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Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Low Activity Waste (Tank Farm Blend) by Fluidized Bed Steam Reformation (FBSR)

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EXECUTIVE SUMMARY

The U.S. Department of Energy's Office of River Protection (ORP) is responsible for the retrieval, treatment, immobilization, and disposal of Hanford's tank waste. 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 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 can be processed irrespective of whether the waste 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 ASTM C1285 (Product Consistency) durability testing. Monolithing of the granular FBSR product was investigated to prevent dispersion during transport or burial/storage. Monolithing in an inorganic geopolymer binder, which is amorphous, macro-encapsulates the granules, and the monoliths pass ANSI/ANS 16.1 and ASTM C1308 durability testing with Re achieving a Leach Index (LI) of 9 (the Hanford Integrated Disposal Facility, IDF, criteria for Tc-99) after a few days and Na achieving an LI of $\geq$6 (the Hanford IDF criteria for Na) in the first few hours. The granular and monolithic waste forms also pass the EPA Toxicity Characteristic Leaching Procedure (TCLP) for all Resource Conservation and Recovery Act (RCRA) components at the Universal Treatment Standards (UTS).

Two identical Benchscale Steam Reformers (BSR) were designed and constructed at SRNL, one to treat non-radioactive 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 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 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.

The granular ESTD and BSR products (radioactive and non-radioactive) were analyzed for total constituents and durability tested as a granular waste form. A subset of the granular material was stabilized in a clay based geopolymer matrix at 42% and 65% FBSR loadings and durability tested as a

monolith waste form. The 65 wt% FBSR loaded monolith made with clay (radioactive) was more durable than the 67-68 wt% FBSR loaded monoliths made from fly ash (non-radioactive) based on short term PCT testing. Long term, 90 to 107 day, ASTM C1308 testing (similar to ANSI/ANS 16.1 testing) was only performed on two fly ash geopolymer monoliths at 67-68 wt% FBSR loading and three clay geopolymer monoliths at 42 wt% FBSR loading. More clay geopolymers need to be made and tested at longer times at higher FBSR loadings for comparison to the fly ash monoliths. Monoliths made with metakaolin (heat treated) clay are of a more constant composition and are very reactive as the heat treated clay is amorphous and alkali activated. The monoliths made with fly ash are subject to the inherent compositional variation found in fly ash as it is a waste product from burning coal and it contains unreactive components such as mullite. However, both the fly ash and the clay based monoliths perform well in long term ASTM C1308 testing.

Extensive testing and characterization of the granular and monolith material were made including the following American Society of Testing and Materials (ASTM) tests:

- ASTM C1285 testing (Product Consistency Test) of granular and monolithic waste forms
    - ➢ Comparison of granular BSR radioactive to ESTD and pilot scale granular non-radioactive waste form made from the Rassat simulant
    - ➢ Comparison of granular radioactive to granular non-radioactive waste form made from the Rassat simulant made using the SRNL BSR
    - ➢ Comparison of monolithic BSR radioactive waste forms to monolithic BSR and ESTD non-radioactive waste forms made of fly ash
    - ➢ Comparison of granular BSR radioactive waste forms to monolithic BSR non-radioactive waste forms made of fly ash
    - ➢ Comparison of granular BSR radioactive waste forms to monolithic BSR non-radioactive waste forms made of clay

- ASTM C1308 Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms
    - ➢ Comparison of BSR non-radioactive waste forms to monolithic ESTD non-radioactive waste forms made from fly ash
    - ➢ Testing of BSR non-radioactive monoliths made from clay for comparison to non-radioactive monoliths made from fly ash

- ASTM C39 Compressive Strength of Cylindrical Concrete Specimens
    - ➢ Comparison of monolithic BSR radioactive waste forms to monolithic BSR and ESTD non-radioactive waste forms

- EPA Manual SW-846 Method 1311, Toxicity Characteristic Leaching Procedure (TCLP)
    - ➢ Comparison of granular BSR radioactive to ESTD and pilot scale granular non-radioactive waste form made from the Rassat simulant
    - ➢ Comparison of granular radioactive to granular non-radioactive waste form made from the Rassat simulant made using the SRNL BSR
    - ➢ Comparison of monolithic BSR radioactive waste forms to monolithic BSR non-radioactive waste forms

