	NA	1.19E-04
Cu	3.04E-05	<7.87E-05	<3.62E-05
Fe	6.96E-04	<8.95E-05	1.74E-04
K	7.33E-02	8.90E-02	7.44E-02
La	<7.92E-06	<2.16E-05	<1.74E-05
Li	<2.74E-05	<4.32E-04	<3.85E-04
Mg	8.26E-05	<2.06E--03	2.35E-04
Mn	<2.20E-05	<5.46E-05	<1.02E-05
Mo	2.63E-04	2.79E-04	2.83E-04
Na	5.03E+00	5.18E+00	5.11E+00
Ni	<1.74E-04	<3.41E-04	<1.76E-05
P	1.12E-02	2.39E-02	9.46E-03
Pb	9.07E-06	<2.41E-04	7.24E-05
Re	1.67E-03	2.03E-05	2.14E-03
S	1.37E-02	1.51E-02	1.41E-02
Sb	<9.39E-05	<4.11E-04	NA
Si	7.61E-03	NA	<1.97E-04
Sn	9.73E-03	NA	<6.26E-05
Sr	6.81E-05	<3.42E-05	<4.47E-06
Th	<6.02E-05	9.91E-06	NA
Ti	2.33E-04	<1.04E-04	<2.25E-05
U	9.89E-06	9.62E-06	NA
Zn	1.68E-04	<7.64E-05	<2.97E-05
Zr	1.25E-04	<5.48E-05	<1.10E-05
	Molar	**Molar**	**Molar**
Cs-137	8.33E-11	9.57E-11	NA
Tc-99	2.00E-05	2.04E-05	NA
I-129	3.92E-06	5.36E-06	NA

NA is Not Analyzed.

Table 4-2. Feed Composition for Module D Simulant and Hanford Tank AN-103 after Re Addition but Prior to Clay, Coal, or Fe Addition (Continued)

Species	SRNL Analysis AN-103	WRPS Analysis AN-103 [95]	SRNL Analysis Simulant D
	Molar	**Molar**	**Molar**
$C_2H_3O_2^-$	NA	7.79E-03	NA
CO_3^{2-}	2.68E-01	5.55E-02	3.15E-01
Cl^-	6.07E-02	5.92E-02	5.70E-02
Br^-	<1.51E-02	<8.06E-04	<3.00E-03
F^-	<6.37E-03	1.84E-02	<1.26E-02
HCO_2^-	6.98E-03	4.80E-03	6.80E-03
$C_2H_3O_3^-$	NA	<1.39E-04	NA
OH^-	1.91E+00	2.12E+00	2.13E+00
I^-	NA	NA	4.19E-03
NO_3^-	1.03E+00	1.02E+00	9.88E-01
NO_2^-	8.01E-01	7.52E-01	8.03E-01
$C_2O_4^{2-}$	5.95E-03	6.27E-03	5.79E-03
PO_4^{3-}	6.44E-03	7.78E-03	6.61E-03
SO_4^{2-}	8.72E-03	1.16E-02	1.06E-02
	Molar	**Molar**	**Molar**
Total Base	2.82E+00	NA	3.09E+00
Other Base Excluding CO_3^{2-}	4.08E-01	NA	3.03E-01
	Wt%	**Wt%**	**Wt%**
Total Solids	28.33	NA	28.90
Dissolved Solids	26.03	NA	27.03
Soluble Solids	25.22	NA	26.34
Insoluble Solids	3.11	NA	2.57
	g/mL	**g/mL**	**g/mL**
Density	NA	1.27	1.28

NA is Not Analyzed.

4.1.3 *Hanford Tank Blend AZ-101/102 (Module E)*

Table 4-3 provides the analysis of the third Hanford Tank sample, a blend of AZ-101 and AZ-102 tank waste, used in Module E and the SRNL simulant that was prepared based upon the SRNL analysis of this tank sample. The tank sample has no visible solids, but there is a minor insoluble solids fraction, 0.09 wt%, in the Module E simulant which appears to be due to Fe precipitation. There appears to be trace complexant materials that are not fully characterized that are able to solubilize (hydrolyze) all of the measurable Fe (as an iron III hydroxide colloid which ages to other oxides) in the radioactive sample. These complexants are not present in the simulant. Once again, the significant Re level measured by SRNL reflects the addition of Re to both the waste tank sample and simulant prior to characterization.

Table 4-3. Feed Composition for Module E Simulant and Hanford Tank Blend AZ-101/AZ-102 after Re Addition but Prior to Clay, Coal, or Fe Addition

Species	SRNL Analysis AZ-101/-102	WRPS Analysis AZ-101/-102	SRNL Analysis Simulant Module E
	Molar	**Molar**	**Molar**
Al	2.41E-01	2.30E-01	2.21E-01
B	<6.51E-04	<2.77E-03	<5.56E-05
Ba	<1.72E-05	<2.18E-05	<3.60E-06
Be	<4.88E-05	<1.11E-04	NA
Ca	1.19E-04	<1.25E-03	1.23E-04
Cd	1.25E-05	<4.45E-05	<1.08E-06
Ce	<1.88E-04	<2.14E-04	<7.92E-06
Co	<5.77E-05	<1.70E-04	<4.91E-06
Cr	1.39E-02	1.48E-02	1.39E-02
Cs	NA	NA	3.28E-05
Cu	<8.94E-05	<7.87E-05	1.52E-05
Fe	2.15E-04	1.45E-04	1.55E-04
Hg	NA	5.08E-08	NA
K	9.50E-02	9.36E-02	7.60E-02
La	<1.84E-05	<2.16E-05	<2.18E-06
Li	<9.97E-04	<4.32E-04	5.42E-05
Mg	<4.11E-05	<2.06E-03	8.87E-05
Mn	<1.46E-05	<5.46E-05	<2.85E-06
Mo	6.60E-04	6.47E-04	6.57E-04
Na	5.32E+00	4.92E+00	4.75E+00
Nb	8.24E-04	5.51E-04	2.89E-04
Ni	<1.60E-04	<3.41E-04	<3.36E-06
P	2.47E-02	2.55E-02	2.21E-02
Pb	5.05E-06	<2.41E-04	<4.98E-06
Re	1.70E-03	NA	1.60E-03
S	1.64E-01	1.52E-01	1.56E-01
Si	2.09E-03	2.02E-03	4.49E-03
Sn	1.59E-04	2.73E-04	<2.23E-05
Sr	<3.20E-06	<3.42E-05	7.76E-07
Th	<8.62E-08	<2.15E-04	NA
Ti	1.53E-04	1.35E-04	8.21E-05
U	1.57E-05	<4.20E-04	NA
Zn	<1.35E-05	<7.64E-05	7.62E-06
Zr	6.24E-05	6.85E-05	6.50E-05
	Molar	**Molar**	**Molar**
Cs-137	4.04E-11	3.18E-11	NA
Tc-99	1.87E-04	1.44E-04	NA
I-129	1.71E-06	1.89E-06	NA

NA is Not Analyzed.

Table 4-3. Feed Composition for Module E Simulant and Hanford Tank Blend AZ-101/AZ-102 after Re Addition but Prior to Clay, Coal, or Fe Addition (Continued)

Species	SRNL Analysis AZ-101/-102	WRPS Analysis AZ-101/-102	SRNL Analysis Simulant Module E
	Molar	**Molar**	**Molar**
$C_2H_3O_2^-$	NA	2.93E-03	NA
CO_3^{2-}	6.91E-01	1.36E-01	5.69E-01
Cl^-	2.90E-02	3.10E-02	3.05E-02
Br^-	<7.66E-03	<7.26E-04	<5.92E-03
F^-	2.64E-02	7.26E-02	2.56E-02
HCO_2^-	8.21E-03	6.98E-03	<1.05E-02
$C_2H_3O_3^-$	NA	7.70E-04	NA
OH^-	4.70E-01	5.64E-01	3.00E-01
I^-	NA	NA	9.44E-03
NO_3^-	1.09E+00	1.25E+00	1.21E+00
NO_2^-	1.23E+00	1.33E+00	1.34E+00
$C_2O_4^{2-}$	1.38E-02	1.60E-02	1.32E-02
PO_4^{3-}	2.18E-02	2.50E-02	2.42E-02
SO_4^{2-}	1.33E-01	1.61E-01	1.52E-01
	Molar	**Molar**	**Molar**
Total Base	1.31E+00	NA	1.33E+00
Other Base Excluding CO_3^{2-}	2.92E-01	NA	2.99E-01
	Wt%	**Wt%**	**Wt%**
Total Solids	NA	NA	27.53
Dissolved	NA	NA	27.47
Soluble Solids	NA	NA	27.44
Insoluble Solids	0	NA	0.09
	g/mL	**g/mL**	**g/mL**
Density	1.24	1.24	1.23

NA is Not Analyzed.

Table 1-5 summarized the molar anion (SO_4,Cl, F, I, P) content to molar sodium content of the Module C and D wastes. The SX-105 Module C waste was considered high anion to sodium LAW and the AN-103 was considered low anion to sodium LAW. However, AZ-101/AZ-102 was higher in SO_4 than either SX-105 or AN-103 (compare analyses in Table 4-3 to Table 4-1 and Table 4-2).

4.2 Prepare Feed for BSR Using MINCALC™ Process Control

In order to control the mineralogy of the FBSR product, a process control methodology was programmed into Microsoft Excel® that calculates the proper clay and coal additives to produce the desired minerals, enhance denitration of the LAW, and control the REDOX range. Control of REDOX drives the various species into the correct valance state such that they make the desired minerals and reduces the amount of unreacted coal in the product. Likewise, temperature control is important to enable the correct mineralization reactions to occur. In engineering scale operations, particle size control is important to maintain a sustainable bed in the DMR.

During FBSR processing, the constituents in the waste feed are converted into highly leach resistant forms by reaction with the aluminosilicate clay additives. The mineral species formed are principally alkali aluminosilicates, also referred to as feldspathoid mineral species. These minerals also incorporate other ions elsewhere in their molecular structures. Examples of the minerals reactions to form nepheline, nosean, and sodalite, are shown Equation 1 forming from NaOH in the LAW.

Equation 1

$$\underbrace{2NaOH}_{waste} + \underbrace{Al_2O_3 \bullet 2SiO_2}_{kaolin\,clay\,additive} \rightarrow 2\,\underbrace{NaAlSiO_4}_{Nepheline\ product} + H_2O$$

$$\underbrace{8NaOH + SO_4^{-2}}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(Na_2SO_4)}_{Nosean\ \ product} + 3H_2O + 2OH^-$$

$$\underbrace{8NaOH + 2Cl^-}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(2NaCl)}_{Sodalite\ product} + 3H_2O + 2OH^-$$

$$\underbrace{8NaOH + 2ReO_4^-}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(2NaReO_4)}_{Sodalite\ product} + 3H_2O + 2OH^-$$

$$\underbrace{6NaAlSiO_4}_{nepheline\ product} + \underbrace{2NaReO_4}_{waste} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(2NaReO_4)}_{Sodalite}$$

If more anions such as Cl, F, and I are present or oxyanions such as TcO_4^- or ReO_4^-, more sodalite forms. If more $SO_4^=$ is present, the sodalite structured phase nosean forms. If anions, $SO_4^=$, Re and Tc are low, then less sodalite and nosean forms and more nepheline forms. Cs and K can be accommodated in either nepheline or sodalite where they substitute for Na. Theoretically[ξ], a pure sodium chloride waste stream would make a chloride sodalite and could accommodate 12.06 wt.% NaCl or 7.32 wt.% Cl. A pure iodide waste stream in sodalite could accommodate 22.03 wt.% I and a pure fluoride sodalite could accommodate 4.06 wt.% F. A pure sodium sulfate waste stream could accommodate up to 9.65 wt.% $SO_4^=$ or 14.28 wt.% as Na_2SO_4 in nosean. Likewise, the Re and Tc sodalites can accommodate 13.31 wt.% Re or 8.00 wt.% Tc-99, respectively. Note that in the Module A WTP-SW FBSR study [27] 1.58 wt.% F was accommodated in the fluoride sodalite of the theoretical 4.06 wt.% F meaning that ~40 wt.% of the waste form was a fluoride sodalite. In the simulant Module E studies reported in Sections 5.1 and 5.2, 3.70 wt.% $SO_4^=$ was accommodated in the nosean or ~40 wt.% of the theoretical $SO_4^=$ that could have been accommodated in the absence of significant quantities of other anions or oxyanions.

[ξ] Calculation is performed as follows: (2NaCl molecular wt./molecular wt. of chloride sodalite), i.e. (58.44*2/969.21)*100=12.06% NaCl, as there are 2NaCl's in sodalite (see atomic formula given in Table 1.1) or (35.45*2/969.21)*100= 7.3 wt.% Cl as there are 2Cl's in each sodalite.

The reactions given in Equation 1 could also have been written with $NaNO_3$ in the LAW as the reactant and N_2 as one of the gaseous products. The cations in the salt waste; Na, Cs, Tc, etc, and other species such as Cl, F, I, and SO_4 are immediately available to react with the added clay as the clay dehydrates at the DMR temperatures and the aluminum atoms in the clay become charge imbalanced as the stabilizing OH^- atoms are lost (Figure 4-4). Once the hydroxides are lost, the clay becomes amorphous (loses its crystalline structure) and very reactive at the FBSR temperatures of 700-750°C. This amorphous clay is called meta-kaolin. Stable crystalline clays (kaolin) are known [96] to become reactive amorphous clays (meta-kaolin) when they lose their hydroxyl groups above 550°C. The cations and other species in the waste react with the reactive amorphous meta-kaolin to form new stable crystalline mineral structures allowing formation and templating of the aluminosilicate structure at the nanoscale at moderate temperatures (see Figure 4-4). In addition, nepheline, once formed by reaction of the waste and clay can further react with the waste to form sodalite(s) as shown in the last reaction above as sodalite is six nepheline unit cells that form a cage structure that surrounds and is bound to $2NaReO_4$.

The stable nepheline and sodalite crystalline structures leave the process as a granular solid product. Kaolin clay has been found to template the feldspathoid group of minerals (nepheline, sodalites, nosean, etc.) for LAW and the illite clays have been found to template the dehydroxylated micas as radionuclide hosts for rare earth species.[9] The IOC stabilizes many of the RCRA hazardous species present in a waste in durable spinel phases, i.e. Cr^{3+}, Ni^{2+}, Pb^{2+} iron oxide minerals.[40] In section 4.6.3 containing TCLP results of granular FBSR/BSR products, the importance of this iron oxide catalyst in sequestering these waste ions will be discussed.

The MINCALC™ process control strategy for the FBSR mineralizing process was developed by SRNL in 2004 for the INL SAIC-STAR FBSR campaigns with SBW and LAW. MINCALC™ is based on composition control in the NAS oxide system (Figure 4-5). MINCALC™ was used during the 2004 INL pilot scale tests [44], the 2008 TTT/HRI ESTD campaigns [29], and the BSR campaigns in 2004 [97] and this study.

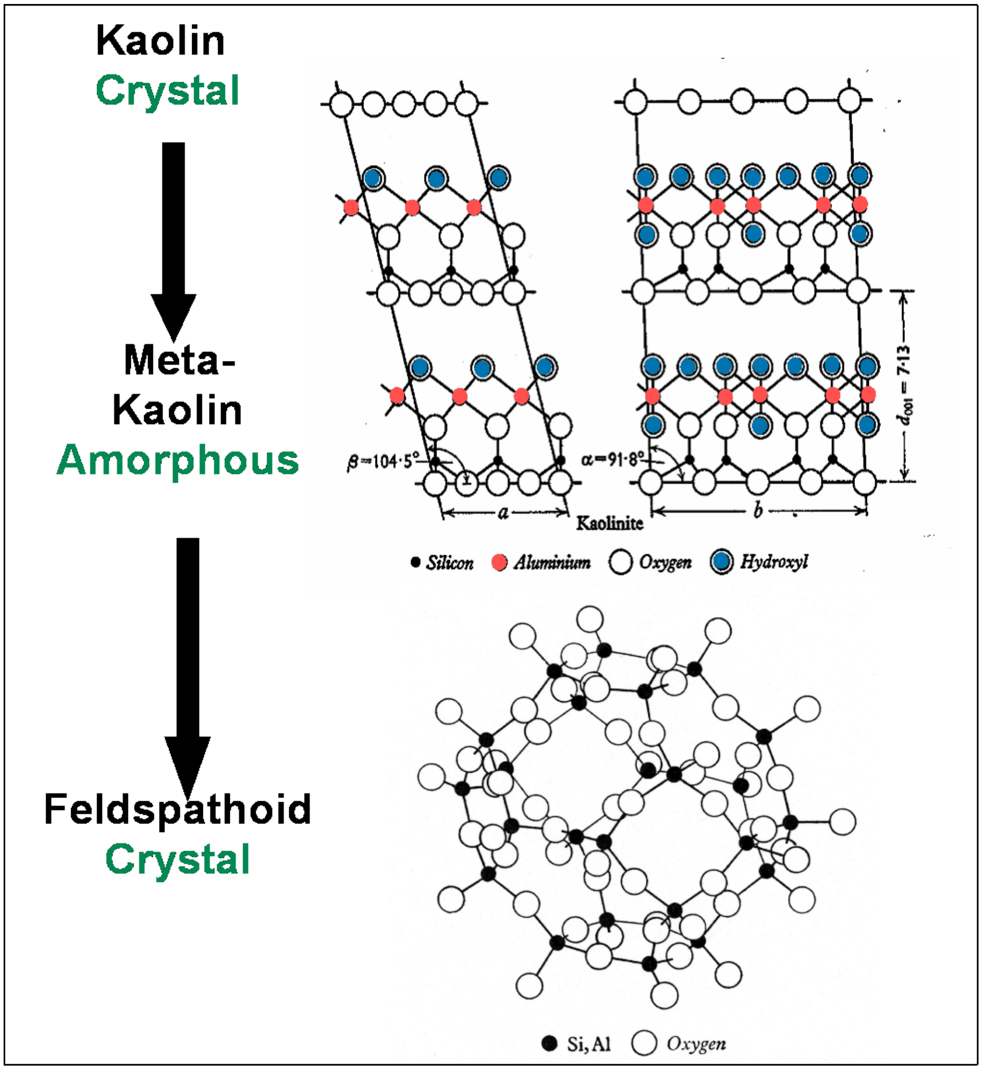

Figure 4-4. Kaolin transformation to meta-kaolin to Feldspathoid (Sodalite) Crystal by loss of hydroxyls and alkali activation as a function of increasing temperature (after reference 96).

MINCALC™ controls the LAW FBSR product in the region of nepheline/sodalite formation (region in Figure 4-5 where the blue rectangle for AN-107 lies). MINCALC™ converts the molar compostions recorded in the tables above to element weight percent on a wet basis and then to oxide weight percent on a dry calcine basis. The Al_2O_3 and SiO_2 from the clay additive and the $(Na,K,Cs)_2O$ and Al_2O_3 contributions from the waste are weighted by waste loading and (100-waste loading), respectively, until the tie-line between the clay composition on the SiO_2-Al_2O_3 binary and the waste composition on $(Na,K,Cs)_2O$-Al_2O_3 binary pass through the AN-107 region of Figure 4-5 where it is known that acceptable FBSR product is made.[35,36,37,38]

The radioactive waste compositions are shown along the Na_2O-Al_2O_3 base of the triangle in Figure 4-5. It is obvious from the positions of the Module D and Module C points on the base of the triangle that AN-103 (Module D) had much more Al_2O_3 in it than SX-105 (Module C). This composition difference is accounted for by the MINCALC™ process control by choosing a clay or a mixture of clays along the

Al_2O_3-SiO_2 side of the triangle that forces the waste-clay mixture through the AN-107 box where it has been determined that the desired NAS minerals are made.[35,36,37,38]

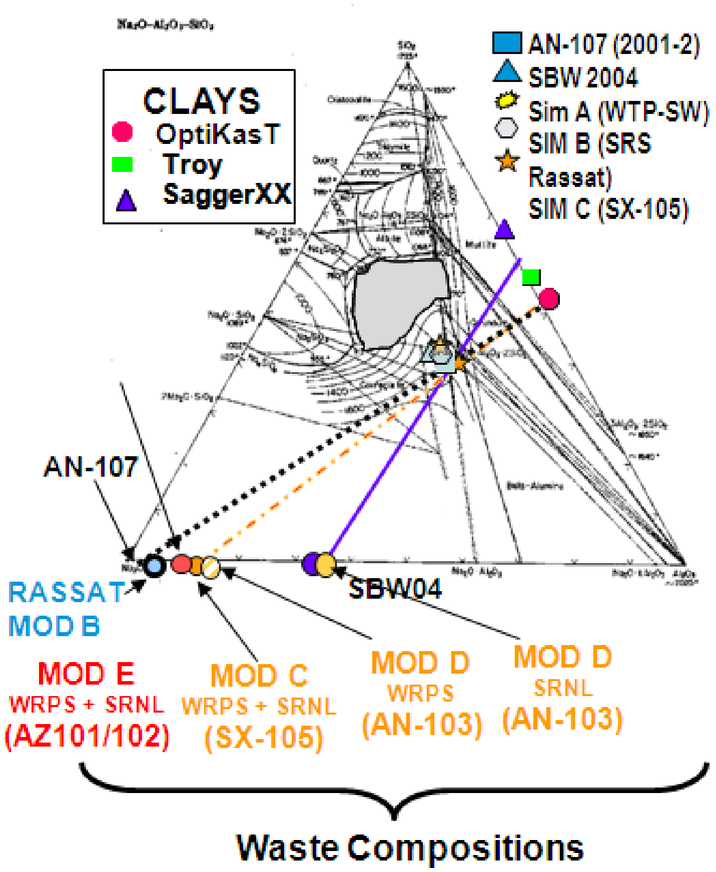

Figure 4-5. Na_2O-Al_2O_3-SiO_2 (NAS) MINCALC™ Process Control Phase Diagram

Note: The composition of the SX-105 (Module C) radioactive waste as analyzed by WRPS and SRNL is shown along the base of the MINCALC™ triangle (Na_2O-Al_2O_3 binary) along with the analyses of AN-103 (Module D) analyzed by WRPS (filtered) and SRNL (unfiltered), and AZ101/AZ102 (Module E) analyzed by WRPS and SRNL. The unfiltered SRNL analyses were used for the AN-103 (Module D) radioactive BSR campaigns. The Rassat simulant (Module B) is shown along the base of the triangle for comparison along the Na_2O-Al_2O_3 binary. The position of the potential clay additives are shown on the Al_2O_3-SiO_2 binary. The OptiKast and SaggerXX clay compositions are presented in Table 4-3 of Reference 29.

MINCALC™ can also be used to calculate the theoretical weight percent of each of the mineral phases. The engineering scale ESTD campaigns were run with excess clay and hence excess Al_2O_3 and SiO_2 usually appear in the species predictions (Table 4-4). The BSR campaigns (non-radioactive and radioactive) were run with minimum excess clay (1-2 wt.%) and even clay deficient. This occurred because the SRNL was trying to maximize LAW content and minimize the aluminosilicate content of the FBSR product. In addition, the radioactive SX-105, AN-103, and AZ-101/AZ-102 were analyzed before the simulants were made and analyzed. So in many cases the original MINCALC™ calculations were performed based on the radioactive analyses and later recalculated based on the simulant analyses. If the simulant and radioactive wastes differed in anions analyses, more sodalite/nosean minerals were made than nepheline as there was always excess Na and K available and often excess Al available as precipitated gibbsite. This occasionally left less excess SiO_2 and Al_2O_3. This is not problematic as many Al and Si deficient nepheline species and sodalites exist and MINCALC™ is designed to give a ±5% estimation. The sum of all predicted phases has not been normalized to 100%, so sums shown at the bottom of Table 4-4 do not add completely to 100% but show how accurate MINCALC™ is in accounting for the major mineral species which, for Module C, Module D, and Module E, are primarily nepheline and nosean which are shaded in Table 4-4.

Table 4-4. Mineral Speciation for Non-Radioactive and Radioactive Module C, D, and E Predicted from MINCALC™-Version 3 SRNL Analyses*

Mineral Component	**Chemical Component**	**Module C with 100% OptiKasT™ Clay**		**Module D with 45 wt% Sagger/55 wt% OptiKast™ Clay**		**Module E With 100% OptiKasT™ Clay**	
		Simulant (wt%)	**Radio-active (wt%)**	**Simulant (wt%)**	**Radio-active (wt%)**	**Simulant (wt%)**	**Radio-active (wt%)**
Na Nepheline	$Na_2Al_2Si_2O_8$	81.86	82.35	86.87	85.13	55.31	64.91
K Nepheline	$K_{0.5}Na_{1.5}Al_2Si_2O_8$ or $K_2Na_6Al_8Si_8O_{32}$	2.48	3.12	9.17	9.10	8.03	8.93
Cl Sodalite	$Na_8Al_6Si_6O_{24}(Cl_2)$	3.22	4.50	3.43	4.11	2.21	1.90
F Sodalite	$Na_8Al_6Si_6O_{24}(F_2)$	BDL	BDL	BDL	0.42	1.79	1.67
I Sodalite	$Na_8Al_6Si_6O_{24}(I_2)$	0.26	2.54E-04	0.398	3.73E-04	0.96	0.0002
Nosean (SO_4-S_2 Sodalite)	$Na_8Al_6Si_6O_{24}(SO_4)$	7.11	6.81	1.47	1.21	22.56	17.90
Re Sodalite	$Na_8Al_6Si_6O_{24}(ReO_4)_2$	0.21	0.22	0.22	0.17	0.18	0.17
Tc Sodalite	$Na_8Al_6Si_6O_{24}(TcO_4)_2$	---	3.54E-07	---	1.84E-03	---	1.47E-02
Free Silica	SiO_2	0.80	-0.17	-3.31	-2.63	2.03	0
Free Alumina	Al_2O_3	1.77	0.88	-0.87	-0.12	2.01	0.28
SUM		97.70	97.88^f	101.57^f	100.14^f	95.09	95.77

* Without any contributions from the ferric nitrate nona-hydrate REDOX indicator or the IOC since the mineral calculations do not include the potential substitution of Fe for Al in nepheline and the sodalites and the IOC forms iron rich spinels

f Sums without negative numbers

For Modules C and E, the feeds were primarily Na_2O species, and OptiKasT® clay was the only clay that had to be added (Table 4-5) to drive the clay-waste mixture into the nepheline forming region of the NAS ternary shown in Figure 4-5. Note that MINCALC™ predicts that the high Na_2O concentration of Module C will make ~ 85% nepheline (combined sodium nepheline and sodium/potassium nepheline) with a small contribution (2.5-3%) from the potassium form of nepheline ($KAlSiO_4$). Module D make about the same concentration of nepheline ($NaAlSiO_4$) but had almost an additional 9-10 wt.% $KAlSiO_4$ so that the overall Na,K-nepheline was in the 94-96% range. Module C had considerably higher nosean concentrations (6.8-7.0 wt.%) due to a higher sulfate content than Module D with nosean ~1.2-1.5 wt.%. It should be noted that had Module E actually been completed it would have produced much more nosean (18-22.5 wt.%) due to a higher sulfate content and much less nepheline (63-74 wt.%) than the other modules (Table 4-4 and Reference 50). About 10 wt.% of the nepheline for Module E would have been

$KAlSiO_4$ instead of $NaAlSiO_4$ at about the same level of $KAlSiO_4$ as Module D (AN-103). These primary phases are highlighted in Table 4-4.

In the Module C (SX-105) and E (AZ-101/AZ-102) campaigns, the OptiKasT® clay was mixed with the salt waste in a large batch to accommodate all the expected runs. Coal and ferric nitrate were also added for REDOX control and REDOX measurement. Module D (AN-103) simulant work started out with Sagger® XX as the only clay based on the low WRPS alumina values that had been determined on a filtered sample (see Table 4-2 and Figure 4-5). When SRNL reanalyzed unfiltered AN-103 which is what was processed in the BSR, a much higher alumina value was determined and SRNL moved to a mixture of 45 wt.% Sagger® XX and 55 wt.% OptiKasT® clays, i.e. MINCALC™ was recalculated and those are the values shown in Table 4-4. Only the Simulant D granular product produced from the dual clay mixture was used in the final composite material. Radioactive Module D was run with the same mixture of the two clays.

A small amount of $Fe(NO_3)_3{\bullet}9H_2O$ was added to the BSR runs to act as an analytical indicator for the REDOX potential in the product (Table 4-5). Note that the iron indicator is ferric nitrate nona-hydrate. Thus an analysis of the $Fe^{2+}/\Sigma Fe$ in the product would indicate how reduced the feed was. The coal addition goal was to provide product within REDOX targets without leaving unused coal as measured by Loss-on-Ignition (LOI). The ferric nitrate was added to provide 1 to 1.5 wt.% Fe in the granular product. The objective was to match the REDOX of the TTT/HRI ESTD campaigns with the Rassat simulant. Originally (Module C), the nitrate from the ferric nitrate nona-hydrate was not included in the coal requirement, but for Module D it was included in the coal calculation. Therefore, all the values for coal in Table 4-5 have been recalculated to put them on a consistent basis that does not include the nitrate from the REDOX indicator.

The same Bestac® coal as was used by the ESTD FBSR was added to the BSR feeds for all modules as a reducing agent and autocatalytic heating source. However, for the BSR, the coal was ground, then sifted through an 80 mesh sieve (177 microns) and mixed with the feed slurry versus the ESTD coal, which was added periodically from a raw materials hopper for autocatalytic heating. The decrease in the coal size at SRNL was necessary due to the small orifice on the BSR feed pump.

Initially, the Module C (SX-105) coal requirement based on the nitrate/nitrite analyses of the simulant was 2.33x. The BSR products were too reduced and the coal target was lowered for the radioactive campaigns to 1.3x (Table 4-5). SRNL had targeted 1.3X coal for Module C based on the WRPS radioactive analyses but this became 1.5x based on the SRNL nitrate/nitrite values (see Table 4-5).

Initially, for Module D, the coal stoichiometry was again 1.3x but the extra nitrate coming from the ferric nitrate non-hydrate REDOX indicator was factored into the coal requirement. Since this had not been done in Modules C and E, the coal stoichiometry was recalculated without including the nitrate from the REDOX indicator and the stoichiometry was 1.9x for Module D. See the coal stoichiometry values in Table 4-5, which are all calculated on a consistent basis ignoring the extra nitrate from the REDOX indicator as it is small compared to the nitrite/nitrate contributions from the LAW feed.

Module E values for coal stoichiometry are given in the same table. The Module E (AZ-101/AZ-102) simulant was run in the BSR but not the radioactive sample, although the MINCALC™ phase distributions and coal requirements were calculated for this campaign.

In the Module C campaigns, the coal was mixed with the salt waste in a large batch to accommodate all the expected runs and this seemed to "blind" the impact of the coal, i.e. it likely became coated in clay and salt waste. In the Module D campaign, the coal was added the day of the run for most of the runs based on the assumption that the coal loses ~40% of its reactivity after sitting in the salt/clay slurry for more than 2 days (it is believed to remain constant after the 3rd day). Radioactive Module C often provided on-spec product (REDOX/LOI) at the 1.3x (which was actually 1.5x in Table 4-5) coal level. Simulant D most often provided on-spec product (REDOX/LOI) at the 1.9x level of coal. All runs for Radioactive Module D were at 1.9x stoichiometric for coal.

Table 4-5. Feed Slurry Composition and Waste Loading from MINCALC™ Based on SRNL Analyses

Module	Target Clay g/L of Initial Solution	Target Coal g/L of Initial Solution	$Fe(NO_3)_3{\cdot}9H_2O$ g/L of Initial Solution	Waste Loading (Dry Calcine Oxide/Anion Basis) wt. %	Waste Loading (Na_2O Calcine Basis) wt.%
Sim C	660 OptiKasT®	255.7 for 2.3x[a]	64.5	25.5	20.52
Rad C	660 OptiKasT®	151.1 for 1.5x[a]	64.5	25.8	20.96
Sim D Batch 1-4	551.4 SaggerXX®	94.27 for 1.9x[b,c]	64.5	33.0	20.10
Sim D Batch 5-6	241.1 Sagger® XX, 294.7 OptiKasT®	94.27 for 1.9x[b,c]	64.5	34.0	21.96
Rad D	241.1 Sagger® XX, 294.7 OptiKasT®	94.27 for 1.9x[b,c]	64.5	33.9	21.67
Sim E	550.8 OptiKasT®	95.36 for 1.3x	64.5	28.0	21.52
Rad E	611.8 OptiKasT®	86.55 for 1.3x	64.5	27.5[d]	21.91[d]

[a] At the time of the Module C simulant and radioactive campaigns, the anion analyses from SRNL were not available for the coal determinations. The coal requirement for denitration was based on the radioactive nitrate/nitrite analyses provided by WRPS: the coal target for Simulant C was 2.33x and the coal target for Rad C was 1.3x as discussed in the text but when the SRNL analyses became available the coal requirement was recalculated as given in this table.

[b] At the time of the Module D simulant and radioactive campaigns, the anion analyses from SRNL were not available for the coal determinations. The coal requirement for denitration was based on the radioactive nitrate/nitrite analyses provided by WRPS: the coal target for Simulant and Rad D was 1.3x as discussed in the text but when the SRNL analyses became available the coal requirement was recalculated as given in this table.

[c] The nitrate from the ferric nitrate nona-hydrate used as a REDOX indicator was included in the coal calculations for the Mod D campaigns but not for the Mod C and E campaigns: all values in this table were recalculated based on the SRNL analyzed nitrite and nitrate values only for consistency.

[d] The calculation was performed but no BSR campaigns were performed.

4.3 Bench Scale Reactor Description: Processing Hanford LAW Samples

This section provides a description of the bench scale reformer equipment and the operational control strategy.

Testing with the non-radioactive BSR always preceded radioactive testing as the run parameters had to be determined so that the product chemistry and the gas reactions in the BSR matched those of the TTT/HRI ESTD pilot scale operations and the MINCALC™ phase predictions. In order to ensure this happened, the following acceptance criteria were established for the non-radioactive BSR and then later applied to the radioactive BSR products:

- BSR product mineralogy after each campaign had to be the same species and qualitatively in similar amounts as that predicted by MINCALC™, which were essentially those found the TTT/HRI ESTD campaigns but in varying weight fractions
- the REDOX measured after each campaign was desired to be in the range of 0.2-0.5 $Fe^{+2}/\Sigma Fe$ to match the ESTD DMR bed product REDOX
- the LOI at 525°C (an indication of the amount of residual coal[f] in the product) was desired to be at a minimum, i.e. in the range of 0-2 wt.%.

4.3.1 *Equipment Description*

The BSR designed at SRNL is a dual reformer (two-stage unit) used to produce the same mineralized products and gases as the ESTD FBSR. Unlike the ESTD FBSR, the BSR is not fluidized since it had to fit in the shielded cells and there is not enough height in the cells to allow for product disengagement. See discussion in the beginning of Section 4.0 as the lack of fluidization does not impact the gaseous or mineralizing reactions but only impacts particle growth which has been determined not to impact product durability.[40]

Steam, the fluidizing media, does flow freely through the product, which is in the form of a porous biscuit. Scanning Electron Microscopy (SEM) analysis shows well reacted particles in the BSR that are similar in morphology and characteristics to those in the FBSR, i.e. fully reacted (Figure 4-6). Only the first reformer, the DMR, was used for this study. A schematic of the single reformer unit as used is shown in Figure 4-7, while the details of the DMR are shown in Figure 4-8.

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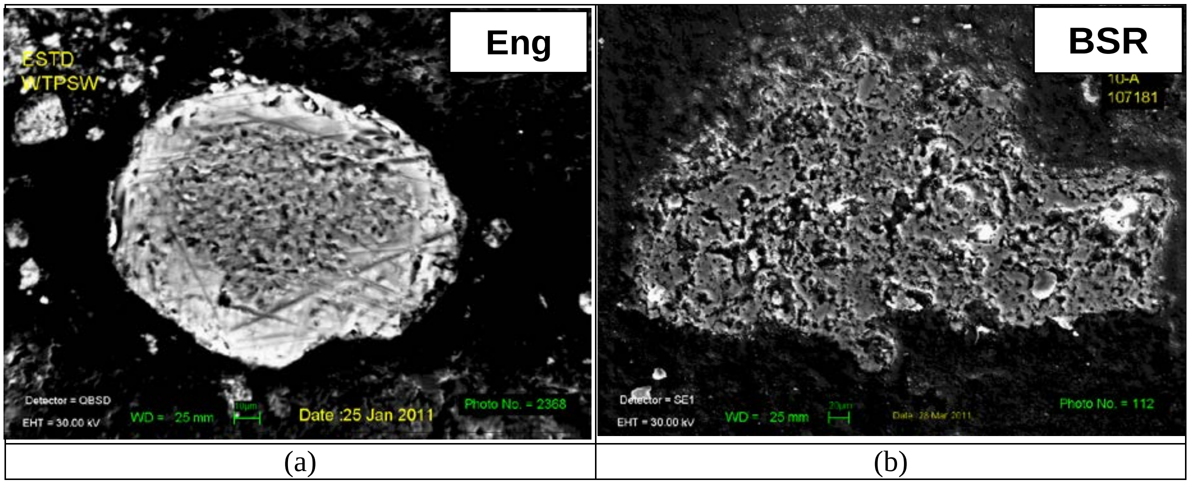
[f] Coal is used in the FBSR as the source of auto-thermally heating and this is described in several papers and patents available at www.thortt.com.



(a) (b)

Figure 4-6. Comparison of the reactivity of an individual particle from the engineering scale (ESTD) and the BSR.

Note the similarity of the reaction textures and the completeness of the reaction.

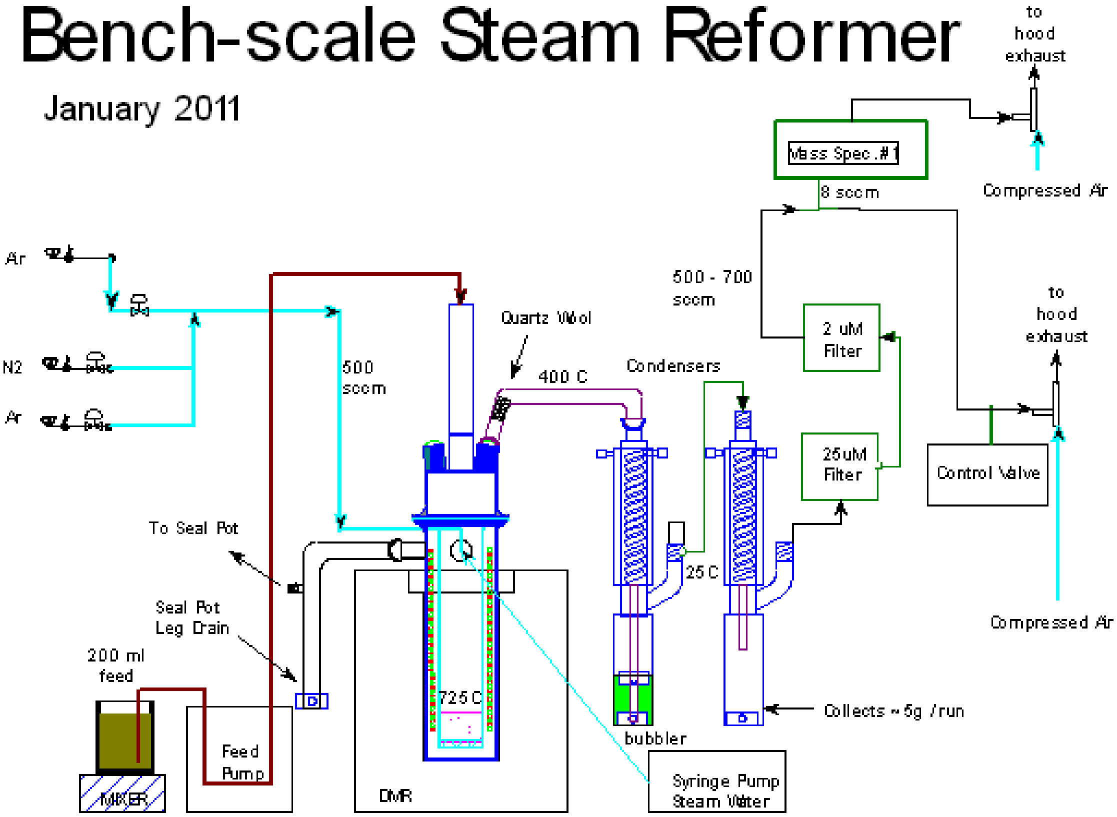


Figure 4-7. Schematic of the Bench-Scale Steam Reformer (BSR)

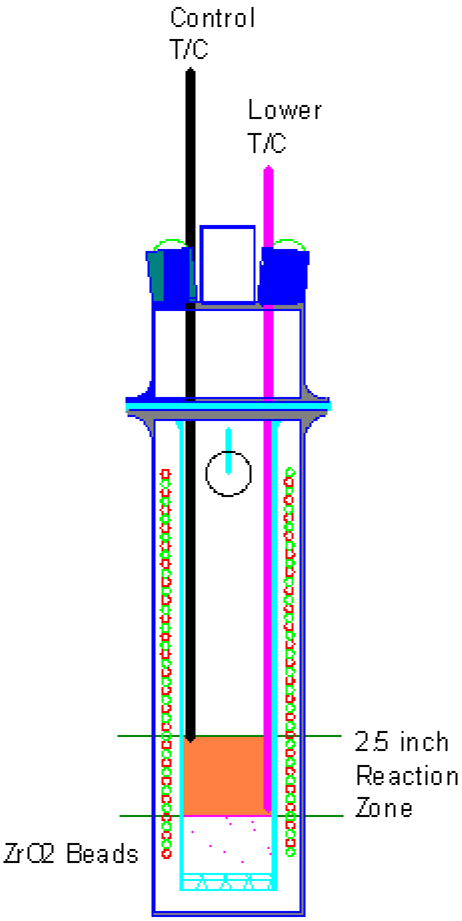


Figure 4-8. The BSR Denitration Mineralization Reformer (DMR)

The nomenclature for the BSR FBSR comes directly from the ESTD FBSR unit. During a typical run, approximately 200 ml of feed slurry was kept agitated with a stir bar mixer, while a peristaltic pump fed the slurry through the center feed port in the lid of the DMR at about 1 ml/min. A mineralized product formed in the DMR in the presence of superheated steam, clay, and carbon and the off-gases flowed toward the DMR condenser.

The DMR off-gas treatment system consists of the quartz wool in the crossover bar from the DMR to the condenser/bubbler, the condenser/bubbler, the second condenser, 25 µm paper filter, and 2 µm paper filter. The quartz wool filtered out most of the particulate carry over as the off-gases passed through it on the way to the condenser. This quartz wool was added at the beginning of Module C after solids carryover into the condenser had been observed in Modules A and B.

The condenser cooled the off-gas stream down to about 25°C and condensed the steam. A bubbler in the trap section of the condenser removed the particulate carry-over. The off-gas was further cooled by a second condenser which condensed out about 5 g of water per run. The off-gas then passed through a 25 µm filter and then a 2 µm filter prior to being measured by a Mass Spectrometer (MS) for H_2, O_2, CO_2, N_2, and Ar. An eductor drew the gases through the system and expelled them into the process exhaust system (chemical hood or shielded cell in SRNL) along with the motive air used to operate it. A control valve bled air into the suction side of the eductor to control the pressure of the DMR outer chamber to -4 inches of water column (inwc).

The DMR received the salt waste mixed with clay and coal as a single stream and converted it to a solid mineralized product in the presence of ~700°C superheated steam and a controlled flow of air, N_2, and Ar.

The SRNL BSR DMR inner reaction chamber is 70mm ID x 385mm tall with a porous bottom. The bottom 50mm (2 inches) is filled with zirconia beads. The zirconia beads were heavy enough not to be suspended by the gases and steam flowing up past them, acted as a base for the product to form on, allowed easy removal of the product from the reaction chamber, allowed easy separation of the product from the beads for analytic purposes, and provided a heat transfer medium for the gases that flow up through them. Zirconia beads are inert at the temperatures and oxygen fugacity at which the DMR operates and the beads do not affect the steam reforming chemistry.

The DMR outer chamber is 120mm ID x 400mm tall and provides connections for the outer chamber pressure relief and measurement line, and each of the two 20 foot coils which are housed between the DMR inner reaction chamber and the outer chamber. The outer chamber is sealed by the top flange of the inner chamber, and thus has a pressure relief line going to a seal pot which relieves at about 15 inwc. Water, N_2, Ar, and air enter the DMR via the coils which are between the inner and outer walls of the DMR and are converted to superheated steam and hot gases with heat provided by the furnace that surrounded the DMR as an external heat source. The steam and gases leave the coils and flow through the bottom of the DMR inner well mixed reaction chamber, the zirconia beads, the product, and out through the top of the DMR to the DMR condenser. The N_2 plus Ar plus Air total flow rate was held at a constant 500 sccm to minimize particle carryover. The relative flow rates are varied in order to control the process REDOX potential.

4.3.2 *BSR Operational Control Strategy*

The DMR lid is 120mm ID x 80mm tall and was sealed to the top of the inner chamber. The lid holds two type K thermocouples, the centered feed line that is cooled with standing water, the inner chamber pressure relief and measurement line, and the off-gas line going to the DMR condenser. In the event of an off-gas line pluggage, the inner chamber and lid have a pressure relief line going to a seal pot which relieves at about 15 inwc. One thermocouple was positioned at the level of the zirconia bead bed and the control thermocouple was positioned 2.5 inches above the surface of the bead bed. This 2.5 inch height was the upper point of the reaction zone in the DMR. The control temperature ranged from 710°C to 760°C in the DMR for all of these runs.

The DMR off-gas treatment system consisted of the quartz wool in the crossover bar, the crossover bar (see Figure 4-9) from the DMR to the condenser/bubbler, the condenser/bubbler, the second condenser, 25 um paper filter, and 2 um paper filter. It was necessary for pretreatment of the off-gas to prevent pluggage or damage to the mass spectrometer. The system treated a combined controlled flow of 500 standard cubic centimeters per minute (sccm) of Ar, N_2, and air along with about ~200 sccm of reaction gases from the reforming process. It condensed 0.4 ml/min water from the superheated steam plus about 0.7 ml/min water from the slurry feed. The condenser/bubbler was capable of reducing the off-gas stream temperature from 400°C down to 25°C.

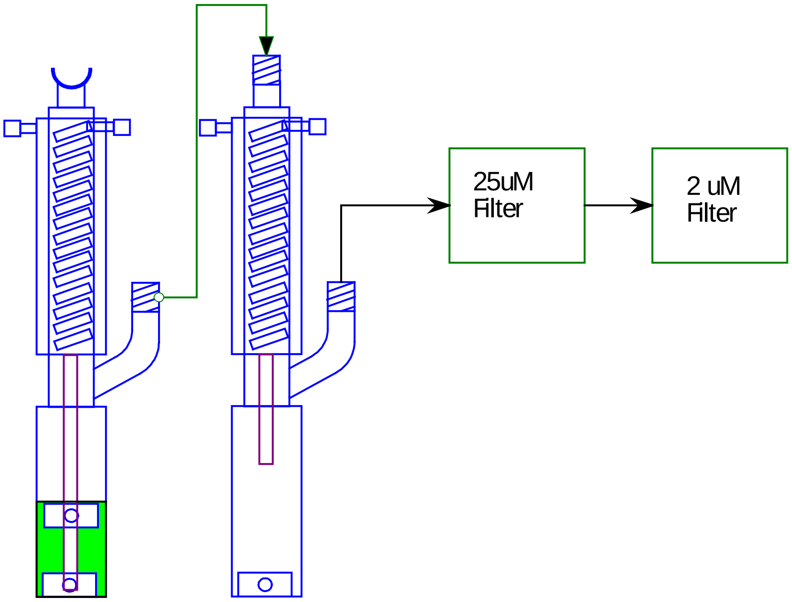


Figure 4-9. BSR DMR Off-Gas Treatment

A removable piece of quartz wool filtered out most of the particulate carry over as the off-gases passed through it on the way to the condenser/bubbler. The off-gases and steam entered at the top of the condenser/bubbler and flowed and condensed down through the center tube which ended at the bottom of a 75 mm deep water reservoir filled with zirconia beads. The condenser cooled the off-gas stream down to about 25°C and removed the steam and feed water. A bubbler in the trap section of the condenser removed the remainder of the particulate carry-over. Excess water from the bubbler would overflow into a sealed reservoir (not shown). The off-gas was further cooled by a second condenser which condensed out about 5 g of water per run. The off-gas then passed through a 25 µm filter and then a 2 µm filter prior to being measured by a Mass Spectrometer. The 25 µm filter trapped most of the vaporized sealing grease (that sealed the DMR flanges) such that the 2 µm filter was seldom blinded. There were no pluggages of the mass spectrometer as a result of this system. The quartz wool and the bubbler water also provided some natural sampling points for off-gas analysis.

The BSR used a Monitor Instruments LAB 3000 Cycloidal MS for the reformer real time off-gas analysis, see Figure 4-10 for schematic. The spectrometer was set up to measure H_2, O_2, N_2, CO_2, and argon. The MS would measure the DMR off-gas on channel 2. Channel 1 was used for the calibration gas. Both channels had 7 micron sintered metal filters in the 1/8” lines going to the instruments to prevent plugging the lines inside the MS.

Since the line pressure near the MS could go down to -25 inwc, it was necessary to run a second eductor and vacuum regulator to draw the sample gases through the MS. The vacuum was controlled to -40 inwc while the flow rate of gases pulled by an MS sample line was kept at 8 sccm. The flow rate of the gases coming from the DMR condenser varied between 500 to 700 sccm.

The MS was controlled by a Personal Computer (PC) with Monitor Instruments proprietary software loaded. Data from the MS computer was transferred to the control computer in real time via a serial connection.

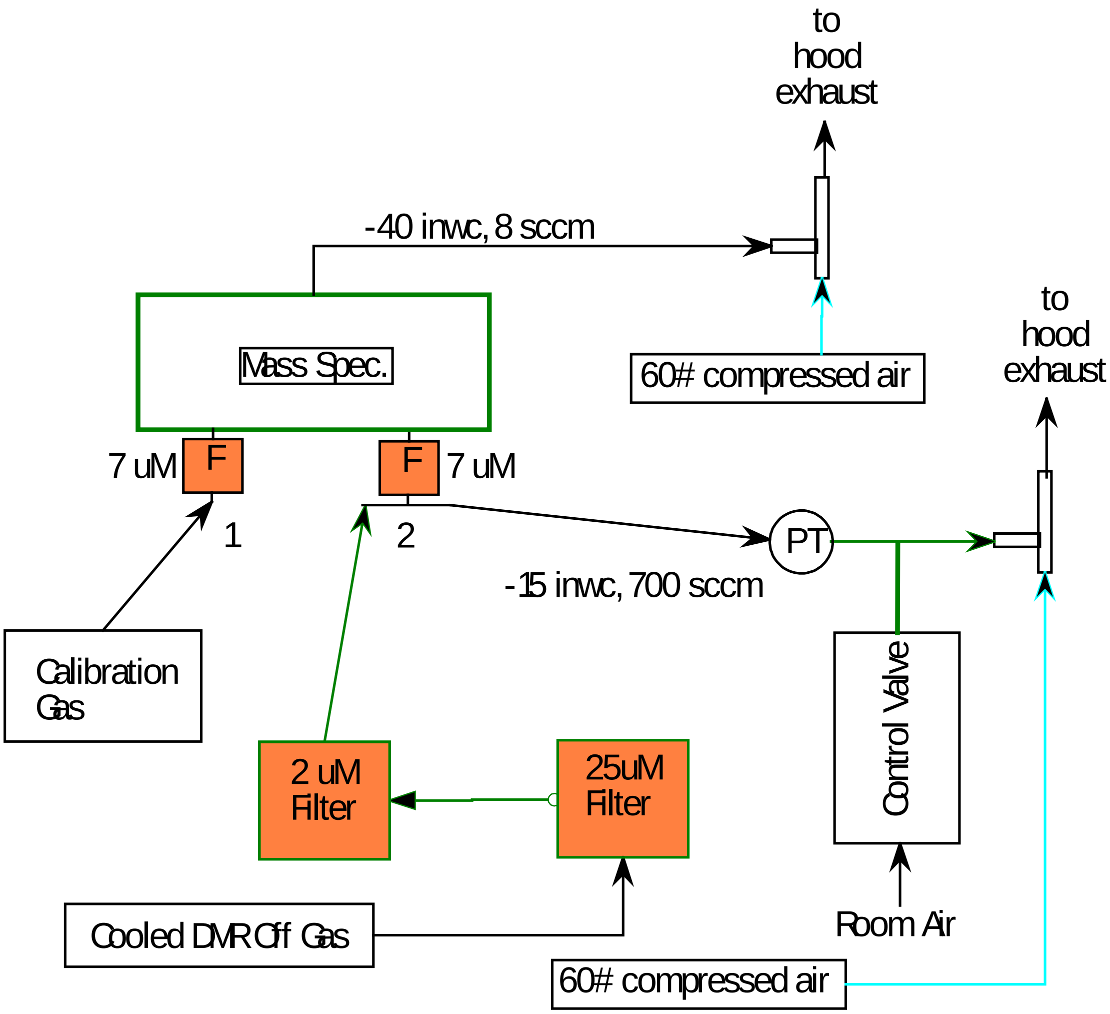


Figure 4-10. The BSR Mass Spectrometer

The DMR H_2 values were continuously trended on the control computer and, originally, operating personnel would manually vary the air flow into the DMR to control the DMR H_2 value between 1.0% and 3.0%. However, from 10/19/10 forward, air flow was controlled to achieve the proper product REDOX based on a gas REDOX correlation.

The LOI was controlled by reacting away the excess coal in the reformer until the cumulative value of CO_2/ml fed to the DMR reached a predetermined endpoint. This ensured the product did not have excessive unreacted coal in it. This was based on an imperfect mass balance of carbon since the MS did not measure CO which also is present in the off-gas.

(Carbon fed into DMR) – (Carbon Leaving as CO_2) = Unreacted carbon in product

The MS would determine and transmit the gas concentration data about once every 14 seconds. However, the lag time between the measurement and the conditions in the DMR ranged between 3 to 4 minutes depending on flow rates. See Figure 4-12 for a diagram of the configuration of the control system in the SRNL Shielded Cells.

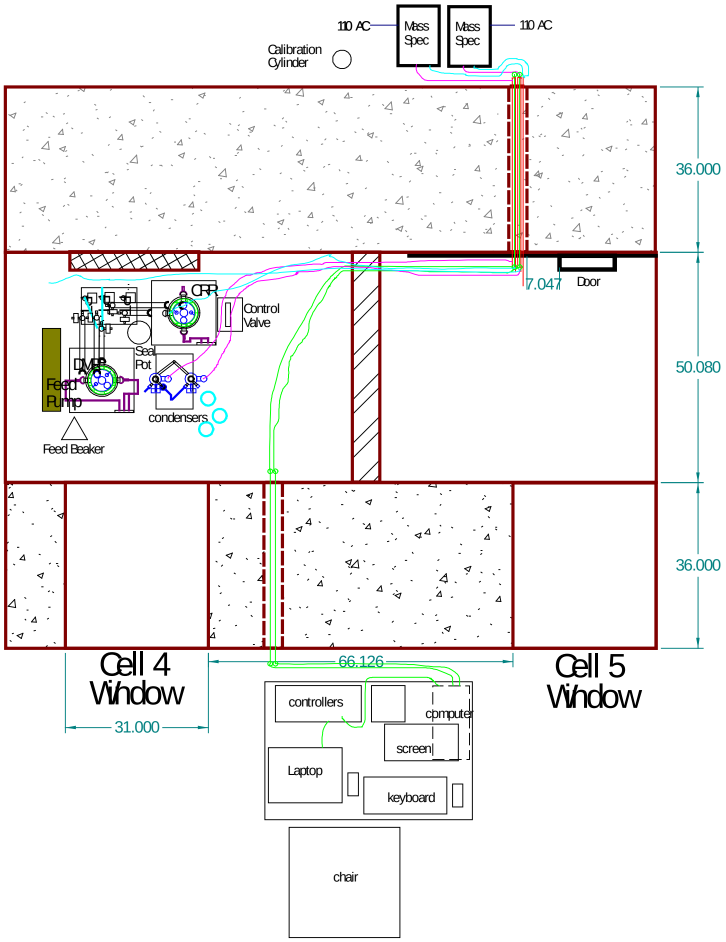


Figure 4-11. Total Rad System Layout at Cell 4 (Simplified)

The computers for the MS and process control system along with the steam water pumps, MKS gas flow controllers, furnace controllers, furnace safety relays, and input/output box are located external to the cell on the operational side. The MS is in a radio-hood behind the cell on the maintenance side. Connections between process and control systems required the use of 9 inner wall connection tubes (known at SRNL as KAPL plugs which were first developed at Knolls Atomic Power Laboratory).

The BSR was controlled by a single PC running Windows XP with 16 serial port connections. Omniserver software was used as the server software to communicate through the serial ports. Intouch software was used as the client software and the main machine interface. Data acquisition was continuous and trended in real time on screen as the process ran. Real time data was also saved to a file on a frequency of once per minute. Control logic was programmed into Intouch to provide operator aid (including a Pressure Indicating Device (PID) pressure controller). A complete schematic of the control set up is given in Figure 4-12.

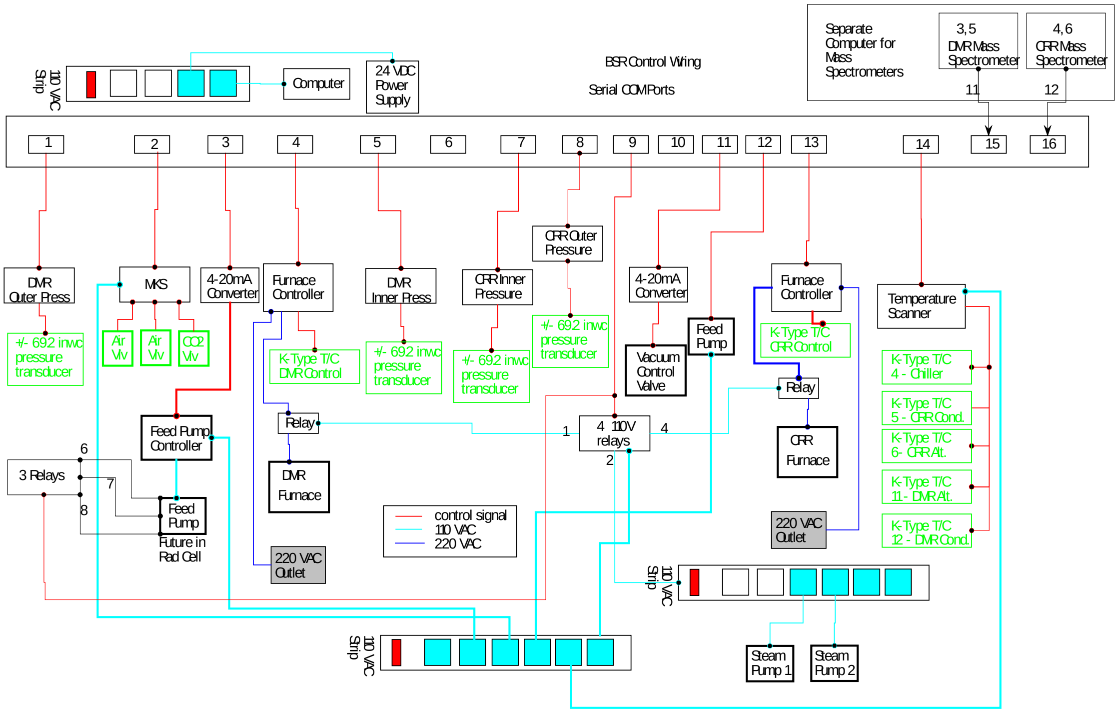


Figure 4-12. BSR Process Controller Diagram

The process parameters measured were:

- Slurry Feed Rate,
- DMR outer pressure,
- DMR Inner Pressure,
- DMR Bed Temperature,
- DMR Control Temperature,
- DMR H_2, O_2, N_2, CO_2, and 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
- DMR Air flow-rate coupled to the N_2 and Ar flowrates.

4.4 Granular Product Characterization

The granular BSR products from the DMR bed, from the off-gas lines, and the seal pots needed to be characterized to facilitate the BSR mass balance strategy outlined in Section 4.5. The BSR granular bed product also needed to be analyzed to normalize leach test results for the performance testing (see Section 4.6).

The BSR product samples were digested by both sealed Teflon® vessel aqua regia (AR) and short duration alkali [Na_2O_2/NaOH] peroxide fusion (PF) in Zr crucibles for elemental composition. The AR and PF digestions were than analyzed by ICP-AES, while the AR digestions were also analyzed by ICP-MS. In the case of the AN-103 (Module D) granular product, both the AR and PF digestions were analyzed by ICP-MS in order to verify that complete recovery of Re was being achieved. Samples for anions, including iodine, were digested by KOH fusion with a water uptake; anions were then determined by IC and iodine by ICP-MS. These techniques were used for both the non-radioactive and radioactive BSR products. Radioactive counting techniques were used for Cs-137, Tc-99, I-125, and I-129. The measured granular product densities were also measured.

The unreacted coal does not contribute to the composition of the mineral product. Therefore, unreacted coal is removed before chemical analysis. This can be done physically by (1) removing large coal manually, (2) roasting the coal out in an oxidized atmosphere, or (3) determining the amount of coal in the sample, performing the analysis with the coal present and then normalizing the composition mathematically for the coal content. Comparative studies have been performed at SRNL with methods 1-3 and the same compositions are achieved.[40,41] Comparative studies have been performed at PNNL of roasted and unroasted samples and the same compositions were also achieved.[98] Heating to remove the carbon was chosen as the preferential method of coal removal before analysis 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 be impossible. Samples before and after this heating were examined by XRD to verify that the phase assemblages had not changed.[40,41]

In order to remove the coal by roasting first the Loss-on-Drying (LOD) is measured as the weight loss at 110°C from adsorbed water. The LOI is then performed at 525°C in air by heating the samples to 525°C overnight. 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 (USGS) procedure [99] for carbon removal in preparation for the analysis of coal combustion by-products.

Unreacted coal is not removed before the $Fe^{+2}/\Sigma Fe$ (REDOX ratio) is measured colorimetrically.[100] If the unreacted coal is present at >10 wt.%, interference can occur with the measurement of the REDOX ratio by the colorimetric procedure. For this reason the unreacted coal concentration was kept as low as reasonably achievable in all the BSR Modules, i.e. <2 w.t%.

The REDOX of certain species in the FBSR process are important because over a certain range of the $Fe^{+2}/\Sigma Fe$ ratio, the oxygen fugacity (f_{O_2}) in the DMR is at an appropriate level to help ensure that the constituents of concern (COC) and the radionuclides are in the right oxidation states to be sequestered in the target mineral phases (see Table 1-1 and Reference 52). The REDOX is a balance between being oxidizing enough so that the Re and Tc are in the +7 state to enter the sodalite cage and not overly oxidizing forcing the chromium to soluble +6 state. To prevent the chromium oxidation, often the IOC is added. [34,40,41] Thus, the REDOX values of the mineral products are determined to confirm that the conditions achieved during BSR processing were consistent with the target conditions from the FBSR ESTD campaigns.

The initial BSR REDOX target for the Rassat simulant (Module B) was between 0.4-0.6 $Fe^{+2}/\Sigma Fe$ which matched the values measured experimentally for the ESTD Module B testing (Table 4-6). The ESTD sample contained the IOC, which has its own REDOX, while the BSR simulant and radioactive products will be tested without the IOC as it complicates the interpretation of the REDOX measurement. The initial target range for Simulant Module C was lowered to allow more oxidizing feeds to be made, i.e. $Fe^{2+}/\Sigma Fe$ of 0.2-0.6 (Table 4-6). The Module C radioactive campaign lowered the upper limit to 0.5, i.e. $Fe^{2+}/\Sigma Fe$ of 0.2-0.5 (Table 4-6). During the course of these studies and in consortium with the ORNL who was measuring the amount of Re and Tc-99 in the sodalite cage, the upper limit $Fe^{+2}/\Sigma Fe$ was reduced to <0.5 as more reduced values volatilized too much SO_4 as $SO_3\uparrow$ or $S_2\uparrow$ gas and left 30-33% of the Re in the reduced oxidation state of Re^{+4} which would not go into the sodalite cage. Therefore, the upper REDOX limit for Module C was lowered to 0.5 to ensure a high percentage of the Re was present as Re^{+7} for the sodalite cage (Table 4-6). For Module D (AN-103), the REDOX target was lowered yet again to match the AN-107 FBSR product value of 0.18, which kept the chromium from leaching but maximized the Re^{+7} incorporation in the sodalite cage. The Module D targets (simulant and radioactive) were 0.15-0.5. The Module E target was lowered again, but the IOC was added to tie up the chromium as it was recognized that without a host phase to sequester the chromium, that the oxidizing REDOX might create soluble chromium +6 species instead of the desired insoluble chromium +3 species.

Table 4-6. REDOX Targets for Hanford Rassat Simulant, SX-105, AN-103 and AZ-101/AZ-102

Demonstration	Measured REDOX	Target REDOX			
	Module B (Rassat Simulant)	Module B (Rassat Simulant)	Module C (SX-105)	Module D (AN-103)	Module E (AZ-101/ AZ-102)
BSR Simulant	0.41	0.4-0.6	0.20-0.60	0.15-0.50	≤0.15
BSR Radioactive	0.36	0.4-0.6	0.20-0.50	0.15-0.50	
ESTD Product Receipt (PR)	0.41-0.58				
Iron Oxide Catalyst (IOC)	0.567				

4.5 BSR Mass Balance

The BSR is a simpler design than the ESTD facility in Golden, CO and so it is easier to perform a mass balance. For Modules C and D, there were five mass balance product vectors and one feed vector. No mass balance was performed for Module E since the test program was stopped before completion of this module. The product vectors were composed of the product solids, the solids in the cross bar that that provided the pathway to the condenser, the solids in the condenser, cross bar rinses used to determine if any species adhered to the crossbar, and the condenser solution. In addition, the glass wool filter in the crossbar was weighed before it was put in place and at the end of each module to determine how much carryover solids had collected onto the glass wool filter.

The mass balance calculational approach for Modules C and D simulant and radioactive campaigns consisted of identifying key input and output streams and then analyzing these streams for key species. Before each radioactive module, a simulant module was performed to identify the proper control parameters and sampling techniques. The mass balance streams that could be analyzed for the simulant campaigns were greater due to the limitations of the radioactive systems, i.e., accessibility to various streams given the physical constraints of the cells operations.

The output streams for the Simulant Module C runs were the solid granular product, the cross bar rinse/ solids, the DMR condenser/bubbler drains, and the seal pot drains/rinses. The output streams for the Radioactive Module C runs were the solid granular product, the cross bar rinse/solids, and the DMR condenser/bubbler drains.

For Module D simulant runs, more output streams were analyzed than the previous campaigns to try to close the mass balance more tightly. To try to capture more of the metal species for a better mass balance, a special solution of 5 wt.% HNO_3, 10 wt.% H_2O_2, 85 wt.% deionized water (hereafter referred to as the Oxidizing Solution) was prepared for Module D. This Oxidizing Solution was used for special rinses of the DMR condenser/bubbler and seal pot legs at the end of the Module D experiments. After the Oxidizing Solution rinse of the DMR condenser/bubbler, a 95 wt.% ethanol solution was used to rinse out the DMR condenser/bubbler to try to capture and characterize the black solids present for Module D. The various output streams for the Simulant Module D runs were the solid granular product, the cross bar solids, the DMR condenser/bubbler drains and Oxidizing Solution rinses, DMR Basket Oxidizing Solution rinses, the seal pot drains and Oxidizing Solution rinses, and the off-gas micron filters.

A special Simulant Module D run was performed to better quantify the masses of the input and output streams for the BSR system. For this special run the Oxidizing Solution was used in the DMR condenser/bubbler instead of deionized water like for the normal Simulant D runs. For this special run, a 5 wt.% Spectrosol[τ] solution (hereafter referred to as the Spectrosol Solution) was used to rinse the crossbar and DMR condenser/bubbler after the Oxidizing Solution rinses. A scrubber with a 5 M KOH caustic solution on the off-gas vent was used to try to capture any volatile species like Iodide. The various output streams for the special Module D run were the solid granular product, the cross bar solids and Oxidizing/ Spectrosol Solution rinses, the DMR condenser/bubbler drains and Oxidizing/Spectrosol Solution rinses, DMR basket Oxidizing Solution rinses, the seal pot drains and Oxidizing Solution rinses, and the off-gas micron filters.

The key input and output streams for the mass balance calculations for the various BSR runs are shown in Table 4-7 and Table 4-8, respectively.

Table 4-7. Key Input Streams for Simulant and Radioactive Modules C and D

Input Stream	Comment
Feed-Supernate	Portion of Feed that is simulant or radioactive waste
Feed-$Fe(NO_3)_3$*$9H_2O$	Portion of Feed that is REDOX indicator
Feed-Coal	Portion of Feed that is unreacted Coal
Feed-Coal Ash	Portion of Feed that is reacted coal or coal ash
Feed-Clay-OptiKasT®	Portion of Feed that is OptiKasT® Clay
Feed-Clay-Sagger XX®	Portion of Feed that is Sagger XX® Clay

[τ] A solution of ultra pure water and 37% fuming hydrochloric acid used to dissolve Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Zn, Sr, Re and radionuclides into solution.

Table 4-8. Key Output Streams for Simulant and Radioactive Modules C and D

Campaign	Module C (Tank SX-105)		Module D (Tank AN-103)		
Output Stream	**Simulant Runs**	**Radioactive Runs**	**Simulant Runs**	**Special Simulant Run**	**Radioactive Runs**
Granular Product	Product Solids	Product Solids	Product Solids	Product Solids	Product Solids
DMR Condenser/Bubbler Drain	Deionized Water Filtrate & Filtered Solids	Deionized Water Filtrate & Filtered Solids	Deionized Water Filtrate & Filtered Solids	Oxidizing Solution Filtrate & Filtered Solids	Deionized Water Filtrate & Filtered Solids
DMR Condenser/Bubbler Rinse	None	None	Oxidizing Rinse Filtrate & Filtered Solids	Unfiltered Oxidizing Rinse	None
DMR Basket Rinse	None	None	Oxidizing Rinse Filtrate & Filtered Solids	Unfiltered Oxidizing Rinse	None
Crossbar Rinse	Deionized Water Rinse Filtrate & Filtered Solids	Deionized Water Rinse Filtrate & Filtered Solids	None	Unfiltered Oxidizing Rinse	Unfiltered Oxidizing Rinse
Crossbar Solids	Quartz Wool Solids	Quartz Wool Solids	Quartz Wool Solids	Quartz Wool Solids	Quartz Wool Solids
Crossbar/DMR Condenser Rinse	None	None	None	Unfiltered Spectrosol Rinse	None
Seal Pot Drain	Filtrate & Filtered Solids	None	Filtrate & Filtered Solids	Unfiltered Drain	None
Seal Pot Rinse	None	None	Oxidizing Rinse Filtrate & Filtered Solids	Unfiltered Oxidizing Rinse	None
25 Micron Off-gas Filter	None	None	Solids	Solids	None
2 Micron Off-gas Filter	None	None	Solids	Solids	None
Off-gas Caustic Scrubber	None	None	None	Unfiltered Drain	None

The key input and output streams for the simulant mass balances are shown pictorially in Figure 4-13 and Figure 4-14. Note that the mass balance input and output streams are in yellow boxes.

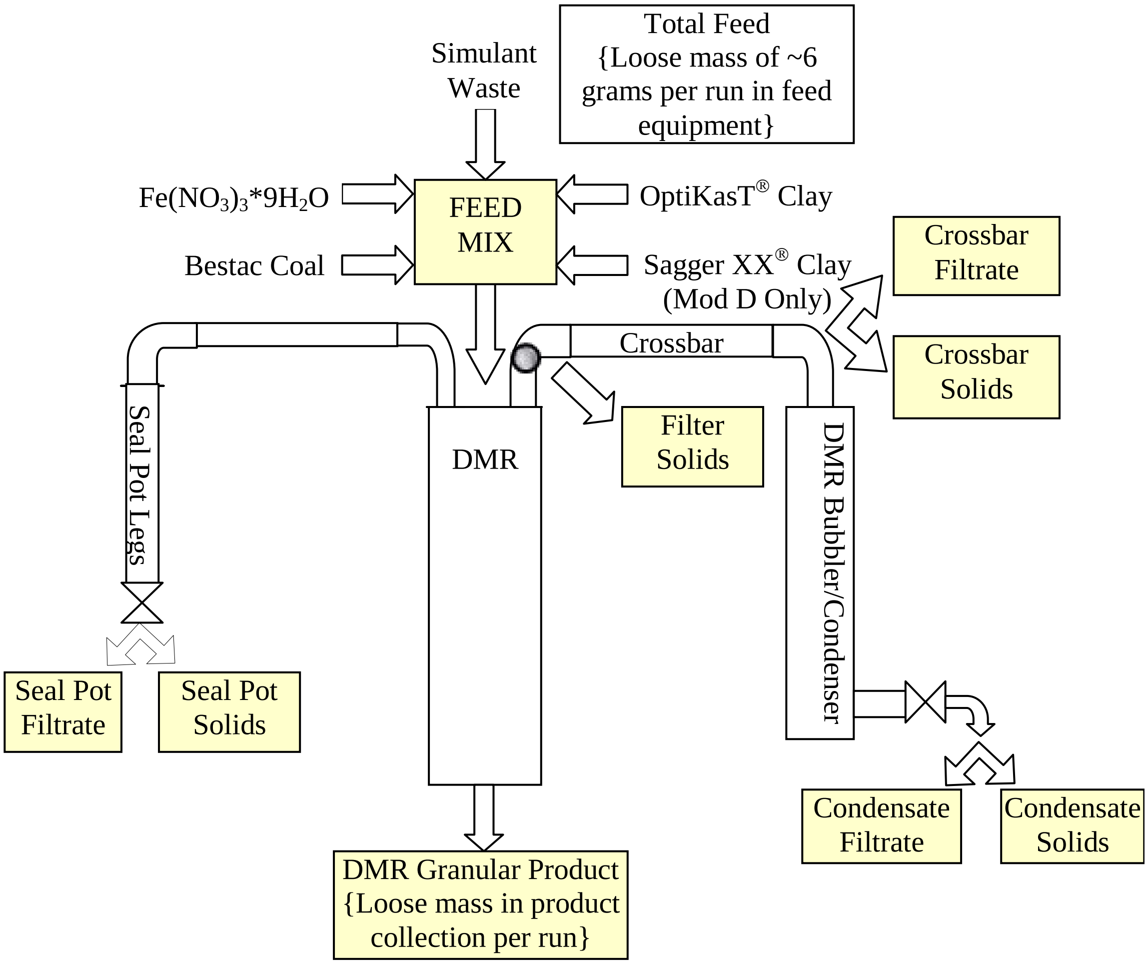


Figure 4-13. Mass Balance Input and Output Streams for Simulant Modules

The key input and output streams for the Module C radioactive mass balances are shown pictorially in Figure 4-14. Due to the timing of the radioactive experiments and the limitations in the Shielded Cells, no seal pot samples were collected.

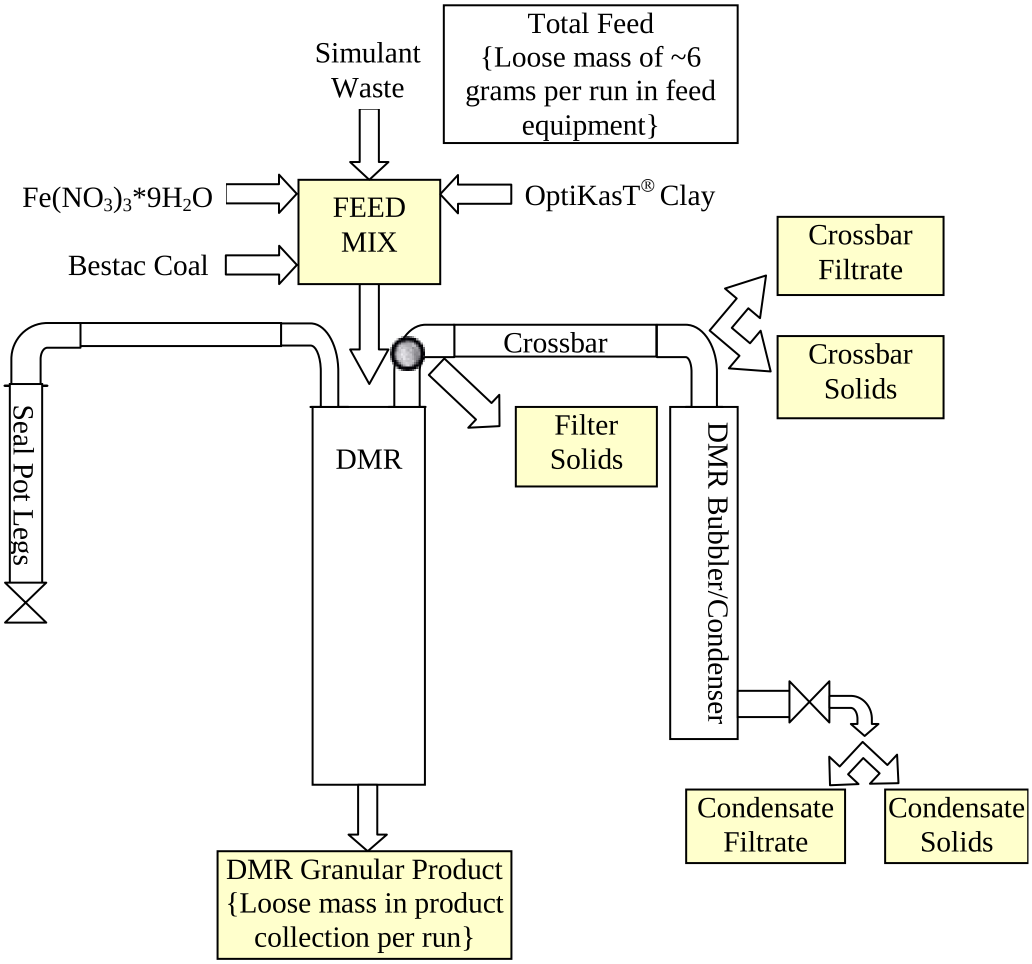


Figure 4-14. Input and Output Streams for Radioactive Module C

The key input and output streams for the regular Module D simulant mass balances are shown pictorially in Figure 4-15. Note that the mass balance input and output streams are in yellow boxes.

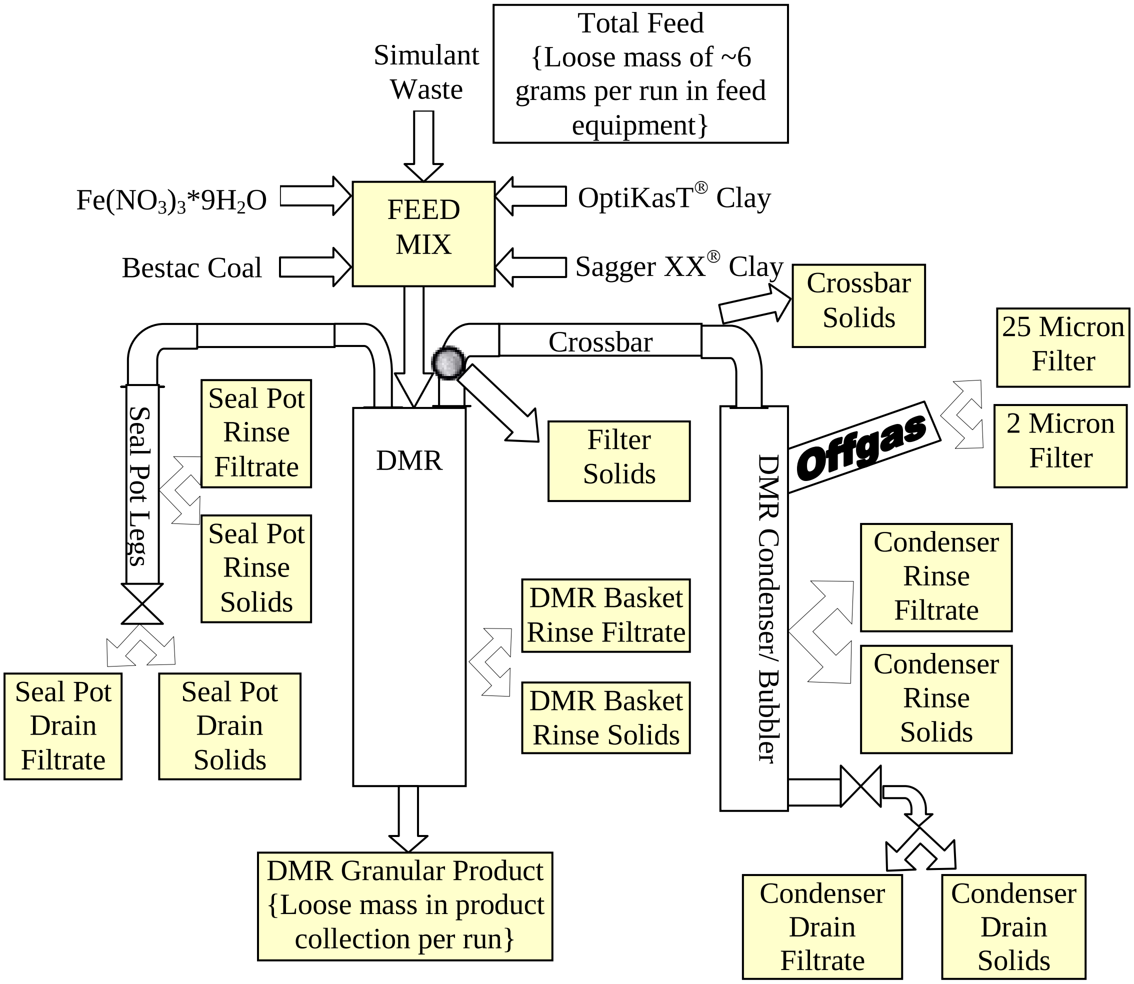


Figure 4-15. Mass Balance Input and Output Streams for Regular Simulant Module D Runs

The key input and output streams for the special Module D simulant run mass balance are shown pictorially in Figure 4-16. Note that the mass balance input and output streams are in yellow boxes. More streams were analyzed for this special run compared to the regular runs to close the mass balance.

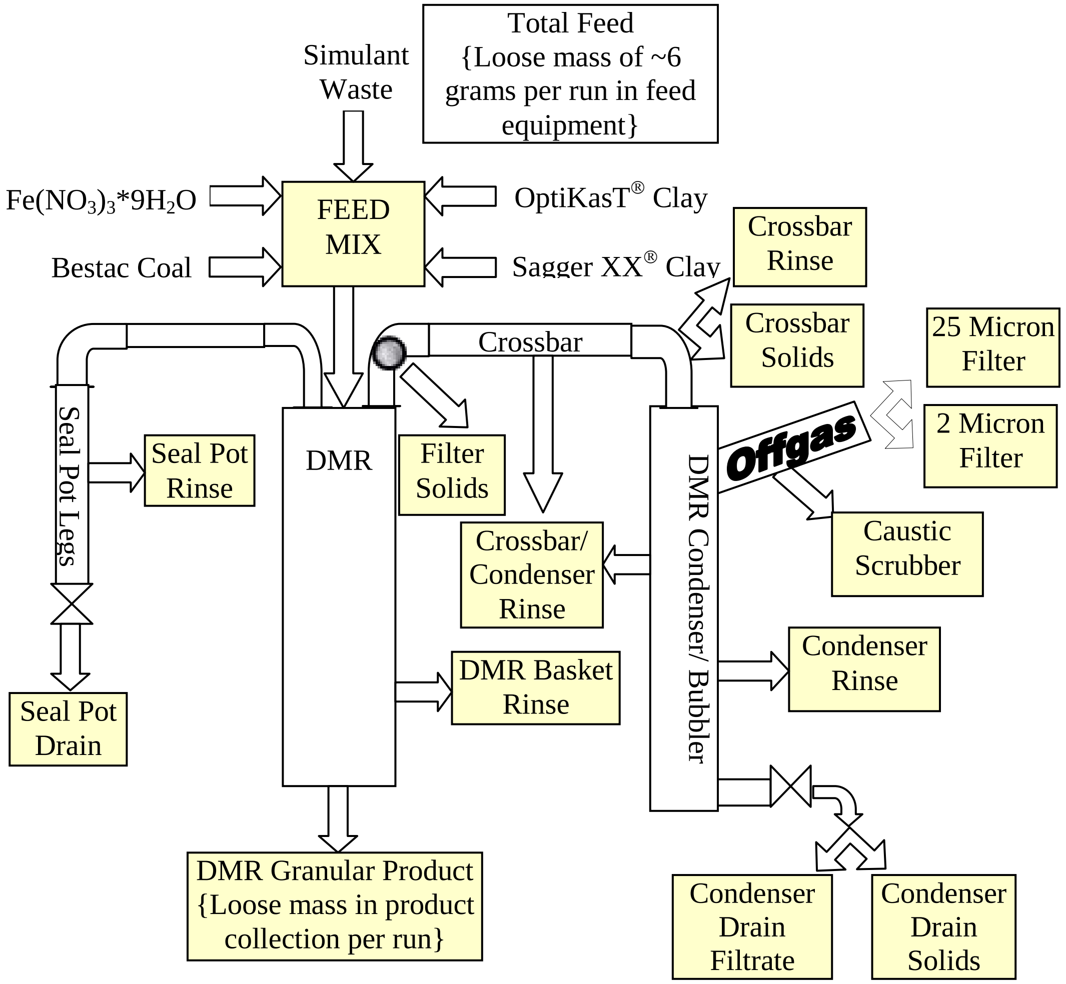


Figure 4-16. Mass Balance Input and Output Streams for Simulant Module D Special Run

The key input and output streams for the radioactive Module D mass balances are the same as in the Module C radioactive runs as shown in Figure 4-14. Due to the timing of the radioactive experiments and the limitations in the Shielded Cells, no seal pot samples were collected and no special rinses were done for the radioactive campaign.

The key species examined in the simulant and radioactive campaigns for the various mass balances are shown in Table 4-9.

Table 4-9. Key Species for Mass Balance

Radioisotope Species	Non-Radioactive Species
Cs-137	Cs-133
I -125	I-127
I -129	
Tc-99	Re
	Al
	Cl
	Cr
	Na
	Si
	SO_4^{2-}

Using the input and output streams described earlier, the mass balance calculational logic for the regular simulant and radioactive runs can be described as shown in Equation 2 noting that some streams are zero if not needed:

Equation 2

$$Waste*w_i + Fe*f_i + Coal_{ash}*ca_i + Coal_{un}*cu_i + O\_Clay*o_i + S\_Clay*s_i = Product*p_i + CD\_fil*cf_i + CD\_sol*cs_i + CDR\_sol*crs_i + CDR\_fil*crf_i + XR\_fil*xf_i + XR\_sol*xs_i + SP\_fil*sf_i + SP\_sol*ss_i + SPR\_fil*srf_i + SPR\_sol*srs_i + BR\_sol*brs_i + BR\_fil*brf_i + F25\_sol*f25_i + F2\_sol*f2_i$$

Where:

i = One of key species identified earlier

Waste = mass of simulant or radioactive waste stream

Fe = mass of $Fe(NO_3)_3 \bullet 9H_2O$ added to waste stream

$Coal_{ash}$ = mass of Bestac® Coal that remains in granular product as coal ash

$Coal_{un}$ = mass of Bestac® Coal that remains unreacted in granular product

O_Clay, S_Clay = mass of OptiKasT® and Sagger XX® Clay added to waste stream, respectively

w_i, f_i, ca_i, cu_i, o_i, s_i are concentrations of species i for waste, $Fe(NO_3)_3*9H_2O$, Coal Ash, Unreacted Coal, OptiKasT® Clay, and Sagger XX® Clay streams, respectively

Product = mass of solid granular product
p_i = concentration of species i in solid granular product

CD_fil = mass of DMR condensate filtrate
cf_i = concentration of species i in DMR condensate filtrate

CD_sol = mass of DMR condensate solids
cs_i = concentration of species i in DMR condensate solids

CDR_sol = mass of DMR Condenser dry solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only) from filtering special rinse
crs_i = concentration of species i in DMR Condenser dry solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only) from filtering special rinse

CDR_fil = mass of DMR Condenser special rinse filtrate (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

crf_i = concentration of species i in DMR Condenser Solids special rinse filtrate (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

XR_fil = mass of crossbar filtrate from rinse and filtering
xf_i = concentration of species i in crossbar filtrate from rinse and filtering

XR_sol = mass of crossbar solids from quartz wool (for modules C and D only) and/or rinse filtering
xs_i = concentration of species i in crossbar solids from quartz wool and/or rinse filtering

SP_fil = mass of seal pot leg filtrate from drains
sf_i = concentration of species i in seal pot leg filtrate from drains

SP_sol = mass of seal pot leg solids from drains
ss_i = concentration of species i in seal pot leg solids from drains

SPR_fil = mass of seal pot leg filtrate from rinses
srf_i = concentration of species i in seal pot leg filtrate from rinses

SPR_sol = mass of seal pot leg solids from rinses
srs_i = concentration of species i in seal pot leg solids from rinses

BR_sol = mass of DMR Basket dry solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only) from special rinse

brs_i = concentration of species i in DMR Basket dry solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only) from special rinse

BR_fil = mass of DMR Basket Solids special rinse filtrate (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

brf_i = concentration of species i in DMR Basket Solids special rinse filtrate (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

F25_sol = mass of 25 micron filter solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

$f25_i$ = concentration of species i in 25 micron filter solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

F2_sol = mass of 2 micron filter solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

$f2_i$ = concentration of species i in 2 micron filter solids (on- and off-specification material were both included in the mass balance as the designations on- and off-specification referred to product REDOX and coal content only)

Due to feed remaining in the feed containers and the feed lines, a special BSR run was performed [28]. This special run was performed to better quantify the masses of the input and output streams for the BSR system. The various output streams for the special run as shown in

Table **4-10** were the solid granular product, the cross bar solids and Oxidizing/Spectrosol Solution rinses, the DMR Condenser/Bubbler drains and Oxidizing/Spectrosol Solution rinses, DMR Basket Oxidizing Solution rinses, the seal pot drains and Oxidizing Solution rinses, and the offgas micron filters. The key input and output streams for the BSR run mass balance are shown pictorially in Figure 4-16 Note that the mass balance input and output streams are in yellow boxes.

Table 4-10. Key Output Streams for Special BSR Run

Output Stream	Special Simulant Run
Granular Product	Product Solids
DMR Condenser/Bubbler Drain	Oxidizing Solution Filtrate & Filtered Solids
DMR Condenser/Bubbler Rinse	Unfiltered Oxidizing Rinse
DMR Basket Rinse	Unfiltered Oxidizing Rinse
Crossbar Rinse	Unfiltered Oxidizing Rinse
Crossbar Solids	Quartz Wool Solids
Crossbar/DMR Condenser Rinse	Unfiltered Spectrosol Rinse
Seal Pot Drain	Unfiltered Drain
Seal Pot Rinse	Unfiltered Oxidizing Rinse
25 Micron Offgas Filter	Solids
2 Micron Offgas Filter	Solids
Offgas Caustic Scrubber	Unfiltered Drain

For the special simulant run for Module D (AN-103), the mass balance uses similar logic shown above and in Equation 2 but the terms are slightly different as shown in Equation 3:

Equation 3

$$\text{Waste}*w_i + \text{Fe}*f_i + \text{Coal}_{ash}*ca_i + \text{Coal}_{un}*cu_i + \text{O\_Clay}*o_i + \text{S\_Clay}*s_i = \text{Product}*p_i + \text{CD\_fil}*cf_i + \text{CD\_sol}*cs_i + \text{CDR}*cr_i + \text{XR}*xr_i + \text{XR\_sol}*xs_i + \text{SP}*sp_i + \text{SPR}*sr_i + \text{BR}*br_i + \text{XRCD}*xrcd_i + \text{F25\_sol}*f25_i + \text{F2\_sol}*f2_i + \text{CAS}*cas_i$$

Where old terms are defined as shown above and new terms are:

CDR = mass of DMR Condenser rinse and residue recovered from Oxidizing rinse
cr_i = concentration of species i in DMR Condenser Oxidizing rinse and residue recovered from special rinse

XR = mass of crossbar Oxidizing rinse and residue recovered from special rinse
xr_i = concentration of species i in crossbar Oxidizing rinse and residue recovered from special rinse

SP = mass of seal pot leg sample from drains
sp_i = concentration of species i in seal pot leg sample from drains

SPR = mass of seal pot leg Oxidizing rinse and residue recovered
sr_i = concentration of species i in seal pot leg Oxidizing rinse and residue recovered

BR = mass of DMR Basket Oxidizing rinse and residue recovered
br_i = concentration of species i in Oxidizing rinse and residue recovered

XRCD = mass of crossbar and DMR Condenser Spectrosol rinse and residue recovered
$xrcd_i$ = concentration of species i in crossbar and DMR Condenser Spectrosol rinse and residue recovered

CAS = mass of off-gas caustic scrubber drains
cas_i = concentration of species i in off-gas caustic scrubber drains

During the special BSR run for Module D, masses of various equipment were taken before and after the run to determine the amount of feed actually fed and the amount of granular product actually produced. These special measurements showed that the feed mass per BSR run was overestimated by about 6 grams per run (feed hold up in the feed bottle and feed tube).

The Module C simulant testing consisted of 6 runs so the total measured feed of about 612.28 g was decreased by 36 grams to about 576.28 g based on the special D run and described in Reference 52 and in the next paragraph. The Module C radioactive campaign had 12 runs but only the first 7 runs were used in the mass balance due to various feed batches being mixed for the last 5 runs. For the first 7 runs of the Module C radioactive campaign, the total measured feed of about 654.95 g was decreased by 42 grams to about 612.95 g.

The simulant campaign for Module D consisted of 10 runs so the total measured feed of about 805.45 g was decreased by 60 grams to about 745.45 g. The special simulant run for Module D consisted of 1 run of total measured feed of about 72.01 g as determined by measuring the masses of various equipment. The Module D radioactive campaign had 10 runs so the total measured feed of about 680.63 g was decreased by 60 grams to about 620.63 g.

The special Module D run also showed that the granular product mass was being underestimated due to losses in the collection and processing of the granular product for each run. Since the granular product collection and processing techniques differed from the simulant versus radioactive modules as well as across different researchers and technicians, a calcine factor for the BSR was developed with respect to the mass of granular product produced per mass of feed coming into the system. This calcine factor was based on data from multiple campaigns as shown in Table 4-11. The average across all campaigns was 0.40 with a standard deviation of 0.03.

Table 4-11. Product to Feed Mass Ratios for BSR Runs

Run	**Module B**		**Module C**		**Module D**
	Simulant Runs	**Radioactive Runs**	**Simulant Runs**	**Radioactive Runs**	**Radioactive Runs**
1	0.42	0.42	0.36	0.36	0.43
2	0.38	0.41	0.43	0.38	0.38
3	0.39	0.40	0.42	0.38	0.41
4	0.39	0.42	0.37	0.44	0.36
5	0.39	0.41	0.42	0.43	0.34
6	0.39	0.42	0.35	0.43	0.40
7	0.39	0.36	----	0.42	0.39
8	0.39	0.43	----	0.38	0.49
9	0.37	0.44	----	0.41	0.37
10	0.40	0.46	----	0.38	----
11	0.40	0.40	----	0.45	----
12	0.39	0.41	----	----	----
13	0.40	0.38	----	----	----
14	0.40	0.46	----	----	----
15	0.39	0.46	----	----	----
16	0.40	0.40	----	----	----
17	0.41	0.38	----	----	----
18	----	0.39	----	----	----
19	----	0.37	----	----	----
Average	**0.39**	**0.41**	**0.39**	**0.41**	**0.40**
Standard Deviation	0.01	0.03	0.04	0.03	0.04

After studying the various granular product masses and corrected feed masses across the simulant and radioactive Module B, C and D activities, it was determined that:

Equation 4

$$C_f = \frac{\text{Product}}{\text{Waste} + \text{O\_Clay} + \text{S\_Clay} + \text{Fe} + \text{Coal}_{ash} + \text{Coal}_{un}} = 0.4$$

Where:

C_f = Calcined factor for BSR

Waste = mass of simulant or radioactive waste stream fed

Fe = mass of $Fe(NO_3)_3{\bullet}9H_2O$ fed

O_Clay, S_Clay = mass of OptiKasT® Clay and/or Sagger XX®Clay fed, respectively

Coal_{ash} = mass of Bestac® Coal that remains in granular product as coal ash

Coal_{un} = mass of Bestac® Coal that remains unreacted in granular product

To calculate the unreacted Bestac® coal remaining after the BSR processing, the LOI and LOD measurements were performed on each run's granular product. Using the LOI and LOD measurements, the wt% carbon remaining in the granular product at the end of each run (c_{wt}%) were calculated using Equation 5:

Equation 5

$c_{wt}\%$ = LOI (wt.% of total mass) – LOD (wt.% of total mass)

The Bestac® coal contains 82.49% wt.% carbon based on analytical data received by SRNL from TTT. Using the c_{wt}% and the known wt% carbon in the Bestac® coal, the amount of unreacted coal per run was calculated using Equation 6:

Equation 6

$$\text{Coal}_{un} = \frac{\text{Product} * c_{wt}\%}{82.49\%}$$

Knowing the total mass of coal fed per run (Coal), the amount of coal that gets ashed per run (Coal_{ashed}) was calculated using Equation 7:

Equation 7

$\text{Coal}_{ashed} = \text{Coal} - \text{Coal}_{un}$

Using the measured wt.% ash in the Bestac® Coal of 5.11%, the mass of coal ash that remains behind in the granular product per run (Coal_{ash}) was then calculated using Equation 8:

Equation 8

$$\text{Coal}_{\text{ash}} = \text{Coal}_{\text{ashed}} * 5.11\%$$

The mass of product produced per run was then calculated using the BSR calcined factor (C_f) and the various output masses as described above:

Equation 9

$$\text{Product} = (\text{Waste} + \text{O\_Clay} + \text{S\_Clay} + \text{Fe} + \text{Coal}_{\text{ash}} + \text{Coal}_{\text{un}}) * 0.4$$

Once the masses and concentrations have been determined, the percent recovery of species i for a particular output stream j was calculated using Equation 10:

Equation 10

$$\text{Rec}_{i,j} = \text{Out}_{i,j}/\text{In}_i$$

Where:

$\text{Rec}_{i,j}$ = Percent Recovery of species i for a particular output stream j

$\text{Out}_{i,j}$ = Output Stream j Mass of Species i, which would be Product*p_i, CD_fil*cf_i, CD_sol*cs_i, XR_fil*xf_i, XR_sol*xs_i for the various streams

In_i = Total Input Mass of Species i = Waste*w_i + Fe*f_i + Coal*c_i + O_Clay*o_i + S_Clay*s_i

The total recovery of species i for all streams j then becomes:

Equation 11

$$\text{Rec}_i = \sum_j \text{Rec}_{i,j}$$

Rec_i = Percent Total Recovery of species i across all output streams

The recovery of species i across j streams was then normalized to 100% by using Equation 12:

Equation 12

$$\overline{\text{Rec}}_{i,j} = \frac{\text{Rec}_{i,j}}{\sum_j \text{Rec}_{i,j}}$$

Where:

$\overline{\text{Rec}}_{i,j}$ = normalized percent recovery of species i in stream j

4.6 Performance and Regulatory Testing

4.6.1 *Product Consistency Test (PCT) - Short Term*

The PCT was conducted on Module C simulant and radioactive granular mineral products following the procedures described in ASTM C 1285-08.[94] The samples were crushed and sieved using ethanol following the ASTM procedure sections 19.5 and 22.5. The samples were washed using only ethanol as described in Section 19.6.1 of the PCT procedure. A portion of the washed and sieved material was analyzed using Brunauer-Emmett-Teller Surface Area (BET-SA) to determine the actual surface area of the BSR product rather than using the geometric hard sphere assumption given in the PCT procedure. Although use of the BET surface area may overestimate the true reactive surface area, the obvious microporosity indicates that use of the geometric surface area will underestimate the true dissolution rate. Therefore, the dissolution rates reported here have been normalized to the BET surface area. The true reactive surface area is probably less than the BET value, but also probably significantly higher than the geometric value.[38] When the durability of the FBSR product is calculated using the BET-SA the durability is ~2 orders of magnitude lower than the leach rate of LAW glass. When the durability of the FBSR product is calculated using the hard sphere geometric surface area, the durability is equivalent to that of LAW glass. Data in this report used the BET-SA but Appendix O contains the necessary data to calculate the durability from either the BET-SA or the hard sphere geometric surface area.