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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
EMF	Electro-Motive Force
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
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
LDRD	Laboratory Directed Research & Development
LI	Leach Index
LAW	Low-Activity Waste
LLW	Low Level Waste
LI	Leaching Index
LOD	Loss on Drying
LOI	Loss on Ignition
MDL	Method Detection Limit
MFC	Materials and Fuels Complex
MSL	Marine Sciences Laboratory

MS	Mass Spectrometer
NAS	Na-Al-Si
NP	Not Present
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
RPP	River Protection Project
SBW	Sodium Bearing Waste
SCDHEC	South Carolina Department of Health and Environmental Control
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
SLM	Standard Liters per Minute
SPFT	Single Pass Flow Through
SST	Single Shell Tank
TDD	Technology Development & Deployment
TIC	Total Inorganic Carbon
TT&QAP	Technical Task & Quality Assurance Plan
TTT	THOR® Treatment Technologies
THOR®	THermal Organic Reduction
TIC	Total Inorganic Carbon
TCLP	Toxicity Characteristic Leaching Procedure
TPA	Tri-Party Agreement
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 form Compliance Plan
WIPP	Waste Isolation Pilot Plant

WRPS	Washington River Protection Services
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. Department of Energy (DOE), Office of River Protection (ORP), through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) 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 high-level waste (HLW) mixture will be sent to the HLW Vitrification Facility, and the pretreated low-activity waste (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). Without additional LAW treatment capacity, the mission would extend an additional 40 years beyond December 31, 2047, the Tri-Party Agreement milestone date for completing all tank waste treatment. 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 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 as durable as LAW glass. Monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage. Considerable durability testing by SRNL and the Pacific Northwest National

Laboratory (PNNL): see Section 1.3 and Reference 2 for a summary of the work already performed 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) [3]. However, crystalline waste forms made from clay have been studied almost continuously since 1953 [3,4]. Often the high temperatures used for sintering created sodalite-cancrinite mineral assemblages. In 1981, Roy [5] 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 [3]. 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 [6,7]. 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 US DOE waste simulants. Illite type clay was tested at the bench scale and 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 [8].

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 temperature 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 [8]. 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 $Na_8[Al_6Si_6O_{24}](Cl_2)$ Na_2MoO_4, $NaTcO_4$, $NaReO_4$. 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 [9]. 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 [10,11] and Ge [12] in the cage like structures. Waste stabilization at the Materials and Fuels Complex (MFC) operated by Battelle Energy Alliance at INL currently uses a glass-bonded sodalite ceramic waste form (CWF) for containment of I from electrorefiner wastes from the EBR II fast breeder reactor [13,14]. 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. [15]

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

Nepheline – Kalsilite Structures*	**Sodalite Structures****	**Nosean Structures**
$Na_xAl_ySi_zO_4$ [21] *where x=1-1.33, y and z = 0.55-1.1*	$[Na_6Al_6Si_6O_{24}](NaCl)_2$ [21]	$[Na_6Al_6Si_6O_{24}](Na_2SO_4)$ [17,21]
$KAlSiO_4$[21]	$[Na_6Al_6Si_6O_{24}](NaFl)_2$ [21]	$[Na_6Al_6Si_6O_{24}](Na_2MoO_4)$ [16,21]
$K_{0.25}Na_{0.75}AlSiO_4$[21]	$[Na_6Al_6Si_6O_{24}](NaI)_2$ [17]	$[Na_6Al_6Si_6O_{24}]((Ca,Na)SO_4)_{1-2}$ [18]
$(Na_2O)_{0.33}NaAlSiO_4$ [9]	$[Na_6Al_6Si_6O_{24}](NaBr)_2$ [17]	$[(Ca,Na)_6Al_6Si_6O_{24}]((Ca,Na)S,SO_{4,}Cl)_x$ [PDF[f] #17-749]
$CsAlSiO_4$ [21]	$[Na_6Al_6Si_6O_{24}](NaReO_4)_2$ [19]	
$RbAlSiO_4$ [21]	$[Na_6Al_6Si_6O_{24}](NaMnO_4)_2$ [20]	
$(Ca_{0.5},Sr_{0.5)}AlSiO_4$ [21]	$[NaAlSiO_4]_6(NaBO_4)_2$ [10,11]	
$(Sr,Ba)Al_2O_4$ [21]	$Mn_4[Be_3Si_3O_{12}]S$ [17]	
$KFeSiO_4$ [21]	$Fe_4[Be_3Si_3O_{12}]S$ [17]	
$(Na,Ca_{0.5})YSiO_4$ [20]	$Zn_4[Be_3Si_3O_{12}]S$ [17]	
$(Na,K)LaSiO_4$[20]		
$(Na,K,Ca_{0.5})NdSiO_4$[20]		