All tests were conducted in triplicate (at a minimum) and the results averaged. The PCTs were performed at 90°C for seven days (PCT-A) in stainless steel vessels. The simulant leachates were then analyzed and the concentration of ions in the leachate measured by ICP-AES, IC, and ICP-MS.

Radioactive leachates were also analyzed using gamma spectroscopy and beta liquid scintillation. The elemental mass release of selected constituents was normalized by the initial concentration of each constituent after adjustment for moisture and unreacted carbon content, and reported in units of g/m^2.

Equation 13

$$NL_i = \frac{c_i(sample)}{f_i \cdot (SA/V)},$$

Where;

NL_i = normalized release, g $_{\text{(waste form)}}$ /m^2,
c_i (sample) = concentration of element "i" in the solution, g_i/L,
f_i = fraction of element "i" in the unleached waste form (unitless), and
SA/V = surface area of the final waste form divided by the leachate volume, m^2/L.

The leached solids were analyzed for phase mineralogy using x-ray diffraction.

4.6.2 *Product Consistency Test (PCT) – Long Term*

The long term PCTs were conducted on Module C non-radioactive and radioactive granular products from the BSR that had been crushed following the procedures described in ASTM C 1285-08.[94] The samples were prepared in the same manner as samples in Section 4.6.1. The PCTs were performed at 90°C for extended times up to one year (PCT-B) in Teflon® vessels. The same analyses were performed on the long term PCT leachates as the short term PCT leachates described in Section 4.6.1. All tests were conducted in duplicate and the results averaged. The elemental mass releases of selected constituents were normalized by the initial concentration of each constituent after adjustment for moisture and unreacted carbon content, and reported in units of g/m^2 as described in Section 4.6.1. The leached solids were analyzed for phase mineralogy using x-ray diffraction.

4.6.3 *Toxicity Characteristic Leaching Procedure (TCLP) Method 1311*

The TCLP [93] was used to assess the release of RCRA metals from the granular BSR products for Modules C, D, and E. Since the BSR REDOX control strategy had not been worked out completely, some of the Module C BSR products had a REDOX more oxidizing than 0.20 (<0.20 $Fe^{2+}/\Sigma Fe$), some were in the desired range (0.20-0.60 $Fe^{2+}/\Sigma Fe$ for the simulant and 0.20-0.50 $Fe^{2+}/\Sigma Fe$ for the radioactive; Table 4-6), and others were more reduced than desired (>0.60 $Fe^{2+}/\Sigma Fe$ for the simulant and >0.5 $Fe^{2+}/\Sigma Fe$ for the radioactive). This allowed SRNL to have the TCLP measured on different REDOX samples to study the impact of REDOX on the Cr leaching. The simulant samples were sent to General Engineering Laboratories (GEL) in Charleston, SC. The radioactive Module C BSR products were in the desired REDOX range, and TCLP was performed on the Module C radioactive material by PNNL.

The Module D simulant was in the correct REDOX range and SRNL submitted it to Davis and Floyd, an EPA certified laboratory for TCLP analyses, in Greenwood, SC. PNNL performed the radioactive Module D TCLP.

Two Module E simulant samples were made at a target REDOX of 0.15 $Fe^{2+}/\Sigma Fe$. One contained no IOC and the ferric nitrate nona-hydrate was the only additional source of iron, and the other contained the IOC and no ferric nitrate nona-hydrate. This was done to help evaluate the impacts of oxidizing REDOX on chromium leaching in the presence and absence of the IOC. Since the IOC has its own REDOX of 0.57 (Table 4-6), having it present can complicate the measurement of the REDOX ratio but attempts will be made to quantify how much IOC is needed at an oxidizing REDOX to retain the chromium as +3 chrome in the spinel mineral phase which is isostructural with the IOC mineral phases.

This Environmental Protection Agency (EPA) approved procedure is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. The main purpose of this procedure was to determine whether the FBSR waste form would meet the requirements of the RCRA LDR since Hanford tank wastes contain hazardous constituents that are listed wastes. The initial focus of the TCLP analyses was on inorganic contaminants, because steam reforming effectively destroys organic materials by pyrolysis. The TCLP data for the granular products are considered inputs to the go / no-go evaluation process.

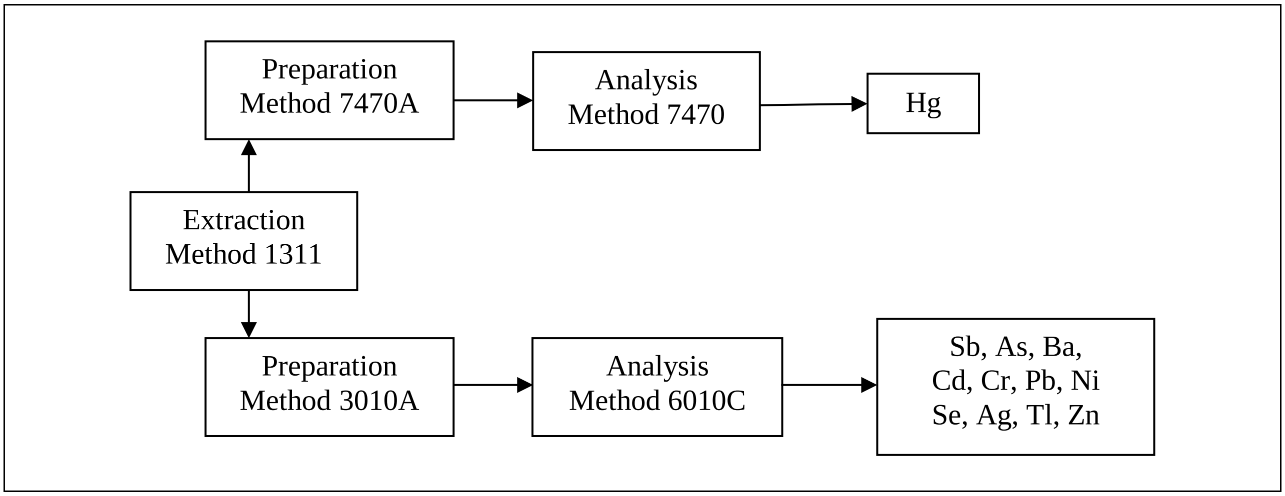


Figure 4-17. TCLP Analysis Sample Flow

5.0 Results and Discussion

5.1 BSR Run Results

This section describes the runs performed for testing the Module C, D, and E simulants and the radioactive runs with the Hanford Tank SX-105 (Module C) and AN-103 (Module D) samples. This section also provides process data from the BSR runs.

The actual run campaign dates are given in Table 5-1 and the run details are given in the associated Appendices. The change in product REDOX and LOI control occurred on October 19, 2010 during the Module B campaigns and all subsequent runs used these improved controls as described in Section 5.1.1 below.

Table 5-1. Timing of Module C, D, and E Campaigns and Location of Run Data Details

Module	Simulant or Radioactive	Start Date	End Date	Run Data Details
C (SX-105)	Simulant	12-13-2010	01-25-2011	Appendix D
	Radioactive	01-26-2011	02-23-2011	Appendix E
	Radioactive Tc-99 Spike	02-24-2011	02-24-2011	
D (AN-103)	Simulant	03-21-2011	04-14-2011	Appendix F
	Radioactive	04-04-2011	05-11-2011	Appendix G
E (AZ-101/AZ-102) with IOC	Simulant	09-06-2011	09-06-2011	Appendix H
E (AZ-101/AZ-102) without IOC	Simulant	10-03-2011	10-03-2011	

5.1.1 *Simulant and Radioactive Module C, D, and E Campaigns*

The BSR did not use scaled values to the ESTD FBSR operation for this study. However, the BSR did feed slurry at about 1/800th the rate that the ESTD FBSR did for reference. The feed rate of 0.9 ml/min for the DMR was established based on the equipment's ability to pump the clay/coal/waste slurries and the desire to minimize particulate carry-over into the condenser. The slurry feed rate of 0.9 ml/min worked well with this unit to form the needed biscuit shaped product, allow adequate pressure control, and minimize product carryover to the off-gas system.

BSR operation was modified to minimize non-condensable gases to reduce the carryover of particles from the reformer. BSR operation was also modified to control product REDOX instead of H_2 concentration. Since the non-radioactive and radioactive BSR systems were identical, the operating parameters determined for the non-radioactive runs were used in the radioactive runs.

Coal was fed at a rate of 0.12 g/min, which is less than the 0.35 g/min scaled equivalent to the ESTD because the BSR is externally heated and does not have to solely rely on the coal to auto-catalytically heat the DMR. In addition, excess unreacted coal in the product is undesirable because it adds unnecessary volume to the FBSR product and causes REDOX measurement problems when present in excess. REDOX is important during the R&D phase of these experiments so it can be correlated with the oxidation state and mineralogical sequestration of REDOX sensitive elements like Tc-99, Re, S, and Cr. Once an optimal REDOX range is defined, a control strategy can be determined in one of several ways, i.e. use of oxygen probes or gas mixture fugacities as done in the steel industry [101] or REDOX process control models as used in the HLW vitrification processing facility at SRS.[102]

Total gas flow in the BSR was as high as reasonable, but limited based on observed solids carry over. The DMR temperatures were the same as the ESTD. The BSR ran at a slightly negative pressure where the ESTD FBSR runs at a slightly positive pressure. All operational conditions were approved by TTT (Brent Evans) as stated in various correspondences, which are documented in the lab notebook SRNL-NB-2009-00115.

The temperature range of 710 – 740°C was specified by TTT. The range was measured across the lower thermocouple at the bottom of the reaction zone and the upper controlled thermocouple at the top of the reaction zone. Typically, the control temperature would start at 725°C and would have to be lowered over the course of a run until it was set to 710°C. Many times slurry feeding was stopped signaling the end of the feeding stage of a run because the lower thermocouple reached 740°C after the control was already at 710°C. Thus, no new product was formed at temperatures above 740°C. However, it was normal for the lower temperature to spike to 760°C at the end of feeding because the temperature control system could not react quickly enough to offset the sudden loss of cold feed entering the DMR. Higher temperatures are typically avoided to avoid making glassy nepheline out of the product. No glassy nepheline was detected visually or by SEM in any of the products formed from the campaigns discussed in this report as temperatures were maintained ~300-350°C lower than the temperature at which glassy nepheline could form.

The total controlled gas flow refers to the sum of the flow of N_2, Ar, and air flowing into the DMR. The control system automatically adjusted the air, N_2, and Ar flows when the operator changed the %air such that the total combined flow always remained at 500 sccm. This total flow is reduced from the ESTD scaled flows in order to reduce product carryover. The important parameter for product formation and REDOX control is O_2 (air) concentration, not flow as long as there is enough O_2 to complete all of the reactions. The ESTD FBSR needed much greater flows to support fluidization which is not a factor for the BSR.

For LOI control, the operator monitored the cumulative value of CO_2/ml fed 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. This was based on a high level mass balance of carbon.

(Carbon fed into DMR) – (Carbon Leaving as CO_2) = Unreacted carbon in product

The CO_2/ml fed endpoint was determined experimentally in the non-rad BSR after REDOX control was established. Since the CO_2/ml fed vs product LOI was a linear relationship, two runs would be performed at different endpoints. A line would be drawn between the two CO_2/ml fed vs product LOI points and the CO_2/ml fed would be determined for the desired product LOI. One confirmation run for each campaign assured the selection of an acceptable target.

The air% was reduced after slurry feeding was stopped for all campaigns. During the Module D campaign, the O_2 level was monitored and the air% was adjusted to keep the O_2 level below 0.05%. No noticeable improvement in product REDOX resulted from keeping the post run O_2 so low. The post run O_2 had sometimes been over 1% in the Module B and Module C campaigns.

Many parameters can affect the REDOX potential in the BSR and they all must be kept as constant as possible (once determined). The parameters that are kept constant are:

- Reactor Temperature (710 – 740°C) during feeding

- Slurry Feed Rate (0.9 ml/min)
- Slurry Feed Concentration (if slurry has to be diluted for better flow property, then the air flow to get the same REDOX must be lowered by a linear amount)
- Air% of the gases fed to the DMR
- O_2 concentration (controlled by air% fed, determined experimentally from REDOX, not measurable by the MS, ~10^{-21} to 10^{-18} atm)
- Time coal is in contact with the Slurry Feed (either by adding coal immediately before run to minimize pre-reaction or allowing coal to react to completion in slurry prior to feeding to BSR)
- The Superheated Steam Rate (0.4 g/min) and Total Gas Flow (Air + N_2 + Argon = 500 sccm) were kept constant and it is unknown at this point how much of a change to REDOX these would affect.

Upon controlling the gas REDOX for Module B runs, it was noticed that good product REDOX was usually attained when the air% of the gases fed to the DMR remained nearly constant. Based on that information, all the Module C, D, and E runs controlled product REDOX by controlling to a constant air% during feeding. Once feeding was completed, the air% was reduced.

The air% to run at was determined experimentally. For a given carbon amount, two or three runs would be performed at different air% settings. The product REDOX would be measured for each of the runs, than the REDOX versus air% would be graphed linearly. The air% that gave the desired product REDOX would then be chosen and usually one confirmation run would assure it.

The REDOX control by use of air% was only partially successful. More work needs to be done to control the product REDOX. The percentage of good runs for Simulant and Radioactive Module C and Simulant and Radioactive Module D were 69%, 72%, 87%, and 60%, respectively. During the Simulant Module D runs, it was discovered that adding the coal just prior to running a campaign gave more consistent results, and 9 out of 9 runs were within the REDOX specification of 0.2 to 0.5. However, when this strategy was used for the Radioactive Module D runs, the results were only 4 out of 10 runs within REDOX specifications. By allowing the coal to age in the Radioactive Module D feed, 8 out of 8 runs were within the REDOX specification. The air% and timing of coal additions needs to be improved by adding REDOX probes to the BSR's in the future for REDOX control.

The Module E simulant runs were purposely run highly oxidized (REDOX < 0.15) first with the IOC catalyst as the only iron source and then with ferric nitrate as the only iron source. It has been noted in earlier studies [40,41,50] that the IOC acts to form the $FeCr_2O_4$ Chromite spinels, which keep the chromium in an oxidation state of +3 which is much less soluble than +6 chromium. The chromium was expected to be in the oxidized +6 state and leachable for the ferric nitrate campaign and it was. The chromium was also soluble for the IOC campaign, which was not expected. This indicated that the IOC concentration was not high enough relative to the amount of Cr in Module E to force the Cr into $FeCr_2O_4$ Chromite spinels. The REDOX results versus TCLP Cr leaching data is given in Section 5.4 and the amount of IOC in oxidized FBSR products that passed the Cr release during TCLP testing, the amount of the IOC added to the Module E sample was under estimated by ~3X. An algorithm for adding the correct amount of IOC for the amount of Cr was derived and is also given in Section 5.4.

Table 5-2. BSR Process Operation Conditions for Modules C, D, and E

Campaign	Module C		Module D		Module E
	Simulant	Radioactive	Simulant	Radioactive	Simulant
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9
DMR Temp (^oC)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam (g/min)	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4
Carbon times Stoichiometric	1.3x – 2.56x	1.3x – 1.54x	2.25x	2.25x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500
Controlled Air% during Feed	50%	50%	24% air w/ new coal	25% w/new coal 15% w/aged coal	15% air w/ new coal
Post Feed Air%	50%	20%	Kept [O_2] < 0.01%	12.75% - 15%	5% - 10%
CO_2/ml fed	34 - 53	25.2 – 36.9	24.5	19.7 – 24.5	16.6 – 17

5.2 Granular Product Characterization

5.2.1 *Constituent Analyses of Simulant and Radioactive Granular Products*

Chemical analyses, REDOX ratio, coal content (LOI-LOD difference), and mineralogy were measured on a Turbula® mixed composite of the "on-spec" granular product for Modules C and D. During Module B, there was an effort to keep the coal content (LOI-LOD) below 2 wt% and this was continued for Modules C, D, and E. The "on-spec" target REDOX ratio was maintained in the ranges shown for Modules C, D, and E testing in Table 4-6. Material with too high a coal content (LOI-LOD difference), and/or too high or low a REDOX ratio were segregated before compositing of the "on-spec" material and are referenced in this document as "off-spec" material. The high coal content samples were rejected because high coal content can impact the REDOX measurement. The high and low REDOX samples were rejected for the reasons specified in Section 4.4. It should be noted that both "on-spec" and "off-spec" granular products had the same mineral phases, and hence this factor was not a discriminating characteristic. The actual LOI, REDOX and calculated oxidation state speciation of rhenium and sulfur from Reference 103 are summarized in Table 5-3.

Table 5-3. LOI, REDOX and Speciation of Rhenium and Sulfur

Waste	Sample	LOI (%)	$Fe^{+2}/\Sigma Fe$	Re^{+7} (%)	SO_4 (%)
Module C (Tank SX-105)	Simulant	1.32	0.34	98	99
	Radioactive	3.50	0.17	100	100
	Radioactive Tc-99 Spike	3.35	0.39	97	98
Module D (Tank AN-103)	Simulant	1.62	0.30	99	100
	Radioactive	6.22	0.18	100	100
Module E (Tank AZ101/AZ102)	Simulant with IOC	0.70	0.13	100	100
	Simulant without IOC	1.15	0.06	100	100

The ESTD P-1B Module B material was made with 640 g wet clay per LAW simulant in the DMR feed, and this provided an excess clay content of 10-15 wt.% expressed as excess SiO_2 and Al_2O_3 in MINCALC™.[28] The BSR campaigns for Module B also used 640 g wet clay per LAW simulant, which provided excess clay (SiO_2 and Al_2O_3) in the range of 12.5 wt.% for the simulant Module B and 8.3 wt.% for the radioactive Module B [28]. Because the simulant Module C (SX-105) campaigns were run using the WRPS radioactive analyses and later recalculated when the simulant SRNL analyses became available only 2.57 wt.% excess clay (SiO_2 and Al_2O_3) was used. The timeline for this compressed R&D program forced the decisions made to use the radioactive analyses, which were available while waiting for the simulant analyses to become available. For the radioactive Module C (SX-105) campaigns, about 1 wt.% excess clay was used (Table 4-4). The Module D (AN-103) campaigns were actually clay deficient by 3-4 wt.% (Table 4-4) because of similar analytic and schedule issues. The Module E (AZ-101/AZ-102) simulant campaigns contained about 4 wt.% excess clay. Due to the flexibility of the nepheline and sodalite structures to accommodate non-stoichiometric amounts of Si and Al, the products with 10-15 wt.% clay versus the products with 1-4 wt.% excess clay and clay deficient products all produced the same mineral assemblages as shown below.

Table 5-4 provides the analyses for Module C and D simulant and radioactive granular product. The measured granular product densities are also provided, which are consistently in the 2.4 – 2.6 g/cc range The Fe detected in the simulant product was not in the simulant feed but was added as the $Fe(NO_3)_3 \cdot 9H_2O$ component for redox measurements and is also be present at trace levels in the added clay.[29] The Ti constituent in the simulant product was not analyzed for the suite of metals from ICP-AES on dissolved simulant product but is present derived from trace levels in the added clay.[29]

Table 5-4. Granular Product Analyses for Simulant and Radioactive Module C and D Samples

Species	**Module C – Tank SX-105**		**Module D - Tank AN-103**	
	Radioactive	**Simulant**	**Radioactive**	**Simulant**
	Wt.%	**Wt.%**	**Wt.%**	**Wt.%**
Al	1.86E+01	1.77E+01	1.84E+01	1.67E+01
As	NA	NA	<1.08E-03	NA
B	1.42E-02	5.93E-03	1.15E-02	5.19E-03
Ba	4.93E-03	4.84E-03	1.18E-02	9.97E-03
Ca	4.05E-02	1.00E-01	6.14E-02	1.16E-01
Cd	<1.01E-03	<5.57E-04	6.89E-04	<1.06E-04
Ce	5.80E-03	<3.28E-03	6.27E-04	6.32E-03
Co	<9.35E-04	<6.72E-04	1.22E-03	<4.42E-04
Cr	1.38E-01	1.20E-01	1.35E-02	1.13E-02
Cs	high blank	6.84E-04	1.58E-04	*~1.35E-02*
Cu	6.60E-03	3.72E-03	7.30E-03	<4.92E-03
Fe*	1.38E+00	1.35E+00	1.76E+00	1.48E+00
K	1.88E-01	1.57E-01	5.71E-01	5.27E-01
La	3.29E-03	3.02E-03	4.05E-03	3.88E-03
Li	5.61E-03	4.37E-03	5.51E-03	2.95E-03
Mg	1.55E-02	1.95E-02	5.48E-02	5.45E-02
Mn	1.04E-03	8.33E-04	1.40E-03	1.14E-03
Mo	<4.92E-03	<1.35E-03	<4.86E-03	3.64E-03
Na	1.58E+01	1.52E+01	1.57E+01	1.57E+01
Ni	<7.31E-03	2.40E-03	<3.59E-03	2.09E-03
P	3.88E-01	3.16E-01	6.04E-02	4.55E-02
Pb	1.35E-03	<3.05E-03	2.64E-03	5.59E-03
Re	2.69E-02	4.70E-02	3.47E-02	4.69E-02
S	2.66E-01	2.92E-01	1.41E-01	1.22E-01
Sb	6.27E-03	NA	<8.25E-02	NA
Se	<2.16E-03	NA	<2.17E-03	NA
Si	1.89E+01	1.85E+01	1.75E+01	1.77E+01
Sn	<3.37E-03	<1.56E-03	<4.42E-03	<8.08E-04
Sr	2.93E-03	3.11E-03	7.68E-03	6.74E-03
Th	1.55E-03	NA	1.40E-03	NA
Ti	7.69E-01	7.33E-01	7.91E-01	8.15E-01
U	2.90E-04	NA	6.28E-04	NA
Zn	5.33E-03	2.65E-03	5.59E-03	2.21E-03
Zr	3.04E-03	<2.49E-03	5.70E-03	4.43E-03
Cs-137	1.66E-08	NA	3.04E-08	NA
Tc-99	3.99E-04	NA	2.23E-04	NA
I-129	3.01E-05	NA	4.68E-05	NA

NA – Not Analyzed, *Fe – Iron constituent was not added to simulant feed but is present in the simulant granular product from both the added $Fe(NO_3)_3{\cdot}9H_2O$ and the added clay; italicized numbers estimated from data in Table 4-2 and waste loading from Table 4-5

Table 5-4. Granular Product Analyses for Simulant and Radioactive Module C and D (Continued)

Species	Module C – Tank SX-105		Module D - Tank AN-103	
	Radioactive	Simulant	Radioactive	Simulant
	Wt.%	**Wt.%**	**Wt.%**	**Wt.%**
Cl^-	2.31E-01	2.06E-01	2.12E-01	2.27E-01
Br^-	NA	NA	NA	<9.46E-02
F^-	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
HCO_2^-	NA	NA	NA	<9.46E-02
I^-	NA	3.17E-02	NA	7.90E-02
	Wt.%	**Wt.%**	**Wt.%**	**Wt.%**
NO_3^-	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
NO_2^-	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
$C_2O_4^{2-}$	7.37E-02	<2.13E-01	<4.69E-02	<9.46E-02
PO_4^{3-}	9.64E-01	9.27E-01	1.81E-01	<4.73E-01
SO_4^{2-}	6.43E-01	6.71E-01	2.56E-01	<9.46E-02
	g/cc	**g/cc**	**g/cc**	**g/cc**
Density	2.60	2.49	NM	NM

NA – Not Analyzed, NM – Not Measured

Table 5-5 provides a summary of the measured $Fe^{2+}/\sum Fe$ REDOX ratio, the difference between the LOI and LOD, which is a measure of the coal content, and the mineral phases measured. The composite REDOX ratio, coal content (LOI-LOD difference), and mineralogy were measured on a Turbula® mixed composite of the “on-spec” granular product. Material with too high a coal content (LOI-LOD difference), and/or too high or low a REDOX ratio were segregated from the composite and are given in the table as “off-spec” material. The high coal content samples were rejected because the high coal content can impact the REDOX measurement. The high and low REDOX samples were rejected as they were not in the REDOX range designated in Table 4-6.

The target range for the REDOX ratio and coal content (LOI-LOD difference) evolved as the program modules progressed (see Table 4-6 and the discussion in Section 4.4). For instance during Module B, there was an effort to keep the coal content (LOI-LOD) below 2 wt%, but this was not possible to achieve during Module D where a larger residual carbon content is observed in both the “on-spec” and “off-spec” granular products.

5.2.2 *Mineralogy Targeted vs. Analyzed*

The mineralogy and qualatiative amounts observed for the BSR non-radioactive and radioactive samples for Modules C, D, and B are the same as those of Module B and the ESTD bed products (see Figure 5-2, Figure 5-3, Figure 5-4). The phases were primarily, two types of nepheline (one of hexagonal symmetry and one of orthorhombic symmetry), and cubic nosean with minor cubic sodalite. The sodalite and nosean peaks do not appear in every XRD. This is because there is a large region of solid solution between sodalite ($Na_8(AlSiO_4)_6Cl_2$) and nosean ($Na_8(AlSiO_4)_6SO_4$) [22,105] as shown in Figure 5-1 because the two species are isostructural. Therefore, when fitting XRD patterns to the “best matching” set of Bragg reflections, sometimes the nosean and sodalite are identified separately and sometimes as one or the other of the two species depending on the relative concentration of each present.

Other minor phases are anatase (TiO_2) which is a clay impurity, quartz, and Al_2O_3 which is the ESTD/HRI startup bed material. The formulas for these species and the reference Powder Diffraction Files (PDFs) are given below Table 5-5 and Figure 5-2. The hexagonal nepheline is the normal crystalline form of $NaAlSiO_4$ and the orthorhombic nepheline is $NaAlSiO_4$. The PDF file for the orthorhombic nepheline states that it may be low-carnegieite, a metastable form of nepheline. However, it is not a hydrated nepheline phase although it is made from a gel that dehydrates at ~800°C.[104] Throughout this document this is referred to as nepheline (O) where the "O" is for orthorhombic but it should be recalled that it may be low-carnegieite.

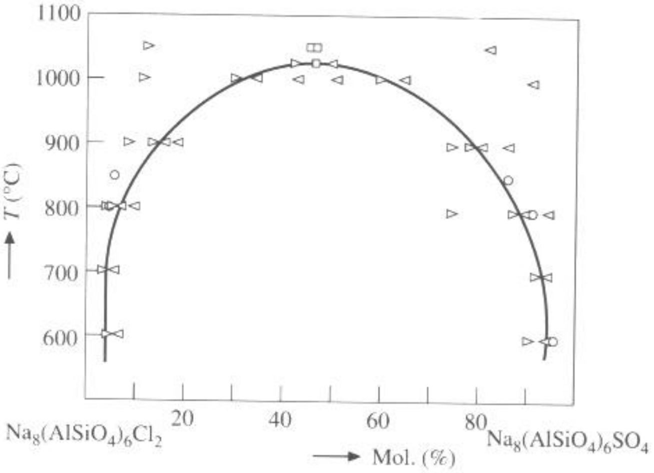


Figure 5-1. Experimentally Determined Sodalite-Nosean Solid Solution [105**]**

For Module C, the mineralogy of the non-radioactive product from the BSR matched the mineralogy of the radioactive product from the BSR (see Table 5-5 and Figure 5-2). The phases observed agree with the predicted mineralogy from MINCALC™ (Table 4-4) of ~ 84-85 wt% nepheline (stronger Bragg reflections) with ~11-12 wt% sodalite and nosean (weaker Bragg reflections). In this case, the nosean is present in larger concentrations than sodalite as there is more SO_4 in the feed than halides.

For Module D, the mineralogy of the non-radioactive product from the BSR matched the mineralogy of the radioactive product from the BSR (see Table 5-5 and Figure 5-3). The phases observed agree with the predicted mineralogy from MINCALC™ (Table 4-4) of ~ 94-96 wt% nepheline (stronger Bragg reflections) with ~5.5-6 wt% sodalite and nosean (weaker Bragg reflections). In this case, the nosean is present in smaller concentrations than sodalite as there is more Cl in the feed than sulfate.

For Module E, the mineralogy from the non-radioactive BSR product matched the phases predicted from MINCALC™ (Table 4-4) as nosean was predicted to be ~20 wt% in the FBSR product. The XRD pattern shown in Figure 5-4 for Module E run with the IOC shows higher concentrations (stronger Bragg reflections) for nosean than those observed in Modules C or D (Figure 5-2 and Figure 5-4).

Table 5-5. Summary of On-Spec and Off-Spec Granular Product Redox ($Fe^{2+}/\sum Fe$), LOI-LOD, and Mineralogy for Module C and D

Module	Type	Composite $Fe^{2+}/\sum Fe$	Range of $Fe^{2+}/\sum Fe$	Composite LOI-LOD	Range of LOI-LOD	Composite Mineralogy	Range of Mineralogy
Simulant Module C	*On-Spec*	0.343	0.194 – 0.414	1.32%	0.50 – 1.90%	Nepheline (H), Nepheline (O), Sodalite, Quartz, Anatase	Nepheline (H), Nepheline (O), Sodalite, Anatase, Quartz
	Off-Spec	*NA*	0.000 – 0.493	NA	0.12 – 8.09%	NA	Nepheline (H), Nepheline (O), Nosean, Sodalite, Anatase, Quartz
Radioactive Module C (SX-105)	*On-Spec*	0.165	0.090 – 0.522	3.50%	0.29 – 4.75%	Nepheline (H), Nepheline (O), Sodalite	Nepheline (H), Nepheline (O), Sodalite, Anatase, Quartz
	Off-Spec	*NA*	0.000 – 0.933	NA	2.48 – 6.89%	NA	Nepheline (H), Nepheline (O), Nosean, Sodalite, Anatase, Quartz
Simulant Module D	*On-Spec*	0.302	0.123 – 0.427	1.62%	0.88 – 2.03%	Nepheline (H), Nepheline (O), Quartz, Sodalite(Cl), Nosean	Nepheline (H), Nepheline (O), Sodalite(Cl), Nosean, Anatase, Quartz
	Off-Spec	*NA*	0.099 – 0.109	NA	0.51 – 0.76%	NA	Nepheline (H), Nepheline (O), Sodalite(Cl), Sodalite, Nosean, Quartz
Radioactive Module D (AN-103)	*On-Spec*	0.184	0.201 – 0.500	6.22%	2.33 – 6.27%	Nepheline (H), Nepheline (O), Quartz, Anatase, Sodalite	Nepheline (H), Nepheline (O), Sodalite(Cl), Sodalite, Nosean, Anatase, Quartz
	Off-Spec	*NA*	0.102 – 0.855	NA	2.88 – 5.22%	NA	Nepheline (H), Nepheline (O), Sodalite(Cl), Sodalite, Anatase, Quartz

Where Nepheline (H) is hexagonal $NaAlSiO_4$ (PDF 00-035-0424)
Nepheline (O) is orthorhombic $NaAlSiO_4$ which “may be synthetic low-carnegieite” [104] (PDF-00-052-1342)
Nosean is cubic $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
Sodalite is cubic $Na_8Al_6Si_6O_{24}Cl_2$ (PDF 00-037-0476)
Anatase is TiO_2 (PDF 00-021-1272)
Quartz is SiO_2 (PDF 00-046-1045)

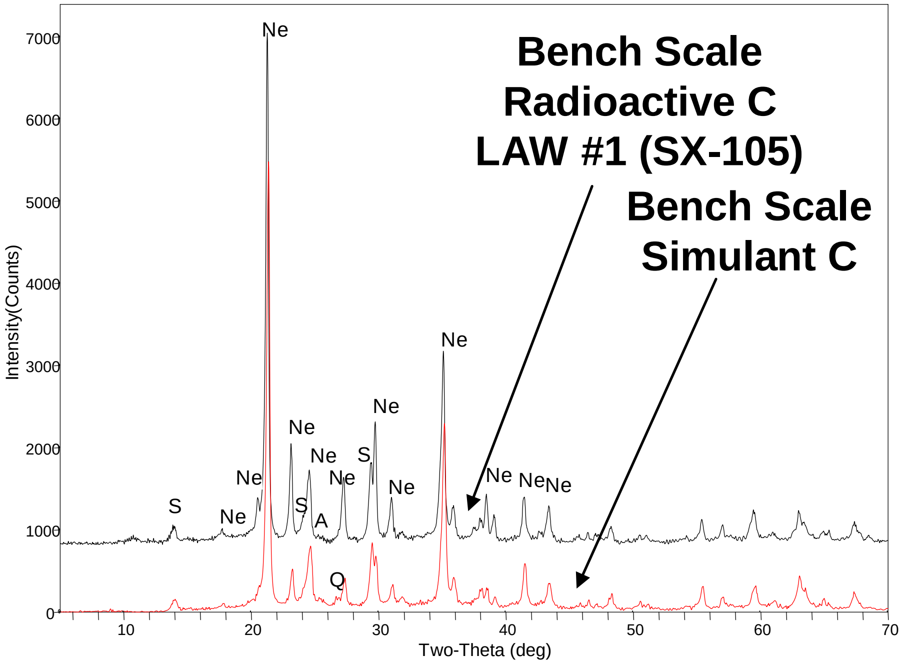


Figure 5-2. Overlay of X-ray Spectra for Module C (SX-105) for the BSR Bench-scale Simulant and Radioactive BSR Products.

Where Ne is Nepheline (H) and Nepheline (O) $NaAlSiO_4$ (PDF 00-035-0424 and PDF00-052-1342)
S is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)
N is Nosean, $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
A is Anatase, TiO_2 (PDF 00-021-1272) a clay impurity
Quartz is SiO_2 (PDF 00-046-1045) a clay impurity
Original XRD spectra fits are in Appendix N

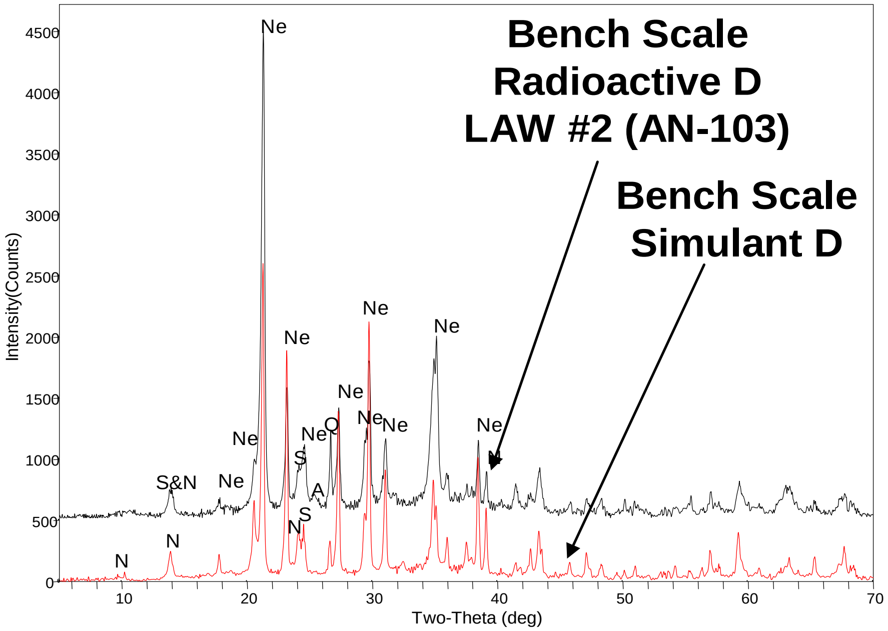


Figure 5-3. Overlay of X-ray Spectra for Module D (AN-103) for the BSR Bench-scale Simulant and Radioactive BSR Products.

Where Ne is Nepheline (H) and Nepheline (O) $NaAlSiO_4$ (PDF 00-035-0424 and PDF00-052-1342)
S is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)
N is Nosean, $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
A is Anatase, TiO_2 (PDF 00-021-1272)
Quartz is SiO_2 (PDF 00-046-1045)
Original XRD spectra fits are in Appendix N

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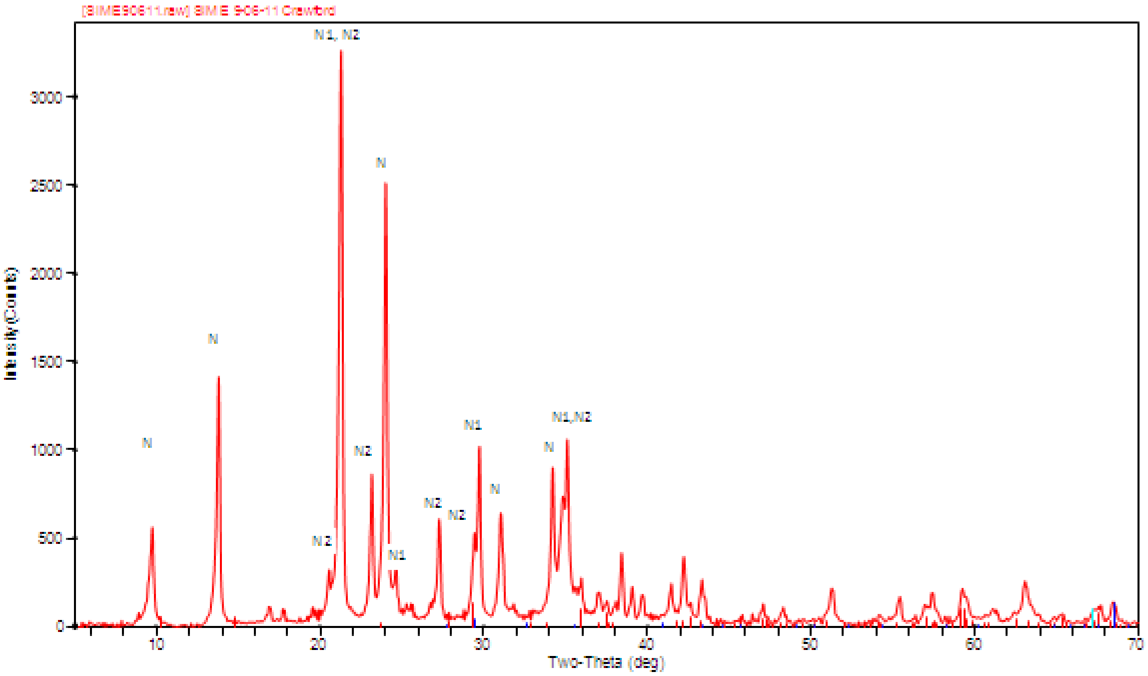


Figure 5-4. X-ray Spectra for Module E (AZ-101/AZ-102) for the BSR Bench-scale Simulant BSR Product run with the IOC.

Where N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
N is Nosean, $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
Original XRD spectra fits are in Appendix N

5.3 Mass Balance

The input and output masses for the various campaigns are shown in Table 5-6 through Table 5-9.

Table 5-6. Input Stream Masses for Module C Campaigns

Input Stream	Simulant Campaign (g)	Radioactive Campaign (g)
Feed-Supernate	322.34	363.94
Feed-$Fe(NO_3)_3$*$9H_2O$	16.57	18.52
Feed-Coal ($Coal_{un}$)	2.69	3.85
Feed-Coal Ash ($Coal_{ash}$)	3.38	2.01
Feed-Clay-OptiKasT®	169.64	187.35
Feed-Clay-Sagger XX®	0.00	0.00

Table 5-7. Output Stream Masses for Module C Campaigns

Output Stream	Simulant Campaign (g)	Radioactive Campaign (g)
Granular Product	204.83	228.80
DMR Condensate Filtrate	1454.55	1487.61
DMR Condensate Solids	0.34	0.0[&]
Crossbar Filtrate	251.77	123.73
Crossbar Solids	0.109	2.166[&]
Seal Pot Filtrate	179.92	None
Seal Pot Solids	0.366	None

[&] The Radioactive Module C condensate solids are negligible since using quartz wool filters in crossbar.

Table 5-8. Input Stream Masses for Module D Campaigns

Input Stream	Simulant Campaign [g]	Simulant Special Run [g]	Radioactive Campaign [g]
Feed-Supernate	499.25	50.09	352.46
Feed-$Fe(NO_3)_3$*$9H_2O$	25.15	2.16	17.71
Feed-Coal (Coal$_{un}$)	5.25	0.00	10.54
Feed-Coal Ash (Coal$_{ash}$)	0.38	0.10	1.75
Feed-Clay-OptiKasT®	114.61	9.83	80.91
Feed-Clay-Sagger XX®	93.72	8.05	66.19

Table 5-9. Output Stream Masses for Module D Campaigns

Output Stream	Regular Simulant Campaign [g]	Simulant Special Run [g]	Radioactive Campaign [g]
Granular Product	293.35	28.09	207.82
DMR Condenser/Bubbler Drain Filtrate	1746.34	238.05	1822.49
DMR Condenser/Bubbler Drain Solids	0.09	0.0003	0.0[&]
DMR Condenser/Bubbler Rinse Filtrate	162.02	89.89	None
DMR Condenser/Bubbler Rinse Solids	0.0566*		None[&]
DMR Basket Rinse Filtrate	110.77	254.77	None
DMR Basket Rinse Solids	0.339		None
Crossbar Filtrate	None	45.48	443.72
Crossbar Solids	2.7816	0.3446	2.655
Seal Pot Drain Filtrate	196.75	27.42	None
Seal Pot Drain Solids	0.0906		None
Seal Pot Rinse Filtrate	135.81	40.72	None
Seal Pot Rinse Solids	0.105		None
25 Micron Off-gas Filter Solids	0.018[#]	0.0049[#]	None
2 Micron Off-gas Filter Solids	0.098[#]	0.0038[#]	None

[&] The radioactive Module D condensate solids negligible and not analyzed since using quartz wool filters in crossbar.
*Includes ethanol rinse to capture remaining solids, #Micron filter solid masses are estimates

The concentrations of key species in the input and output streams are shown in Table 5-10 through Table 5-18. Some cells are marked as 'BDL' for below detection limits.

Table 5-10. Key Species Concentrations for Module C Simulant Input and Output Streams

Method	Non-Radioactive Species$^+$	Feed-Supernate [ug/L]	Feed-Coal [wt%]	Feed-Coal Ash [wt%]	Feed-Clay-OptiKasT® [wt%]	Feed-Clay-Sagger XX® [wt%]	Granular Product [wt%]	Condensate Filtrate [ug/L] *	Condensate Solids [wt%]*	Crossbar Filtrate [ug/L]*	Crossbar Solids [wt%]*	Seal Pot Filtrate [ug/L] *	Seal Pot Solids [wt%]*
ICP-MS	Cs-133	5.33E+03	0.00	0.00	0.00	0.00	0.0007	8.55E+00	0.003	1.85E+00	0.0015	2.54E+01	0.0011
	Re	3.95E+05	0.00	0.00	0.00	0.00	0.05	1.05E+03	0.02	1.95E+01	0.05	1.70E+03	0.01
	I-127	3.78E+05	0.00	0.00	0.00	0.00	0.03	4.82E+03	0.01	2.02E+02	0.05	9.94E+03	0.01
ICP-ES	Al	1.04E+07	0.71	13.81	19.98	16.66	17.68	4.29E+02	16.30	< 1.09E+02	13.31	3.50E+02	14.71
	Cr	8.97E+05	0.00	0.00	0.00	0.00	0.12	< 3.83E+01	0.12	< 2.80E+01	0.09	< 2.80E+01	0.10
	Na	1.26E+08	0.02	0.36	0.01	0.07	15.17	2.85E+04	9.20	3.87E+03	8.41	5.77E+04	6.80
	Si	0.00E+00	1.45	28.40	20.88	25.75	18.47	3.47E+03	15.50	1.26E+03	0.02	6.87E+03	10.99
IC	Cl	1.81E+06	0.00	0.00	0.00	0.00	0.21	4.90E+04	< 0.44	< 1.00E+04	3.57	4.73E+04	0.17
	SO_4^{2-}	5.29E+06	1.40	1.02	0.00	0.00	0.67	2.99E+04	0.33	< 1.00E+04	7.77	3.78E+04	0.14

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-11. Key Species Concentrations for Module C Radioactive Campaign Input and Output Streams

Method	Non-Radioactive Species	Feed-Supernate [ug/L]	Feed-Coal [wt%]	Feed-Coal Ash [wt%]	Feed-Clay-OptiKasT® [wt%]	Feed-Clay-Sagger XX® [wt%]	Granular Product [wt%]	Condensate Filtrate [ug/L]*	Crossbar Filtrate [ug/L]*	Crossbar Solids [wt%]*
ICP-MS	Cs-133	0.00E+00	0.00	0.00	0.00	0.00	0.00	0.00E+00	0.00E+00	0.00
	Re	3.13E+05	0.00	0.00	0.00	0.00	0.03	1.97E+02	8.24E+01	0.06
	I-127	0.00E+00	0.00	0.00	0.00	0.00	0.00	0.00E+00	0.00E+00	0.00
ICP-ES	Al	1.01E+07	0.71	13.81	19.98	16.66	18.63	3.52E+02	< 1.88E+02	6.79
	Cr	1.04E+06	0.00	0.00	0.00	0.00	0.14	< 2.10E+01	< 2.10E+01	0.04
	Na	1.23E+08	0.02	0.36	0.01	0.07	15.77	1.00E+04	6.76E+03	7.23
	Si	1.39E+05	1.45	28.40	20.88	25.75	18.87	4.46E+03	5.58E+02	0.00
IC	Cl	2.55E+06	0.00	0.00	0.00	0.00	0.23	5.00E+03	3.00E+03	1.30
	SO_4^{2-}	5.10E+06	1.40	1.02	0.00	0.00	0.64	1.00E+04	3.00E+03	1.97

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-12. Key Radioactive Species Concentrations for Module C Radioactive Run Input and Output Streams

Method	Radioactive Species	Feed-Supernate [dpm/mL]	Granular Product [dpm/g]	Condensate Filtrate [dpm/mL]*	Crossbar Filtrate [dpm/mL]*	Crossbar Solids [dpm/g]*
Radiochem	Cs-137	1.72E+03	3.24E+04	2.75E+02	2.05E+02	3.80E+05
	Tc-99	1.53E+05	1.50E+05	5.96E+01	2.35E+01	2.81E+05
	I-129	1.47E+02	1.18E+02&	3.51E-01	< 1.77E-01	1.76E+03
	I-125	BDL	BDL	BDL	BDL	BDL

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream, &I-129 granular product average 118 dpm/g had high variability (19.39% RSD) which gives a 95% confidence interval of 92-143 dpm/g

Table 5-13. Key Species Concentrations for Module D Simulant Input Streams

Method	Non-Radioactive Species+	Feed-Supernate [ug/L]	Feed-Coal [wt%]	Feed-Coal Ash [wt%]	Feed-Clay-OptiKasT® [wt%]	Feed-Clay-Sagger XX® [wt%]
ICP-MS	Cs-133	1.58E+04	0.00	0.00	0.00	0.00
	Re	3.98E+05	0.00	0.00	0.00	0.00
	I-127	5.32E+05	0.00	0.00	0.00	0.00
ICP-ES	Al	4.05E+07	0.71	13.81	19.98	16.66
	Cr	1.69E+04	0.00	0.00	0.00	0.00
	Na	1.18E+08	0.02	0.36	0.01	0.07
	Si	0.00E+00	1.45	28.40	20.88	25.75
IC	Cl	2.02E+06	0.00	0.00	0.00	0.00
	SO_4^{2-}	1.02E+06	1.40	1.02	0.00	0.00

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-14. Key Species Concentrations for Module D Simulant Output Streams

Method	Non-Radioactive Species$^+$	Granular Product [wt%]	Condenser Drain Filtrate [ug/L]*	Condenser Drain Solids [wt%]*	Condenser Rinse Filtrate [ug/L]*	Condenser Rinse Solids [wt%]*	Basket Rinse Filtrate [ug/L]	Basket Rinse Solids [wt%]	Crossbar Solids [wt%]*	Seal Pot Drain Filtrate [ug/L]*	Seal Pot Drain Solids [wt%]*	Seal Pot Rinse Filtrate [ug/L]*	Seal Pot Rinse Solids [wt%]*
ICP-MS	Cs-133	0.013	1.45E+01	0.013	1.45E+01	0.008	1.96E+02	0.0007	0.003	5.98E+01	0.0022	3.55E+01	0.001
	Re	0.046	2.48E+02	0.008	1.16E+02	0.008	5.15E+03	0.006	0.068	1.26E+03	0.0070	3.70E+02	0.012
	I-127	0.079	9.63E+02	0.001	9.86E+01	0.014	7.05E+01	0.006	0.14	6.76E+03	0.0093	3.90E+02	0.025
ICP-ES	Al	16.73	6.59E+02	5.14	6.04E+04	5.02	1.45E+06	7.29	8.06	9.99E+02	7.36	3.61E+05	5.39
	Cr	0.011	0.00E+00	0.0044	< 1.00E+02	0.018	5.31E+02	0.017	0.014	<1.00E+02	0.006	< 1.00E+02	0.02
	Na	15.73	9.22E+03	5.19	4.03E+04	1.16	1.81E+06	2.27	11.64	9.49E+04	5.98	2.43E+05	1.05
	Si	17.70	6.78E+03	0.00	6.13E+04	2.85	1.50E+06	0.40	1.51	9.51E+03	3.81	3.91E+05	1.14
IC	Cl	0.23	<1.00E+04	<0.55	<1.00E+05	<2.75	<1.00E+05	<0.087	0.13	1.16E+04	<1.10	< 1.00E+02	<0.48
	SO_4^{2-}	0.10	<1.00E+04	<0.55	4.21E+05	<2.75	1.30E+06	0.09	1.71	2.60E+04	<1.10	6.49E+05	0.48

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-15. Key Species Concentrations for Module D Simulant Special Run Input Streams

Method	Non-Radioactive Species$^+$	Feed-Supernate [ug/L]	Feed-Coal [wt%]	Feed-Coal Ash [wt%]	Feed-Clay-OptiKasT® [wt%]	Feed-Clay-Sagger XX® [wt%]
ICP-MS	Cs-133	1.58E+04	0.00	0.00	0.00	0.00
	Re	3.98E+05	0.00	0.00	0.00	0.00
	I-127	5.32E+05	0.00	0.00	0.00	0.00
ICP-ES	Al	4.05E+07	0.71	13.81	19.98	16.66
	Cr	1.69E+04	0.00	0.00	0.00	0.00
	Na	1.18E+08	0.02	0.36	0.01	0.07
	Si	0.00E+00	1.45	28.40	20.88	25.75
IC	Cl	2.02E+06	0.00	0.00	0.00	0.00
	SO_4^{2-}	1.02E+06	1.40	1.02	0.00	0.00

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-16. Key Species Concentrations for Module D Simulant Special Run Output Streams

Method	Non-Radioactive Species$^+$	Granular Product [wt%]	Condenser Drain Filtrate [ug/L]*	Condenser Drain Solids [wt%]*	Condenser Rinse [ug/L]*	Basket Rinse [ug/L]	Crossbar Rinse [ug/L]	Crossbar Solids [wt%]*	Crossbar/ Condenser Spectrosol Rinse [ug/L]*	Seal Pot Drain [ug/L]*	Seal Pot Rinse [ug/L]*	25 Micron Filter Solids [wt%]*	2 Micron Filter Solids [wt%]*	Caustic Scrubber Drain [ug/L]
ICP-MS	Cs-133	0.0015	< 1.50E+01	0.879	2.07E+00	9.06E+01	4.13E+00	0.0090	3.52E+00	4.87E+01	1.74E+01	0.109	0.010	7.38E+02
	Re	0.43	7.72E+02	0.098	1.91E+02	1.28E+04	1.77E+02	0.78	6.91E+01	5.77E+03	1.87E+03	6.312	0.0058	< 1.00E+01
	I-127	0.075	3.24E+02	0.212	6.59E+01	1.23E+02	8.02E+01	0.00	3.74E+01	5.67E+03	9.32E+02	NM	NM	1.68E+02
ICP-ES	Al	17.50	NM	< 12.73	NM	NM	NM	10.15	NM	NM	NM	9.72	11.06	NM
	Cr	0.0091	NM	< 1.57	NM	NM	NM	0.019	NM	NM	NM	0.039	0.047	NM
	Na	15.90	NM	6.95	NM	NM	NM	14.05	NM	NM	NM	1.23	1.08	NM
	Si	< 0.003	NM	5.97	NM	NM	NM	2.14	NM	NM	NM	0.00	0.00	NM
IC	Cl	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
	SO_4^{2-}	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM

NM=Not Measured, *Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-17. Key Species Concentrations for Module D Radioactive Campaign Input and Output Streams

Method	Non-Radioactive Species	Feed-Supernate [ug/L]	Feed-Coal [wt%]	Feed-Coal Ash [wt%]	Feed-Clay-OptiKasT® [wt%]	Feed-Clay-Sagger XX® [wt%]	Granular Product [wt%]	Condensate Filtrate [ug/L]*	Crossbar Filtrate [ug/L]*	Crossbar Solids [wt%]*
ICP-MS	Cs-133	0.00E+00	0.00	0.00	0.00	0.00	0.00	<5.00E-01	0.00E+00	0.00
	Re	3.10E+05	0.00	0.00	0.00	0.00	0.04	1.63E+02	3.71E+01	0.08
	I-127	0.00E+00	0.00	0.00	0.00	0.00	0.00067	0.00E+00	0.00E+00	0.00
ICP-ES	Al	4.13E+07	0.71	13.81	19.98	16.66	18.35	9.45E+02	8.40E+01	7.04
	Cr	2.06E+04	0.00	0.00	0.00	0.00	0.01	< 1.50E+01	< 1.50E+01	0.005
	Na	1.16E+08	0.02	0.36	0.01	0.07	15.67	5.90E+03	2.16E+03	5.65
	Si	2.14E+05	1.45	28.40	20.88	25.75	17.50	4.55E+03	2.43E+02	0.066
IC	Cl	1.78E+05	0.00	0.00	0.00	0.00	0.21	<5.00E+03	<5.00E+03	0.59
	SO_4^{2-}	6.93E+04	1.40	1.02	0.00	0.00	0.26	<5.00E+03	<5.00E+03	0.99

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.

Table 5-18. Key Radioactive Species Concentrations for Module D Radioactive Run Input and Output Streams

Method	Radioactive Species	Feed-Supernate [dpm/mL]	Granular Product [dpm/g]	Condensate Filtrate [dpm/mL]*	Crossbar Filtrate [dpm/mL]*	Crossbar Solids [dpm/g]*
Radiochem	Cs-137	2.20E+03	5.86E+04	3.16E+02	1.15E+02	8.98E+05
	Tc-99	7.46E+04	8.38E+04	2.80E+01	7.79E+00	1.39E+05
	I-129	1.98E+02	1.83E+02	1.28E-01	< 1.49E-01	6.35E+03
	I-125	BDL	BDL	BDL	BDL	BDL

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream; BDL is Below Detection Limit

The total recoveries of the key species for the key streams were calculated for the Module C campaigns using the logic presented in Section 4.5. The recoveries for Module C simulant from the BSR processing campaign are shown in Table 5-19. More details of the mass balance are shown in Appendix I. The non-radioactive Cs-133 recovery was 105% for the simulant campaign. This recovery was good since the concentration of Cs-133 in the feed was about 5,331 ug/L with a total Cs fed of about 1.37 milligrams over 7 runs. The Re recovery was 98% and the I-127 recovery was 76% for the simulant campaign. The SO_4 recovery was about 114%. The SO_4 recovery is very dependent on the SO_4 coming in via the coal in the feed mix and how much of the coal in the feed is ashed. The approach on how to handle the feed coal SO_4 and other species is discussed in Section 4.5.

Table 5-19. Recoveries for Key Streams and Species for Simulant Module C

Method	Element	Total Recovery (%)	Normalized Recoveries					
			Product %	Condensate Filtrate %	Crossbar Filtrates %	Crossbar Solids %	Seal Pot Filtrates %	Seal Pot Solids %
ICP-MS	Cs-133	104.96	97.77	0.87	0.03	0.12	0.32	0.29
	Re	97.69	97.98	1.55	0.00	0.05	0.31	0.04
	I-127	76.38	87.86	9.48	0.07	0.07	2.42	0.05
ICP-ES	Al	98.07	99.66	0.00	0.00	0.04	0.00	0.15
	Cr	107.46	99.65	BDL	BDL	0.04	BDL	0.15
	Na	96.31	99.62	0.13	0.00	0.03	0.03	0.08
	Si	104.13	99.74	0.01	0.00	0.00	0.00	0.11
IC	Cl	102.89	88.35	8.77	BDL	0.82	1.78	0.29
	SO_4^{2-}	100.86	95.54	3.02	BDL	0.59	0.47	0.30

BDL is Below Detection Limit

The recoveries for the Module C radioactive campaign are shown in Table 5-20. The radiochemistry and mass spectrometer recoveries were lower than expected and may be due to a mixing of the various feed batches for the runs. More details of the mass balance are shown in Appendix J. The recoveries for the radionuclides in the Module C radioactive campaign were in the range of 71% to 83%. The I-129 granular product average concentration of 118 dpm/g had a high variability (19.39% RSD), which gives a 95% confidence interval of 92-143 dpm/g. Using the upper 95% confidence value of the I-129 granular product concentration, the total recovery of I-129 becomes 89%. The Cs-137 level is indeterminate because of the low concentrations in the feed and contamination from the shielded cells operations. Comparison of the total recoveries shown in Table 5-20 to the percent of each species in the product (Product % column) suggests that most analytes remain predominately with the granular product in processing the feed slurries in the BSR.

Table 5-20. Recoveries for Key Streams and Species for the Module C Radioactive Campaign

Method	Element	Total Recovery (%)	Normalized Recoveries			
			Product %	Condensate Filtrate %	Crossbar Filtrates %	Crossbar Solids %
Radiochem	Cs-137	Indeterminate				
	I-129[&]	74.60 (88.70)[&]	86.15 (88.35)[&]	1.67 (1.41)[&]	BDL (BDL)[&]	12.18 (10.24)[&]
	Tc-99	80.24	98.00	0.25	0.01	1.74
ICP-MS	Tc-99	82.51	97.96	0.29	0.02	1.74
	Re	70.73	97.64	0.47	BDL	1.89
ICP-ES	Al	105.35	99.65	0.00	BDL	0.34
	Cr	107.75	99.73	BDL	BDL	0.27
	Na	103.82	99.52	0.04	0.00	0.43
	Si	108.52	99.98	0.02	0.00	0.00
IC	Cl	77.73	93.64	1.32	0.07	4.98
	SO_4^{2-}	100.33	96.23	0.97	BDL	2.79

[&] I-129 recoveries using upper 95% confidence interval value for granular product of 143 dpm/g; BDL is Below Detection Limit

The total recoveries of the key species for the key streams were calculated for the Module D campaigns using the logic presented in Section 4.5. The recoveries for Module D simulant from the BSR processing campaign are shown in Table 5-21. More details of the Module D simulant mass balance are shown in Appendix K.

To try to better close the mass balance around the BSR system, the DMR condenser/bubbler, the DMR product basket, and DMR seal pots for the simulant campaign were rinsed with a 5-wt% HNO_3, 10-wt% H_2O_2 solution (balance is deionized water) to try to recover as many residue solids as possible. These special rinses were then filtered through 45-μm filters and the filtrates and solids submitted for analyses. The extra analyses showed that for key species there were about 0.3-0.4 wt % in the DMR product basket, about 0.01-0.02 wt % in the DMR condenser/bubbler, and about 0.04-0.10 wt % in the Seal Pots. The 25 and 2 micron cellulose filters on the off-gas going to the mass spectrometer were also analyzed to see what species were making it to this point in the system. Note that these filters were in series, the 25 micron followed by the 2 micron filter. The analyses of the filters showed that very little of the key species make it to the filters. There was about 0.21% of the Re on the 25 micron filter but then below detection limit on the 2 micron filter. These additional analyses showed that the bulk of the BSR product remains in the granular product, crossbar solids, and DMR condenser/bubbler.

The non-radioactive Cs-133 recovery was indeterminate for the Module D simulant campaign due to the low amount in the feed (about 0.006 grams). The Re recovery was 90% and the I-127 recovery was 115% for the simulant campaign. The SO_4 recovery was about 134%. The SO_4 recovery is very dependent on the SO_4 coming in via the coal in the feed mix and how much of the coal in the feed is ashed. The approach on how to handle the feed coal SO_4 and other species is discussed in Section 4.5.

There was a special run for the Module simulant to try to quantify the feed and product mass losses in the other runs. The total recoveries of the key species for the key streams were calculated for this special Module D run using the logic presented in Section 4.5. The recoveries for Module D simulant special run are shown in Table 5-22. More details of the special Module D simulant mass balance are shown in Appendix L.

The non-radioactive Cs-133 recovery for the Module D simulant special run was about 87%. There was high variability in Cs-133 measurements across campaigns so caution should be used in drawing any conclusions from the reported values. The Re recovery was about 95% and the I-127 recovery was about 104% for the special simulant run. The special off-gas caustic scrubber showed very little I-127 present (0.05%). This finding plus the operational problems of the caustic scrubber led to not using a caustic scrubber in future campaigns. The SO_4 recovery was indeterminate. The SO_4 recovery is very dependent on the SO_4 coming in via the coal in the feed mix and how much of the coal in the feed is ashed. The approach on how to handle the feed coal SO_4 and other species was discussed in Section 4.5.

The recoveries for the Module D radioactive campaign are shown in Table 5-23. Note that fewer streams were analyzed for the radioactive campaign due to physical limitations imposed by the Shield Cells Operations or remote cell operations. More details of the mass balance are shown in Appendix M. The recoveries for the radionuclides in the Module D radioactive campaign were in the range of 86% to 100%. The Cs-137 level is indeterminate because of the low concentrations in the feed and contamination from the shielded cells operations. Comparison of the total recoveries shown in Table 5-23 to the percent of each species in the product (Product % column) suggests that most analytes remain predominately with the granular product in processing the feed slurries in the BSR.

Table 5-21. Recoveries for Key Streams and Species for Module D Simulant Runs

Method	Element	Total Recovery (%)	Normalized Recoveries													
			Granular Product	Conden-sate Filtrate	Conden-sate Solids	Condenser Rinse Filtrate	Condenser Rinse Solids	Basket Rinse Filtrate	Basket Rinse Solids	Crossbar Solids	Seal Pot Drain Filtrate	Seal Pot Drain Solids	Seal Pot Rinse Filtrate	Seal Pot Rinse Solids	25 Micron Filter Solids	2 Micron Filter Solids
ICP-MS	Cs-137	Indeterminate														
	Re	90.35	97.45	0.31	0.005	0.01	0.002	0.4	0.02	1.36	0.18	0.005	0.04	0.01	0.21	BDL
	I-127	115.43	97.01	0.70	0.0002	0.01	0.001	0.003	0.01	1.64	0.56	0.004	0.02	0.01	0.02	0.004
ICP-ES	Al	91.24	98.99	0.00	0.01	0.02	0.003	0.3	0.05	0.45	0.0004	0.013	0.10	0.01	0.003	0.02
	Cr	Indeterminate														
	Na	102.33	98.60	0.03	0.01	0.01	0.001	0.4	0.02	0.69	0.04	0.01	0.07	0.002	0.01	0.07
	Si	108.22	99.44	0.02	0.00	0.02	0.001	0.3	0.003	0.08	0.004	0.01	0.10	0.002	0.0004	0.00003
IC	Cl	85.64	99.11	BDL	BDL	BDL	BDL	BDL	BDL	0.55	0.34	BDL	BDL	BDL	0.0002	BDL
	SO_4^{2-}	134.27	44.35	BDL	BDL	10.73	BDL	22.7	0.05	7.47	0.81	BDL	13.87	0.08	0.0004	0.00002

BDL is Below Detection Limit

Table 5-22. Recoveries for Key Streams and Species for Module D Simulant Special Run

Method	Element	Total Recovery (%)	Normalized Recoveries											
			Granular Product	Condenser Drain Filtrate	Condenser Drain Solids	Condenser Rinse	Basket Rinse	Crossbar Rinse	Crossbar Solids	Spectrosol Crossbar/ Condenser Rinse	Seal Pot Drain	Seal Pot Rinse	25 Micron Filter Solids	2 Micron Filter Solids	Caustic Scrubber Solution
ICP-MS	Cs-137	87.08	79.32	BDL	0.50	0.04	4.36	0.04	5.84	0.09	0.25	0.13	0.79	0.09	8.55
	Re	95.39	94.75	0.15	0.00	0.01	2.58	0.01	2.12	0.01	0.13	0.06	0.19	0.0002	BDL
	I-127	103.58	98.48	0.36	0.00	0.03	0.15	0.02	0.00	0.02	0.72	0.18	NM	NM	0.05
ICP-ES	Al	101.09	99.28	NM	BDL	NM	NM	NM	0.71	NM	NM	NM	0.008	0.011	NM
	Cr	Indeterminate													
	Na	98.39	98.93	NM	0.0005	NM	NM	NM	1.07	NM	NM	NM	0.001	0.001	NM
	Si	Indeterminate													
IC	Cl	Indeterminate													
	SO_4^{2-}	Indeterminate													

NM=Not Measured

Table 5-23. Recoveries for Key Streams and Species for the Module D Radioactive Campaign

Method	Element	Total Recovery (%)	Normalized Recoveries			
			Product	Condensate Filtrate	Crossbar Filtrates	Crossbar Solids
Radiochem	Cs-137	Indeterminate				
	I-129	100.26	69.04	0.42	BDL	30.54
	Tc-99	86.15	97.62	0.29	0.02	2.08
ICP-MS	Tc-99	82.85	97.60	BDL	BDL	2.40
	Re	87.69	96.76	0.39	0.02	2.83
ICP-ES	Al	98.35	99.51	0.0045	0.0001	0.49
	Cr	Indeterminate				
	Na	101.70	99.51	0.03	0.003	0.46
	Si	105.00	99.97	0.023	0.0003	0.005
IC	Cl	Indeterminate				
	SO_4^{2-}	Indeterminate				

. BDL is Below Detection Limit

5.4 Regulatory Testing

5.4.1 *Toxicity Characteristic Leaching Procedure (TCLP) for Granular Module C, D, and E*

During the Module C simulant campaigns, different REDOX conditions were achieved; those that were considered "on-spec" (Table 5-5) and those that were either more reduced or more oxidized than the target values given in Table 4-4. For the Module C simulant, the designation "off spec" included a reduced sample with a $Fe^{2+}/\Sigma Fe>0.6$ and an oxidized sample with a $Fe^{2+}/\Sigma Fe<0.2$. Two replicates of each sample type (1) off-spec (oxidized), (2) on-spec, and (3) off spec (reduced) were submitted to GEL Laboratories for TCLP analysis. Duplicate samples of FBSR products that were >0.6 $Fe^{+2}/\Sigma Fe$, <0.15 $Fe^{+2}/\Sigma Fe$, and 0.34 $Fe^{+2}/\Sigma Fe$ were selected to aid in defining how the product REDOX impacted the TCLP response in the absence of the IOC. PNNL performed TCLP analysis of the radioactive Module C granules prepared with a REDOX of 0.17 $Fe^{+2}/\Sigma Fe$, which was below the oxidized REDOX limit set in Table 4-4 since this FBSR product was prepared without the IOC, which would act as an alternate Cr host in an oxidized FBSR product.

TCLP results in Table 5-24 show that the simulant sample deemed too oxidized exceeded the UTS limits for chromium implying that soluble chromium +6 was present. Analysis performed by PNNL on the Module C radioactive product also exceeded the UTS limits for chromium. This indicates a sensitivity of the chromium release to REDOX in the absence of the IOC spinel host. The "on spec" REDOX sample passed TCLP testing at the UTS for chromium indicating that the REDOX forced the chromium to Cr_2O_3 (Cr^{3+}) in the absence of the IOC spinel host. The sample designated "more reduced" in Table 5-24 also passed the TCLP testing at the UTS indicating the presence of Cr_2O_3 or an insoluble iron chrome spinel where chromium is in the +3 oxidation state. Analytes detected but at concentrations too low to determine quantitatively have been flagged with the "J" qualifier.

Table 5-24. TCLP Results for Non-Radioactive and Radioactive FBSR Products from Module C (SX-105).

	Simulant Module C Granular Product						**Radioactive Module C Granular Product* (REDOX =0.17)**	**Reporting Limit (RL)**	**Method Detection Limit (MDL)**	**TCLP Characteristic of Toxicity 40CFR 261.24**	**UTS 40CFR 268.48 (Non-waste water standard)**
	“Off-Spec” (REDOX < 0.15)		**“On Spec” (REDOX = 0.34)**		**“Off-Spec” (REDOX = >0.6)**						
	1	2	1	2	1	2	4	--	--	--	--
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sb	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0004	0.1	0.03	- - -	1.15
As	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.15	0.05	5	5
Ba	0.0449^{J}	0.0566	0.0891	0.057	0.0208^{J}	0.0211^{J}	0.269-0.310	0.05	0.01	100	21
Cd	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0026-0.00265	0.05	0.01	1	0.11
Cr	***0.790***	***0.826***	0.393	0.243	0.207	0.244	***0.69-0.72***	0.05	0.02	5	0.6
Pb	0.0947^{J}	0.110	0.0786^{J}	0.129	0.0336^{J}	0.0440^{J}	<MDL	0.1	0.025	5	0.75
Se	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.028-0.033	0.15	0.05	1	5.7
Ag	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.05	0.01	5	0.14
Hg	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.012	0.002	0.0003	0.2	0.025
Ni	<MDL	<MDL	<MDL	<MDL	0.0204^{J}	MDL	<MDL	0.05	0.01	- - -	11
Tl	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	0.05	- - -	0.2
Zn	0.115	0.115	0.0681^{J}	0.0599^{J}	0.0335^{J}	0.0408^{J}	<MDL	0.1	0.02	- - -	4.3

*Measured by PNNL; J are analytes detected but at concentrations too low to determine quantitatively; MDL is Method Detection Limit

The Module D TCLP results are given in Table 5-25 and show that the non-radioactive sample was below the UTS for all contaminants of concern. The measured REDOX of the non-radioactive sample was $Fe^{2+}/\Sigma Fe = 0.30$ and the measured REDOX of the radioactive sample was $Fe^{2+}/\Sigma Fe = 0.18$. The Cr response for both the non-radioactive and the radioactive sample passed the TCLP at the UTS limits. Analytes detected but at concentrations too low to determine quantitatively have been flagged with the "J" qualifier.

Table 5-25. TCLP Results for Non-Radioactive and Radioactive FBSR Products from Module D (AN-103)

	Simulant Module D Granular Product			Radioactive Module D Granular Product*		Reporting Limit (RL)	Method Detection Limit (MDL)	TCLP Charact-eristic of Toxicity 40CFR 261.24	UTS 40CFR 268.48 (Non-waste water standard)
	REDOX <0.15	REDOX = 0.30	REDOX >0.5	REDOX = 0.18					
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sb	<MDL	<MDL	<MDL	0.00093	0.00086	0.1	0.1	- - -	1.15
As	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1	5	5
Ba	1.66	1.57	1.38	0.0565	0.0527	0.2	0.2	100	21
Cd	<MDL	<MDL	<MDL	<MDL	<MDL	0.05	0.05	1	0.11
Cr	0.184	0.120	0.165	0.07	0.0688	0.1	0.1	5	0.6
Pb	<MDL	<MDL	<MDL	0.0017^{J}	ND	0.1	0.1	5	0.75
Se	<MDL	<MDL	<MDL	0.0209	0.0244	0.1	0.1	1	5.7
Ag	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1	5	0.14
Hg	<MDL	<MDL	<MDL	0.00167^{J}	<MDL	0.002	0.002	0.2	0.025
Ni	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	0.2	- - -	11
Tl	<MDL	<MDL	<MDL	<MDL	<MDL	0.04	0.04	- - -	0.2
Zn	<MDL	<MDL	<MDL	0.406	<MDL	0.2	0.2	- - -	4.3

*Measured by PNNL – duplicate results; U=unreportable due to interference; J are analytes detected but at concentrations too low to determine quantitatively; MDL is Method Detection Limit

The non-radioactive Module E TCLP results are given in Table 5-26 and show that the oxidized FBSR product with the IOC failed TCLP at the UTS limits only for chromium. The non-radioactive Module E TCLP results for the oxidized FBSR product without the IOC also failed TCLP at the UTS limits for chromium. All other contaminants of concern passed the TCLP for the non-radioactive TCLP. The measured REDOX of the non-radioactive samples with and without the IOC were $Fe^{2+}/\Sigma Fe = 0.13$ and 0.06, respectively (Table 5-26).

Table 5-26. TCLP Results for Non-Radioactive FBSR Products from Module E (AZ-101/AZ-102) With and Without the IOC

	Simulant Module E Granular Product with IOC	**Simulant Module E Granular Product without IOC**	**Reporting Limit (RL)**	**Method Detection Limit (MDL)**	**TCLP Characteristic of Toxicity 40CFR 261.24**	**UTS 40CFR 268.48 (Non-waste water standard)**
	REDOX = 0.13	**REDOX= 0.06**				
	(mg/L)	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**
Sb	<MDL	<MDL	0.1	0.1	- - -	1.15
As	<MDL	<MDL	0.1	0.1	5	5
Ba	0.474	0.567	0.2	0.2	100	21
Cd	<MDL	<MDL	0.05	0.05	1	0.11
Cr	***12.2***	***10.3***	0.1	0.1	5	0.6
Pb	<MDL	<MDL	0.1	0.1	5	0.75
Se	<MDL	<MDL	0.1	0.1	1	5.7
Ag	<MDL	<MDL	0.1	0.1	5	0.14
Hg	<MDL	<MDL	0.002	0.002	0.2	0.025
Ni	0.221	<MDL	0.2	0.2	- - -	11
Tl	<MDL	<MDL	0.04	0.04	- - -	0.2
Zn	1.39	0.625	0.2	0.2	- - -	4.3

MDL is Method Detection Limit

Using the data in Table 5-27 for the TCLP response of Cr from the simulant and radioactive Modules B, C, and D (Reference 28 and this study), one can derive a dependency of Cr leaching on the product REDOX as noted already in Table 5-24 above for the Module C (SX-105) oxidized, on specification, and overly reduced FBSR products. For all of the BSR campaigns and data in Table 5-27, the IOC catalyst was not added to sequester chromium into the iron oxide mineral structure as $FeCr_2O_4$. Therefore, it is likely that the reducing REDOX forced the chromium into a Cr_2O_3 structure instead. This Cr leaching versus REDOX dependency is shown in Figure 5-5.

Table 5-27. Measured Cr_2O_3, REDOX and TCLP Response for Module B, C, and D FBSR Product without the IOC Catalyst Present

BSR Feed	Sample ID	Cr_2O_3 (wt.%) in FBSR Product$^{\xi}$	Measured REDOX $Fe^{2+}/\Sigma Fe$	Pass or Fail Cr UTS during TCLP Testing
Module B	Radioactive	0.0989	0.41	Pass
	Simulant	0.0998	0.36	Fail
Module C	Radioactive	0.2017	0.17	Fail
	Simulant On Spec	0.1754	0.34	Pass
	Simulant Oxidized	0.1754	0.15	Fail
	Simulant Reduced	0.1754	0.55	Pass
Module D	Radioactive	0.01973	0.18	Pass
	Simulant	0.01652	0.30	Pass

ξ calculation performed on Cr+3 as that was the desited Cr REDOX in the FBSR product

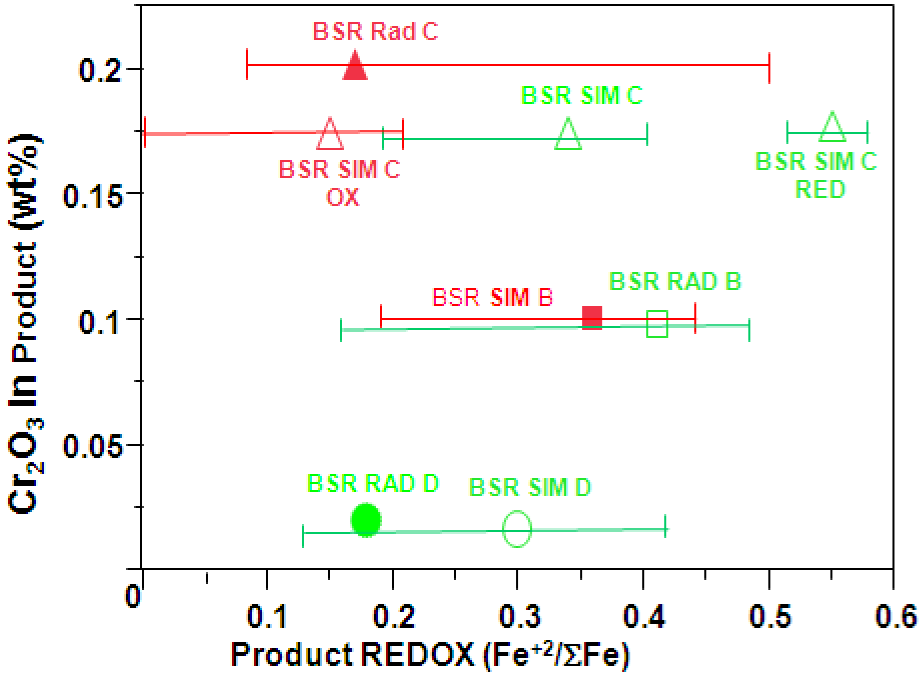


Figure 5-5. Dependency of Cr_2O_3 Leaching on FBSR Product REDOX.

Note: The red symbols denote samples that failed TCLP for chromium leaching, while the green symbols denote samples that passed TCLP for chromium leaching. While the error bands on the REDOX measurements are large (as explained in the text), samples that failed chromium leaching in TCLP were definitely more oxidized than those that passed the TCLP testing.

Figure 5-5 shows the radioactive campaigns as solid symbols and the simulant campaigns as open symbols. Because “on specification” FBSR product was a composite of multiple runs with multiple measured REDOX values, the average value of the turbula mixed sample is plotted in Figure 5-5 and the ranges from Table 5-5 in this study and Table 5-8 in Reference 28 are given as error bars. The wide ranges of the REDOX error bars complicates the interpretation of Figure 5-5 but in general the samples below (more oxidized) than an $Fe^{2+}/\Sigma Fe$ of <0.25-0.3 fail TCLP for chromium leaching at the UTS levels implying that chromium is present in the soluble +6 form. Samples that are more reduced ($Fe^{2+}/\Sigma Fe$ >0.30) pass TCLP for chromium leaching at the UTS levels implying that chromium is present in the non-soluble +3 form, i.e. likely Cr_2O_3. More data is needed to better define the Cr leaching limit on samples that have not been composited. Additional data is needed due to the poor reproducibility of the TCLP test response and the complications imposed by compositing the samples. The errors from compositing will be minimized when the BSR can be run with REDOX control using either REDOX probes or effluent gas mixtures as is done in the steel industry.[101]

Because more oxidizing values are favorable to the retention of Re and Tc-99 in the sodalite cage (see discussion in Reference 52), an alternative way to sequester the chromium at oxidizing REDOX ranges is to provide the Fe_3O_4 host IOC which forms the isostructural $FeCr_2O_4$ spinel where the chromium is in the +3 oxidation state. There is limited data available to look at the impacts of the IOC and the available data are presented in Table 5-28.

Table 5-28. Measured Cr_2O_3, REDOX and TCLP Response for Module B, C, and D FBSR Product with the IOC Catalyst Present

Sample ID	IOC (g/100 grams wet feed)	Cr_2O_3 (wt.%) in FBSR product	Measured REDOX $Fe^{2+}/\Sigma Fe$	Pass or Fail Cr UTS during TCLP Testing
HRI Module B	14	0.1069	0.5	Pass
HRI Module B	14	0.1069	0.5	Pass
BSR Simulant Module E	17	0.16	0.13	Fail
AN-107 (TTT 2001)	14	0.0497	0.15	Pass
IOC	100	0	0.567	N/A

This limited data set was used to demonstrate that a “control strategy” can be developed for adding the necessary amount of IOC to sequester the chromium in the FBSR product in an iron chrome spinel while keeping the overall REDOX of the FBSR more oxidizing so that the Re and Tc-99 oxidation states are oxidizing enough to enter the sodalite structures. Using the same dependent axis (Cr_2O_3 in the FBSR product) as in Figure 5-5 above an x axis was derived which uses the IOC algorithm given below in

$$desired\,REDOX * \left(\frac{IOC(\,g\,/\,100g\,wet\ feed\,)}{100} \right) * 0.567$$

where 0.567 is the $Fe^{2+}/\Sigma Fe$ of 100% pure IOC from Table 5-28. Plotting the IOC algorithm against the Cr_2O_3 in the FBSR product gives Figure 5-6 so that the amount of IOC can be calculated from the known Cr_2O_3 in the sample (via MINCALC™) and the REDOX desired to keep the Re and Tc-99 in the correct oxidation states for incorporation into sodalite. Since there are only 3 data points to fit the IOC algorithm, the intercept of the equation shown in Figure 5-6 is assumed to be zero. From this equation, the necessary IOC (in grams per 100 grams of wet feed/100) for chromium leaching control is back calculated to be

$$\left(\frac{IOC(\,g\,/\,100g\,wet\ feed\,)}{100} \right) \geq \frac{Cr_2O_3\,in\,FBSR\,product}{1.167 * desired\,REDOX}$$

From Figure 5-6, it can be seen that the Module E BSR simulant feed (AZ-101/AZ-102) did not have enough IOC added to ensure that all the chromium was tied up in an iron chrome spinel. Clearly, the data used from Table 5-28 indicates that FBSR products can be made at oxidizing REDOX with the IOC and that the presence of the IOC, when sufficient, ties up the chromium in the waste in an insoluble mineral phase related to the IOC structure.

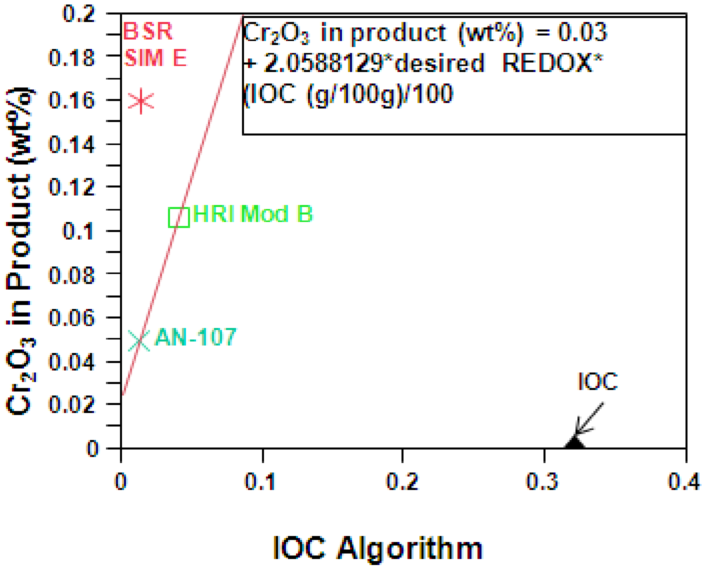


Figure 5-6. Dependency of the IOC on the Cr_2O_3 content of the FBSR product and the desired REDOX.

5.5 Wasteform Performance Testing Results

5.5.1 *Product Consistency Test (PCT) - Short Term on FBSR Granular Product*

The 7-day PCT was conducted on the BSR Module C simulant and radioactive SX-105 BSR products as described in Section 4.6.1. All data is provided in Table 5-29 and Appendix O and all the release rates are below 2 g/m^2. Rhenium was added to the Module C radioactive Hanford salt solutions to link durability release (performance) between these two species and, thus, between the simulant and radioactive products. As can be seen from the data in Table 5-29, the release of rhenium is consistent between the simulant and radioactive FBSR granular products made from the SX-105 solutions in the non-radioactive BSR and the radioactive BSR. Re and Tc-99 releases are shown to track each other well. Thus, the FBSR minerals have been found to retain Re in the cage structure (~100%) of the granular mineral products and varying percentages of Tc-99 depending on the REDOX conditions.[90] The release rates from Module C FBSR granular products are also comparable to the Module B radioactive and simulant FBSR granular products reported in Reference 28.

Table 5-29. 7-Day PCT Results for Granular FBSR Product Prepared from Module C Simulant and SX-105 Radioactive Waste

Normalized Elemental Release (g/m^2)	Module C Simulant (g/m^2)	Module C Simulant Std. Dev.	Normalized Elemental Release (g/m^2)	Radioactive Module C (g/m^2)	Radioactive Module C Std. Dev.
Al	3.43E-03	1.93E-04	**Al**	3.41-03	2.21E-04
S	1.51E-01	4.87E-03	**S**	1.64E-01	9.30E-03
Cs-133	7.60E-03	1.67E-03	**Cs-137**	1.03E-02	1.52E-03
Re	2.86E-02	1.45E-03	**Re**	1.49E-02	1.35E-03
Na	1.34E-02	6.88E-04	**Na**	1.65E-02	1.06E-03
Si	3.71E-04	2.35E-05	**Si**	2.50E-04	2.04E-05
I-127	2.35E-03	3.37E-05	**I-129**	<0.1644	N/A
			Tc-99	2.61E-02	7.17E-03
pH	10.79	0.04	**pH**	10.87	0.02

The short term PCT leachate data are shown graphically in Figure 5-7. These short-term PCT data are in agreement with the data generated in 2001 on AN-107 [35] and the 2004 SAIC-STAR facility samples with the Rassat simulant.[40,41] The correlations shown in Figure 5-7 were generated with the 7 available PCT responses from the 2001 and 2004 testing of both the bed and the fines. The HRI/TTT 2008 engineering-scale studies are overlain for comparison for the LAW samples (P-1B bed samples, and High Temperature Filter, HTF, fines), which appear as "x" marks on the graphs. The HRI/TTT 2008 engineering-scale studies for the WTP-SW are overlain (bed and fines) as open diamonds. The BSR data for non-radioactive and radioactive Modules B and C are overlain with "doughnut" shaped circles around them for emphasis. Note that the data plotted in Figure 5-7 is plotted as the log of the release rates shown in Table 5-29.

As with the 2001, 2004 and Module B data, the pH increases (becomes more caustic) as the surface area of the material is decreased (see Figure 5-7a). For glass waste forms, pH usually increases with increasing surface area. This indicates that a buffering mechanism is occurring for the BSR products. Based on the trend of alkali (Na) release being co-linear with Al release (Figure 5-7b), it was hypothesized that this was an aluminosilicate buffering mechanism.[40,41]

The Na release and Cs release are colinear with the Al release in the BSR and 2008 engineering scale data, as well as in the historical 2001 and 2004 data, as seen in Figure 5-7b and Figure 5-7f. All the other cations appear to be released as a function of the solution pH (Figure 5-7c, d and e) for the Si, S, and Re and Tc-99. This is also in agreement with the historical data and data from other leach testing and thermodynamic modeling.[53,90,106,107]

The Re release plot for the BSR (radioactive and simulant Module C/SX-105 and Module B/Rassat 68 Tank Blend from SRS Tank 50), the 2008 engineering scale, and the historic data appear in Figure 5-7d. Due to the low concentration of rhenium, it is a difficult element to measure. It is noteworthy that the Re release from the Module C simulant PCT tracks close to the Re release measured at SRNL for the radioactive Module C granular product. Note that the simulant Module C Re release tracks with the radioactive Tc-99 release. This demonstrates that Re and Tc-99 release is within experimental error of one another. This was also shown in the Re and Tc-99 leaching and with the Rassat simulant as shown in

Figure 5-7d and reported in Reference 28. The “tie back” strategy is, therefore, proven based on the fact that the radioactive and simulant BSR campaign products match the historic and engineering scale data.

Due to funding and scope cutbacks, short term leaching was not performed on Module D (AN-103) non-radioactive or radioactive BSR products. Short term leaching was also not performed on Module E simulant BSR products (there were only 2 campaign runs) and no radioactive FBSR product was made with the Module E (AZ-101/AZ-102) radioactive LAW.

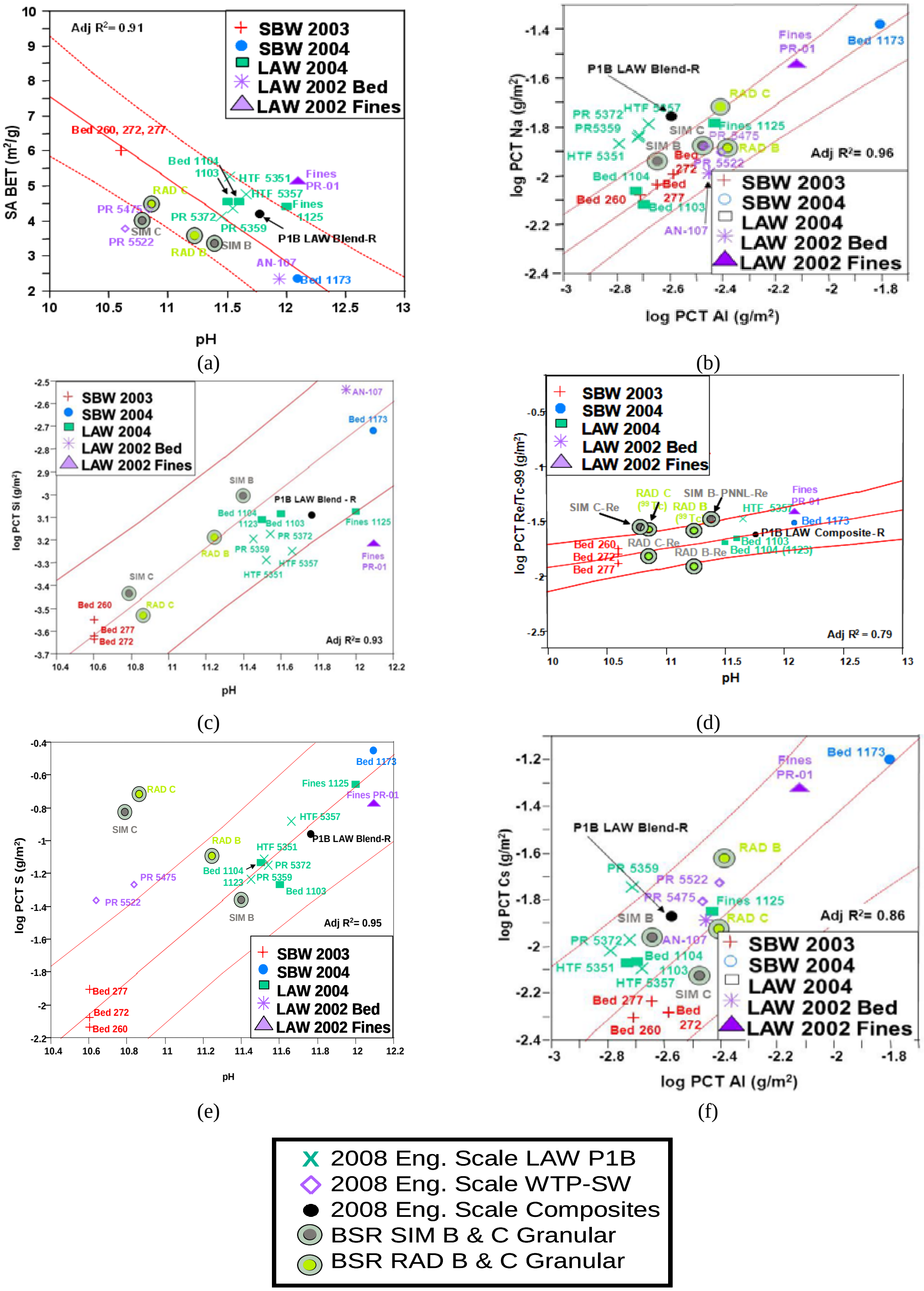


Figure 5-7. **Short Term PCT Testing (ASTM C1285) Correlation Developed with INL Pilot-scale Test Results with Rassat Simulant from 2003-2004, and HRI/TTT Testing of LAW AN-107 Samples from 2001-2002 Testing with Current Module B PCT data from Engineering Scale ESTD samples and BSR samples Modules B and C (non-radioactive and radioactive).**

5.5.2 *Product Consistency Test (PCT) - Long Term on FBSR Granular Product*

Long term PCT tests are performed in the same manner as the short term tests but PCT Method B allows for longer time intervals, in this case, 1 month, 3 month, 6 month, and/or 12 month tests. PCT-B tests are useful for generating concentrated solutions to study chemical affinity effects on the dissolution rate. PCT Method B tests at high temperatures and high glass/solution mass ratios can be used to promote the formation of alteration phases to (1) identify the kinetically favored alteration phases, (2) determine their propensity to sequester radionuclides, and (3) evaluate the effect of their formation on the continued waste form dissolution rate. XRD was used as a tool to identify alteration phases but it should be noted that XRD sensitivity to minor phases is, in general, not very good.

Short term PCT results (7 day) are shown along with release results from samples leached for 1, 3, 6 and 12 months in Table 5-30 and Appendix O for Module C non-radioactive granular product. For each of the elements analyzed, the release was relatively consistent over the 1 year of testing, i.e. same order of magnitude. Silicon release was decreasing slightly indicating solution saturation. Cesium release was decreasing as the silicon release was decreasing. All of the data is shown graphically in Figure 5-8. Releases of other species were each of the same magnitude from one time interval to the other over the one year of testing indicating that the FBSR granular product was not undergoing a significant degradation. Al and I were released at similar rates. Re, Na and Cs were all released at about the same rate but S was released at an elevated rate. The same composite sample was used in each long term PCT and the composite REDOX was 0.34 $Fe^{2+}/\Sigma Fe$.

Table 5-30. Long Term PCT Results for Module C (SX-105) Simulant Granular Product

Normalized Elemental Release (g/m^2)	**Module C (SX-105) Simulant Granular Test Interval**				
	7 Days	**1 Month**	**3 Month**	**6 Month**	**1 Year**
Al	3.43E-03	3.88E-03	3.53E-03	4.29E-03	3.77E-03
S	1.51E-01	1.64E-01	2.03E-01	1.87E-01	1.68E-01
Cs-133	7.60E-03	8.38E-03	8.69E-03	13.0E-03	10.4E-03
Re	2.86E-02	2.70E-02	2.92E-02	3.18E-02	3.04E-02
Na	1.34E-02	1.62E-02	1.66E-02	1.96-02	1.85E-02
Si	3.71E-04	3.20E-04	3.10E-04	2.60E-04	2.60E-04
I-127	2.35E-03	2.86E-03	3.10E-03	3.66E-03	3.62E-03
pH	10.79 ±0.04	10.52 ±0.00	10.29 ±0.02	10.04 ±0.00	10.15 ±0.06

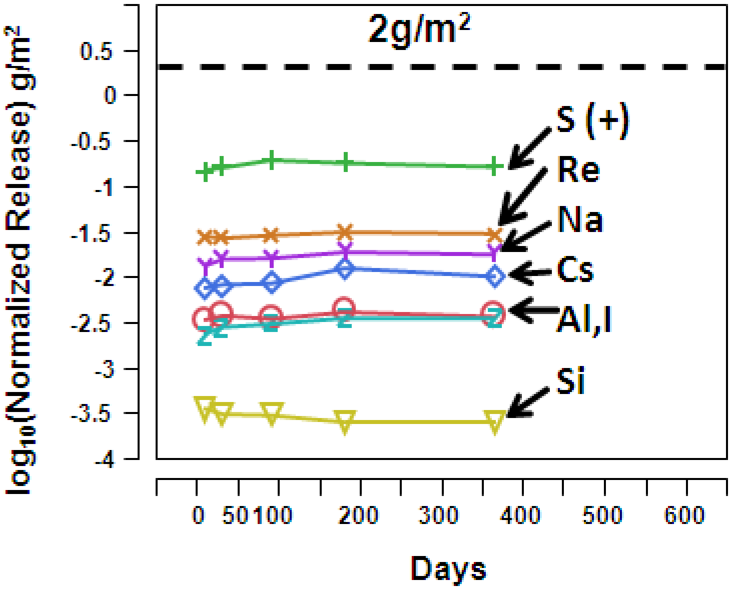
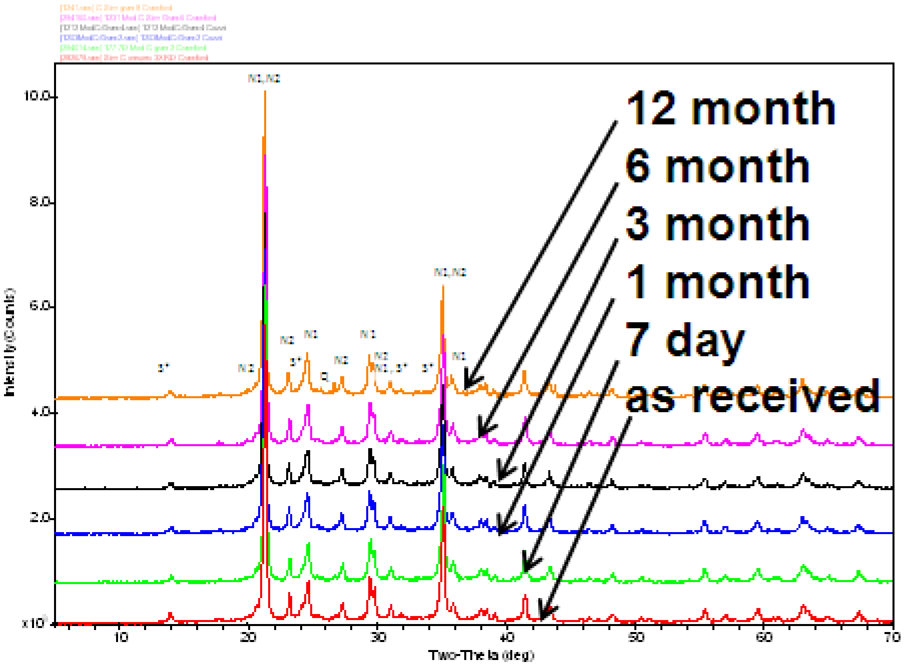


Figure 5-8. Release of elements from non-radioactive SX-105 simulant during 7 day, 1 month, 3 month, 6 month and 12 month long term PCT testing.

Figure 5-9 is an overlay of the XRD patterns of the Module C (SX-105) FBSR simulant granules as received and after each short term and long term leach interval. It is significant that all of the crystalline peaks of nepheline and sodalite have remained sharp and clear and of approximately the same height (intensity). This consistency implies that there has been little degradation to the mineral product throughout the 1 year leaching at 90°C. This is in agreement with the minimal change in leach rate over time shown in Figure 5-8. No reaction products were found after one year of leaching at 90°C by XRD analysis.



S*-sodalite/Zeolite A structure ($NaAlSiO_4$); N1 and N2 are the hexagonal and cubic nephelines discussed in Table 5-5

Figure 5-9. XRD patterns of FBSR Module C (SX-105) FBSR Simulant Granules As-Received and After PCT Leaching.

Where N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
S* is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)
Quartz is SiO_2 (PDF 00-046-1045) from excess SiO_2 in Table 4-4
Original XRD spectra fits are in Appendix N

For the Module C radioactive BSR granular product, the 7-day results are shown with release results from samples leached for 1, 3, and 12 months in Table 5-31, Appendix O, and Figure 5-10. No 6 month interval was performed on the radioactive samples based on the results from the non-radioactive testing. For each of the elements analyzed, the release was relatively consistent over the 1 year of testing, i.e. same order of magnitude. Silicon release was decreasing, while the other releases held constant over the one year of testing indicating that the FBSR granular product was not undergoing significant degradation of the mineral species. Tc-99, Na, Cs, and Re were all released at almost identical rates (each of the same magnitude from one time interval to the other) for the one year duration (Figure 5-10), which is similar to their congruent release with each other in glass. The sample REDOX was 0.17 $Fe^{2+}/\Sigma Fe$, which is considered ideal for Re and Tc-99 to be in the sodalite cage structure. All I-129 releases were below detection limit, $< -1.43 \log_{10}$ g/m^2 (Table 5-31) which puts the I-129 leaching in the same range as the Tc-99, Na, Cs, and Re releases in Figure 5-10.

Table 5-31. Long Term PCT Results for the Module C (SX-105) Radioactive FBSR Granular Product

Normalized Elemental Release (g/m^2)	BSR Radioactive Module C granular Test Interval			
	7 Days	1 Month	3 Month	1 Year
Al	3.41E-03	3.72E-03	3.91E-03	3.40E-03
S	1.64E-01	1.60E-01	1.85E-01	1.65E-01
Cs-137	1.03E-02	1.81E-02	1.64E-02	1.36E-02
Re	1.49E-02	1.55E-02	1.86E-02	1.76E-02
Na	1.65E-02	1.93E-02	2.21E-02	2.17E-02
Si	2.50E-04	2.90E-04	2.40E-04	1.60E-04
I-129	<0.1644	<0.04538	<0.05968	<0.0368
Tc-99	2.61E-02	2.00E-02	2.75E-02	2.55E-02
pH	10.87 ±0.02	10.61 ±0.04	10.33 ±0.04	10.02 ±0.06

Figure 5-11 is an overlay of the XRD patterns of the Module C (SX-105) radioactive FBSR granular product as received and after each short term and long term leach interval. The XRD pattern for the as-received sample is on the bottom of the figure and the patterns are stacked with increasing leach duration. It can be noted from the figure that the intensity and width of the major phases persists through all the leach intervals, indicating minimal degradation of the mineral species. All of the original phases (sodalite and the two varieties of nepheline) from the BSR campaigns (radioactive Module C) appear in the XRD spectra and there are no reaction products present after one year of leaching at 90°C.

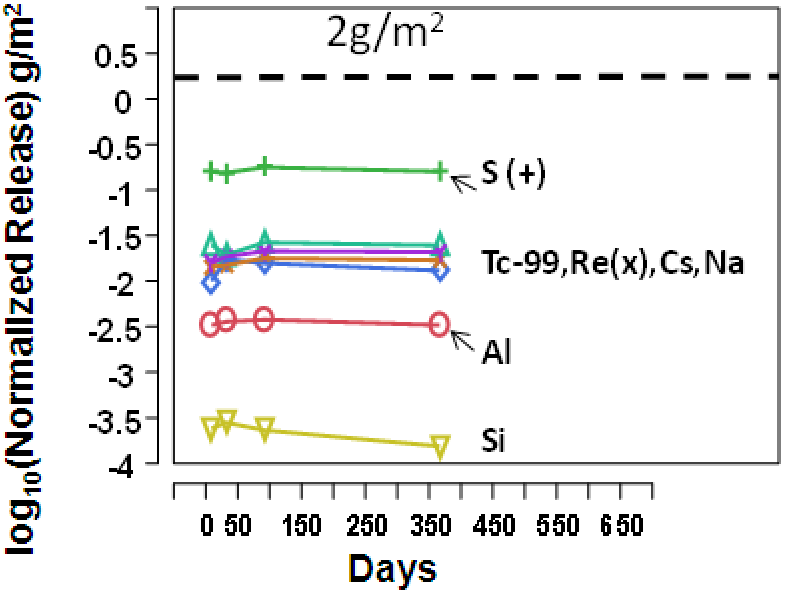
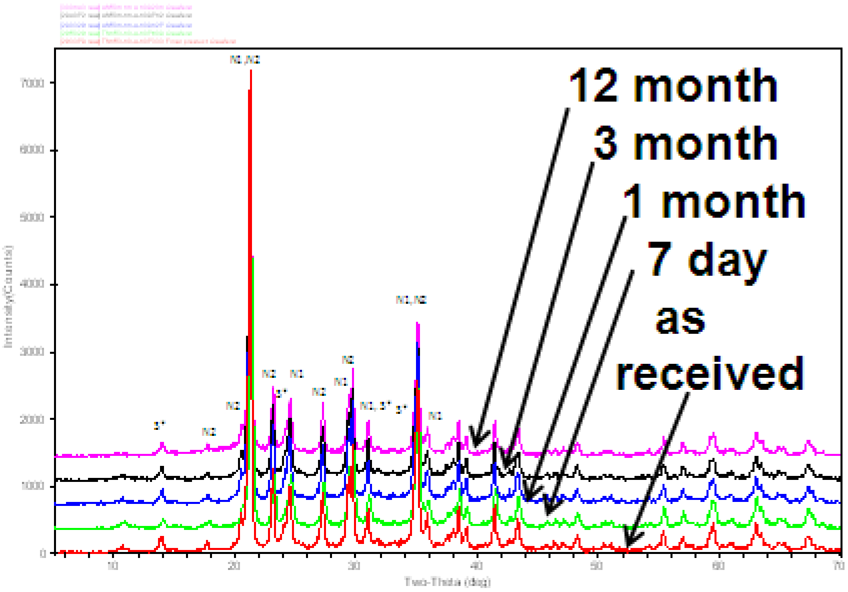


Figure 5-10. Release of elements from BSR radioactive Module C granular product during 7 day, 1 month, 3 month and 12 month long term PCT testing.



S*-sodalite/Zeolite A structure ($NaAlSiO_4$); N1 and N2 are the hexagonal and cubic nephelines discussed in Table 5-5

Figure 5-11. XRD patterns of Module C Radioactive Granules As-Made and After Long – Term PCT Leaching

Where N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
S* is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)
Original XRD spectra fits are in Appendix N

Nephelines are known to have survived anywhere from 879-1169 million years in nature as measured by K-Ar dating.[108] Weathering products from natural nephelines include but are not limited to analcite ($NaAlSi_2O_6$), Boehmite (AlOOH), hydronepheline (nepheline with attached water molecules), Kaolinite, muscovite, natrolite, and/or sodalite.[108] So the stability of the non-radioactive and radioactive nepheline and sodalite granular mineral phases in 90°C deionized water for periods of up to one year was anticipated and demonstrated.

6.0 Conclusions

Fluidized Bed Steam Reforming (FBSR) is a robust technology for the immobilization of a wide variety of radioactive wastes. Applications have been tested at the pilot scale for the high sodium, sulfate, halide, organic and nitrate wastes at the Hanford site, the Idaho National Laboratory (INL), and the Savannah River Site (SRS). Due to the moderate processing temperatures, halides, sulfates, and technetium are retained in mineral phases of the feldspathoid family (nepheline, sodalite, nosean, carnegieite, etc). The feldspathoid minerals bind the contaminants such as Tc-99 in cage (sodalite, nosean) or ring (nepheline) structures to surrounding aluminosilicate tetrahedra in the feldspathoid structures. The granular FBSR mineral waste form that is produced has a comparable durability to LAW glass based on the short term PCT testing in this study, the INL studies, SPFT and PUF testing from previous studies as given in the columns in Table 1-3 that represent the various durability tests. Monolithing of the granular product was shown to be feasible in a separate study. Macro-encapsulating the granular product provides a decrease in leaching compared to the FBSR granular product when the geopolymer is correctly formulated. The impact of monolithing on element release is probably due to several reasons: 1) the monolith has less surface area available to leach in comparison to the granular product, 2) dilution of the FBSR granular product by the monolith matrix, 3) transport properties of the monolith (diffusion and solubility controlled release) and 4) a combination of all three.

The significant findings to date of the testing primarily from the Hanford Tank SX-105 (Module C), Hanford Tank AN-103 (Module D), and Hanford Tank Blend AZ-101/102 (Module E) samples are given below and generally follow the order of the success criteria given in Section 3.0:

- ➢ The mineralogy of the radioactive and simulant products from the BSR for LAW SX-105, AN-103, and AZ-101/AZ-102 are nephelines, nosean, and sodalite;
  - the same mineral phases as the Rassat 68 tank Hanford LAW blend run in the BSR (non-radioactive and radioactive), in the Engineering-scale Test Demonstration (ESTD) in 2008, and in the 2001 and 2004 pilot studies at INL SAIC-STAR and TTT/HRI
  - the same mineral phases predicted by MINCALC™ qualitatively at the same wt.% given in MINCALC™

- ➢ The skeletal density of the radioactive and simulant products, the $Fe^{2+}/\Sigma Fe$ REDOX ratio of the radioactive and simulant products, and the coal content of the radioactive and simulant products are given in the table below:

Waste	Sample	Skeletal Density (g/cc)	Coal (%)	$Fe^{+2}/\Sigma Fe$
Module C (Tank SX-105)	Simulant	2.6	1.32	0.34
	Radioactive	2.49	3.50	0.17
Module D (Tank AN-103)	Simulant	Not Measured	1.62	0.30
	Radioactive		6.22	0.18
Module E (Tank AZ101/AZ102)	Simulant with IOC		0.70	0.13
	Simulant without IOC		1.15	0.06

- ➢ The skeletal densities for the SX-105 are in the range of the Module B Rassat 68 tank blend BSR campaigns (2.59 g/cc and 2.39 g/cc for the radioactive and non-radioactive, respectively) and the ESTD non-radioactive campaigns for the same Rassat simulant (2.39 g/cc)

- The coal content (except for the radioactive AN-103 and SX-105) were in the <2-wt% range like the Module B BSR and ESTD FBSR bed products and the radioactive AN-103 was <5 wt% coal

- The REDOX was targeted to be more oxidizing than the ESTD Module B Rassat 68 tank blend, which was in the 0.41-0.6 $Fe^{+2}/\Sigma Fe$ range and more oxidizing than the radioactive and non-radioactive (0.41 and 0.36 respectively) BSR Module B campaigns in an effort to keep the Tc-99 and the Re in the +7 oxidation state so it would be incorporated into the sodalite cage structure as $NaTcO_4$ and $NaReO_4$

- XAS studies reported elsewhere have shown all the Re to be in the sodalite cage and most of the Tc-99 to be in the sodalite cage; when Tc-99 is not in the sodalite cage it is present as insoluble technecium sulfide

- The mass balances of Tc-99, Re, Cs-137/Cs-133, and I-129/I-125/I-127 were determined in the BSR system.
  - Good mass balance closure was achieved on Tc-99, Re, Cs, I and chloride in the Module C (SX-105) and Module D (AN-103) campaigns. The Module E (AZ-101/AZ-102) simulant consisted of only one run and a mass balance was not performed.
  - Module C – Hanford LAW Tank SX-105
    - 71-98% recovery of Re in the product streams for radioactive and simulant campaigns, respectively for once through processing, which is ~3X greater retention than LAW glass for once through processing
    - 80-83% recovery of Tc-99 for once through processing, which is ~2.5X greater retention than LAW glass for once through processing
    - depending on analytical measurement technique used, radiochemistry vs. ICP-MS, respectively
    - ~75% recovery of I-127 (non-radioactive) and I-129 (radioactive)
    - 78-100% recovery of chloride, radioactive and non-radioactive, respectively
    - ~100% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns in the SCO
  - Module D – Hanford LAW Tank AN-103
    - 90-95% recovery of Re in simulant runs, 88% recovery in radioactive campaign for once through processing, which is ~3X greater retention than LAW glass for once through processing
    - 83-86% recovery of Tc-99 for once through processing, which is ~2.5X greater retention than LAW glass for once through processing
    - 100% recovery of I-127 (non-radioactive) in two simulant campaign and 100% recovery of I-129 (radioactive) in the radioactive campaign
    - 86% recovery of Cl in the simulant campaigns
    - 87% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns in the SCO

- The data indicates Tc-99, Re, Cs, and I (all isotopes) report preferentially to the mineral product with only minor amounts partitioning to the off-gas.

- Tc-99 and Re show similar behavior in partitioning between the product and off-gas: for mass balance Re is an acceptable simulant for Tc-99.

- The FBSR minerals were found to retain Re in the cage structure (~100%) of the granular mineral products and varying percentages of Tc-99 depending on the REDOX conditions.

- TCLP data are acceptable when REDOX is >0.30 $Fe^{2+}/\Sigma Fe$ or an IOC is present as a spinel host for Cr
  - An IOC algorithm was derived to quantify how much IOC is needed to stabilize chromium in an iron chrome spinel if REDOX targets <0.30 $Fe^{2+}/\Sigma Fe$ are found necessary to stabilize the Tc-99 and Re in the +7 oxidation state for incorporation into the sodalite host as $NaTcO_4$ and/or $NaReO_4$

- The successful processing of AN-103, which contained copious amounts of gibbsite ($Al(OH)_3$), demonstrated that precipitates do not have to be removed before FBSR processing.
  - precipitated solids were shown to behave like the clay additive in the FBSR process, i.e. at the FBSR processing temperature the hydroxides are removed from the gibbsite and the activated aluminum will react and become part of the mineral product in an identical fashion to how the hydroxides are removed from the clay additives and become reactive
  - excess Al is easily accounted for in the MINCALC™ process control spreadsheet as demonstrated in the Module D (AN-103) campaign where the clay content was adjusted for the additional alumina in the waste

- Granular waste form performance testing using ASTM C1285 (short term 7 day) was completed on Module C (SX-105)
  - ASTM C1285 (Product Consistency Test) testing is below 2 g/m^2 LAW glass leach rate limit for the constituents of concern (COC) by 2 orders of magnitude or 100-200X
  - Use of BET surface area to account for the surface roughness of the mineral granules demonstrates that the FBSR product is 2 orders of magnitude lower than the 2 g/m^2 LAW glass leach rate limit
  - Use of the geometric surface area, which ignores the surface roughness of the mineral granules and assumes the granules are hard spheres which is incorrect, gives an equivalent leach rate to LAW vitreous waste forms
  - All the durability results from Module C (non-radioactive and radioactive) are in agreement with the data from the Module B BSR testing (non-radioactive and radioactive) and the ESTD testing in 2008 and pilot scale testing from 2001 and 2004
  - Re is a good surrogate for Tc-99 during leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only and also prove the “tie back” strategy.
  - An aluminum buffering mechanism appears to control the leachate pH and all other element releases are released as function of solution pH for all radioactive and non-radioactive LAW wastes tested
    - The pH dependence is the same conclusions reached by SPFT and PUF testing of the Rassat FBSR ESTD and BSR products

- Long term testing (1, 3, 6 month and/or 1 year) at 90°C by ASTM C1285 of Module C (SX-105) non-radioactive and radioactive has not shown any significant change in the mineral assemblages as analyzed by X-Ray Diffraction (XRD)
  - Since excess clay was not present in the SX-105 FBSR products, halloysite ($Al_2Si_2O_5(OH)_4$ which can form from as a reaction product from excess clay was not present.
  - Silica concentrations in solution are decreasing with time indicating solution supersaturation: if reaction products were going to form, they would have formed when the solution saturates or supersaturates.
  - Re is a good surrogate for Tc-99 during long term leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only proving the “tie back” strategy.

Coupling the results of this study with previous radioactive BSR studies demonstrates that when anions such as Cl, F, and I are present or oxyanions such as TcO_4^- or ReO_4^-, more sodalite forms. If more $SO_4^=$ is present the sodalite structured phase nosean forms. If anions, $SO_4^=$, Re and Tc are low, then less sodalite/nosean forms and more nepheline forms. Cs and K can be accommodated in either nepheline or sodalite where they substitute for Na.

Theoretically, a pure sodium chloride waste stream would make a chloride sodalite and could accommodate 12.06 wt.% NaCl or 7.32 wt.% Cl. A pure iodide waste stream in sodalite could accommodate 22.03 wt.% I and a pure fluoride sodalite could accommodate 4.06 wt.% F. A pure sodium sulfate waste stream could accommodate up to 9.90 wt.% $SO_4^=$ or 14.65 wt.% as Na_2SO_4 in nosean. Likewise the Re and Tc sodalites can accommodate 25.22 wt.% Re or 15.20 wt.% Tc-99, respectively. Note that in the Module A WTP-SW FBSR study that 0.89 wt.% F was accommodated in the fluoride sodalite of the theoretical 4.06 wt.% F meaning that ~22 wt.% of the waste form was a fluoride sodalite. In the simulant Module E studies 2.18 wt.% $SO_4^=$ was accommodated in the nosean or ~22 wt.% of the theoretical $SO_4^=$ that could have been accommodated. The chemistry of the wastes that were tested, were relatively low in I, Cl, and Tc-99. Based on the mass balances reported in this study 85-100% of these species were retained in the FBSR minerals. The high mineral retentions mean that the following anion or oxyanion mineral incorporations were achieved which are well below the theoretical mineral retentions shown in the last column:

Anion or Oxyanion	**WTP-SW Radioactive**	**Hanford 68 Tank Blend Radioactive**	**LAW Tank SX-105 Radioactive**	**LAW Tank AN-103 Radioactive**	**LAW Tank AZ-101 /AZ-102 Simulant**	**Theoretical Pure Anion Stream**
	Wt.%	**Wt.%**	**Wt.%**	**Wt.%**	**Wt.%**	**Wt.%**
F^-	0.89	0.05	Below Detection Level	0.02	0.07	4.06
Cl^-	0.87	0.27	0.33	0.30	0.16	7.32
I^-	3.68E-03	0.25	5.61E-05	8.21E-05	0.21	22.03
$SO_4^=$	0.16	1.12	0.66	0.12	2.18	9.90
Tc^{+7}	2.13E-03	8.57E-05	5.33E-08	2.77E-04	non radioactive	15.20
Re^{+7}	0.05	0.04	0.05	0.04	0.04	25.22

The anion and oxyanion concentrations that can be accommodated in the sodalite/nosean mineral waste form are 10-20X what can be accommodated in LAW glass at equivalent Na_2O wt.% waste loadings. After monolithing, the 10-20X factor decreases by ~33% (100%-67% FBSR loading per monolith) and that still provides a 6.6-13.2X higher solubility for anions and oxyanions in FBSR LAW at moderate temperatures that do not volatilize these anions and oxyanions or create the need for complex recycle loops during processing during LAW vitrification.

7.0 Future Work

1. In order to match the BSR REDOX to the ESTD REDOX, the addition of reductants such as coal, IOC, and control of gas inputs were adjusted during the BSR campaigns. An optimized REDOX control strategy needs to be developed to ensure the COC's are in the correct oxidation states. For example:
   - REDOX control is an integral part of steel manufacturing and this type of control can be implemented.
   - ➢ Oxygen fugacity probes can be used to develop calibration curves that relate oxygen fugacity to the ratio of the gases already monitored in the FBSR pilot-scale tests as part of the process control for auto-catalytically heating the DMR.
   - ➢ The use of oxygen fugacity probes will allow more oxidized REDOX ranges to be targeted and achieved so that higher concentrations of Tc-99 (>80%) can enter the sodalite cage structure.

2. The amounts of the IOC needed for denitration vs. sequestration of the RCRA metals should be optimized as currently an excess is added which may not be necessary. A preliminary algorithm was derived in this study but is based only on three data points.

3. Geopolymer optimization was not a rigorous part of this study. More work needs to be performed with the clay based geopolymers and an optimization study performed. After binder optimization, more short and long term monolith testing (ASTM C1285, ASTM C1308/ANSI/ANS 16.1, SPFT and PUF) should be pursued to better determine the transport properties of the monolithed waste form.

4. Longer term leach testing and SEM are needed to determine what reaction products form on the granular and monolithic waste forms.

5. Geochemical modeling of the short and long term granular and optimized monolith leachates should be performed to determine long term waste form stability.

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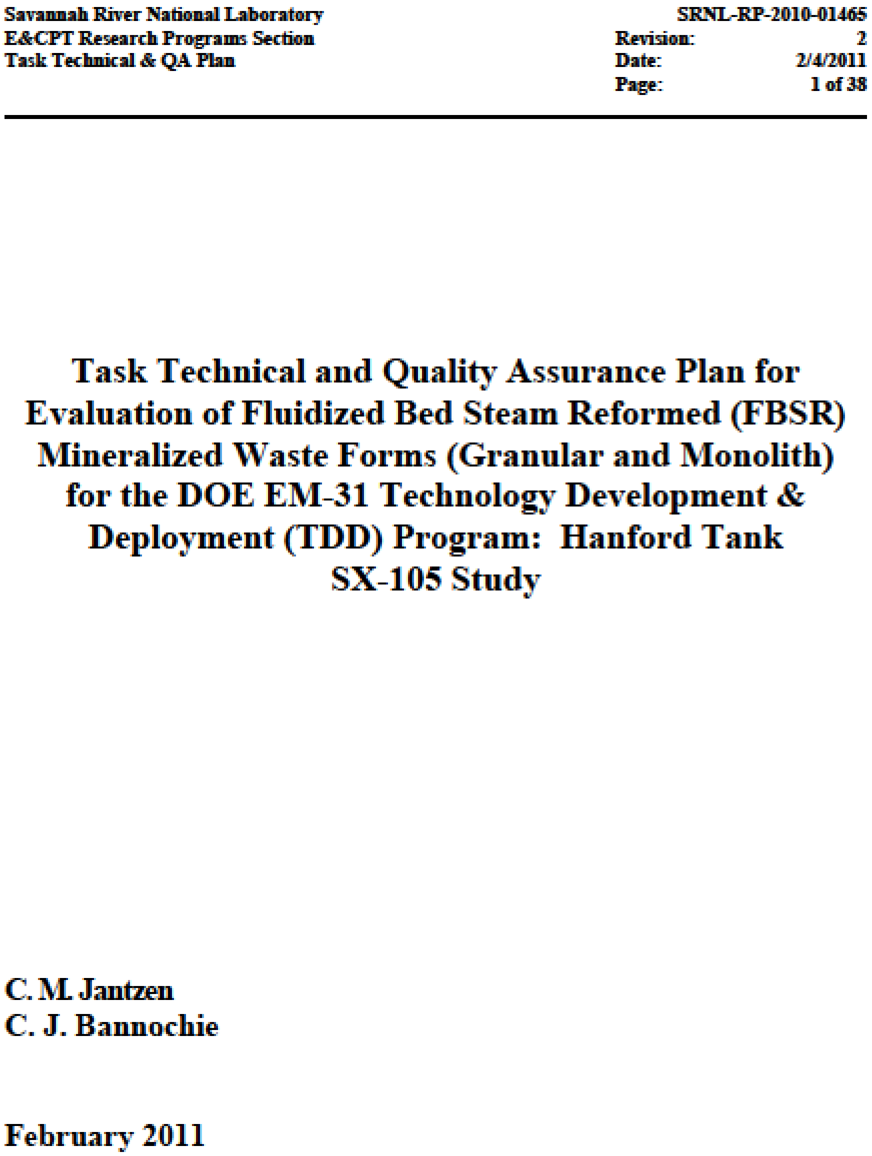
Appendix A. Task Technical & Quality Assurance Plan for Module C



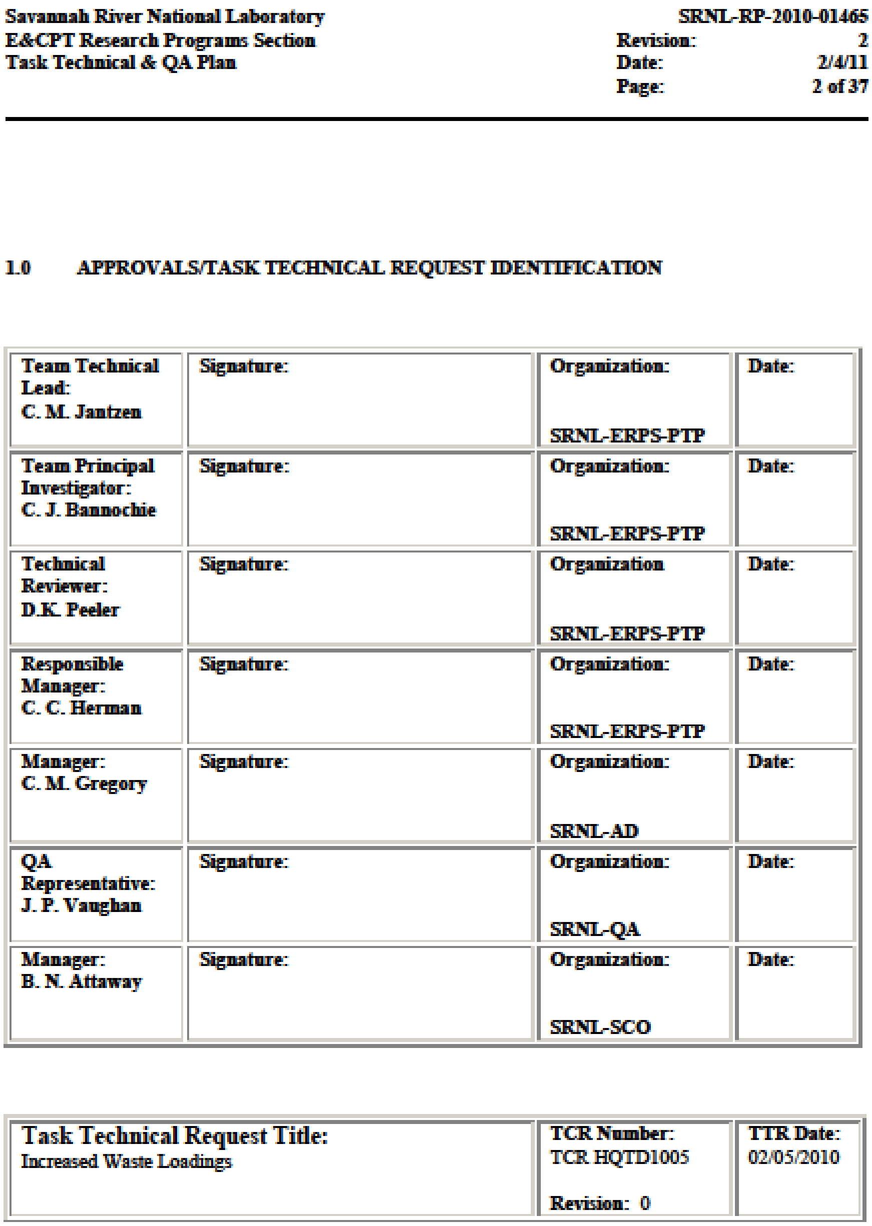
Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

	SRNL-RP-2010-01465
Revision:	2
Date:	2/4/2011
Page:	1 of 38

Task Technical and Quality Assurance Plan for Evaluation of Fluidized Bed Steam Reformed (FBSR) Mineralized Waste Forms (Granular and Monolith) for the DOE EM-31 Technology Development & Deployment (TDD) Program: Hanford Tank SX-105 Study

C. M. Jantzen
C. J. Bannochie

February 2011



Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01465
Revision: 2
Date: 2/4/11
Page: 2 of 37

1.0 APPROVALS/TASK TECHNICAL REQUEST IDENTIFICATION

Team Technical Lead: **C. M. Jantzen**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Team Principal Investigator: **C. J. Bannochie**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Technical Reviewer: **D.K. Peeler**	**Signature:**	**Organization** **SRNL-ERPS-PTP**	**Date:**
Responsible Manager: **C. C. Herman**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Manager: **C. M. Gregory**	**Signature:**	**Organization:** **SRNL-AD**	**Date:**
QA Representative: **J. P. Vaughan**	**Signature:**	**Organization:** **SRNL-QA**	**Date:**
Manager: **B. N. Attaway**	**Signature:**	**Organization:** **SRNL-SCO**	**Date:**

Task Technical Request Title: Increased Waste Loadings	**TCR Number:** TCR HQTD1005 **Revision:** 0	**TTR Date:** 02/05/2010

LIST OF REVISIONS

Revision Number	Summary of Changes	Date
0	Initial Issuance	11/23/10
1	• Removed text references to Tc by ICP-MS to reconcile text with Table 4. • Revised Table 1, PO$_4^{3-}$ value from 0.7871 to 0.07871. • Table 2 and 3, clarified descriptions of product sums • Table 2, quantity of non-radioactive product required for testing increased to make 4 non-radioactive monoliths. • Added IC analyses for PCT leachates of granular product and monoliths. • Table 4, added AA As and AA Se analysis on radioactive granular product and monoliths and their PCT leachates. • Table 4, replaced lithium metaborate preps with closed vessel aqua regia digestions. • Table 4, added Sim C and Rad C characterization prior to clay/coal/Fe addition. • Added test detail and durations about Long Term PCT on radioactive and non-radioactive granular product and monoliths. • Changed minimum Fe limit in the final product to ≥1.5 wt% Fe instead of ≥3 wt% Fe as testing has indicated that 1.5 wt% Fe is adequate for reproducible REDOX measurements. • Details of what granular and monolithic samples get shipped to PNNL for testing and which remain at SRNL for testing. • Corrected volume of radioactive waste received from Hanford to 950 mL instead of 900 mL.	1/21/11
2	• Corrected LT-PCT sampling intervals for non-radioactive granular product and monoliths which were given incorrectly. • Added option of performing short-term PCT in Teflon® vessels. • Section 2.1.3, removed requirement to verify Tc-99, Re, and I-127 on the doped feed sample due to lack of material for these analyses. • Table 4, added total base and TIC measurements needed on SX-105 feed. • Table 4, added SX-105 analyses needed for final mass balance calculations. • Table 4, adjusted radiochemistry turn-around-times from 15 to 20 days. • Table 4, clarified PCT leachate analyses for acidified and non-acidified samples. • Table 4, added conductivity and pH measurements to PCT leachates. • Section 4.2, corrected the number of non-radioactive monoliths from five to four.	2/4/11

2.0 INTRODUCTION

2.1 Task Definition

2.1.1 Introduction

The baseline treatment plan for Hanford is to vitrify their salt supernate wastes also known as Low Activity Waste (LAW). This task plan deals with the feasibility of an alternative or supplemental treatment for LAW waste known as Fluidized Bed Steam Reforming (FBSR) and so the investigations are not considered to be baseline. The Waste Treatment Plant (WTP) is currently under construction to treat all of the High Level Waste (HLW) and a portion of the LAW via vitrification. However, the LAW will be generated at over twice the rate that the currently designed LAW vitrification facility can treat the waste. Either a second LAW vitrification facility or other supplemental LAW treatment technology is needed to meet schedule objectives and approved tank closure deadlines.

One of the supplemental LAW treatment technologies being considered is FBSR. Recently, THOR® Treatment Technologies (TTT) has successfully demonstrated the FBSR technology at the Engineering Scale Technology Demonstration (ESTD) pilot scale on a non-radioactive Hanford LAW simulant[1] that represents a 68 tank blend of Hanford wastes. This simulant is known as the Rassat[2] simulant. As part of the Washington River Protection Solutions (WRPS) supplemental treatment technology evaluation and Department of Energy (DOE) EM-31 Technology Development and Deployment (TDD) programs[3], the Savannah River National Laboratory (SRNL) has been requested to successfully demonstrate the FBSR technology on waste streams representative of Hanford's LAW at the Benchscale Steam Reformer (BSR) scale and compare the results to the products formed at the pilot scale. The first demonstration[4] was a radioactive Savannah River Site (SRS) salt supernate that had been compositionally trimmed to look like the Hanford Rassat 68 tank blend that TTT processed non-radioactive. The second demonstration of LAW is a Hanford waste from Tank SX-105 and will be known as Module C for SRNL tracking purposes. Module C is the focus of this Task Technical and Quality Assurance Plan (TTQAP).

FBSR treatment offers a low temperature (700-750°C) continuous method by which LAW may be processed into a crystalline ceramic (mineral) waste form regardless of whether the wastes are high in organics, nitrates, sulfates/sulfides, other anions or components. The FBSR process produces no secondary liquid waste streams. Based on previous testing[5,6,7,8,9,10,11,12,13,14], the granular waste form that is produced by co-processing the LAW with kaolin clay has been shown to be as durable as LAW glass. However, monolithing of the granular product is being pursued since monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage. Once again, it is not believed to be necessary to meet performance criteria.

To support SRS implementation of the FBSR technology for Tank 48 (T48), SRNL has successfully operated a Bench scale Steam Reformer (BSR) in the SRNL Shielded Cells Facility (SCF).[15,16] The BSR is a unique SRNL design and this radioactive capability does not exist commercially nor at any other DOE site. All related safety basis documentation for operation of the BSR in the

SRNL SCF was completed for the T48 demonstration and will need to be updated to cover the stream being treated for this scope and additional Hanford streams that will be covered in future task plans. SRNL also has unique expertise, analytical chemistry skills, and equipment for monolithing the granular FBSR product and measuring durability of waste forms.[17,18]

The scope of work addressed in this task planning document consists of SRNL making a simulant of Hanford's Tank SX-105 LAW and testing the simulant in the non-radioactive BSR in 735-11A to provide

- optimization of processing parameters for radioactive testing,
- non-radioactive granular samples for testing the durability response of the SX-105 BSR product compared with previous testing of pilot scale FBSR products[17] and previous BSR products,[4,17] and
- granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from previously tested pilot and BSR products.[4,17] Tank SX-105 LAW is a high anion containing waste with high concentrations of S, Cl, F and P.
- Radioactive BSR testing will also be performed (see next paragraph) and the response of the non-radioactive granular and monolithed products will also be compared to the radioactive granular and monolithed products produced.

The scope of work addressed in this task planning document also consists of SRNL mineralizing a radioactive Hanford LAW sample from Tank SX-105 that has been supplied by Hanford and has already been chemically analyzed.[19] However, if any data is missing or if validation of the Cs, I, and Tc levels is necessary, then SRNL will perform the analysis. The Tank SX-105 LAW will be processed in the BSR in the SCF to provide

- radioactive granular samples for testing the durability response of BSR product compared to product from the TTT pilot scale runs from WFO-09-003[17] and other BSR campaigns with Waste Treatment Plant Secondary Waste (WTP-SW)[17] and Hanford's Rassat simulant[4,17] and the non radioactive testing in the scope above and
- radioactive granular products to monolith and compare (durability and compressive strength) to the non-radioactive monolithic waste forms prepared under WFO-09-003,[17] Hanford's Rassat simulant,[4] and in the scope described above.

Because of the lack of complete fluidization and less residence time in the BSR than in the ESTD pilot, the particle size will be mostly fines as particle size growth is minimized in the absence of long residence times and intense fluidization. This is not problematic as the ESTD bed product is an agglomeration of finer particles that grow in the long residence times in the FBSR.

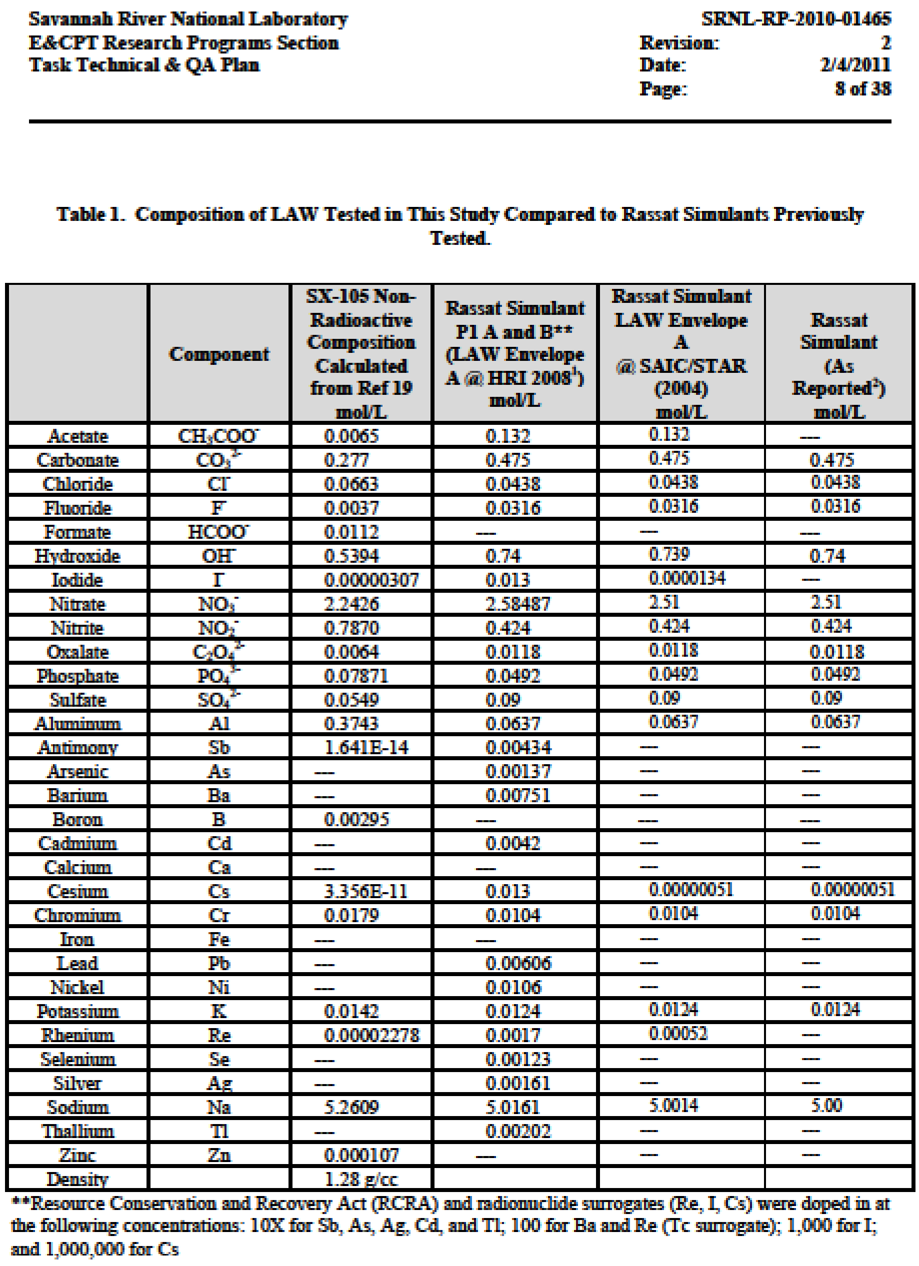
2.1.2 Non-Radioactive Tests

The SX-105 simulant will be developed by SRNL from the chemical analysis provided by WRPS as shown in Table 1[19]. The target concentration for the LAW Resource Conservation and Recovery Act (RCRA) metals will not be increased over what is already present in the waste. The Re (Tc surrogate) will be increased by 100; the I by 1,000; and 1,000,000 for Cs as done in the TTT pilot scale demonstrations of the Rassat simulant[1] in order to observe their behavior during mass balance of the process. Ferric nitrate nona-hydrate will be added to have $\geq$1.5 wt% Fe in the final product as a REDOX indicator as there is little to no iron in the waste. Knowing the iron REDOX helps determine the oxidation state of many other REDOX active species such as Re^{+7} vs. Re^{+4} and Cr^{+6} vs. Cr^{+3}.

Once the simulant recipe is developed it will be used to determine the optimum non-radioactive BSR operational conditions and then these same operational conditions will be used in the radioactive BSR tests in the SCF. Partitioning of the Cs, I, and Re to the off-gas versus the overall solid mineralized product will be assessed by whole element chemistry of the off-gas condensate and the solid product. Additionally, off-gas lines in-between the reaction chamber known as the Denitration and Mineralizing Reactor (DMR) and the off-gas condenser will be rinsed with a known amount of deionized water and analyzed to determine the species that have been trapped or retained in the lines. The data will be used to calculate a mass balance of the system. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) will be used for analyses of the Cs, Re, and I in the solids and off-gas due to their presence at very low concentrations.

In addition, partitioning of the Cs, Re, and I amongst the solid phases, e.g. nepheline vs. sodalite, will also be determined by quantitative X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and possibly Transmission Electron Microscopy (TEM) and Selected Area Diffraction (SAD). Since the sodalite phases, including nosean, are present in small quantities which for low anion containing feeds may be below the detection limit of the XRD, a total amount of "sodalite vs. nepheline" may be the only quantitative analyses that are reportable. Phase pure standards (see Section 2.1.4) are being made to develop quantitative XRD calibration curves.

Sufficient non-radioactive granular product must be made to provide five 1"OD x 2"H monoliths and 56 g of granular product for durability testing at SRNL. Therefore, a total of ~181 ((154 x 0.65) + 56) g is required as shown in Table 2. After the 28 day curing, two of the monoliths will be compression tested at SRNL. Upon passing the 500 psi compression test minimum requirement, SRNL will retain the entire non-radioactive product for durability testing.



Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01465
Revision: 2
Date: 2/4/2011
Page: 8 of 38

Table 1. Composition of LAW Tested in This Study Compared to Rassat Simulants Previously Tested.

	Component	SX-105 Non-Radioactive Composition Calculated from Ref 19 mol/L	Rassat Simulant P1 A and B** (LAW Envelope A @ HRI 2008[1]) mol/L	Rassat Simulant LAW Envelope A @ SAIC/STAR (2004) mol/L	Rassat Simulant (As Reported[2]) mol/L
Acetate	CH_3COO^-	0.0065	0.132	0.132	—
Carbonate	CO_3^{2-}	0.277	0.475	0.475	0.475
Chloride	Cl^-	0.0663	0.0438	0.0438	0.0438
Fluoride	F^-	0.0037	0.0316	0.0316	0.0316
Formate	$HCOO^-$	0.0112	—	—	—
Hydroxide	OH^-	0.5394	0.74	0.739	0.74
Iodide	I^-	0.00000307	0.013	0.0000134	—
Nitrate	NO_3^-	2.2426	2.58487	2.51	2.51
Nitrite	NO_2^-	0.7870	0.424	0.424	0.424
Oxalate	$C_2O_4^{2-}$	0.0064	0.0118	0.0118	0.0118
Phosphate	PO_4^{3-}	0.07871	0.0492	0.0492	0.0492
Sulfate	SO_4^{2-}	0.0549	0.09	0.09	0.09
Aluminum	Al	0.3743	0.0637	0.0637	0.0637
Antimony	Sb	1.641E-14	0.00434	—	—
Arsenic	As	—	0.00137	—	—
Barium	Ba	—	0.00751	—	—
Boron	B	0.00295	—	—	—
Cadmium	Cd	—	0.0042	—	—
Calcium	Ca	—	—	—	—
Cesium	Cs	3.356E-11	0.013	0.00000051	0.00000051
Chromium	Cr	0.0179	0.0104	0.0104	0.0104
Iron	Fe	—	—	—	—
Lead	Pb	—	0.00606	—	—
Nickel	Ni	—	0.0106	—	—
Potassium	K	0.0142	0.0124	0.0124	0.0124
Rhenium	Re	0.00002278	0.0017	0.00052	—
Selenium	Se	—	0.00123	—	—
Silver	Ag	—	0.00161	—	—
Sodium	Na	5.2609	5.0161	5.0014	5.00
Thallium	Tl	—	0.00202	—	—
Zinc	Zn	0.000107	—	—	—
Density		1.28 g/cc			

**Resource Conservation and Recovery Act (RCRA) and radionuclide surrogates (Re, I, Cs) were doped in at the following concentrations: 10X for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs

Table 2. BSR Product Requirements in Grams (Non-Radioactive Testing)

MODULE C PRODUCT REQUIREMENTS BY TEST AND LABORATORY		
Testing	Granular SRNL (g)	Monolith SRNL (g)
Product Consistency Test (PCT) Short Term	24	24
PCT Long Term	12	12
Toxicity Characteristic Leaching Procedure (TCLP)	20	20
ASTM C1308	0	98
Compression Testing**	0	0
TOTAL MATERIAL SUM	56	154
BSR GRANULAR PRODUCT EQUIVALENTS		125*
TOTAL GRANULAR PRODUCT	181	

* Monolith Product x 0.65 BSR Loading x 1.25, makes four monoliths at ~33 g BSR per monolith. Two monoliths will be crushed and two will be used in tact for ASTM C1308 testing.

** Compression tested samples will be used for PCT and TCLP

SRNL will perform analyses to measure properties of the non-radioactive granular products and the monolithed simulated waste forms generated from the granular products produced during the simulant BSR campaigns. This will include loss-on-drying (LOD) tests at 110°C to determine moisture content and loss-on-ignition (LOI) tests at 525°C to determine the coal fraction in the samples which is the difference between the LOI and the LOD weight losses. The temperature of 525°C removes the carbon left in the raw coal after processing in the BSR as the hydrogen, oxygen, and moisture from the coal have been removed during the BSR processing. However, this temperature does not vaporize the sulfur in the coal or the BSR product phases. For these experiments, where SRNL is using the carbon LOI to assess the impact of carbon on the REDOX measurement, this temperature has been found to be sufficient and it is the temperature recommended by a US Geological Survey procedure developed for coal analyses.[20] Different subsamples will be sent for REDuction/OXidation (REDOX) analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the SEM using Energy Dispersive Spectroscopy (EDS) to determine if Re and I are retained in a sodalite structure and if Cs substitutes for Na in nepheline and/or sodalite or both.

The non-radioactive granular and monolithed waste form products will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by qualified personnel at SRNL. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The time durations are to be one month, three month, six month and an additional time to be determined (TBD) which may be up to one year or longer. The tests will be performed in Teflon® vessels. A minimum of 1 g of sample must be tested at a mass ratio of 1 g of solids to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume will be determined once the Brunauer, Emmett, and Teller (BET) surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA); and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC.

The Toxicity Characteristic Leaching Procedure (TCLP) will be performed by an Environmental Protection Agency (EPA) certified laboratory in South Carolina for the non-radioactive simulant.

The non-radioactive granular product will be made into monoliths using the optimized monolith binder defined by the completion of the SRNL WFO-08-003[18] matrix or the testing performed as part of EM-31 Task 5.2.1. The monolith will be characterized as described above and compression tested. Diffusion coefficients for Re, Cs, and I will be determined using the 3 month long ASTM C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form.

2.1.3 Radioactive Tests

The Tank SX-105 Hanford LAW sample has been analyzed by WRPS.[19] WRPS decided to filter the waste through a 2 micron and then a 0.7 micron filter and so there should be no solids. The density of the waste has been measured by WRPS to be 1.28g/cc.

Hanford has provided ~950 mL of SX-105 and all will be processed to make the 422 g of radioactive product calculated in Table 3. Re will be added to the waste to have $\geq$150 µg/g in the final product and ferric nitrate nona-hydrate will be added to have $\geq$1.5 wt% Fe in the final product. The ferric nitrate is added as a REDOX indicator in order to determine the oxidation state of Re, Tc, and the RCRA metals from an already developed Electro-Motive Force (EMF) diagram for FBSR. The concentration of Re will be verified after doping. The addition of the ferric nitrate is accounted for during the balancing of oxidants and reductants in the feed.

During the demonstration, ~90% of the waste will be processed as received with only Re and ferric nitrate added. The remaining ~10% of the waste will be doped with Tc^{99}, Re, and I^{127} (non-radioactive) at a minimum of 150 µg/g in the solid product as this is the level needed to detect these species during follow on extended x-ray absorption fine structure (EXAFS) testing at the Stanford

Synchrotron Radiation Lightsource (formerly Stanford Synchrotron Radiation Laboratory) to determine the local bonding of the Tc^{99} and I^{127} in the mineral waste form. Iodine-125, -127 and -129 will all be present and expected to partition to the same sodalite phase and the Synchroton sensors can pick up all three isotopes but is most specific for I^{127}. The ~10% of the feed will be processed at the end of the campaign, after the off-gas condensate is sampled and lines are flushed. This will ensure that the mass balance and leaching tests described below are not compromised by the elevated concentrations required by the EXAFS testing.

Non-radioactive Re is added to determine the effectiveness of Re as a surrogate for Tc^{99} during BSR processing, i.e. do they track each other in the off-gas, do they substitute for each other in the solid products or does one preferentially partition to the sodalite over the other, and do they respond similarly to the reduction/oxidation (REDOX) in the BSR. This will be compared to their response during subsequent durability testing.

Partitioning of the radionuclides (Cs, Tc, and I) and Re to the off-gas and to the solid mineralized product will be assessed by analysis of the off-gas condensate and analysis of the solid product. Off-gas lines in-between the reaction chamber known as the DMR and the off-gas condenser will be rinsed with a known amount of deionized water and analyzed to determine the species that have been trapped or retained in the lines. A mass balance will be performed. A combination of ICP-MS and radiometric methods will be used for analyses of these components as they should be present at very low concentrations.

During the BSR processing in the SCF, kaolin clay will be added to the SX-105 sample to form the mineralized waste form between 725°-750°C. Because the waste is concentrated during processing while also being diluted by the non-radioactive clay added, the resulting radioactive dose of the final product will be different than the starting material. Assuming the measured dose is low enough to work in a radioactive hood, characterization and testing of the samples will be performed in a 773-A laboratory. If not, the characterization and testing will be performed in the SCF.

Adequate radioactive granular product must be produced in the BSR in the SCF to fabricate five 1"OD x 2"H monoliths and provide granular product for durability testing at PNNL and SRNL (Table 3). After the required 28 day curing, two of the monoliths will be sent to PNNL for future testing and three will be retained at SRNL for testing.

If the 950 mL of SX-105 does not make the required 422 g of granular product, then the amounts given in Table 3 will have to be adjusted accordingly, e.g. fewer monoliths, fewer samples, or fewer tests. This will be agreed upon with input from the customer and stakeholders.

SRNL will perform analysis of chemical and physical properties of the radioactive granular products and monoliths generated from the granular products produced during the BSR campaigns in the SCF. This will include LOD tests at 110°C to determine moisture content and LOI tests at 525°C to determine the coal fraction in the sample. Different subsamples will be sent for REDOX analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the Contained Scanning Electron Microscope

(CSEM) using EDS to determine if Tc, I and Re are retained in a sodalite structure and whether Cs substitutes for Na in the nepheline and/or sodalite structures. The coal in the product will also be examined for retention of radionuclides.

Table 3. BSR Product Requirements in Grams (Radioactive Testing)

MODULE C PRODUCT REQUIREMENTS BY TEST AND LABORATORY				
Testing	Granular PNNL (g)	Granular SRNL (g)	Monolith PNNL (g)	Monolith SRNL (g)
Single-Pass Flow-Through (SPFT)	144	0	72	0
Pressurized Unsaturated Flow (PUF)	40	0	40	0
Product Consistency Test (PCT) Short Term	0	24	0	24
PCT Long Term	0	12	0	12
Toxicity Characteristic Leaching Procedure (TCLP)	20	0	20	0
ASTM C1308	0	0	0	98
SUMS BY LABORATORY	204	36	132	134
TOTAL MATERIAL SUM	240		266	
BSR GRANULAR PRODUCT EQUIVALENTS	NA		182*	
TOTAL GRANULAR PRODUCT	422			

* Monolith Product x 0.65 BSR loading x 1.05, makes 5.5 monoliths at ~33 g BSR per monolith. Of these 5.5 monoliths two uncrushed monoliths remain at SRNL for ASTM C1308 testing; three monoliths are compression tested; 2.75 crushed monoliths are sent to PNNL for testing; 0.75 crushed monoliths are retained at SRNL for short term and long term PCT.

The radioactive granular waste form product will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by SRNL. The radioactive granular product will be made into monoliths using the optimized monolith binder defined by simulant testing. The monoliths will then be re-characterized and subjected to the ASTM C1285-08 test (long and short term) and a compression test. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The radiation dose from the sample must be calculated to ensure that the Teflon® vessels are acceptable per the dose requirements given in the PCT procedure, e.g. doses up to 1 x 10^5 rad of beta or gamma radiation have been shown not to damage TFE-fluorocarbon (Teflon®). The time durations are to be one month, six month, and an additional time to be determined (TBD) which could be up to one year. The tests will be performed in Teflon® vessels. A minimum of 1 g of sample must be tested at a mass ratio of 1g of solid to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume ratio will be determined once the Brunauer, Emmett, and Teller (BET) surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA), and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC. Cs, I, and Tc will be measured radio-metrically.

Diffusion coefficients for Tc, Re, Cs, and I will be determined using the three month long C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form.

Both the granular product and the monolith product will be leach-tested using the EPA TCLP procedure. Because SX-105 is a listed waste the samples (granular and monolithic) will be sent to PNNL who will subcontract with an EPA certified laboratory.

2.2 Customer/Requester

Terry Samms, Manager of WTP Technology and Development, is the customer/requester as the ultimate user of the technology. Steve Schneider, Director (Acting) Office of Waste Processing is the HQ customer/requester for the overall program.

2.3 Task Responsibilities

Environmental & Chemical Processing Technology Research Programs (ERPS) personnel will be primarily responsible for the scope described in this task plan. Durability testing being performed on the granular and monolithic samples (non-radioactive and radioactive) being sent to PNNL is not covered in this task plan. SRNL support will be provided by personnel in the Shielded Cells, AD, and the Regulatory Integration and Environmental Services organization. C. J. Bannochie is the overall Principal Investigator for the Hanford BSR program, while C. M. Jantzen is the overall technical lead for the program and is responsible for this task plan and any revisions. P. R. Burket is considered the Subject Matter Expert (SME) for the BSR equipment (non-radioactive and radioactive) and control system design and set-up. A. D. Cozzi is the lead for the waste form qualification and testing. C. C. Herman is the responsible manager for the program. The responsible manager (or designee) is responsible for reviewing and approving all procedures and task plans, assessing the preparedness to carry out this task, and reviewing and approving all reports.

Overall responsibilities of the ERPS BSR team include the following:

- Coordinating all activities and ensuring that they are completed in a timely manner
- Ensuring that all results are documented
- Preparing the records for this task
- Ensuring that sample tracking and document controls are followed
- Ensuring that the latest revisions of procedures are used to complete the task activities

For the simulant BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the Hazards Analysis Package (HAP) for the testing, providing guidance on the equipment performance parameters, ensuring the BSR is set up to perform testing, and performing the BSR testing.
- R. E. Eibling (or designee) is responsible for overseeing the production of the necessary simulant, including verifying acceptability of the simulant.
- W. E. Daniel (or designee) is responsible for preparing the equipment for simulant demonstrations, analyzing the simulant and ensuring product samples are submitted for characterization.
- C. L. Crawford and A. D. Cozzi (or designees) are responsible for characterization and testing of the granular product, production of the monoliths, and characterization and testing of the monoliths. C. L. Crawford will interface with W. L. Mhyre of Quality Control Testing to perform the necessary compression testing.
- ERPS technicians are responsible for performing the LOI measurements and PCT.
- Support for the above tasks will be provided by personnel within the ERPS section.
- AD is responsible for performing Brunauer-Emmett-Teller (BET) surface area measurements on the simulant samples.

For the radioactive BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the HAP for the testing and overseeing performance of the BSR testing.
- C. L. Crawford (or designee) is responsible for characterization and spiking of the radioactive sample.
- C. L. Crawford and C. J. Bannochie (or designees) are responsible for characterization of the granular product, monoliths, and offgas condensates/rinses.
- A. D. Cozzi (or designee) is responsible for testing of the granular product, production of the monoliths, and testing of the monoliths.
- J. H. Scogin (or designee) is responsible for performing BET surface area measurements on the radioactive samples.
- M. G. Bronikowski (or designee) is responsible for performing skeletal density measurements on the radioactive samples.
- ERPS technicians are responsible for performing the LOI measurements and PCT if the samples can be removed from the Shielded Cells. If the samples cannot be removed, Shielded Cells personnel will perform the LOI measurements and PCT under the guidance of ERPS personnel.
- Support for the above tasks will be provided by personnel within the ERPS section and by SCF personnel as necessary.

As necessary, C. L. Crawford (or designee) will be responsible for developing or modifying existing HAPs for the waste form characterization, production, or testing. C. L. Crawford (or designee) will be the PI for the treatability study. He will have primary responsibility for working with the Inventory Authority, H. K. Hall (or designee), to track generated samples and residue throughout the performance of the task until completion of the studies and disposition of all material. All other researchers working with the actual Hanford material will also be required to comply with the guidelines of L29, ITS-0167 for tracking and disposition of samples and residue.

The Process Science Analytical Laboratory (PSAL) will be responsible for analyzing simulant and product streams using the following methods or equipment: Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Ion Chromatography (IC), Parr Anton density meter, REDOX, and LOD/LOI. PSAL will perform the necessary digestions or dilutions to allow the samples to be analyzed by these methods. PSAL will follow approved procedures to perform these measurements and will assign a unique ID to each sample to maintain traceability. PSAL will ensure that the appropriate standards are used and that equipment calibration is maintained during performance of the testing. Appropriate analytic standards will be submitted with all samples for a cross comparison between non-radioactive samples analyses by PSAL and radioactive sample analyses by Analytic Development (AD).

SRNL – SCO (Shielded Cells Operations) personnel are responsible for:

- Reviewing and approving this TTQAP
- Readying and maintaining the facility for operation
- Checking and installing the equipment necessary for tasks to be performed in the Shielded Cells
- Providing SRNL – Quality Assurance (QA) access to training and qualification records for SCO personnel for surveillances or audits
- Ensuring the latest revisions of procedures are used to complete the task activities

SRNL – AD Laboratory personnel are responsible for:

- Reviewing and approving this TTQAP
- Analyzing radioactive waste samples and simulant and product streams using the following methods or equipment: ICP-AES, ICP-MS, IC, particle size distribution (PSD), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Contained Scanning Electron Microscopy (CSEM), and radiometric analyses
- Providing personnel resources and equipment necessary to perform REDOX via remote handling in SCF (not an AD established method)
- Providing SRNL – QA access to training and qualification records for AD personnel for surveillances or audits
- Performing QA checks (i.e., using standards and ensuring calibrations are valid) on instrumentation involved in this task
- Analyzing the samples per the Turn Around Times (TAT) specified in this TTQAP
- Reviewing the sample results prior to reporting them
- Ensuring the latest revisions of procedures are used to complete the task activities
- Communicating needed method development validation work to be performed on radioactive materials produced as part of the Task Plan

SRNL QA is responsible for reviewing and approving this task plan and providing guidance and oversight for this task.

WRPS and EM-31 WP-5 personnel are responsible for providing guidance and input on the requirements of their associated qualification program and CD-1 package needs. They are requested to provide written requests to SRNL specifying any changes/deviations to the scope of this TTQAP. The WRPS and EM-31 WP-5 team will be responsible for reviewing the final reports associated with this task. Any changes or addition to scope will be agreed upon by SRNL after considering the impact to budget and schedule. K. Ryan, of TTT, is responsible for providing BSR operational parameters and providing the coal and clays to be used by SRNL if needed.

2.4 Task Deliverables

1. An approved Task Technical and QA Plan (this document).
2. Mass balance of Re, I, and Cs during non-radioactive BSR operation.

3. Interim documentation of the results of the non-radioactive BSR run and the characterization of the granular and mineralized product including subsequent product characterization and testing.
4. Production and testing of five non-radioactive monoliths and ~36 g granular product for further testing for SRNL.
5. Mass balance of Tc^{99}, I^{129}, and Cs^{137} during radioactive BSR operation.
6. Interim documentation and a final approved report documenting the results of the radioactive BSR mineralized product and subsequent product characterization and testing.
7. Shipment of two radioactive monoliths and ~204 g granular product to PNNL for further testing.
8. Three radioactive monoliths and ~36 g granular product for SRNL testing.
9. Shipment of granular products made from Hanford SX-105 waste at an elevated solids spiking of 150μg/g Tc^{99} and I^{129} for Synchrotron testing at Stanford Synchrotron Radiation Lightsource or an equivalent facility.

3.0 TASK ACCEPTANCE CRITERIA

Acceptance testing is not part of this task.

4.0 TASK ACTIVITIES

4.1 Task Initiation

- Draft/review/issue TTQAP.
- Conduct R&D/Hazards Assessment Package (HAP)/Safety review for simulant BSR testing including initiation of the Environmental Evaluation Checklist (EEC).
- Conduct R&D/HAP/Safety review for radioactive BSR testing including approval of the necessary national emissions standards for hazardous air pollutants NESHAPS analysis and EEC.
- Conduct R&D/HAP/Safety review for the fabrication, characterization, and testing of the granular and monolithic waste forms as necessary including the EEC for simulant and radioactive testing.

4.2 Simulant and BSR Product Formation

- Develop an SX-105 simulant.
- Make ample non-radioactive simulant (1-2 Liters) to make ~181 g (Table 2) of non-radioactive BSR product for further testing.
- Analyze non-radioactive SX-105 simulant to confirm critical parameters.
- Determine the simulant BSR operating parameters (clay levels, coal levels, input gases/flow rates) by scaling of the ESTD operation parameters down to the BSR scale. SRNL will obtain concurrence with the simulant BSR operating parameters from TTT before proceeding with the BSR operation.
- Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases and sufficient carbon to provide the necessary reductant for the non-radioactive BSR campaigns.
- Run the non-radioactive BSR in 735-11A between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each simulant run will use a minimum of 60 mL and maximum of 250 mL of feed. It is estimated that five runs with ~60 mL each of non-radioactive simulant are needed to produce enough granular product to be analyzed and tested. The estimated

required granular product mass is 181 g (four 1" x 2" monolith cylinders and 56 g of granular product).

4.3 Simulant Product Analysis and Off-Gas Mass Balance

- Analyze the composited BSR products for whole element chemistry of all cations and anions by ICP-AES and IC, REDuction/OXidation or REDOX ratio to determine $Fe^{+2}/\Sigma Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Re concentrations by ICP-MS.
- Analyze the off-gas condensate for all cations and anions by ICP-AES and for Cs, I, and Re by ICP-MS. This may facilitate speciation of the type of carryover occurring, if any. For example Cs may be carried over as vapor as Cs_2O, CsCl, CsF, $CsNO_3$ or as particulates such as $CsAlSiO_4$.
- Rinse the off-gas line(s) between the DMR and the condenser with a known volume of water and/or acid and analyze for all cations and anions by ICP-AES and for Cs, I, and Re by ICP-MS.
- Perform mass balances on elements of concern with special attention to Cs, I, and Re.

4.4 Simulant Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR granular products. The surface area to volume ratios will be determined once the particle size distribution from the BSR runs for this simulant is known.
- Perform long term ASTM C1285 - PCT on the BSR granular products. Sample and analyze at one, three, six, and TBD month intervals. At the end of each sampling, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. Geochemist's Workbench (GWB).
- Send a subset of the granular product for TCLP testing by a certified EPA laboratory.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003)[18].

4.5 Simulant Monolith Production and Product Testing

- Use a portion of the BSR granular products from the non-radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined in WFO-2009-003[17] and/or EM-31 Task 5.2.1 to produce 10 separate 1" x 2" monoliths.
- After curing for 28 days, perform compression testing on the non-radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.

- Compression test the monoliths with both a penetrometer and the ASTM compression test to calibrate the penetrometer for use with the radioactive monoliths since radioactive ASTM compression testing capability is not available
- Using crushed segments returned from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR monolith products.
- Perform long term ASTM C1285 - PCT on the BSR monolith products. Sample and analyze at one, three, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB.
- Send a subset of the crushed samples from compression testing for TCLP testing by a certified EPA laboratory.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1)[3,4,17].
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths. This is a 90 day test.

4.6 Radioactive BSR Product Formation

- Transport SX-105 Hanford Waste to the SRNL SCF.
- Perform Treatability Study sample handling and processing in the SCF in accordance with SRNL Procedure Manual L1, 6.04 'Hazardous/Mixed Waste Treatability Studies' and Procedure Manual L29, ITS-0167 'Hanford Treatability Study and Materials Handling'.
- Ensure that enough of the radioactive dopants (Tc^{99}, Cs^{137}, I^{129} or I^{125}) have been procured and available to process the last 100 mL of SX-105.
- Dope 800 mL of the SX-105 sample with Re and ferric nitrate
- Analyze the trimmed Tank SX-105 after doping.
- Dope the remaining 100 mL of the SX-105 sample with Re, ferric nitrate, Tc^{99} and I^{127} to the levels needed to achieve 150μg/g of each in the solid samples for EXAFS testing.
- Ship Tc^{99} and I^{127} doped sample to Synchrotron Radiation source defined by customer.
- Determine the BSR operating parameters (clay levels, coal levels, input gases/flow rates) based on the BSR simulant testing. Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases (wet clay basis) and sufficient carbon to provide the necessary reductant (Bestac carbon) for the radioactive BSR campaigns. The carbon will be calculated for the actual amount of NO_3 and NO_2 in the radioactive sample using 1.3X the value calculated by the SRNL developed MINCALC Version #3. Obtain concurrence with the BSR operating parameters from TTT before proceeding with the radioactive BSR operation.
- As necessary, install the BSR in the SCF after preliminary testing in the Shielded Cells Mock-up Facility. If already located in the SCF, install new glass ware and BSR components to perform the radioactive demonstration.
- Run the radioactive BSR in the SCF between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity.

Each radioactive doped SX-105 run will use a minimum of 60 mL of feed. It is estimated that somewhere around 15 runs with ~60 mL each of SX-105 are needed to produce enough granular product to be analyzed and tested. The estimated required granular product mass is ~422 g (five 1" x 2" monolith cylinders and 240 g of granular product - see Table 3).

- Analyze the BSR product for whole element chemistry of all cations and anions by ICP-AES, ICP-MS, AA, and IC, REDuction/OXidation or REDOX to determine $Fe^{+2}/\sum Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Tc concentrations by ICP-MS and/or radiometric methods.
- Analyze the off-gas condensate for Cs, I and Tc by ICP-MS and/or radiometric methods.
- Rinse the off-gas line(s) at the end of the nominal concentration runs between the DMR and the condenser with a known volume of water and/or acid and analyze for Cs, I, and Tc by ICP-MS and/or radiometric methods.
- Perform mass balances for Tc, Cs, and I.

4.8 Radioactive Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the FBSR granular products.
- Perform long term ASTM C1285 - PCT on the BSR granular products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides to the alteration phases.
- Send a subset of the granular product (see Table 3) to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003),[4,17,18] to data gathered during Hanford Module A and B testing, and to the durability response of the non-radioactive granular product produced in this task plan.

4.9 Radioactive Monolith Production and Product Durability Testing

- Use a portion of the BSR granular products from the radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined from the simulant monolith testing in this task plan.
- After curing for a minimum of 28 days, perform compression testing on two radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.
- Compression test the monoliths with the pre-calibrated penetrometer or an ASTM C39 compression tester.
- Upon passing the compression test at 500 psi ship two of the radioactive monoliths to PNNL (one whole and one broken from compression testing) along with ~204

g of radioactive granular product.

- Using crushed segments from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 – PCT on the BSR radioactive monolith products.
- Perform long term ASTM C1285 - PCT on the BSR radioactive monolith products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides in the alteration phases.
- Send a subset of the crushed samples from compression testing (see Table 3) to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1),[3,17,18] to data gathered during Hanford Module A and B testing, and in the non-radioactive portion of this task plan.
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths and run for 90 days.

4.10 Data Analysis and Documentation

- Analyze data as each module is completed.
- Provide interim technical reports as necessary to meet WRPS project commitments.
- Draft, approve, and issue a final report(s) after all the phases are complete.

5.0 TASK SCHEDULE

The timing of the individual activities will be maintained in the ERPS schedule. A higher level schedule is also being maintained by WRPS and is being updated on a weekly basis with all parties.

Table 4 summarizes the various runs/campaigns and the associated testing. The acronym in parenthesis after the test method indicates the organization that will perform the analyses. PSAL is denoted separately so that they can plan their resource load accordingly and to distinguish from AD. The radioactive sample PCTs will be performed by ERPS or SCF personnel if not able to remove the samples from the cells and the leachates will be submitted to AD. Radioactive sample BET will be performed in a glovebox using existing instrumentation maintained by ERPS personnel.

Table 4. Summary of Sample Types and Methods. Required Turnaround Times are in Work Days (* = Calendar Days) and Responsible Organization (A = AD, C = E&CPT/SSP, N = N-Area, O = Offsite, Op - = Optional, P = PSAL, U = E&CPT/PTP)

	No. of Samples[†]	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Pre-Clay/Coal/Fe (no dissolution)	3																						3 U		
Simulant Pre-Clay/Coal/Fe (AR Digestion)	5	15 A	15 A																						
Simulant Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	4			15 A	2 P																				
Simulant Post-Clay/Coal/Fe	2																							2 U	
Simulant Granular Product Production Subsamples (no dissolution)	20 ‡											2 A	2 P									1 P			
Simulant Granular Product (no dissolution)	3											5 A	3 P	15 A	10 U	180 U					30 O	3 P		2 U	15 A

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Granular Product (AR Digestion)	**5**	15 A	15 A																						
Simulant Granular Product (PF Digestion)	**5**	15 A																							
Simulant Granular Product (KOH/H_2O Digest)	**4**			15 A	2 P																				
Simulant Granular Product PCT Leachates (Non-Acidified)	**36**			15 A	5 P												3 U	3 U							
Simulant Granular Product PCT Leachates (Acidified)	**36**	5 P	15 A																						
Simulant Granular Product LT PCT Solids	**8**											15 A													
Simulant Condensate	**3**	5 P	15 A	15 A	5 P																				

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Condensate Solids (no digestion)	1										Op	Op													
Simulant Condensate Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Condensate Solids (PF Digestion)	2	5 A																							
Simulant Condensate Solids (KOH/H_2O Digest)	2				15 A																				
Simulant Rinsed Lines	3	5 P	15 A	15 A	5 P																				
Simulant Rinsed Lines Solids	1										Op	Op													
Simulant Rinsed Lines Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Rinsed Lines Solids (PF Digestion)	2	5 A																							

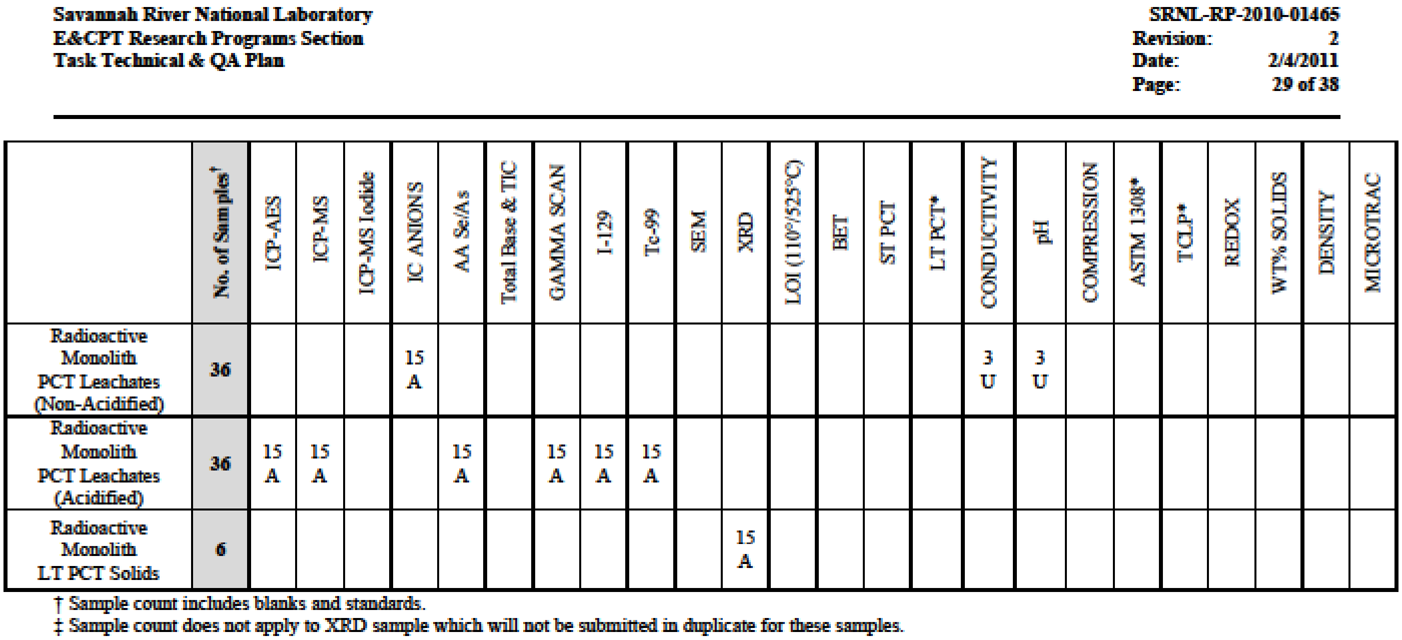
	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Rinsed Lines Solids (KOH/H_2O Digest)	**2**				15 **A**																				
Simulant Monoliths (no dissolution)	**3**											15 **A**	3 **U**	15 **A**	10 **U**	180 **U**			5 **U**	90 **U**	30 **O**			2 **U**	15 **A**
Simulant Monoliths (AR Digestion)	**9**	15 **A**	15 **A**																						
Simulant Monoliths (PF Digestion)	**9**	15 **A**																							
Simulant Monoliths (KOH/H_2O Digest)	**4**			15 **A**	2 **P**																				
Simulant Monoliths PCT Leachates (Non-Acidified)	**36**			15 **A**	5 **P**												3 **U**	3 **U**							
Simulant Monoliths PCT Leachates (Acidified)	**36**	5 **P**	15 **A**																						

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Monoliths LT PCT Solids	8											15 A													
Radioactive Feed Pre-Clay/Coal/Fe (no dissolution)	4						15 A	20 A	20 A														3 U		
Radioactive Feed Pre-Clay/Coal/Fe (AR Digestion)	5	15 A	15 A							20 A															
Radioactive Feed Pre-Clay/Coal/Fe (PF Digestion)	5	15 A																							
Radioactive Feed Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	4				15 A																				
Radioactive Feed Post-Clay/Coal/Fe	2																							2 U	
Radioactive Granular Product Production Subsamples (no dissolution)	30 ‡											2 A	2 U									1 A			

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Granular Product (no dissolution)	**3**								**20 A**		**15 A**	**15 A**	**3 U**	**15 C**	**10 U**	**180 U**					**30 O**	**15 A**		**15 U**	**15 A**
Radioactive Granular Product (AR Digestion)	**9**	**15 A**	**15 A**			**15 A**				**20 A**															
Radioactive Granular Product (PF Digestion)	**9**	**15 A**						**20 A**																	
Radioactive Granular Product (KOH/H$_2$O Digest)	**4**				**15 A**																				
Radioactive Granular Product PCT Leachates (Non-Acidified)	**36**				**15 A**												**3 U**	**3 U**							
Radioactive Granular Product PCT Leachates (Acidified)	**36**	**15 A**	**15 A**			**15 A**		**20 A**	**20 A**	**20 A**															
Radioactive Granular Product LT PCT Solids	**6**											**15 A**													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Condensate	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Condensate Solids (no digestion)	2								20 A		Op	Op													
Radioactive Condensate Solids (AR Digestion)	2	15 A	15 A					20 A	20 A	20 A															
Radioactive Condensate Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Condensate Solids (KOH/H_2O Digest)	2				15 A																				
Radioactive Rinsed Lines	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Rinsed Lines Solids (no dissolution)	2								20 A		Op	Op													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Rinsed Lines Solids (AR Digestion)	2	15 A	15 A							20 A															
Radioactive Rinsed Lines Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Rinsed Lines Solids (KOH/H_2O Digest)	2				15 A																				
Radioactive Monolith (no dissolution)	3								20 A			15 A	3 U	15 C	10 U	180 U			5 U	90 U	30 O			2 U	15 A
Radioactive Monolith (AR Digestion)	9	15 A	15 A			15 A				20 A															
Radioactive Monolith (PF Digestion)	9	15 A						20 A																	
Radioactive Monolith (KOH/H_2O Digest)	4				15 A																				



	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT‡	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308‡	TCLP‡	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Monolith PCT Leachates (Non-Acidified)	**36**				15 A												3 U	3 U							
Radioactive Monolith PCT Leachates (Acidified)	**36**	15 A	15 A			15 A		15 A	15 A	15 A															
Radioactive Monolith LT PCT Solids	**6**											15 A													

† Sample count includes blanks and standards.
‡ Sample count does not apply to XRD sample which will not be submitted in duplicate for these samples.

6.0 RESEARCH FACILITY PLANNING

6.1 Effects of the Task on Equipment, Personnel, and Research Facilities' Physical Plant

The receipt, analyses, and handling of radioactive samples such as the SX-105 salt supernate are routine tasks performed in the Shielded Cells. The entire task will be evaluated using the SRNL Conduct of R&D Manual. A calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution. An e-mail will be sent to the coordinator for the Radionuclide Inventory – Administrative Control (RI-AC) computer system to make sure the use of these samples for this testing is within the authorization basis of the SRNL Documented Safety Analysis (DSA).

Activities surrounding the analysis of the samples and the running of the BSR will be shown on the SRNL Shielded Cells Operations and ERPS schedules. Appropriate documentation will be completed prior to the start of activities.

Activities need to stay on schedule to support WRPS's supplemental LAW treatment technology selection.

Because the SX-105 waste is an Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) listed waste, special procedures for handling and segregating this waste are being implemented in SRNL including a tracking mechanism for all samples, and sample residues.[21]

6.2 Products and By-Products of Task

Any solids created by the radioactive sample processing will be stored in a Satellite Accumulation Area (SAA) at the end of the treatability study. It is anticipated that all the SX-105 will be processed and there will be no SX-105 to return to Hanford. Disposition and return of solids to Hanford after analysis will be accomplished through consultation with the SRNL Environmental Compliance Authority (ECA) and in compliance with the EEC. All remaining solutions (from condensates derived from the BSR process and from the dissolutions of the product for analyses and from PCT leachates) and solid residues from completed testing will be returned to Hanford. All job control waste will be disposed of as manifested waste returns to Hanford. Some solid samples will be retained at SRNL for follow on characterization and testing after the treatability study has ended, i.e. under the "sample exclusion." Residues (liquid and solid) from this characterization and testing will also be tracked and the residues returned to Hanford. ERPS will work with the SRNL ECA to disposition these residues.

Samples for PNNL, except those for Synchrotron testing, will be sent after the treatability study has ended, i.e. once the samples have been archived, they will be sent to PNNL under the sample exclusion rule rather than as part of the treatability study.

Disposition of Test Equipment

Upon completion of the radioactive BSR processing additional follow-on work is to be performed, i.e., radioactive Hanford LAW processing and the equipment will remain in the SCF. However, non-containers that come in contact with the Hanford material will

be treated as job control waste for that stream. The simulant BSR will also be used for additional testing and thus will remain set-up until subsequent Hanford testing is completed.

6.3 Exposure of Personnel

Samples that are radioactive will be handled remotely in the Shielded Cells. Samples with high levels of radiation that have to be removed from the Shielded Cells for analyses by AD will be diluted in the cells so that only a small portion of the radioactivity is removed from the cell. If the BSR products are at a low enough radiation level to be handled in SRNL radioactive hoods (i.e., meet existing hood limits), they will be removed from the Shielded Cells and handled in ERPS laboratories. This includes preparation for characterization, production of the monoliths, and testing of the granular and monolith products. The radioactive samples may be contact handled by Shielded Cells technicians, ERPS personnel (in radioactive hoods and radiobenches), and AD technicians (in radioactive hoods and radiobenches). These samples will be controlled and comply with standing radiological work plans. If a sample is expected to exceed standing radiological work plan limits, a job specific radiological work plan will be implemented after implementation of all engineering and administrative controls and when no other choice exists.

7.0 PROGRAMMATIC RISK REVIEW

Per the L1 manual, Procedure 7.10, a programmatic risk review has been performed for the tasks listed in this TTQAP. The SRNL Conduct of R&D manual will be used to complete a review for all tasks listed in the TTQAP. Results of the risk review are given below in Table 5.

Table 5. Programmatic Risk Review

Question	Response
Could an inadvertent or premature failure of equipment result in unacceptable added programmatic costs or schedule delays?	Yes. All preventive measures will be taken in order to maintain schedule and budget. Back-up BSR equipment has been procured. Spare parts are available for the components. One spare controller is available and two spare Mass Spectrometers are being procured. A schedule delay would be experienced to place the backup or new equipment into service and recover from the point of failure. A delay in the return to service date of any SRNL – AD analytical instrumentation will result in a schedule delay since back-up options for most of the required analyses are limited.
Is the activity on a critical path or is the activity significant to a major site program/process, milestone, or objective?	No. However, this activity is in support of a multi-year DOE EM-31 funded proposal and is on a critical path for Hanford Waste Form Qualification (WFQ) and the WRPS Supplemental LAW Treatment selection.
Does the activity involve long lead time items whose failure would exceed the allowable programmatic schedule?	Yes. Failure of the controller system or the Mass Spectrometer before the spare is obtained and operational will result in a delay to the program. In addition, an AD instrumentation failure(s) resulting in the need for replacement equipment would exceed the allowable programmatic schedule.
Does this activity involve high risk technology whose development, if not successful, could exceed allowable programmatic cost or schedule?	No. The technology has been used for previous experimentation and the primary change is the feed stream. Decisions will be made for the remaining Hanford BSR program based on the results of this program. Decisions will be made for Hanford implementing this technology as the supplemental technology for LAW at Hanford based on the results of this program.
Could the activity or failure of the activity significantly impact the facility or other programs in proximity of the activity?	Potential exists. Cells 3 and 4 of the Shielded Cells will be dedicated to the BSR runs for several months. This could impact needed space for other SRR and EM programs. Cell 6 may be used for analytical support if needed. This could impact the analytical support for other sample processing that will be going on at the same time. If Cell 6 is not used, then resources (i.e., hoods in ERPS laboratories) will be utilized which may impact other programs. During the running of the BSR in the SCF, facility support will be required to monitor the SCF ventilation system since the BSR system generates appreciable quantities of flammable hydrogen. No physical impacts to the facility are anticipated.
If quantities of accountable radioisotopes (per L7.7, 1.07) are received into the SRNL facilities, what impact will the planned activity have on SRNL facilities?	The SX-105 sample has already been received at SRNL. However, a calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution prior to use and after doping with the necessary quantities of additives. If any radionuclide quantity is predicted to exceed the SRNL reportable quantities, the appropriate section of procedure 1.07 of the L7.7 manual will be followed. An e-mail will be sent to the coordinator for the RIAC database system to make sure the receipt of these samples is within the authorization basis of the SRNL DSA. If the sample has an impact on the Authorization Basis, a schedule delay would be experienced though not expected.

8.0 R&D HAZARDS SCREENING

Before any laboratory work is initiated, a review of L1, 7.02, will be performed to determine the hazards and controls required. At a minimum, three HAPs are expected to be generated to support this task.

9.0 QUALITY ASSURANCE

9.1 Documents Requiring Requester Approval

Document	Management		Customer		QA	
	Yes	No	Yes	No	Yes	No
Task Technical and QA Plan	X			X	X	
Final Report	X		X			X

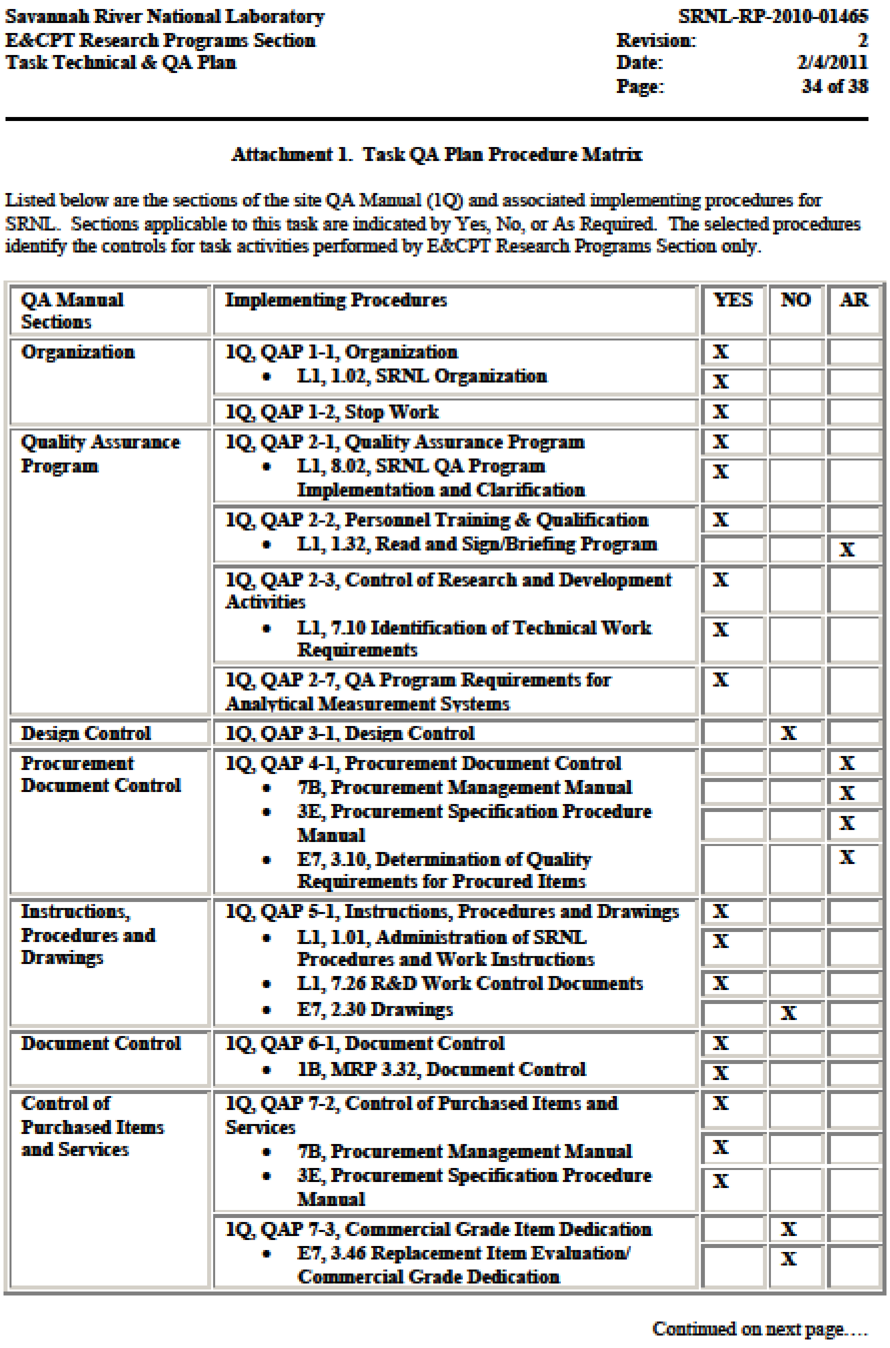
9.2 Records Generated During Task Performance

Description	YES	NO	AR*
Task Technical and QA Plan	X		
Controlled Laboratory Notebooks	X		
Task Technical Reports	X		
Data Qualification Reports		X	
Supporting Documentation			X

*** AR = As Required**

9.3 Task QA Plan Procedure Matrix

See Attachment 1.



Attachment 1. Task QA Plan Procedure Matrix

Listed below are the sections of the site QA Manual (1Q) and associated implementing procedures for SRNL. Sections applicable to this task are indicated by Yes, No, or As Required. The selected procedures identify the controls for task activities performed by E&CPT Research Programs Section only.

QA Manual Sections	Implementing Procedures	YES	NO	AR
Organization	**1Q, QAP 1-1, Organization**	X		
	• **L1, 1.02, SRNL Organization**	X		
	1Q, QAP 1-2, Stop Work	X		
Quality Assurance Program	**1Q, QAP 2-1, Quality Assurance Program**	X		
	• **L1, 8.02, SRNL QA Program Implementation and Clarification**	X		
	1Q, QAP 2-2, Personnel Training & Qualification	X		
	• **L1, 1.32, Read and Sign/Briefing Program**			X
	1Q, QAP 2-3, Control of Research and Development Activities	X		
	• **L1, 7.10 Identification of Technical Work Requirements**	X		
	1Q, QAP 2-7, QA Program Requirements for Analytical Measurement Systems	X		
Design Control	**1Q, QAP 3-1, Design Control**		X	
Procurement Document Control	**1Q, QAP 4-1, Procurement Document Control**			X
	• **7B, Procurement Management Manual**			X
	• **3E, Procurement Specification Procedure Manual**			X
	• **E7, 3.10, Determination of Quality Requirements for Procured Items**			X
Instructions, Procedures and Drawings	**1Q, QAP 5-1, Instructions, Procedures and Drawings**	X		
	• **L1, 1.01, Administration of SRNL Procedures and Work Instructions**	X		
	• **L1, 7.26 R&D Work Control Documents**	X		
	• **E7, 2.30 Drawings**		X	
Document Control	**1Q, QAP 6-1, Document Control**	X		
	• **1B, MRP 3.32, Document Control**	X		
Control of Purchased Items and Services	**1Q, QAP 7-2, Control of Purchased Items and Services**	X		
	• **7B, Procurement Management Manual**	X		
	• **3E, Procurement Specification Procedure Manual**	X		
	1Q, QAP 7-3, Commercial Grade Item Dedication		X	
	• **E7, 3.46 Replacement Item Evaluation/ Commercial Grade Dedication**		X	

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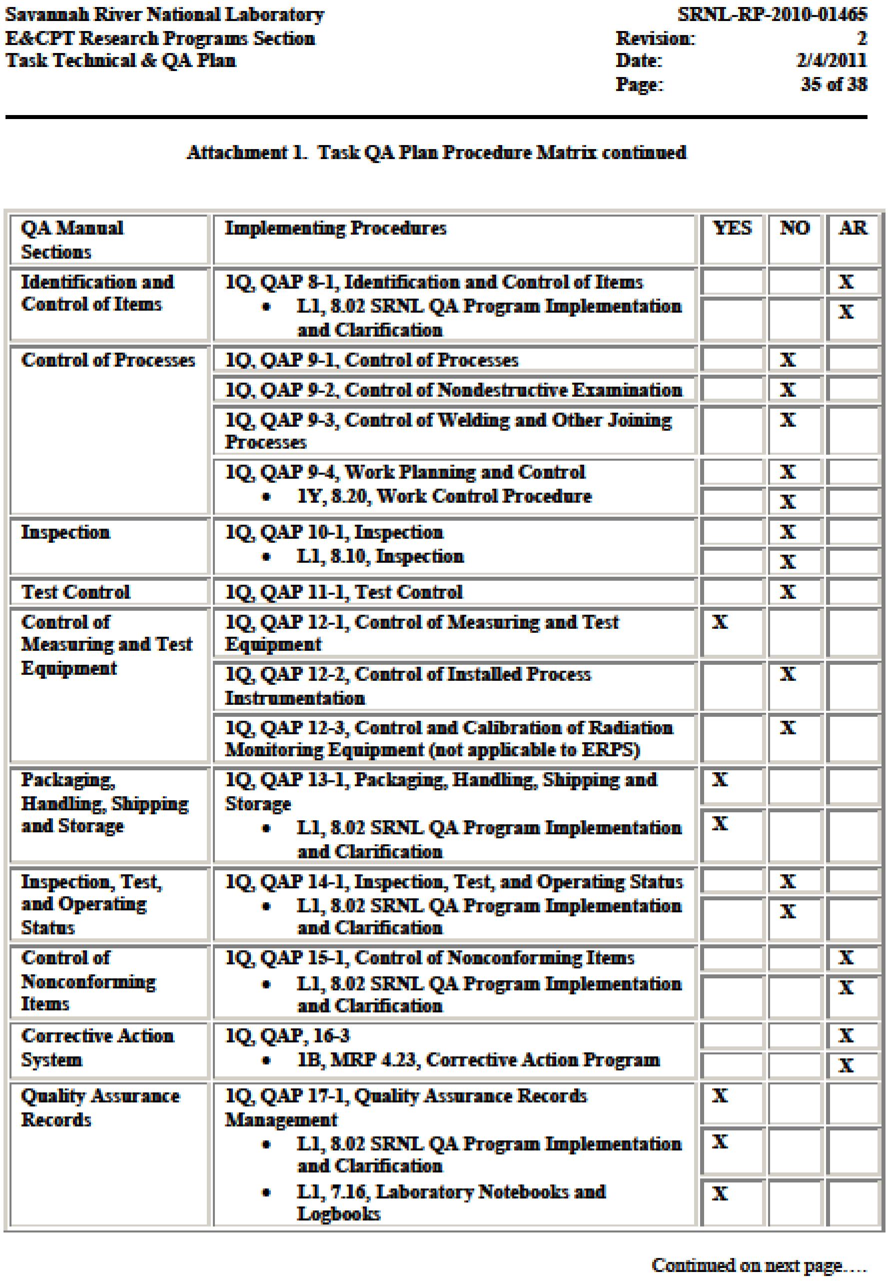

Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01465
Revision: 2
Date: 2/4/2011
Page: 35 of 38

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Identification and Control of Items	1Q, QAP 8-1, Identification and Control of Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Control of Processes	1Q, QAP 9-1, Control of Processes		X	
	1Q, QAP 9-2, Control of Nondestructive Examination		X	
	1Q, QAP 9-3, Control of Welding and Other Joining Processes		X	
	1Q, QAP 9-4, Work Planning and Control		X	
	• 1Y, 8.20, Work Control Procedure		X	
Inspection	1Q, QAP 10-1, Inspection		X	
	• L1, 8.10, Inspection		X	
Test Control	1Q, QAP 11-1, Test Control		X	
Control of Measuring and Test Equipment	1Q, QAP 12-1, Control of Measuring and Test Equipment	X		
	1Q, QAP 12-2, Control of Installed Process Instrumentation		X	
	1Q, QAP 12-3, Control and Calibration of Radiation Monitoring Equipment (not applicable to ERPS)		X	
Packaging, Handling, Shipping and Storage	1Q, QAP 13-1, Packaging, Handling, Shipping and Storage	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
Inspection, Test, and Operating Status	1Q, QAP 14-1, Inspection, Test, and Operating Status		X	
	• L1, 8.02 SRNL QA Program Implementation and Clarification		X	
Control of Nonconforming Items	1Q, QAP 15-1, Control of Nonconforming Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Corrective Action System	1Q, QAP, 16-3			X
	• 1B, MRP 4.23, Corrective Action Program			X
Quality Assurance Records	1Q, QAP 17-1, Quality Assurance Records Management	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
	• L1, 7.16, Laboratory Notebooks and Logbooks	X		

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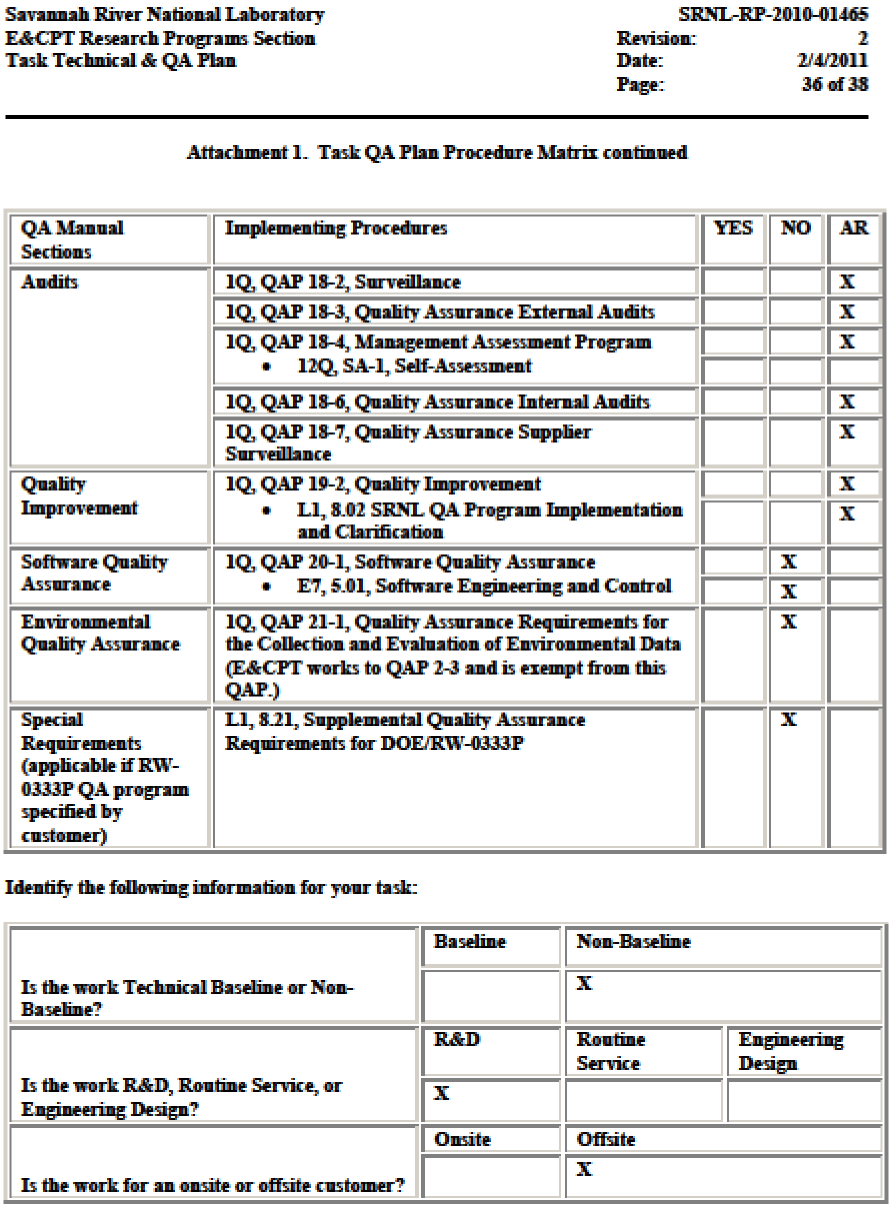

Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01465
Revision: 2
Date: 2/4/2011
Page: 36 of 38

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Audits	1Q, QAP 18-2, Surveillance			X
	1Q, QAP 18-3, Quality Assurance External Audits			X
	1Q, QAP 18-4, Management Assessment Program			X
	• 12Q, SA-1, Self-Assessment			
	1Q, QAP 18-6, Quality Assurance Internal Audits			X
	1Q, QAP 18-7, Quality Assurance Supplier Surveillance			X
Quality Improvement	1Q, QAP 19-2, Quality Improvement			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Software Quality Assurance	1Q, QAP 20-1, Software Quality Assurance		X	
	• E7, 5.01, Software Engineering and Control		X	
Environmental Quality Assurance	1Q, QAP 21-1, Quality Assurance Requirements for the Collection and Evaluation of Environmental Data (E&CPT works to QAP 2-3 and is exempt from this QAP.)		X	
Special Requirements (applicable if RW-0333P QA program specified by customer)	L1, 8.21, Supplemental Quality Assurance Requirements for DOE/RW-0333P		X	

Identify the following information for your task:

Is the work Technical Baseline or Non-Baseline?	Baseline	Non-Baseline	
		X	
Is the work R&D, Routine Service, or Engineering Design?	R&D	Routine Service	Engineering Design
	X		
Is the work for an onsite or offsite customer?	Onsite	Offsite	
		X	

10.0 REFERENCES

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Appendix B. Task Technical & Quality Assurance Plan for Module D

Task Technical and Quality Assurance Plan for Evaluation of Fluidized Bed Steam Reformed (FBSR) Mineralized Waste Forms (Granular and Monolith) for the DOE EM-31 Technology Development & Deployment (TDD) Program: Hanford Tank AN-103 Study

C. M. Jantzen
C. J. Bannochie

February 2011

1.0 APPROVALS/TASK TECHNICAL REQUEST IDENTIFICATION

Team Technical Lead: **C. M. Jantzen**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Team Principal Investigator: **C. J. Bannochie**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Technical Reviewer: **D.K. Peeler**	**Signature:**	**Organization** **SRNL-ERPS-PTP**	**Date:**
Responsible Manager: **C. C. Herman**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
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Task Technical Request Title: Increased Waste Loadings	**TCR Number:** TCR HQTD1005 **Revision:** 0	**TTR Date:** 02/05/2010

LIST OF REVISIONS

Revision Number	Summary of Changes	Date
0	Initial Issuance	2/4/11

2.0 INTRODUCTION

2.1 Task Definition

2.1.1 Introduction

The baseline treatment plan for Hanford is to vitrify their salt supernate wastes also known as Low Activity Waste (LAW). This task plan deals with the feasibility of an alternative or supplemental treatment for LAW waste known as Fluidized Bed Steam Reforming (FBSR) and so the investigations are not considered to be baseline. The Waste Treatment Plant (WTP) is currently under construction to treat all of the High Level Waste (HLW) and a portion of the LAW via vitrification. However, the LAW will be generated at over twice the rate that the currently designed LAW vitrification facility can treat the waste. Either a second LAW vitrification facility or other supplemental LAW treatment technology is needed to meet schedule objectives and approved tank closure deadlines.