Iron, Ti^{3+}, Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in nepheline.[21]

** 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 [20]

f Powder Diffraction File

The sodalites are classified [22] as "clathrasils", which are structures with large polyhedral cavities that 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 19. 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 through the crystal.[22]

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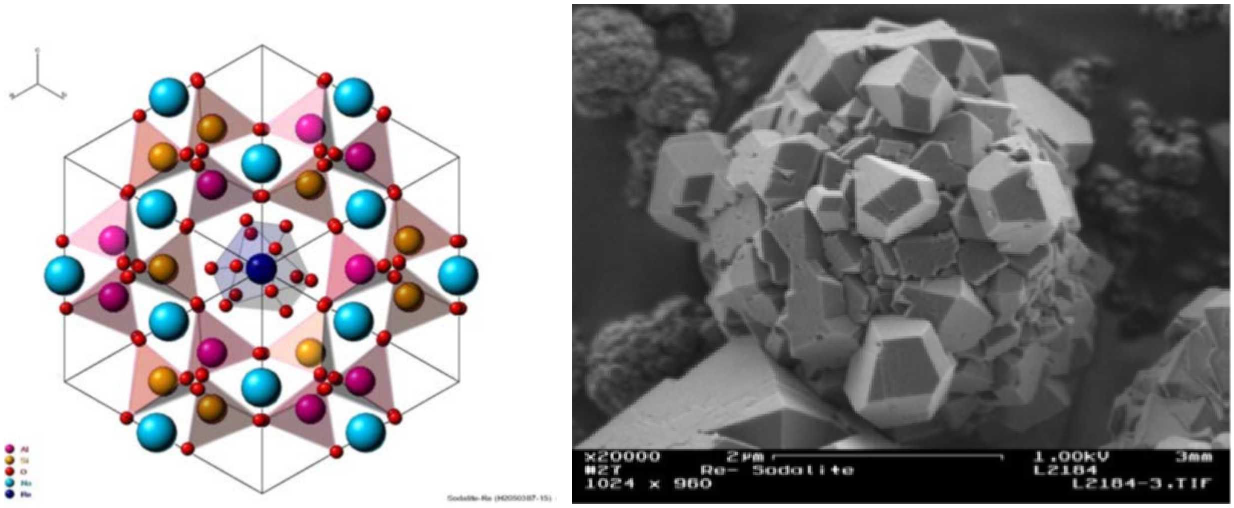
[f] Powder Diffraction File (PDF) #39-0101

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

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.[22]



(a) (b)

Figure 1-1. Structure of a Re-sodalite (left) and a scanning electron microscope image of the same Re sodalite[19].

1.2 <u>FBSR Technology</u>

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 Idaho National Laboratory (INL) for treatment of their Sodium Bearing Waste (SBW) for potential disposal in the Waste Isolation Pilot Plant (WIPP) (Table 1-3). Another facility has been 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) [23,24].

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).[25] 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. [25] 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. 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, Bestac, 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 Defense Waste Processing Facility (DWPF).[26] Additional testing with the radioactive and non-radioactive Rassat 68 tank blend are discussed in this report. Other Hanford radioactive and non-radioactive LAW compositions (Tank SX-105, Tank AN-103, and a blend of AZ-101/AZ-102) are discussed briefly in Section 1.4 and in more detail in Reference 27.

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 and 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). 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).[28] This will be discussed in Section 2 in more detail.