One of the supplemental LAW treatment technologies being considered is FBSR. Recently, THOR® Treatment Technologies (TTT) has successfully demonstrated the FBSR technology at the Engineering Scale Technology Demonstration (ESTD) pilot scale on a non-radioactive Hanford LAW simulant[1] that represents a 68 tank blend of Hanford wastes. This simulant is known as the Rassat[2] simulant. As part of the Washington River Protection Solutions (WRPS) supplemental treatment technology evaluation and Department of Energy (DOE) EM-31 Technology Development and Deployment (TDD) programs[3], the Savannah River National Laboratory (SRNL) has been requested to successfully demonstrate the FBSR technology on waste streams representative of Hanford's LAW at the Benchscale Steam Reformer (BSR) scale and compare the results to the products formed at the pilot scale. The first demonstration[4] was a radioactive Savannah River Site (SRS) salt supernate that had been compositionally trimmed to look like the Hanford Rassat 68 tank blend that TTT processed non-radioactive. The second demonstration of LAW is a Hanford waste from Tank SX-105 and will be known as Module C for SRNL tracking purposes. The third demonstration of LAW is a Hanford waste from Tank AN-103 and will be known as Module D for SRNL tracking purposes. Module D is the focus of this Task Technical and Quality Assurance Plan (TTQAP).

FBSR treatment offers a low temperature (700-750°C) continuous method by which LAW may be processed into a crystalline ceramic (mineral) waste form regardless of whether the wastes are high in organics, nitrates, sulfates/sulfides, other anions or components. The FBSR process produces no secondary liquid waste streams. Based on previous testing [5,6,7,8,9,10,11,12,13,14], the granular waste form that is produced by co-processing the LAW with kaolin clay has been shown to be as durable as LAW glass. However, monolithing of the granular product is being pursued since monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage. Once again, it is not believed to be necessary to meet performance criteria.

To support SRS implementation of the FBSR technology for Tank 48 (T48), SRNL has successfully operated a Bench scale Steam Reformer (BSR) in the SRNL Shielded Cells Facility (SCF).[15,16] The BSR is a unique SRNL design and this radioactive capability does not exist commercially nor at any other DOE site. All related safety basis documentation for operation of the BSR in the SRNL SCF was completed for the T48 demonstration and will need to be updated to cover the stream being treated for this scope and additional Hanford streams that will be covered in future task plans. SRNL also has unique expertise, analytical chemistry skills, and equipment for monolithing the granular FBSR product and measuring durability of waste forms.[17,18]

The scope of work addressed in this task planning document consists of SRNL making a simulant of Hanford's Tank AN-103 LAW and testing the simulant in the non-radioactive BSR in 735-11A to provide

- optimization of processing parameters for radioactive testing,
- non-radioactive granular samples for testing the durability response of the AN-103 BSR product compared with previous testing of pilot scale FBSR products[17] and previous BSR products,[4,17] and
- granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from previously tested pilot and BSR products.[4,17] Tank AN-103 LAW is a low anion containing waste with high concentrations of S, Cl, F and P.
- Radioactive BSR testing will also be performed (see next paragraph) and the response of the non-radioactive granular and monolithed products will also be compared to the radioactive granular and monolithed products produced.

The scope of work addressed in this task planning document also consists of SRNL mineralizing a radioactive Hanford LAW sample from Tank AN-103 that has been supplied by Hanford and has already been chemically analyzed.[19] Considerable solids have precipitated in the radioactive AN-103 sample since it was shipped to SRNL from Hanford. Re-characterization of a subsample of a well stirred/mixed AN-103 sample will be necessary. The re-characterization will include determination of weight percent solids (wt. %) and density. The slurry will be dissolved and analyzed for cations, anions, elemental composition, and Tc-99, I-129, and Cs-137. The solids will be analyzed by XRD and/or XRF.

In parallel to the analysis of a well mixed subsample of the radioactive AN-103, a simulant will be made that represents the chemistry of the AN-103 after ion exchange and filtration at Hanford, e.g. the state of the AN-103 sample at the time of shipping. This "as shipped" simulant will be allowed to age to see if similar precipitates form. Non-radioactive testing of the AN-103 "as shipped" simulant with precipitated solids will be performed to determine if BSR processing with the particulates is problematic. Since TTT has experience with processing solids in the ESTD campaigns (Appendix A) and the clay additives are themselves particulate slurries, it may not be necessary to remove the precipitates before BSR processing.

The Tank AN-103 LAW will be processed in the BSR in the SCF to provide

- radioactive granular samples for testing the durability response of BSR product compared to product from the TTT pilot scale runs from WFO-

09-003[17] and other BSR campaigns with Waste Treatment Plant Secondary Waste (WTP-SW)[17] and Hanford's Rassat simulant,[4,17] AN-103, and the non radioactive testing in the scope above and

- radioactive granular products to monolith and compare (durability and compressive strength) to the non-radioactive monolithic waste forms prepared under WFO-09-003,[17] Hanford's Rassat simulant,[4] AN-103, and in the scope described above.

Because of the lack of complete fluidization and shorter residence times in the BSR than in the ESTD pilot, the particle size will be mostly fines as particle size growth is minimized in the absence of long residence times and intense fluidization. This is not problematic as the ESTD bed product is an agglomeration of finer particles that grow in the long residence times in the FBSR.

2.1.2 Radioactive Sample Characterization

The AN-103 radioactive sample will be mixed, shimmed with $NaReO_4$ to 1.7 mmol/L, and an analytical subsample of ~ 50mL taken. The subsample will be analyzed to verify parameters needed for simulant formulation and for mass balance calculations. See Table 4 for specific analyses to be performed.

2.1.3 Non-Radioactive Tests

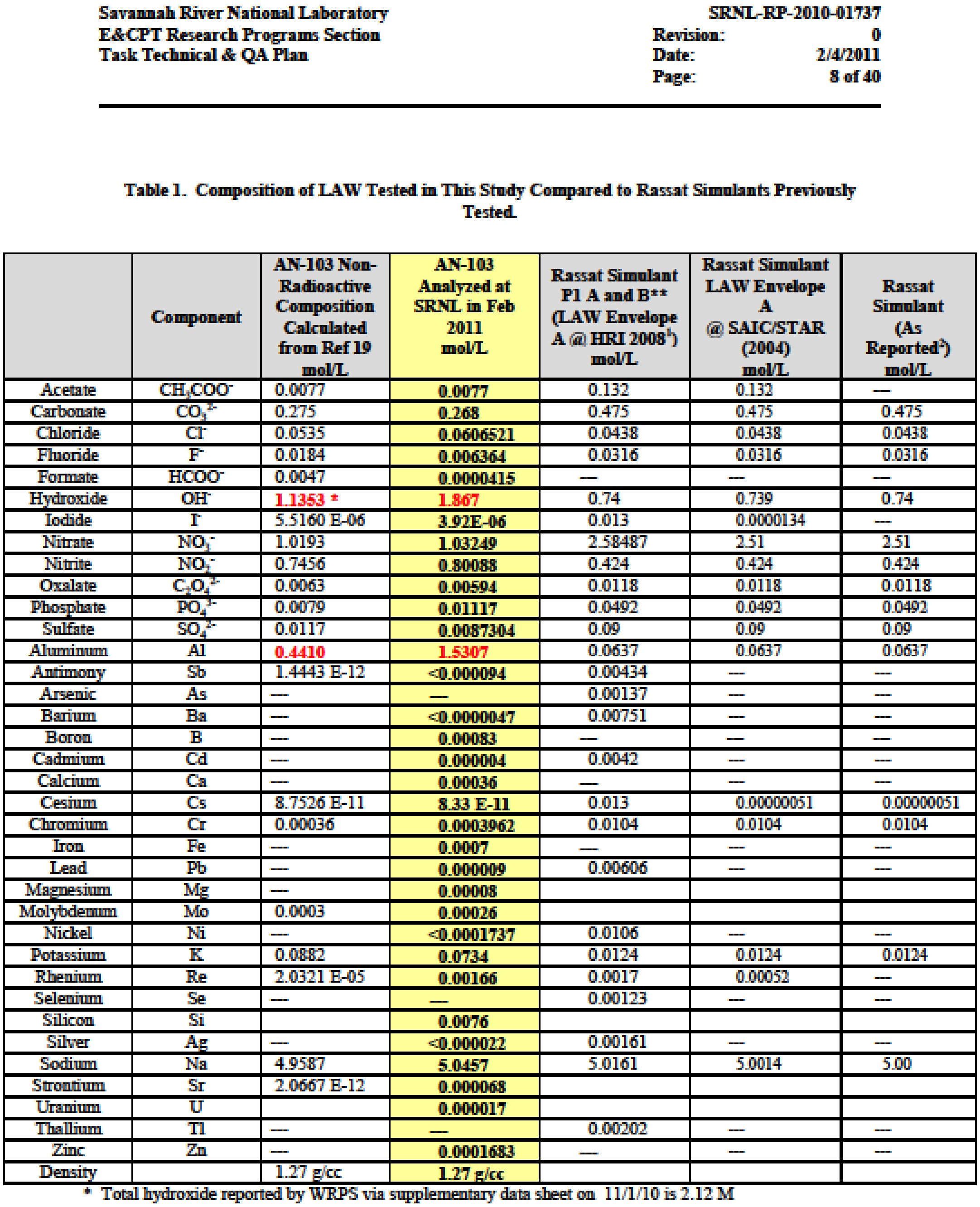
The AN-103 simulant will be developed by SRNL from the chemical analysis provided by WRPS as shown in Table 1[19] and analyses performed by SRNL. This simulant will be labeled the "as shipped" simulant and left to age for approximately two weeks to determine if similar precipitates form to what has been visually observed in the AN-103 radioactive sample. The target concentration for the LAW Resource Conservation and Recovery Act (RCRA) metals will not be increased over what is already present in the waste. The Re (Tc surrogate) will be increased by 100; the I by 1,000; and 1,000,000 for Cs as done in the TTT pilot scale demonstrations of the Rassat simulant[1] in order to observe their behavior during mass balance of the process. Ferric nitrate nona-hydrate will be added to have ≥1.5 wt% Fe in the final product as a REDOX indicator as there is little to no iron in the waste. Knowing the iron REDOX helps determine the oxidation state of many other REDOX active species such as Re^{7+} vs. Re^{4+} and Cr^{6+} vs. Cr^{3+}.

If precipitates develop a subsample of a well mixed "as shipped" simulant will be taken and analyzed as outlined in 2.1.2 for the radioactive sample to ensure that the same types of precipitates have formed. Once the subsample is taken, BSR processing of the well mixed "as shipped" simulant with precipitates will begin. It is anticipated that the clay particulates will keep these precipitates buoyant once the clay and simulant are mixed. Processing the "as shipped" simulant with precipitates will determine whether or not the AN-103 as received sample can be processed without first removing the precipitates. If the simulant with the precipitates can be processed in the BSR, then the radioactive sample will be processed as received.

Once the "as shipped" simulant recipe is developed it will be used to determine the optimum non-radioactive BSR operational conditions and then these same operational conditions will be used in the radioactive BSR tests in the SCF. If the "as shipped" simulant cannot be processed then the optimal non-radioactive BSR operational conditions will be determined on a heated "as shipped" simulant or a filtered simulant. Partitioning of the Cs, I, and Re to the off-gas versus the overall solid mineralized product will be assessed by whole element chemistry of the off-gas condensate and the solid product. Additionally, off-gas lines in-between the reaction chamber known as the Denitration and Mineralizing Reactor (DMR) and the off-gas condenser will be rinsed with a known amount of deionized water and analyzed to determine the species that have been trapped or retained in the lines. The data will be used to calculate a mass balance of the system. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) will be used for analyses of the Cs, Re, and I in the solids and off-gas due to their presence at very low concentrations.

In addition, partitioning of the Cs, Re, and I amongst the solid phases, e.g. nepheline vs. sodalite, will also be determined by quantitative X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and possibly Transmission Electron Microscopy (TEM) and Selected Area Diffraction (SAD). Since the sodalite phases, including nosean, are present in small quantities which for low anion containing feeds may be below the detection limit of the XRD, a total amount of "sodalite vs. nepheline" may be the only quantitative analyses that are reportable. Phase pure standards are being made to develop quantitative XRD calibration curves.

Sufficient non-radioactive granular product must be made to provide four 1"OD x 2"H monoliths and 56 g of granular product for durability testing at SRNL. Therefore, a total of ~181 ((154 x 0.65) + 56) g is required as shown in Table 2. After the 28 day curing, two of the monoliths will be compression tested at SRNL. Upon passing the 500 psi compression test minimum requirement, SRNL will retain the entire non-radioactive product for durability testing.



Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01737
Revision: 0
Date: 2/4/2011
Page: 8 of 40

Table 1. Composition of LAW Tested in This Study Compared to Rassat Simulants Previously Tested.

	Component	AN-103 Non-Radioactive Composition Calculated from Ref 19 mol/L	AN-103 Analyzed at SRNL in Feb 2011 mol/L	Rassat Simulant P1 A and B** (LAW Envelope A @ HRI 2008[1]) mol/L	Rassat Simulant LAW Envelope A @ SAIC/STAR (2004) mol/L	Rassat Simulant (As Reported[2]) mol/L
Acetate	CH_3COO^-	0.0077	**0.0077**	0.132	0.132	—
Carbonate	CO_3^{2-}	0.275	**0.268**	0.475	0.475	0.475
Chloride	Cl^-	0.0535	**0.0606521**	0.0438	0.0438	0.0438
Fluoride	F^-	0.0184	**0.006364**	0.0316	0.0316	0.0316
Formate	$HCOO^-$	0.0047	**0.0000415**	—	—	—
Hydroxide	OH^-	1.1353 *	**1.867**	0.74	0.739	0.74
Iodide	I^-	5.5160 E-06	**3.92E-06**	0.013	0.0000134	—
Nitrate	NO_3^-	1.0193	**1.03249**	2.58487	2.51	2.51
Nitrite	NO_2^-	0.7456	**0.80088**	0.424	0.424	0.424
Oxalate	$C_2O_4^{2-}$	0.0063	**0.00594**	0.0118	0.0118	0.0118
Phosphate	PO_4^{3-}	0.0079	**0.01117**	0.0492	0.0492	0.0492
Sulfate	SO_4^{2-}	0.0117	**0.0087304**	0.09	0.09	0.09
Aluminum	Al	0.4410	**1.5307**	0.0637	0.0637	0.0637
Antimony	Sb	1.4443 E-12	**<0.000094**	0.00434	—	—
Arsenic	As	—	**—**	0.00137	—	—
Barium	Ba	—	**<0.0000047**	0.00751	—	—
Boron	B	—	**0.00083**	—	—	—
Cadmium	Cd	—	**0.000004**	0.0042	—	—
Calcium	Ca	—	**0.00036**	—	—	—
Cesium	Cs	8.7526 E-11	**8.33 E-11**	0.013	0.00000051	0.00000051
Chromium	Cr	0.00036	**0.0003962**	0.0104	0.0104	0.0104
Iron	Fe	—	**0.0007**	—	—	—
Lead	Pb	—	**0.000009**	0.00606	—	—
Magnesium	Mg	—	**0.00008**			
Molybdemum	Mo	0.0003	**0.00026**			
Nickel	Ni	—	**<0.0001737**	0.0106	—	—
Potassium	K	0.0882	**0.0734**	0.0124	0.0124	0.0124
Rhenium	Re	2.0321 E-05	**0.00166**	0.0017	0.00052	—
Selenium	Se	—	**—**	0.00123	—	—
Silicon	Si		**0.0076**			
Silver	Ag	—	**<0.000022**	0.00161	—	—
Sodium	Na	4.9587	**5.0457**	5.0161	5.0014	5.00
Strontium	Sr	2.0667 E-12	**0.000068**			
Uranium	U		**0.000017**			
Thallium	Tl	—	**—**	0.00202	—	—
Zinc	Zn	—	**0.0001683**	—	—	—
Density		1.27 g/cc	**1.27 g/cc**			

* Total hydroxide reported by WRPS via supplementary data sheet on 11/1/10 is 2.12 M

Resource Conservation and Recovery Act (RCRA) and radionuclide surrogates (Re, I, Cs) were doped in at the following concentrations: 10X for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs **TOTAL BASE IS 2.76.

Table 2. BSR Product Requirements in Grams (Non-Radioactive Testing)

MODULE D PRODUCT REQUIREMENTS BY TEST AND LABORATORY		
Testing	Granular SRNL (g)	Monolith SRNL (g)
Product Consistency Test (PCT) Short Term	24	24
PCT Long Term	12	12
Toxicity Characteristic Leaching Procedure (TCLP)	20	20
ASTM C1308	0	98
Compression Testing**	0	0
TOTAL MATERIAL SUM	56	154
BSR GRANULAR PRODUCT EQUIVALENTS		125*
TOTAL GRANULAR PRODUCT	181	

* Monolith Product x 0.65 BSR Loading x 1.25, makes 4 monoliths at ~33 g FBSR per monolith. Two monoliths will be crushed and two will be used in tact for ASTM C1308 testing.

** Compression tested samples will be used for PCT and TCLP

SRNL will perform analyses to measure properties of the non-radioactive granular products and the monolithed simulated waste forms generated from the granular products produced during the simulant BSR campaigns. This will include loss-on-drying (LOD) tests at 110°C to determine moisture content and loss-on-ignition (LOI) tests at 525°C to determine the coal fraction in the samples which is the difference between the LOI and the LOD weight losses. The temperature of 525°C removes the carbon left in the raw coal after processing in the BSR as the hydrogen, oxygen, and moisture from the coal have been removed during the BSR processing. However, this temperature does not vaporize the sulfur in the coal or the BSR product phases. For these experiments, where SRNL is using the carbon LOI to assess the impact of carbon on the REDOX measurement, this temperature has been found to be sufficient and it is the temperature recommended by a US Geological Survey procedure developed for coal analyses.[20] Different subsamples will be sent for REDuction/OXidation (REDOX) analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the SEM using Energy Dispersive Spectroscopy (EDS) to determine if Re and I are retained in a sodalite structure and if Cs substitutes for Na in nepheline and/or sodalite or both.

The non-radioactive granular and monolithed waste form products will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by qualified personnel at SRNL. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The time durations are to be one month, three month, six month and an additional time to be determined (TBD) which may be up to 1 year or longer. The tests will be performed in Teflon® vessels. A minimum of 1 gram of sample must be tested at a mass ratio of 1 gram of solids to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume will be determined once the Brunauer, Emmett, and Teller (BET) surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA); and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC.

The Toxicity Characteristic Leaching Procedure (TCLP) will be performed by an Environmental Protection Agency (EPA) certified laboratory in South Carolina for the non-radioactive simulant.

The non-radioactive granular product will be made into monoliths using the optimized monolith binder defined by the completion of the SRNL WFO-08-003[18] matrix or the testing performed as part of EM-31 Task 5.2.1. The monolith will be characterized as described above and compression tested. Diffusion coefficients for Re, Cs, and I will be determined using the 3 month long ASTM C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form

2.1.4 Radioactive Tests

The Tank AN-103 Hanford LAW sample has been analyzed by WRPS.[19] At the time of shipping by WRPS, the sample contained precipitated solids. The density of the waste has been measured by WRPS to be 1.27g/cc.

Hanford has provided ~900 mL of AN-103 and all will be processed to make the 422 g of radioactive product calculated in Table 3. Re will be added to the waste to have ≥150 μg/g in the final product and ferric nitrate nona-hydrate will be added to have ≥1.5 wt% Fe in the final product. The ferric nitrate is added as a REDOX indicator in order to determine the oxidation state of Re, Tc, and the RCRA metals from an already developed Electro-Motive Force (EMF) diagram for FBSR. The concentration of Re will be verified after doping. The addition of the ferric nitrate is accounted for during the balancing of oxidants and reductants in the feed.

During the demonstration, ~90% of the waste will be processed as received with only Re and ferric nitrate added. The remaining ~10% of the waste will be doped with Tc^{99}, Re, and I^{127} (non-radioactive) at a minimum of 150 μg/g in the solid product as this is the level needed to detect these species during follow on extended x-ray absorption fine structure (EXAFS) testing at the Stanford Synchrotron Radiation Lightsource (formerly Stanford Synchrotron Radiation

Laboratory) to determine the local bonding of the Tc^{99} and I^{127} in the mineral waste form. Iodine-125, -127 and -129 will all be present and expected to partition to the same sodalite phase and the Synchroton sensors can pick up all three isotopes but is most specific for I^{127}. The ~10% of the feed will be processed at the end of the campaign, after the off-gas condensate is sampled and lines are flushed. This will ensure that the mass balance and leaching tests described below are not compromised by the elevated concentrations required by the EXAFS testing.

Non-radioactive Re is added to determine the effectiveness of Re as a surrogate for Tc^{99} during BSR processing, i.e. do they track each other in the off-gas, do they substitute for each other in the solid products or does one preferentially partition to the sodalite over the other, and do they respond similarly to the reduction/oxidation (REDOX) in the BSR. This will be compared to their response during subsequent durability testing.

Partitioning of the radionuclides (Cs, Tc, and I) and Re to the off-gas and to the solid mineralized product will be assessed by analysis of the off-gas condensate and analysis of the solid product. Off-gas lines in-between the reaction chamber known as the DMR and the off-gas condenser will be rinsed with a known amount of deionized water and analyzed to determine the species that have been trapped or retained in the lines. A mass balance will be performed. A combination of ICP-MS and radiometric methods will be used for analyses of these components as they should be present at very low concentrations.

During the BSR processing in the SCF, kaolin clay will be added to the AN-103 sample to form the mineralized waste form between 725°-750°C. Because the waste is concentrated during processing while also being diluted by the non-radioactive clay added, the resulting radioactive dose of the final product will be different than the starting material. Assuming the measured dose is low enough to work in a radioactive hood, characterization and testing of the samples will be performed in a 773-A laboratory. If not, the characterization and testing will be performed in the SCF.

Adequate radioactive granular product must be produced in the BSR in the SCF to fabricate five 1"OD x 2"H monoliths and provide granular product for durability testing at PNNL and SRNL (Table 3). After the required 28 day curing, two of the monoliths will be sent to PNNL for future testing and three will be retained at SRNL for testing.

If the 900 mL of AN-103 does not make the required 422 g of granular product, then the amounts given in Table 3 will have to be adjusted accordingly, e.g. fewer monoliths, fewer samples, or fewer tests. This will be agreed upon with input from the customer and stakeholders.

SRNL will perform analysis of chemical and physical properties of the radioactive granular products and monoliths generated from the granular products produced during the BSR campaigns in the SCF. This will include LOD tests at 110°C to determine moisture content and LOI tests at 525°C to determine the coal fraction in the sample. Different subsamples will be sent for REDOX analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the Contained Scanning Electron Microscope (CSEM) using EDS to determine if Tc, I and Re are retained in a sodalite structure and whether Cs substitutes for Na in the nepheline and/or sodalite structures. The coal in the product will also be examined for retention of radionuclides.

Table 3. BSR Product Requirements in Grams (Radioactive Testing)

MODULE D PRODUCT REQUIREMENTS BY TEST AND LABORATORY				
Testing	Granular PNNL (g)	Granular SRNL (g)	Monolith PNNL (g)	Monolith SRNL (g)
Single-Pass Flow-Through (SPFT)	144	0	72	0
Pressurized Unsaturated Flow (PUF)	40	0	40	0
Product Consistency Test (PCT) Short Term	0	24	0	24
PCT Long Term	0	12	0	12
Toxicity Characteristic Leaching Procedure (TCLP)	20	0	20	0
ASTM C1308	0	0	0	98
SUMS BY LABORATORY	204	36	132	134
TOTAL MATERIAL SUM	240		266	
BSR GRANULAR PRODUCT EQUIVALENTS	NA		182*	
TOTAL GRANULAR PRODUCT	422			

* Monolith Product x 0.65 BSR loading x 1.05, makes 5.5 monoliths at ~33 g FBSR per monolith. Of these 5.5 monoliths two uncrushed monoliths remain at SRNL for ASTM C1308 testing; three monoliths are compression tested; 2.75 crushed monoliths are sent to PNNL for testing; 0.75 crushed monoliths are retained at SRNL for short term and long term PCT.

The radioactive granular waste form product will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by SRNL. The radioactive granular product will be made into monoliths using the optimized monolith binder defined by simulant testing. The monoliths will then be re-characterized and subjected to the ASTM C1285-08 test (long and short term) and a compression test. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The radiation dose from the sample must be calculated to ensure that the Teflon® vessels are acceptable per the dose requirements given in the PCT procedure, e.g. doses up to 1 x 10^5 rad of beta or gamma radiation have been shown not to damage TFE-fluorocarbon (Teflon®). The time durations are to be one month, six month, and an additional time to be determined (TBD) which could be up to one year.

The tests will be performed in Teflon® vessels. A minimum of 1 g of sample must be tested at a mass ratio of 1 g of solid to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume ratio will be determined once the Brunauer, Emmett, and Teller (BET) surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA), and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC. Cs, I, and Tc will be measured radio-metrically.

Diffusion coefficients for Tc, Re, Cs, and I will be performed using the 3 month long C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form.

Both the granular product and the monolith product will be leach-tested using the EPA TCLP procedure. Because AN-103 is a listed waste the samples (granular and monolithic) will be sent to PNNL who will subcontract with an EPA certified laboratory.

2.2 Customer/Requester

Terry Samms, Manager of WTP Technology and Development, is the customer/requester as the ultimate user of the technology. Steve Schneider, Director (Acting) Office of Waste Processing is the HQ customer/requester for the overall program.

2.3 Task Responsibilities

Environmental & Chemical Processing Technology Research Programs (ERPS) personnel will be primarily responsible for the scope described in this task plan. Durability testing being performed on the granular and monolithic samples (non-radioactive and radioactive) being sent to PNNL is not covered in this task plan. SRNL support will be provided by personnel in the Shielded Cells, AD, and the Regulatory Integration and Environmental Services organization. C. J. Bannochie is the overall Principal Investigator for the Hanford BSR program, while C. M. Jantzen is the overall technical lead for the program and is responsible for this task plan and any revisions. P. R. Burket is considered the Subject Matter Expert (SME) for the BSR equipment (non-radioactive and radioactive) and control system design and set-up. A. D. Cozzi is the lead for the waste form qualification and testing. C. C. Herman is the responsible manager for the program. The responsible manager (or designee) is responsible for reviewing and approving all procedures and task plans, assessing the preparedness to carry out this task, and reviewing and approving all reports.

Overall responsibilities of the ERPS BSR team include the following:

- Coordinating all activities and ensuring that they are completed in a timely manner
- Ensuring that all results are documented
- Preparing the records for this task
- Ensuring that sample tracking and document controls are followed
- Ensuring that the latest revisions of procedures are used to complete the task activities

For the simulant BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the Hazards Analysis Package (HAP) for the testing, providing guidance on the equipment performance parameters, ensuring the BSR is set up to perform testing, and performing the BSR testing.
- R. E. Eibling (or designee) is responsible for overseeing the production of the necessary simulant, including verifying acceptability of the simulant.
- W. E. Daniel (or designee) is responsible for preparing the equipment for simulant demonstrations, analyzing the simulant and ensuring product samples are submitted for characterization.
- C. L. Crawford and A. D. Cozzi (or designees) are responsible for characterization and testing of the granular product, production of the monoliths, and characterization and testing of the monoliths. C. L. Crawford will interface with W. L. Mhyre of Quality Control Testing to perform the necessary compression testing.
- ERPS technicians are responsible for performing the LOI measurements and PCT.
- Support for the above tasks will be provided by personnel within the ERPS section.
- AD is responsible for performing Brunauer-Emmett-Teller (BET) surface area measurements on the simulant samples.

For the radioactive BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the HAP for the testing and overseeing performance of the BSR testing.
- C. L. Crawford (or designee) is responsible for characterization and spiking of the radioactive sample.
- C. L. Crawford and C. J. Bannochie (or designees) are responsible for characterization of the granular product, monoliths, and offgas condensates/rinses.
- A. D. Cozzi (or designee) is responsible for testing of the granular product, production of the monoliths, testing of the monoliths, and performing skeletal density measurements on the radioactive samples.
- J. H. Scogin (or designee) is responsible for performing BET surface area measurements on the radioactive samples.
- ERPS technicians are responsible for performing the LOI measurements and PCT if the samples can be removed from the Shielded Cells. If the samples cannot be removed, Shielded Cells personnel will perform the LOI measurements and PCT under the guidance of ERPS personnel.
- Support for the above tasks will be provided by personnel within the ERPS section and by SCF personnel as necessary.

As necessary, C. L. Crawford (or designee) will be responsible for developing or modifying existing HAPs for the waste form characterization, production, or testing. C. L. Crawford (or designee) will be the PI for the treatability study. He will have primary responsibility for working with the Inventory Authority, H. K. Hall (or designee), to track generated samples and residue throughout the performance of the task until completion of the studies and disposition of all material. All other researchers working with the actual Hanford material will also be required to comply with the guidelines of L29, ITS-0167 for tracking and disposition of samples and residue.

The Process Science Analytical Laboratory (PSAL) will be responsible for analyzing simulant and product streams using the following methods or equipment: Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Ion Chromatography (IC), Parr Anton density meter, REDOX, and LOD/LOI. PSAL will perform the necessary digestions or dilutions to allow the samples to be analyzed by these methods. PSAL will follow approved procedures to perform these measurements and will assign a unique ID to each sample to maintain traceability. PSAL will ensure that the appropriate standards are used and that equipment calibration is maintained during performance of the testing. Appropriate analytic standards will be submitted with all samples for a cross comparison between non-radioactive samples analyses by PSAL and radioactive sample analyses by Analytic Development (AD).

SRNL – SCO (Shielded Cells Operations) personnel are responsible for:

- Reviewing and approving this TTQAP
- Readying and maintaining the facility for operation
- Checking and installing the equipment necessary for tasks to be performed in the Shielded Cells
- Providing SRNL – Quality Assurance (QA) access to training and qualification records for SCO personnel for surveillances or audits
- Ensuring the latest revisions of procedures are used to complete the task activities

SRNL – AD Laboratory personnel are responsible for:

- Reviewing and approving this TTQAP
- Analyzing radioactive waste samples and simulant and product streams using the following methods or equipment: ICP-AES, ICP-MS, IC, particle size distribution (PSD), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Contained Scanning Electron Microscopy (CSEM), and radiometric analyses
- Providing personnel resources and equipment necessary to perform REDOX via remote handling in SCF (not an AD established method)
- Providing SRNL – QA access to training and qualification records for AD personnel for surveillances or audits
- Performing QA checks (i.e., using standards and ensuring calibrations are valid) on instrumentation involved in this task
- Analyzing the samples per the Turn Around Times (TAT) specified in this TTQAP
- Reviewing the sample results prior to reporting them
- Ensuring the latest revisions of procedures are used to complete the task activities
- Communicating needed method development validation work to be performed on radioactive materials produced as part of the Task Plan

SRNL QA is responsible for reviewing and approving this task plan and providing guidance and oversight for this task.

WRPS and EM-31 WP-5 personnel are responsible for providing guidance and input on the requirements of their associated qualification program and CD-1 package needs. They are requested to provide written requests to SRNL specifying any changes/deviations to the scope of this TTQAP. The WRPS and EM-31 WP-5 team will be responsible for reviewing the final reports associated with this task. Any changes or addition to scope will be agreed upon by SRNL after considering the impact to budget and schedule. K. Ryan, of TTT, is responsible for providing BSR operational parameters and providing the coal and clays to be used by SRNL if needed.

2.4 Task Deliverables

1. An approved Task Technical and QA Plan (this document).
2. Mass balance of Re, I, and Cs during non-radioactive BSR operation.

3. Interim documentation of the results of the non-radioactive BSR run and the characterization of the granular and mineralized product including subsequent product characterization and testing.
4. Production and testing of four non-radioactive monoliths and ~36 g granular product for further testing for SRNL.
5. Mass balance of Tc^{99}, I^{129}, and Cs^{137} during radioactive BSR operation.
6. Interim documentation and a final approved report documenting the results of the radioactive BSR mineralized product and subsequent product characterization and testing.
7. Shipment of two radioactive monoliths and ~204 g granular product to PNNL for further testing.
8. Three radioactive monoliths and ~36 g granular product for SRNL testing.
9. Shipment of granular products made from Hanford AN-103 waste at an elevated solids spiking of 150μg/g Tc^{99} and I^{129} for Synchrotron testing at Stanford Synchrotron Radiation Lightsource or an equivalent facility.

3.0 TASK ACCEPTANCE CRITERIA

Acceptance testing is not part of this task.

4.0 TASK ACTIVITIES

4.1 Task Initiation

- Draft/review/issue TTQAP.
- Conduct R&D/Hazards Assessment Package (HAP)/Safety review for simulant BSR testing including initiation of the Environmental Evaluation Checklist (EEC).
- Conduct R&D/HAP/Safety review for radioactive BSR testing including approval of the necessary national emissions standards for hazardous air pollutants NESHAPS analysis and EEC.
- Conduct R&D/HAP/Safety review for the fabrication, characterization, and testing of the granular and monolithic waste forms as necessary including the EEC for simulant and radioactive testing.

4.2 Simulant and BSR Product Formation

- Analyze the precipitated AN-103 and determine the precipitate composition.
- Develop an "as shipped" AN-103 simulant which should be the same as the "as dissolved" simulant.
- Develop an "as filtered" AN-103 simulant only if necessary
- Make ample non-radioactive simulant (1-2 Liters) to make ~181 g (Table 2) of non-radioactive BSR product for further testing.
- Analyze non-radioactive AN-103 simulant to confirm critical parameters.
- Determine the simulant BSR operating parameters (clay levels, coal levels, input gases/flow rates) by scaling of the ESTD operation parameters down to the BSR scale. SRNL will obtain concurrence with the simulant BSR operating parameters from TTT before proceeding with the BSR operation.
- Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases and sufficient carbon to provide the necessary reductant for the non-radioactive BSR campaigns.
- Run the non-radioactive BSR in 735-11A between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity.

Each simulant run will use a minimum of 60 mL and maximum of 250 mL of feed. It is estimated that five runs with ~60 mL each of non-radioactive simulant are needed to produce enough granular product to be analyzed and tested. The estimated required granular product mass is 181 g (four 1" x 2" monolith cylinders and 56 g of granular product).

4.3 Simulant Product Analysis and Off-Gas Mass Balance

- Analyze the composited BSR products for whole element chemistry of all cations and anions by ICP-AES and IC, REDuction/OXidation or REDOX ratio to determine $Fe^{+2}/\sum Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Re concentrations by ICP-MS.
- Analyze the off-gas condensate for all cations and anions by ICP-AES and for Cs, I, and Re by ICP-MS. This may facilitate speciation of the type of carryover occurring, if any. For example Cs may be carried over as vapor as Cs_2O, CsCl, CsF, $CsNO_3$ or as particulates such as $CsAlSiO_4$.
- Rinse the off-gas line(s) between the DMR and the condenser with a known volume of water and/or acid and analyze for all cations and anions by ICP-AES and for Cs, I, and Re by ICP-MS.
- Perform mass balances on elements of concern with special attention to Cs, I, and Re.

4.4 Simulant Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR granular products. The surface area to volume ratios will be determined once the particle size distribution from the BSR runs for this simulant is known.
- Perform long term ASTM C1285 - PCT on the BSR granular products. Sample and analyze at one, three, six, and TBD month intervals. At the end of each sampling, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. Geochemist's Workbench (GWB).
- Send a subset of the granular product for TCLP testing by a certified EPA laboratory.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003)[18].

4.5 Simulant Monolith Production and Product Testing

- Use a portion of the BSR granular products from the non-radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined in WFO-2009-003[17] and/or EM-31 Task 5.2.1 to produce 10 separate 1" x 2" monoliths.
- After curing for 28 days, perform compression testing on the non-radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.
- Compression test the monoliths with both a penetrometer and the ASTM compression test to calibrate the penetrometer for use with the radioactive monoliths since radioactive ASTM compression testing capability is not available
- Using crushed segments returned from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR monolith products.
- Perform long term ASTM C1285 - PCT on the BSR monolith products. Sample and analyze at one, three, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB.
- Send a subset of the crushed samples from compression testing for TCLP testing by a certified EPA laboratory.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1)[3,4,17].
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths. This is a 90 day test.

4.6 Radioactive BSR Product Formation

- Transport AN-103 Hanford Waste to the SRNL SCF.
- Perform Treatability Study sample handling and processing in the SCF in accordance with SRNL Procedure Manual L1, 6.04 'Hazardous/Mixed Waste Treatability Studies' and Procedure Manual L29, ITS-0167 'Hanford Treatability Study and Materials Handling'.
- Ensure that enough of the radioactive dopants (Tc^{99}, Cs^{137}, I^{129} or I^{125}) have been procured and available to process the last 100mL of AN-103.
- Dope 800 mL of the AN-103 sample with Re and ferric nitrate
- Analyze the trimmed Tank AN-103 after doping.
- Dope the remaining 100 mL of the AN-103 sample with Re, ferric nitrate, Tc^{99} and I^{127} to the levels needed to achieve 150µg/g of each in the solid samples for EXAFS testing.
- Ship Tc^{99} and I^{127} doped sample to Synchrotron Radiation source defined by customer.
- Determine the BSR operating parameters (clay levels, coal levels, input gases/flow rates) based on the BSR simulant testing. Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases (wet clay basis) and sufficient carbon to provide the necessary reductant (Bestac carbon) for the radioactive BSR

campaigns. The carbon will be calculated for the actual amount of NO_3 and NO_2 in the radioactive sample using 1.3X the value calculated by the SRNL developed MINCALC Version #3. Obtain concurrence with the BSR operating parameters from TTT before proceeding with the radioactive BSR operation.

- As necessary, install the BSR in the SCF after preliminary testing in the Shielded Cells Mock-up Facility. If already located in the SCF, install new glass ware and BSR components to perform the radioactive demonstration.
- Run the radioactive BSR in the SCF between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each radioactive doped AN-103 run will use a minimum of 60 mL of feed. It is estimated that somewhere around 15 runs with ~60 mL each of AN-103 are needed to produce enough granular product to be analyzed and tested. The estimated required granular product mass is ~422 g (five 1" x 2" monolith cylinders and 240 g of granular product – see Table 3).
- Analyze the BSR product for whole element chemistry of all cations and anions by ICP-AES and IC, REDuction/OXidation or REDOX to determine $Fe^{+2}/\sum Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Tc concentrations by ICP-MS and/or radiometric methods.
- Analyze the off-gas condensate for Cs, I and Tc by ICP-MS and/or radiometric methods.
- Rinse the off-gas line(s) at the end of the nominal concentration runs between the DMR and the condenser with a known volume of water and/or acid and analyze for Cs, I, and Tc by ICP-MS and/or radiometric methods.
- Perform mass balances for Tc, Cs, and I.

4.8 Radioactive Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the FBSR granular products.
- Perform long term ASTM C1285 - PCT on the FBSR granular products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides to the alteration phases.
- Send a subset of the granular product (see Table 3) to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003),[4,17,18] to data gathered during Hanford Module A, B, and C testing, and to the durability response of the non-radioactive granular product produced in this task plan.

4.9 Radioactive Monolith Production and Product Durability Testing

- Use a portion of the BSR granular products from the radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined from the simulant monolith testing in this task plan.
- After curing for 28 days, perform compression testing on two radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.
- Compression test the monoliths with the pre-calibrated penetrometer.
- Upon passing the compression test at 500 psi ship two of the radioactive monoliths to PNNL (one whole and one broken from compression testing) along with ~204 g of radioactive granular product.
- Using crushed segments from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 – PCT on the BSR radioactive monolith products.
- Perform long term ASTM C1285 - PCT on the BSR radioactive monolith products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides in the alteration phases.
- Send a subset of the crushed samples from compression testing to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1),[3,17,18] to data gathered during Hanford Module A and B testing, and in the non-radioactive portion of this task plan.
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths and run for 90 days.

4.10 Data Analysis and Documentation

- Analyze data as each module is completed.
- Provide interim technical reports as necessary to meet WRPS project commitments.
- Draft, approve, and issue a final report(s) after all the phases are complete.

5.0 TASK SCHEDULE

The timing of the individual activities will be maintained in the ERPS schedule. A higher level schedule is also being maintained by WRPS and is being updated on a weekly basis with all parties.

Table 4 summarizes the various runs/campaigns and the associated testing. The acronym in parenthesis after the test method indicates the organization that will perform the analyses. PSAL is denoted separately so that they can plan their resource load accordingly and to distinguish from AD. The radioactive sample PCTs will be performed by ERPS or SCF personnel if not able to remove the samples from the cells and the leachates will be submitted to AD. Radioactive sample BET and skeletal density will be performed in a glovebox using existing instrumentation maintained by ERPS personnel.

Table 4. Summary of Sample Types and Methods. Required Turnaround Times are in Work Days (* = Calendar Days) and Responsible Organization (A = AD, C = E&CPT/SSP, N = N-Area, O = Offsite, Op - = Optional, P = PSAL, U = E&CPT/PTP)

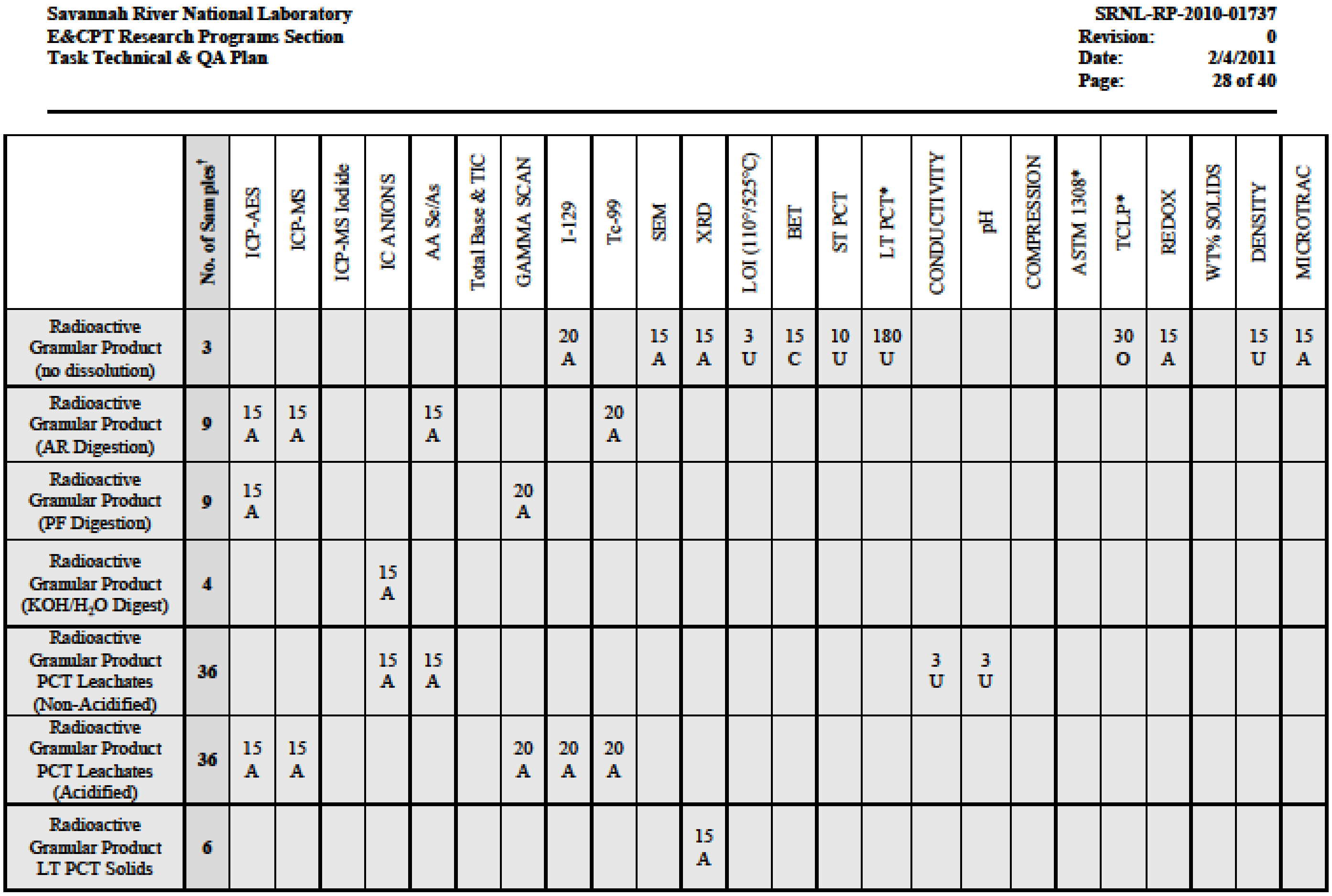
	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Pre-Clay/Coal/Fe (no dissolution)	**3**																						3 U		
Simulant Pre-Clay/Coal/Fe (AR Digestion)	**5**	15 A	15 A																						
Simulant Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	**4**			15 A	2 P																				
Simulant Post-Clay/Coal/Fe	**3**																							2 U	
Simulant Granular Product Production Subsamples (no dissolution)	**20** ‡											2 A	2 P									1 P			
Simulant Granular Product (no dissolution)	**3**											5 A	3 P	15 A	10 U	180 U					30 O	3 P		2 U	15 A

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Granular Product (AR Digestion)	**5**	15 A	15 A																						
Simulant Granular Product (PF Digestion)	**5**	15 A																							
Simulant Granular Product (KOH/H_2O Digest)	**4**			15 A	2 P																				
Simulant Granular Product PCT Leachates (Non-Acidified)	**36**			15 A	5 P												3 U	3 U							
Simulant Granular Product PCT Leachates (Acidified)	**36**	5 P	15 A																						
Simulant Granular Product LT PCT Solids	**8**											15 A													
Simulant Condensate	**3**	5 P	15 A	15 A	5 P																				

	No. of Samples[†]	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Condensate Solids (no digestion)	1										Op	Op													
Simulant Condensate Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Condensate Solids (PF Digestion)	2	5 A																							
Simulant Condensate Solids (KOH/H_2O Digest)	2				15 A																				
Simulant Rinsed Lines	3	5 P	15 A	15 A	5 P																				
Simulant Rinsed Lines Solids	1										Op	Op													
Simulant Rinsed Lines Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Rinsed Lines Solids (PF Digestion)	2	5 A																							

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Rinsed Lines Solids (KOH/H_2O Digest)	2				15 A																				
Simulant Monoliths (no dissolution)	3											15 A	3 U	15 A	10 U	180 U			5 U	90 U	30 O			2 U	15 A
Simulant Monoliths (AR Digestion)	9	15 A	15 A																						
Simulant Monoliths (PF Digestion)	9	15 A																							
Simulant Monoliths (KOH/H_2O Digest)	4			15 A	2 P																				
Simulant Monoliths PCT Leachates (Non-Acidified)	36			15 A	5 P												3 U	3 U							
Simulant Monoliths PCT Leachate (Acidified)	36	5 P	15 A																						
Simulant Monoliths LT PCT Solids	8											15 A													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Feed Pre-Clay/Coal/Fe (no dissolution)	4						2 A	20 A	20 A														3 U		
Radioactive Feed Pre-Clay/Coal/Fe Solids												5 A													
Radioactive Feed Pre-Clay/Coal/Fe (AR Digestion)	5	5 A	5 A							20 A															
Radioactive Feed Pre-Clay/Coal/Fe (PF Digestion)	5	5 A																							
Radioactive Feed Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	4				2 A																				
Radioactive Feed Post-Clay/Coal/Fe	2																							2 U	
Radioactive Granular Product Production Subsamples (no dissolution)	30 ‡											2 A	2 U									1 A			



	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Granular Product (no dissolution)	**3**								20 A		15 A	15 A	3 U	15 C	10 U	180 U					30 O	15 A		15 U	15 A
Radioactive Granular Product (AR Digestion)	**9**	15 A	15 A			15 A				20 A															
Radioactive Granular Product (PF Digestion)	**9**	15 A						20 A																	
Radioactive Granular Product (KOH/H_2O Digest)	**4**				15 A																				
Radioactive Granular Product PCT Leachates (Non-Acidified)	**36**				15 A	15 A											3 U	3 U							
Radioactive Granular Product PCT Leachates (Acidified)	**36**	15 A	15 A					20 A	20 A	20 A															
Radioactive Granular Product LT PCT Solids	**6**											15 A													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Condensate	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Condensate Solids (no digestion)	2								20 A		Op	Op													
Radioactive Condensate Solids (AR Digestion)	2	15 A	15 A					20 A	20 A	20 A															
Radioactive Condensate Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Condensate Solids (KOH/H$_2$O Digest)	2				15 A																				
Radioactive Rinsed Lines	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Rinsed Lines Solids (no dissolution)	2								20 A		Op	Op													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Rinsed Lines Solids (AR Digestion)	2	15 A	15 A							20 A															
Radioactive Rinsed Lines Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Rinsed Lines Solids (KOH/H_2O Digest)					15 A																				
Radioactive Monolith (no dissolution)	3								20 A			15 A	3 U	15 C	10 U	180 U			5 U	90 U	30 O			2 U	15 A
Radioactive Monolith (AR Digestion)	9	15 A	15 A			15 A				20 A															
Radioactive Monolith (PF Digestion)	9	15 A						20 A																	
Radioactive Monolith (KOH/H_2O Digest)	4				15 A																				

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Monolith PCT Leachates (Non-Acidified)	**36**				15 A	15 A											3 U	3 U							
Radioactive Monolith PCT Leachates (Acidified)	**36**	15 A	15 A					20 A	20 A	20 A															
Radioactive Monolith LT PCT Solids	**6**											15 A													

† Sample count includes blanks and standards.
‡ Sample count does not apply to XRD sample which will not be submitted in duplicate for these samples.

6.0 RESEARCH FACILITY PLANNING

6.1 Effects of the Task on Equipment, Personnel, and Research Facilities' Physical Plant

The receipt, analyses, and handling of radioactive samples such as the AN-103 salt supernate are routine tasks performed in the Shielded Cells. The entire task will be evaluated using the SRNL Conduct of R&D Manual. A calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution. An e-mail will be sent to the coordinator for the Radionuclide Inventory – Administrative Control (RI-AC) computer system to make sure the use of these samples for this testing is within the authorization basis of the SRNL Documented Safety Analysis (DSA).

Activities surrounding the analysis of the samples and the running of the BSR will be shown on the SRNL Shielded Cells Operations and ERPS schedules. Appropriate documentation will be completed prior to the start of activities.

Activities need to stay on schedule to support WRPS's supplemental LAW treatment technology selection.

Because the AN-103 waste is an Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) listed waste, special procedures for handling and segregating this waste are being implemented in SRNL including a tracking mechanism for all samples, and sample residues.[21]

6.2 Products and By-Products of Task

Any solids created by the radioactive sample processing will be stored in a Satellite Accumulation Area (SAA) at the end of the treatability study. It is anticipated that all the AN-103 will be processed and there will be no AN-103 to return to Hanford. Disposition and return of solids to Hanford after analysis will be accomplished through consultation with the SRNL Environmental Compliance Authority (ECA) and in compliance with the EEC. All remaining solutions (from condensates derived from the BSR process and from the dissolutions of the product for analyses and from PCT leachates) and solid residues from completed testing will be returned to Hanford. All job control waste will be disposed of as manifested waste returns to Hanford. Some solid samples will be retained at SRNL for follow on characterization and testing after the treatability study has ended, i.e. under the "sample exclusion." Residues (liquid and solid) from this characterization and testing will also be tracked and the residues returned to Hanford. ERPS will work with the SRNL ECA to disposition these residues.

Samples for PNNL, except those for Synchrotron testing, will be sent after the treatability study has ended, i.e. once the samples have been archived, they will be sent to PNNL under the sample exclusion rule rather than as part of the treatability study.

Disposition of Test Equipment

Upon completion of the radioactive BSR processing additional follow-on work is to be performed, i.e., radioactive Hanford LAW processing and the equipment will remain in the SCF. However, non-containers that come in contact with the Hanford material will

be treated as job control waste for that stream. The simulant BSR will also be used for additional testing and thus will remain set-up until subsequent Hanford testing is completed.

6.3 Exposure of Personnel

Samples that are radioactive will be handled remotely in the Shielded Cells. Samples with high levels of radiation that have to be removed from the Shielded Cells for analyses by AD will be diluted in the cells so that only a small portion of the radioactivity is removed from the cell. If the BSR products are at a low enough radiation level to be handled in SRNL radioactive hoods (i.e., meet existing hood limits), they will be removed from the Shielded Cells and handled in ERPS laboratories. This includes preparation for characterization, production of the monoliths, and testing of the granular and monolith products. The radioactive samples may be contact handled by Shielded Cells technicians, ERPS personnel (in radioactive hoods and radiobenches), and AD technicians (in radioactive hoods and radiobenches). These samples will be controlled and comply with standing radiological work plans. If a sample is expected to exceed standing radiological work plan limits, a job specific radiological work plan will be implemented after implementation of all engineering and administrative controls and when no other choice exists.

7.0 PROGRAMMATIC RISK REVIEW

Per the L1 manual, Procedure 7.10, a programmatic risk review has been performed for the tasks listed in this TTQAP. The SRNL Conduct of R&D manual will be used to complete a review for all tasks listed in the TTQAP. Results of the risk review are given below in Table 5.

Table 5. Programmatic Risk Review

Question	Response
Could an inadvertent or premature failure of equipment result in unacceptable added programmatic costs or schedule delays?	Yes. All preventive measures will be taken in order to maintain schedule and budget. Back-up BSR equipment has been procured. Spare parts are available for the components. One spare controller is available and two spare Mass Spectrometers are being procured. A schedule delay would be experienced to place the backup or new equipment into service and recover from the point of failure. A delay in the return to service date of any SRNL – AD analytical instrumentation will result in a schedule delay since back-up options for most of the required analyses are limited.
Is the activity on a critical path or is the activity significant to a major site program/process, milestone, or objective?	No. However, this activity is in support of a multi-year DOE EM-31 funded proposal and is on a critical path for Hanford Waste Form Qualification (WFQ) and the WRPS Supplemental LAW Treatment selection.
Does the activity involve long lead time items whose failure would exceed the allowable programmatic schedule?	Yes. Failure of the controller system or the Mass Spectrometer before the spare is obtained and operational will result in a delay to the program. In addition, an AD instrumentation failure(s) resulting in the need for replacement equipment would exceed the allowable programmatic schedule.
Does this activity involve high risk technology whose development, if not successful, could exceed allowable programmatic cost or schedule?	No. The technology has been used for previous experimentation and the primary change is the feed stream. Decisions will be made for the remaining Hanford BSR program based on the results of this program. Decisions will be made for Hanford implementing this technology as the supplemental technology for LAW at Hanford based on the results of this program.
Could the activity or failure of the activity significantly impact the facility or other programs in proximity of the activity?	Potential exists. Cells 3 and 4 of the Shielded Cells will be dedicated to the BSR runs for several months. This could impact needed space for other SRR and EM programs. Cell 6 may be used for analytical support if needed. This could impact the analytical support for other sample processing that will be going on at the same time. If Cell 6 is not used, then resources (i.e., hoods in ERPS laboratories) will be utilized which may impact other programs. During the running of the BSR in the SCF, facility support will be required to monitor the SCF ventilation system since the BSR system generates appreciable quantities of flammable hydrogen. No physical impacts to the facility are anticipated.
If quantities of accountable radioisotopes (per L7.7, 1.07) are received into the SRNL facilities, what impact will the planned activity have on SRNL facilities?	The AN-103 sample has already been received at SRNL. However, a calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution prior to use and after doping with the necessary quantities of additives. If any radionuclide quantity is predicted to exceed the SRNL reportable quantities, the appropriate section of procedure 1.07 of the L7.7 manual will be followed. An e-mail will be sent to the coordinator for the RIAC database system to make sure the receipt of these samples is within the authorization basis of the SRNL DSA. If the sample has an impact on the Authorization Basis, a schedule delay would be experienced though not expected.

8.0 R&D HAZARDS SCREENING

Before any laboratory work is initiated, a review of L1, 7.02, will be performed to determine the hazards and controls required. At a minimum, three HAPs are expected to be generated to support this task.

9.0 QUALITY ASSURANCE

9.1 Documents Requiring Requester Approval

Document	**Management**		**Customer**		**QA**	
	Yes	**No**	**Yes**	**No**	**Yes**	**No**
Task Technical and QA Plan	X			X	X	
Final Report	X		X			X

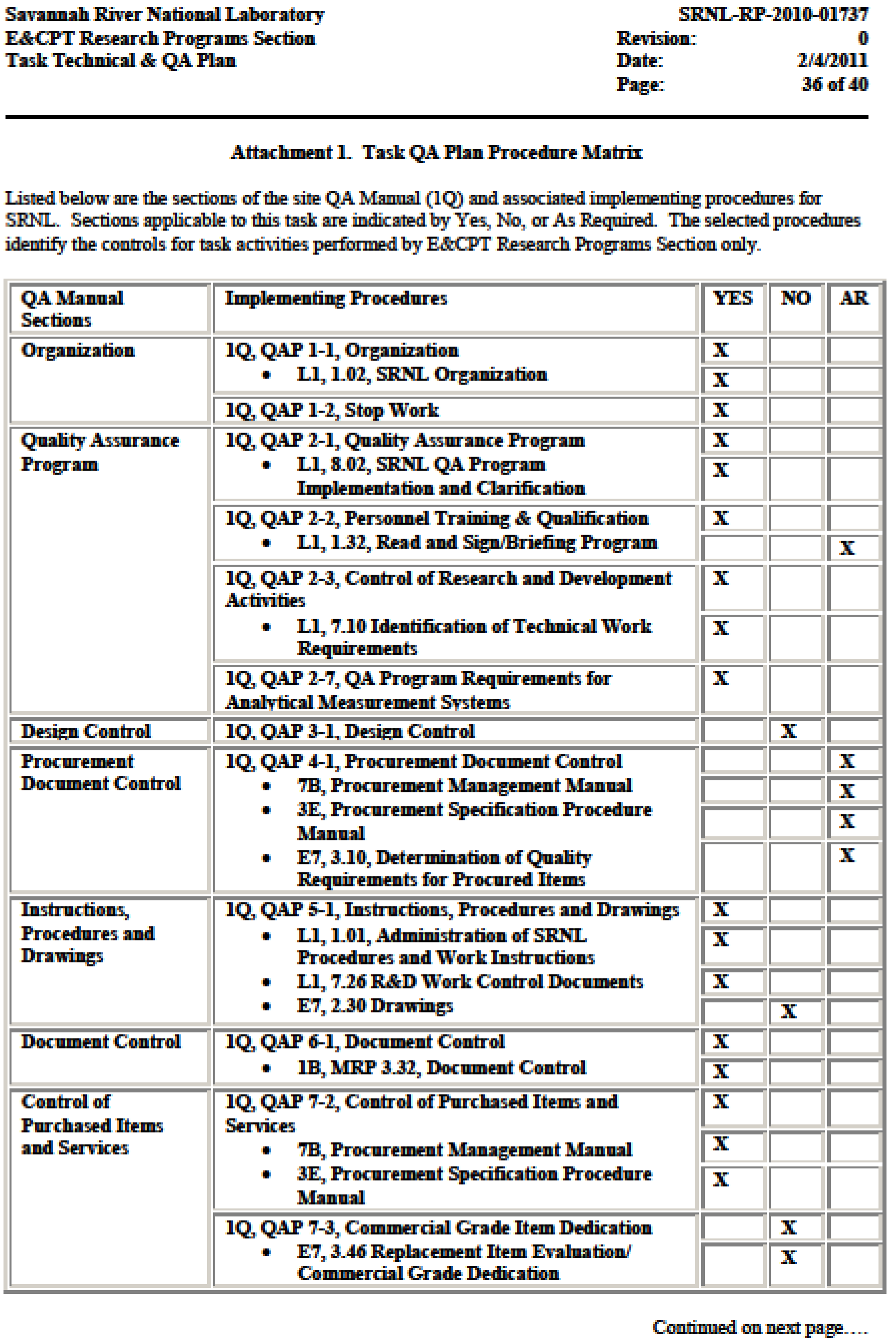
9.2 Records Generated During Task Performance

Description	**YES**	**NO**	**AR***
Task Technical and QA Plan	X		
Controlled Laboratory Notebooks	X		
Task Technical Reports	X		
Data Qualification Reports		X	
Supporting Documentation			X

*** AR = As Required**

9.3 Task QA Plan Procedure Matrix

See Attachment 1.



Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2010-01737
Revision: 0
Date: 2/4/2011
Page: 36 of 40

Attachment 1. Task QA Plan Procedure Matrix

Listed below are the sections of the site QA Manual (1Q) and associated implementing procedures for SRNL. Sections applicable to this task are indicated by Yes, No, or As Required. The selected procedures identify the controls for task activities performed by E&CPT Research Programs Section only.

QA Manual Sections	Implementing Procedures	YES	NO	AR
Organization	1Q, QAP 1-1, Organization	X		
	• L1, 1.02, SRNL Organization	X		
	1Q, QAP 1-2, Stop Work	X		
Quality Assurance Program	1Q, QAP 2-1, Quality Assurance Program	X		
	• L1, 8.02, SRNL QA Program Implementation and Clarification	X		
	1Q, QAP 2-2, Personnel Training & Qualification	X		
	• L1, 1.32, Read and Sign/Briefing Program			X
	1Q, QAP 2-3, Control of Research and Development Activities	X		
	• L1, 7.10 Identification of Technical Work Requirements	X		
	1Q, QAP 2-7, QA Program Requirements for Analytical Measurement Systems	X		
Design Control	1Q, QAP 3-1, Design Control		X	
Procurement Document Control	1Q, QAP 4-1, Procurement Document Control			X
	• 7B, Procurement Management Manual			X
	• 3E, Procurement Specification Procedure Manual			X
	• E7, 3.10, Determination of Quality Requirements for Procured Items			X
Instructions, Procedures and Drawings	1Q, QAP 5-1, Instructions, Procedures and Drawings	X		
	• L1, 1.01, Administration of SRNL Procedures and Work Instructions	X		
	• L1, 7.26 R&D Work Control Documents	X		
	• E7, 2.30 Drawings		X	
Document Control	1Q, QAP 6-1, Document Control	X		
	• 1B, MRP 3.32, Document Control	X		
Control of Purchased Items and Services	1Q, QAP 7-2, Control of Purchased Items and Services	X		
	• 7B, Procurement Management Manual	X		
	• 3E, Procurement Specification Procedure Manual	X		
	1Q, QAP 7-3, Commercial Grade Item Dedication		X	
	• E7, 3.46 Replacement Item Evaluation/ Commercial Grade Dedication		X	

Continued on next page….

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Identification and Control of Items	1Q, QAP 8-1, Identification and Control of Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Control of Processes	1Q, QAP 9-1, Control of Processes		X	
	1Q, QAP 9-2, Control of Nondestructive Examination		X	
	1Q, QAP 9-3, Control of Welding and Other Joining Processes		X	
	1Q, QAP 9-4, Work Planning and Control		X	
	• 1Y, 8.20, Work Control Procedure		X	
Inspection	1Q, QAP 10-1, Inspection		X	
	• L1, 8.10, Inspection		X	
Test Control	1Q, QAP 11-1, Test Control		X	
Control of Measuring and Test Equipment	1Q, QAP 12-1, Control of Measuring and Test Equipment	X		
	1Q, QAP 12-2, Control of Installed Process Instrumentation		X	
	1Q, QAP 12-3, Control and Calibration of Radiation Monitoring Equipment (not applicable to ERPS)		X	
Packaging, Handling, Shipping and Storage	1Q, QAP 13-1, Packaging, Handling, Shipping and Storage	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
Inspection, Test, and Operating Status	1Q, QAP 14-1, Inspection, Test, and Operating Status		X	
	• L1, 8.02 SRNL QA Program Implementation and Clarification		X	
Control of Nonconforming Items	1Q, QAP 15-1, Control of Nonconforming Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Corrective Action System	1Q, QAP, 16-3			X
	• 1B, MRP 4.23, Corrective Action Program			X
Quality Assurance Records	1Q, QAP 17-1, Quality Assurance Records Management	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
	• L1, 7.16, Laboratory Notebooks and Logbooks	X		

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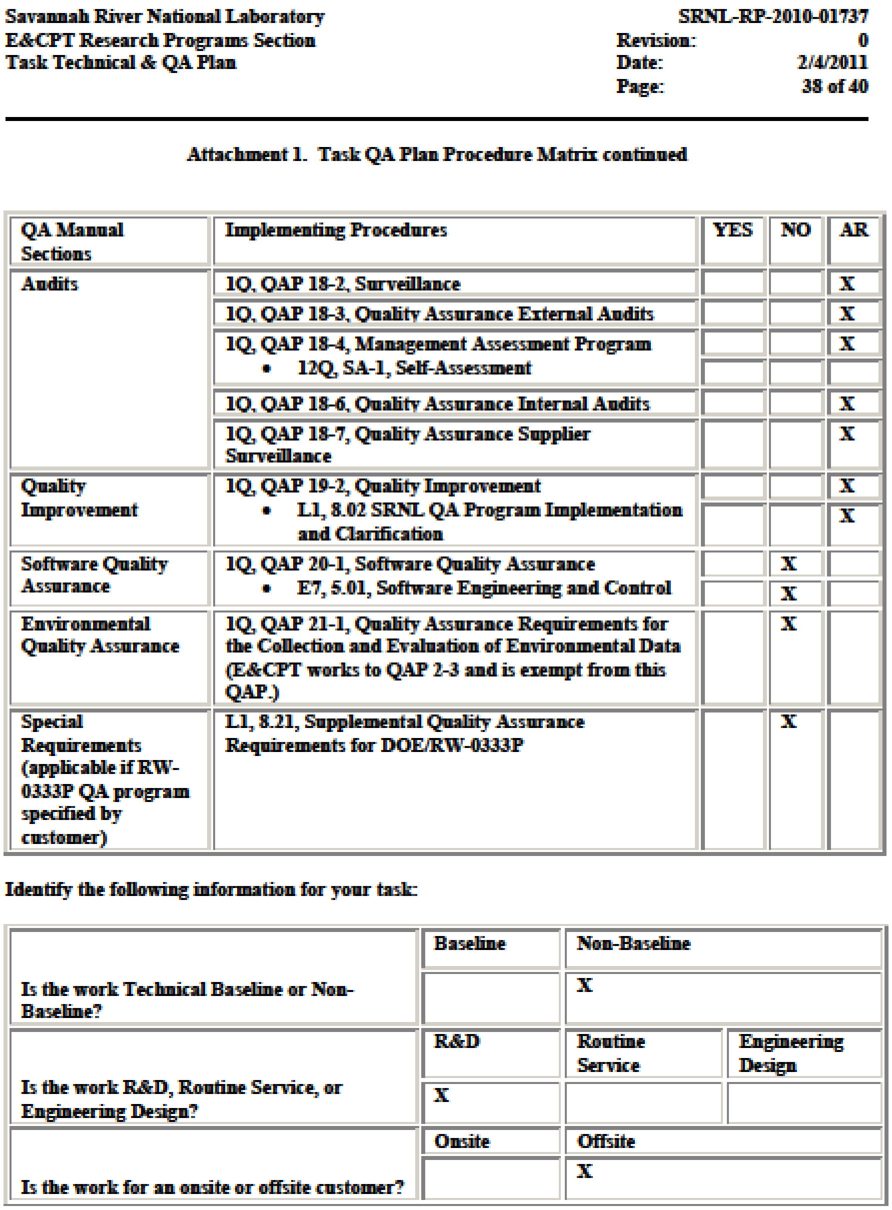

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Audits	1Q, QAP 18-2, Surveillance			X
	1Q, QAP 18-3, Quality Assurance External Audits			X
	1Q, QAP 18-4, Management Assessment Program			X
	• 12Q, SA-1, Self-Assessment			
	1Q, QAP 18-6, Quality Assurance Internal Audits			X
	1Q, QAP 18-7, Quality Assurance Supplier Surveillance			X
Quality Improvement	1Q, QAP 19-2, Quality Improvement			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Software Quality Assurance	1Q, QAP 20-1, Software Quality Assurance		X	
	• E7, 5.01, Software Engineering and Control		X	
Environmental Quality Assurance	1Q, QAP 21-1, Quality Assurance Requirements for the Collection and Evaluation of Environmental Data (E&CPT works to QAP 2-3 and is exempt from this QAP.)		X	
Special Requirements (applicable if RW-0333P QA program specified by customer)	L1, 8.21, Supplemental Quality Assurance Requirements for DOE/RW-0333P		X	

Identify the following information for your task:

Is the work Technical Baseline or Non-Baseline?	Baseline	Non-Baseline	
		X	
Is the work R&D, Routine Service, or Engineering Design?	R&D	Routine Service	Engineering Design
	X		
Is the work for an onsite or offsite customer?	Onsite	Offsite	
		X	

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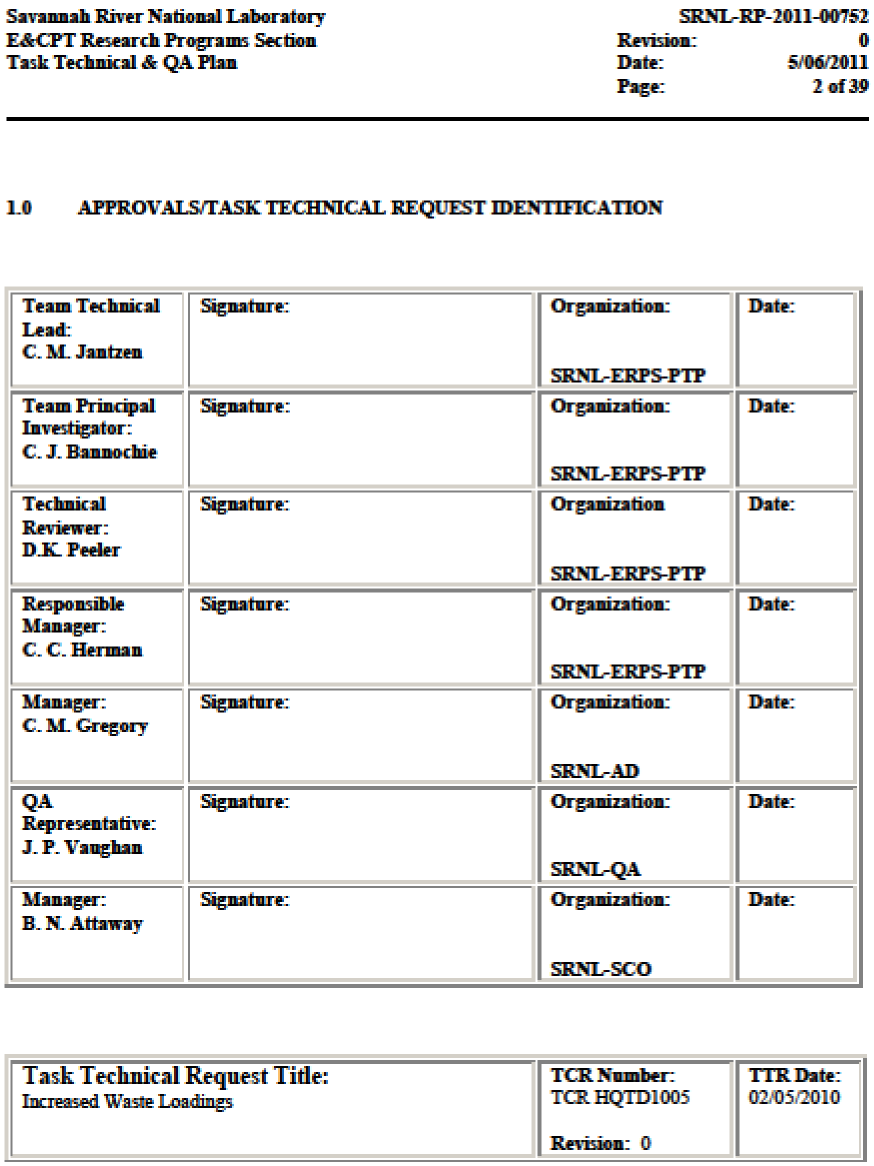
Appendix C. Task Technical & Quality Assurance Plan for Module E

Task Technical and Quality Assurance Plan for Evaluation of Fluidized Bed Steam Reformed (FBSR) Mineralized Waste Forms (Granular and Monolith) for the DOE EM-31 Technology Development & Deployment (TDD) Program: Hanford Tank AZ-101/AZ-102 Study

C. M. Jantzen
C. J. Bannochie

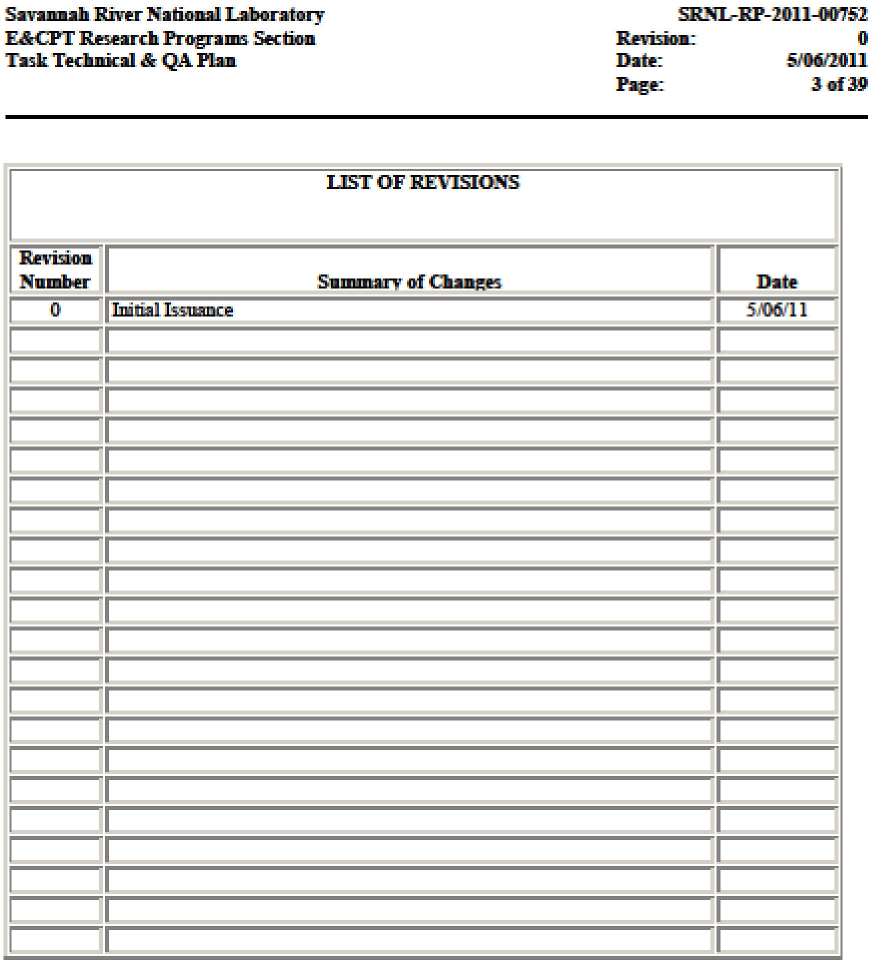
May 2011



1.0 APPROVALS/TASK TECHNICAL REQUEST IDENTIFICATION

Team Technical Lead: **C. M. Jantzen**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Team Principal Investigator: **C. J. Bannochie**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Technical Reviewer: **D.K. Peeler**	**Signature:**	**Organization** **SRNL-ERPS-PTP**	**Date:**
Responsible Manager: **C. C. Herman**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Manager: **C. M. Gregory**	**Signature:**	**Organization:** **SRNL-AD**	**Date:**
QA Representative: **J. P. Vaughan**	**Signature:**	**Organization:** **SRNL-QA**	**Date:**
Manager: **B. N. Attaway**	**Signature:**	**Organization:** **SRNL-SCO**	**Date:**

Task Technical Request Title: Increased Waste Loadings	**TCR Number:** TCR HQTD1005 **Revision:** 0	**TTR Date:** 02/05/2010



Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2011-00752
Revision: **0**
Date: **5/06/2011**
Page: **3 of 39**

LIST OF REVISIONS

Revision Number	Summary of Changes	Date
0	Initial Issuance	5/06/11

2.0 INTRODUCTION

2.1 Task Definition

2.1.1 Introduction

The baseline treatment plan for Hanford is to vitrify their salt supernate wastes also known as Low Activity Waste (LAW). This task plan deals with the feasibility of an alternative or supplemental treatment for LAW waste known as Fluidized Bed Steam Reforming (FBSR) and so the investigations are not considered to be baseline. The Waste Treatment Plant (WTP) is currently under construction to treat all of the High Level Waste (HLW) and a portion of the LAW via vitrification. However, the LAW will be generated at over twice the rate that the currently designed LAW vitrification facility can treat the waste. Either a second LAW vitrification facility or other supplemental LAW treatment technology is needed to meet schedule objectives and approved tank closure deadlines.

One of the supplemental LAW treatment technologies being considered is FBSR. Recently, THOR® Treatment Technologies (TTT) has successfully demonstrated the FBSR technology at the Engineering Scale Technology Demonstration (ESTD) pilot scale on a non-radioactive Hanford LAW simulant[1] that represents a 68 tank blend of Hanford wastes. This simulant is known as the Rassat[2] simulant. As part of the Washington River Protection Solutions (WRPS) supplemental treatment technology evaluation and Department of Energy (DOE) EM-31 Technology Development and Deployment (TDD) programs[3], the Savannah River National Laboratory (SRNL) has been requested to successfully demonstrate the FBSR technology on waste streams representative of Hanford's LAW at the Bench scale Steam Reformer (BSR) scale and compare the results to the products formed at the pilot scale. The first demonstration[4] was a radioactive Savannah River Site (SRS) salt supernate that had been compositionally trimmed to look like the Hanford Rassat 68 tank blend that TTT processed non-radioactive, this is referred to as Module B testing at SRNL since Module A testing involved secondary waste and not LAW. The second demonstration of LAW is a Hanford waste from Tank SX-105 and was designated as Module C for SRNL tracking purposes. The third demonstration of LAW is a Hanford waste from Tank AN-103 and was designated as Module D for SRNL tracking purposes. The fourth demonstration of LAW is a Hanford waste from tanks AZ-101/AZ-102 and is designated as Module E. Module E is the focus of this Task Technical and Quality Assurance Plan (TTQAP).

FBSR treatment offers a low temperature (700-750°C) continuous method by which LAW may be processed into a crystalline ceramic (mineral) waste form regardless of whether the wastes are high in organics, nitrates, sulfates/sulfides, other anions or components. The FBSR process produces no secondary liquid waste streams. Based on previous testing [5,6,7,8,9,10,11,12,13,14], the granular waste form that is produced by co-processing the LAW with kaolin clay has been shown to be very durable. However, monolithing of the granular product is being pursued since monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage and/or meet compressive strength for Hanford land disposal requirements. Once again, monolithing is not believed to be necessary to meet any durability performance criteria since compressive strength could be achieved through other means.

To support SRS implementation of the FBSR technology for Tank 48 (T48), SRNL has successfully operated a Bench scale Steam Reformer (BSR) in the SRNL Shielded Cells Facility (SCF).[15,16] The BSR is a unique SRNL design and this radioactive capability does not exist commercially nor at any other DOE site. All related safety basis documentation for operation of the BSR in the SRNL SCF was completed for the T48 demonstration and has been updated to cover the streams being treated for the Hanford LAW scope. SRNL also has unique expertise, analytical chemistry skills, and equipment for monolithing the granular FBSR product and measuring durability of waste forms.[17,18]

The scope of work addressed in this task planning document consists of SRNL making a simulant of Hanford's Tank AZ-101/AZ-102 LAW and testing the simulant in the non-radioactive BSR in 735-11A to provide

- optimization of processing parameters for radioactive testing,
- non-radioactive granular samples for testing the durability response of the AZ-101/AZ-102 BSR product compared with previous testing of pilot scale FBSR products[17] and previous simulant and radioactive BSR products,[4,17,19,20] and
- granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from previously tested pilot and BSR products.[4,17,19,20] Tank AZ-101/AZ-102 LAW is a high Cr_2O_3 containing tank mixture with high concentrations of sulfur.

The scope of work addressed in this task planning document also consists of SRNL mineralizing a radioactive Hanford LAW sample from Tank AZ-101/AZ-102 that has been supplied by Hanford. Re-characterization of Module C and Module D Hanford wastes was determined to be necessary even though the sample had been analyzed at Hanford before shipping.[21] Re-characterization of a subsample of a well stirred/mixed AZ-101/AZ-102 sample will be necessary to develop the simulant and to provide data with equivalent analytical uncertainty for the mass balance. The re-characterization will include determination of weight percent solids (wt. %) and density. The slurry will be dissolved and analyzed for cations, anions, elemental composition, and Tc-99, I-129, and Cs-137. The solids, if any, will be analyzed by XRD and/or XRF.

A simulant will be made that represents the chemistry of the Tank AZ-101/AZ-102 LAW after ion exchange and filtration at Hanford, e.g. the state of the AZ-101/AZ-102 sample at the time of shipping. This "as shipped" simulant will be allowed to age to see if precipitates form. Non-radioactive testing of the AZ-101/AZ-102 "as shipped" simulant will be performed whether it has particulates present or not. Since TTT has experience with processing solids in the ESTD campaigns (Appendix A) and the clay additives are themselves particulate slurries, it was determined during the Module C and D testing that the precipitates did not have to be removed before BSR processing.

The Tank AZ-101/AZ-102 LAW will be processed in the BSR in the SCF to provide

- radioactive granular samples for testing the durability response of BSR product compared to product from the TTT pilot scale runs from WFO-09-003[17] and other BSR campaigns with Waste Treatment Plant Secondary Waste (WTP-SW)[17] and Hanford's Rassat simulant,[4,17], Tank SX-105,19 Tank AN-103,[20] and the non radioactive testing in the scope above and

- radioactive granular products to monolith and compare (durability and compressive strength) to the non-radioactive monolithic waste forms prepared under WFO-09-003,[17] Hanford's Rassat simulant,[4] Tank SX-105, Tank AN-103, and in the scope described above.

Because of the lack of complete fluidization and shorter residence times in the BSR than in the ESTD pilot, the particle size will be mostly fines as particle size growth is minimized in the absence of long residence times and intense fluidization. This is not problematic as the ESTD bed product is an agglomeration of finer particles that grow in the long residence times in the FBSR.

2.1.2 Radioactive Sample Characterization

The AZ-101/AZ-102 radioactive sample will be mixed, shimmed with NaReO$_4$ to 1.7 mmol/L, and an analytical subsample of ~ 50mL taken. The subsample will be analyzed to verify parameters needed for simulant formulation and for mass balance calculations. See Table 4 for specific analyses to be performed.

2.1.3 Non-Radioactive Tests

The AZ-101/AZ-102 simulant will be developed by SRNL using chemical analysis provided by SRNL as shown in Table 1. The target concentration for the LAW Resource Conservation and Recovery Act (RCRA) metals will not be increased over what is already present in the waste. The Re (Tc surrogate) will be increased by 100; the I by 1,000; and 1,000,000 for Cs as done in the TTT pilot scale demonstrations of the Rassat simulant[1] in order to observe their behavior during mass balance of the process. SphereOx, a denitration catalyst used in FBSR processing at the pilot scale, will be substituted for the ferric nitrate nona-hydrate used in Modules B, C, and D to force RCRA constituents into insoluble spinel phases. The iron will also act as a REDOX indicator as there is little to no iron in the waste. Knowing the iron REDOX helps determine the oxidation state of many other REDOX active species such as Re^{7+} vs. Re^{4+} and Cr^{6+} vs. Cr^{3+}.

If precipitates develop, a subsample of a well mixed "as shipped" simulant will be taken and analyzed as outlined in 2.1.2 for the radioactive sample to ensure that the same types of precipitates have formed. Once the subsample is taken, BSR processing of the well mixed "as shipped" simulant with precipitates will begin. It is anticipated that the clay particulates will keep these precipitates buoyant once the clay and simulant are mixed. Processing the "as shipped" simulant with precipitates will determine whether or not the AZ-101/AZ-102 as received sample can be processed without first removing the precipitates. If the simulant with the precipitates can be processed in the BSR, then the radioactive sample will be processed as received.

Once the "as shipped" simulant recipe is developed it will be used to determine the optimum non-radioactive BSR operational conditions to guide the operational conditions to be used in the radioactive BSR tests in the SCF. Partitioning of the Cs, I, and Re to the off-gas versus the overall solid mineralized product will be assessed by whole element chemistry of the off-gas condensate and the solid product. Since the testing of the deposits in the off-gas lines in-between the reaction chamber known as the Denitration and Mineralizing Reactor (DMR) and the off-gas condenser during Modules B and C, have shown that only minimal amounts (<0.05%) of any of the elements of concern reside in this line, the line will no longer be rinsed with a known amount of deionized water and analyzed to determine the species that have been trapped or retained in the lines. The data will be used to calculate a mass balance of the system. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) will be used for analyses of the Cs, Re, and I in the solids and off-gas due to their presence at very low concentrations.

In addition, partitioning of the Cs, Re, and I amongst the solid phases, e.g. nepheline vs. sodalite, will also be determined by quantitative X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and possibly Transmission Electron Microscopy (TEM) and Selected Area Diffraction (SAD). Since the sodalite phases, including nosean, are present in small quantities which for low anion containing feeds may be below the detection limit of the XRD, a total amount of "sodalite vs. nepheline" may be the only quantitative analyses that are reportable. Phase pure standards are being made to develop quantitative XRD calibration curves.

Sufficient non-radioactive granular product must be made to provide eight 1"OD x 2"H monoliths and ~272 g of granular product for durability testing at SRNL. Therefore, a total of ~530 ((396.3 x 0.65) + 272.3) g is required as shown in Table 2. After the 28 day curing (or longer curing times if necessary), two of the monoliths will be compression tested at SRNL. Upon passing the minimum 500 psi compression test requirement, SRNL will retain the entire non-radioactive product for durability testing.

Table 1. Composition of LAW Tested in This Study Compared to Rassat Simulants Previously Tested.

	Component	AZ-101/AZ-102 Hanford data mol/L	AZ-101/AZ-102 SRNL data after Re spike mol/L	Rassat Simulant (LAW @ HRI 2008[1])** mol/L	Rassat Simulant (LAW @ SAIC/STAR 2004) mol/L	Rassat Simulant (As Reported[2]) mol/L
Acetate	CH_3COO^-	2.93E-03	Not analyzed	0.132	0.132	—
Glycolate	$C_2H_3O_3^-$	7.81E-04	Not analyzed	—	—	—
Carbonate	CO_3^{2-}	6.82E-01	6.91E-01	0.475	0.475	0.475
Chloride	Cl^-	3.10E-02	2.90E-02	0.0438	0.0438	0.0438
Fluoride	F^-	7.26E-02	2.64E-02	0.0316	0.0316	0.0316
Formate	$HCOO^-$	6.98E-03	8.21E-03	—	—	—
Hydroxide	OH^-	5.65E-01	4.70E-01	0.74	0.739	0.74
Iodide	I^-	1.89E-06	1.71E-06	0.013	0.0000134	—
Nitrate	NO_3^-	1.25E+00	1.09E+00	2.58487	2.51	2.51
Nitrite	NO_2^-	1.33E+00	1.23E+00	0.424	0.424	0.424
Oxalate	$C_2O_4^{2-}$	1.60E-02	1.38E-02	0.0118	0.0118	0.0118
Phosphate	PO_4^{3-}	2.50E-02	2.18E-02	0.0492	0.0492	0.0492
Sulfate	SO_4^{2-}	1.61E-01	1.33E-01	0.09	0.09	0.09
Aluminum	Al	2.30E-01	2.41E-01	0.0637	0.0637	0.0637
Antimony	Sb	—	—	0.00434	—	—
Arsenic	As	—	—	0.00137	—	—
Barium	Ba	—	—	0.00751	—	—
Cadmium	Cd	—	1.25E-05	0.0042	—	—
Calcium	Ca	—	1.19E-04			
Cesium	Cs	3.18 E-11	4.04E-11	0.013	0.00000051	0.00000051
Chromium	Cr	1.47E-02	1.13E-02	0.0104	0.0104	0.0104
Iron	Fe	1.45E-04	2.15E-04	—	—	—
Lead	Pb	—	5.05E-06	0.00606	—	—
Molybdenum	Mo	6.47E-04	6.60E-04			
Nickel	Ni	—	—	0.0106	—	—
Niobium	Nb	5.51E-04	8.24E-04	—	—	—
Potassium	K	9.36E-02	9.5E-02	0.0124	0.0124	0.0124
Rhenium	Re	—	1.7E-03	0.0017	0.00052	—
Selenium	Se	—	—	0.00123	—	—
Silicon	Si	2.02E-03	2.09E-03	—	—	—
Silver	Ag	—	—	0.00161	—	—
Sodium	Na	4.92E+00	5.32E+00	5.0161	5.0014	5.00
Technetium	Tc	1.44E-04	1.87E-04	—	—	—
Thallium	Tl	—	—	0.00202	—	—
Titanium	Ti	1.34E-04	1.53E-04	—	—	—
Uranium	U	—	1.57E-05	—	—	—
Zirconium	Zr	6.85E-05	6.24E-05	—	—	—
Density		1.236g/cc	1.24 g/cc	—	—	—

**Resource Conservation and Recovery Act (RCRA) and radionuclide surrogates (Re, I, Cs) were doped in at the following concentrations: 10X for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs

Table 2. BSR Product Requirements in Grams (Non-Radioactive Testing)

MODULE E PRODUCT REQUIREMENTS BY TEST AND LABORATORY				
Testing	Granular PNNL (g)	Granular SRNL (g)	Monolith PNNL (g)	Monolith SRNL (g)
Single-Pass Flow-Through (SPFT)	144	0	72	0
Product Consistency Test (PCT) Short Term ƒ	30	30‡	30	30‡
PCT Long Term	0	28‡	0	28‡
Toxicity Characteristic Leaching Procedure (TCLP)	20	20	20	20
ASTM C1308	0	0	98	98
SUMS BY LABORATORY	194	78	220	176
TOTAL MATERIAL SUM	272		396	
BSR GRANULAR PRODUCT EQUIVALENTS	NA		258*	
TOTAL GRANULAR PRODUCT	530			

ƒ (includes surface area measurement by BET, density, loss on drying, coal measurement by loss on ignition, and particle size distribution)

* Monolith Product x 0.65 BSR loading, makes eight monoliths at ~33 g FBSR per monolith. Of these eight monoliths two uncrushed monoliths remain at SRNL for ASTM C1308 testing and two uncrushed monoliths get sent to PNNL for testing; four monoliths are compression tested; 122 grams of crushed monoliths are sent to PNNL for testing; 77.9 grams of crushed monoliths are retained at SRNL for short term and long term PCT and TCLP.

‡ Increased quantities required compared to Modules A-D due to 20% loss during ethanol wash and only 30% yield of required particle size for PCT testing

SRNL will perform analyses to measure properties of the non-radioactive granular products and the monolithed simulated waste forms generated from the granular products produced during the simulant BSR campaigns. This will include loss-on-drying (LOD) tests at 110°C to determine moisture content and loss-on-ignition (LOI) tests at 525°C to determine the coal fraction in the samples which is the difference between the LOI and the LOD weight losses. The temperature of 525°C removes the carbon left in the raw coal after processing in the BSR as the hydrogen, oxygen, and moisture from the coal have been removed during the BSR processing. However, this temperature does not vaporize the sulfur in the coal or the BSR product phases. For these experiments, where SRNL is using the carbon LOI to assess the impact of carbon on the REDOX measurement, this temperature has been found to be sufficient and it is the temperature recommended by a US Geological Survey procedure developed for coal analyses.[22] Different subsamples will be sent for REDuction/OXidation (REDOX) analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the SEM using Energy Dispersive Spectroscopy (EDS) to determine if Re and I are retained in a sodalite structure and if Cs substitutes for Na in nepheline and/or sodalite or both.