The engineering scale technology demonstration (ESTD) product characterization simulant testing is reported in reference 29 and summarized in Table 1-3. Prior to the reference 29 studies, the FBSR bed products and fines had been studied independently to determine the leaching mechanisms and appropriate leach tests to perform. In reference 29, 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. [30,31,32] The durability of the monolithed FBSR waste forms were then compared to the granular product responses.[32]

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 Distri-bution (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 33	6”	LAW Env. C	Ref. 34	Ref 33,34	Ref 35, 36 And PUF testing 37)	Ref. 38	Bed	Removed By Hand	Gaussian	No	N/A			
		6”	LAW Env. C	Ref 39,40,41		None	“Tie-back” Strategy	Fines	Removed by 525°C Roasting						
SAIC/ STAR	7/03 Ref 42	6”	SBW			None	None	Bed			Yes (Samples were combined; 20% LAW, 32 % SBW and 45% Startup Bed	Ref 30,31	N/A		
SAIC/ STAR	8/04 Ref. 43	6”	LAW Rassat			Ref 41,44,45 and PUF 46	Data from Ref 41,44,45 “Tie-back” Strategy	Bed and Fines Separate							
SAIC/ STAR	7/04 and 11/04 Ref. 47	6”	SBW			Ref 41,44	None								
HRI/ TTT	12/06	15”	SBW	Ref 48		None	None				No	N/A			
HRI/ TTT	2008 Ref. 28		LAW Rassat	Ref 29, 32,49, 50,51	Ref 32,49, 50,51	52	“Tie-back” Strategy	Bed and Fines Together	Not removed	Bi-Modal	Yes	Ref 32	PNNL	This Study	This Study
			WTP-SW			None	None						None	Ref 26,53	32,49, 50,51
Radioactive Testing															
SRNL/ BSR	2010-2011	2.75”	LAW Rassat	51,54 This Study		52	“Tie-back” Strategy	Bed and Fines Together	Not removed	Gaussian	Yes	This Study	PNNL	This Study	This Study
			WTP-SW	26,51,54		None	None					26	None	26	26

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; PNNL Test Results are Complete and being documented; N/A – not applicable.

The ESTD simulant tests [28], including characterization, monolithing, and durability testing [28,29,32] formed the basis for performing the comparative LAW BSR radioactive tests reported on in this study, and referred to as BSR Module B (Table 1-5). The 2008 ESTD simulant tests [28], including characterization, monolithing, and durability testing [28,29,32] also formed the basis for the studies on other LAW waste streams (Table 1-5 and reference 27).

1.3 Performance Assessment Testing

1.3.1 *Durability Requirements*

For HLW, Waste Acceptance Product Specifications (WAPS) [55] and a Waste Compliance Plan (WCP) [56] 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.[57] 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 [58]."
>
> 1.3.1 Acceptance Criteria
> "The consistency of the waste form shall be demonstrated using the Product Consistency Test (PCT).[f] 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 [59]…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} weight % in the waste form, has been shown to be released at the

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[f] 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).

same maximum normalized concentration as boron, lithium, and sodium. [60,61,62,63,64,65,66,67,68] Tc-99 is the radionuclide released 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 [60-68] 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.[69] The PCT is used to determine the waste form leaching and durability in conjunction with ANSI/ANS-16.1 [70] and the PCT is used for determining waste form stability.[57] The Hanford contract [71] 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.”

[‡] 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.

In addition, the Hanford contract [71] requires durability testing for LAW glass by the Vapor Hydration Test (VHT) [72] 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 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, [57] 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.

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.[19, 73] 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.[35,36,38] 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) [38].

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 to be disposed of in the facility although there have been several draft waste acceptance criteria proposed. Initial draft waste acceptance criteria for a secondary waste form are based on the draft IDF waste acceptance criteria [74] 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 [75]:

- 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 [76]
- Leachability Index (LI): The waste form shall have a sodium LI greater than 6.0 when tested in deionized water using the American National Standards Institute/American National Standards (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 [77] and on early waste disposal risk assessments (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 American Society for Testing and Materials (ASTM) C39/C39M (ASTM 2010c). This is based on the Nuclear Regulatory Commission's Technical Position on Waste Forms [77], 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 ANSI/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.[78]