The non-radioactive granular and monolithed waste form products will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by qualified personnel at SRNL. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The time durations are to be one month, three month, six month and an additional time to be determined (TBD) which may be up to 1 year or longer. The tests will be performed in Teflon® vessels. A minimum of 1 gram of sample must be tested at a mass ratio of 1 gram of solids to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume will be determined once the Brunauer, Emmett, and Teller (BET) surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA); and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC.

The Toxicity Characteristic Leaching Procedure (TCLP) will be performed by an Environmental Protection Agency (EPA) certified laboratory in South Carolina for the non-radioactive simulant granular product.

The non-radioactive granular product will be made into monoliths using an optimized monolith binder formulation defined by the testing performed as part of the Hanford LAW supplemental treatment testing funded by EM-31. The monolith will be characterized as described above and compression tested. Diffusion coefficients for Re, Cs, and I will be determined using the 3 month long ASTM C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form

2.1.4 Radioactive Tests

The Tank AZ-101/AZ-102 Hanford LAW sample has been analyzed by WRPS, but, based on lessons learned from from Modules C and D; SRNL will re-analyze the AZ-101/AZ-102 sample to ensure that a representative simulant is fabricated and that the mass balance can be completed with reduced uncertainty. At the time of shipping the density of the waste has been measured by WRPS to be 1.236 g/cc.

Hanford has provided ~1379 mL of Tank AZ-101/AZ-102 LAW and all will be processed in an attempt to produce the 491g of radioactive product estimated to be needed, see Table 3. Re will be added to the waste to have ≥150 μg/g in the final product and SphereOx as a denitration catalyst. The iron oxide also acts as a REDOX indicator in order to determine the oxidation state of Re, Tc, and the

RCRA metals from an already developed Electro-Motive Force (EMF) diagram for FBSR. The concentration of Re will be verified after doping.

During the demonstration, at least one run with the radioactive waste will be spiked with Tc^{99}, Re, and I^{127} (non-radioactive) at a minimum of 150 μg/g in the solid product. This level is needed to detect these species during follow on extended x-ray absorption fine structure (EXAFS) testing at the Stanford Synchrotron Radiation Lightsource (formerly Stanford Synchrotron Radiation Laboratory) to determine the local bonding of the Tc^{99} and I^{127} in the mineral waste form. Iodine-125, -127 and -129 will all be present and expected to partition to the same sodalite phase and the Synchroton sensors can pick up all three isotopes but is most specific for I^{127}. The spiked feed will be processed at the end of the campaign, after the off-gas condensate is sampled and lines are flushed. This will ensure that the mass balance and leaching tests described below are not compromised by the elevated concentrations required by the EXAFS testing.

Non-radioactive Re is added to determine the effectiveness of Re as a surrogate for Tc^{99} during BSR processing, i.e. do they track each other in the off-gas, do they substitute for each other in the solid products or does one preferentially partition to the sodalite over the other, and do they respond similarly to the reduction/oxidation (REDOX) in the BSR. This will be compared to their response during subsequent durability testing.

Partitioning of the radionuclides (Cs, Tc, and I) and Re to the off-gas and to the solid mineralized product will be assessed by analysis of the off-gas condensate and analysis of the solid product. A mass balance will be performed. A combination of ICP-MS and radiometric methods will be used for analyses of these components as they should be present at very low concentrations.

During the BSR processing in the SCF, kaolin clay will be added to the AZ-101/AZ-102 sample to form the mineralized waste form between 725°-750°C. Because the waste is concentrated during processing while also being diluted by the non-radioactive clay added, the resulting radioactive dose of the final product will be different than the starting material. Assuming the measured dose is low enough to work in a radioactive hood, characterization and testing of the samples will be performed in a 773-A laboratory. If not, the characterization and testing will be performed in the SCF.

Adequate radioactive granular product must be produced in the BSR in the SCF to fabricate eight 1"OD x 2"H monoliths and provide granular and monolith product for durability testing at PNNL and SRNL (Table 3). After the required curing time, two whole monoliths will be sent to PNNL for testing and two whole monoliths will be retained at SRNL for testing. Of the crushed monoliths, 163 grams will be sent to PNNL for testing and 58 grams of crushed monoliths will be retained at SRNL for short and long term PCT testing (Table 3).

If the 1397 mL of AZ-101/AZ-102 does not make the required 491 g of granular product, then the amounts given in Table 3 will have to be adjusted accordingly, e.g. fewer monoliths, fewer samples, or fewer tests. This will be agreed upon with input from the customer and stakeholders.

SRNL will perform analysis of chemical and physical properties of the radioactive granular products and monoliths generated from the granular products produced during the BSR campaigns in the SCF. This will include LOD tests at 110°C to determine moisture content and LOI tests at 525°C to determine the coal fraction in the sample. Different subsamples will be sent for REDOX analyses, characterization by XRD, and whole element chemistry. Samples will be examined on the Contained Scanning Electron Microscope (CSEM) using EDS to determine if Tc, I and Re are retained in a sodalite structure and whether Cs substitutes for Na in the nepheline and/or sodalite structures. The coal in the product will also be examined for retention of radionuclides.

Table 3. BSR Product Requirements in Grams (Radioactive Testing)

MODULE E PRODUCT REQUIREMENTS BY TEST AND LABORATORY				
Testing	Granular PNNL (g)	Granular SRNL (g)	Monolith PNNL (g)	Monolith SRNL (g)
Single-Pass Flow-Through (SPFT)	72	0	72	0
Pressurized Unsaturated Flow (PUF)	40	0	40	0
Product Consistency Test (PCT) Short Term	30	30‡	30	30‡
PCT Long Term	0	28‡	0	28‡
Toxicity Characteristic Leaching Procedure (TCLP)	20	0	20	0
ASTM C1308	0	0	98	98
SUMS BY LABORATORY	162	58	260	156
TOTAL MATERIAL SUM	220		416	
BSR GRANULAR PRODUCT EQUIVALENTS	NA		271*	
TOTAL GRANULAR PRODUCT	491			

* Monolith Product x 0.65 BSR loading, makes eight monoliths at ~33 g FBSR per monolith. Of these eight monoliths two uncrushed monoliths remain at SRNL for ASTM C1308 testing and two uncrushed monoliths get sent to PNNL for testing; four monoliths are compression tested; 162 grams of crushed monoliths are sent to PNNL for testing; 58 grams of crushed monoliths are retained at SRNL for short term and long term PCT.

‡ Increased quantities required compared to Modules A-D due to 20% loss during ethanol wash and only 30% yield of required particle size for PCT testing

The radioactive granular waste form product will be tested using the ASTM C1285-08 (Product Consistency Test – long and short term) by SRNL. The radioactive granular product will be made into monoliths using the optimized monolith binder defined by simulant testing. The monoliths will then be re-characterized and subjected to the ASTM C1285-08 test (long and short term) and a compression test. The short term testing will be the seven day PCT and will be performed in stainless steel or Teflon® vessels at the reference 100-200 mesh called for in the PCT-A procedure. The long term testing will be performed using PCT-B which allows for longer time testing at different sample mass to solution volume ratios in steel or Teflon® vessels. The radiation dose from the sample must be calculated to ensure that the Teflon® vessels are acceptable per the dose requirements given in the PCT procedure, e.g. doses up to 1 x 10^5 rad of beta or gamma radiation have been shown not to damage TFE-fluorocarbon (Teflon®). The time durations are to be one month, six month, and an additional time to be determined (TBD) which could be up to one year. The tests will be performed in Teflon® vessels. A minimum of 1 g of sample must be tested at a mass ratio of 1 g of solid to 10 g of water per the procedure. Duplicate samples will be tested at each time interval. The exact surface area to solution volume ratio will be determined once the BET surface area of the FBSR product is measured. The solids and leachates will be chemically analyzed for the major species (Al, Na, Si, Fe) by ICP-ES; for the minor species (Ag, Ba, Cr, K, P, S, Tl, Zr) by ICP-ES; for other minor constituents (Cs, I, Re, Pb, Cd) by ICP-MS, (As, Se) by atomic absorption spectroscopy (AA), and for anions (F^-, Cl^-, I^-, SO_4^{2-}, PO_4^{3-}) by IC. Cs, I, and Tc will be measured radio-metrically.

Diffusion coefficients for Tc, Re, Cs, and I will be performed using the 3 month long C1308 monolith test, which is an improved version of ANSI 16.1 that does not allow back reactions to form.

Both the granular product and the monolith product will be leach-tested using the EPA TCLP procedure. Because AZ-101/AZ-102 is a listed waste the samples (granular and monolithic) will be sent to PNNL who will subcontract with an EPA certified laboratory.

2.2 Customer/Requester

Leo Thompson, Manager of WTP Technology and Development, is the customer/requester as the ultimate user of the technology. Steve Schneider, Director (Acting) Office of Waste Processing is the HQ customer/requester for the overall program.

2.3 Task Responsibilities

Environmental & Chemical Processing Technology Research Programs (ERPS) personnel will be primarily responsible for the scope described in this task plan. Durability testing being performed on the granular and monolithic samples (non-radioactive and radioactive) being sent to PNNL is not covered in this task plan. SRNL support will be provided by personnel in the Shielded Cells, AD, and the Regulatory Integration and Environmental Services organization. C. J. Bannochie is the overall Principal Investigator for the Hanford BSR program, while C. M. Jantzen is the overall technical lead for the program and is responsible for this task plan and any revisions. P. R. Burket is considered the Subject Matter Expert (SME) for the BSR equipment (non-radioactive and radioactive) and control system design and set-up. A. D. Cozzi is the lead for the waste form qualification and testing. C. C. Herman is the responsible manager for the program. The responsible manager (or designee) is responsible for reviewing and approving all procedures and task plans, assessing the preparedness to carry out this task, and reviewing and approving all reports.

Overall responsibilities of the ERPS BSR team include the following:

- Coordinating all activities and ensuring that they are completed in a timely manner
- Ensuring that all results are documented
- Preparing the records for this task
- Ensuring that sample tracking and document controls are followed
- Ensuring that the latest revisions of procedures are used to complete the task activities

For the simulant BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the Hazards Analysis Package (HAP) for the testing, providing guidance on the equipment performance parameters, ensuring the BSR is set up to perform testing, and performing the BSR testing.
- R. E. Eibling (or designee) is responsible for overseeing the production of the necessary simulant, including verifying acceptability of the simulant.
- W. E. Daniel (or designee) is responsible for preparing the equipment for simulant demonstrations, analyzing the simulant and ensuring product samples are submitted for characterization.
- C. L. Crawford and A. D. Cozzi (or designees) are responsible for characterization and testing of the granular product, production of the monoliths, and characterization and testing of the monoliths. C. L. Crawford will interface with W. L. Mhyre of Quality Control Testing as necessary to perform compression testing.
- ERPS technicians are responsible for performing the LOD/LOI measurements and PCT.
- Support for the above tasks will be provided by personnel within the ERPS section.
- AD is responsible for performing Brunauer-Emmett-Teller (BET) surface area measurements on the simulant samples.

For the radioactive BSR testing, the following responsibilities are delineated:

- P. R. Burket (or designee) is responsible for preparing the HAP for the testing and overseeing performance of the BSR testing.
- C. L. Crawford (or designee) is responsible for characterization and spiking of the radioactive sample.
- C. L. Crawford and C. J. Bannochie (or designees) are responsible for characterization of the granular product, monoliths, and offgas condensates/rinses.
- A. D. Cozzi (or designee) is responsible for testing of the granular product, production of the monoliths, testing of the monoliths, and performing skeletal density measurements on the radioactive samples.
- J. H. Scogin (or designee) is responsible for performing BET surface area measurements on the radioactive samples.
- ERPS technicians are responsible for performing the LOD/LOI measurements and PCT if the samples can be removed from the Shielded Cells. If the samples cannot be removed, Shielded Cells personnel will perform the LOD/LOI measurements and PCT under the guidance of ERPS personnel.
- Support for the above tasks will be provided by personnel within the ERPS section and by SCF personnel as necessary.

As necessary, C. L. Crawford (or designee) will be responsible for developing or modifying existing HAPs for the waste form characterization, production, or testing. C.

L. Crawford (or designee) will be the PI for the treatability study. He will have primary responsibility for working with the Inventory Authority, H. K. Hall (or designee), to track generated samples and residue throughout the performance of the task until completion of the studies and disposition of all material. All other researchers working with the actual Hanford material will also be required to comply with the guidelines of L29, ITS-0167 for tracking and disposition of samples and residue.

The Process Science Analytical Laboratory (PSAL) will be responsible for analyzing simulant and product streams using the following methods or equipment: Parr Anton density meter, REDOX, and LOD/LOI. PSAL will perform the necessary digestions or dilutions to allow the samples to be analyzed by these methods. PSAL will follow approved procedures to perform these measurements and will assign a unique ID to each sample to maintain traceability. PSAL will ensure that the appropriate standards are used and that equipment calibration is maintained during performance of the testing. Appropriate analytical standards will be submitted with all samples for a cross comparison between non-radioactive analyses by PSAL and radioactive sample analyses by Analytical Development (AD).

SRNL – SCO (Shielded Cells Operations) personnel are responsible for:

- Reviewing and approving this TTQAP
- Readying and maintaining the facility for operation
- Checking and installing the equipment necessary for tasks to be performed in the Shielded Cells
- Providing SRNL – Quality Assurance (QA) access to training and qualification records for SCO personnel for surveillances or audits
- Ensuring the latest revisions of procedures are used to complete the task activities

SRNL – AD Laboratory personnel are responsible for:

- Reviewing and approving this TTQAP
- Analyzing radioactive waste samples and simulant and product streams using the following methods or equipment: Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Ion Chromatography (IC), ICP-MS, particle size distribution (PSD), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Contained Scanning Electron Microscopy (CSEM), and radiometric analyses
- Providing personnel resources and equipment necessary to perform REDOX via remote handling in SCF (not an AD established method)
- Providing SRNL – QA access to training and qualification records for AD personnel for surveillances or audits
- Performing QA checks (i.e., using standards and ensuring calibrations are valid) on instrumentation involved in this task
- Analyzing the samples per the Turn Around Times (TAT) specified in this TTQAP
- Reviewing the sample results prior to reporting them
- Ensuring the latest revisions of procedures are used to complete the task activities
- Communicating needed method development validation work to be performed on radioactive materials produced as part of the Task Plan

SRNL QA is responsible for reviewing and approving this task plan and providing guidance and oversight for this task.

WRPS and EM-31 WP-5 personnel are responsible for providing guidance and input on the requirements of their associated qualification program and CD-1 package needs.

They are requested to provide written requests to SRNL specifying any changes/deviations to the scope of this TTQAP. The WRPS and EM-31 WP-5 team will be responsible for reviewing the final reports associated with this task. Any changes or addition to scope will be agreed upon by SRNL after considering the impact to budget and schedule. K. Ryan, of TTT, is responsible for providing BSR operational parameters and providing the coal and clays to be used by SRNL if needed.

2.4 Task Deliverables

1. An approved Task Technical and QA Plan (this document).
2. Mass balance of Re, I, and Cs during non-radioactive BSR operation.
3. Interim documentation of the results of the non-radioactive BSR run and the characterization of the granular and mineralized product including subsequent product characterization and testing.
4. Production and testing of eight non-radioactive monoliths and ~272 g granular product for further testing for SRNL and PNNL.
5. Mass balance of Tc^{99}, I^{129}, and Cs^{137} during radioactive BSR operation.
6. Interim documentation and a final approved report documenting the results of the radioactive BSR mineralized product and subsequent product characterization and testing.
7. Shipment of two radioactive monoliths and ~162 g granular product to PNNL for further testing.
8. Six radioactive monoliths and ~58 g granular product for SRNL testing.
9. Shipment of granular products made from Hanford AZ-101/AZ-102 waste at an elevated solids spiking of 150µg/g Tc^{99} and I^{129} for Synchrotron testing at Stanford Synchrotron Radiation Lightsource or an equivalent facility.

3.0 TASK ACCEPTANCE CRITERIA

Acceptance testing is not part of this task.

4.0 TASK ACTIVITIES

4.1 Task Initiation

- Draft/review/issue TTQAP.
- Conduct R&D/Hazards Assessment Package (HAP)/Safety review for simulant BSR testing including initiation of the Environmental Evaluation Checklist (EEC).
- Conduct R&D/HAP/Safety review for radioactive BSR testing including approval of the necessary national emissions standards for hazardous air pollutants NESHAPS analysis and EEC.
- Conduct R&D/HAP/Safety review for the fabrication, characterization, and testing of the granular and monolithic waste forms as necessary including the EEC for simulant and radioactive testing.

4.2 Simulant and BSR Product Formation

- Analyze the AZ-101/AZ-102 sample and determine if precipitation has occurred.
- Develop an AZ-101/AZ-102 simulant
- Make ample non-radioactive simulant (4 Liters) to make ~530 g (Table 2) of non-radioactive BSR product for further testing.
- Analyze non-radioactive AZ-101/AZ-102 simulant to confirm critical parameters.

- Determine the simulant BSR operating parameters (clay levels, coal levels, input gases/flow rates) by scaling of the ESTD operation parameters down to the BSR scale. SRNL will obtain concurrence with the simulant BSR operating parameters from TTT before proceeding with the BSR operation.
- Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases and sufficient carbon to provide the necessary reductant for the non-radioactive BSR campaigns. Use SphereOx as a catalyst to assess the impacts of this co-reactant. Quantity will be decided upon by SRNL and TTT.
- Run the non-radioactive BSR in 735-11A between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each simulant run will use a minimum of 20 mL and maximum of 120 mL of feed with the volume of feed being dependant on operating conditions. It is estimated that ~30 runs will be required to generate 530 grams of product for analysis and testing. The estimated required granular product mass is 530 g (eight 1" x 2" monolith cylinders requiring 258 grams of granular product and 272 g of granular product).

4.3 Simulant Product Analysis and Off-Gas Mass Balance

- Analyze the composited BSR products for whole element chemistry of all cations and anions by ICP-AES and IC, REDuction/OXidation or REDOX ratio to determine $Fe^{+2}/\sum Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Re concentrations by ICP-MS.
- Analyze the off-gas condensate for all cations and anions by ICP-AES and for Cs, I, and Re by ICP-MS. This may facilitate speciation of the type of carryover occurring, if any. For example Cs may be carried over as vapor as Cs_2O, CsCl, CsF, $CsNO_3$ or as particulates such as $CsAlSiO_4$.
- Rinsing of the off-gas line(s) between the DMR and the condenser is no longer needed since it has been shown that less than 0.05% of any constituent resides in this line during Module C and D testing with the quartz wool filter. The quartz wool is still weighed before and after use to ensure that >0.05% of the product is retained by the filter.
- Perform mass balances on elements of concern with special attention to Cs, I, and Re.

4.4 Simulant Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR granular products. The surface area to volume ratios will be determined once the particle size distribution from the BSR runs for this simulant is known.
- Perform long term ASTM C1285 - PCT on the BSR granular products. Sample and analyze at one, three, six, and TBD month intervals. At the end of each sampling, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. Geochemist's Workbench (GWB).
- Send a subset of the granular product for TCLP testing by a certified EPA laboratory.

- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003)[18].

4.5 Simulant Monolith Production and Product Testing

- Use a portion of the BSR granular products from the non-radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined in EM-31 testing with the earlier Module wastes to produce eight separate 1" x 2" monoliths.
- After curing for 28 days or the appropriate time, perform compression testing on the non-radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.
- Compression test the monoliths with both a penetrometer and the ASTM compression test to calibrate the penetrometer for use with the radioactive monoliths since radioactive ASTM compression testing capability is not available
- Using crushed segments returned from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the BSR monolith products.
- Perform long term ASTM C1285 - PCT on the BSR monolith products. Sample and analyze at one, three, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB.
- Send a subset of the crushed samples from compression testing for TCLP testing by a certified EPA laboratory.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1)[3,4,17].
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths. This is a 90 day test.

4.6 Radioactive BSR Product Formation

- Transport AZ-101/AZ-102 Hanford Waste to the SRNL SCF.
- Perform Treatability Study sample handling and processing in the SCF in accordance with SRNL Procedure Manual L1, 6.04 'Hazardous/Mixed Waste Treatability Studies' and Procedure Manual L29, ITS-0167 'Hanford Treatability Study and Materials Handling'.
- Ensure that enough of the radioactive dopants (Tc^{99}, Cs^{137}, I^{129} or I^{125}) have been procured and available to process the last 100mL of AZ-101/AZ-102.
- Dope all but 100ML of the 1379 mL of the AZ-101/AZ-102 sample with Re and SphereOx
- Analyze the trimmed Tank AZ-101/AZ-102 after doping.
- Dope the remaining 100 mL of the AZ-101/AZ-102 sample with Re, SphereOx, Tc^{99} and I^{127} to the levels needed to achieve 150μg/g of each in the solid samples for EXAFS testing.

- Ship Tc^{99} and I^{127} doped sample to Synchrotron Radiation source defined by customer.
- Determine the BSR operating parameters (clay levels, coal levels, input gases/flow rates) based on the BSR simulant testing. Use OptiKasT kaolin clays at the appropriate ratio to form the desired mineral phases (wet clay basis) and sufficient carbon to provide the necessary reductant (Bestac carbon) for the radioactive BSR campaigns. The carbon will be calculated for the actual amount of NO_3 and NO_2 in the radioactive sample using 1.3X the value calculated by the SRNL developed MINCALC Version #3. Obtain concurrence with the BSR operating parameters from TTT before proceeding with the radioactive BSR operation.
- As necessary, install the BSR in the SCF after preliminary testing in the Shielded Cells Mock-up Facility. If already located in the SCF, install new glass ware and BSR components to perform the radioactive demonstration.
- Run the radioactive BSR in the SCF between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each radioactive doped AZ-101/AZ-102 run will use between 20-120 mL of feed. It is estimated that somewhere around 30 runs are needed to produce enough granular product for analysis and testing. The estimated required granular product mass is ~491 g (eight 1" x 2" monolith cylinders and 220 g of granular product – see Table 3).
- Analyze the BSR product for whole element chemistry of all cations and anions by ICP-AES and IC, REDuction/OXidation or REDOX to determine $Fe^{+2}/\sum Fe$ ratio, XRD for mineral formation, moisture content by LOD at 110°C, and coal determination by LOI at 525°C. Analyze the Cs, I, and Tc concentrations by ICP-MS and/or radiometric methods.
- Analyze the off-gas condensate for Cs, I and Tc by ICP-MS and/or radiometric methods.
- Perform mass balances for Tc, Cs, and I.

4.8 Radioactive Granular Product Durability Testing

- Prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 - PCT on the FBSR granular products.
- Perform long term ASTM C1285 - PCT on the FBSR granular products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides to the alteration phases.
- Send a subset of the granular product (see Table 3) to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003),[4,17,18] to data gathered during Hanford Module A, B, C and D testing, and to the durability response of the non-radioactive granular product produced in this task plan.

4.9 Radioactive Monolith Production and Product Durability Testing

- Use a portion of the BSR granular products from the radioactive campaigns to produce monoliths with the monolithing agent (cement or geopolymer) determined from the simulant monolith testing in this task plan.
- After curing for 28 days, perform compression testing on two radioactive monoliths and analyze for whole element chemistry (all cations and anions) and x-ray diffraction.
- Compression test the monoliths with the pre-calibrated penetrometer.
- Upon passing the compression test at 500 psi ship two of the radioactive monoliths to PNNL (one whole and one broken from compression testing) along with ~162 g of radioactive granular product.
- Using crushed segments from the compression testing, prepare granular sample subsets for ASTM C1285 - PCT. Variation to the standard PCT protocol will be implemented since samples will be wet sieved in ultra pure ethyl alcohol, not sonicated, and not water washed as part of the PCT sample preparation. Analyze the prepared and washed samples for BET surface area, particle size analysis, and skeletal density by pycnometry.
- Perform the short term (seven day) ASTM C1285 – PCT on the BSR radioactive monolith products.
- Perform long term ASTM C1285 - PCT on the BSR radioactive monolith products. Sample and analyze at one, six, and TBD month intervals. At the end of the testing, the secondary alteration phases will be analyzed and the leachates will be analyzed for all components including Al, Fe, Mn, etc. in order to perform geochemical modeling using EQ3/6 or equivalent, e.g. GWB. CSEM with EDS may be performed to determine the partitioning of radionuclides in the alteration phases.
- Send a subset of the crushed samples from compression testing to PNNL for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to the original waste generator, WRPS.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1),[3,17,18] to data gathered during Hanford Module A, B, C, D testing, and in the non-radioactive portion of this task plan.
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths and run for 90 days.

4.10 Data Analysis and Documentation

- Analyze data as each module is completed.
- Provide interim technical reports as necessary to meet WRPS project commitments.
- Draft, approve, and issue a final report(s) after all the phases are complete.

5.0 TASK SCHEDULE

The timing of the individual activities will be maintained in the ERPS schedule. A higher level schedule is also being maintained by WRPS and is being updated on a weekly basis with all parties.

Table 4 summarizes the various runs/campaigns and the associated testing. The acronym in parenthesis after the test method indicates the organization that will perform the analyses. PSAL is denoted separately so that they can plan their resource load accordingly and to distinguish from

AD. The radioactive sample PCTs will be performed by ERPS or SCF personnel if not able to remove the samples from the cells and the leachates will be submitted to AD. Radioactive sample BET and skeletal density will be performed in a glovebox using existing instrumentation maintained by ERPS personnel.

Table 4. Summary of Sample Types and Methods. Required Turnaround Times are in Work Days (* = Calendar Days) and Responsible Organization (A = AD, C = E&CPT/SSP, N = N-Area, O = Offsite, Op - = Optional, P = PSAL, U = E&CPT/PTP)

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Pre-Clay/Coal/Fe (no dissolution)	3																						3 U		
Simulant Pre-Clay/Coal/Fe (AR Digestion)	5	15 A	15 A																						
Simulant Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	4			15 A	2 P																				
Simulant Post-Clay/Coal/Fe	3																							2 U	
Simulant Granular Product Production Subsamples (no dissolution)	20 ‡											2 A	2 P									1 P			
Simulant Granular Product (no dissolution)	3											5 A	3 P	15 A	10 U	180 U					30 O	3 P		2 U	15 A

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Granular Product (AR Digestion)	5	15 A	15 A																						
Simulant Granular Product (PF Digestion)	5	15 A																							
Simulant Granular Product (KOH/H_2O Digest)	4			15 A	2 P																				
Simulant Granular Product PCT Leachates (Non-Acidified)	36			15 A	5 P												3 U	3 U							
Simulant Granular Product PCT Leachates (Acidified)	36	5 P	15 A																						
Simulant Granular Product LT PCT Solids	8											15 A													
Simulant Condensate	3	5 P	15 A	15 A	5 P																				

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Condensate Solids (no digestion)	1										Op	Op													
Simulant Condensate Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Condensate Solids (PF Digestion)	2	5 A																							
Simulant Condensate Solids (KOH/H_2O Digest)	2				15 A																				
Simulant Rinsed Lines	3	5 P	15 A	15 A	5 P																				
Simulant Rinsed Lines Solids	1										Op	Op													
Simulant Rinsed Lines Solids (AR Digestion)	2	5 A	15 A	15 A																					
Simulant Rinsed Lines Solids (PF Digestion)	2	5 A																							

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Simulant Rinsed Lines Solids (KOH/H_2O Digest)	**2**				15 A																				
Simulant Monoliths (no dissolution)	**3**											**15 A**	**3 U**	**15 A**	**10 U**	**180 U**			**5 U**	**90 U**	**30 O**			**2 U**	**15 A**
Simulant Monoliths (AR Digestion)	**9**	**15 A**	**15 A**																						
Simulant Monoliths (PF Digestion)	**9**	**15 A**																							
Simulant Monoliths (KOH/H_2O Digest)	**4**			**15 A**	**2 P**																				
Simulant Monoliths PCT Leachates (Non-Acidified)	**36**			**15 A**	**5 P**												**3 U**	**3 U**							
Simulant Monoliths PCT Leachate (Acidified)	**36**	**5 P**	**15 A**																						
Simulant Monoliths LT PCT Solids	**8**											**15 A**													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Feed Pre-Clay/Coal/Fe (no dissolution)	**4**						2 **A**	20 **A**	20 **A**														**3** **U**		
Radioactive Feed Pre-Clay/Coal/Fe Solids												5 **A**													
Radioactive Feed Pre-Clay/Coal/Fe (AR Digestion)	**5**	5 **A**	5 **A**							20 **A**															
Radioactive Feed Pre-Clay/Coal/Fe (PF Digestion)	**5**	5 **A**																							
Radioactive Feed Pre-Clay/Coal/Fe (KOH/H_2O Digest or Wt. Dil.)	**4**				2 **A**																				
Radioactive Feed Post-Clay/Coal/Fe	**2**																							2 **U**	
Radioactive Granular Product Production Subsamples (no dissolution)	**30** **‡**											2 **A**	2 **U**									1 **U**			

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Granular Product (no dissolution)	3								20 A		15 A	15 A	3 U	15 C	10 U	180 U					30 O	15 A		15 U	15 A
Radioactive Granular Product (AR Digestion)	9	15 A	15 A			15 A				20 A															
Radioactive Granular Product (PF Digestion)	9	15 A						20 A																	
Radioactive Granular Product (KOH/H_2O Digest)	4				15 A																				
Radioactive Granular Product PCT Leachates (Non-Acidified)	36				15 A	15 A											3 U	3 U							
Radioactive Granular Product PCT Leachates (Acidified)	36	15 A	15 A					20 A	20 A	20 A															
Radioactive Granular Product LT PCT Solids	6											15 A													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Condensate	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Condensate Solids (no digestion)	2								20 A		Op	Op													
Radioactive Condensate Solids (AR Digestion)	2	15 A	15 A					20 A	20 A	20 A															
Radioactive Condensate Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Condensate Solids (KOH/H_2O Digest)	2				15 A																				
Radioactive Rinsed Lines	3	15 A	15 A		15 A			20 A	20 A	20 A															
Radioactive Rinsed Lines Solids (no dissolution)	2								20 A		Op	Op													

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Rinsed Lines Solids (AR Digestion)	2	15 A	15 A							20 A															
Radioactive Rinsed Lines Solids (PF Digestion)	2	15 A						20 A																	
Radioactive Rinsed Lines Solids (KOH/H_2O Digest)					15 A																				
Radioactive Monolith (no dissolution)	3								20 A			15 A	3 U	15 C	10 U	180 U			5 U	90 U	30 O			2 U	15 A
Radioactive Monolith (AR Digestion)	9	15 A	15 A			15 A				20 A															
Radioactive Monolith (PF Digestion)	9	15 A						20 A																	
Radioactive Monolith (KOH/H_2O Digest)	4				15 A																				

	No. of Samples†	ICP-AES	ICP-MS	ICP-MS Iodide	IC ANIONS	AA Se/As	Total Base & TIC	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	CONDUCTIVITY	pH	COMPRESSION	ASTM 1308*	TCLP*	REDOX	WT% SOLIDS	DENSITY	MICROTRAC
Radioactive Monolith PCT Leachates (Non-Acidified)	**36**				15 A	15 A											3 U	3 U							
Radioactive Monolith PCT Leachates (Acidified)	**36**	15 A	15 A					20 A	20 A	20 A															
Radioactive Monolith LT PCT Solids	**6**											15 A													

† Sample count includes blanks and standards.

‡ Sample count does not apply to XRD sample which will not be submitted in duplicate for these samples.

6.0 RESEARCH FACILITY PLANNING

6.1 Effects of the Task on Equipment, Personnel, and Research Facilities' Physical Plant

The receipt, analyses, and handling of radioactive samples such as the AZ-101/AZ-102 salt supernate are routine tasks performed in the Shielded Cells. The entire task will be evaluated using the SRNL Conduct of R&D Manual. A calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution. An e-mail will be sent to the coordinator for the Radionuclide Inventory – Administrative Control (RI-AC) computer system to make sure the use of these samples for this testing is within the authorization basis of the SRNL Documented Safety Analysis (DSA).

Activities surrounding the analysis of the samples and the running of the BSR will be shown on the SRNL Shielded Cells Operations and ERPS schedules. Appropriate documentation will be completed prior to the start of activities.

Activities need to stay on schedule to support WRPS's supplemental LAW treatment technology selection.

Because the AZ-101/AZ-102 waste is an Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) listed waste, special procedures for handling and segregating this waste are being implemented in SRNL including a tracking mechanism for all samples, and sample residues.[23]

6.2 Products and By-Products of Task

Any solids created by the radioactive sample processing will be stored in a Satellite Accumulation Area (SAA) at the end of the treatability study. It is anticipated that all the AZ-101/AZ-102 will be processed and there will be no AZ-101/AZ-102 to return to Hanford. Disposition and return of solids to Hanford after analysis will be accomplished through consultation with the SRNL Environmental Compliance Authority (ECA) and in compliance with the EEC. All remaining solutions (from condensates derived from the BSR process and from the dissolutions of the product for analyses and from PCT leachates) and solid residues from completed testing will be returned to Hanford. All job control waste will be disposed of as manifested waste returns to Hanford. Some solid samples will be retained at SRNL for follow on characterization and testing after the treatability study has ended, i.e. under the "sample exclusion." Residues (liquid and solid) from this characterization and testing will also be tracked and the residues returned to Hanford. ERPS will work with the SRNL ECA to disposition these residues.

Samples for PNNL, except those for Synchrotron testing, will be sent after the treatability study has ended, i.e. once the samples have been archived, they will be sent to PNNL under the sample exclusion rule rather than as part of the treatability study.

Disposition of Test Equipment

Upon completion of the radioactive BSR processing additional follow-on work is to be performed, i.e., radioactive Hanford LAW processing and the equipment will remain in the SCF. However, non-containers that come in contact with the Hanford material will

be treated as job control waste for that stream. The simulant BSR will also be used for additional testing and thus will remain set-up until subsequent Hanford testing is completed.

6.3 Exposure of Personnel

Samples that are radioactive will be handled remotely in the Shielded Cells. Samples with high levels of radiation that have to be removed from the Shielded Cells for analyses by AD will be diluted in the cells so that only a small portion of the radioactivity is removed from the cell. If the BSR products are at a low enough radiation level to be handled in SRNL radioactive hoods (i.e., meet existing hood limits), they will be removed from the Shielded Cells and handled in ERPS laboratories. This includes preparation for characterization, production of the monoliths, and testing of the granular and monolith products. The radioactive samples may be contact handled by Shielded Cells technicians, ERPS personnel (in radioactive hoods and radiobenches), and AD technicians (in radioactive hoods and radiobenches). These samples will be controlled and comply with standing radiological work plans. If a sample is expected to exceed standing radiological work plan limits, a job specific radiological work plan will be implemented after implementation of all engineering and administrative controls and when no other choice exists.

7.0 PROGRAMMATIC RISK REVIEW

Per the L1 manual, Procedure 7.10, a programmatic risk review has been performed for the tasks listed in this TTQAP. The SRNL Conduct of R&D manual will be used to complete a review for all tasks listed in the TTQAP. Results of the risk review are given below in Table 5.

Table 5. Programmatic Risk Review

Question	Response
Could an inadvertent or premature failure of equipment result in unacceptable added programmatic costs or schedule delays?	Yes. All preventive measures will be taken in order to maintain schedule and budget. Back-up BSR equipment has been procured. Spare parts are available for the components. One spare controller is available and two spare Mass Spectrometers are being procured. A schedule delay would be experienced to place the backup or new equipment into service and recover from the point of failure. A delay in the return to service date of any SRNL – AD analytical instrumentation will result in a schedule delay since back-up options for most of the required analyses are limited.
Is the activity on a critical path or is the activity significant to a major site program/process, milestone, or objective?	No. However, this activity is in support of a multi-year DOE EM-31 funded proposal and is on a critical path for Hanford Waste Form Qualification (WFQ) and the WRPS Supplemental LAW Treatment selection.
Does the activity involve long lead time items whose failure would exceed the allowable programmatic schedule?	Yes. Failure of the controller system or the Mass Spectrometer before the spare is obtained and operational will result in a delay to the program. In addition, an AD instrumentation failure(s) resulting in the need for replacement equipment would exceed the allowable programmatic schedule.
Does this activity involve high risk technology whose development, if not successful, could exceed allowable programmatic cost or schedule?	No. The technology has been used for previous experimentation and the primary change is the feed stream. Decisions will be made for the remaining Hanford BSR program based on the results of this program. Decisions will be made for Hanford implementing this technology as the supplemental technology for LAW at Hanford based on the results of this program.
Could the activity or failure of the activity significantly impact the facility or other programs in proximity of the activity?	Potential exists. Cells 3 and 4 of the Shielded Cells will be dedicated to the BSR runs for several months. This could impact needed space for other SRR and EM programs. Cell 6 may be used for analytical support if needed. This could impact the analytical support for other sample processing that will be going on at the same time. If Cell 6 is not used, then resources (i.e., hoods in ERPS laboratories) will be utilized which may impact other programs. During the running of the BSR in the SCF, facility support will be required to monitor the SCF ventilation system since the BSR system generates appreciable quantities of flammable hydrogen. No physical impacts to the facility are anticipated.
If quantities of accountable radioisotopes (per L7.7, 1.07) are received into the SRNL facilities, what impact will the planned activity have on SRNL facilities?	The AZ-101/AZ-102 sample has already been received at SRNL. However, a calculation will be performed to estimate the reportable and/or accountable radionuclides in the solution prior to use and after doping with the necessary quantities of additives. If any radionuclide quantity is predicted to exceed the SRNL reportable quantities, the appropriate section of procedure 1.07 of the L7.7 manual will be followed. An e-mail will be sent to the coordinator for the RIAC database system to make sure the receipt of these samples is within the authorization basis of the SRNL DSA. If the sample has an impact on the Authorization Basis, a schedule delay would be experienced though not expected.

8.0 R&D HAZARDS SCREENING

Before any laboratory work is initiated, a review of L1, 7.02, will be performed to determine the hazards and controls required. At a minimum, three HAPs are expected to be generated to support this task.

9.0 QUALITY ASSURANCE

9.1 Documents Requiring Requester Approval

Document	Management		Customer		QA	
	Yes	No	Yes	No	Yes	No
Task Technical and QA Plan	X			X	X	
Final Report	X		X			X

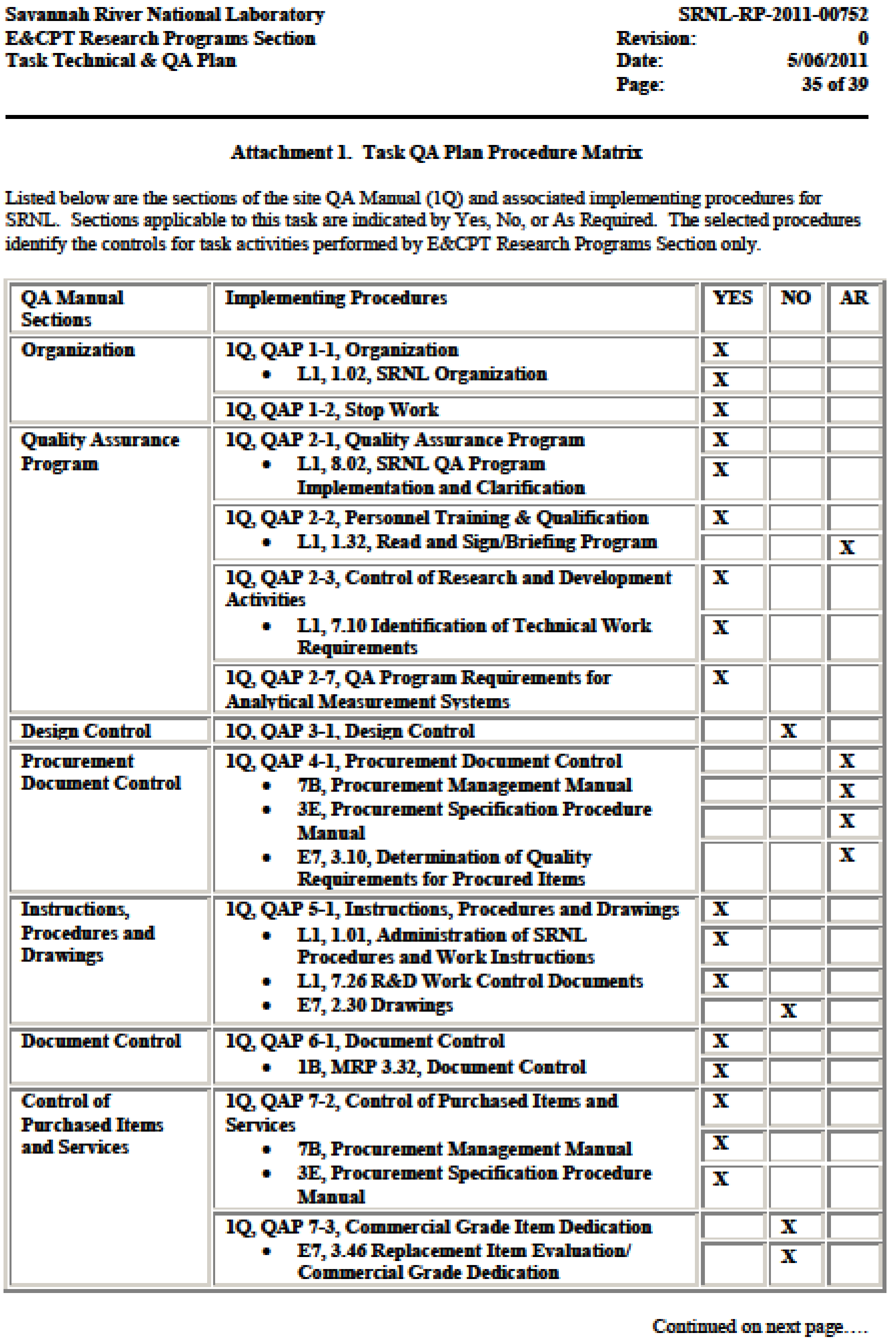
9.2 Records Generated During Task Performance

Description	YES	NO	AR*
Task Technical and QA Plan	X		
Controlled Laboratory Notebooks	X		
Task Technical Reports	X		
Data Qualification Reports		X	
Supporting Documentation			X

*** AR = As Required**

9.3 Task QA Plan Procedure Matrix

See Attachment 1.



Attachment 1. Task QA Plan Procedure Matrix

Listed below are the sections of the site QA Manual (1Q) and associated implementing procedures for SRNL. Sections applicable to this task are indicated by Yes, No, or As Required. The selected procedures identify the controls for task activities performed by E&CPT Research Programs Section only.

QA Manual Sections	Implementing Procedures	YES	NO	AR
Organization	**1Q, QAP 1-1, Organization**	**X**		
	• **L1, 1.02, SRNL Organization**	**X**		
	1Q, QAP 1-2, Stop Work	**X**		
Quality Assurance Program	**1Q, QAP 2-1, Quality Assurance Program**	**X**		
	• **L1, 8.02, SRNL QA Program Implementation and Clarification**	**X**		
	1Q, QAP 2-2, Personnel Training & Qualification	**X**		
	• **L1, 1.32, Read and Sign/Briefing Program**			**X**
	1Q, QAP 2-3, Control of Research and Development Activities	**X**		
	• **L1, 7.10 Identification of Technical Work Requirements**	**X**		
	1Q, QAP 2-7, QA Program Requirements for Analytical Measurement Systems	**X**		
Design Control	**1Q, QAP 3-1, Design Control**		**X**	
Procurement Document Control	**1Q, QAP 4-1, Procurement Document Control**			**X**
	• **7B, Procurement Management Manual**			**X**
	• **3E, Procurement Specification Procedure Manual**			**X**
	• **E7, 3.10, Determination of Quality Requirements for Procured Items**			**X**
Instructions, Procedures and Drawings	**1Q, QAP 5-1, Instructions, Procedures and Drawings**	**X**		
	• **L1, 1.01, Administration of SRNL Procedures and Work Instructions**	**X**		
	• **L1, 7.26 R&D Work Control Documents**	**X**		
	• **E7, 2.30 Drawings**		**X**	
Document Control	**1Q, QAP 6-1, Document Control**	**X**		
	• **1B, MRP 3.32, Document Control**	**X**		
Control of Purchased Items and Services	**1Q, QAP 7-2, Control of Purchased Items and Services**	**X**		
	• **7B, Procurement Management Manual**	**X**		
	• **3E, Procurement Specification Procedure Manual**	**X**		
	1Q, QAP 7-3, Commercial Grade Item Dedication		**X**	
	• **E7, 3.46 Replacement Item Evaluation/ Commercial Grade Dedication**		**X**	

Continued on next page….

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Identification and Control of Items	1Q, QAP 8-1, Identification and Control of Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Control of Processes	1Q, QAP 9-1, Control of Processes		X	
	1Q, QAP 9-2, Control of Nondestructive Examination		X	
	1Q, QAP 9-3, Control of Welding and Other Joining Processes		X	
	1Q, QAP 9-4, Work Planning and Control		X	
	• 1Y, 8.20, Work Control Procedure		X	
Inspection	1Q, QAP 10-1, Inspection		X	
	• L1, 8.10, Inspection		X	
Test Control	1Q, QAP 11-1, Test Control		X	
Control of Measuring and Test Equipment	1Q, QAP 12-1, Control of Measuring and Test Equipment	X		
	1Q, QAP 12-2, Control of Installed Process Instrumentation		X	
	1Q, QAP 12-3, Control and Calibration of Radiation Monitoring Equipment (not applicable to ERPS)		X	
Packaging, Handling, Shipping and Storage	1Q, QAP 13-1, Packaging, Handling, Shipping and Storage	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
Inspection, Test, and Operating Status	1Q, QAP 14-1, Inspection, Test, and Operating Status		X	
	• L1, 8.02 SRNL QA Program Implementation and Clarification		X	
Control of Nonconforming Items	1Q, QAP 15-1, Control of Nonconforming Items			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Corrective Action System	1Q, QAP, 16-3			X
	• 1B, MRP 4.23, Corrective Action Program			X
Quality Assurance Records	1Q, QAP 17-1, Quality Assurance Records Management	X		
	• L1, 8.02 SRNL QA Program Implementation and Clarification	X		
	• L1, 7.16, Laboratory Notebooks and Logbooks	X		

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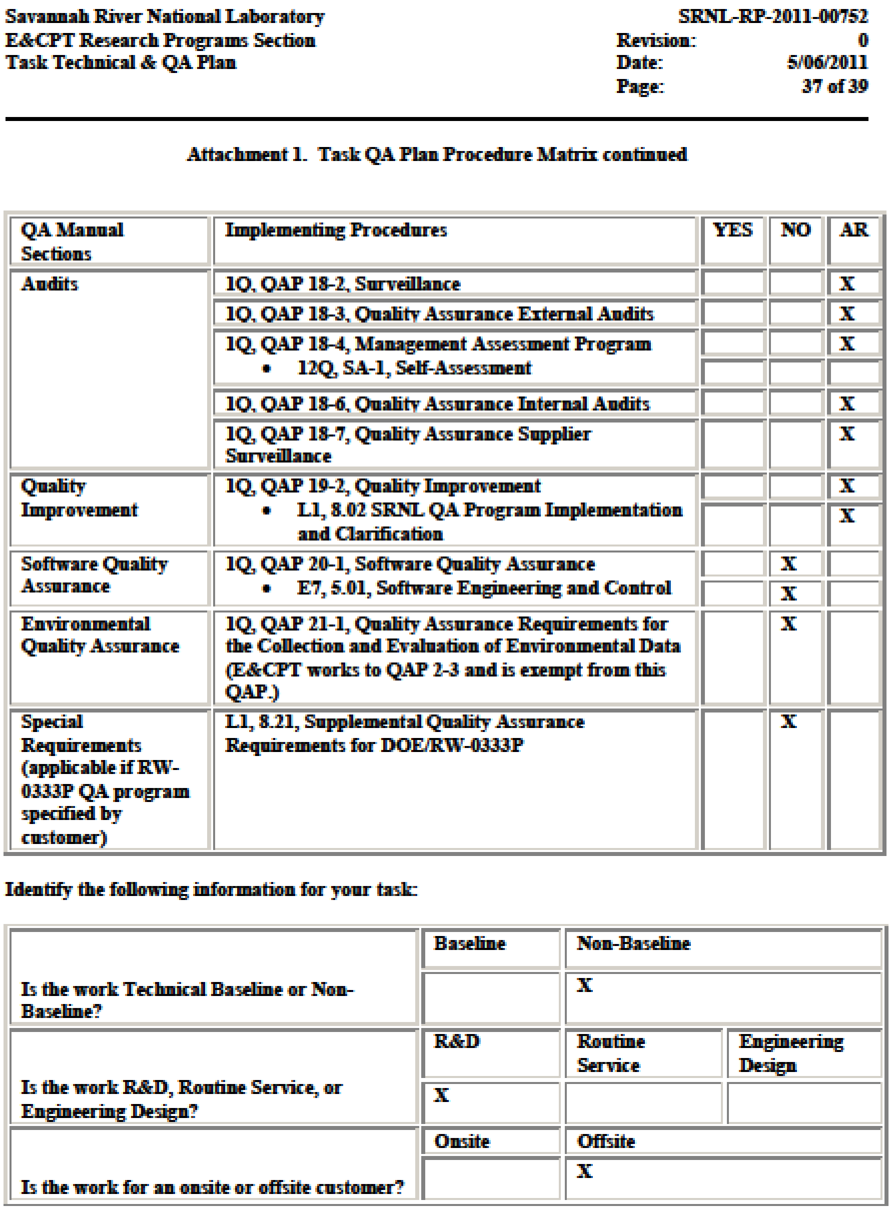

Savannah River National Laboratory
E&CPT Research Programs Section
Task Technical & QA Plan

SRNL-RP-2011-00752
Revision: 0
Date: 5/06/2011
Page: 37 of 39

Attachment 1. Task QA Plan Procedure Matrix continued

QA Manual Sections	Implementing Procedures	YES	NO	AR
Audits	1Q, QAP 18-2, Surveillance			X
	1Q, QAP 18-3, Quality Assurance External Audits			X
	1Q, QAP 18-4, Management Assessment Program			X
	• 12Q, SA-1, Self-Assessment			
	1Q, QAP 18-6, Quality Assurance Internal Audits			X
	1Q, QAP 18-7, Quality Assurance Supplier Surveillance			X
Quality Improvement	1Q, QAP 19-2, Quality Improvement			X
	• L1, 8.02 SRNL QA Program Implementation and Clarification			X
Software Quality Assurance	1Q, QAP 20-1, Software Quality Assurance		X	
	• E7, 5.01, Software Engineering and Control		X	
Environmental Quality Assurance	1Q, QAP 21-1, Quality Assurance Requirements for the Collection and Evaluation of Environmental Data (E&CPT works to QAP 2-3 and is exempt from this QAP.)		X	
Special Requirements (applicable if RW-0333P QA program specified by customer)	L1, 8.21, Supplemental Quality Assurance Requirements for DOE/RW-0333P		X	

Identify the following information for your task:

Is the work Technical Baseline or Non-Baseline?	Baseline	Non-Baseline	
		X	
Is the work R&D, Routine Service, or Engineering Design?	R&D	Routine Service	Engineering Design
	X		
Is the work for an onsite or offsite customer?	Onsite	Offsite	
		X	

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Appendix D. BSR Process Operation Conditions & Trends for Simulant Module C Runs

Table D - 1. BSR Process Operation Conditions & Results for Simulant C Accepted Runs

Run Date	**12/13/10 days**	**12/13/10 nights**	**12/16/10**	**1/20/11 days**	**1/20/11 nights**	**1/25/11**
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Coal (stoichiometry)	1.3x	1.72x	2.56x	2.56x	2.56x	2.56x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	15.5	MS problem	MS problem	15.2	na	13.6
CO_2/ml	27.8	27.8	na	39.2	40.68	37
Post Feed Run Time (min)	127	211	120	120	180	130
Product REDOX	0.254	0.197	0.331	0.224	0.414	0.194
Product LOI	0.87%	0.50%	1.51%	1.02%	1.90%	0.84%
Product Quantity (g)	33.35	38.19	34.38	26.79	31.40	25.03
Feed Quantity (g)	110.48	108.70	103.56	96.30	98.25	94.99

na = not available

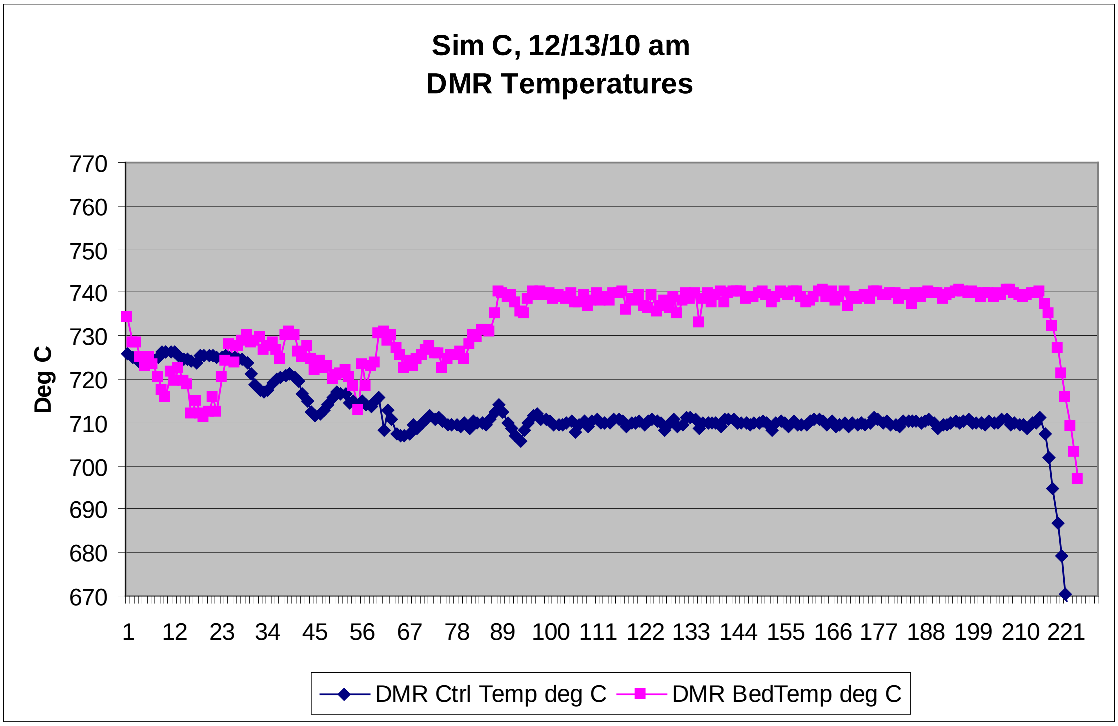

Figure D - 1. Run 12/13/10 days Temperatures in DMR

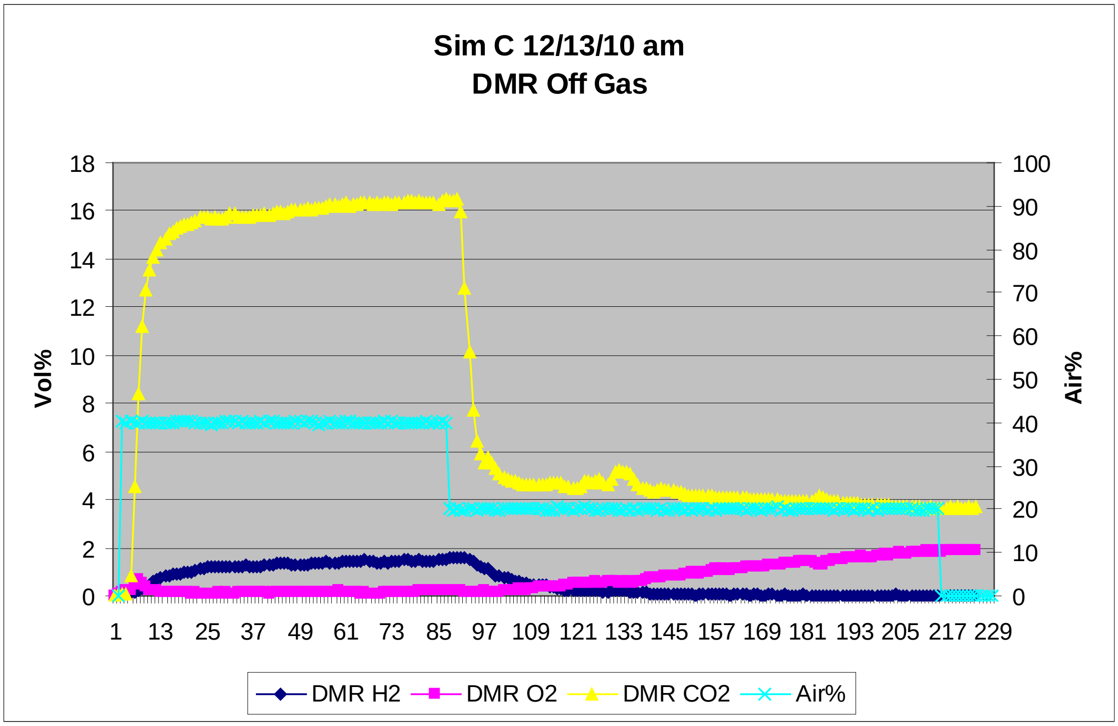

Figure D - 2. Run 12/13/10 days Off-gas Concentrations and Air% Fed

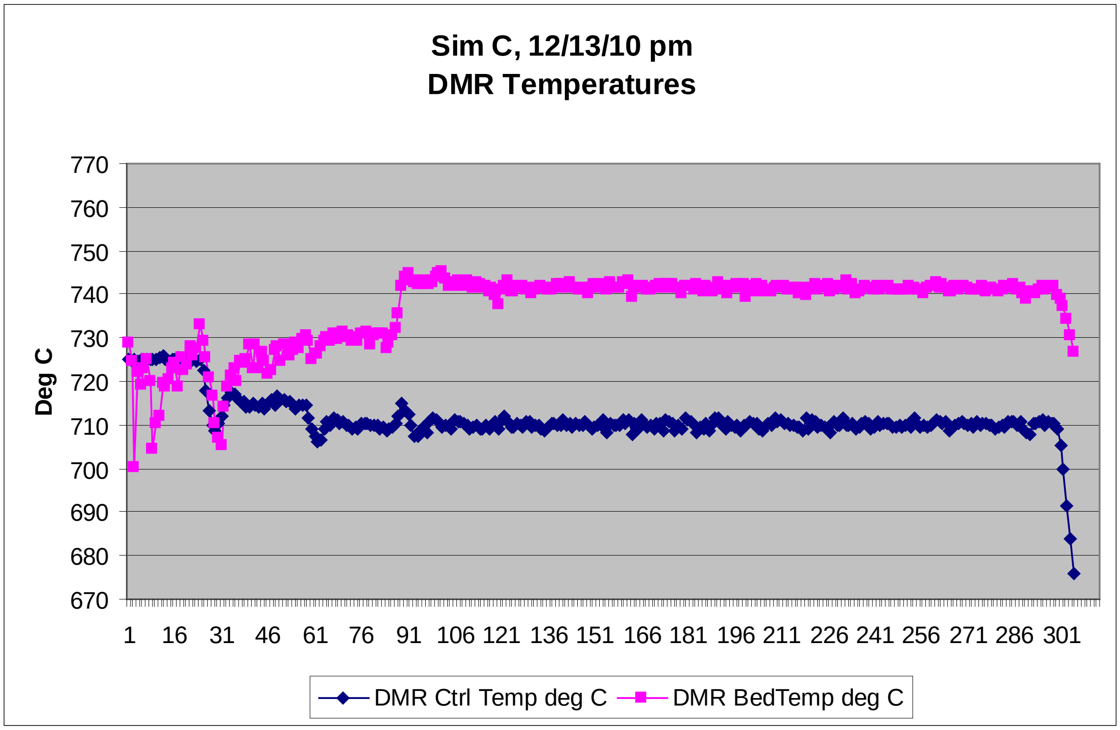

Figure D - 3. Run 12/13/10 Nights Temperatures in DMR

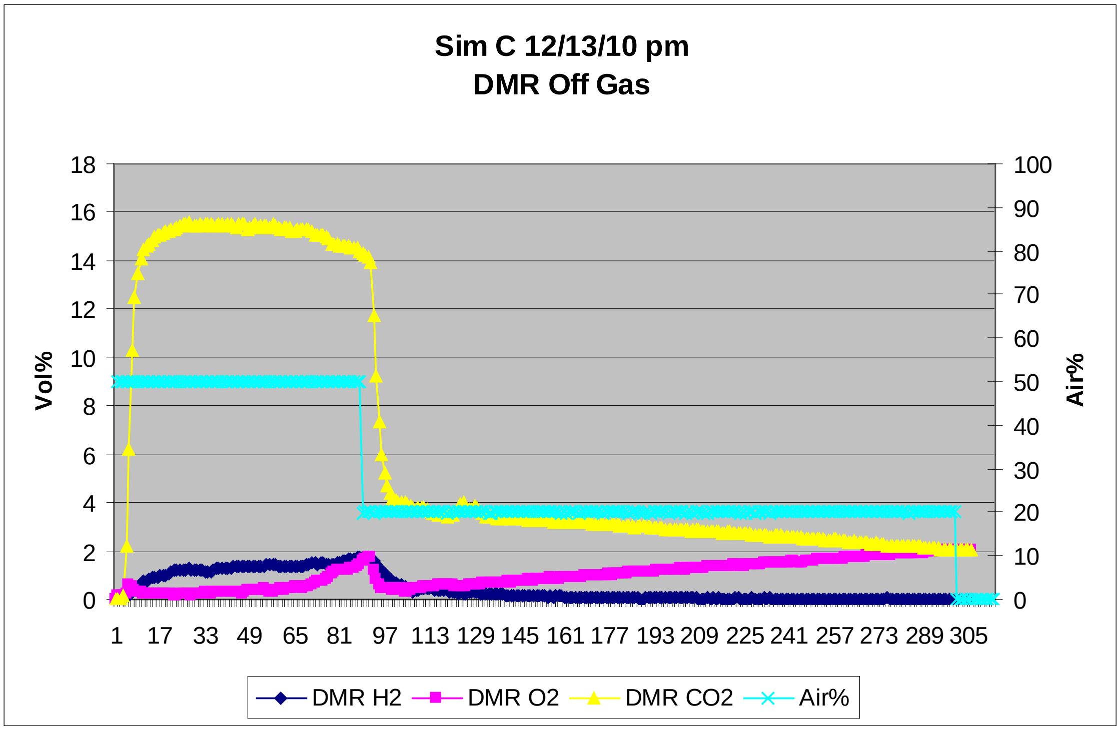

Figure D - 4. Run 12/13/10 Nights Off-gas Concentrations and Air% Fed

Appendix E. BSR Process Operation Conditions & Trends for Radioactive Module C Runs

Table E - 1. BSR Process Operation Conditions & Results for Radioactive C Accepted Runs

Run Date	**1/26/11**	**1/29/11**	**1/31/11**	**2/2/11**	**2/3/11**	**2/4/11**	**2/6/11**
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4	-4
Coal (stoichiometry)	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500	500
CO_2/ml	27.8	27.8	27.8	28.8	26.5	25.9	25.2
Post Feed Run Time (min)	106	125	173	60	198	210	200
Product REDOX	0.290	0.522	0.363	0.145	0.127	0.090	0.091
Product LOI	1.66%	1.50%	1.58%	0.80%	1.58%	2.23%	0.29%
Product Quantity (g)	27.27	28.32	24.33	31.46	34.57	34.56	31.14
Feed Quantity (g)	95.46	93.88	83.42	90.30	106.00	104.68	99.44
Run Date	**2/11/11**	**2/17/11**	**2/19/11**	**2/20/11**	**2/23/11**	**2/24/11**	
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9	
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40	
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4	
Coal (stoichiometry)	1.84x	1.54x	1.54x	1.54x	1.54x	1.54x	
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500	
CO_2/ml	na	na	37.4	36.9	36.9	31.5	
Post Feed Run Time (min)	107	180	240	240	188	240	
Product REDOX	0.254	0.395	0.159	0.168	0.244	0.388	
Product LOI	4.32%	3.67%	2.85%	4.75%	3.55%	3.35%	
Product Quantity (g)	17.78	20.15	21.06	23.67	22.68	24.37	
Feed Quantity (g)	65.42	76.85	73.92	86.57	71.65	98.18	

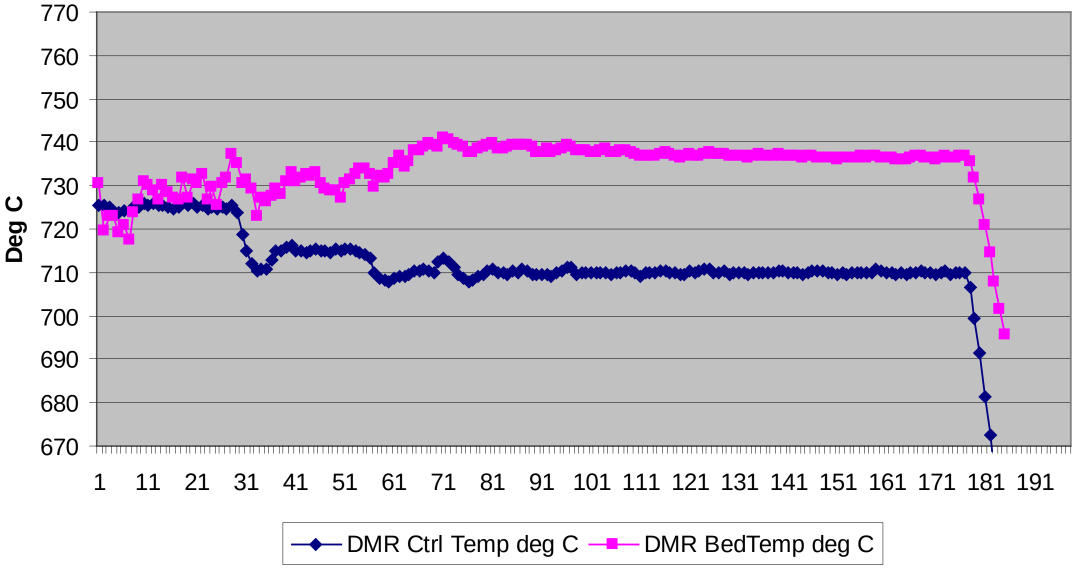

Figure E - 1. Run 1/26/11 Temperatures in DMR

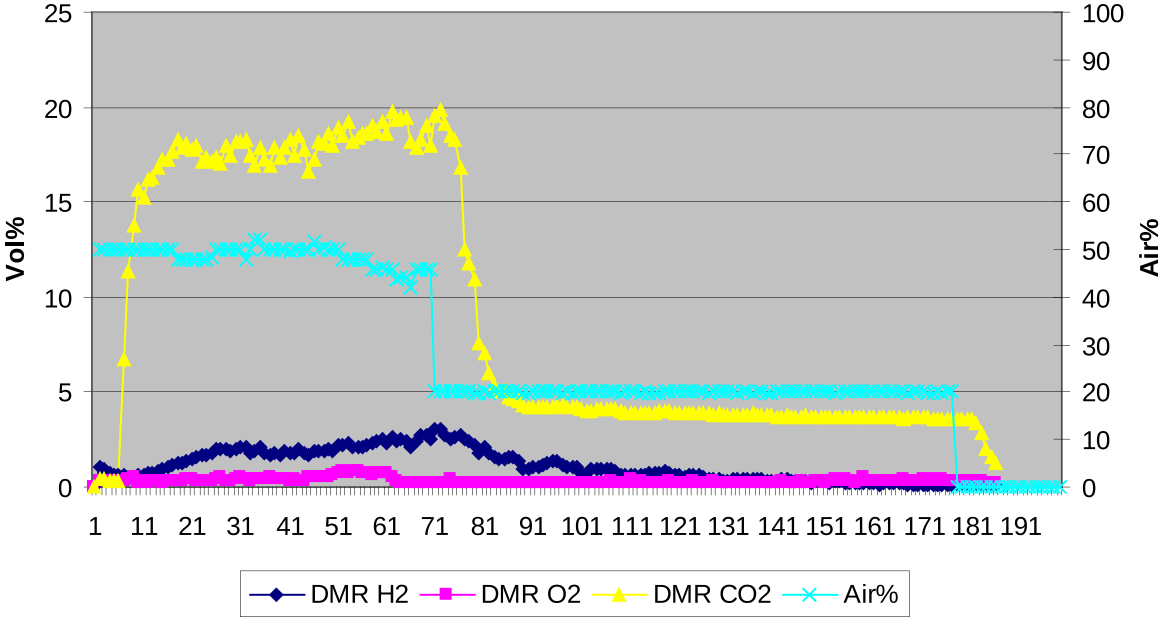

Figure E - 2. Run 1/26/11 Off-gas Concentrations and Air% Fed

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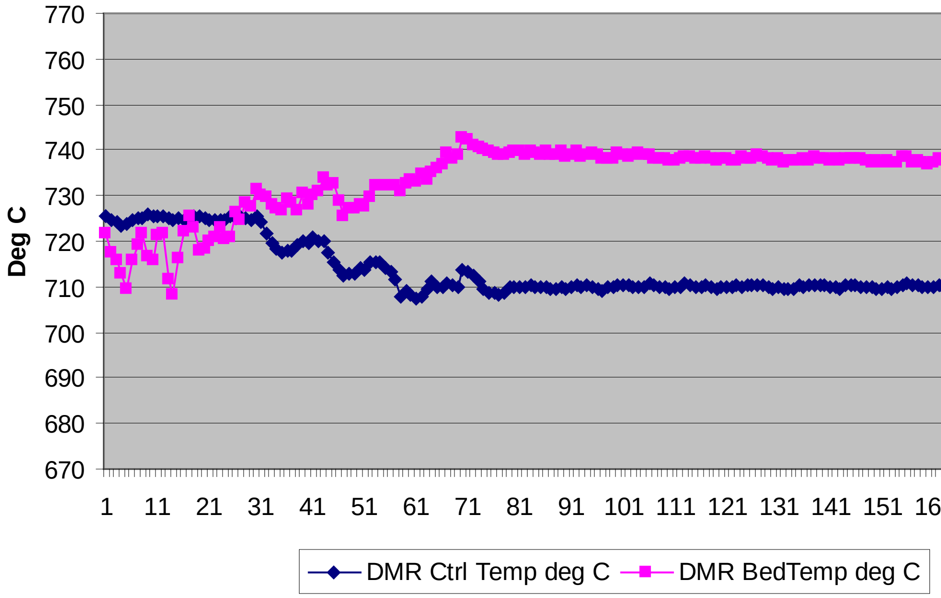

Figure E - 3. Run 1/29/11 Temperatures in DMR

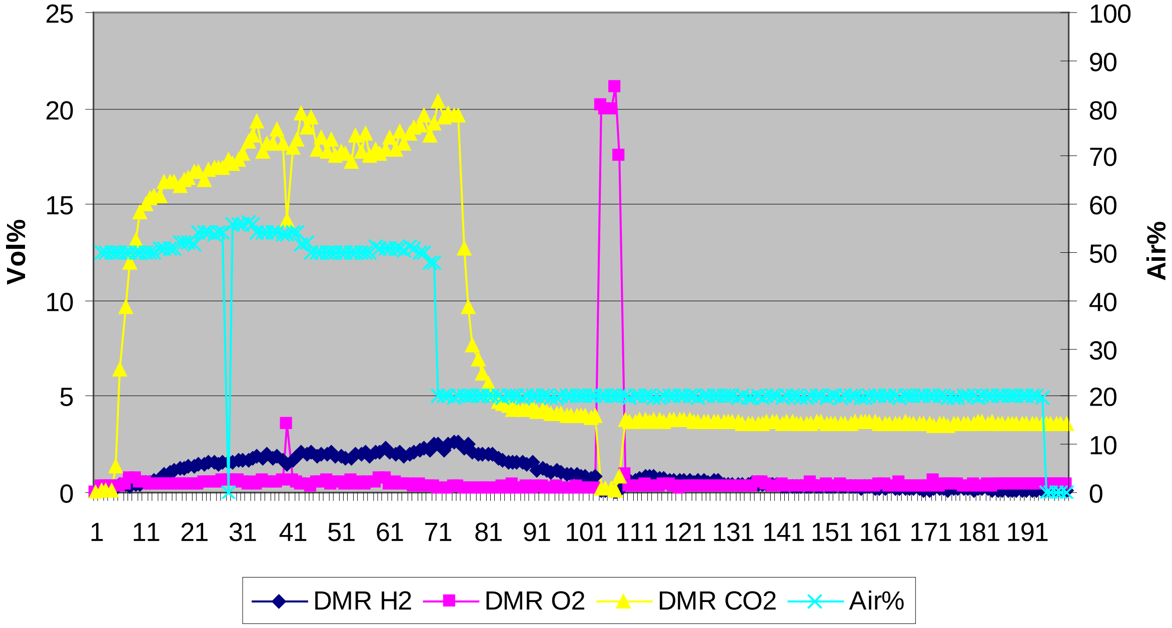

Figure E - 4. Run 1/29/11 Off-gas Concentrations and Air% Fed

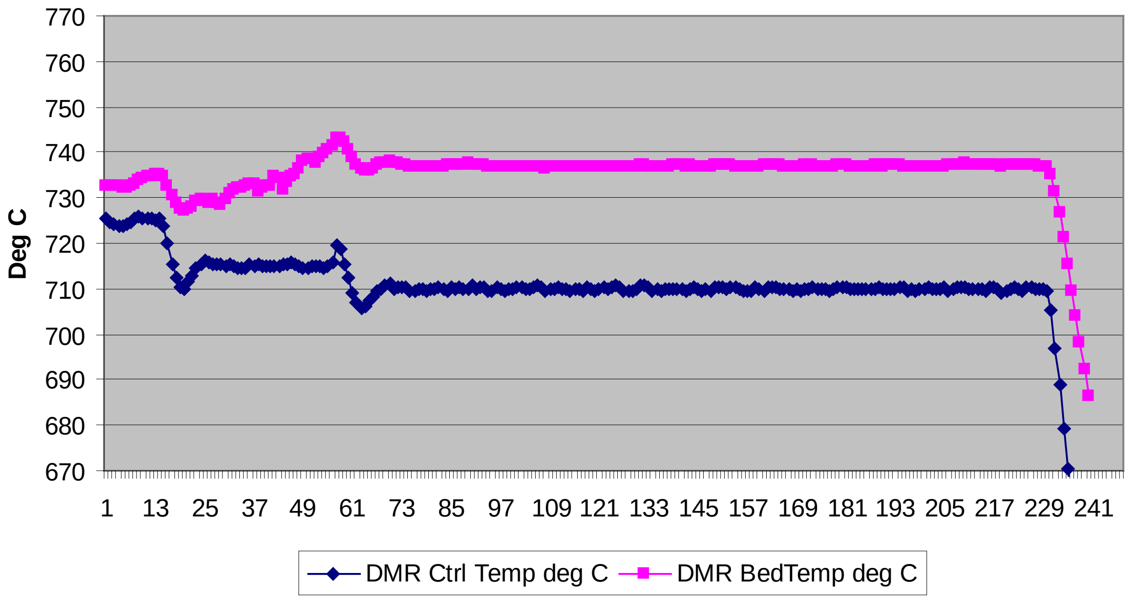

Figure E - 5. Run 1/31/11 Temperatures in DMR

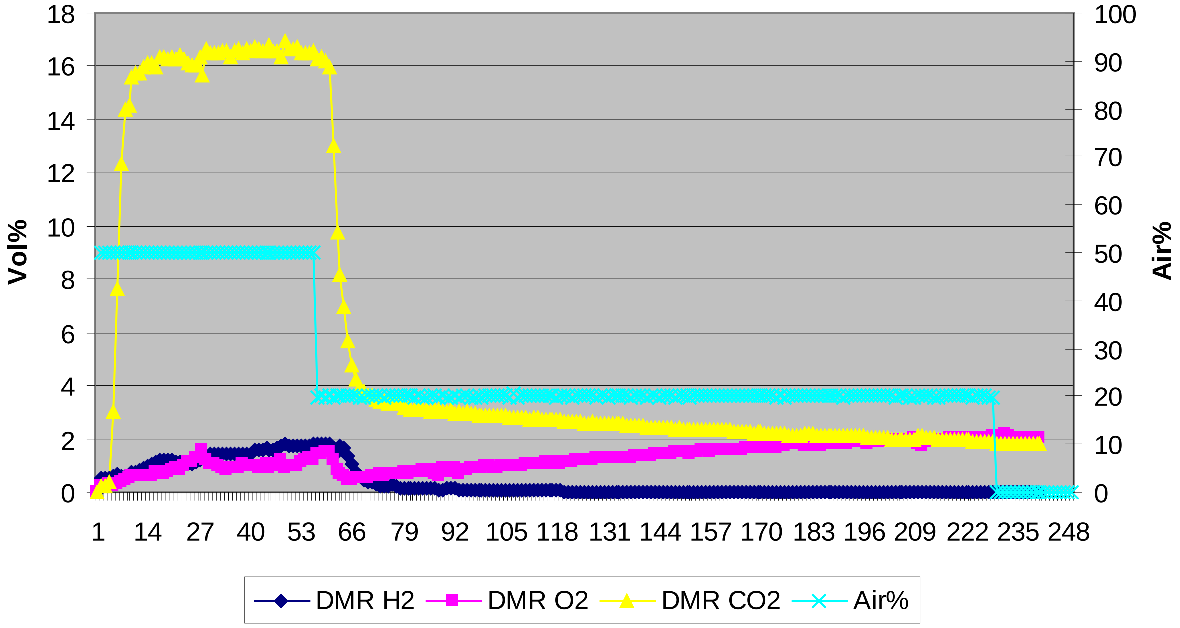

Figure E - 6. Run 1/31/11 Off-gas Concentrations and Air% Fed

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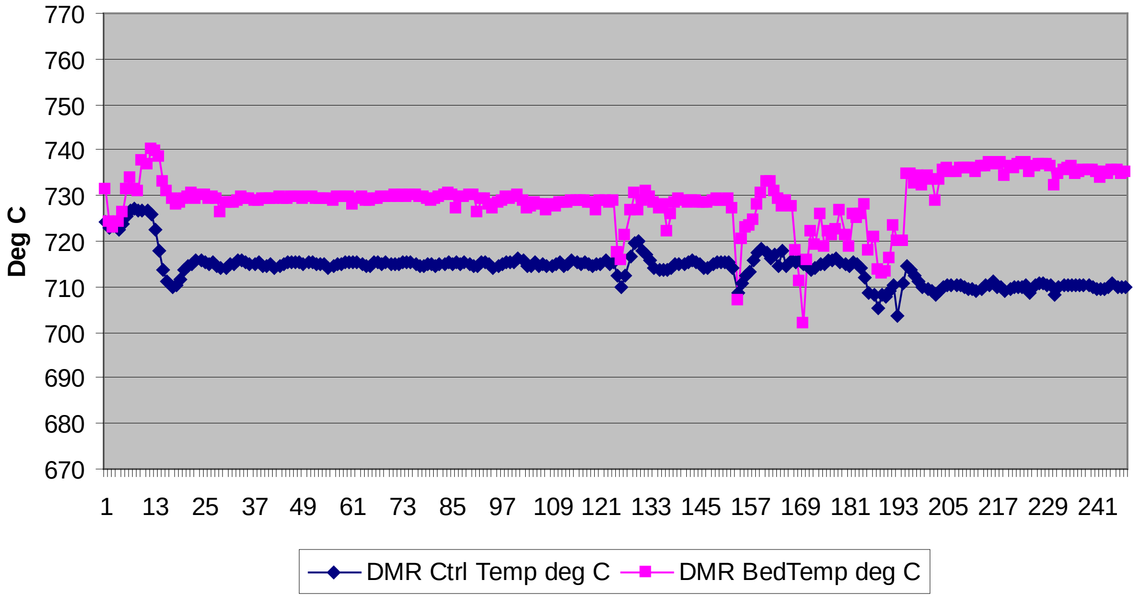

Figure E - 7. Run 2/2/11 Temperatures in DMR

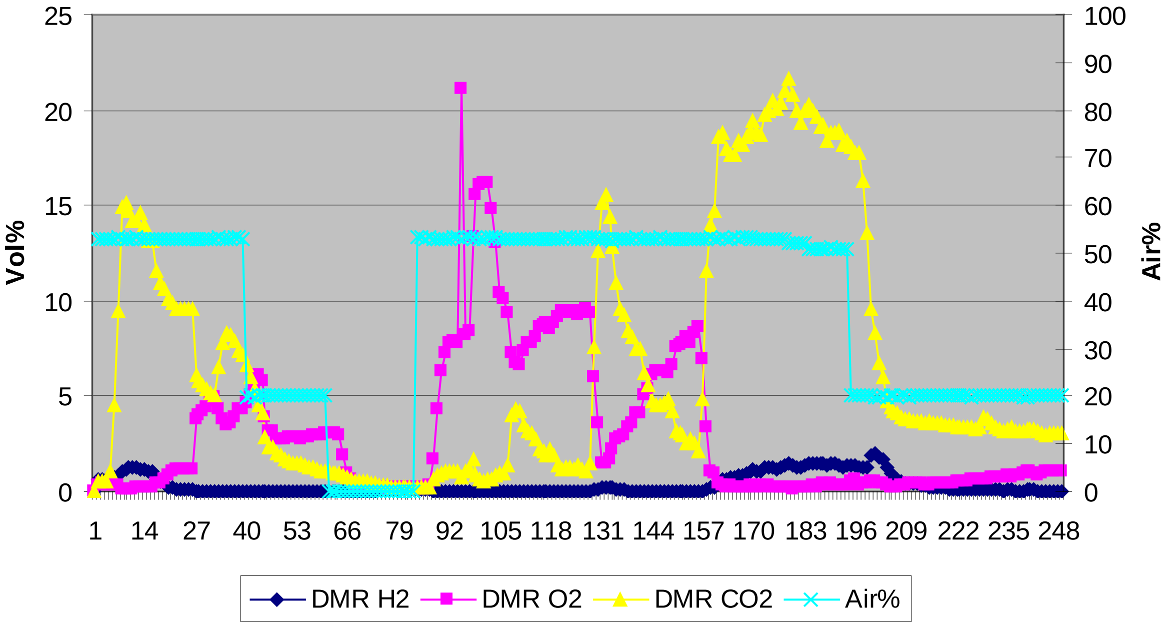

Figure E - 8. Run 2/2/11 Off-gas Concentrations and Air% Fed

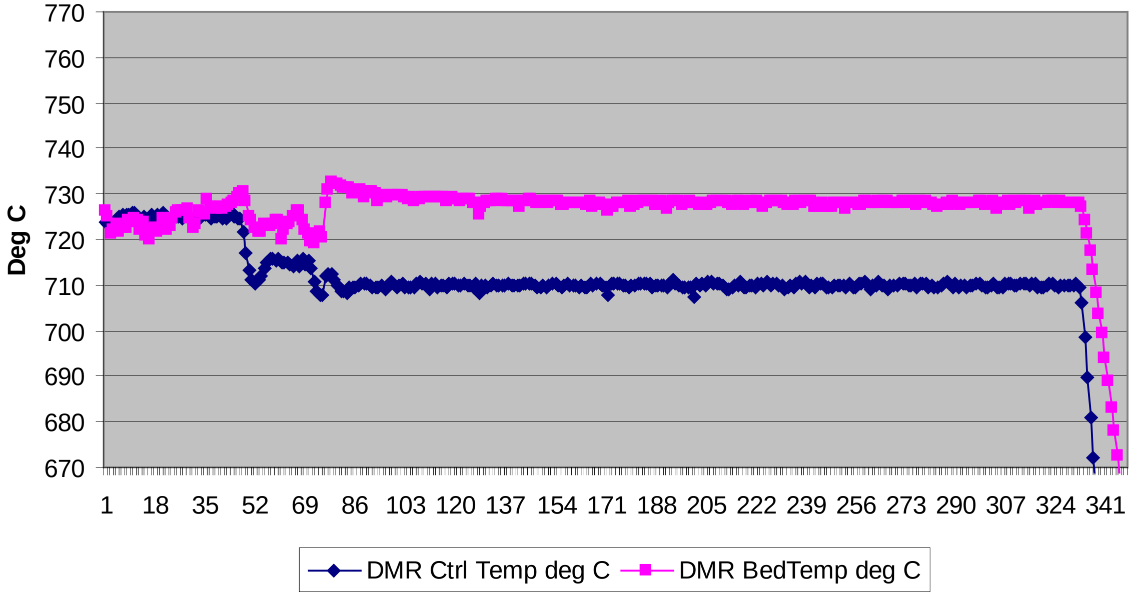

Figure E - 9. Run 2/3/11 Temperatures in DMR

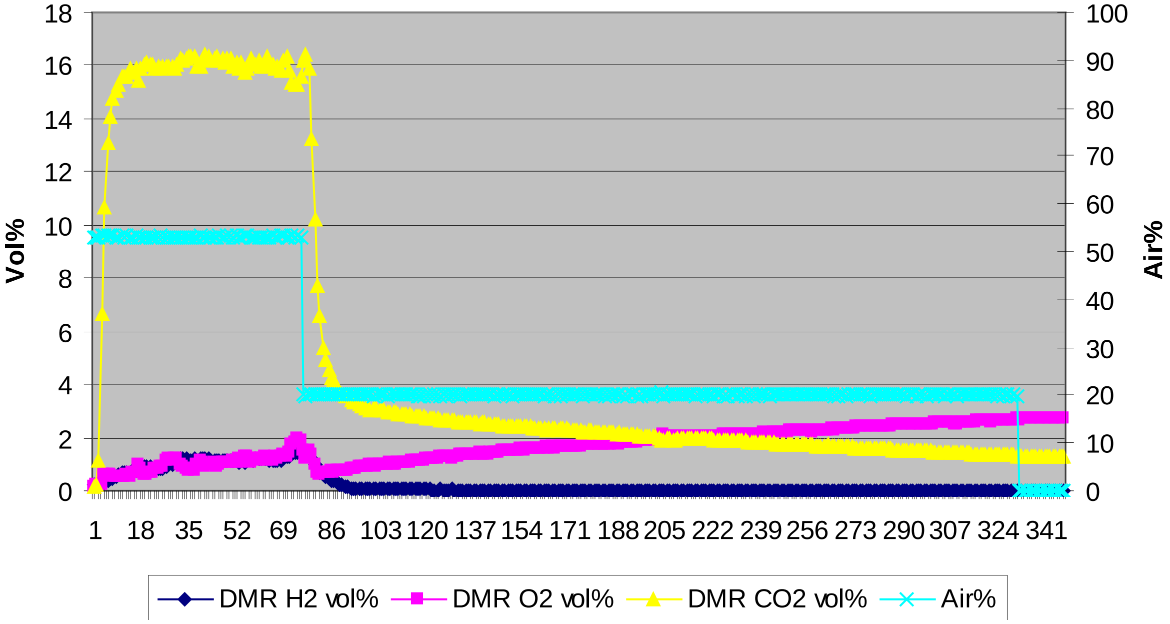

Figure E - 10. Run 2/3/11 Off-gas Concentrations and Air% Fed

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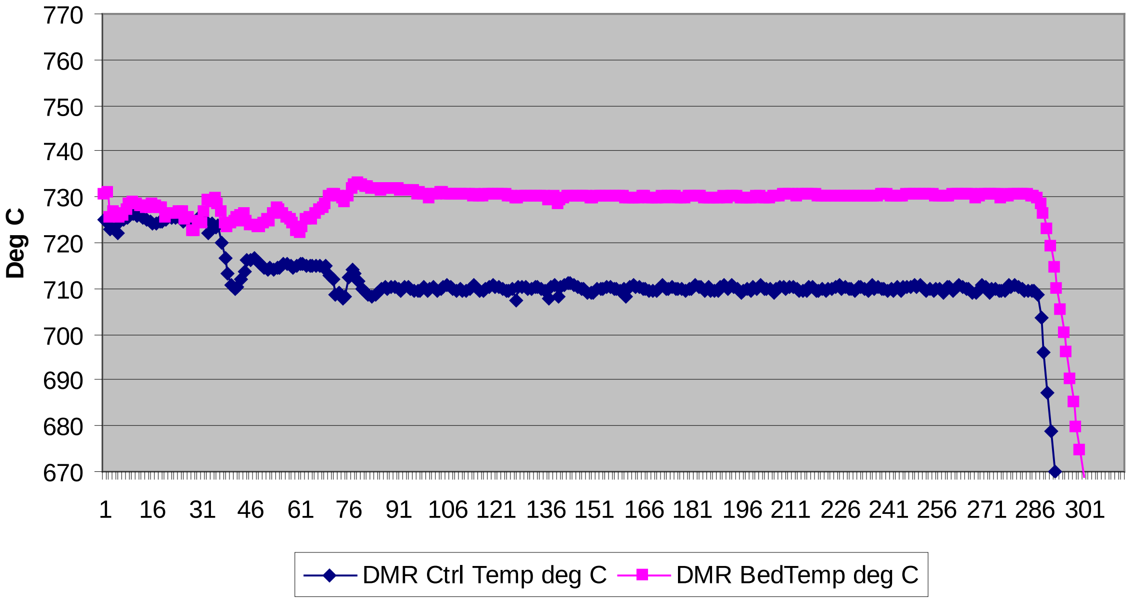