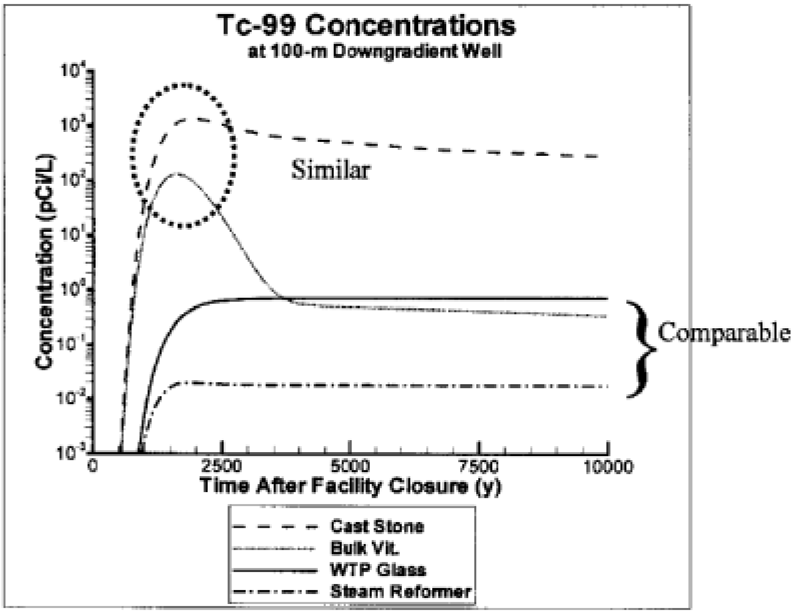

Figure 1-2. Comparison of Tc-99 concentration in a well 100 m downgradient of the IDF as a function of time from Mann et.al. (2003) RA. [38]

1.3.3 *Compressive Strength*

In the 1983 (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 Portlant 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.[77]

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 Performance Assessment. 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 [71] 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"

Because OPC mortars achieve ~75% of their 28 day strength in 7 days of curing [79], some samples were only cured for 7 days and then compression tested with the assumption that any monolith cured for 7 days that would pass the compression test would, therefore, pass after a total of 28 days of curing under the same conditions. Seven day versus 28 day cures are noted in the data tables in Sections 5.6.2 and 5.6.4.

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) [71] 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 [39,40] 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. Therefore, the FBSR loading in a monolith should be ~ 67 wt% for Envelope A type wastes to be comparable to LAW glass. FBSR far exceeds the Na_2O waste loading criteria for Envelope B and C type wastes. 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.[75] There is an LDR requirement that solvent/organics not leach from grout waste forms either.[75] 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 glass (wt%)	67
Toxic 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] and data has been generated on the granular waste form to demonstrate preliminary acceptance in the IDF [1,2,3,4,5,6,8,14,16,19].

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

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 the SRNL BSR using three actual Hanford tank waste samples to demonstrate the range of Hanford LAW to be treated by FBSR (representing the the middle 80% of the total LAW feeds based on anion content). See Table 1-5 for a description of the associated Hanford BSR testing. The data resulting from the demonstration test program and data in previous publications and this study 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 [81] summarizing all previous and current leaching results and their impact on acceptance of the granular FBSR waste form in the IDF.

Prior to performing tests with actual Hanford LAW, a test with a radioactive SRS secondary waste sample from DWPF that was compositionally adjusted to reflect the expected composition of a Hanford WTP secondary waste was performed. [26] An additional SRS LAW sample was shimmed to be compositionally the same as the Rassat 68 tank blend waste simulant recently 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 BSR was performed with the SRS LAW sample to complete the tie-back strategy, which is discussed in the next section.

The SRS LAW tests, documented in this report, provide 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 shown in Table 1-3 and Table 1-5, while some of the granular radioactive and non-radioactive products were monolithed and retested using the same regulatory and performance testing protocols. The data and resulting analysis will be used to minimize technical risk regarding waste form performance 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 benchscale research precedes pilot scale testing, the FBSR process has been run at the pilot and engineering scale (Table 1-3 and Table 1-5) with simulants but not at the benchscale with either simulants or radioactive wastes. SRNL has successfully operated a BSR in the SRNL Shielded Cells Facility (SCF). [82,83] 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. SRNL used two BSR's – one for non-radioactive testing and one for radioactive testing.

Non-radioactive Re was added to the radioactive feed 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.

During the radioactive BSR campaigns, ~90% of the waste was processed with the Tc-99, Re, and I levels equivalent to the Rassat ESTD simulant processed by TTT, while the remaining ~10% of the waste (see Table 1-6 for exact amounts) was doped with Tc-99, and Re at a minimum of 150 μg/g. This level was 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 Re in the mineral waste form. The 10% portion of the feed was processed at the end of the BSR campaigns, after the off-gas condensate was sampled and lines were flushed to ensure that the mass balance and leaching tests were not compromised by the elevated concentrations required by the XAFS.