Figure E - 11. Run 2/4/11 Temperatures in DMR

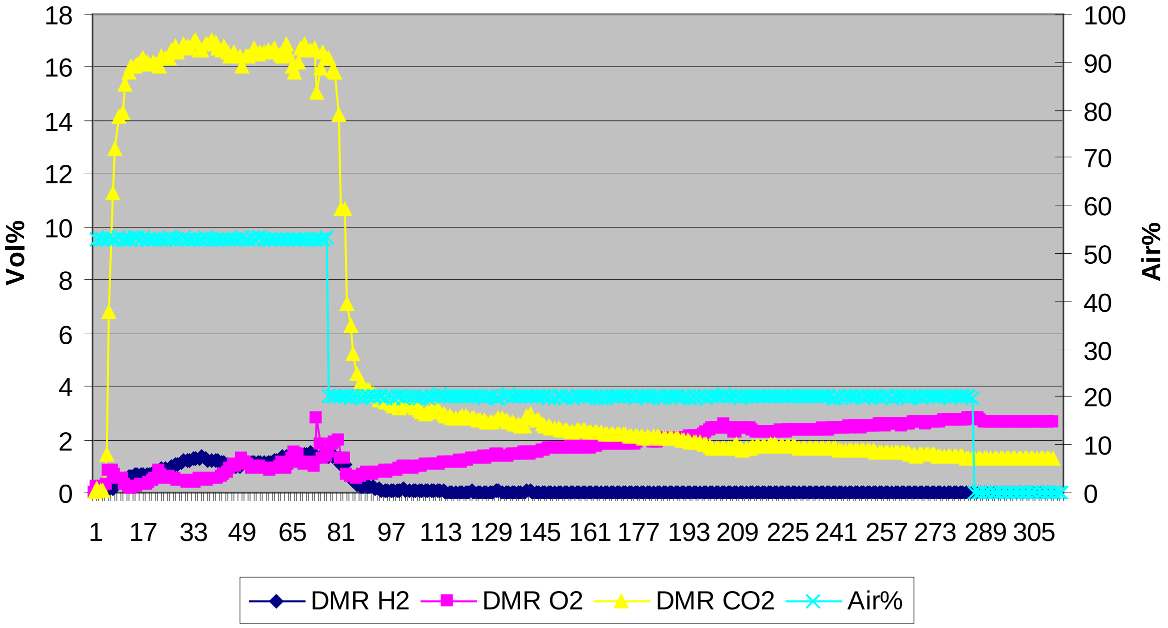

Figure E - 12. Run 2/4/11 Off-gas Concentrations and Air% Fed

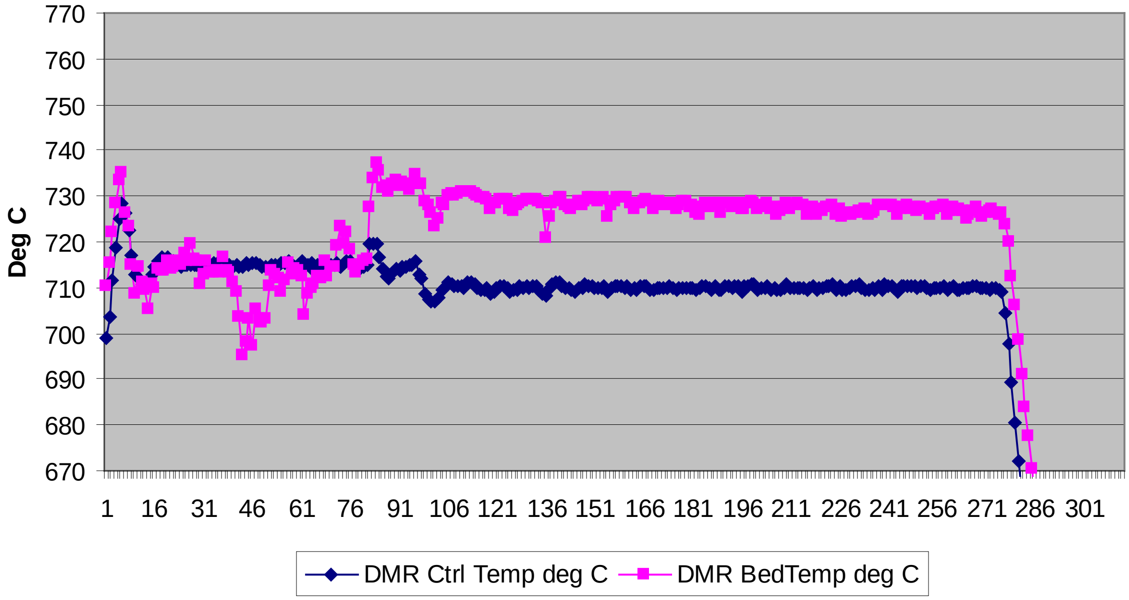

Figure E - 13. Run 2/6/11 Temperatures in DMR

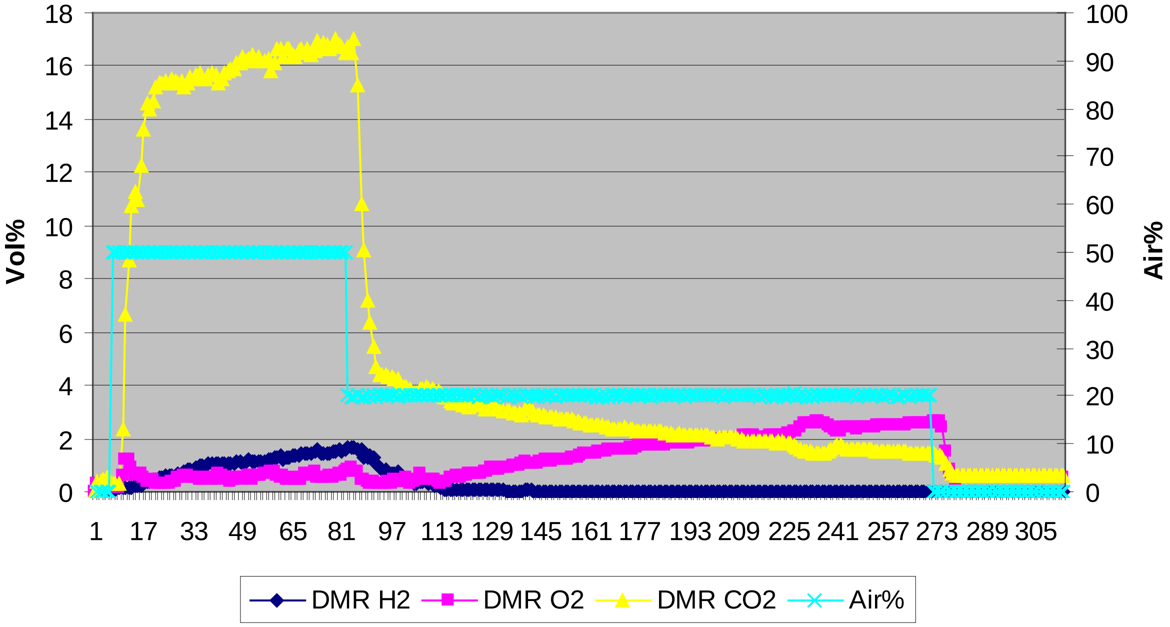

Figure E - 14. Run 2/6/11 Off-gas Concentrations and Air% Fed

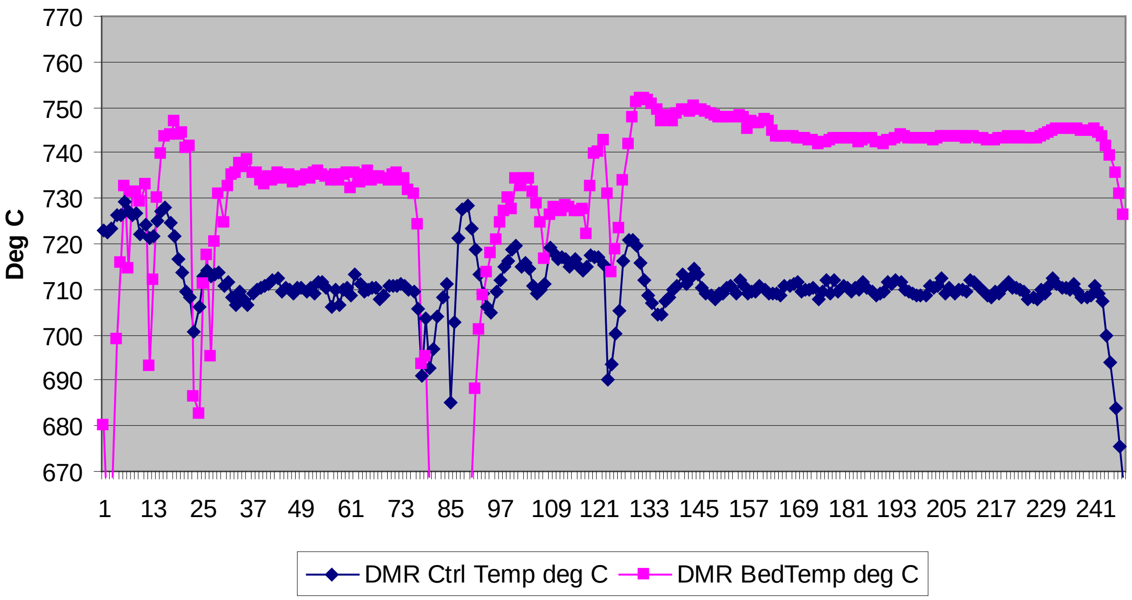

Figure E - 15. Run 2/11/11 Temperatures in DMR

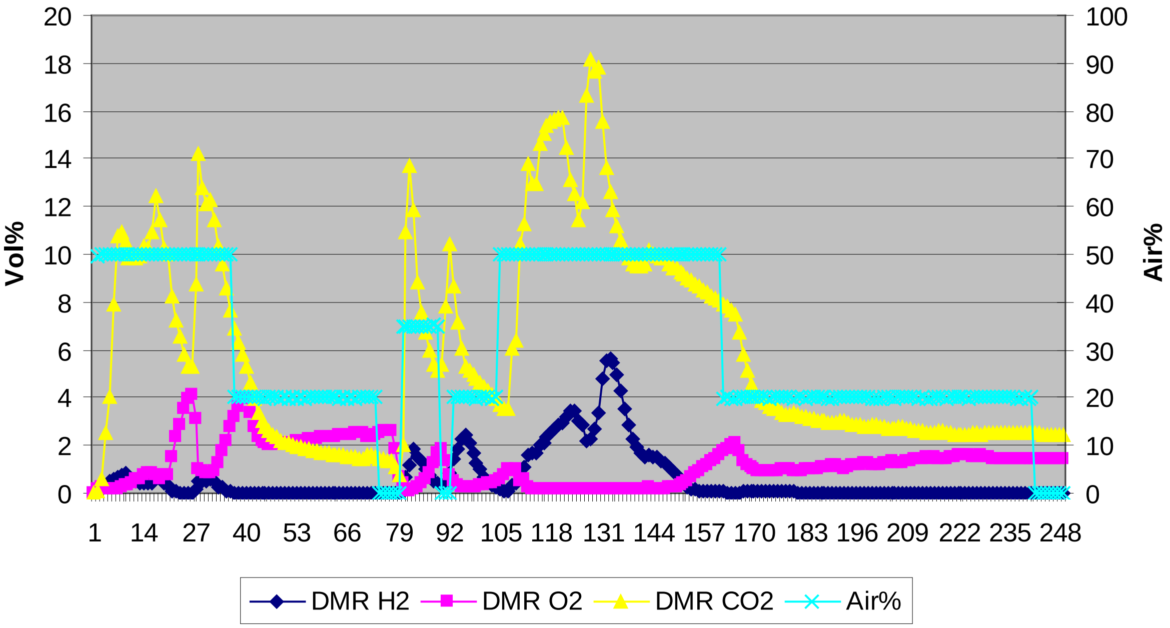

Figure E - 16. Run 2/11/11 Off-gas Concentrations and Air% Fed

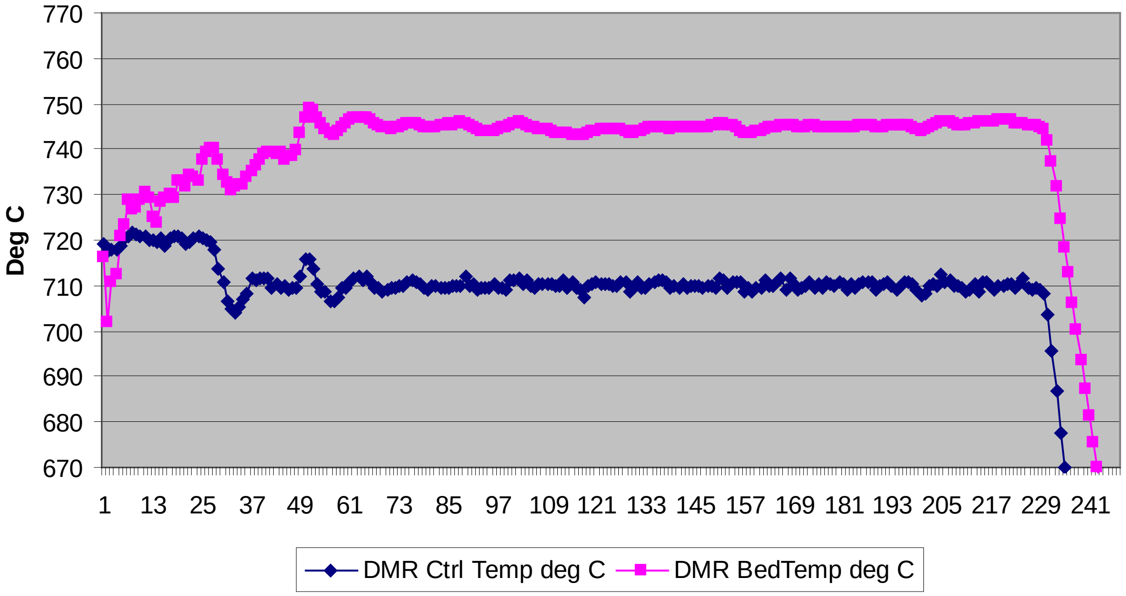

Figure E - 17. Run 2/17/11 Temperatures in DMR

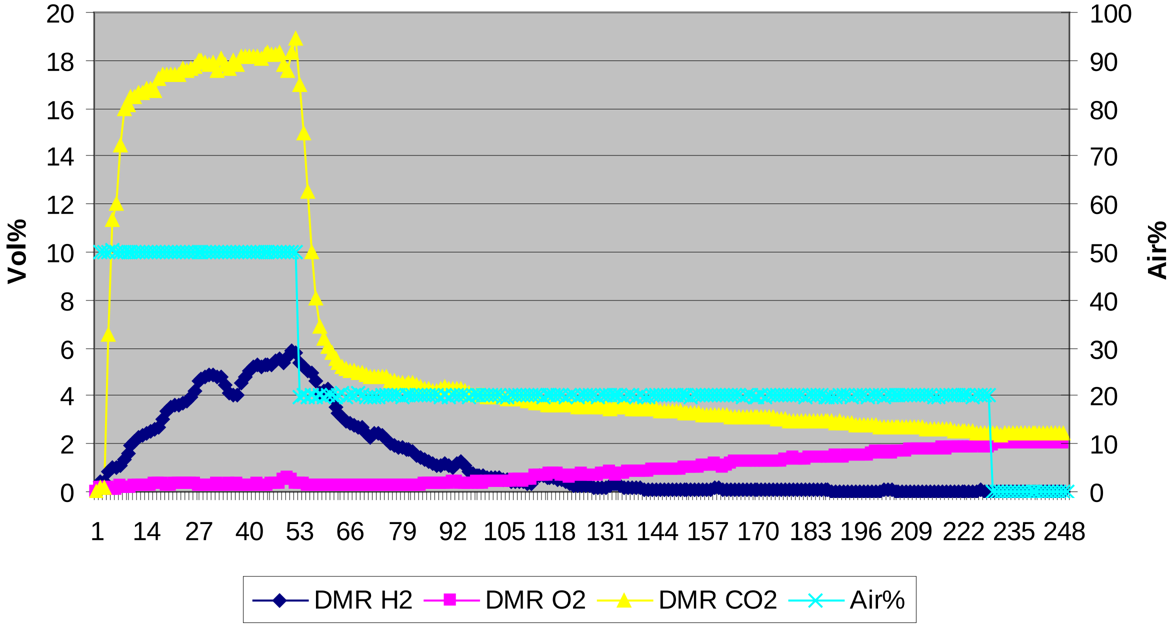

Figure E - 18. Run 2/17/11 Off-gas Concentrations and Air% Fed

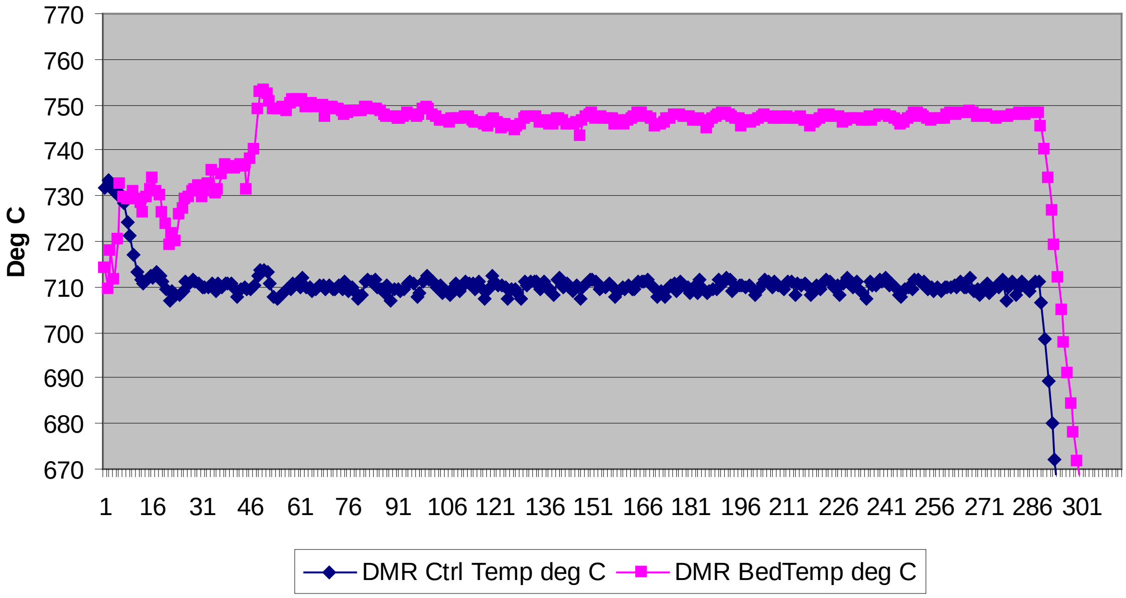

Figure E - 19. Run 2/19/11 Temperatures in DMR

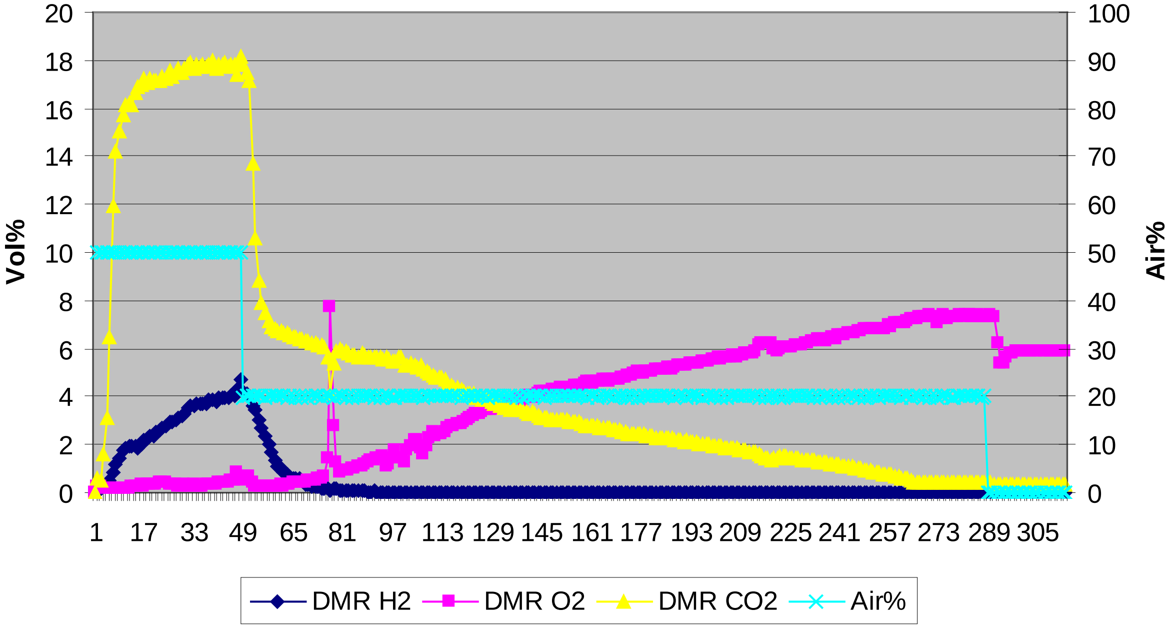

Figure E - 20. Run 2/19/11 Off-gas Concentrations and Air% Fed

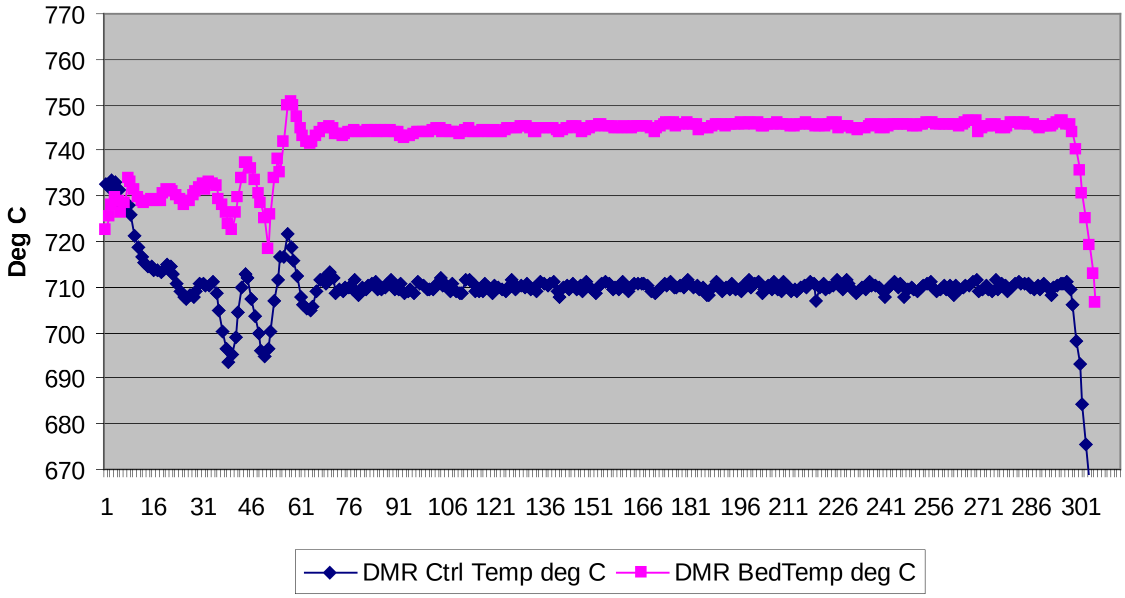

Figure E - 21. Run 2/20/11 Temperatures in DMR

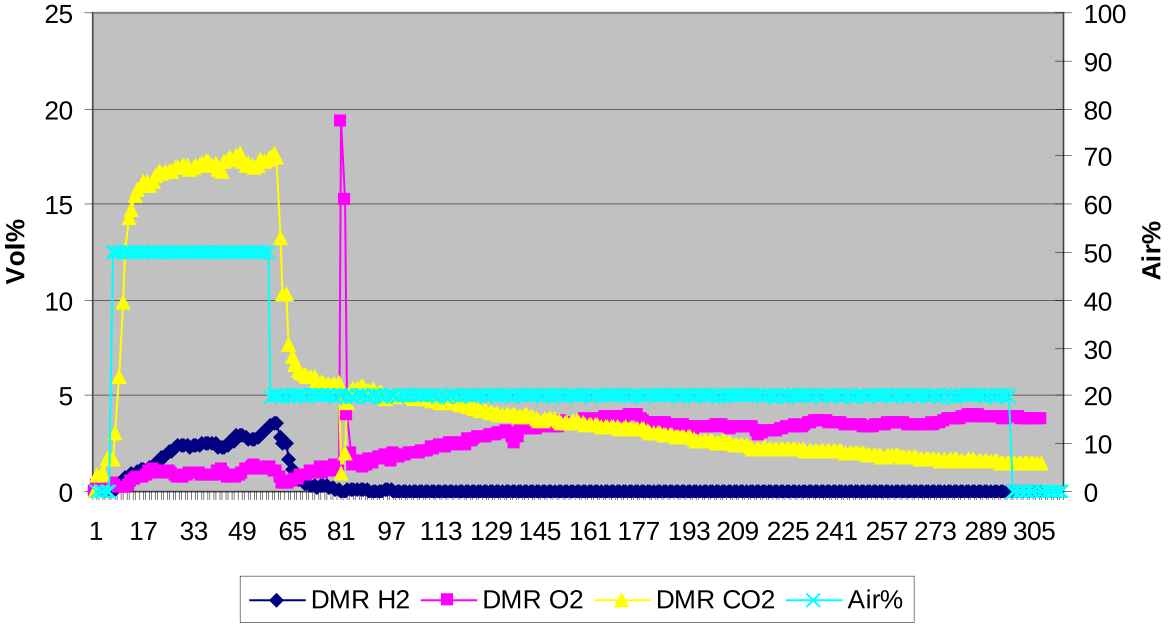

Figure E - 22. Run 2/20/11 Off-gas Concentrations and Air% Fed

.

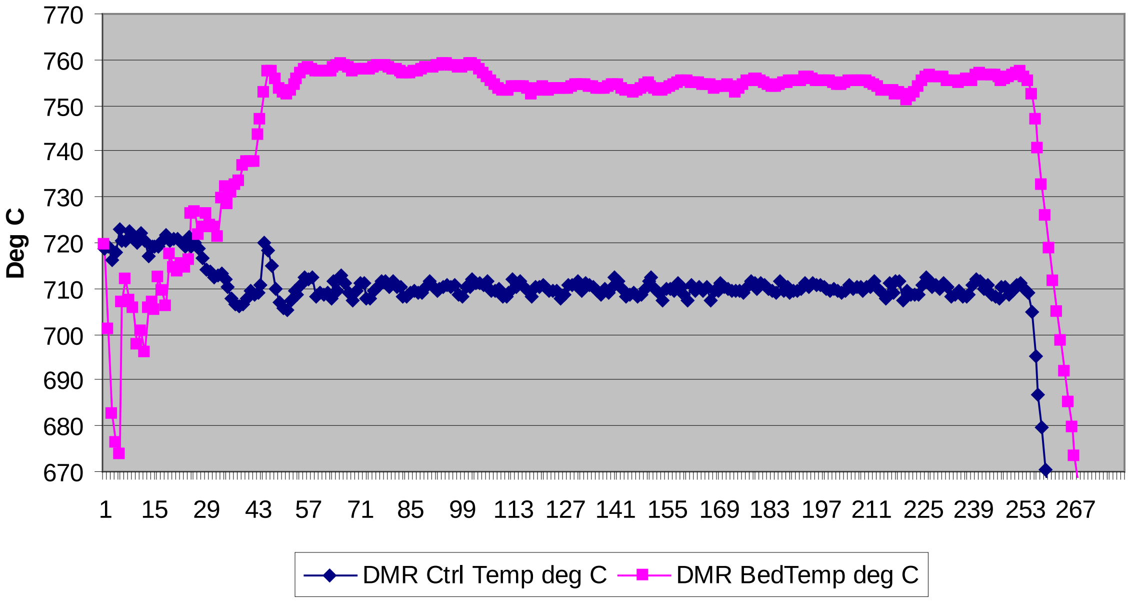

Figure E - 23. Run 2/23/11 Temperatures in DMR

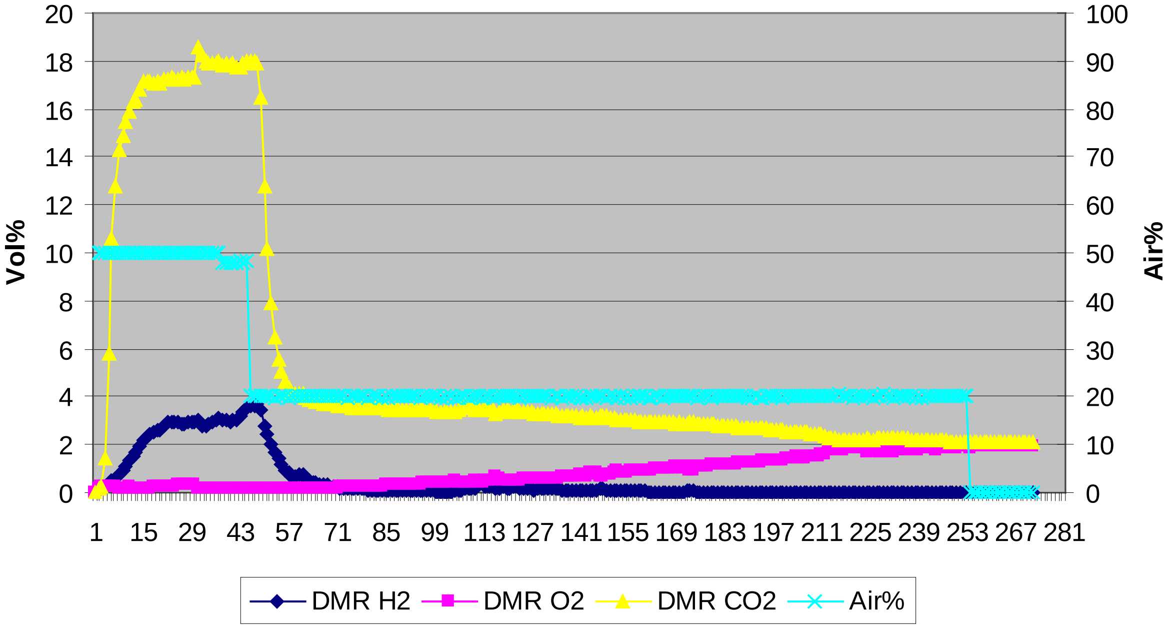

Figure E - 24. Run 2/23/11 Off-gas Concentrations and Air% Fed

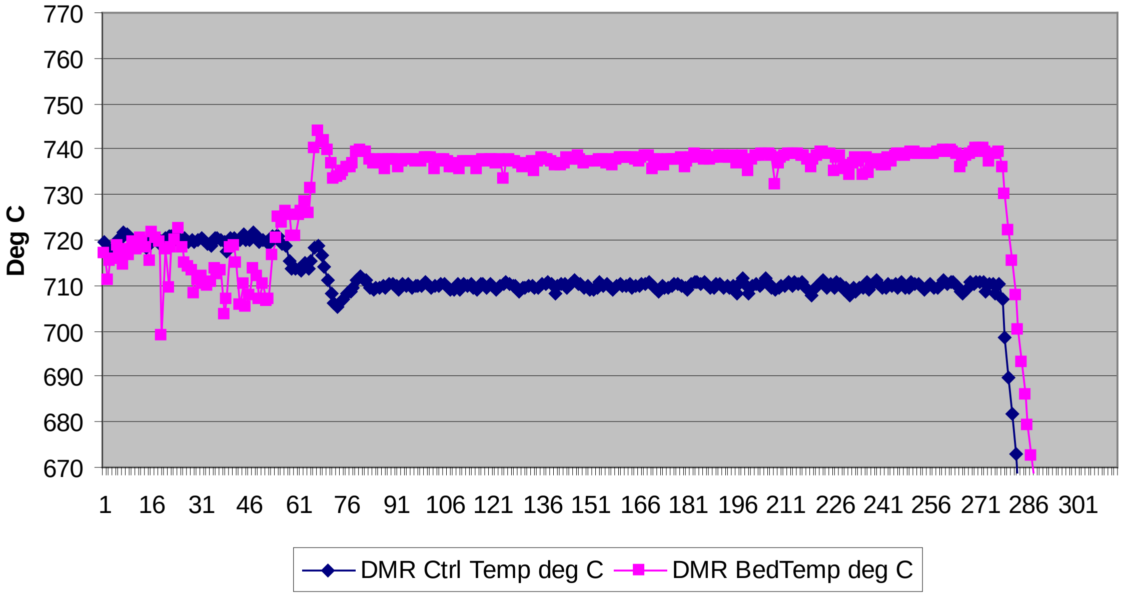

Figure E - 25. Spiked Run 2/24/11 Temperatures in DMR

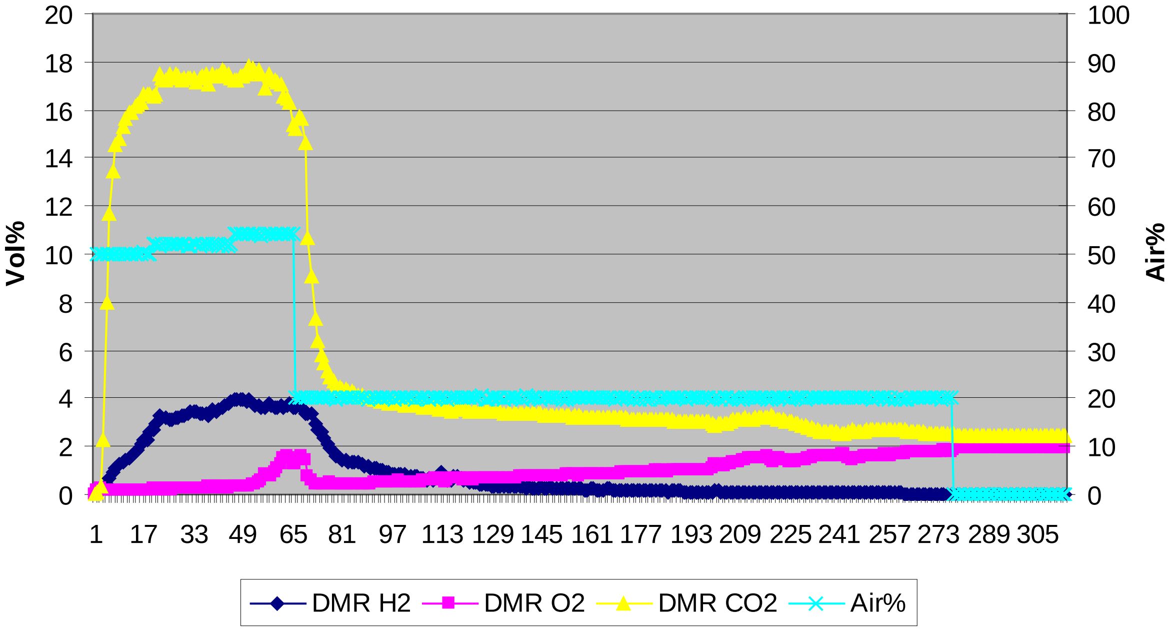

Figure E - 26. Spiked Run 2/24/11 Off-gas Concentrations and Air% Fed

Appendix F. BSR Process Operation Conditions & Trends for Simulant Module D Runs

Table F - 1. BSR Process Operation Conditions & Results for Simulant D Accepted Runs

Run Date	**3/21/11**	**3/22/11**	**3/23/11**	**3/28/11**	**3/29/11**	**3/30/11**	**4/4/11**
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4	-4
Coal (stoichiometry)	2.25x	2.25x	2.25x	2.25x	2.25x	2.25x	2.25x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500	500
CO_2/ml	14.52	17	25.02	24.55	23	24.5	24.5
Post Feed Run Time (min)	41	94	59	109	87	95	108
Product REDOX	0.251	0.236	0.234	0.123	0.129	0.239	0.257
Product LOI	2.52%	2.74%	2.80%	0.88%	1.25%	1.91%	1.56%
Product Quantity (g)	23.14	20.15	31.23	21.51	24.97	22.92	23.81
Feed Quantity (g)	78.38	87.96	81.44	75.90	83.00	81.99	78.20
Run Date	**4/6/11**	**4/7/11**	**4/11/11**	**4/12/11**	**4/13/11**	**4/14/11**	
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9	
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40	
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4	
Coal (stoichiometry)	2.25x	2.25x	2.25x	2.25x	2.25x	2.25x	
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500	
CO_2/ml	24.52	24.5	24.5	24.5	24.5	24.5	
Post Feed Run Time (min)	104	95	128	126	161	129	
Product REDOX	0.244	0.196	0.353	0.298	0.427	0.356	
Product LOI	1.54%	1.22%	2.03%	1.38%	1.45%	1.43%	
Product Quantity (g)	22.55	24.83	22.93	21.22	24.04	22.00	
Feed Quantity (g)	78.60	79.85	89.19	76.52	82.50	79.70	

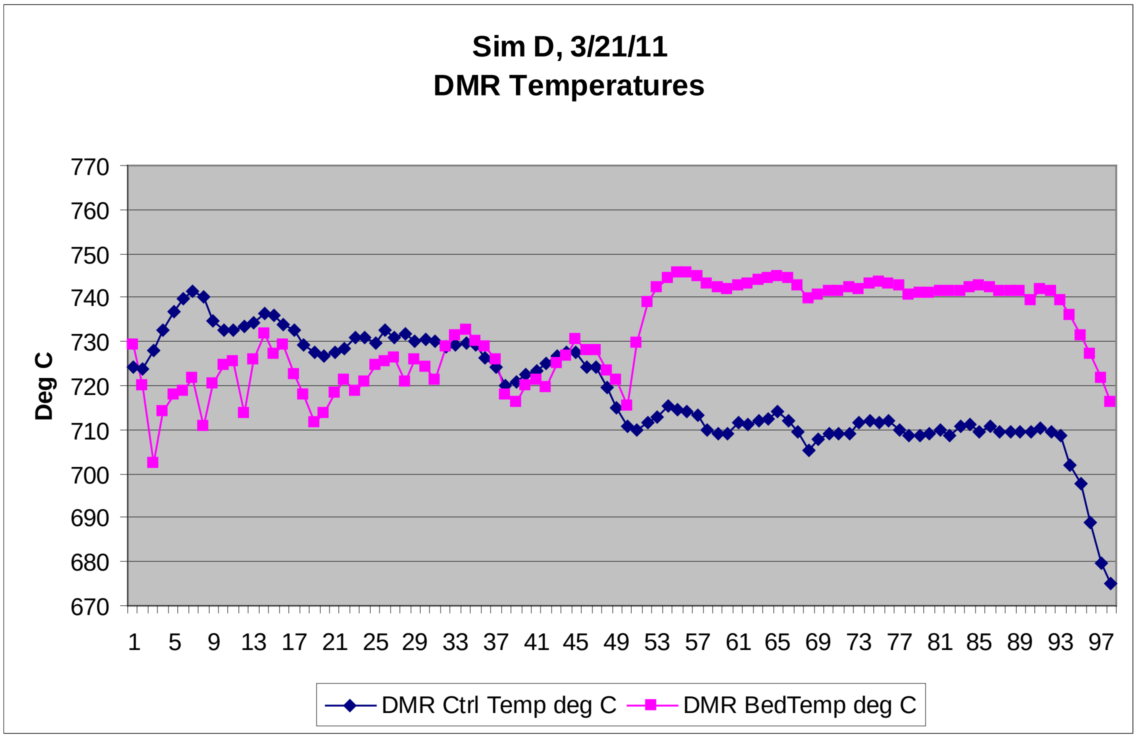

Figure F - 1. Run 3/21/11 Temperatures in DMR

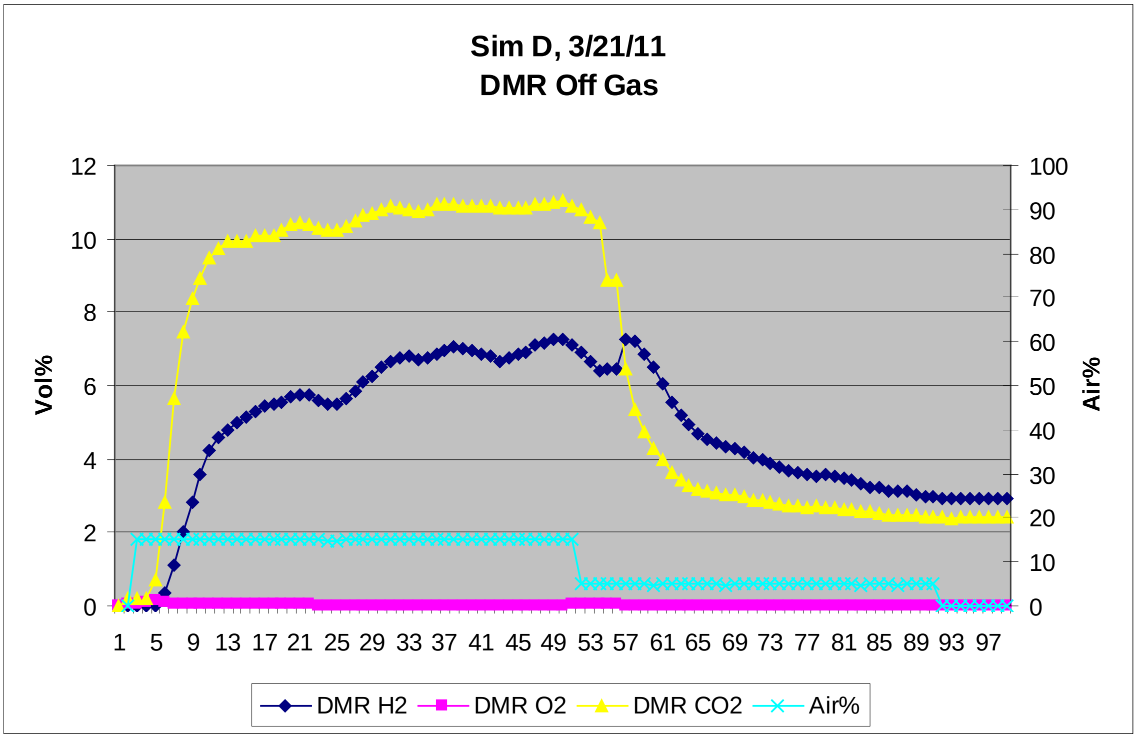

Figure F - 2. Run 3/21/11 Off-gas Concentrations and Air% Fed

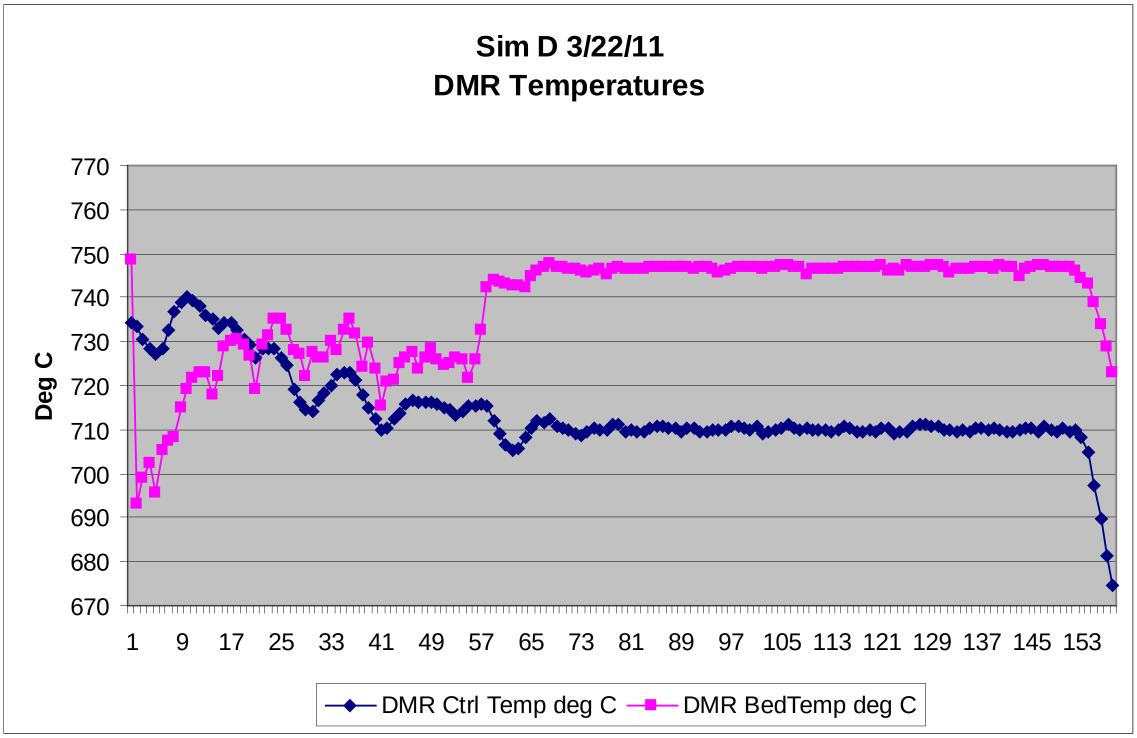

Figure F - 3. Run 3/22/11 Temperatures in DMR

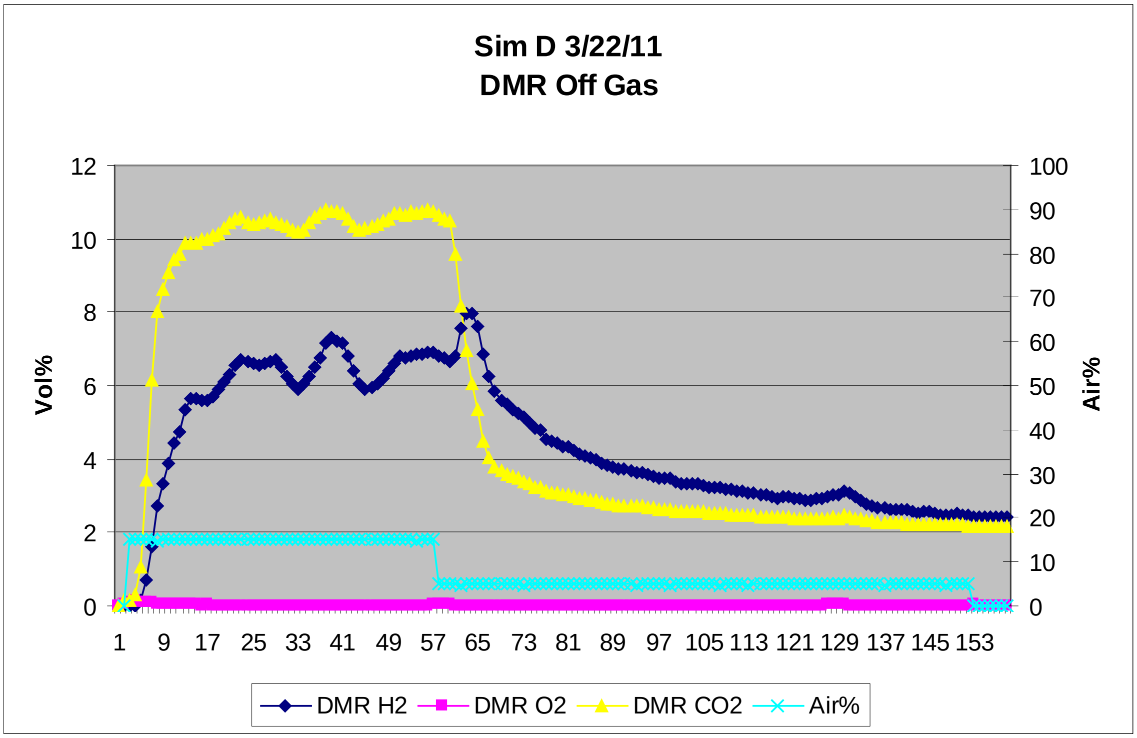

Figure F - 4. Run 3/22/11 Off-gas Concentrations and Air% Fed

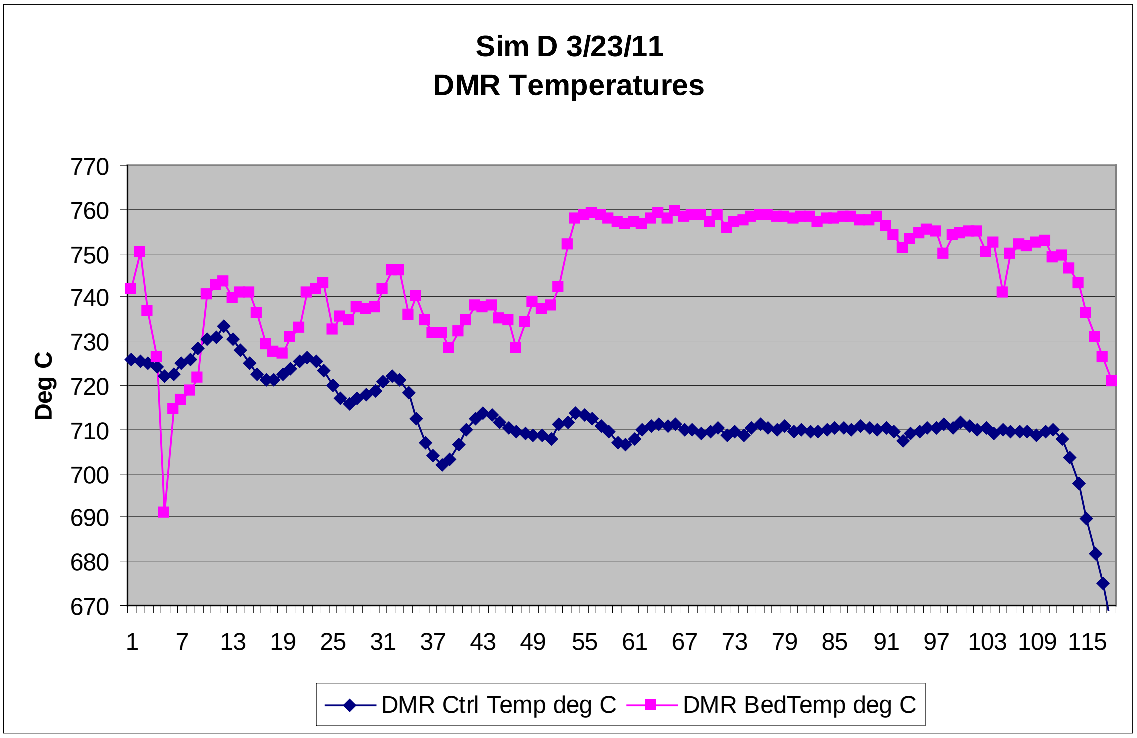

Figure F - 5. Run 3/23/11 Temperatures in DMR

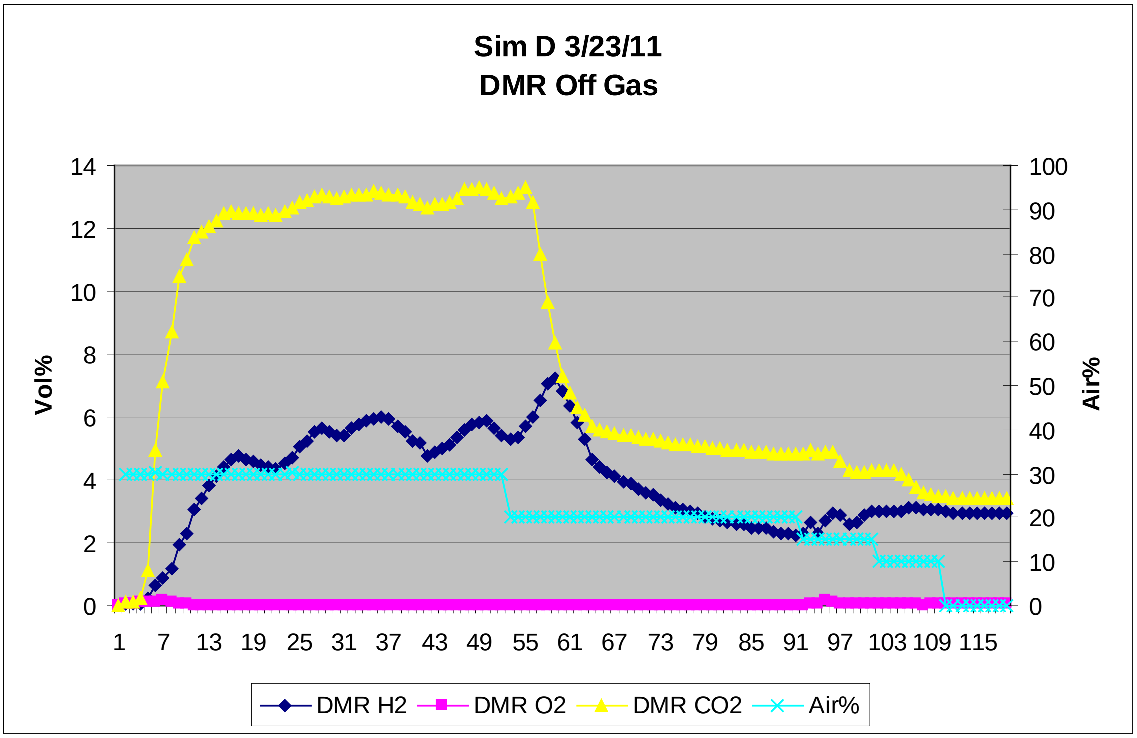

Figure F - 6. Run 3/23/11 Off-gas Concentrations and Air% Fed

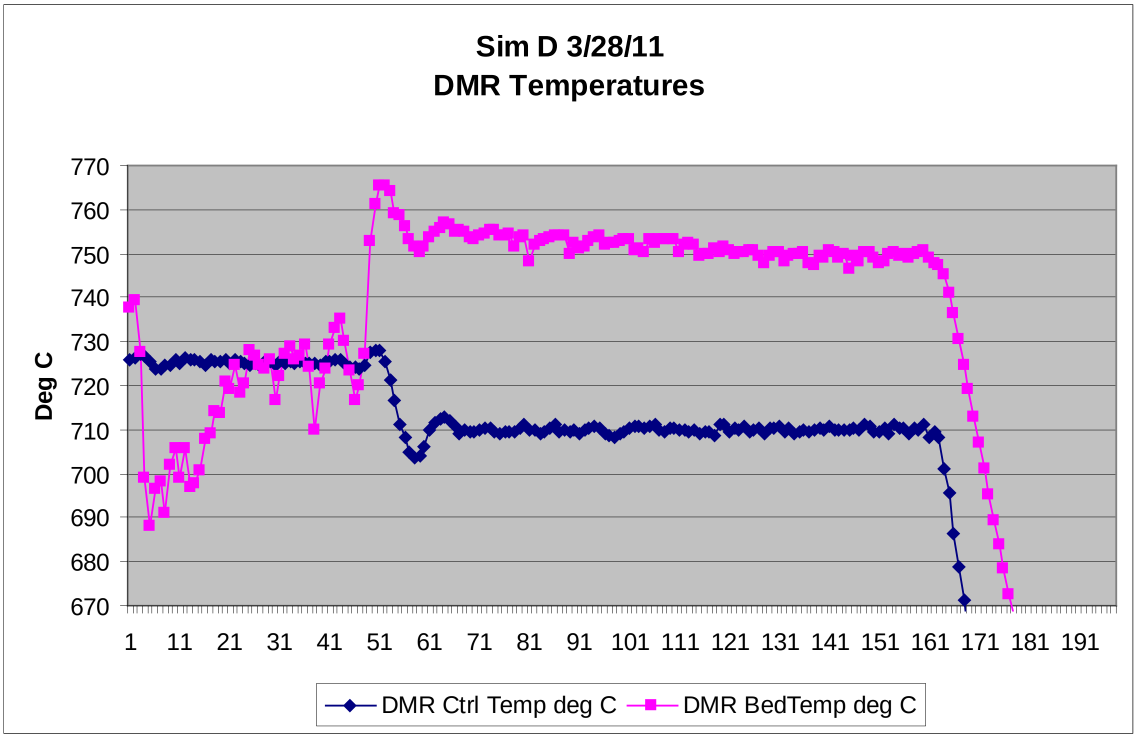

Figure F - 7. Run 3/28/11 Temperatures in DMR

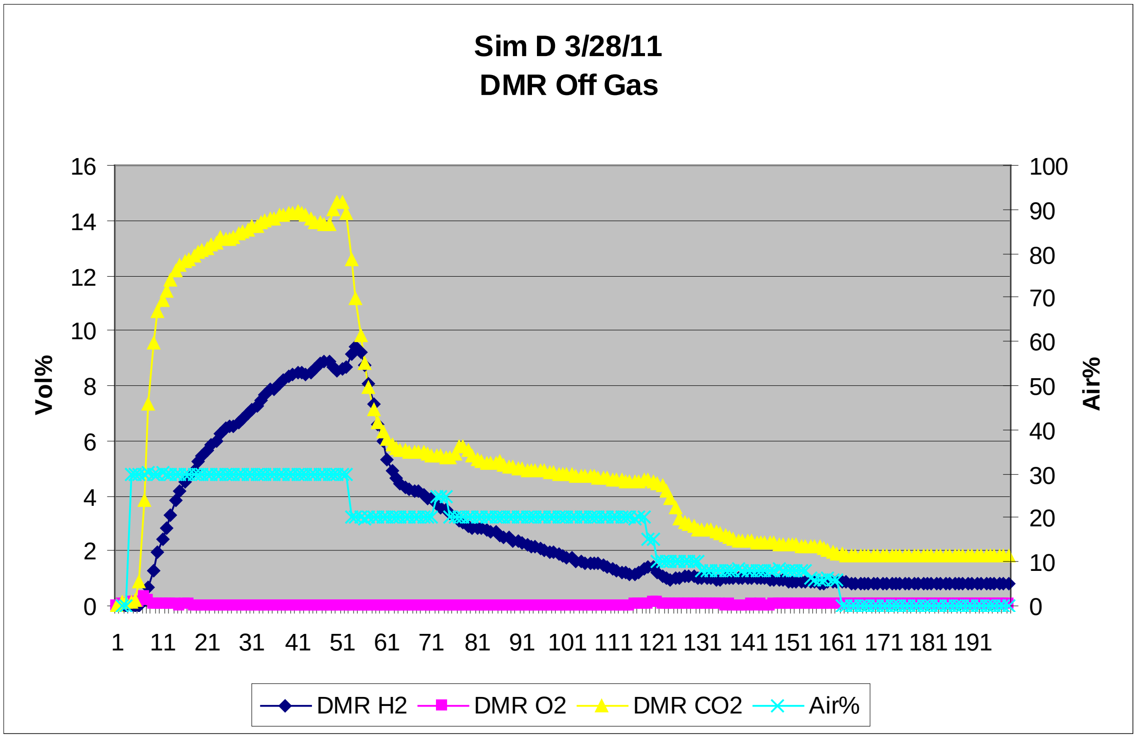

Figure F - 8. Run 3/28/11 Off-gas Concentrations and Air% Fed

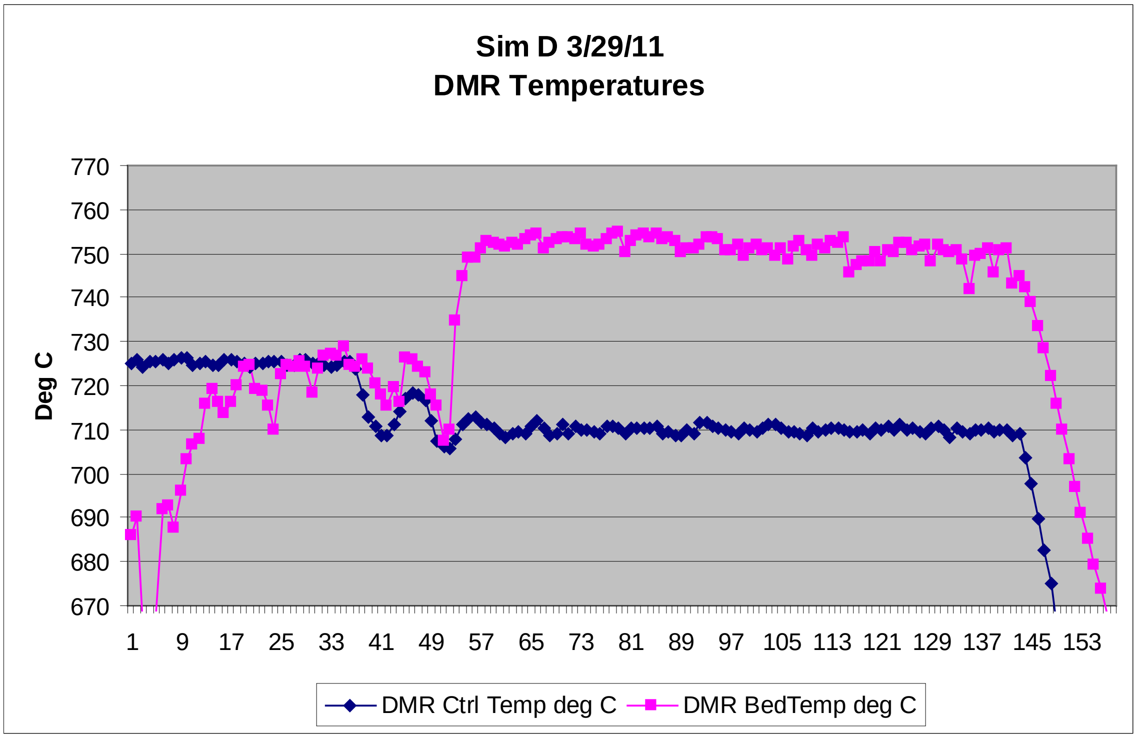

Figure F - 9. Run 3/29/11 Temperatures in DMR

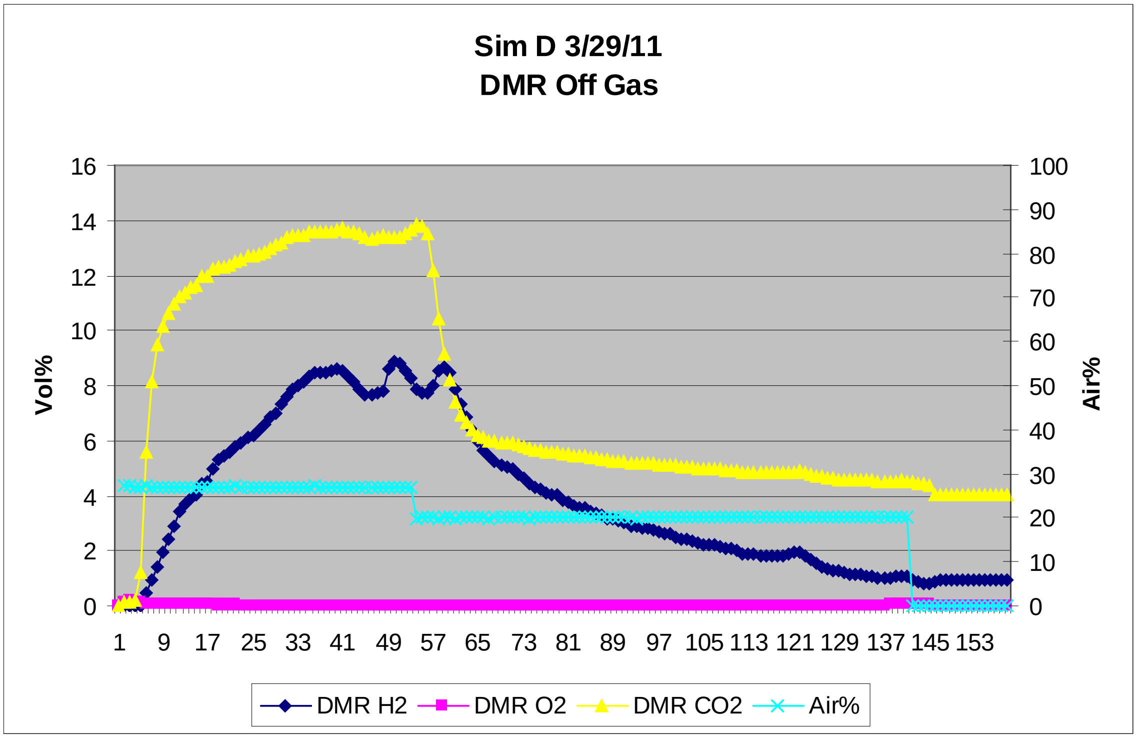

Figure F - 10. Run 3/29/11 Off-gas Concentrations and Air% Fed

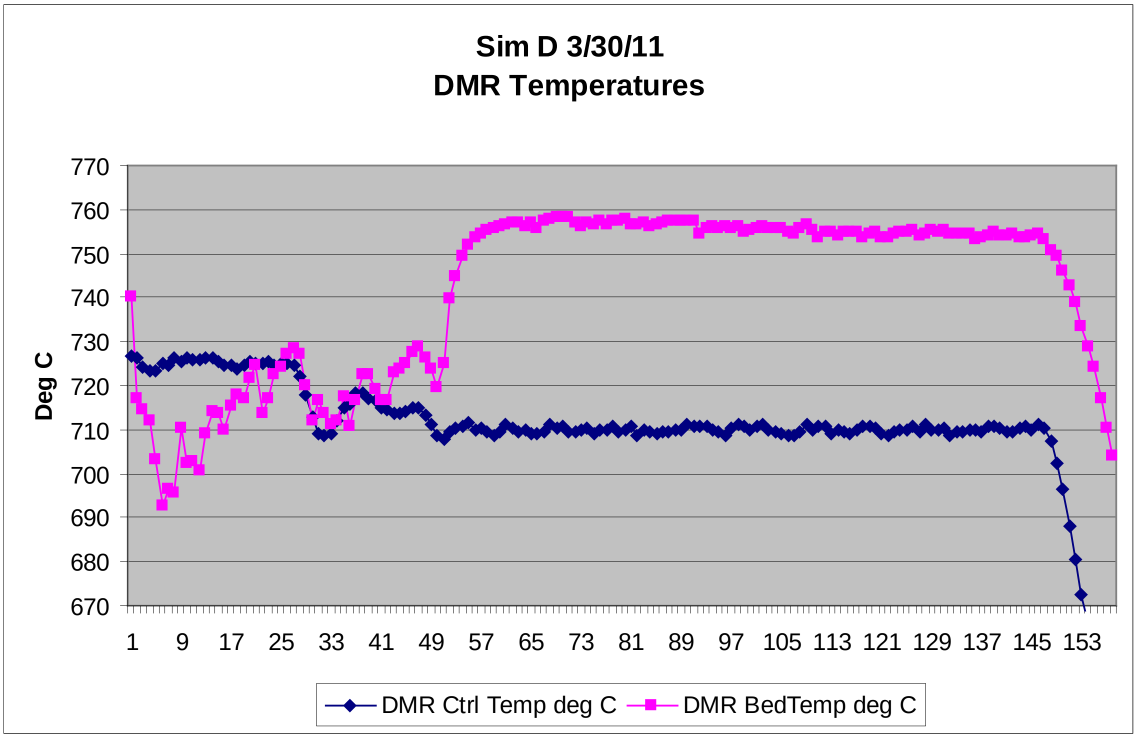

Figure F - 11. Run 3/30/11 Temperatures in DMR

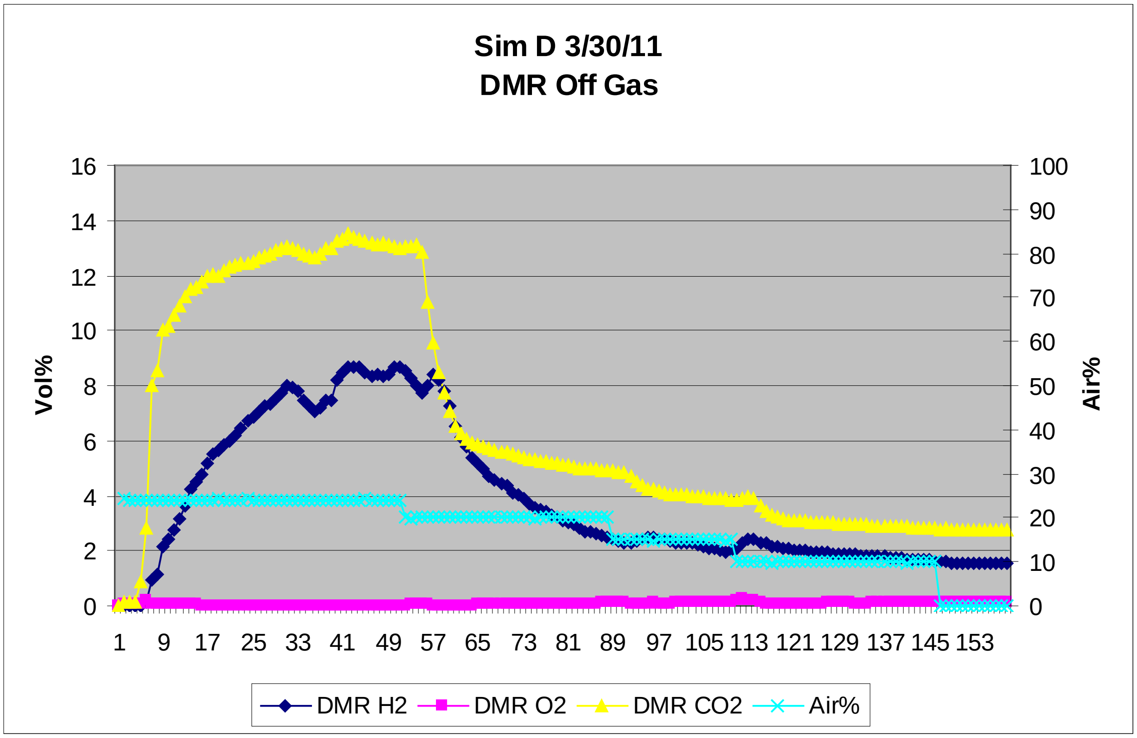

Figure F - 12. Run 3/30/11 Off-gas Concentrations and Air% Fed

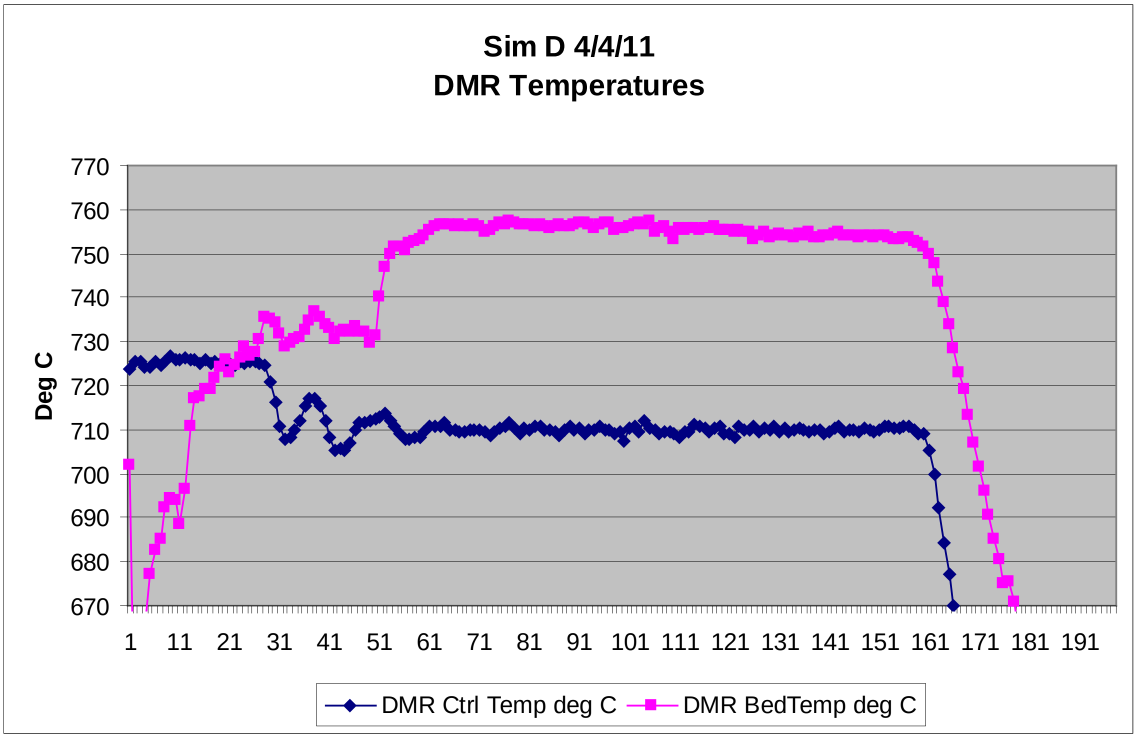

Figure F - 13. Run 4/4/11 Temperatures in DMR

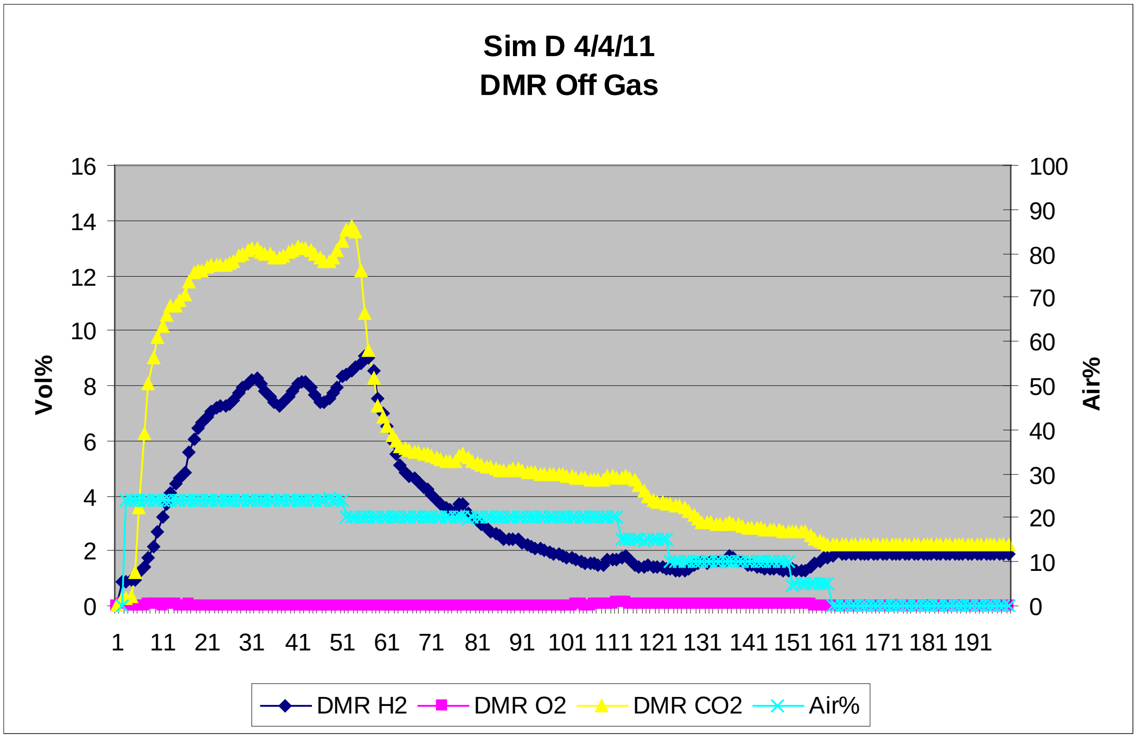

Figure F - 14. Run 4/4/11 Off-gas Concentrations and Air% Fed

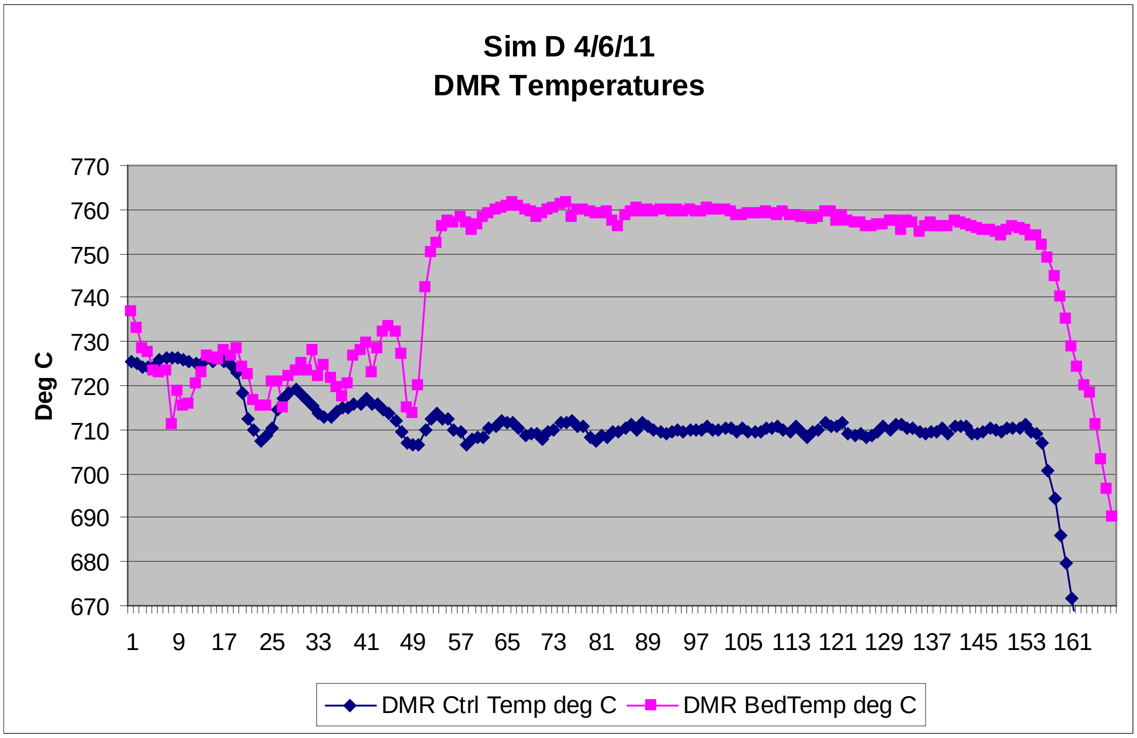

Figure F - 15. Run 4/6/11 Temperatures in DMR

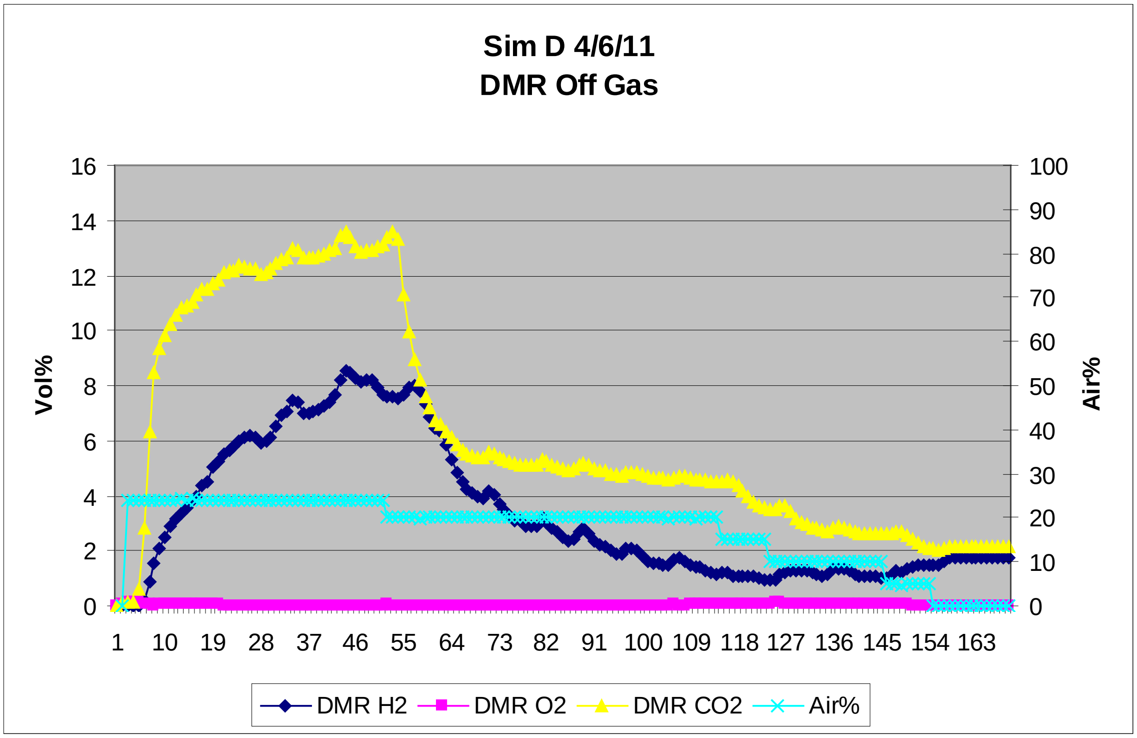

Figure F - 16. Run 4/6/11 Off-gas Concentrations and Air% Fed

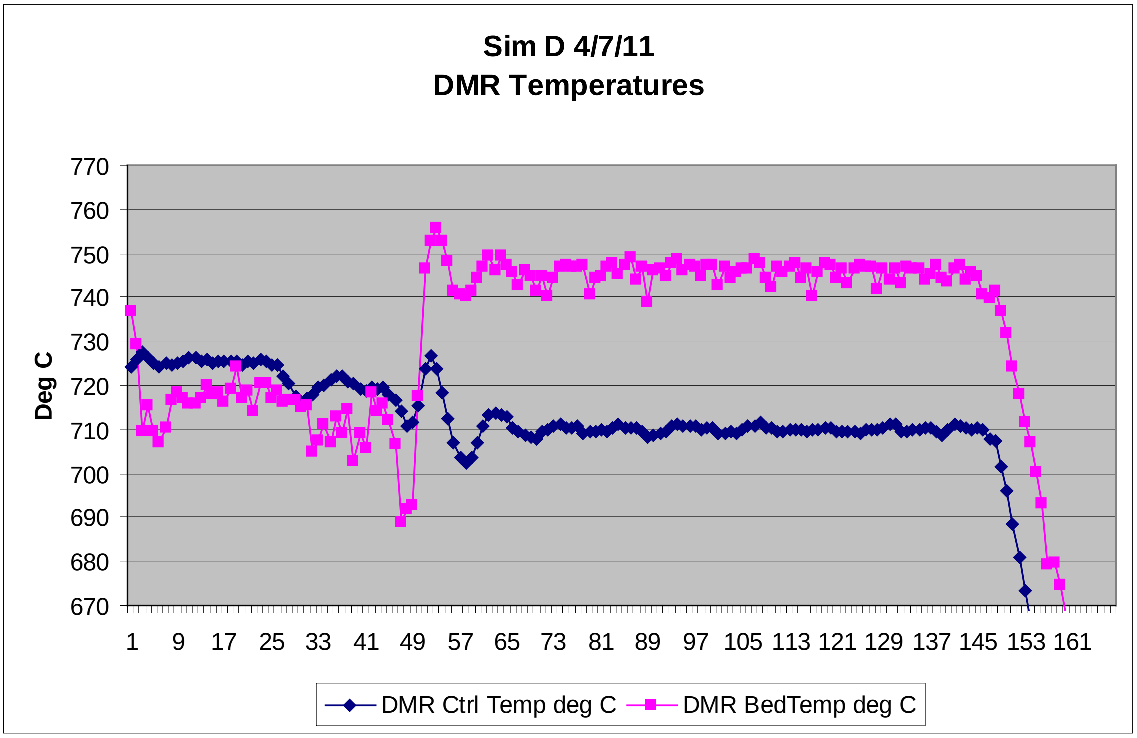

Figure F - 17. Run 4/7/11 Temperatures in DMR

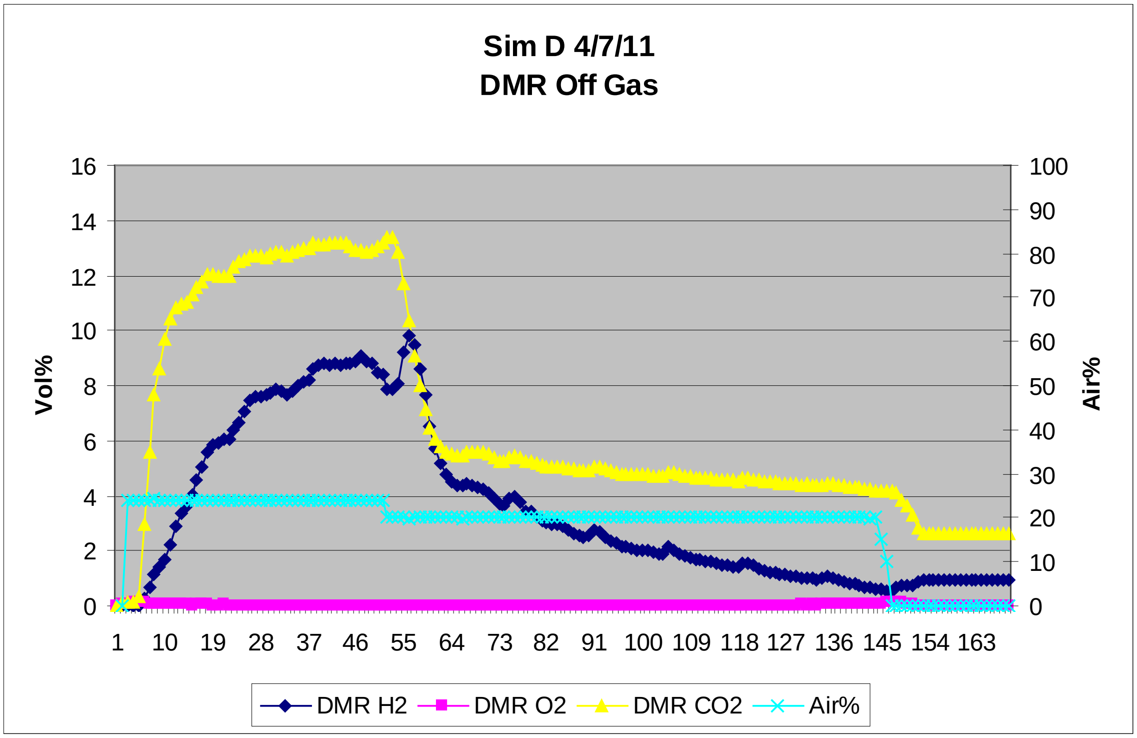

Figure F - 18. Run 4/7/11 Off-gas Concentrations and Air% Fed

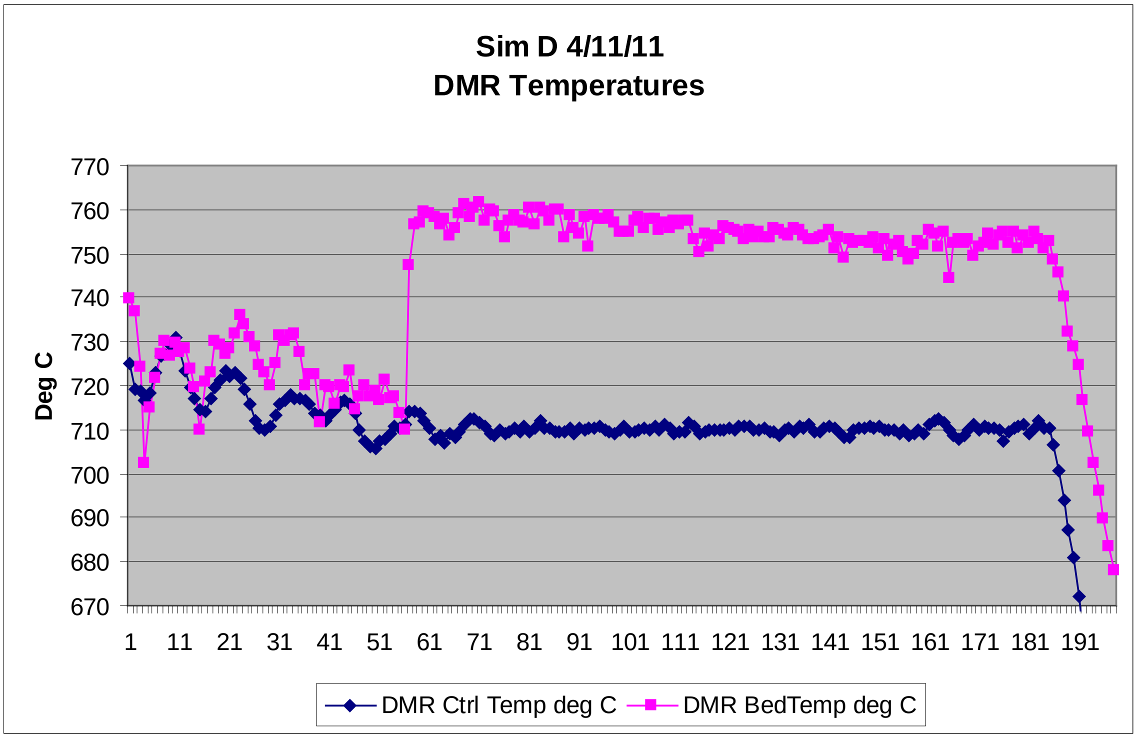

Figure F - 19. Run 4/11/11 Temperatures in DMR

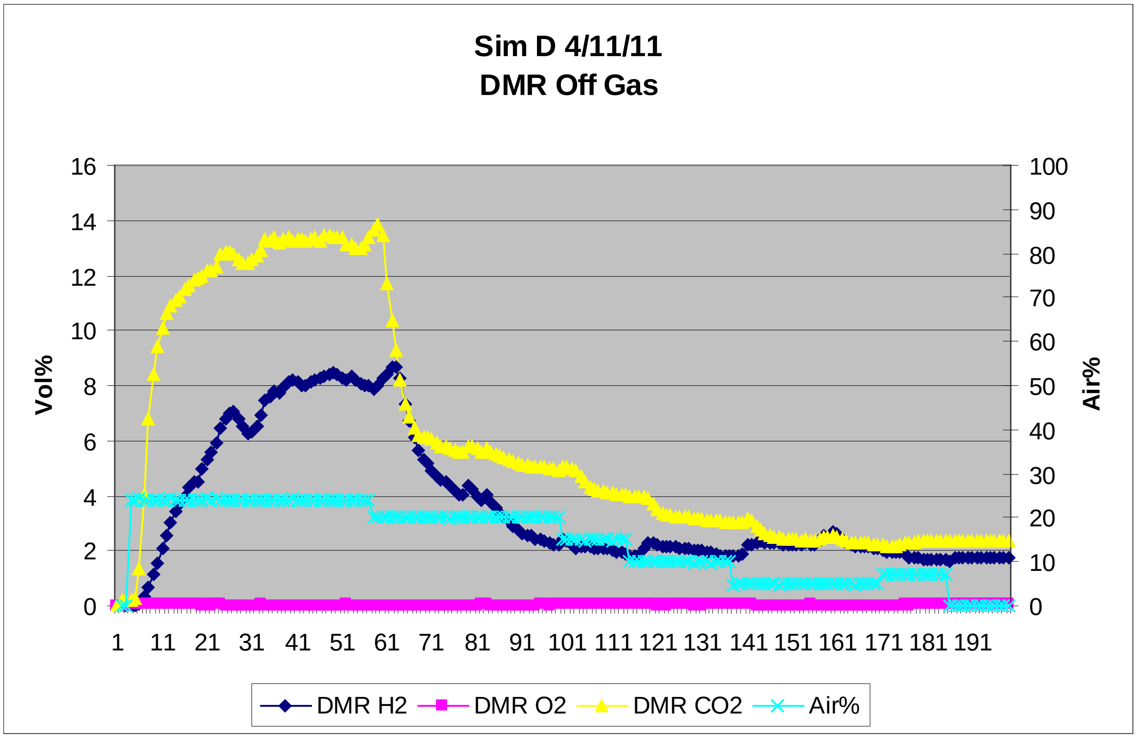

Figure F - 20. Run 4/11/11 Off-gas Concentrations and Air% Fed

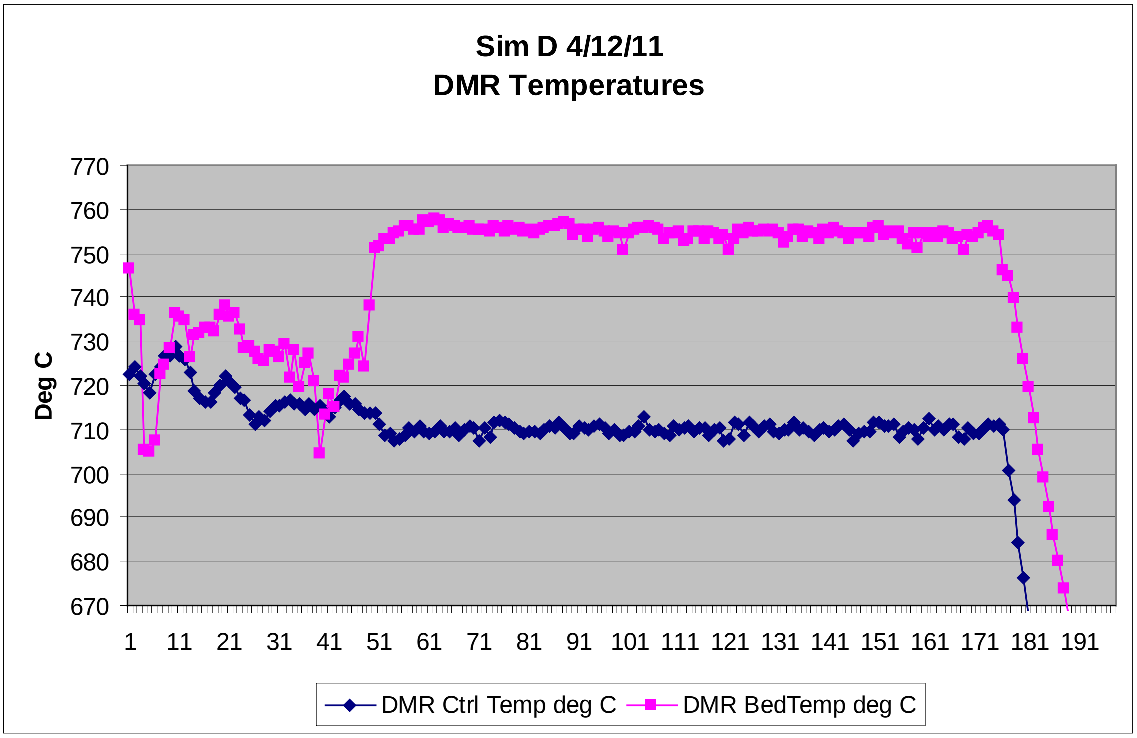

Figure F - 21. Run 4/12/11 Temperatures in DMR

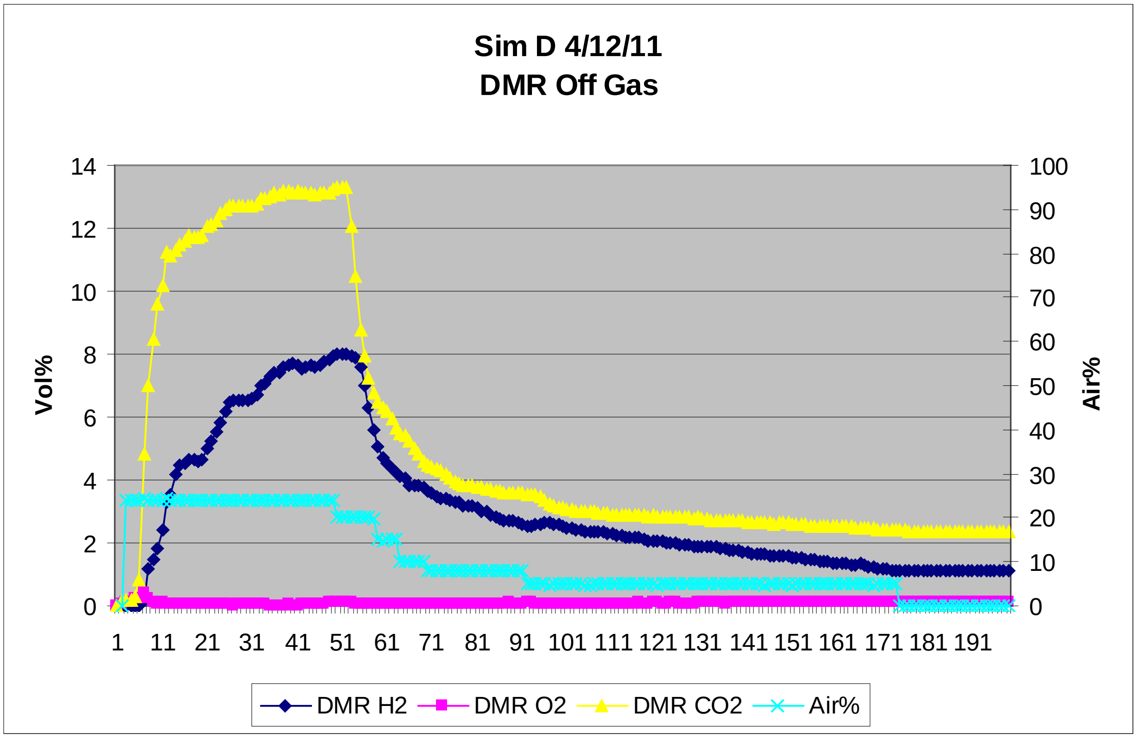

Figure F - 22. Run 4/12/11 Off-gas Concentrations and Air% Fed

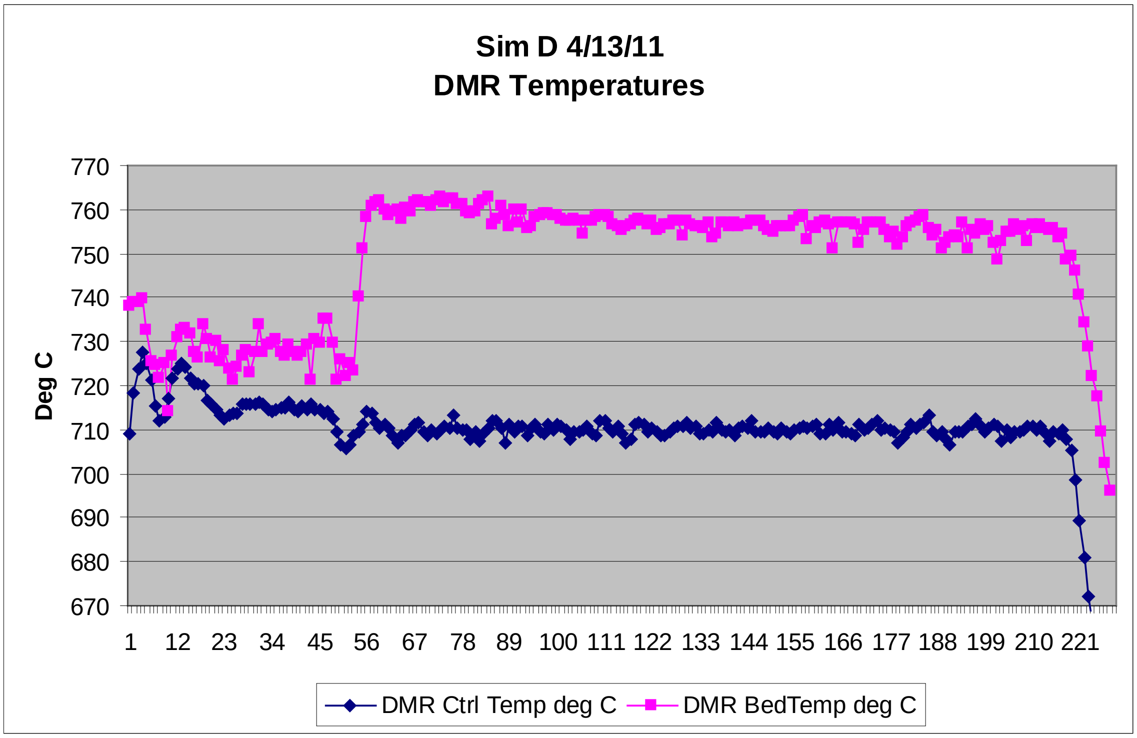

Figure F - 23. Run 4/13/11 Temperatures in DMR

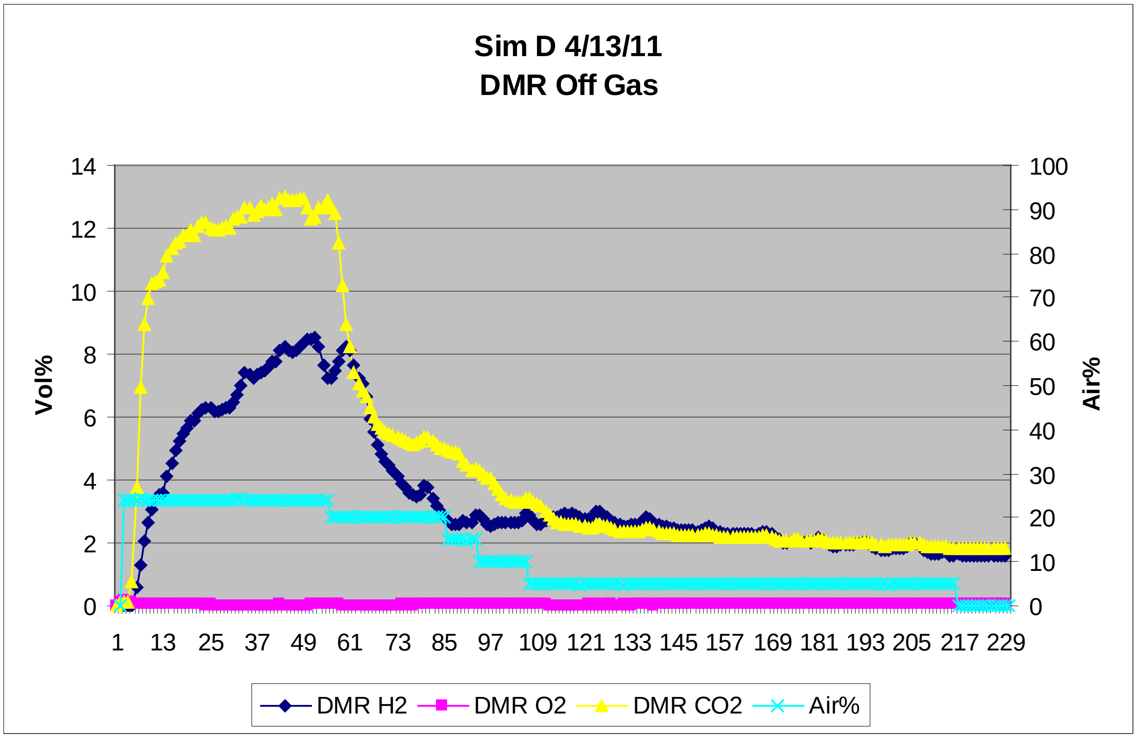

Figure F - 24. Run 4/13/11 Off-gas Concentrations and Air% Fed

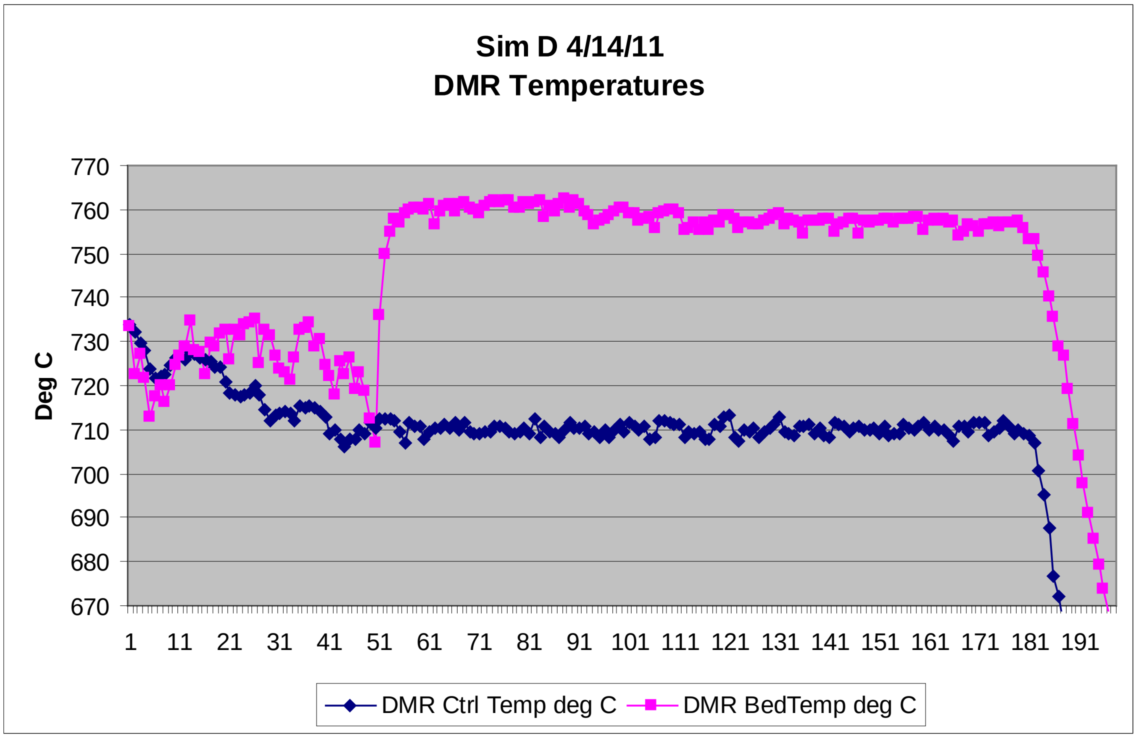

Figure F - 25. Run 4/14/11 Temperatures in DMR

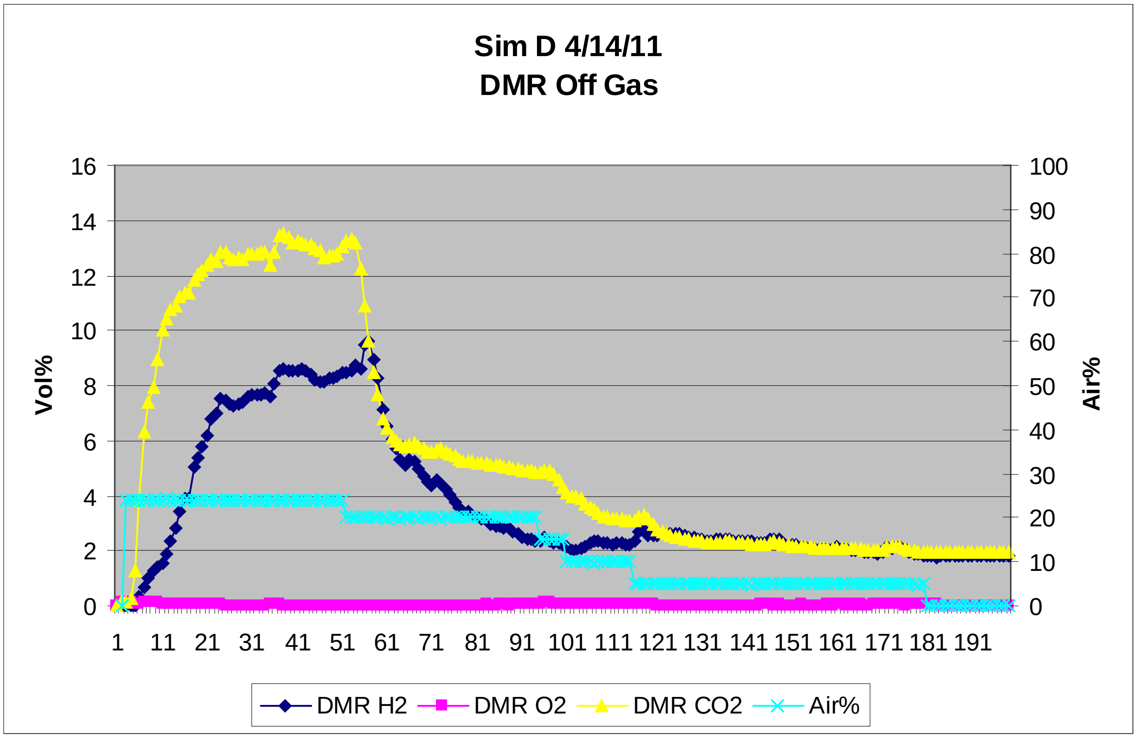

Figure F - 26. Run 4/14/11 Off-gas Concentrations and Air% Fed

Appendix G. BSR Process Operation Conditions & Trends for Radioactive Module D Runs

Table G - 1. BSR Process Operation Conditions & Results for Radioactive D Accepted Runs

Run Date	**4/4/11**	**4/7/11**	**4/8/11**	**4/9/11**	**4/15/11**	**4/18/11**
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Coal (stoichiometry)	2.25x	2.25x	2.25x	2.25x	2.25x	2.25x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
CO_2/ml	24.5	24.5	24.5	24.5	19.7	uncertain
Post Feed Run Time (min)	240	258	232	155	101	180
Product REDOX	0.303	0.500	0.245	0.412	0.486	0.371
Product LOI	4.40%	3.95%	3.67%	4.72%	3.27%	5.47%
Product Quantity (g)	17.75	27.25	31.41	20.98	27.28	17.86
Feed Quantity (g)	84.76	76.65	96.50	64.78	81.53	59.64
Run Date	**4/19/11**	**4/20/11**	**5/5/11**	**5/9/11**	**5/10/11**	**5/11/11**
Slurry Feed Rate (ml/min)	0.9	0.9	0.9	0.9	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Coal (stoichiometry)	2.25x	2.25x	2.25x	2.25x	2.25x	2.25x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
(CO_2+H_2)/ml	40	40	40	40	39	uncertain
Post Feed Run Time (min)	135	177	310	216	270	180
Product REDOX	0.433	0.306	0.205	0.393	0.402	0.201
Product LOI	5.85%	5.37%	6.27%	5.74%	6.17%	4.66%
Product Quantity (g)	13.96	11.92	16.55	18.59	19.13	9.92
Feed Quantity (g)	40.85	46.34	53.48	60.96	70.88	46.80

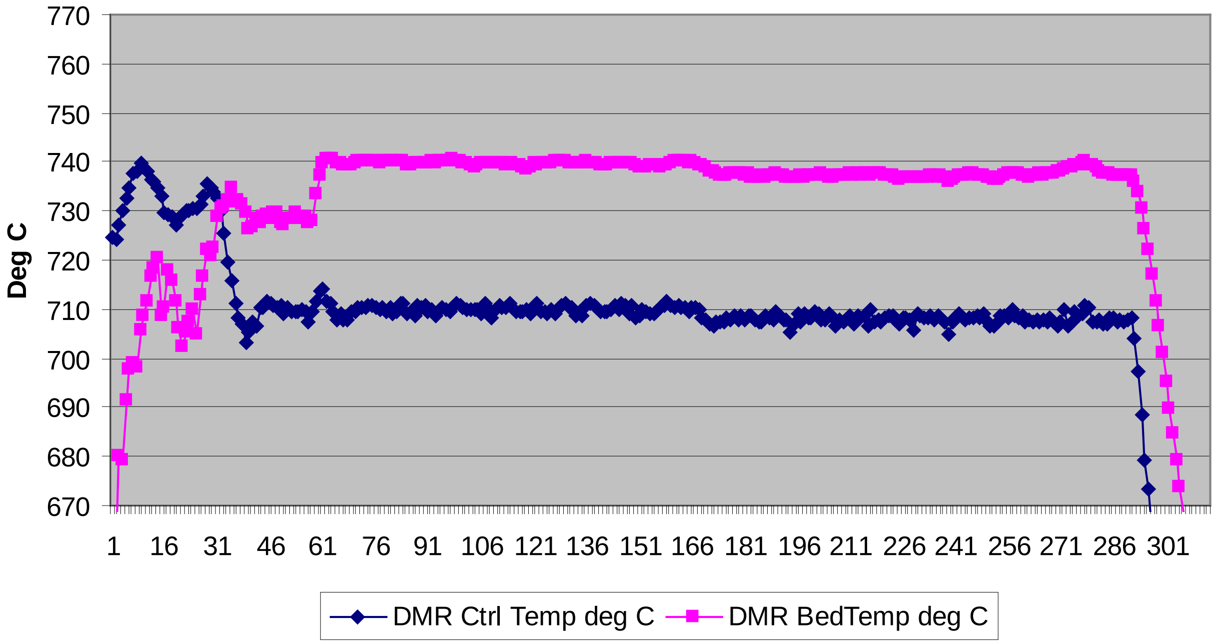

Figure G - 1. Run 4/4/11 Temperatures in DMR

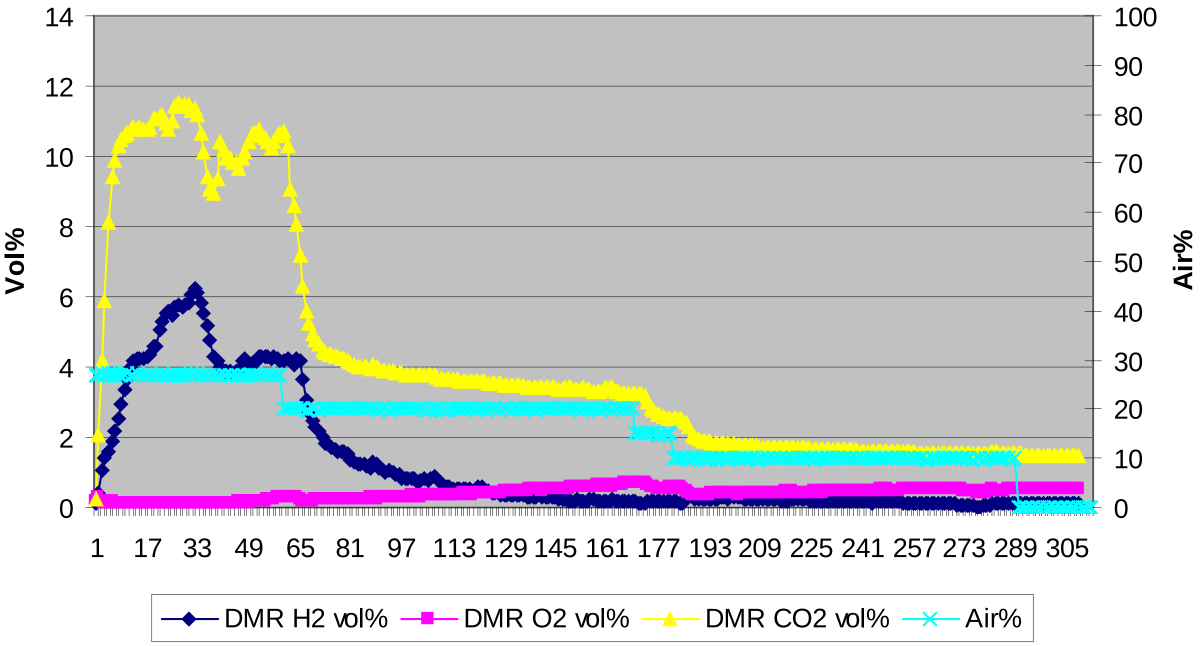

Figure G - 2. Run 4/4/11 Off-gas Concentrations and Air% Fed

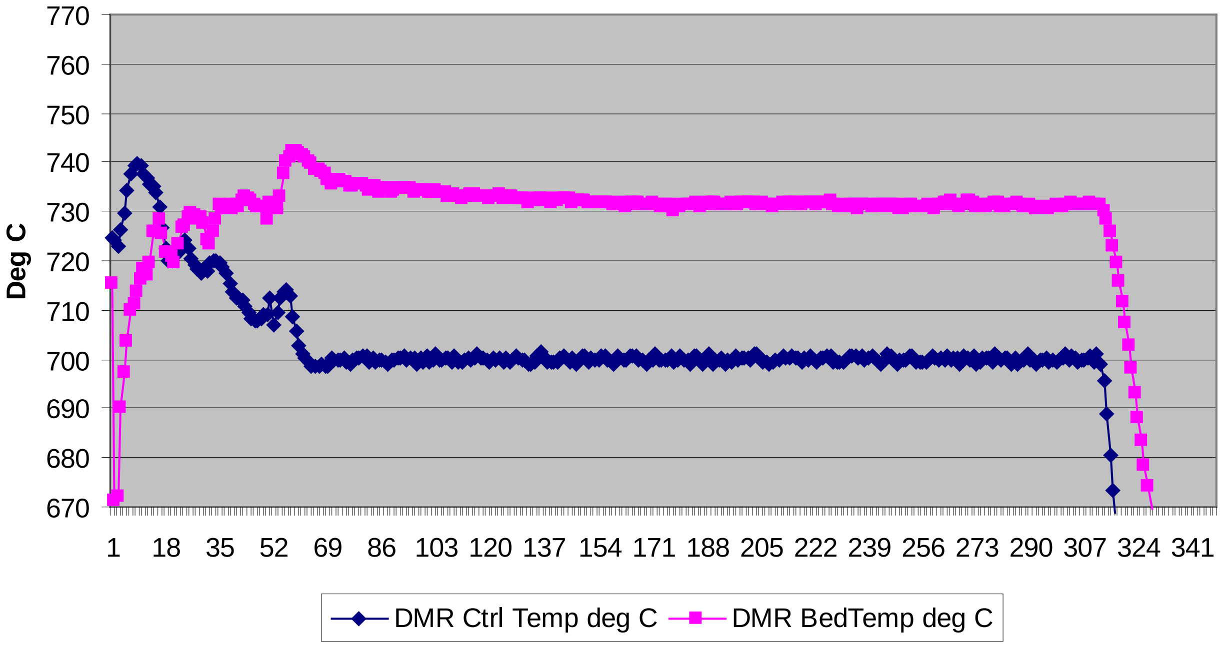

Figure G - 3. Run 4/7/11 Temperatures in DMR

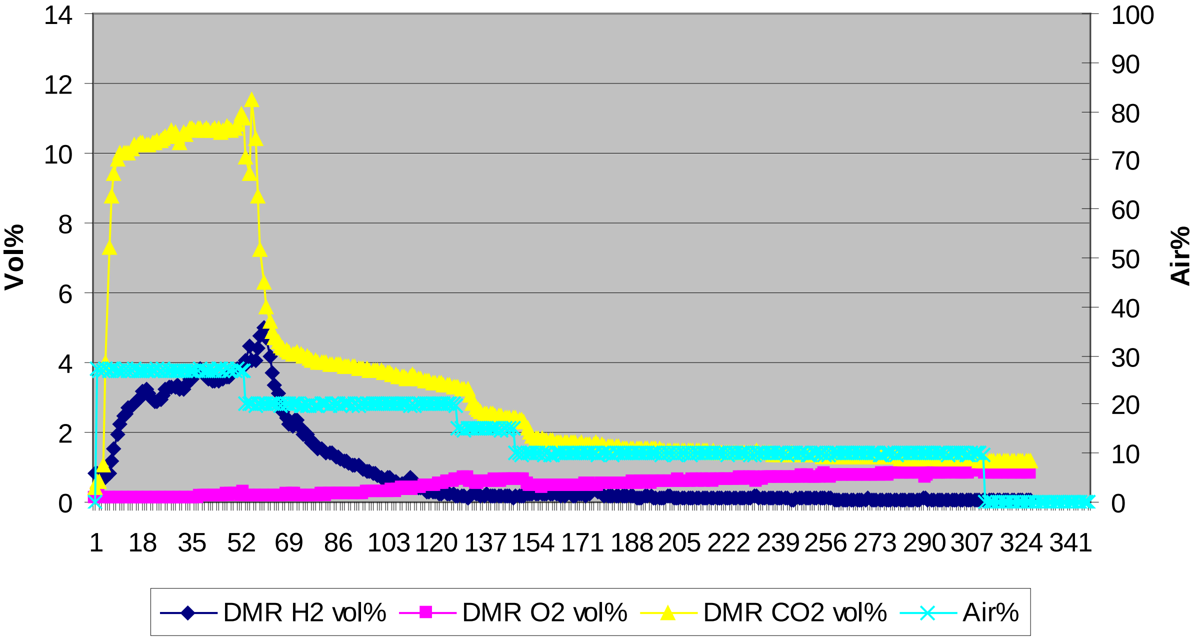

Figure G - 4. Run 4/7/11 Off-gas Concentrations and Air% Fed

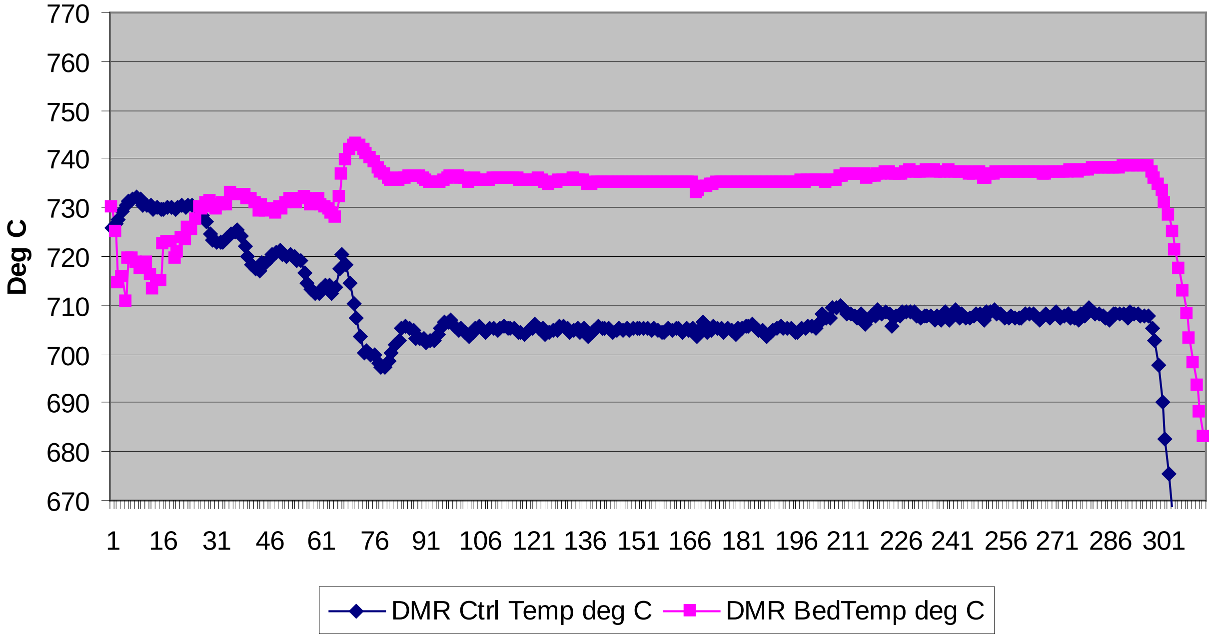

Figure G - 5. Run 4/8/11 Temperatures in DMR

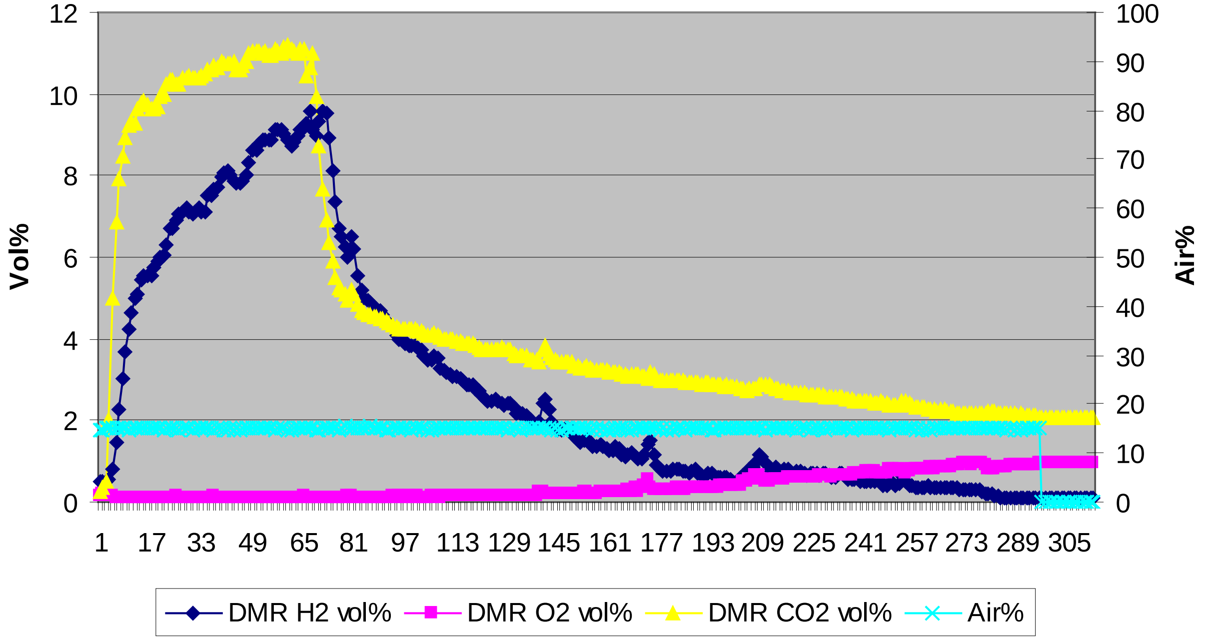

Figure G - 6. Run 4/8/11 Off-gas Concentrations and Air% Fed

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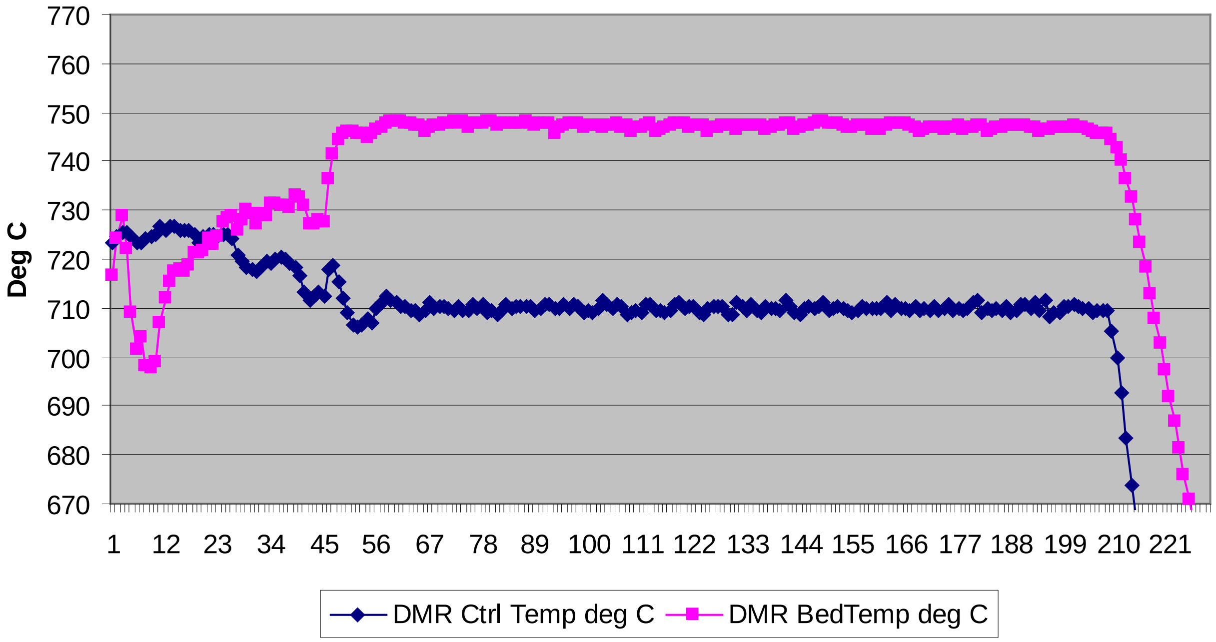

Figure G - 7. Run 4/9/11 Temperatures in DMR

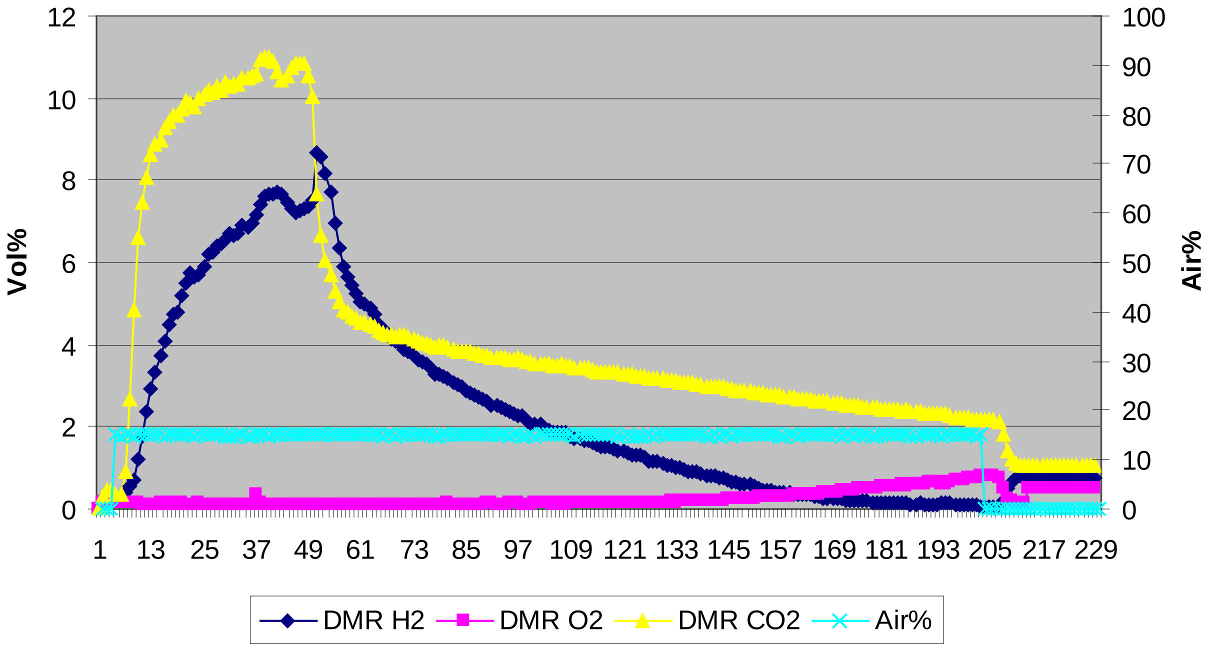

Figure G - 8. Run 4/9/11 Off-gas Concentrations and Air% Fed

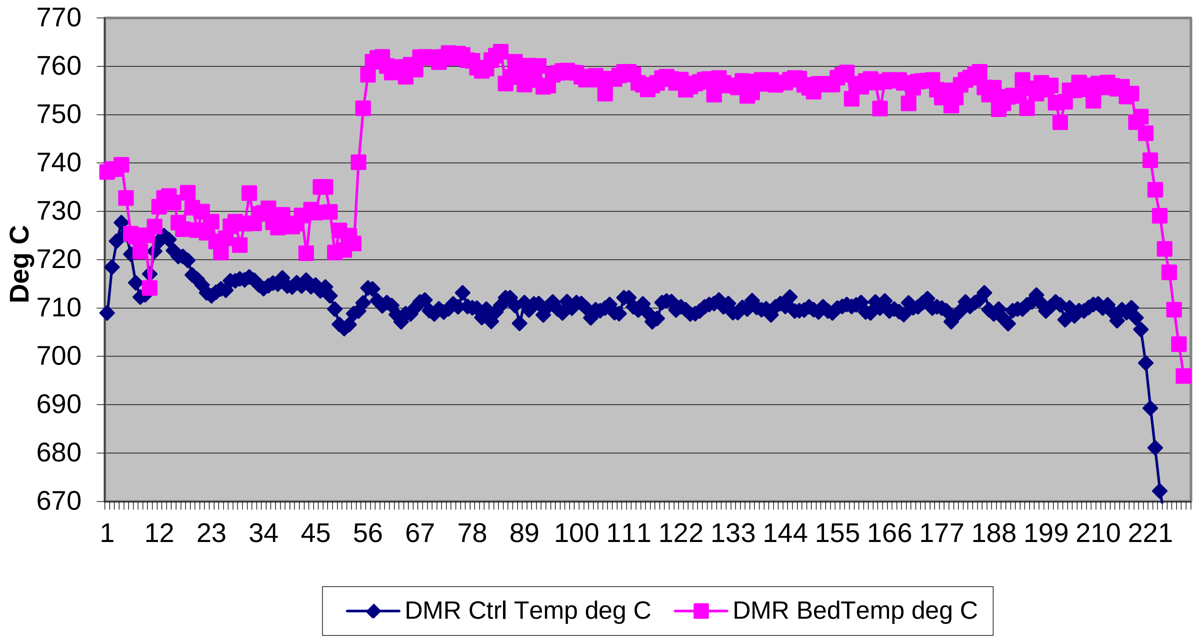

Figure G - 9. Run 4/13/11 Temperatures in DMR

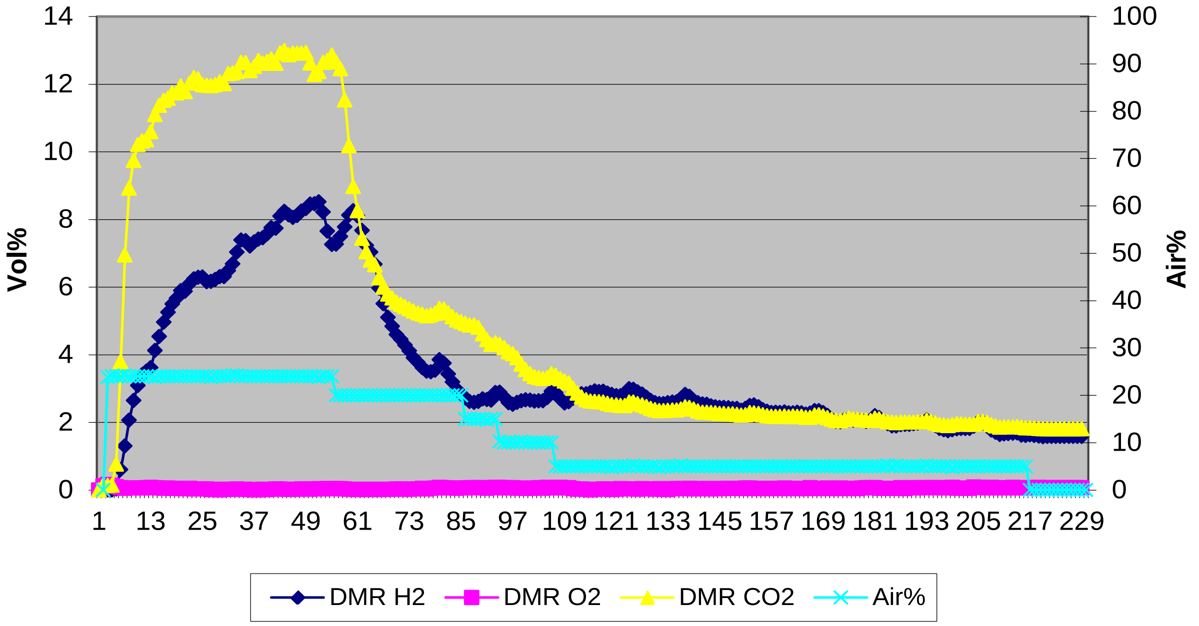

Figure G - 10. Run 4/13/11 Off-gas Concentrations and Air% Fed

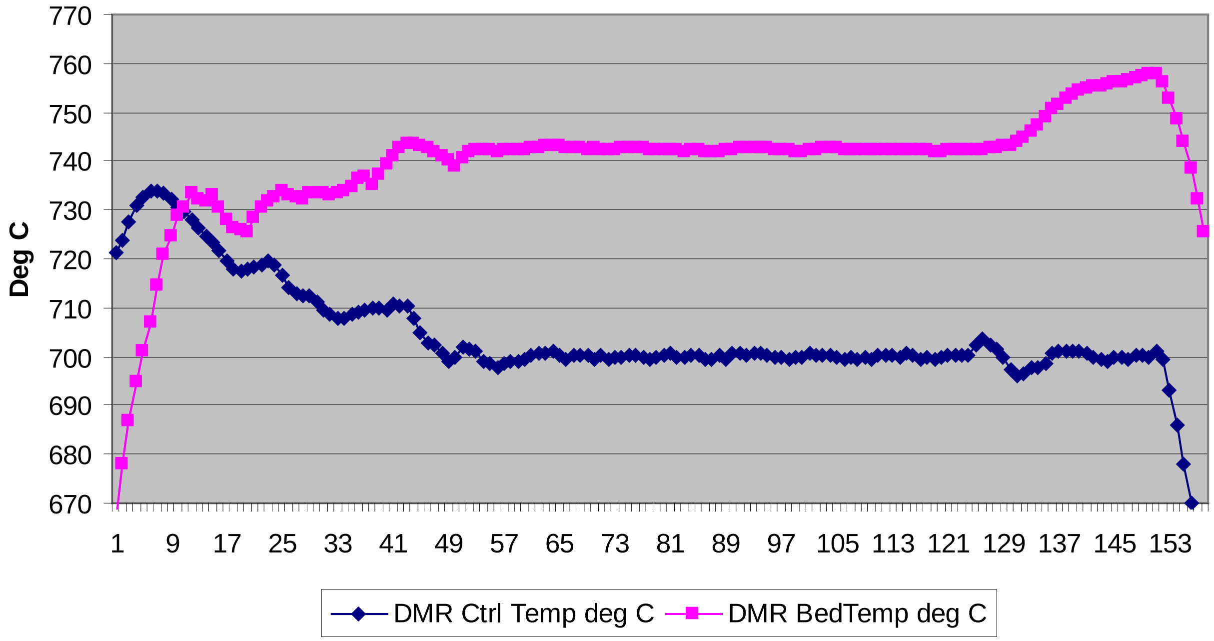

Figure G - 11. Run 4/15/11 Temperatures in DMR

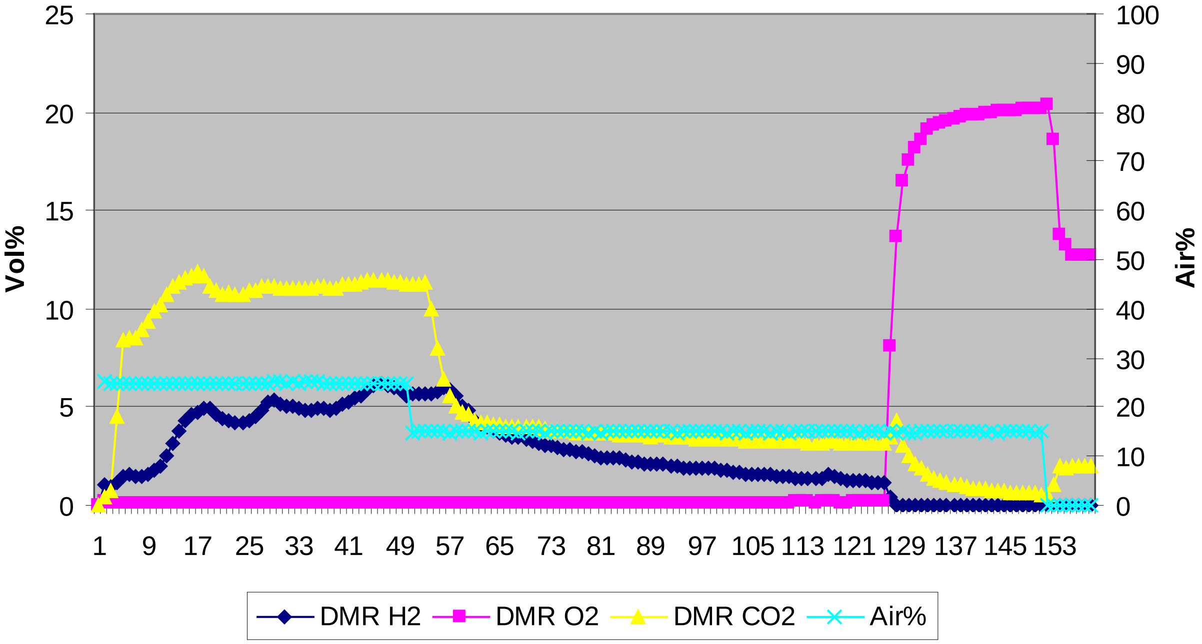

Figure G - 12. Run 4/15/11 Off-gas Concentrations and Air% Fed

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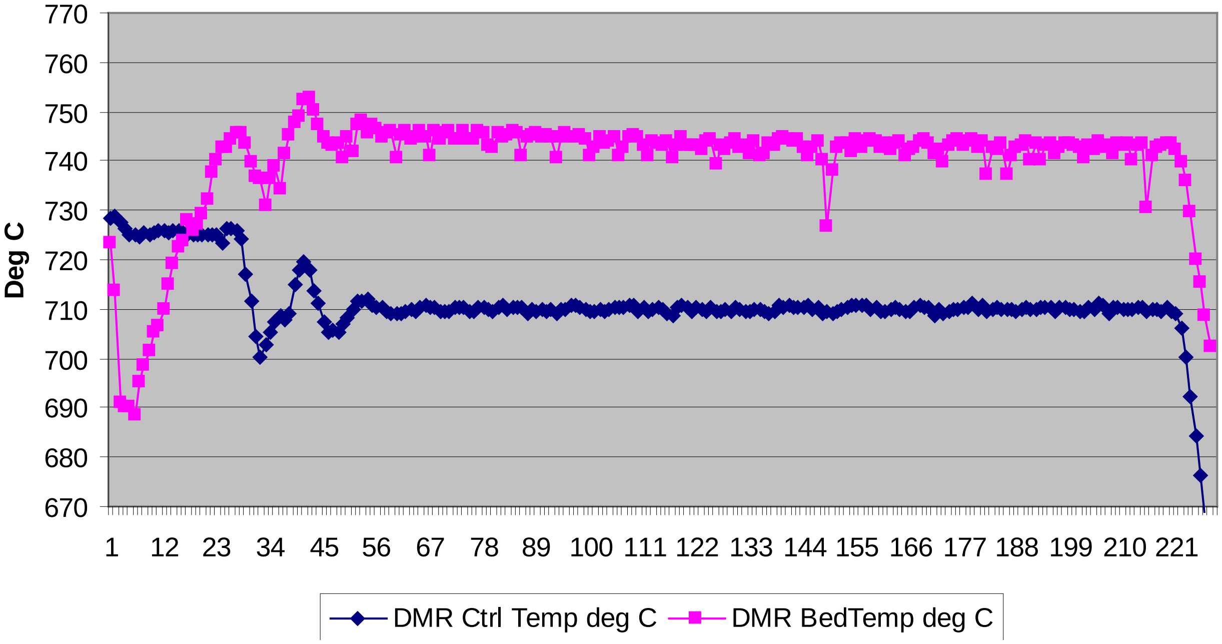

Figure G - 13. Run 4/18/11 Temperatures in DMR

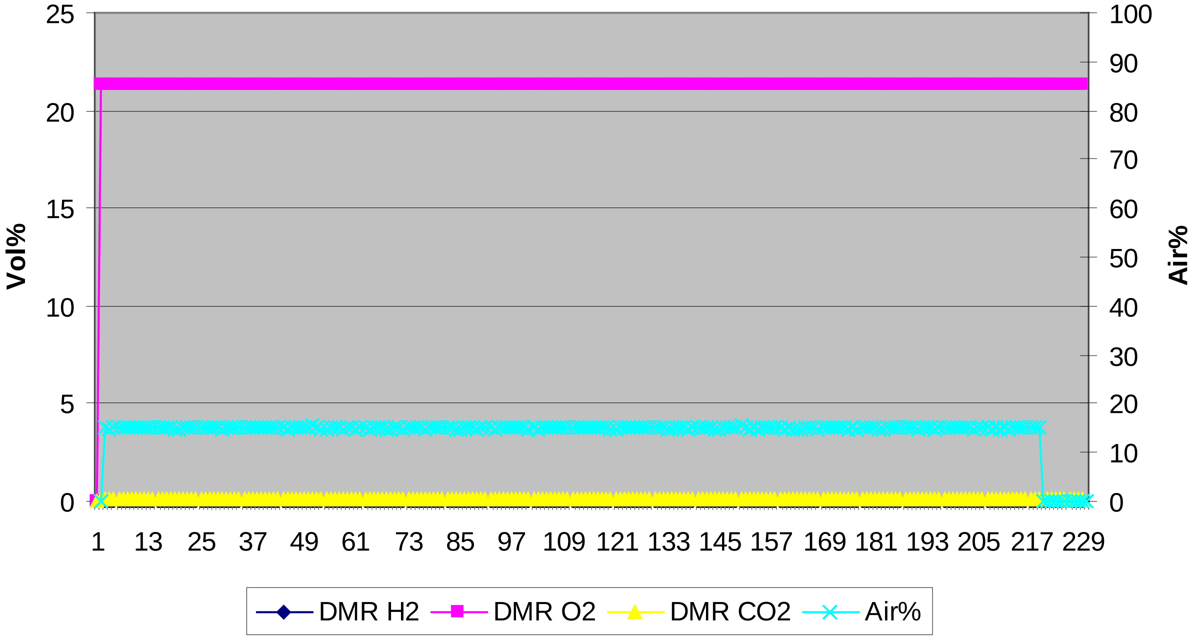

Figure G - 14. Run 4/18/11 Off-gas Concentrations and Air% Fed

Note: Mass Spec broken in this run.

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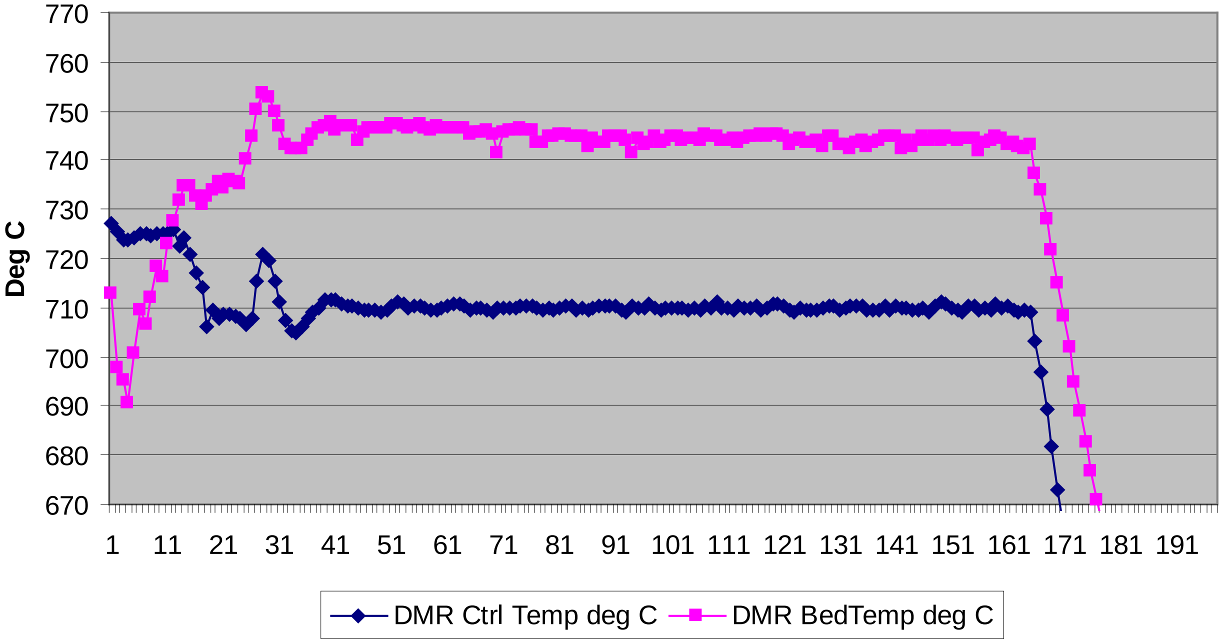

Figure G - 15. Run 4/19/11 Temperatures in DMR

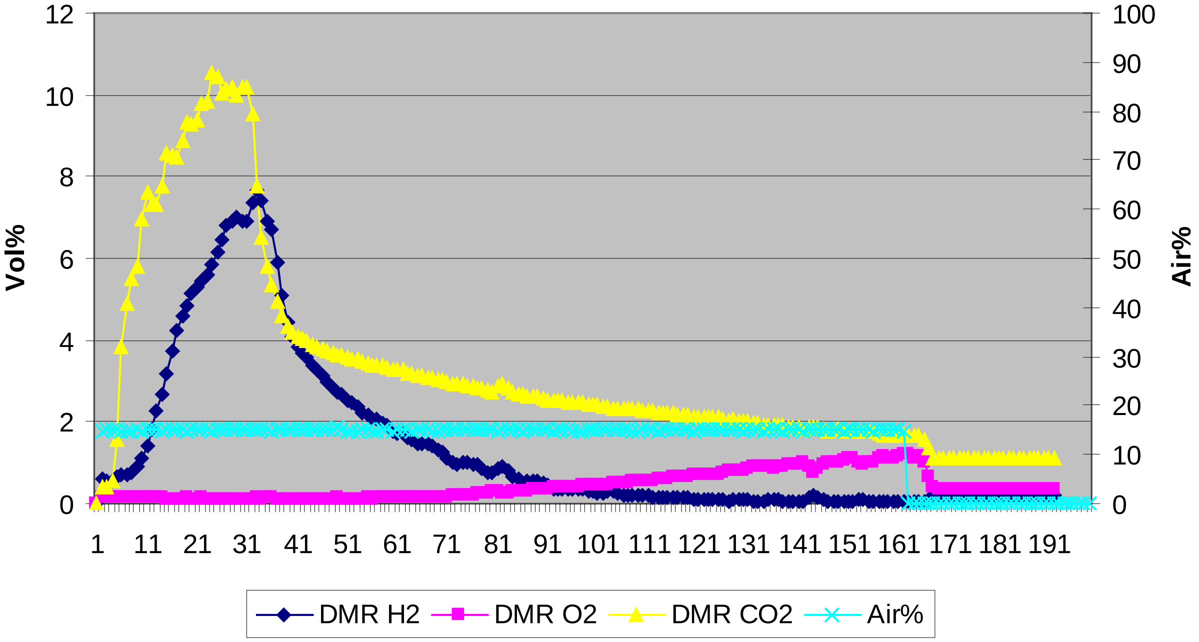

Figure G - 16. Run 4/19/11 Off-gas Concentrations and Air% Fed

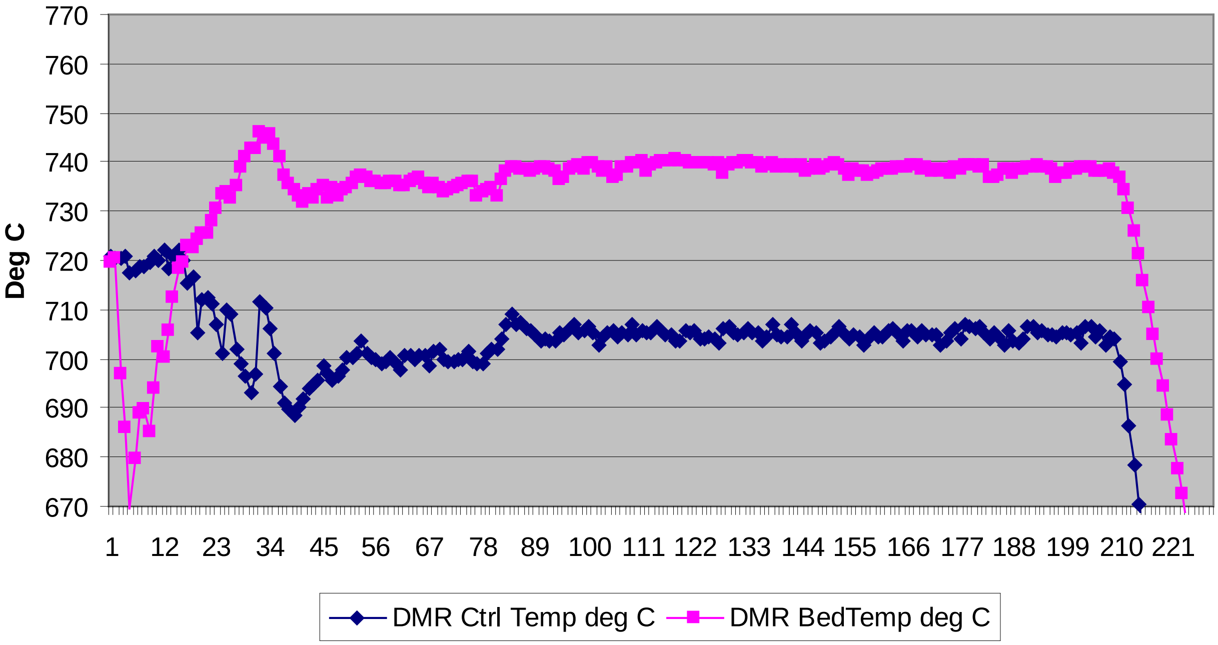

Figure G - 17. Run 4/20/11 Temperatures in DMR

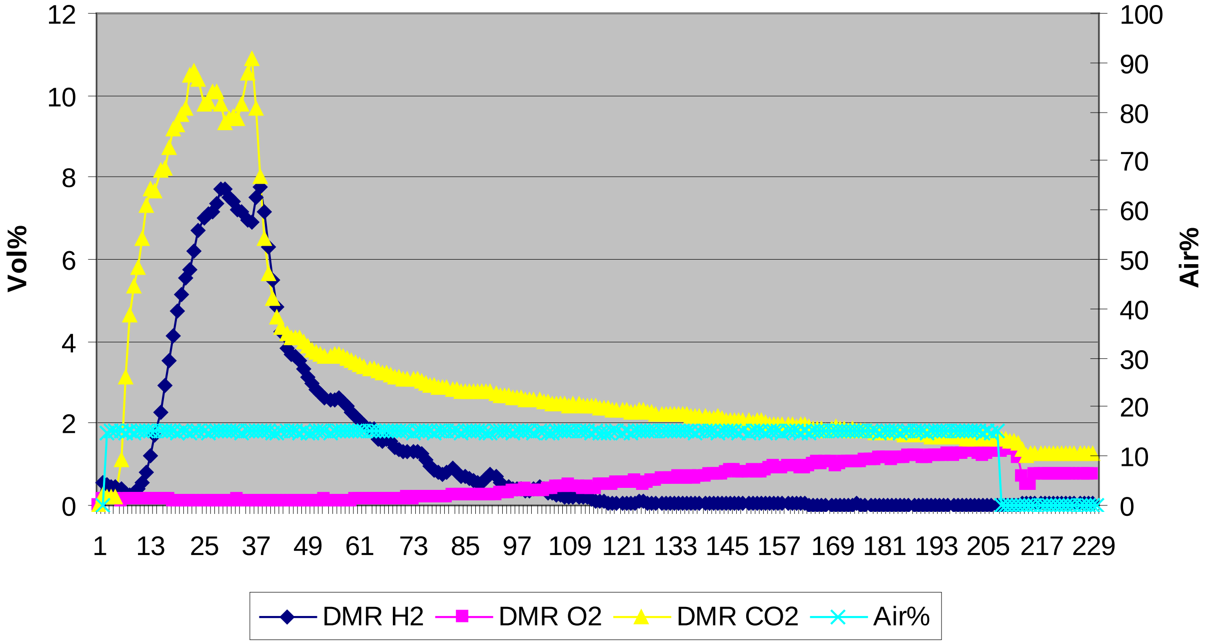

Figure G - 18. Run 4/20/11 Off-gas Concentrations and Air% Fed

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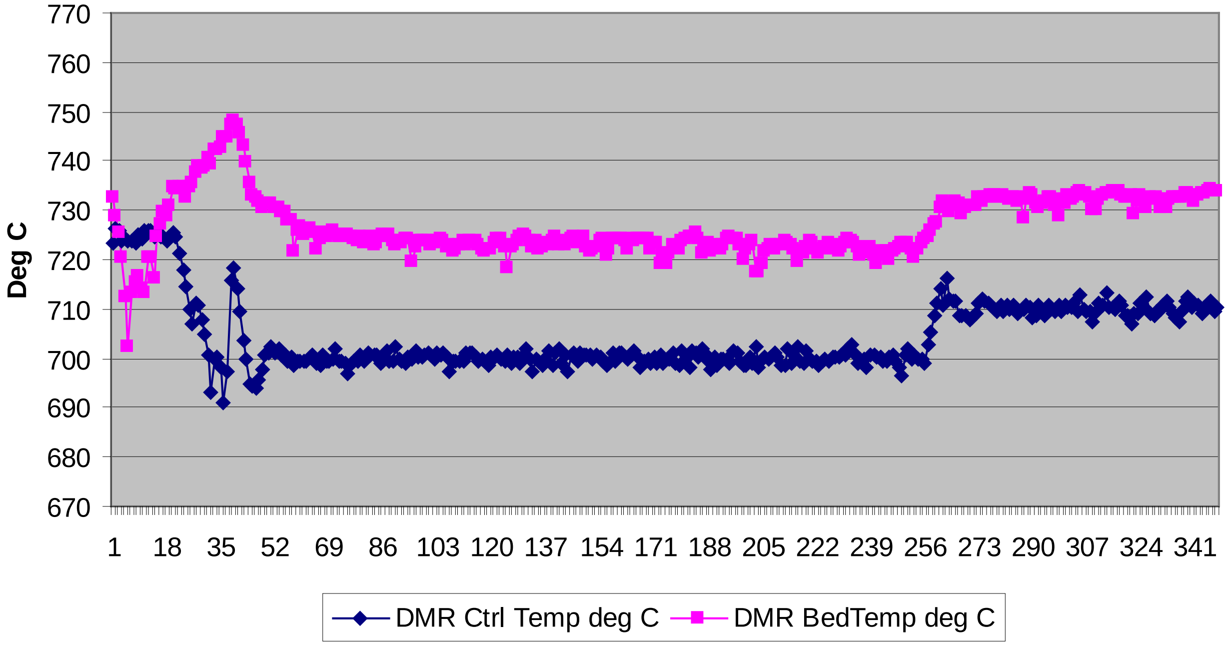

Figure G - 19. Run 5/5/11 Temperatures in DMR

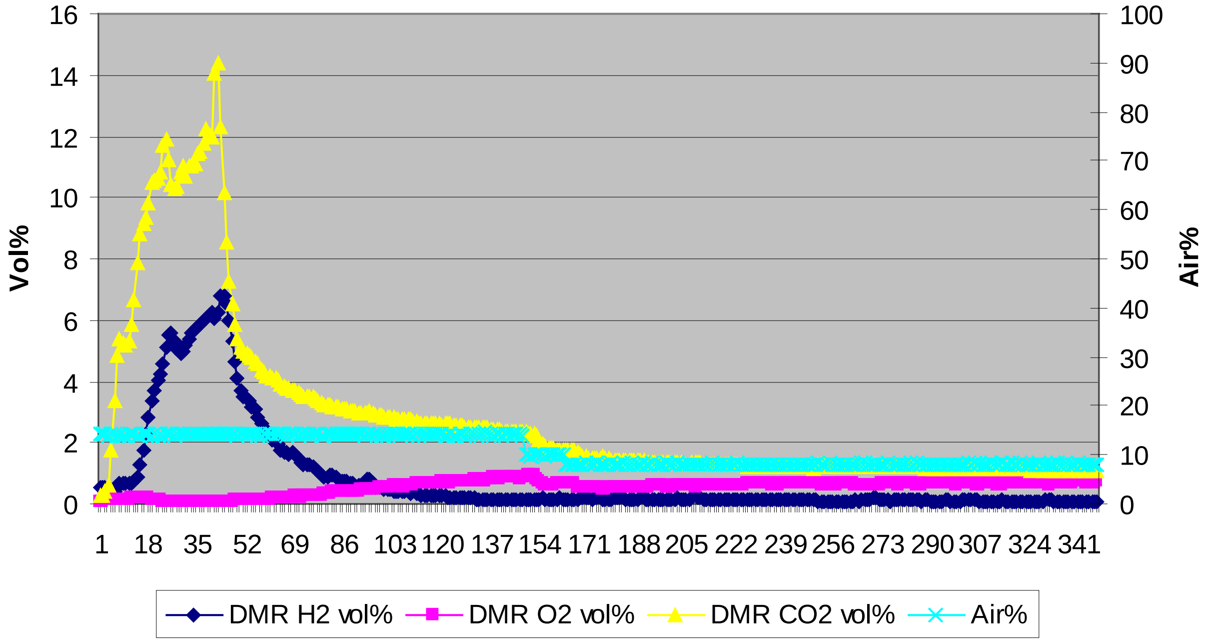

Figure G - 20. Run 5/5/11 Off-gas Concentrations and Air% Fed

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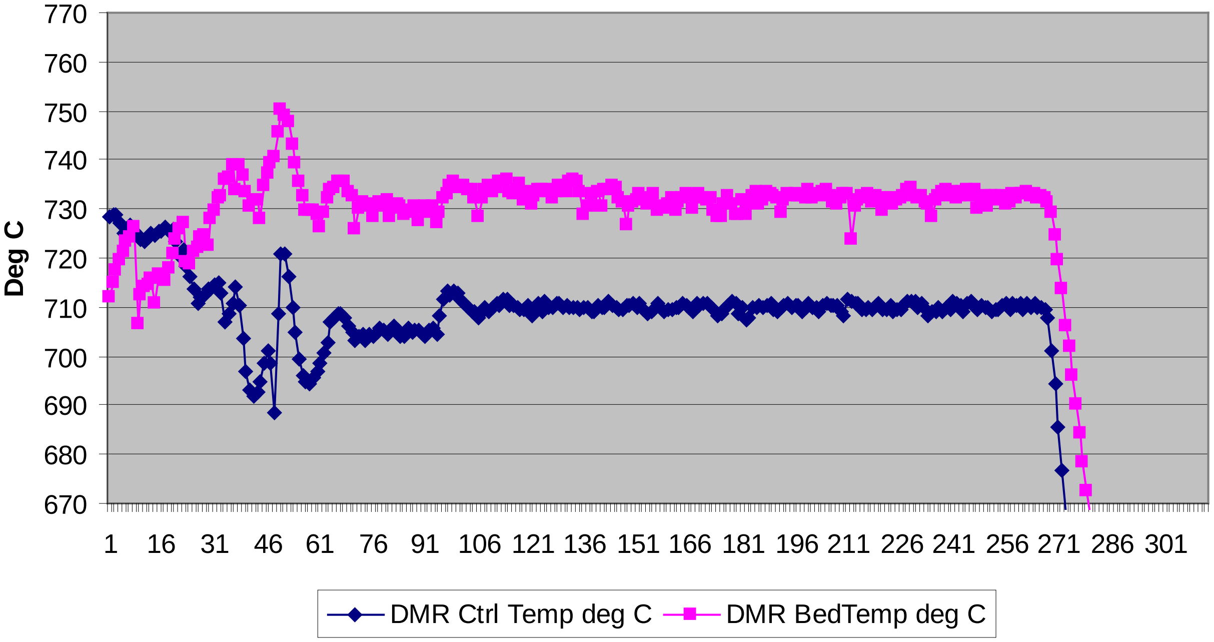

Figure G - 21. Run 5/9/11 Temperatures in DMR

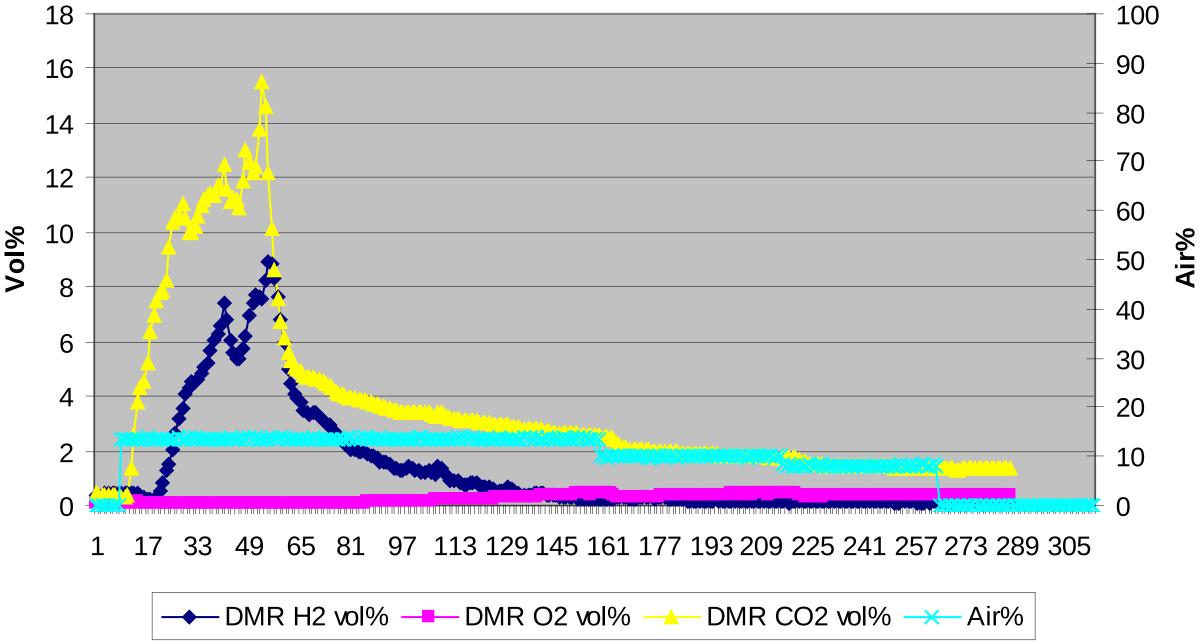

Figure G - 22. Run 5/9/11 Off-gas Concentrations and Air% Fed

.

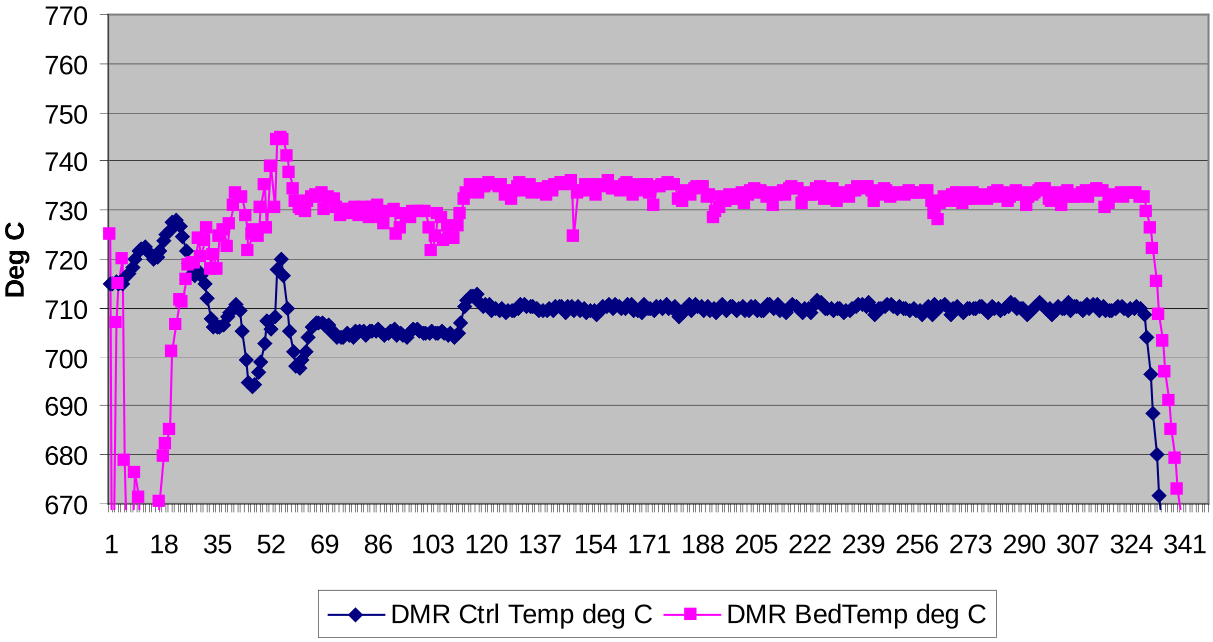

Figure G - 23. Run 5/10/11 Temperatures in DMR

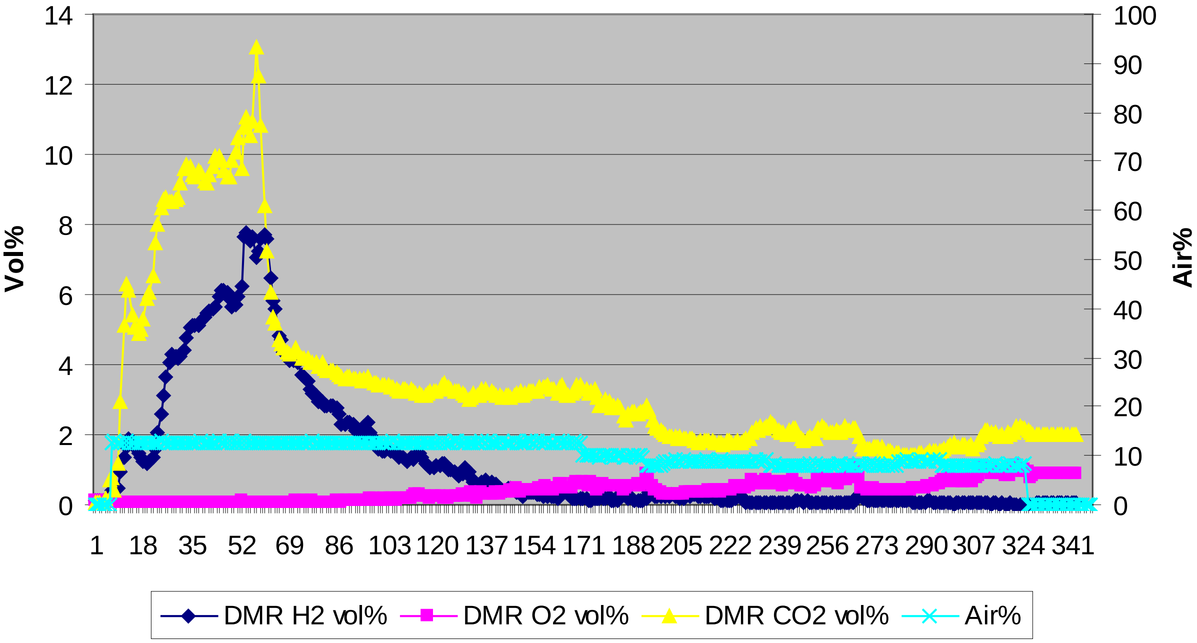

Figure G - 24. Run 5/10/11 Off-gas Concentrations and Air% Fed

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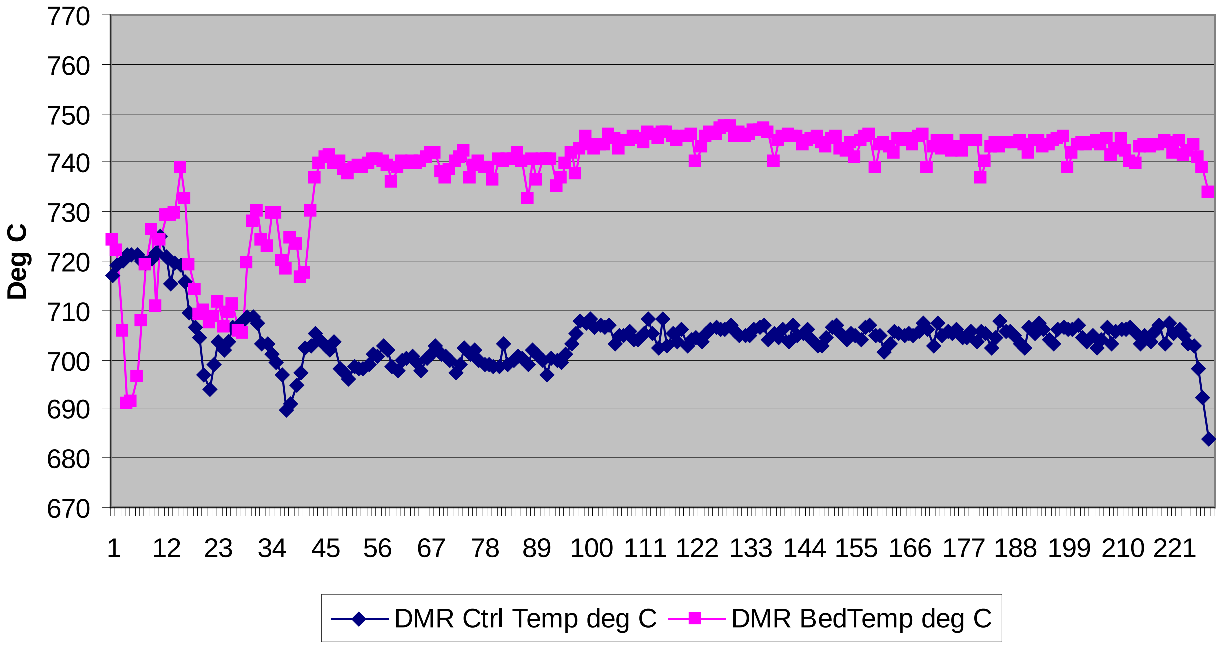

Figure G - 25. Run 5/11/11 Temperatures in DMR

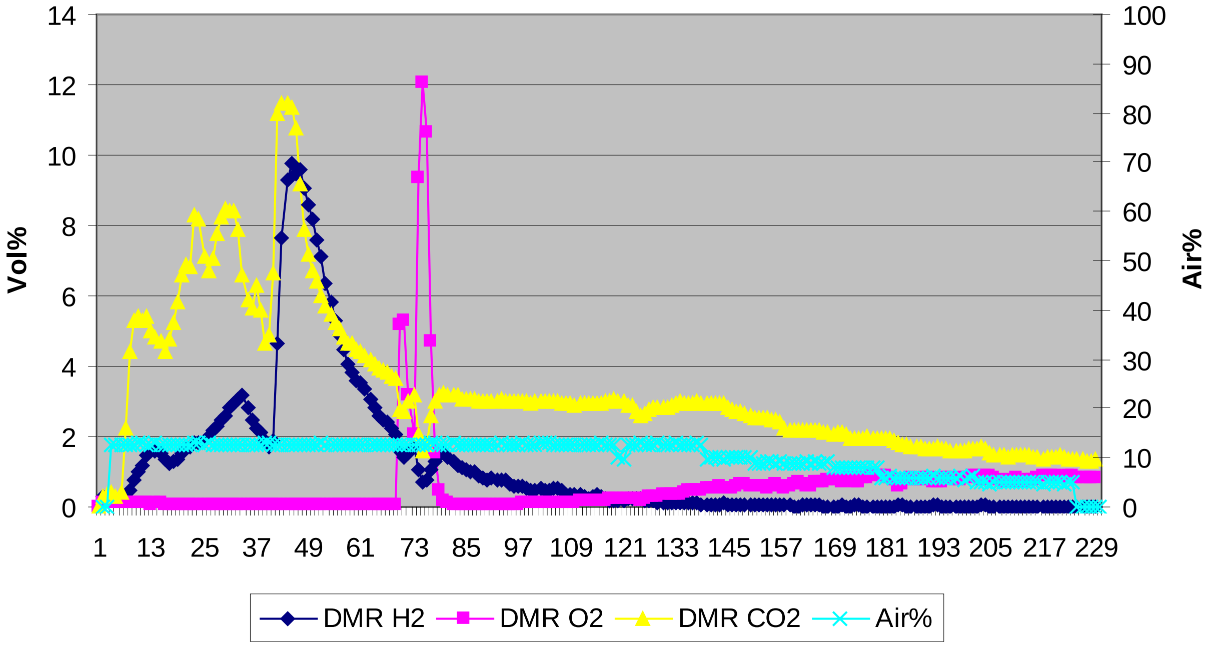

Figure G - 26. Run 5/11/11 Off-gas Concentrations and Air% Fed

Appendix H. BSR Process Operation Conditions & Trends for Simulant Module E Runs

Table H - 1. BSR Process Operation Conditions & Results for Simulant E Accepted Runs

Run Date	**9/6/11**	**10/3/11**
Iron Source	SphereOX	$FeNO_3$
Slurry Feed Rate (ml/min)	0.9	0.9
DMR Bed Temp (°C)	710 – 740	710 – 740
Superheated Steam Flow Rate (g/min)	0.40	0.40
DMR Control Pressure (inwc)	-4	-4
Coal (stoichiometry)	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500
CO_2/ml	17	16.6
Post Feed Run Time (min)	53	92
Product REDOX	0.13	0.06
Product LOI	0.703%	1.149%
Product Quantity (g)	19.41	20.33

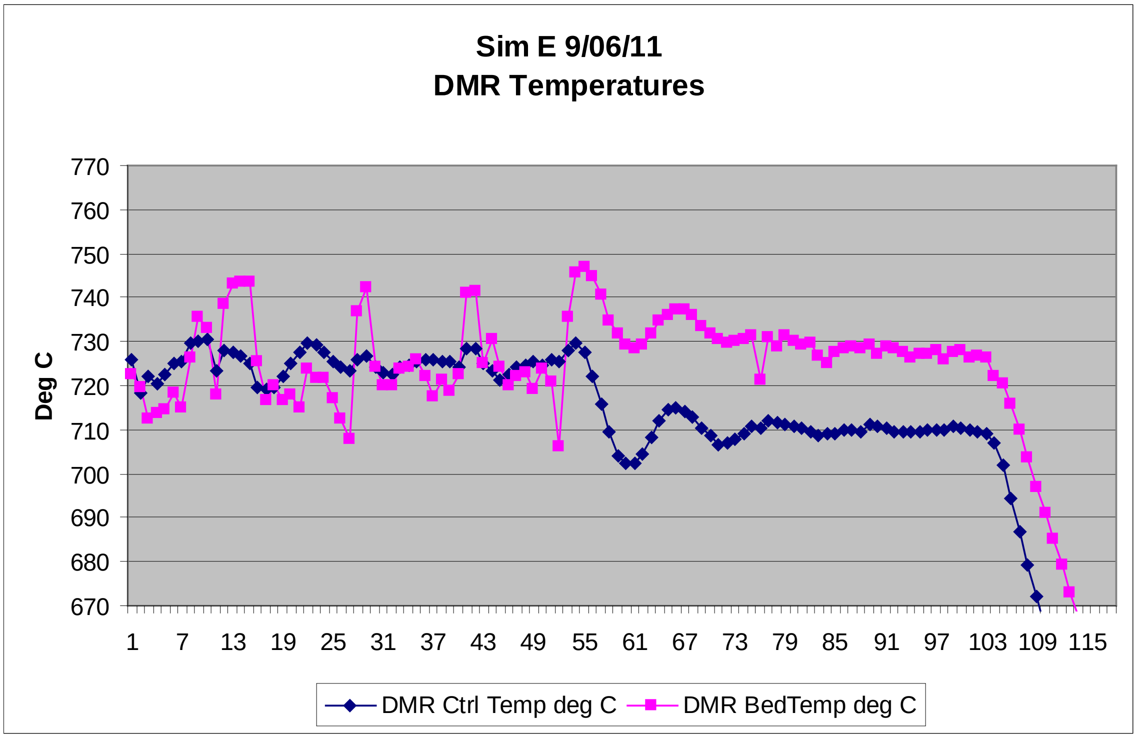

Figure H - 1. Run 9/6/11 Temperatures in DMR

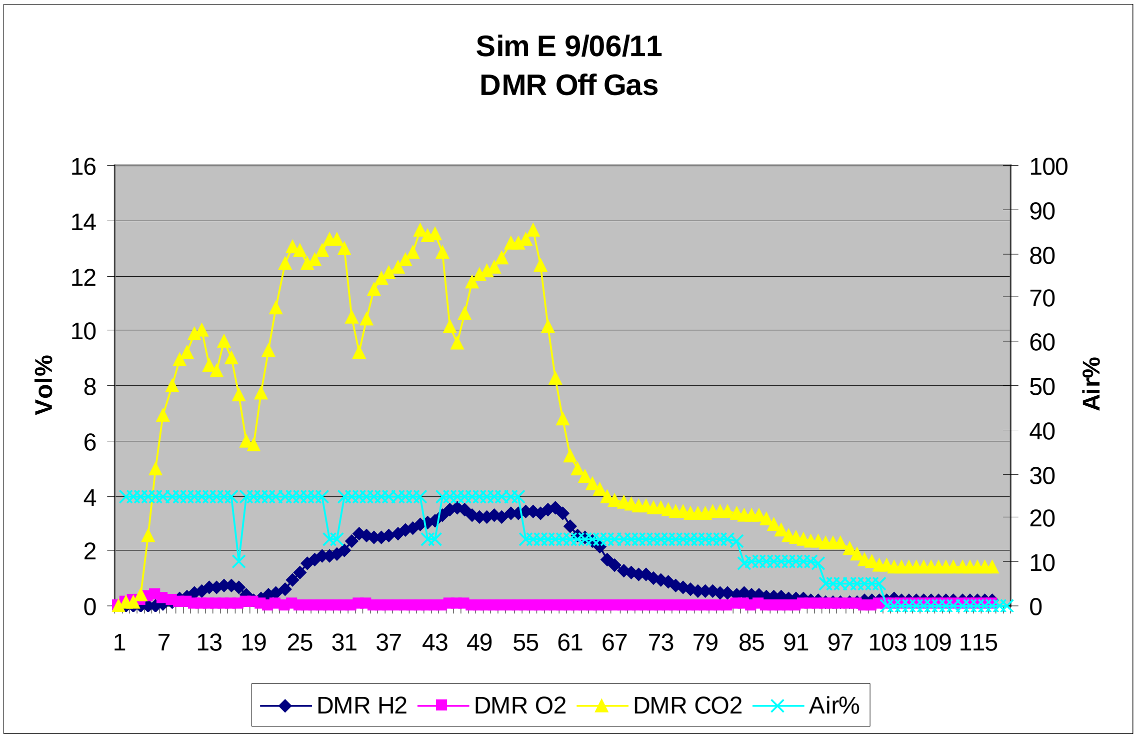

Figure H - 2. Run 9/6/11 Off-gas Concentrations and Air% Fed

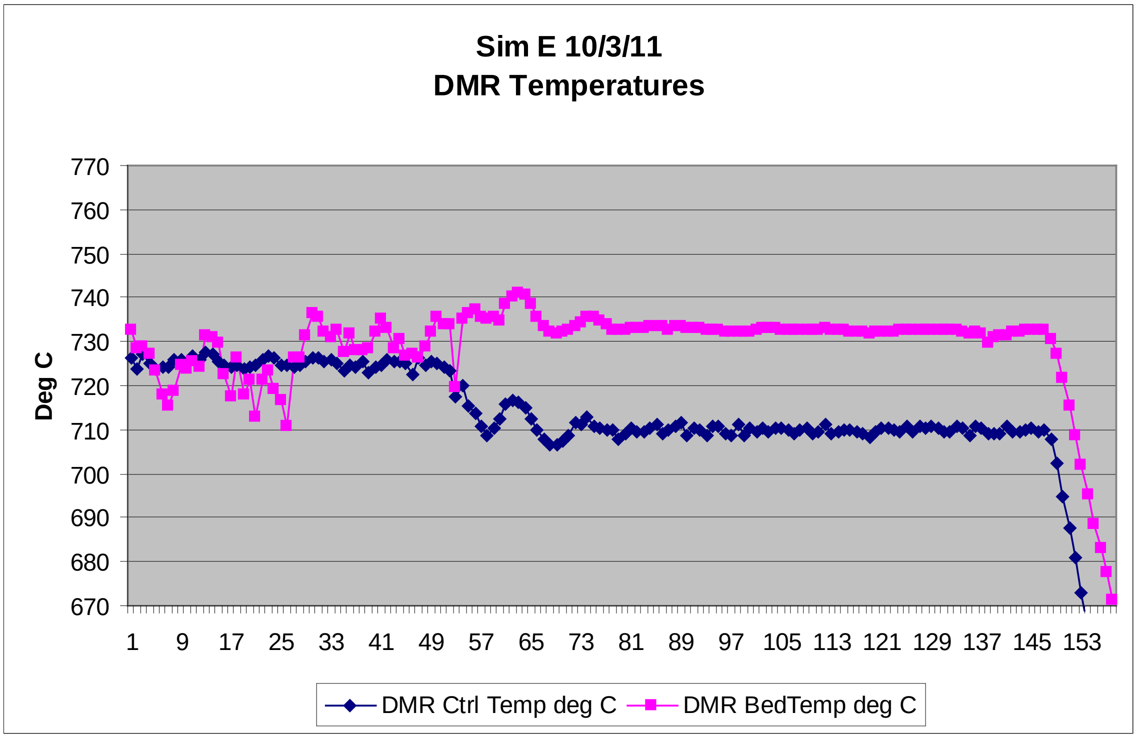

Figure H - 3. Run 10/3/11 Temperatures in DMR

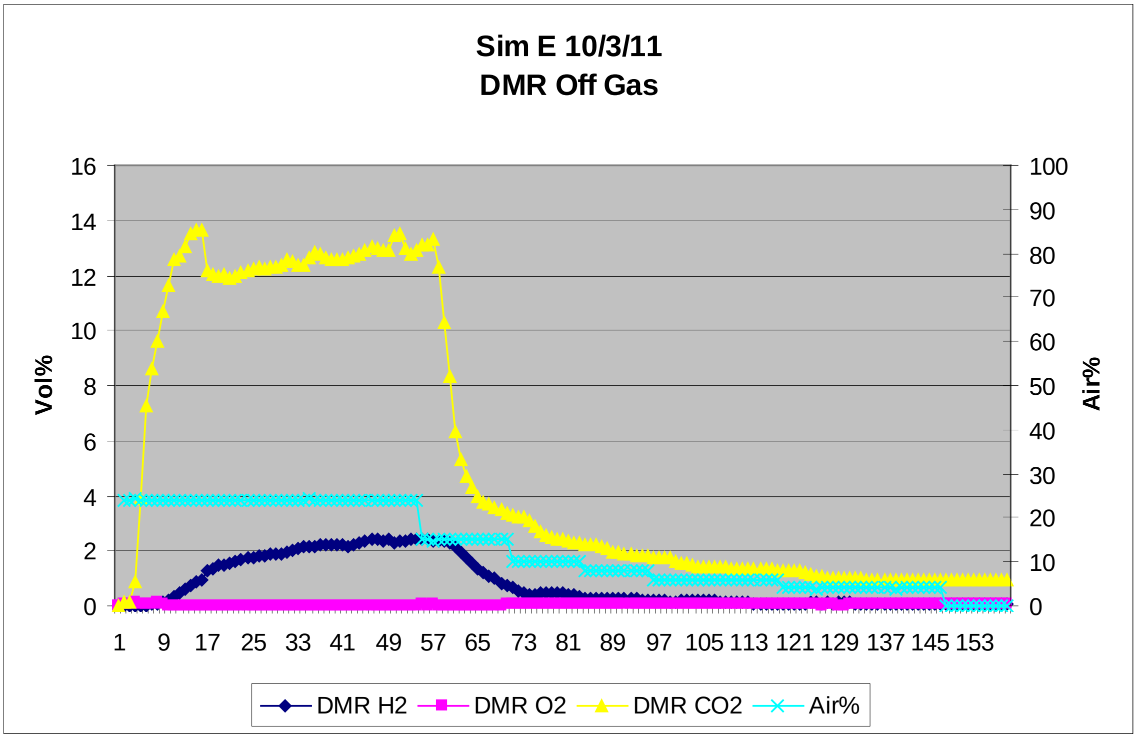

Figure H - 4. Run 10/3/11 Off-gas Concentrations and Air% Fed

Appendix I. Simulant Module C Mass Balance Analytical Data

Table I - 1 through Table I - 3 give the ICPES, IC, and ICPMS concentrations for the Simulant Mod C (Tank SX-105) granular product samples. The total mass of the composite granular product was 204.83 g and the average concentrations shown were used in the mass balance.

Table I - 1. Simulant Module C Granular Composite Product ICPES

Sample	Elemental Concentration (wt%)										
	Ag	**Al**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.0013	17.40	0.121	0.163	14.80	0.00243	0.33	< 0.0035	0.27	18.40	0.0027
2	< 0.0012	17.90	0.120	0.154	15.20	0.00241	0.33	< 0.0031	0.28	18.30	0.0027
3	< 0.0014	17.80	0.119	0.154	15.50	0.00236	0.33	< 0.0038	0.28	18.70	0.0025
4		17.60					0.29		0.31		
5		17.70					0.31		0.29		
6		17.70					0.31		0.32		
Average	**< 0.0013**	**17.68**	**0.120**	**0.157**	**15.17**	**0.0024**	**0.32**	**< 0.0034**	**0.29**	**18.47**	**0.0026**
Std. Dev.	0.0001	0.17	0.001	0.005	0.35	0.00004	0.02	0.0004	0.02	0.21	0.0001
%RSD	10.17	0.97	3.31	3.31	2.32	1.50	5.07	10.42	6.74	1.13	4.21

Table I - 2. Simulant Module C Granular Composite Product IC

Sample	Species Concentration (wt%)					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	< 0.23	0.21*	< 0.23	< 0.23	0.69	0.94
2	< 0.18		< 0.18	< 0.18	0.67	0.95
3	< 0.24		< 0.24	< 0.24	0.66	0.89
Average	**< 0.21**	**0.21***	**< 0.21**	**< 0.21**	**0.67**	**0.93**
Std. Dev.	0.03	0.00	0.03	0.03	0.01	0.03
%RSD	15.31	0.00	15.31	15.31	2.23	3.23

*Cl value from Neutron Activation Analysis

Table I - 3. Simulant Module C Granular Composite Product ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	**Re**	**I**
1	0.0006	0.045	0.033
2	0.0008	0.048	0.030
3	0.0007	0.048	0.032
Average	**0.0007**	**0.047**	**0.032**
Std. Dev.	0.0001	0.002	0.001
%RSD	12.23	3.50	3.82

The DMR condensate filtrate cation or ICPES concentrations from the runs for Simulant Module C runs are shown in Table I - 4. The DMR condensate filtrates were separated into three batches. The first and second batches represent condensate material collected before the use of quartz wool in the off-gas crossbar of the DMR. The third batch represents the condensate material collected after the use of quartz wool in the off-gas crossbar of the DMR. The first batch condensate samples were not filtered at the time of collection but filtered later. The second and third batch condensate samples were filtered at the time of collection. For the mass balance, a composite DMR condensate filtrate was calculated based on each batch average times the volume per batch. For example, the aluminum composite concentration in mg/L was calculated as:

$$xf_{Al} = \frac{(0.6467 * 5.13E-01) + (0.2086 * 4.10E-01) + (0.5993 * 3.45E-01)}{0.6467 + 0.2086 + 0.5993} = \frac{6.24E-01}{1.4546} = 4.29E-01$$

Note that if one batch had a less than or below detection limit value and the other batch had a measured value then only the measured value was used in the composite calculation. For example, the potassium composite concentration in mg/L was calculated as:

$$xf_{K} = \frac{(0.2086 * 5.88E-01)}{0.6467 + 0.2086 + 0.5993} = \frac{1.23E-01}{1.4546} = 8.43E-02$$

The cation or ICPES concentrations based on this method for the DMR condensate filtrate composite filtrate are shown in Table I - 5 and these values were used in the mass balance.

Table I - 4. Simulant Module C Condensate Filtrates ICPES

Batch	Volume (L)	Sample	Elemental Concentration (mg/L)									
			Ag	Al	Cr	K	Na	Ni	P	Pb	S	Si	Zn
1 (Filtered Later & Before Quartz Wool)	0.6467	1	< 8.50E-02	4.67E-01	< 2.80E-02	< 4.89E-01	5.58E+01	< 3.80E-02	3.75E-01	< 9.20E-02	1.93E+01	3.21E+00	< 3.60E-02
		2	< 8.50E-02	4.43E-01	< 2.80E-02	< 4.89E-01	5.48E+01	< 3.80E-02	3.80E-01	< 9.20E-02	1.96E+01	3.42E+00	< 3.60E-02
		3	< 8.50E-02	6.28E-01	< 2.80E-02	< 4.89E-01	5.56E+01	< 3.80E-02	3.92E-01	< 9.20E-02	1.95E+01	3.31E+00	< 3.60E-02
		Average	**< 8.50E-02**	**5.13E-01**	**< 2.80E-02**	**< 4.89E-01**	**5.54E+01**	**< 3.80E-02**	**3.82E-01**	**< 9.20E-02**	**1.95E+01**	**3.31E+00**	**< 3.60E-02**
		Std. Dev.	na	1.01E-01	na	na	5.29E-01	na	8.74E-03	na	1.53E-01	1.05E-01	na
		%RSD	na	19.62%	na	na	0.96%	na	2.29%	na	0.78%	3.17%	na
2 (Filtered Immediately & Before Quartz Wool)	0.2086	1	< 8.50E-02	4.11E-01	< 2.80E-02	6.05E-01	1.77E+01	4.60E-02	2.30E-01	< 9.20E-02	1.32E+01	4.57E+00	6.30E-02
		2	< 8.50E-02	4.26E-01	< 2.80E-02	<4.89E-01	1.76E+01	5.70E-02	2.39E-01	< 9.20E-02	1.39E+01	4.34E+00	5.70E-02
		3	< 8.50E-02	3.94E-01	< 2.80E-02	5.71E-01	1.76E+01	4.90E-02	2.08E-01	< 9.20E-02	1.35E+01	3.96E+00	6.00E-02
		Average	**< 8.50E-02**	**4.10E-01**	**< 2.80E-02**	**5.88E-01**	**1.76E+01**	**5.07E-02**	**2.26E-01**	**< 9.20E-02**	**1.35E+01**	**4.29E+00**	**6.00E-02**
		Std. Dev.	na	1.60E-02	na	2.40E-02	5.77E-02	5.69E-03	1.59E-02	na	3.51E-01	3.08E-01	3.00E-03
		%RSD	na	3.90%	na	4.09%	0.33%	11.22%	7.07%	na	2.59%	7.18%	5.00%
3 (Filtered Immediately & After Quartz Wool)	0.5993	1	< 8.70E-02	3.42E-01	< 5.30E-02	< 1.22E+00	3.31E+00	< 4.30E-02	< 1.38E-01	3.09E-01	1.79E+01	3.37E+00	< 4.10E-02
		2	< 8.70E-02	3.42E-01	< 5.30E-02	< 1.22E+00	3.39E+00	< 4.30E-02	< 1.38E-01	<2.30E-01	1.82E+01	3.39E+00	< 4.10E-02
		3	< 8.70E-02	3.51E-01	< 5.30E-02	< 1.22E+00	3.27E+00	< 4.30E-02	< 1.38E-01	<2.30E-01	1.82E+01	3.29E+00	< 4.10E-02
		Average	**< 8.70E-02**	**3.45E-01**	**< 5.30E-02**	**< 1.22E+00**	**3.32E+00**	**< 4.30E-02**	**< 1.38E-01**	**3.09E-01**	**1.81E+01**	**3.35E+00**	**< 4.10E-02**
		Std. Dev.	na	5.20E-03	na	na	6.11E-02	na	na	na	1.73E-01	5.29E-02	na
		%RSD	na	1.51%	na	na	1.84%	na	na	na	0.96%	1.58%	na

na=not applicable

Table I - 5. Simulant Module C Condensate Composite Filtrate ICPES

Batch	Volume (L)	Elemental Concentration (mg/L)									
		Ag	Al	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	1.4546	< 8.58E-02	4.29E-01	< 3.83E-02	8.43E-02	2.85E+01	7.27E-03	2.02E-01	1.27E-01	1.81E+01	3.47E+00	8.60E-03

The DMR condensate filtrates were separated into three batches and the anion or IC analyses performed on each batch are shown in Table I - 6. For the mass balance, a composite DMR condensate filtrate was calculated based on each batch average times the volume per batch. For example, the nitrite composite concentration in mg/L was calculated as:

$$xf_{NO2} = \frac{(0.6467 * 5.84E + 05) + (0.2086 * 8.43E + 04) + (0.5993 * 4.57E + 04)}{0.6467 + 0.2086 + 0.5993} = \frac{4.224E + 05}{1.4546} = 2.90E + 05$$

Note that if one batch had a less than or below detection limit value and the other batch had a measured value then only the measured value was used in the composite calculation. For example, the nitrate composite concentration in mg/L was calculated as:

$$xf_{NO3} = \frac{(0.6467 * 5.70E + 04)}{0.6467 + 0.2086 + 0.5993} = \frac{3.69E + 04}{1.4546} = 2.53E + 04$$

The DMR condensate composite filtrate anion or IC concentrations for the Simulant Module C runs are shown in Table I - 7. and these values were used in the mass balance.

Table I - 6. Simulant Module C Condensate Filtrates IC

Batch	**Volume (L)**	**Sample**	**Species Concentration (ug/L)**					
			F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1 (Filtered Later & Before Quartz Wool)	0.6467	1	< 5.00E+03	6.10E+04	6.46E+05	5.70E+04	3.90E+04	< 1.00E+04
		2	< 5.00E+03	6.10E+04	5.80E+05	5.70E+04	3.90E+04	< 1.00E+04
		3	< 5.00E+03	6.10E+04	5.25E+05	5.70E+04	3.90E+04	< 1.00E+04
		Average	**< 5.00E+03**	**6.10E+04**	**5.84E+05**	**5.70E+04**	**3.90E+04**	**< 1.00E+04**
		Std. Dev.	na	0.00E+00	6.06E+04	0.00E+00	0.00E+00	na
		%RSD	na	0.00%	10.38%	0.00%	0.00%	na
2 (Filtered Immediately & Before Quartz Wool)	0.2086	1	< 5.00E+03	1.10E+04	8.20E+04	< 5.00E+03	1.70E+04	< 5.00E+03
		2	< 5.00E+03	1.20E+04	8.40E+04	< 5.00E+03	1.80E+04	< 5.00E+03
		3	< 5.00E+03	1.20E+04	8.70E+04	< 5.00E+03	1.80E+04	< 5.00E+03
		Average	**< 5.00E+03**	**1.17E+04**	**8.43E+04**	**< 5.00E+03**	**1.77E+04**	**< 5.00E+03**
		Std. Dev.	na	5.77E+02	2.52E+03	na	5.77E+02	na
		%RSD	na	4.95%	2.98%	na	3.27%	na
3 (Filtered Immediately & After Quartz Wool)	0.5993	1	< 5.00E+03	< 5.00E+03	4.60E+04	< 5.00E+03	2.50E+04	< 5.00E+03
		2	< 5.00E+03	< 5.00E+03	4.50E+04	< 5.00E+03	2.40E+04	< 5.00E+03
		3	< 5.00E+03	< 5.00E+03	4.60E+04	< 5.00E+03	2.40E+04	< 5.00E+03
		Average	**< 5.00E+03**	**< 5.00E+03**	**4.57E+04**	**< 5.00E+03**	**2.43E+04**	**< 5.00E+03**
		Std. Dev.	na	na	5.77E+02	na	5.77E+02	na
		%RSD	na	na	1.26%	na	2.37%	na

na=not applicable

Table I - 7. Simulant Module C Condensate Composite Filtrates IC

Sample	**Species Concentration (ug/L)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	< 5.00E+03	2.88E+04	2.90E+05	2.53E+04	2.99E+04	< 7.22E+03

The DMR condensate filtrates were separated into three batches and the trace elemental or ICPMS analyses performed on each batch are shown in Table I - 8. For the mass balance, a composite DMR condensate filtrate was calculated based on each batch average times the volume per batch. For example, the cesium composite concentration in mg/L was calculated as:

$$xf_{cs} = \frac{(0.6467 * 1.49E+01) + (0.2086 * 7.20E+00) + (0.5993 * 2.17E+00)}{0.6467 + 0.2086 + 0.5993} = \frac{1.244E+01}{1.4546} = 8.55E+00$$

The trace elemental or ICPMS concentrations for the DMR condensate composite filtrate are shown in Table I - 9.

Table I - 8. Simulant Module C Condensate Filtrates ICPMS

Batch	**Volume (L)**	**Elemental Concentration (ug/L)**			
		Sample	**Cs**	**Re**	**I**
1 (Filtered Later & Before Quartz Wool)	0.6467	1	1.50E+01	1.97E+03	9.67E+03
		2	1.47E+01	2.00E+03	9.60E+03
		3	1.50E+01	1.99E+03	9.60E+03
		Average	**1.49E+01**	**1.99E+03**	**9.62E+03**
		Std. Dev.	1.73E-01	1.53E+01	4.04E+01
		%RSD	1.16%	0.77%	0.42%
2 (Filtered Immediately & Before Quartz Wool)	0.2086	1	7.19E+00	6.46E+02	1.67E+03
		2	7.36E+00	6.46E+02	1.70E+03
		3	7.04E+00	6.42E+02	1.68E+03
		Average	**7.20E+00**	**6.45E+02**	**1.68E+03**
		Std. Dev	1.60E-01	2.31E+00	1.53E+01
		%RSD	2.22%	0.36%	0.91%
3 (Filtered Immediately & After Quartz Wool)	0.5993	1	2.35E+00	1.91E+02	7.20E+02
		2	2.03E+00	1.87E+02	7.23E+02
		3	2.13E+00	1.95E+02	7.21E+02
		Average	**2.17E+00**	**1.91E+02**	**7.21E+02**
		Std. Dev	1.64E-01	4.00E+00	1.53E+00
		%RSD	7.54%	2.09%	0.21%

na=not applicable

Table I - 9. Simulant Module C Condensate Composite Filtrate ICPMS

Run	**Volume (L)**	**Elemental Concentration (ug/L)**		
		Cs	**Re**	**I**
Composite	1.4546	8.55E+00	1.05E+03	4.82E+03

The DMR condensate composite filtered solids concentrations from the Simulant Module C are shown in Table I - 10. The DMR condensate composite filtered solids mass was 0.34 g and the average concentrations shown were used in the mass balance.

Table I - 10. Simulant Module C Condensate Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.0022	16.20	0.021	0.123	0.357	9.20	0.005	0.289	0.091	0.109	15.500	0.005
2		16.40		0.110								
Average	**< 0.0022**	**16.30**	**0.021**	**0.12**	**0.36**	**9.200**	**0.005**	**0.289**	**0.09**	**0.109**	**15.50**	**0.005**
Standard Deviation	na	0.14	na	0.01	na	na	na	na	na	na	na	na
%RSD	na	0.87	na	7.89	na	na	na	na	na	na	na	na

na=not applicable

Anion or IC analyses were performed on the Simulant Module C condensate filtered solid samples but gave concentrations for F, Cl, NO_2, NO_3, SO_4, and PO_4 at or below detection limits. For the mass balance, the SO_4 and PO_4 concentrations were estimated from the S and P analyses discussed in the prior section using the following logic:

$$cs_{SO4} = \frac{cs_S * MW_{SO4}}{MW_S}$$

$$cs_{PO4} = \frac{cs_S * MW_{PO4}}{MW_P}$$

The SO_4 and PO_4 concentrations for the DMR Condensate Composite Filtered Solids for Simulant Module C can be calculated as follows:

$$cs_{SO4} = \frac{0.109\% * 96.0636}{32.0660} = 0.33\%$$
$$cs_{PO4} = \frac{0.289\% * 94.9714}{30.9738} = 0.89\%$$

The estimated SO_4 and PO_4 concentrations for the condensate filtered solid samples are shown in Table I - 11 and were used in the mass balance. The DMR condensate composite filtered solids mass was 0.34 g and the concentrations shown were used in the mass balance.

Table I - 11. Simulant Module C Condensate Composite Filtered Solids Estimated IC

Sample	**Elemental Concentration (wt%)**	
	SO_4	**PO_4**
Composite	0.33	0.89

The Cs, Re, and I wt% concentrations for the DMR Condensate Composite Filtered Solids are shown in Table I - 12. The DMR condensate composite filtered solids mass was 0.34 g and the average concentrations were used in the mass balance.

Table I - 12. Simulant Module C Condensate Composite Filtered Solids ICPMS

Sample	**Elemental Concentration (wt%)**		
	Cs	**Re**	**I**
1	0.002	0.015	0.010
2	0.004	0.016	
Average	**0.003**	**0.015**	**0.010**
Std. Dev.	0.001	0.001	na
%RSD	53.83	5.58	na

The crossbar rinse filtrate cation or ICPES concentrations from the runs for Simulant Module C are shown in Table I - 13. For the mass balance the average concentrations were used.

Table I - 13. Simulant Module C Crossbar Rinse Filtrates ICPES

Volume (L)	Sample	Elemental Concentration (mg/L)										
		Ag	**Al**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
0.2518	1	< 8.50E-02	< 1.09E-01	< 2.80E-02	< 4.89E-01	3.84E+00	< 3.80E-02	< 9.60E-02	< 9.20E-02	< 2.94E-01	1.36E+00	< 3.60E-02
	2	< 8.50E-02	< 1.09E-01	< 2.80E-02	< 4.89E-01	3.91E+00	< 3.80E-02	< 9.60E-02	< 9.20E-02	< 2.94E-01	1.21E+00	< 3.60E-02
	3	< 8.50E-02	< 1.09E-01	< 2.80E-02	< 4.89E-01	3.85E+00	< 3.80E-02	< 9.60E-02	< 9.20E-02	< 2.94E-01	1.22E+00	< 3.60E-02
	Average	**< 8.50E-02**	**< 1.09E-01**	**< 2.80E-02**	**< 4.89E-01**	**3.87E+00**	**< 3.80E-02**	**< 9.60E-02**	**< 9.20E-02**	**< 2.94E-01**	**1.26E+00**	**< 3.60E-02**
	Std. Dev.	na	na	na	na	3.79E-02	na	na	na	na	8.39E-02	na
	%RSD	na	na	na	na	0.98%	na	na	na	na	6.64%	na

na=not applicable

The crossbar rinse filtrate anion or IC concentrations for the Simulant Module C are shown in Table I - 14. For the mass balance the average concentrations were used.

Table I - 14. Simulant Module C Crossbar Rinse Filtrates IC

Volume (L)	Sample	Species Concentration (ug/L)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
0.2518	1	< 5.00E+03	< 1.00E+04	< 1.00E+04	< 5.00E+03	< 1.00E+04	< 1.00E+04
	2	< 5.00E+03	< 1.00E+04	< 1.00E+04	< 5.00E+03	< 1.00E+04	< 1.00E+04
	3	< 5.00E+03	< 1.00E+04	< 1.00E+04	< 5.00E+03	< 1.00E+04	< 1.00E+04
	Average	**< 5.00E+03**	**< 1.00E+04**	**< 1.00E+04**	**< 5.00E+03**	**< 1.00E+04**	**< 1.00E+04**
	Std Dev.	na	na	na	na	na	na
	%RSD	na	na	na	na	na	na

na=not applicable

The crossbar rinse filtrate trace elemental or ICPMS concentrations for the Simulant Module C are shown in Table I - 15. For the mass balance the average concentrations were used.

Table I - 15. Simulant Module C Crossbar Rinse Filtrates ICPMS

Volume (L)	Batch	Elemental Concentration (ug/L)		
		Cs	Re	I
0.2518	1	2.11E+00	1.94E+01	2.03E+02
	2	1.90E+00	1.90E+01	2.02E+02
	3	1.53E+00	2.01E+01	2.01E+02
	Average	**1.85E+00**	**1.95E+01**	**2.02E+02**
	Std Dev.	2.94E-01	5.57E-01	1.00E+00
	%RSD	15.90%	2.86%	0.50%

The crossbar solids were separated into two batches. The first batch represented crossbar rinse solids collected before the use of quartz wool in the off-gas crossbar of the DMR. The second batch represented the crossbar solids collected from quartz wool used in the off-gas crossbar of the DMR. The crossbar solids cation or ICPES analyses for each batch are shown in Table I - 16. For the mass balance, composite crossbar solids concentrations were calculated based on each batch average times the mass per batch. For example, the aluminum composite concentration in wt% was calculated as:

$$xs_{Al} = \frac{0.0693 * 17.10\% + 0.0398 * 6.70\%}{0.0693 + 0.0398} = \frac{0.01452}{0.1091} = 13.31\%$$

The cation or ICPES concentrations based on this method for the crossbar solids are shown in and these values were used in the mass balance.

Table I - 16. Simulant Module C Crossbar Solids ICPES

Batch	Mass (g)	Sample	Elemental Concentration (wt%)											
			Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Before Quartz Wool	0.0693	1	< 0.004	17.10	0.02	0.11	0.12	8.68	0.004	0.27	0.01	0.10	0.01	0.01
After Quartz Wool	0.0398	1	< 0.008	6.70	0.02	0.05	0.05	7.93	0.01	0.25	0.02	2.83	0.05	0.01

Table I - 17. Simulant Module C Crossbar Composite Solids ICPES

Run	Mass (g)	Elemental Concentration (wt%)											
		Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	0. 1091	< 0.005	13.31	0.02	0.09	0.09	8.41	0.01	0.26	0.01	1.10	0.02	0.01

The crossbar solids were separated into two batches as discussed earlier and the crossbar solids Anion or IC analyses for each batch are shown in Table I - 18. For the mass balance, composite crossbar solids concentrations were calculated based on each batch average times the mass per batch. For example, the chloride composite concentration in wt% was calculated as:

$$xs_{Cl} = \frac{0.0693 * 0.61\% + 0.0398 * 8.73\%}{0.0693 + 0.0398} = \frac{0.003897}{0.1091} = 3.57\%$$

Note that if one batch had a less than or below detection limit value and the other batch had a measured value then only the measured value was used in the composite calculation. For example, the fluoride composite concentration in wt% was calculated as:

$$xs_F = \frac{(0.0398 * 1.25\%)}{0.0693 + 0.0398} = \frac{0.0004975}{0.1091} = 0.46\%$$

These composite concentrations are shown in Table I - 19 and were used in the mass balance.

Table I - 18. Simulant Module C Crossbar SolIDS IC

Batch	Mass (g)	Species Concentration (wt%)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
1	0.0693	< 0.18	0.61	< 0.18	< 0.18	0.43	< 0.18
2	0.0398	1.25	8.73	< 0.21	0.35	20.55	< 0.21

Table I - 19. Simulant Module C Crossbar Composite Solids IC

Run	Mass (g)	Species Concentration (wt%)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	0. 1091	0.46	3.57	< 0.19	0.13	7.77	< 0.19

The crossbar solids trace elemental or ICPMS concentrations from the two batches for Simulant Module C are shown in Table I - 20. Using the same logic shown earlier, the two batches of crossbar solids data was represented as one mass of 0.1091 g with the composite concentrations shown in Table I - 21. The composite concentrations were used in the mass balance.

Table I - 20. Simulant Module C Crossbar Rinse Composite Filtered Solids ICPMS

Batch	Mass (g)	Elemental Concentration (wt%)		
		Cs	Re	I
1	0.0693	0.0009	0.0097	0.0134
2	0.0398	0.0026	0.116	0.113

Table I - 21. Simulant Module C Crossbar Rinse Composite Filtered Solids ICPMS

Run	Mass (g)	Elemental Concentration (wt%)		
		Cs	Re	I
Composite	0. 1091	0.002	0.048	0.050

Appendix J. Radioactive Module C Mass Balance Analytical Data

Table J - 1 through Table J - 3 gives the ICPES, IC, and ICPMS concentrations for the Radioactive Module C granular product samples. The average concentrations were used in the mass balance.

Table J - 1. Radioactive Module C Granular Composite Product ICPES

Sample	**Elemental Concentration (wt%)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.0015	18.60	0.0143	0.139	0.18	16.40	< 0.0074	0.39	0.0090	0.28	18.70	0.0053
2	< 0.0015	18.60	0.0141	0.137	0.19	15.50	< 0.0074	0.37	0.0094	0.26	18.90	0.0047
3	< 0.0015	18.70	0.0142	0.139	0.20	15.40	< 0.0073	0.36	0.0090	0.26	19.00	0.0046
4								0.39				0.0064
5								0.41				0.0050
6								0.41				0.0060
Average	**< 0.0015**	**18.63**	**0.014**	**0.138**	**0.19**	**15.77**	**< 0.0074**	**0.39**	**0.009**	**0.27**	**18.87**	**0.0053**
Std. Dev.	0.00001	0.06	0.0001	0.001	0.01	0.55	0.00004	0.02	0.0003	0.01	0.15	0.0007
%RSD	0.78	0.31	0.70	0.83	4.66	3.49	0.59	4.79	2.91	5.13	0.81	13.88

Table J - 2. Radioactive Module C Granular Composite Product IC

Sample	**Species Concentration (wt%)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	< 0.050	0.24	< 0.050	< 0.050	0.67	0.96
2	< 0.050	0.23	< 0.050	< 0.050	0.64	0.97
3	< 0.051	0.22	< 0.051	< 0.051	0.62	0.96
Average	**< 0.050**	**0.23**	**< 0.050**	**< 0.050**	**0.64**	**0.96**
Std. Dev.	0.0003	0.01	0.0003	0.0003	0.03	0.01
%RSD	0.62	3.86	0.62	0.62	4.20	0.55

Table J - 3. Radioactive Module C Granular Composite Product ICPMS

Sample	**Re* (wt%)**
1	0.028
2	0.026
3	0.026
4	0.028
5	0.027
6	0.026
Average	**0.027**
Std. Dev.	0.001
%RSD	3.61

*Re from ICPMS sweep with mass of 185 at 37.40% and 187 at 62.60%

The radio isotopes of the granular product by gamma analysis for the Radioactive Module C are shown in Table J - 4 and the average values were used in the mass balance. Note that the I-129 concentration has a high variability (19.39% RSD) and a broader 95% confidence interval of 9.19E+01 to 1.43E+02 dpm/g for the granular product concentration.

Table J - 4. Radioactive Module C Granular Composite Product Gamma

Sample	**Concentration (dpm/g)**	
	I-129	**Tc-99**
1	1.05E+02	1.57E+05
2	1.44E+02	1.47E+05
3	1.04E+02	1.45E+05
Average	**1.18E+02**	**1.50E+05**
Std. Dev	2.28E+01	6.43E+03
%RSD	19.39%	4.30%

The DMR condensate filtrate cation or ICPES concentrations from the Radioactive Module C runs are shown in Table J - 5. The DMR condensate filtrates have a volume of 1.4876 L with a density of 1.00 g/ml. The average cation or ICPES concentrations were the values used in the mass balance.

The DMR condensate composite filtrate anion or IC concentrations from the Radioactive Module C runs are shown in Table J - 6. The DMR condensate composite filtrate was 1.4876 L and the average condensate composite concentrations were used in the mass balance.

The DMR condensate filtrate trace elemental or ICPMS concentrations from the Radioactive Module C are shown in Table J - 7. The average concentrations for the DMR condensate filtrates were used in the mass balance.

The radio isotopes of the DMR Condensate filtrate by gamma analysis for the Radioactive Module C are shown in Table J - 8. There was only one sample so those concentrations were used in the mass balance.

The crossbar rinse filtrate cation or ICPES concentrations from the runs for Radioactive Module C are shown in Table J - 9. The crossbar rinse filtrate total volume was 0.1237 L. The average cation or ICPES concentrations in Table J - 9 are used in the mass balance.

Table J - 5. Radioactive Module C Condensate Composite Filtrate ICPES

Sample	Elemental Concentration (mg/L)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	< 3.70E-02	3.52E-01	1.23E-01	< 2.10E-02	< 6.98E-01	1.00E+01	< 1.86E-01	< 6.74E-01	< 8.15E-01	1.26E+01	4.46E+00	7.60E-03

Table J - 6. Radioactive Module C Condensate Composite Filtrate IC

Sample	Species Concentration (mg/L)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 1	5	643	88	10	< 1

Table J - 7. Radioactive Module C Condensate Composite Filtrate ICPMS

Sample	Re (ug/L)
1	2.01E+02
2	1.93E+02
Average	**1.97E+02**
Std. Dev.	5.12E+00
%RSD	2.60%

Table J - 8. Radioactive Module C Condensate Composite Filtrate Gamma

Sample	Concentration (dpm/mL)		
	Cs-137	I-129	Tc-99
Composite	2.75E+02	3.51E-01	5.96E+01

Table J - 9. Radioactive Module C Crossbar Rinse Composite Filtrate ICPES

Sample	Elemental Concentration (mg/L)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	< 3.72E-02	< 1.88E-01	< 3.52E-02	< 2.10E-02	< 6.98E-01	6.76E+00	< 1.86E-01	< 6.74E-01	< 8.15E-01	1.57E+00	5.58E-01	< 4.40E-03

Anion or IC analyses for the Radioactive Module C crossbar rinse filtrate are shown in Table J - 10. The average anion or IC concentrations were used in the mass balance.

Table J - 10. Radioactive Module C Crossbar Rinse Composite Filtrate IC

Sample	**Species Concentration (mg/L)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	< 1	3	1	3	3	< 1

The crossbar rinse filtrate trace elemental or ICPMS concentrations for Radioactive B module are shown in Table J - 11. The crossbar rinse filtrate had a volume of 0.1237 L. The average trace elemental or ICPMS concentrations in Table J - 11 were used in the mass balance.

Table J - 11. Radioactive Module C Crossbar Rinse Composite Filtrate ICPMS

Sample	**Re (ug/L)**
1	8.61E+01
2	7.88E+01
Average	**8.24E+01**
Std. Dev.	5.19E+00
%RSD	6.30%

The radio isotopes of the crossbar rinse filtrate by gamma analysis for the Radioactive Module C are shown in Table J - 12. The composite average concentrations shown in Table J - 12 were used in the mass balance.

Table J - 12. Radioactive Module C Crossbar Rinse Composite Filtrate Gamma

Sample	**Species Concentration (dpm/mL)**		
	Cs-137	**I-129**	**Tc-99**
Composite	2.05E+02	< 1.77E-01	2.35E+01

The crossbar solids were captured in Quartz Wool samples in the off-gas crossbar from the DMR. It is impossible to separate out all the solids from the quartz wool material so the entire quartz wool samples with solids were first water leached followed by Aqua Regia dissolution. The water leach concentrations were then added to the aqua regia concentrations to give a total species concentration in the solids. The total solids in the quart wool was obtained by weighing the quartz wool before the experiment then drying it after the experiment and re-weighing to get the crossbar solids dry weight.

The crossbar solids cation or ICPES concentrations for the Radioactive Module C runs are shown in Table J - 13. The crossbar solids total mass was 2.166 g. The composite cation or ICPES concentrations for the crossbar solids were used in the mass balance.

Table J - 13. Radioactive Module C Crossbar Solids ICPES

Sample	Elemental Concentration wt%											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Water Leach	< 0.00007	0.02	0.00	0.00	0.00	2.24	< 0.00021	0.032	< 0.00033	0.96	0.00	0.000
Aqua Regia	< 0.00017	6.77	0.00	0.04	0.07	4.99	0.006	0.143	< 0.00609	0.11	0.00	0.002
Composite	< 0.00024	6.79	0.00	0.04	0.07	7.23	0.006	0.175	< 0.00642	1.07	0.00	0.002

Anion or IC analyses for the Radioactive Module C Crossbar Solids samples came from the Water Leach preparations and are shown in Table J - 14. These values were used in the mass balance.

Table J - 14. Radioactive Module C Crossbar Solids IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	0.27	1.30	0.23	0.14	1.97	0.032

The crossbar solids trace elemental or ICPMS concentrations for Radioactive Module C are shown in Table J - 15. The crossbar solids mass was 2.166 g. The composite concentrations were used in the mass balance.

Table J - 15. Radioactive Module C Crossbar Rinse Composite Filtered Solids ICPMS

Run	Species Concentration (wt%)		
	Cs-137	Re	Tc-99
Water Leach	0.000003	0.048	0.0004
Aqua Regia	0.000221	0.007	0.0004
Composite	0.000224	0.055	0.0008

The radio isotopes of the crossbar solids by gamma analysis for the Radioactive Module C are shown in Table J - 16. The average composite concentrations are shown in Table J - 16 and were used in the mass balance.

Table J - 16. Radioactive Module C Crossbar Rinse Filtered Solids Gamma

Run	Species Concentration (dpm/g)	
	^{137}Cs	^{129}I
Composite	3.80E+05	1.76E+03

Appendix K. Simulant Module D Mass Balance Analytical Data

Table K - 1 through Table K - 3 give the ICPES, IC, and ICPMS concentrations for the Simulant Module D (Tank AN-103) granular product samples. The total mass of the composite granular product was 293.35 g and the average concentrations shown were used in the mass balance.

Table K - 1. Simulant Module D Granular Composite Product ICPES

Sample	Elemental Concentration (wt%)										
	Ag	**Al**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.00041	15.90	0.010	0.54	16.10	0.0023	0.05	0.006	0.12	17.60	0.0025
2	< 0.00036	16.00	0.012	0.53	15.70	0.0020	0.05	0.005	0.12	18.10	0.0022
3	< 0.00038	15.90	0.011	0.52	15.40	0.0021	0.05	0.006	0.12	17.40	0.0020
4		17.30					0.03		0.13		
5		17.50					0.04		0.13		
6		17.80					0.05				
Average	**< 0.00038**	**16.73**	**0.011**	**0.53**	**15.73**	**0.0021**	**0.05**	**0.006**	**0.12**	**17.70**	**0.0022**
Std. Dev.	0.00003	0.89	0.001	0.01	0.35	0.0002	0.01	0.0005	0.01	0.36	0.0002
%RSD	6.66	5.33	9.32	1.99	2.23	8.08	15.41	8.32	4.42	2.04	10.81

Table K - 2. Simulant Module D Granular Composite Product IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
1	< 0.095	0.247	< 0.095	< 0.095	< 0.095	< 0.474
2	< 0.099	0.217	< 0.099	< 0.099	< 0.099	< 0.494
3	< 0.095	0.218	< 0.095	< 0.095	< 0.095	< 0.473
Average	**< 0.096**	**0.227**	**< 0.096**	**< 0.096**	**< 0.096**	**< 0.480**
Std. Dev.	0.002	0.017	0.002	0.002	0.002	0.012
%RSD	2.43	7.39	2.43	2.43	2.43	2.43

Table K - 3. Simulant Module D Granular Composite Product ICPMS

Sample	Elemental Concentration (wt%)	
	Re	**I**
1	0.047	0.080
2	0.046	0.079
3	0.046	0.078
Average	**0.046**	**0.079**
Std. Dev.	0.001	0.001
%RSD	1.84	1.03

The DMR Condenser/Bubbler Drain filtrate cation or ICPES concentrations from the runs for Simulant Module D are shown in Table K - 4 and the average values were used in the mass balance.

Table K - 4. Simulant Module D Condenser/Bubbler Drain Filtrates ICPES

Sample	Volume (L)	Sample	Elemental Concentration (mg/L)					
			Al	Cr	K	Na	Pb	Si
Composite	1.7463	1	6.69E-01	< 1.00E-01	1.70E+00	9.27E+00	< 1.00E-01	8.51E+00
		2	6.44E-01	< 1.00E-01	1.67E+00	9.19E+00	< 1.00E-01	6.14E+00
		3	6.63E-01	< 1.00E-01	1.69E+00	9.19E+00	< 1.00E-01	5.70E+00
		Average	**6.59E-01**	**< 1.00E-01**	**1.69E+00**	**9.22E+00**	**< 1.00E-01**	**6.78E+00**
		Std. Dev.	1.31E-02	na	1.53E-02	4.62E-02	na	1.51E+00
		%RSD	1.98	na	0.91	0.50	na	22.28

na=not applicable

The DMR Condenser/Bubbler Drain filtrates anion or IC analyses are shown in Table K - 5 and the average values were used in the mass balance.

Table K - 5. Simulant Module D Condenser/Bubbler Drain Filtrates IC

Sample	Volume (L)	Sample	Species Concentration (ug/L)					
			F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	1.7463	1	< 1.00E+04	< 1.00E+04	1.67E+04	< 1.00E+04	< 1.00E+04	< 1.00E+04
		2	< 1.00E+04	< 1.00E+04	1.66E+04	< 1.00E+04	< 1.00E+04	< 1.00E+04
		3	< 1.00E+04	< 1.00E+04	1.65E+04	< 1.00E+04	< 1.00E+04	< 1.00E+04
		Average	**< 1.00E+04**	**< 1.00E+04**	**1.66E+04**	**< 1.00E+04**	**< 1.00E+04**	**< 1.00E+04**
		Std. Dev.	na	na	1.00E+02	na	na	na
		%RSD	na	na	0.60	na	na	na

na=not applicable

The DMR Condenser/Bubbler Drain filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table K - 6. The average values were used in the mass balance.

Table K - 6. Simulant Module D Condenser/Bubbler Drain Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	1.7463	1	1.43E+01	2.48E+02	9.70E+02
		2	1.50E+01	2.48E+02	9.58E+02
		3	1.43E+01	2.48E+02	9.62E+02
		Average	**1.45E+01**	**2.48E+02**	**9.63E+02**
		Std. Dev.	4.04E-01	0.00E+00	6.11E+00
		%RSD	2.78	0.00	0.63

The DMR Condenser/Bubbler Drain composite filtered solids concentrations from the Simulant Module D runs are shown in Table K - 7. Note there was only one sample analyzed for the DMR Condenser/Bubbler Drain composite filtered solids mass of 0.0917 g and the values in Table K - 7 were used in the mass balance.

Table K - 7. Simulant Module D Condenser/Bubbler Drain Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	< 0.002	5.14	0.02	0.005	0.18	5.19	0.012	0.027	0.009	0.22	0.40	0.006

Anion or IC analyses for the Simulant Module D condensate filtered solid samples are shown in Table K - 8 and were used in the mass balance. These values were used in the mass balance.

Table K - 8. Simulant Module D Condenser/Bubbler Drain Composite Filtered Solids Estimated IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 0.55	< 0.55	< 0.55	0.82	< 0.55	< 0.55

The Cs, Re, and I wt% concentrations for the DMR Condenser/Bubbler Drain Composite Filtered Solids are shown in Table K - 9. These values were used in the mass balance.

Table K - 9. Simulant Module D Condenser/Bubbler Drain Composite Filtered Solids ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	Re	I
Composite	0.013	0.0075	0.00061

The DMR Condenser/Bubbler rinse filtrate cation or ICPES concentrations from the runs for Simulant Module D are shown in Table K - 10 and the average values were used in the mass balance.

Table K - 10. Simulant Module D Condenser/Bubbler Rinse Filtrates ICPES

Sample	Volume (L)	Sample	Elemental Concentration (mg/L)					
			Al	Cr	K	Na	Pb	Si
Composite	0.1620	1	6.05E+01	< 1.00E-01	3.07E+00	4.57E+01	< 1.00E-01	6.17E+01
		2	6.04E+01	< 1.00E-01	3.06E+00	3.76E+01	< 1.00E-01	6.10E+01
		3	6.04E+01	< 1.00E-01	3.07E+00	3.75E+01	< 1.00E-01	6.11E+01
		Average	**6.04E+01**	**< 1.00E-01**	**3.07E+00**	**4.03E+01**	**< 1.00E-01**	**6.13E+01**
		Std. Dev.	5.77E-02	na	5.77E-03	4.71E+00	na	3.79E-01
		%RSD	0.10%	na	0.19%	11.69%	na	0.62%

na=not applicable

The DMR Condenser/Bubbler rinse filtrates anion or IC analyses are shown in Table K - 11 and the average values were used in the mass balance.

Table K - 11. Simulant Module D Condenser/Bubbler Rinse Filtrates IC

Sample	Volume (L)	Sample	Species Concentration (ug/L)					
			F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	0.1620	1	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.62E+07	3.87E+05	< 1.00E+05
		2	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.71E+07	4.34E+05	< 1.00E+05
		3	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.84E+07	4.42E+05	< 1.00E+05
		Average	**< 1.00E+05**	**< 1.00E+05**	**< 1.00E+05**	**5.72E+07**	**4.21E+05**	**< 1.00E+05**
		Std. Dev.	na	na	na	1.11E+06	2.97E+04	na
		%RSD	na	na	na	1.93%	7.06%	na

na=not applicable

The DMR Condenser/Bubbler rinse filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table K - 12. The average values were used in the mass balance.

Table K - 12. Simulant Module D Condenser/Bubbler Rinse Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.1620	1	1.56E+01	1.12E+02	9.80E+01
		2	1.39E+01	1.20E+02	9.69E+01
		3	1.40E+01	1.17E+02	1.01E+02
		Average	**1.45E+01**	**1.16E+02**	**9.86E+01**
		Std. Dev.	9.54E-01	4.04E+00	2.12E+00
		%RSD	6.58%	3.47%	2.15%

The DMR Condenser/Bubbler Oxidizing Solution /Ethanol rinse composite filtered solids from the Simulant Module D runs are shown in Table K - 13. The DMR Condenser/Bubbler Drain composite filtered solids mass was 0.0566 g and the values in Table K - 13 were used in the mass balance.

Table K - 13. Simulant Module D Condenser/Bubbler Rinse Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	0.0038	2.36	0.06	0.015	< 0.14	0.58	0.10	0.04	0.0097	0.62	1.29	0.01

Anion or IC analyses for the Simulant Module D Condenser/Bubbler rinse composite filtered solid samples are shown in Table K - 14 and were used in the mass balance.

Table K - 14. Simulant Module D Condenser/Bubbler Rinse Composite Filtered Solids Estimated IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 1.77	< 1.77	< 1.77	1.41	< 1.77	< 1.77

The Cs, Re, and I wt% concentrations for the DMR Condenser/Bubbler rinse Composite Filtered Solids are shown in Table K - 15. These values were used in the mass balance.

Table K - 15. Simulant Module D Condenser/Bubbler Rinse Composite Filtered Solids ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	Re	I
Composite	0.0062	0.0053	0.0057

The DMR basket rinse filtrate cation or ICPES concentrations from the runs for Simulant Module D are shown in Table K - 16 and the average values were used in the mass balance.

Table K - 16. Simulant ModuleD Basket Rinse Filtrates ICPES

Sample	Volume (L)	Sample	Elemental Concentration (mg/L)					
			Al	Cr	K	Na	Pb	Si
Composite	0.1108	1	1.45E+03	5.25E-01	1.13E+02	1.81E+03	2.05E+01	1.48E+03
		2	1.45E+03	5.38E-01	1.14E+02	1.81E+03	2.06E+01	1.51E+03
		3	1.45E+03	5.31E-01	1.14E+02	1.81E+03	2.07E+01	1.51E+03
		Average	**1.45E+03**	**5.31E-01**	**1.14E+02**	**1.81E+03**	**2.06E+01**	**1.50E+03**
		Std. Dev.	0.00E+00	6.51E-03	5.77E-01	0.00E+00	1.00E-01	1.73E+01
		%RSD	0.00%	1.22%	0.51%	0.00%	0.49%	1.15%

The DMR basket rinse filtrates anion or IC analyses are shown in Table K - 17 and the average values were used in the mass balance.

Table K - 17. Simulant Module D Basket Rinse Filtrates IC

Sample	Volume (L)	Sample	Species Concentration (ug/L)					
			F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	0.1108	1	< 1.00E+05	< 1.00E+05	< 1.00E+05	6.11E+07	1.25E+06	< 1.00E+05
		2	< 1.00E+05	< 1.00E+05	< 1.00E+05	6.26E+07	1.33E+06	< 1.00E+05
		3	< 1.00E+05	< 1.00E+05	< 1.00E+05	6.25E+07	1.32E+06	< 1.00E+05
		Average	**< 1.00E+05**	**< 1.00E+05**	**< 1.00E+05**	**6.21E+07**	**1.30E+06**	**< 1.00E+05**
		Std. Dev.	na	na	na	8.39E+05	4.36E+04	na
		%RSD	na	na	na	1.35%	3.35%	na

na=not applicable

The DMR basket rinse filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table K - 18. The average values were used in the mass balance.

Table K - 18. Simulant Module D Basket Rinse Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	**Cs**	**Re**	**I**
Composite	0.1108	1	1.94E+02	5.23E+03	6.98E+01
		2	1.96E+02	5.13E+03	7.49E+01
		3	1.99E+02	5.09E+03	6.68E+01
		Average	**1.96E+02**	**5.15E+03**	**7.05E+01**
		Std. Dev.	2.52E+00	7.21E+01	4.10E+00
		%RSD	1.28%	1.40%	5.81%

The DMR basket rinse composite filtered solids concentrations from the Simulant Module D runs are shown in Table K - 19. Note there was only one sample analyzed for the DMR basket rinse composite filtered solids mass of 0.339 g and the values in Table K - 19 were used in the mass balance.

Table K - 19. Simulant Module D Basket Rinse Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	< 0.0004	7.29	0.026	0.017	0.059	2.27	0.018	0.024	0.011	0.074	0.40	0.008

Anion or IC analyses for the Simulant Module D basket rinse composite filtered solid samples are shown in Table K - 20 and were used in the mass balance.

Table K - 20. Simulant Module D Basket Rinse Composite Filtered Solids Estimated IC

Sample	Species Concentration (wt%)					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	< 0.087	< 0.087	< 0.087	11.70	0.09	< 0.087

The Cs, Re, and I wt% concentrations for the DMR basket rinse Composite Filtered Solids are shown in Table K - 21. These values were used in the mass balance.

Table K - 21. Simulant Module D Basket Rinse Composite Filtered Solids ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	**Re**	**I**
Composite	0.00073	0.0065	0.0061

The crossbar solids composite cation or ICPES analyses are shown in Table K - 22. These values were used in the mass balance.

Table K - 22. Simulant Module D Crossbar Solids ICPES

Sample	Mass (g)	Elemental Concentration (wt%)											
		Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	2.7816	0.00006	8.06	0.009	0.014	0.30	11.64	< 0.00014	0.051	0.001	0.998	1.51	0.003

The crossbar solids Anion or IC analyses are shown in Table K - 23. These values were used in the mass balance.

Table K - 23. Simulant Module D Crossbar Composite Solids IC

Sample	Mass (g)	Species Concentration (wt%)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	2.7816	0.28	0.13	< 0.02	< 0.02	1.71	< 0.02

The crossbar solids trace elemental or ICPMS concentrations for Simulant Module D runs are shown in Table K - 24**Error! Reference source not found.**. The composite concentrations were used in the mass balance.

Table K - 24. Simulant Module D Crossbar Rinse Composite Filtered Solids ICPMS

Sample	Mass (g)	Species Concentration (wt%)		
		Cs	Re	I
Composite	2.7816	0.0034	0.068	0.14

The seal pot drain filtrate cation or ICPES concentrations from the runs for Simulant Module D are shown in Table K - 25 and the average values were used in the mass balance.

Table K - 25. Simulant Module D Seal Pot Drain Filtrates ICPES

Sample	Volume (L)	Sample	Elemental Concentration (mg/L)					
			Al	Cr	K	Na	Pb	Si
Composite	0.1968	1	1.00E+00	< 1.00E-01	5.13E+00	9.25E+01	< 1.00E-01	9.63E+00
		2	9.92E-01	< 1.00E-01	5.08E+00	9.71E+01	< 1.00E-01	9.52E+00
		3	1.00E+00	< 1.00E-01	5.06E+00	9.51E+01	< 1.00E-01	9.38E+00
		Average	**9.99E-01**	**< 1.00E-01**	**5.09E+00**	**9.49E+01**	**< 1.00E-01**	**9.51E+00**
		Std. Dev.	6.64E-03	na	3.64E-02	2.31E+00	na	1.24E-01
		%RSD	0.66%	na	0.71%	2.43%	na	1.30%

na=not applicable

The DMR seal pot drain filtrates anion or IC analyses are shown in Table K - 26 and the average values were used in the mass balance.

Table K - 26. Simulant Module D Seal Pot Drain Filtrates IC

Sample	Volume (L)	Sample	Species Concentration (ug/L)					
			F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	0.1968	1	< 1.00E+04	1.15E+04	2.70E+05	9.96E+03	2.60E+04	< 1.00E+04
		2	< 1.00E+04	1.15E+04	2.71E+05	9.92E+03	2.60E+04	< 1.00E+04
		3	< 1.00E+04	1.16E+04	2.74E+05	9.83E+03	2.60E+04	< 1.00E+04
		Average	**< 1.00E+04**	**1.16E+04**	**2.72E+05**	**9.90E+03**	**2.60E+04**	**< 1.00E+04**
		Std. Dev.	na	5.14E+01	2.37E+03	6.79E+01	6.37E+00	na
		%RSD	na	0.44%	0.87%	0.69%	0.02%	na

na=not applicable

The DMR seal pot drain filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table K - 27. The average values were used in the mass balance.

Table K - 27. Simulant Module D Seal Pot Drain Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.1968	1	6.07E+01	1.27E+03	6.75E+03
		2	6.03E+01	1.26E+03	6.76E+03
		3	5.83E+01	1.25E+03	6.75E+03
		Average	**5.98E+01**	**1.26E+03**	**6.76E+03**
		Std. Dev.	1.29E+00	8.18E+00	6.76E+00
		%RSD	2.16%	0.65%	0.10%

The DMR seal pot drain composite filtered solids concentrations from the Simulant Module D runs are shown in Table K - 28. Note there was only one sample analyzed for the DMR seal pot drain composite filtered solids mass of 0.0906 g and these values were used in the mass balance.

Table K - 28. Simulant Module D Seal Pot Drain Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	< 0.005	7.36	0.036	0.006	0.20	5.98	0.00	0.07	0.004	0.20	3.81	0.003

Anion or IC analyses for the Simulant D seal pot drain filtered solid samples are shown in Table K - 29 and were used in the mass balance.

Table K - 29. Simulant Module D Seal Pot Drain Composite Filtered Solids Estimated IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 1.10	< 1.10	< 1.10	< 1.10	< 1.10	< 1.10

The Cs, Re, and I wt% concentrations for the DMR Seal pot drain Composite Filtered Solids are shown in Table K - 30. These values were used in the mass balance.

Table K - 30. Simulant Module D Seal Pot Drain Composite Filtered Solids ICPMS

Sample	**Elemental Concentration (wt%)**		
	Cs	**Re**	**I**
Composite	0.0022	0.0070	0.0093

The DMR seal pot rinse filtrate cation or ICPES concentrations from the runs for Simulant Module D are shown in Table K - 31 and the average values were used in the mass balance.

Table K - 31. Simulant Module D Seal Pot Rinse Filtrates ICPES

Sample	**Volume (L)**	**Sample**	**Elemental Concentration (mg/L)**					
			Al	**Cr**	**K**	**Na**	**Pb**	**Si**
Composite	0.1358	1	3.61E+02	< 1.00E-01	1.59E+01	2.41E+02	< 1.00E-01	3.92E+02
		2	3.61E+02	< 1.00E-01	1.59E+01	2.44E+02	< 1.00E-01	3.91E+02
		3	3.60E+02	< 1.00E-01	1.59E+01	2.43E+02	< 1.00E-01	3.90E+02
		Average	**3.61E+02**	**< 1.00E-01**	**1.59E+01**	**2.43E+02**	**< 1.00E-01**	**3.91E+02**
		Std. Dev.	5.77E-01	na	0.00E+00	1.53E+00	na	1.00E+00
		%RSD	0.16%	na	0.00%	0.63%	na	0.26%

na=not applicable

The DMR seal pot rinse filtrates anion or IC analyses are shown in Table K - 32 and the average values were used in the mass balance.

Table K - 32. Simulant Module D Seal Pot Rinse Filtrates IC

Sample	**Volume (L)**	**Sample**	**Species Concentration (ug/L)**					
			F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	0.1358	1	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.98E+07	6.20E+05	< 1.00E+05
		2	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.95E+07	6.68E+05	< 1.00E+05
		3	< 1.00E+05	< 1.00E+05	< 1.00E+05	5.91E+07	6.59E+05	< 1.00E+05
		Average	**< 1.00E+05**	**< 1.00E+05**	**< 1.00E+05**	**5.95E+07**	**6.49E+05**	**< 1.00E+05**
		Std. Dev.	na	na	na	3.51E+05	2.55E+04	na
		%RSD	na	na	na	0.59%	3.93%	na

na=not applicable

The DMR seal pot rinse filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table K - 33. The average values were used in the mass balance.

Table K - 33. Simulant Module D Seal Pot Rinse Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.1358	1	3.64E+01	3.69E+02	3.86E+02
		2	3.53E+01	3.74E+02	3.89E+02
		3	3.49E+01	3.67E+02	3.95E+02
		Average	**3.55E+01**	**3.70E+02**	**3.90E+02**
		Std. Dev.	7.77E-01	3.61E+00	4.58E+00
		%RSD	2.19%	0.97%	1.18%

The DMR seal pot rinse composite filtered solids concentrations from the Simulant Module D are shown in Table K - 34. Note there was only one sample analyzed for the DMR seal pot rinse composite filtered solids mass of 0.105 g and the values in Table K - 34 were used in the mass balance.

Table K - 34. Simulant Module D Seal Pot Rinse Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Composite	< 0.002	5.39	0.019	0.018	0.21	1.05	0.0323	0.037	0.0025	0.37	1.14	0.0046

Anion or IC analyses for the Simulant Module D seal pot drain rinse composite filtered solid samples are shown in Table K - 35 and were used in the mass balance.

Table K - 35. Simulant Module D Seal Pot Rinse Composite Filtered Solids Estimated IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 0.48	< 0.48	< 0.48	5.21	0.48	< 0.48

The Cs, Re, and I wt% concentrations for the seal pot drain rinse Composite Filtered Solids are shown in Table K - 36. These values were used in the mass balance.

Table K - 36. Simulant Module D Seal Pot Rinse Composite Filtered Solids ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	Re	I
Composite	0.0012	0.012	0.025

The off-gas 25 micron (front) and 2 micron (back) cellulose filters right before the mass spectrometer were analyzed for cation concentrations for the Simulant Module D as shown in Table K - 37. Note the relative solid mass on each filter was estimated based on the analyses performed and the total number of runs performed. The 25 and 2 micron filters were analyzed like the Quartz Wool and the filtered samples performing a water leach followed by Aqua Regia dissolution. There was only one sample analyzed for each Micron Filter. The values shown in Table K - 37 were used in the mass balance.

Table K - 37. Simulant Module D Off-gas Micron Filter Solids ICPES

Sample	Estimated Mass (g)	Elemental Concentration (wt%)											
		Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
25 μm (front)	0.018	< 0.013	8.57	8.64	0.01	8.56	37.98	0.02	0.07	0.07	7.69	1.26	8.26
2 μm (back)	0.098	< 0.001	12.21	14.70	0.00	11.18	33.85	0.00	0.01	0.01	0.23	0.02	14.60

Anion or IC analyses for the Simulant Module D micron filter solids samples are shown in Table K - 38 and were used in the mass balance.

Table K - 38. Simulant Module D Off-gas Micron Filter Solids Estimated IC

Sample	Estimated Mass (g)	Species Concentration (wt%)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
25 μm (front)	0.018	0.003	0.009	< 0.001	0.006	0.014	< 0.001
2 μm (back)	0.098	< 0.0001	< 0.0001	< 0.0001	0.001	0.0002	< 0.0001

The Cs, Re, and I wt% concentrations for the DMR seal pot drain rinse Composite Filtered Solids are shown in Table K - 39. These values were used in the mass balance.

Table K - 39. Simulant Module D Off-gas Micron Filter Solids ICPMS

Sample	Estimated Mass (g)	Elemental Concentration (wt%)		
		Cs	Re	I
25 μm (front)	0.018	0.051	1.673	0.312
2 μm (back)	0.098	0.00013	< 0.0001	0.0086

Appendix L. Simulant Module D Special Run Mass Balance Analytical Data

Table L - 1 through Table L - 2 give the ICPES and ICPMS concentrations for Simulant Module D granular product samples for the special run where trying to close the mass balance. The total mass of the composite granular product was 28.09 g and the average concentrations shown were used in the mass balance.

Table L - 1. Special Run Simulant Module D Granular Composite Product ICPES

Sample	Elemental Concentration (wt%)										
	Ag	**Al**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.00171	16.40	0.0087	0.56	15.50	0.0024	0.049	0.010	0.12	< 0.00313	0.0037
2	< 0.00172	18.40	0.0092	0.58	15.70	0.0026	0.049	0.008	0.13	< 0.00315	0.0034
3	< 0.00168	17.70	0.0094	0.58	16.50	0.0028	0.054	0.008	0.12	< 0.00307	0.0030
Average	**< 0.00170**	**17.50**	**0.0091**	**0.57**	**15.90**	**0.0026**	**0.051**	**0.009**	**0.12**	**< 0.00312**	**0.0034**
Std. Dev.	0.00002	1.01	0.0004	0.01	0.53	0.0002	0.003	0.001	0.01	0.00	0.0003
%RSD	1.22	5.80	3.93	2.57	3.33	7.49	5.86	11.33	4.64	1.34	10.34

Table L - 2. Special Run Simulant Module D Granular Composite Product ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	**Re**	**I**
1	0.0016	0.441	0.072
2	0.0014	0.410	0.075
3			0.079
Average	**0.0015**	**0.425**	**0.075**
Std. Dev.	0.0002	0.022	0.003
%RSD	11.41	5.17	4.51

The DMR Condenser/Bubbler Drain filtrates trace elemental or ICPMS analyses performed on each batch are shown in Table L - 3. The average values were used in the mass balance.

Table L - 3. Special Run Simulant Module D Condenser/Bubbler Drain Filtrates ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	**Cs**	**Re**	**I**
Composite	0.2381	1	< 1.50E+01	7.80E+02	3.31E+02
		2	< 1.50E+01	7.83E+02	3.22E+02
		3	< 1.50E+01	7.54E+02	3.18E+02
		Average	**< 1.50E+01**	**7.72E+02**	**3.24E+02**
		Std. Dev.	na	1.59E+01	6.66E+00
		%RSD	na	2.06%	2.06%

na=not applicable

It was impossible to separate out all the solids from the 0.45 μm nylon filter so the entire filter sample with solids was first water leached followed by Aqua Regia dissolution. The water leach concentrations were then added to the aqua regia concentrations to give a total species concentration in the solids. The DMR Condenser/Bubbler Drain composite filtered solids concentrations from the Simulant Module D Special Run are shown in Table L - 4. Note there was only one sample analyzed for the DMR Condenser/ Bubbler Drain composite filtered solids mass of 0.0003 g and the values in Table L - 4 were used in the mass balance.

Table L - 4. Special Run Simulant Module D Condenser/Bubbler Drain Composite Filtered Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	Al	B	Cr	K	Na	Ni	P	Pb	S	Si	Zn
Water Leach	< 1.15	< 3.63	< 2.28	< 0.45	< 16.22	6.95	4.40	< 3.20	< 1.53	< 4.90	< 2.12	< 0.55
Aqua Regia	< 2.88	< 9.10	< 5.73	< 1.12	< 40.67	< 9.33	1.78	< 8.00	< 3.83	< 12.27	5.97	< 1.38
Composite	< 4.03	< 12.73	< 8.02	< 1.57	< 56.88	6.95	6.18	< 11.20	< 5.37	< 17.17	5.97	< 1.93

The Cs, Re, and I wt% concentrations for the DMR Condenser/Bubbler Drain Composite Filtered Solids are shown in Table L - 5. The DMR Condenser/Bubbler Drain Composite Filtered Solids were analyzed like the condensate filtered solids where the filtered samples underwent a water leach followed by Aqua Regia dissolution. There was only one sample analyzed for these solids and the composite values were used in the mass balance.

Table L - 5. Special Run Simulant Module D Condenser/Bubbler Drain Composite Filtered Solids ICPMS

Sample	Elemental Concentration (wt%)		
	Cs	Re	I
Water Leach	0.502	0.047	0.212
Aqua Regia	0.377	0.051	
Composite	0.879	0.098	0.212

The DMR Condenser/Bubbler rinse trace elemental or ICPMS analyses performed are shown in Table L - 6. The average values were used in the mass balance.

Table L - 6. Special Run Simulant Module D Dmr Condenser/Bubbler Rinse ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.0899	1	2.20E+00	1.91E+02	6.60E+01
		2	2.16E+00	1.90E+02	6.58E+01
		3	1.85E+00	1.92E+02	6.58E+01
		Average	**2.07E+00**	**1.91E+02**	**6.59E+01**
		Std. Dev.	1.92E-01	1.00E+00	1.15E-01
		%RSD	9.25%	0.52%	0.18%

The DMR basket rinse trace elemental or ICPMS analyses performed are shown in Table L - 7. The average values were used in the mass balance.

Table L - 7. Special Run Simulant Module D Basket Rinse ICPMS

Sample	**Volume (L)**	**Elemental Concentration (ug/L)**			
		Sample	**Cs**	**Re**	**I**
Composite	0.2548	1	9.06E+01	1.28E+04	1.34E+02
		2	9.05E+01	1.29E+04	1.20E+02
		3		1.26E+04	1.15E+02
		Average	**9.06E+01**	**1.28E+04**	**1.23E+02**
		Std. Dev.	7.07E-02	1.53E+02	9.85E+00
		%RSD	0.08%	1.20%	8.01%

The crossbar solids were captured in Quartz Wool samples in the off-gas crossbar from the DMR. It is impossible to separate out all the solids from the quartz wool material so the entire quartz wool samples with solids were first water leached followed by Aqua Regia dissolution. The water leach concentrations were then added to the aqua regia concentrations to give a total species concentration in the solids. The total solids in the quart wool was obtained by weighing the quartz wool before the experiment then drying it after the experiment and re-weighing to get the crossbar solids dry weight. The crossbar solids cation or ICPES analyses are shown in Table L - 8. The composite values were used in the mass balance.

Table L - 8. Special Run Simulant Module D Crossbar Solids ICPES

Sample	**Mass (g)**	**Elemental Concentration (wt%)**											
		Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Water Leach		< 0.0010	0.08	< 0.0000	0.011	0.04	3.51	0.00	0.01	0.00	0.64	0.00	< 0.000
Aqua Regia		< 0.0025	10.07	< 0.0050	0.007	0.39	10.53	0.01	0.06	0.02	0.49	2.14	0.009
Composite	0.3446	< 0.0035	10.15	< 0.0050	0.019	0.43	14.05	0.01	0.07	0.02	1.12	2.14	0.009

The crossbar solids trace elemental or ICPMS concentrations for the Simulant Module D Special Run are shown in Table L - 9. The composite concentrations were used in the mass balance.

Table L - 9. Special Run Simulant Module D Crossbar Solids ICPMS

Sample	**Mass (g)**	**Species Concentration (wt%)**		
		Cs	**Re**	**I**
Water Leach		0.0004	0.44	0.000009
Aqua Regia		0.0086	0.34	
Composite	0.3446	0.0090	0.775	0.000009

The DMR seal pot drain trace elemental or ICPMS analyses performed are shown in Table L - 10. The average values were used in the mass balance.

Table L - 10. Special Run Simulant Module D Seal Pot Drain ICPMS

Sample	**Volume (L)**	**Elemental Concentration (ug/L)**			
		Sample	**Cs**	**Re**	**I**
Composite	0.0274	1	4.98E+01	5.69E+03	5.65E+03
		2	4.75E+01	5.84E+03	5.68E+03
		Average	4.87E+01	5.77E+03	5.67E+03
		Std. Dev.	1.63E+00	1.06E+02	2.12E+01
		%RSD	3.34%	1.84%	0.37%

The DMR seal pot rinse trace elemental or ICPMS analyses are shown in Table L - 11. The average values were used in the mass balance.

Table L - 11. Special Run Simulant Module D Seal Pot Rinse ICPMS

Sample	**Volume (L)**	**Elemental Concentration (ug/L)**			
		Sample	**Cs**	**Re**	**I**
Composite	0.0407	1	1.71E+01	1.85E+03	8.91E+02
		2	1.76E+01	1.89E+03	9.72E+02
		Average	**1.74E+01**	**1.87E+03**	**9.32E+02**
		Std. Dev.	3.54E-01	2.83E+01	5.73E+01
		%RSD	2.04%	1.51%	6.15%

The off-gas 25 μm (front) and 2 μm (back) cellulose filters right before the mass spectrometer were analyzed for cation concentrations for the Simulant Module D special run as shown in Table L - 12. Note the relative solid mass on each filter was estimated based on the analyses performed and the total number of runs performed. The 25 and 2 μmfilters were analyzed like the Quartz Wool where the samples underwent a water leach followed by Aqua Regia dissolution. There was only one sample analyzed for each Micron Filter. The values shown in Table L - 12 were used in the mass balance.

Table L - 12. Special Run Simulant Module D Off-gas Micron Filter Solids ICPES

Sample	**Estimated Mass (g)**	**Elemental Concentration (wt%)**											
		Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
25 μm (front)	0.0038	< 0.32	9.72	12.79	0.039	21.20	1.23	0.34	0.33	< 0.42	1.69	0.00	14.53
2 μm (back)	0.0049	< 0.25	11.06	16.41	0.047	13.42	1.08	0.04	0.26	< 0.33	1.88	0.00	15.42

The Cs, Re, and I wt% concentrations for the off-gas 25 μm (front) and 2 μm (back) cellulose filters are shown in Table L - 13. These values were used in the mass balance.

Table L - 13. Special Run Simulant Module D Micron Filter Solids ICPMS

Sample	Estimated Mass (g)	Elemental Concentration (wt%)	
		Cs	Re
25 µm (front)	0.0038	0.11	6.31
2 µm (back)	0.0049	0.010	0.006

The caustic scrubber solution trace elemental or ICPMS analyses performed are shown in Table L - 14. The average values were used in the mass balance.

Table L - 14. Special Run Simulant Module D Caustic Scrubber Solution ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.2548	1	7.44E+02	< 1.00E+01	1.62E+02
		2	7.32E+02	< 1.00E+01	1.78E+02
		3		< 1.00E+01	1.65E+02
		Average	**7.38E+02**	**< 1.00E+01**	**1.68E+02**
		Std. Dev.	8.49E+00	na	8.50E+00
		%RSD	1.15%	na	5.05%

na=not applicable

A special rinse of the DMR off-gas crossbar and condenser was performed using a 5-wt% Spectrosol solution. The trace elemental or ICPMS analyses performed for this Spectrosol rinse are shown in Table L - 15. The average values were used in the mass balance.

Table L - 15. Special Run Simulant Module D Crossbar and Condenser Spectrosol Rinse ICPMS

Sample	Volume (L)	Elemental Concentration (ug/L)			
		Sample	Cs	Re	I
Composite	0.1356	1	3.67E+00	6.79E+01	3.80E+01
		2	3.37E+00	7.27E+01	3.68E+01
		3		6.67E+01	3.73E+01
		Average	3.52E+00	6.91E+01	3.74E+01
		Std. Dev.	2.12E-01	3.17E+00	6.03E-01
		%RSD	6.03%	4.59%	1.61%

Appendix M. Radioactive Module D Mass Balance Analytical Data

Table M - 1 through Table M - 3 gives the ICPES, IC, and ICPMS concentrations for the Radioactive Module D granular product samples. The average concentrations were used in the mass balance.

Table M - 1. Radioactive Module D Granular Composite Product ICPES

Sample	**Elemental Concentration (wt)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.00115	17.40	0.011	0.012	0.57	14.60	< 0.004	0.059	< 0.042		16.30	0.0055
2	< 0.00118	19.70	0.012	0.014	0.60	16.60	< 0.004	0.064	< 0.043	0.15	17.90	0.0059
3	< 0.00114	18.90	0.012	0.015	0.54	15.80	< 0.004	0.058	< 0.042	0.13	18.30	0.0051
4		17.10										0.0057
5		18.20										< 0.01
6		18.80										0.0057
Average	**< 0.00116**	**18.35**	**0.011**	**0.014**	**0.57**	**15.67**	**< 0.004**	**0.060**	**< 0.042**	**0.14**	**17.50**	**0.0056**
Std. Dev.	0.00002	0.98	0.001	0.001	0.03	1.01	0.0001	0.003	0.0008	0.02	1.06	0.0003
RSD	1.80	5.35	7.31	10.25	4.48	6.43	1.87	5.14	1.97	12.04	6.05	5.32

Table M - 2. Radioactive Module D Granular Composite Product IC

Sample	**Species Concentration (wt%)**					
	F	**Cl**	**NO$_2$**	**NO$_3$**	**SO$_4$**	**PO$_4$**
1	< 0.047	0.206	< 0.047	< 0.047	0.262	0.178
2	< 0.047	0.216	< 0.047	< 0.047	0.262	0.178
3	< 0.047	0.216	< 0.047	< 0.047	0.244	0.187
Average	**< 0.047**	**0.212**	**< 0.047**	**< 0.047**	**0.256**	**0.181**
Std. Dev.	na	0.005	na	na	0.011	0.005
%RSD	na	2.55	na	na	4.22	2.99

na=not applicable

Table M - 3. Radioactive Module D Granular Composite Product ICPMS

Sample	**Species Concentration (wt%)**		
	Re**	**I**	**Tc-99**
1	0.0345	0.00069	0.00021
2	0.0353	0.00065	0.00023
3	0.0356		0.00021
4	0.0345		
5	0.0358		
6	0.0353		
Average	**0.0352**	**0.00067**	**0.000217**
Std. Dev.	0.0005	0.00003	0.00002
%RSD	1.54	4.14	6.93

**Re from ICPMS sweep with mass of 185 at 37.40% and 187 at 62.60%

The radio isotopes of the granular product by gamma analysis for the Radioactive Module D are shown in Table M - 4 and the average values were used in the mass balance.

Table M - 4. Radioactive Module D Granular Composite Product Gamma

Sample	**Concentration (dpm/g)**	
	^{129}I	^{99}Tc
1	1.83E+02	8.22E+04
2	1.65E+02	8.29E+04
3	2.02E+02	8.62E+04
Average	**1.83E+02**	**8.38E+04**
Std. Dev.	1.85E+01	2.14E+03
%RSD	10.09%	2.55%

The DMR condensate filtrate cation or ICPES concentrations from the Radioactive Module D runs are shown in Table M - 5. The DMR condensate filtrates have a volume of 1.8225 L with a density of 1.00 g/ml. There was only one sample analyzed and these values were used in the mass balance.

The DMR condensate composite filtrate anion or IC concentrations from the Radioactive Module C runs are shown in Table M - 6. The DMR condensate composite filtrate was 1.8225 L and the average condensate composite concentrations were used in the mass balance.

The DMR condensate filtrate trace elemental or ICPMS concentrations from the Radioactive Module D runs are shown in Table M - 7. The average concentrations for the DMR condensate filtrates were used in the mass balance.

The radioisotopes of the DMR Condensate filtrate by gamma analysis for the Radioactive Module D runs are shown in Table M - 8. There was only one sample so those concentrations were used in the mass balance.

The crossbar rinse filtrate cation or ICPES concentrations from the runs for Radioactive Module D runs are shown in Table M - 9. The crossbar rinse filtrate total volume was 0.4437 L. The average cation or ICPES concentrations in Table M - 9 are used in the mass balance

Table M - 5. Radioactive Module D Condensate Composite Filtrate ICPES

Sample	**Elemental Concentration (mg/L)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	< 2.90E-02	9.45E-01	< 2.80E-02	< 1.50E-02	< 5.13E-01	5.90E+00	< 9.10E-02	< 3.28E-01	< 1.43E-01	2.72E+00	4.55E+00	< 1.30E-02

Table M - 6. Radioactive Module D Condensate Composite Filtrate IC

Sample	**Species Concentration (mg/L)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	< 5	< 5	10	< 5	< 5	< 5

Table M - 7. Radioactive Module D Condensate Composite Filtrate ICPMS

Sample	**Species Concentration (ug/L)**	
	Re	**Tc-99**
1	1.64E+02	<1.25E+00
2	1.61E+02	
Average	**1.63E+02**	**<1.25E+00**
Std. Dev.	2.19E+00	na
%RSD	1.34%	na

na=not applicable

Table M - 8. Radioactive Module D Condensate Composite Filtrate Gamma

Sample	**Concentration (dpm/mL)**		
	Cs-137	**I-129**	**Tc-99**
Composite	3.16E+02	<1.28E-01	2.80E+01

Table M - 9. Radioactive Module D Crossbar Rinse Composite Filtrate ICPES

Sample	**Elemental Concentration (mg/L)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	< 2.90E-02	8.40E-02	< 2.80E-02	< 1.50E-02	< 5.13E-01	2.16E+00	< 9.10E-02	< 3.28E-01	< 1.43E-01	< 1.50E+00	2.43E-01	< 1.30E-02

Anion or IC analyses for the Radioactive Module D crossbar rinse filtrate are shown in Table M - 10. The average anion or IC concentrations were used in the mass balance.

Table M - 10. Radioactive Module D Crossbar Rinse Composite Filtrate IC

Sample	Species Concentration (mg/L)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 5	< 5	< 5	< 5	< 5	< 5

The crossbar rinse filtrate trace elemental or ICPMS concentrations for Radioactive Module D runs are shown in Table M - 11. The crossbar rinse filtrate had a volume of 0.1237 L. The average trace elemental or ICPMS concentrations in Table M - 11 were used in the mass balance.

Table M - 11. Radioactive Module D Crossbar Rinse Composite Filtrate ICPMS

Sample	Concentration (ug/L)	
	Re	Tc-99
1	3.66E+01	<2.50E-01
2	3.75E+01	
Average	**3.71E+01**	**<2.50E-01**
Std. Dev.	6.43E-01	na
%RSD	1.73	na

na=not applicable

The radioisotopes of the crossbar rinse filtrate by gamma analysis for the Radioactive Module D runs are shown in Table M - 12. The composite average concentrations shown in Table M - 12 were used in the mass balance.

Table M - 12. Radioactive Module D Crossbar Rinse Composite Filtrate Gamma

Sample	Concentration (dpm/mL)		
	Cs-137	I-129	Tc-99
Composite	1.15E+02	< 1.49E-01	7.79E+00

The crossbar solids were captured in Quartz Wool samples in the off-gas crossbar from the DMR. It is impossible to separate out all the solids from the quartz wool material so the entire quartz wool samples with solids were first water leached followed by Aqua Regia dissolution. The water leach concentrations were then added to the aqua regia concentrations to give a total species concentration in the solids. The total solids in the quart wool was obtained by weighing the quartz wool before the experiment then drying it after the experiment and re-weighing to get the crossbar solids dry weight.

The crossbar solids cation or ICPES concentrations for the Radioactive Module C run are shown in Table M - 13. The crossbar solids total mass was 2.655 g. The composite cation or ICPES concentrations for the crossbar solids were used in the mass balance.

Table M - 13. Radioactive Module D Crossbar Solids ICPES

Sample	Elemental Concentration (wt%)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Water Leach	< 0.00014	0.11	0.0004	< 0.0001	< 0.0028	2.22	< 0.0002	0.001	< 0.0007	0.36	0.066	< 0.0001
Aqua Regia	< 0.00014	6.92		0.005	0.21	3.424	< 0.0004	0.033	0.005	0.01		0.0073
Composite	< 0.00027	7.04	0.0004	0.005	0.21	5.65	< 0.0006	0.034	0.005	0.37	0.066	0.0073

Anion or IC analyses for the Radioactive Module D Crossbar Solids samples came from the Water Leach preparations and are shown in Table M - 14. These values were used in the mass balance.

Table M - 14. Radioactive Module D Crossbar Solids IC

Sample	**Species Concentration (wt%)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
Composite	0.46	0.59	0.11	0.055	0.99	<0.009

The crossbar solids trace elemental or ICPMS concentrations for Radioactive Module C runs are shown in Table M - 15. The crossbar solids mass was 2.655 g. The composite concentrations were used in the mass balance.

Table M - 15. Radioactive Module D Crossbar Rinse Composite Filtered Solids ICPMS

Run	**Concentration (wt%)**	
	Re	**Tc-99**
Water Leach	0.0605	0.0002
Aqua Regia	0.0199	0.0002
Composite	0.080	0.0004

The radioisotopes of the crossbar solids by gamma analysis for the Radioactive Module D runs are shown in Table M - 16. The average composite concentrations are shown in Table M - 16 and were used in the mass balance.

Table M - 16. Radioactive Module D Crossbar Rinse Filtered Solids Gamma

Run	**Concentration (dpm/g)**	
	I-129	**Tc-99**
Composite	6.35 E+03	1.39E+05

Appendix N. X-Ray Diffraction Spectra

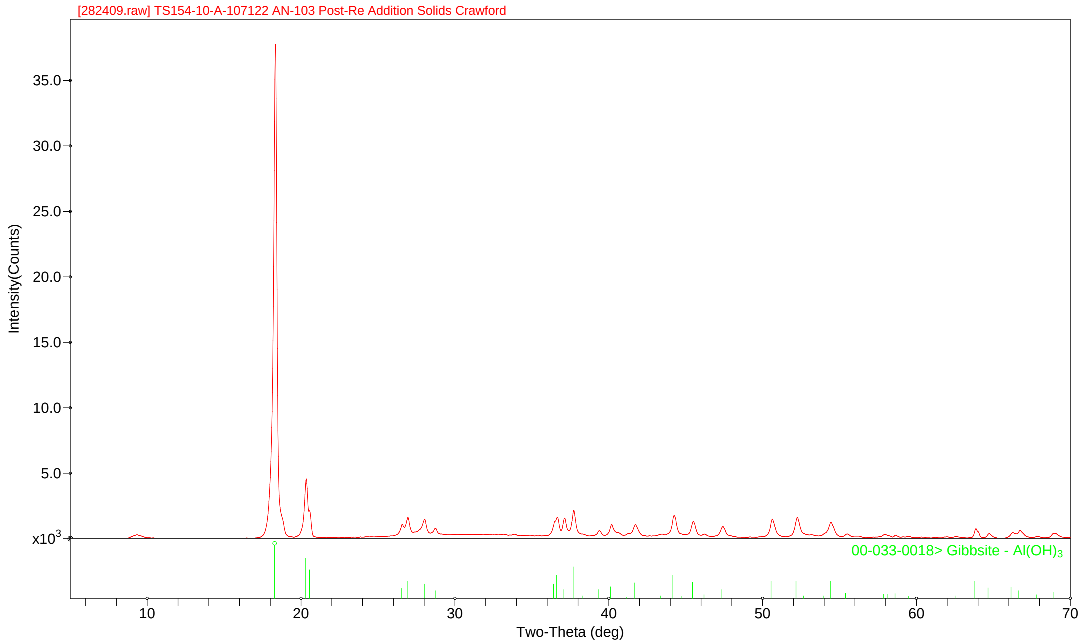

Figure N - 1. X-Ray Spectra for Figure 4-2

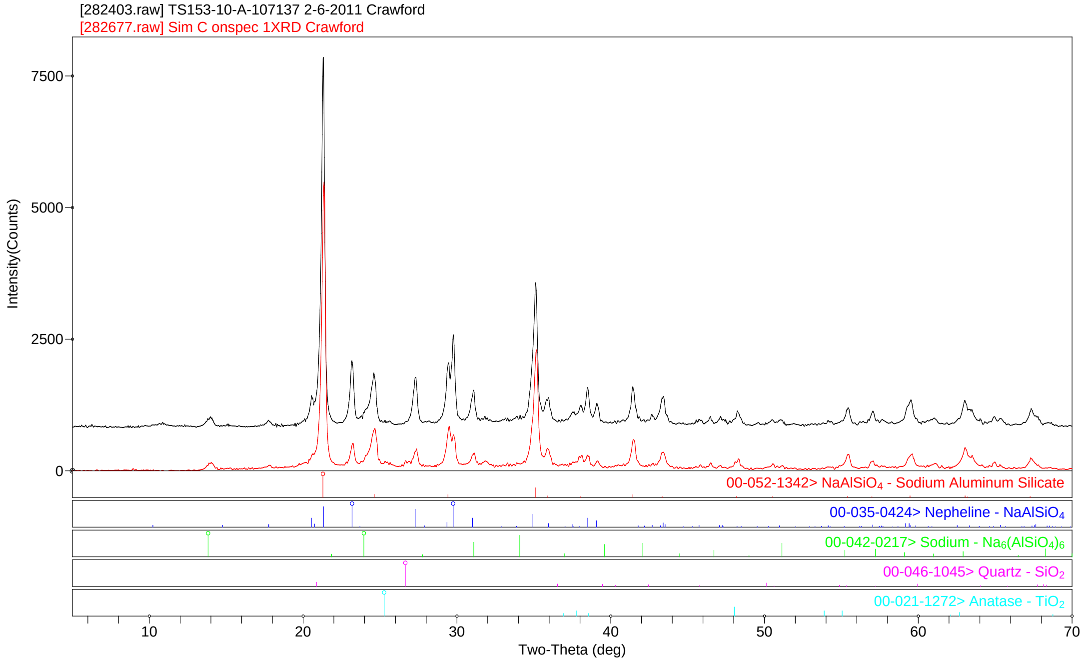

Figure N - 2. X-Ray Spectra for Figure 5-2 Overlays

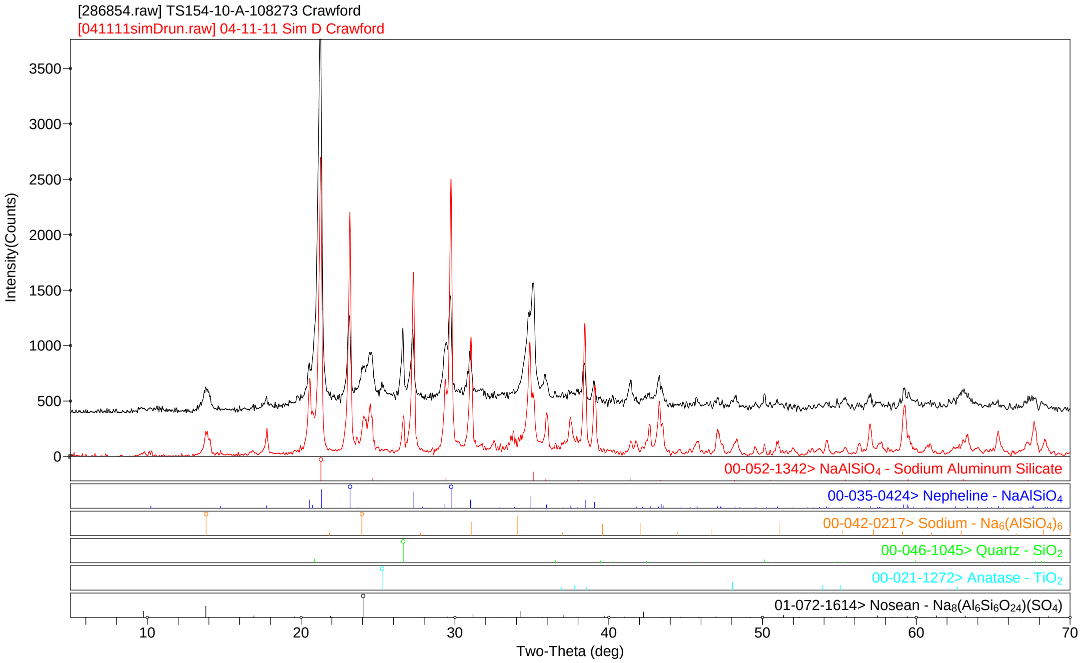

Figure N - 3. X-Ray Spectra for Figure 5-3 Overlays

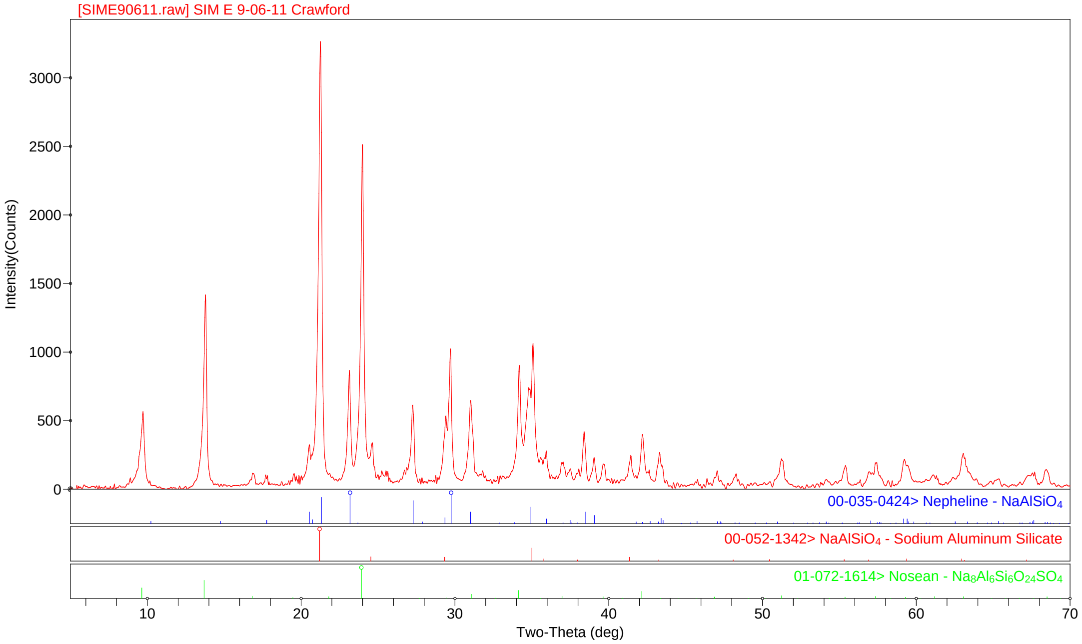

Figure N - 4. X-Ray Spectra for Figure 5-4 Overlays

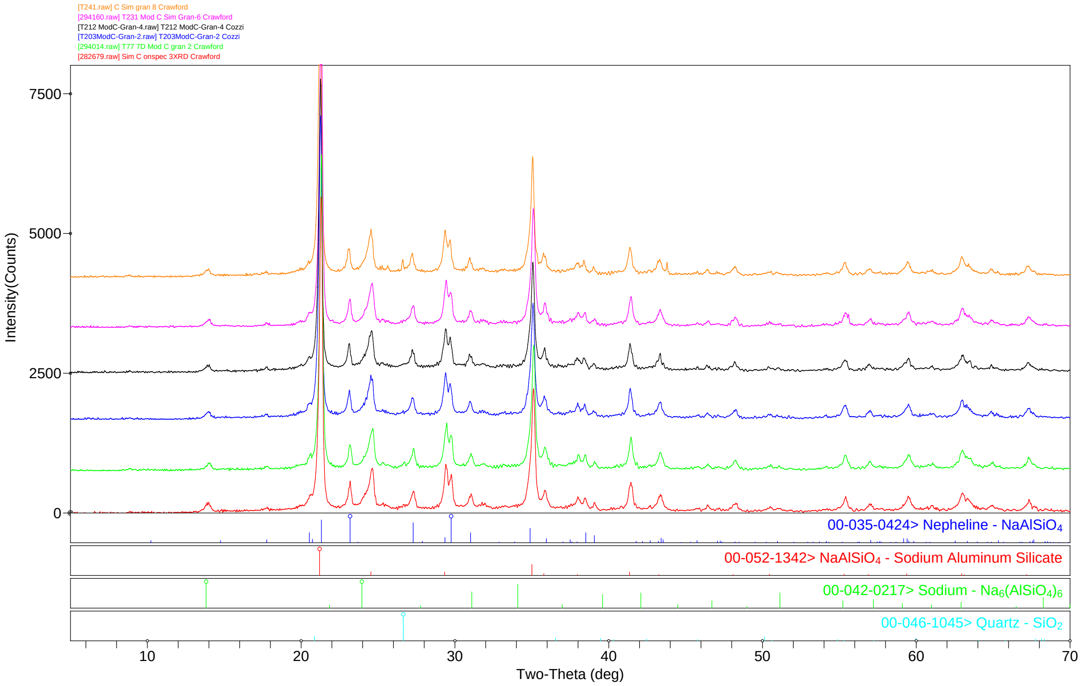

Figure N - 5. X-Ray Spectra for Figure 5-9 Overlays

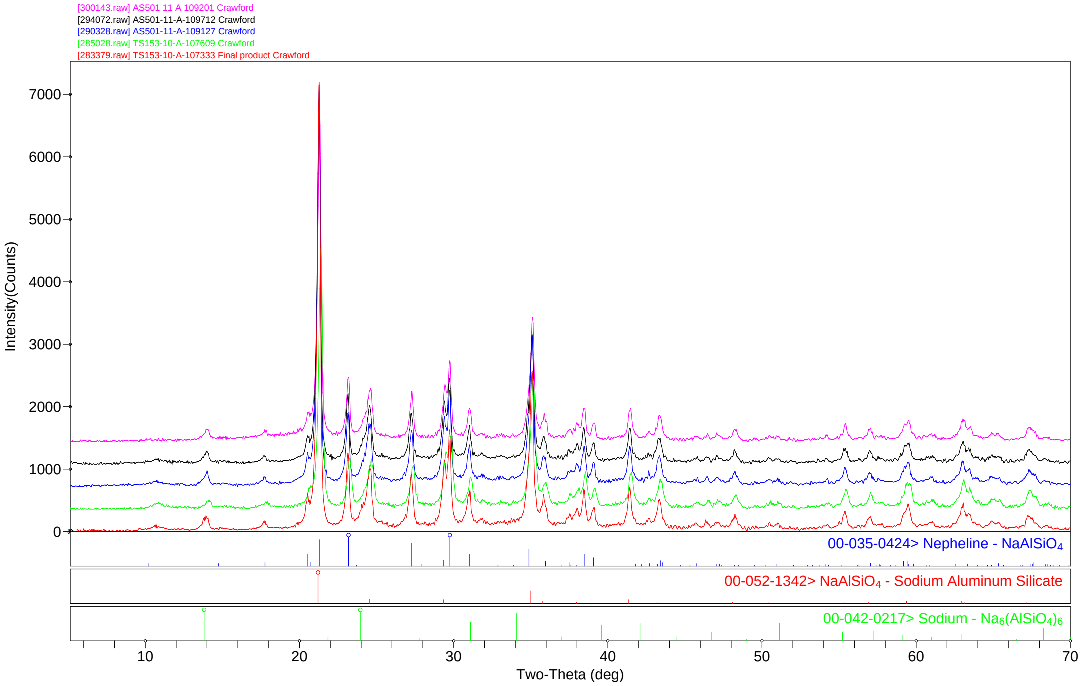

Figure N - 6. X-Ray Spectra for Figure 5-11 Overlays

Appendix O. Short-Term and Long-Term Product Consistency Testing

PCT Data for Short Term Tests

All short term PCT data includes ARM and LRM glass leachate data for comparison to referenced leachate concentrations. **Error! Reference source not found.** shows as measured leachate concentrations (mg/L) for Simulant Module C granular product short term tests. These data are corrected for dilution and shown as g/L values along with the various matrix and leachant masses, dilution factors and measured BET Surface Areas in **Error! Reference source not found.**.

As measured leachate and corrected leachate data are shown in **Error! Reference source not found.** and **Error! Reference source not found.** for the Radioactive Module C granular product short term tests.

These short term PCT data show that all the measured ARM glass Na and Si leachate data are within the reference range of 0.029 to 0.043 g/L Na and 0.049 to 0.073 g/L Si.[1] These data also show that all the measured LRM glass Na and Si leachate data compare with the reference range of 0.13 to 0.19 g/L Na and 0.066 to 0.098 g/L Si.[2] Thus these data indicate that the short term PCTs were properly prepared with 100-200 mesh washed particles at the 1 g product to 10 mL leachant ratio and controlled to the appropriate 7-day durations and 90°C temperature.

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[1] WSRC-TR-93-672, Rev. 1

[2] W.L. Ebert and S.F. Wolf, J. Nucl. Matls., 282 (2000) 112-124

Table O- 1. Leachate Data for BSR Simulant Module C Granular Short Term PCT

Sample	Al	Cr	Fe	K	Na	P	Pb	S	Si	Ti	Zr	Cl	F	I	Cs	Re
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L
BLK-1	<0.100	<0.100	<0.100	<10.0	8.50	<10.0	<1.00	<1.00	<1.00	<1.00	<0.100					
BLK-2	<0.100	<0.100	<0.100	<10.0	1.59	<10.0	<1.00	<1.00	<1.00	<1.00	<0.100					
ARM-1	3.67	<0.100	<0.100	<10.0	22.89	<10.0	<1.00	<1.00	37.85	<1.00	<0.100					
ARM-2	3.58	<0.100	<0.100	<10.0	26.26	<10.0	<1.00	<1.00	41.21	<1.00	<0.100					
ARM-3	3.69	<0.100	<0.100	<10.0	25.34	<10.0	<1.00	<1.00	41.31	<1.00	<0.100					
LRM-1	8.27	<0.100	1.31	<10.0	105.74	<10.0	<1.00	<1.00	55.69	<1.00	0.79					
LRM-2	8.40	<0.100	1.38	<10.0	111.23	<10.0	<1.00	<1.00	55.97	<1.00	0.86					
LRM-3	8.69	<0.100	1.39	<10.0	112.01	<10.0	<1.00	<1.00	57.93	<1.00	0.90					
7D Sim Mod C gran-1	139.00	1.71	<0.100	<10.0	468.79	86.28	<1.00	103.22	15.80	<1.00	<0.100	<10.0	<10.0	364	10.20	3110
7D Sim Mod C gran-2	154.95	1.94	<0.100	<10.0	498.55	97.72	<1.00	109.34	17.84	<1.00	<0.100	<10.0	<10.0	365	15.70	3420
7D Sim Mod C gran-3	147.23	1.88	<0.100	<10.0	514.13	90.02	<1.00	107.41	16.69	<1.00	<0.100	<10.0	<10.0	353	12.50	3310

Table O- 2. Corrected Leachate Data, pH and BET SA for Simulant Module C Granular Short Term PCT

Sample ID	**BLK**		**ARM**			**LRM**			**7D Sim Mod C granular**		
Replicate ID	**BLK-1**	**BLK-2**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**gran-1**	**gran-2**	**gran-3**
Vessel ID	**t64**	**t66**	**t67**	**t68**	**t69**	**t70**	**t71**	**t73**	**t75**	**t77**	**t79**
pH	7.60	7.10	10.12	10.1	10.18	10.87	10.91	10.94	10.82	10.8	10.75
Empty Mass (g)	112.395	113.208	108.783	111.378	113.312	111.119	111.314	113.402	113.328	111.546	114.504
Mass w/Sample (g)	NA	NA	110.283	112.878	114.814	112.618	112.81	114.905	114.332	112.546	115.5
Mass w/Water and Sample (g)	127.370	128.201	125.261	127.884	129.826	127.566	127.784	129.89	124.305	122.516	125.489
Mass w/Lug, Start (g)	127.370	128.201	125.261	127.884	129.826	127.566	127.784	129.89	124.305	122.516	125.489
Mass w/Lug, Finish (g)	126.634	128.117	124.439	126.73	129.7	127.44	127.647	129.752	123.812	122.205	125.383
Use PCT A Surface Area / Volume?	NA	NA	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No
Measured Surface Area (m2/g)	NA	NA	NA	NA	NA	NA	NA	NA	4	4	4
Leachate Dilution Factor	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
Element	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**
Al	<1.0E-04	<1.0E-04	6.1E-03	6.0E-03	6.2E-03	1.4E-02	1.4E-02	1.5E-02	2.3E-01	2.6E-01	2.5E-01
Cr	<1.0E-04	<1.0E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.9E-03	3.2E-03	3.1E-03
Fe	<1.0E-04	<1.0E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.2E-03	2.3E-03	2.3E-03	<1.7E-04	<1.7E-04	<1.7E-04
K	<1.0E-02	<1.0E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02
Na	8.5E-03	1.6E-03	3.8E-02	4.4E-02	4.2E-02	1.8E-01	1.9E-01	1.9E-01	7.8E-01	8.3E-01	8.6E-01
P	<1.0E-02	<1.0E-02	<1.7E-02	<1.67E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	1.4E-01	1.6E-01	1.5E-01
Pb	<1.0E-03	<1.0E-03	<1.7E-03	<1.67E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03
S	<1.0E-03	<1.0E-03	<1.7E-03	<1.67E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	1.72E-01	1.83E-01	1.79E-01
Si	<1.0E-03	<1.0E-03	6.3E-02	6.9E-02	6.9E-02	9.3E-02	9.3E-02	9.7E-02	2.6E-02	3.0E-02	2.8E-02
Ti	<1.0E-03	<1.0E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03
Zr	<1.0E-04	<1.0E-04	<1.7E-04	<1.7E-04	<1.7E-04	1.3E-03	1.43E-03	1.51E-03	<1.7E-04	<1.7E-04	<1.7E-04
Cl									<8.4E-03	<8.4E-03	<8.4E-03
F									<8.4E-03	<8.4E-03	<8.4E-03
I									3.0E-04	3.0E-04	2.9E-04
Cs									1.7E-05	2.6E-05	2.1E-05
Re									5.2E-03	5.7E-03	5.5E-03

Table O- 3. Leachate Data for BSR Radioactive Module C Granular Short Term PCT

Sample	Al	Cr	Fe	K	Na	P	Pb	S	Si	Ti	Zr	Cl	F	I-129	Cs-137	Tc-99	Re
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	dpm/mL	dpm/mL	dpm/mL	ug/L
BLK-1	<0.38	<0.04	<0.02	<1.40	0.46	0.62	<0.29	<3.00	0.17	<0.01	<0.02	<5.00	<5.00				
BLK-2	<0.38	<0.04	<0.02	<1.40	0.46	0.62	<0.29	<3.00	0.17	<0.01	<0.02	<5.00	<5.00				
ARM-1	1.03	<0.02	0.02	<0.70	6.52	0.21	<0.15	1.5	10.8	0.006	<0.01						
ARM-2	0.99	<0.02	0.01	<0.70	6.62	0.226	<0.15	<1.5	10.8	0.005	<0.01						
ARM-3	0.99	<0.02	0.02	<0.70	6.36	0.21	<0.15	<1.5	10.4	0.006	<0.01						
LRM-1	2.66	0.06	0.53	<0.70	35	<0.17	<0.15	<1.5	16	0.031	0.30						
LRM-2	2.65	0.06	0.53	<0.70	34.3	0.194	<0.15	<1.5	16.4	0.03	0.31						
LRM-3	2.6	0.06	0.52	<0.70	33.7	0.185	<0.15	<1.5	15.9	0.03	0.30						
7D Rad MOD C gran-1	58.2	3.92	0.05	<0.70	238	49.1	<0.15	39.6	4.46	0.02	<0.01	<5	<5	<1.3	3.3E+01	2.5E+02	3.4E+02
7D Rad MOD C gran-2	58.2	3.82	0.07	<0.70	238	49	<0.15	39.7	4.46	0.02	<0.01	<5	<5	<3.41	2.9E+01	3.9E+02	3.5E+02
7D Rad MOD C gran-3	58.1	4.02	0.04	<0.70	238	49.6	<0.15	40.5	4.28	0.02	<0.01	<5	<5	<1.25	3.0E+01	4.8E+02	4.2E+02

Table O- 4. Corrected Leachate Data, pH and BET SA for BSR Radioactive Module C Granular Short Term PCT

Sample ID	**BLK**		**ARM**			**LRM**			**7D Rad Module C granular**		
Replicate ID	**BLK-1**	**BLK-2**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**7D gran-1**	**7D gran-2**	**7D gran-3**
Vessel ID	**t41**	**t42**	**t43**	**t44**	**t46**	**t47**	**t48**	**t53**	**t56**	**t61**	**t62**
pH									10.87	10.89	10.85
Empty Mass (g)	113.859	114.764	111.207	113.238	112.952	112.991	111.124	114.551	108.904	114.568	112.28
Mass w/Sample (g)	NA	NA	112.194	114.226	113.932	113.983	112.103	115.548	109.9068	115.6407	113.362
Mass w/Water and Sample (g)	123.697	124.622	122.035	124.08	123.775	123.838	121.949	125.375	120.254	125.62	123.323
Mass w/Lug, Start (g)	123.697	124.622	122.035	124.08	123.775	123.838	121.949	125.375	120.254	125.62	123.323
Mass w/Lug, Finish (g)											
Use PCT A Surface Area / Volume?	NA	NA	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No
Measured Surface Area (m2/g)	NA	NA	NA	NA	NA	NA	NA	NA	4.5	4.5	4.5
Leachate Dilution Factor	5	5	5	5	5	5	5	5	5	5	5
Element	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**
Al	<3.8E-04	<3.8E-04	5.2E-03	4.9E-03	5.0E-03	1.3E-02	1.3E-02	1.3E-02	2.9E-01	2.9E-01	2.9E-01
Cr	<4.2E-05	<4.2E-05	<1.1E-04	<1.1E-04	<1.1E-04	3.2E-04	3.1E-04	3.1E-04	2.0E-02	1.9E-02	2.0E-02
Fe	<2.3E-05	<2.3E-05	1.2E-04	6.2E-05	7.5E-05	2.7E-03	2.6E-03	2.6E-03	2.7E-04	3.3E-04	2.2E-04
K	<1.4E-03	<1.4E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03	<3.5E-03
Na	<4.6E-04	<4.6E-04	3.3E-02	3.3E-02	3.2E-02	1.8E-01	1.7E-01	1.7E-01	1.2E+00	1.2E+00	1.2E+00
P	<6.2E-04	<6.2E-04	1.1E-03	1.1E-03	1.1E-03	<8.5E-04	9.7E-04	9.3E-04	2.5E-01	2.5E-01	2.5E-01
Pb	<2.9E-04	<2.9E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04	<7.3E-04
S	<3.0E-03	<3.0E-03	7.5E-03	<7.5E-03	<7.5E-03	<7.5E-03	<7.5E-03	<7.5E-03	2.0E-01	2.0E-01	2.0E-01
Si	1.7E-04	1.7E-04	5.4E-02	5.4E-02	5.2E-02	8.0E-02	8.2E-02	8.0E-02	2.2E-02	2.2E-02	2.1E-02
Ti	<7.0E-06	<7.0E-06	3.1E-05	2.7E-05	3.1E-05	1.5E-04	1.5E-04	1.5E-04	1.1E-04	9.8E-05	7.9E-05
Zr	<1.9E-05	<1.9E-05	<4.7E-05	<4.7E-05	<4.7E-05	1.51E-03	1.53E-03	1.49E-03	<4.7E-05	<4.7E-05	<4.7E-05
Cl	<5.0E-03	<5.0E-03							<2.5E-02	<2.5E-02	<2.5E-02
F	<5.0E-03	<5.0E-03							<2.5E-02	<2.5E-02	<2.5E-02
I-129									<1.7E-05	<4.4E-05	<1.6E-05
Cs-137									8.6E-10	7.4E-10	7.7E-10
Tc-99									3.3E-05	5.1E-05	6.4E-05
Re									1.7E-03	1.7E-03	2.1E-03

PCT Data for Long Term Tests

The as measured and corrected leachate data for long term PCTs for the Simulant Module C granular products are shown in Table O- 5 and Table O- 6. Similar as measured and corrected leachate data for long term PCTs for the Radioactive Module C granluar product are shown in Table O- 7 and

Table O- 8. These long term tests conducted for up to twelve months did not include any ARM or LRM glass samples.

Table O- 5. Leachate Data for Simulant Module C Granular LongTerm PCT

Sample	Al	Cr	Fe	K	Na	P	Pb	S	Si	Ti	Zr	Cl	F	I	Cs	Re
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L
1M Sim MOD C gran-1	137.00	1.51	1.34	<10.0	487.00	82.90	<1.00	95.20	12.40	<1.00	<0.100	<10.0	<10.0	370	11.60	2520
1M Sim MOD C gran-2	140.00	1.56	1.41	<10.0	505.00	85.30	<1.00	97.50	11.80	<1.00	<0.100	<10.0	<10.0	362	11.50	2610
3M Sim MOD C gran-1	127.88	2.27	<0.100	<10.0	508.00	117.56	<1.00	121.63	11.54	<1.00	<0.100	<10.0	<10.0	396	11.80	2800
3M Sim MOD C gran-2	123.29	2.23	<0.100	<10.0	503.00	112.65	<1.00	116.37	11.24	<1.00	<0.100	<10.0	<10.0	394	12.10	2750
6M Sim MOD C gran-1	152.67	2.00	<0.100	<10.0	592.00	97.13	<1.00	108.63	9.41	<1.00	<1.00	<10.0	<10.0	475	18.20	3010
6M Sim MOD C gran-2	151.34	2.03	<0.100	<10.0	602.00	95.89	<1.00	110.11	9.60	<1.00	<1.00	<10.0	<10.0	456	17.40	3010
12M Sim MOD C gran-1	125.00	1.56	0.101	<0.100	543.53	81.85	<1.00	92.07	9.44	<1.00	<1.00	<10.0	<10.0	429	14.39	2746
12M Sim MOD C gran-2	143.00	1.78	0.1	<0.100	583.90	94.98	<1.00	104.10	9.70	<1.00	<1.00	<10.0	<10.0	494	14.11	3019

Table O- 6. Corrected Leachate Data, pH and BET SA for Simulant Module C Granular LongTerm PCT

Sample ID	1M Sim MOD C gran		3M Sim MOD C gran		6M Sim MOD C gran		12M Sim MOD C gran	
Replicate ID	**1M gran-1**	**1M gran-2**	**3M gran-1**	**3M gran-2**	**6M gran-1**	**6M gran-2**	**12M gran-1**	**12M gran-2**
Vessel ID	**t198**	**t203**	**t206**	**t212**	**t220**	**t231**	**t239**	**t241**
pH	10.52	10.52	10.3	10.27	10.04	10.04	10.19	10.1
Empty Mass (g)	114.627	113.37	113.45	113.387	114.617	113.462	115.068	114.425
Mass w/Sample (g)	115.627	114.362	114.447	114.377	115.605	114.457	116.067	115.359
Mass w/Water and Sample (g)	125.599	124.351	124.418	124.375	125.596	124.452	126.057	124.85
Mass w/Lug, Start (g)	125.599	124.351	124.418	124.375	125.596	124.452	126.057	124.85
Mass w/Lug, Finish (g)	125.286	124.033	123.725	123.681	124.219	123.075	124.908	123.617
Use PCT A Surface Area / Volume?	No	No	No	No	No	No	No	No
Measured Surface Area (m2/g)	4	4	4	4	4	4	4	4
Leachate Dilution Factor	2	2	2	2	2	2	2	2
Element	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**
Al	2.7E-01	2.8E-01	2.6E-01	2.5E-01	3.1E-01	3.0E-01	2.5E-01	2.9E-01
Cr	3.0E-03	3.1E-03	4.5E-03	4.5E-03	4.0E-03	4.1E-03	3.1E-03	3.6E-03
Fe	2.7E-03	2.8E-03	<2.0E-04	<2.0E-04	<2.0E-04	<2.0E-04	2.0E-04	2.0E-04
K	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-04	<2.0E-04
Na	9.7E-01	1.0E+00	1.0E+00	1.0E+00	1.2E+00	1.2E+00	1.1E+00	1.2E+00
P	1.7E-01	1.7E-01	2.4E-01	2.3E-01	1.9E-01	1.9E-01	1.6E-01	1.9E-01
Pb	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
S	1.9E-01	2.0E-01	2.4E-01	2.3E-01	2.2E-01	2.2E-01	1.8E-01	2.1E-01
Si	2.5E-02	2.4E-02	2.3E-02	2.2E-02	1.9E-02	1.9E-02	1.9E-02	1.9E-02
Ti	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
Zr	<2.0E-04	<2.0E-04	<2.0E-04	<2.0E-04	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
Cl	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
F	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
I	3.7E-04	3.6E-04	4.0E-04	3.9E-04	4.8E-04	4.6E-04	4.3E-04	4.9E-04
Cs	2.3E-05	2.3E-05	2.4E-05	2.4E-05	3.6E-05	3.5E-05	2.9E-05	2.8E-05
Re	5.0E-03	5.2E-03	5.6E-03	5.5E-03	6.0E-03	6.0E-03	5.5E-03	6.0E-03

Table O- 7. Leachate Data for BSR Radioactive Module C Granular Long Term PCT

Sample	Al	Cr	Fe	K	Na	P	Pb	S	Si	Ti	Zr	Cl	F	I-129	Cs-137	Tc-99	Re
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	dpm/mL	dpm/mL	dpm/mL	ug/L
1M Rad MOD C gran-1	60.6	4.27	<0.02	<0.60	265	48	<0.14	36.6	4.79	<0.01	<0.01	<5	<5	<0.66	5.9E+01	2.8E+02	3.6E+02
1M Rad MOD C gran-2	61.6	4.37	<0.02	<0.60	272	50	<0.14	38.6	4.71	<0.01	<0.01	<5	<5	<0.33	4.5E+01	2.5E+02	3.7E+02
3M Rad MOD C gran-1-1	105	7.48	<0.10	<2.57	502	87.6	<0.72	67.9	6.68	<0.04	<0.03						7.2E+02
3M Rad MOD C gran-2-1												<10	<10	<1.52	6.5E+01	5.5E+02	
3M Rad MOD C gran-1-2	102	7.31	<0.10	<2.57	490	85.4	<0.72	72.6	6.24	<0.04	<0.03						7.0E+02
3M Rad MOD C gran-2-2												<10	<10	<0.68	9.0E+01	6.5E+02	
12M Rad MOD C gran-1-1	91.5	7.66	0.12	<1.7	516	84	<0.88	67.2	3.75	<0.02	<0.03						7.3E+02
12M Rad MOD C gran-2-1												<10	<10	<0.60	6.7E+01	7.3E+02	
12M Rad MOD C gran-1-2	114	8.7	0.09	<1.7	588	98.5	<0.88	74.6	6.3	<0.02	<0.03						7.9E+02
12M Rad MOD C gran-2-2												<10	<10	<1.42	1.3E+02	9.1E+02	

Table O- 8. Corrected Leachate Data, pH and BET SA for Radioactive Module C Granular LongTerm PCT

Sample ID	1M Rad MOD C gran		3M Rad MOD C gran-1		3M Rad MOD C gran-2		12M Rad MOD C gran-1		12M Rad MOD C gran-2	
Replicate ID	**1M gran-1**	**1M gran-2**	**3M gran-1-1**	**3M gran-1-2**	**3M gran-2-1**	**3M gran-2-2**	**12M gran-1-1**	**12M gran-1-2**	**12M gran-2-1**	**12M gran-2-2**
Vessel ID	**t155**	**t167**	**t166**	**t181**	**t166**	**t181**	**t185**	**t199**	**t185**	**t199**
pH	10.64	10.58	10.36	10.3	10.36	10.3	10.06	9.97	10.06	9.97
Empty Mass (g)	113.324	108.691	115.3	114.67	115.3	114.67	110.807	113.295	110.807	113.295
Mass w/Sample (g)	114.315	109.682	116.306	115.578	116.306	115.578	111.795	114.845	111.795	114.845
Mass w/Water and Sample (g)	124.182	119.559	126.19	125.56	126.19	125.56	121.697	130.374	121.697	130.374
Mass w/Lug, Start (g)	124.182	119.559	126.19	125.56	126.19	125.56	121.697	130.374	121.697	130.374
Mass w/Lug, Finish (g)	123.89	118.834	125.3434	124.773	125.3434	124.773	120.804	129.956	120.804	129.956
Use PCT A Surface Area / Volume?	No	No	No	No	No	No	No	No	No	No
Measured Surface Area (m2/g)	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Leachate Dilution Factor	5	5	2.97	2.97	2.83	3.02	2.98	2.48	2.42	1.76
Element	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**	**(g/L)**
Al	3.0E-01	3.1E-01	3.1E-01	3.0E-01			2.7E-01	2.8E-01		
Cr	2.1E-02	2.2E-02	2.2E-02	2.2E-02			2.3E-02	2.2E-02		
Fe	<9.5E-05	<9.5E-05	<2.9E-04	<2.9E-04			3.5E-04	2.2E-04		
K	<3.0E-03	<3.0E-03	<7.6E-03	<7.6E-03			<5.1E-03	<4.2E-03		
Na	1.3E+00	1.4E+00	1.5E+00	1.5E+00			1.5E+00	1.5E+00		
P	2.4E-01	2.5E-01	2.6E-01	2.5E-01			2.5E-01	2.4E-01		
Pb	7.2E-04	<7.2E-04	<2.1E-03	<2.1E-03			<2.6E-03	<2.2E-03		
S	1.8E-01	1.9E-01	2.0E-01	2.2E-01			2.0E-01	1.9E-01		
Si	2.4E-02	2.4E-02	2.0E-02	1.9E-02			1.1E-02	1.6E-02		
Ti	4.0E-05	4.0E-05	1.1E-04	<1.13E-04			<6.0E-05	<5.0E-05		
Zr	<5.5E-05	<5.5E-05	<7.4E-05	<7.4E-05			<9.5E-05	<7.9E-05		
Cl	<2.5E-02	<2.5E-02			<2.8E-02	<3.0E-02			<2.4E-02	<1.8E-02
F	<2.5E-02	<2.5E-02			<2.8E-02	<3.0E-02			<2.4E-02	<1.8E-02
I-129	<8.5E-06	<4.3E-06			<1.1E-05	<5.2E-06			<3.7E-06	<6.4E-06
Cs-137	1.5E-09	1.2E-09			9.6E-10	1.4E-09			8.4E-10	1.2E-09
Tc-99	3.7E-05	3.3E-05			4.1E-05	5.2E-05			4.7E-05	4.2E-05
Re	1.8E-03	1.9E-03	2.13E-03	2.09E-03			2.2E-03	2.0E-03		

Distribution:

T. B. Brown, 773-A
D. R. Click, 999-W
A. P. Fellinger, 773-41A
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A

C. J. Bannochie, 773-42A
P. R. Burket, 773-42A
A. D. Cozzi, 999-W
C. L. Crawford, 773-42A
W. E. Daniel, 999-W
D. H. Miller, 999-W
D. M. Missimer, 773-A
C. A. Nash, 773-42A
M. F. Williams, 999-W

P. R. Jackson, 703-46A

T. W. Fletcher, DOE-ORP
S. H. Pfaff, DOE-ORP

D. J. Swanberg, WRPS
P. A. Cavanah, WRPS
W. G. Ramsey, WRPS
R. A. Robbins, WRPS
L. E. Thompson, WRPS

C. Brown, PNNL
N. Quafoku, PNNL
R. A. Peterson, PNNL
G. L. Smith, PNNL

E. M. Pierce, ORNL