Table 1-5. Module B Testing on ESTD and BSR Scale Tests

Task	**Rassat Recipe for LAW (Module B)**		
	ESTD Simulant	**BSR Simulant**	**BSR Radioactive (SRS Tank 50)**
Mass Balance	●	●	●
Prepare Monolith	●	●	●
REDOX vs Tc, Re, Cr	●	●	●
TCLP (Granular)	●/▲	●/▲	●/▲
TCLP (Monolith)	●/▲	●/▲	●
Mineral Characterization (Gran vs. Mono)	●/●	●/●	●/●
SPFT (ASTM 1662)	▲	▲	▲
Diffusion (Mono only) (ASTM C1308)	●	●	○
PUF Testing	▲		
Short Term PCT (Gran vs Mono) ASTM C1285	●/●	●/●	●/●
Long Term PCT (Gran vs. Mono) ASTM C1285	●/●	●/●	●/○
Tc & Re Speciation	■	■	
Pure Phase Mineral Testing	■		

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

1.4.2 *Defining the "Tie-Back" Strategy*

The importance of BSR Module B with radioactive SRS LAW is intended to assess the performance of the FBSR process and waste form in the treatment of Hanford LAW. The test is important because the actual SRS LAW that was used from Tank 50 was chemically adjusted to represent the 68 tank blend of Hanford LAW known as the Rassat simulant [25]. This provides a tie back to the 2008 ESTD FBSR tests at HRI by TTT which used the same simulant [28] and the 2004 pilot-scale FBSR tests at SAIC-STAR [43] (see Figure 2-1).

Since the monolith work performed at SRNL between 2008-2009 [30,31] was generated using the granular FBSR product produced from the Rassat simulant tested at HRI/TTT [28], and the monolith work performed from 2005-2006 [30,31,84] was generated using the granular FBSR product produced from the Rassat simulant tested at SAIC-STAR test program, [43,47] this work can also be compared using the "tie-back" strategy. Thus, the early data from the SRS LAW test using actual radionuclides will provide an important correlation to previous tests using surrogates at the bench and engineering scales. Ties will also be made between granular and monolith mineralized products from testing.

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 sensitive than tests with radioactive wastes. Specifically the following correlations can be derived between the Rassat simulant and a radioactive SRS LAW shimmed to be like the Rassat simulant:

- Correlate radioactive bench scale reformer to 15" HRI/TTT engineering scale reformer tests
- Correlate radioactive bench scale reformer to non-radioactive bench scale reformer tests
- Correlate non-radioactive bench scale reformer to 15" HRI/TTT engineering scale reformer tests
- Correlate the non-radioactive 15" HRI/TTT engineering scale reformer to the 6" SAIC-STAR facility engineering scale reformer tests at INL

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 1-6) in order to facilitate all the testing needed for the tie-back strategy.

Table 1-6. 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	26	SRS WTP-SW	Shim of SRS DWPF melter recycle to resemble Hanford WTP- Secondary Waste	96	188
B	This Study	SRS-LAW	Shim of SRS LAW (Tank 50) to resemble Hanford LAW based upon Hanford 68 tank blend	640*	645
C	27	Hanford LAW Sample #1 (medium S, Cl, F, and P)	Hanford Tank SX105	317[f]	189
D		Hanford LAW Sample #2 (low S, Cl, F, and P)	Hanford Tank AN103	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.

2.0 Quality Assurance

The overarching Task Plan for the FBSR studies supported by SRNL, PNNL, and ORNL is the DOE EM-31 Technology Development & Deployment (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 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 Module B the TT&QAP "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 68 Tank Blend Study" [85] was followed. It is attached as Appendix A.

The SRNL results are summarized in the current document. The original BSR non-radioactive run data can be found in notebook SRNL-NB-2009-00115 and the radioactive run data in SRNL-NB-2010-00160. The data produced from these runs can be found in notebooks SRNL-NB-2010-00143, SRNL-NB-2010-00172, SRNL-NB-2010-00178, and SRNL-NB-2010-00081.

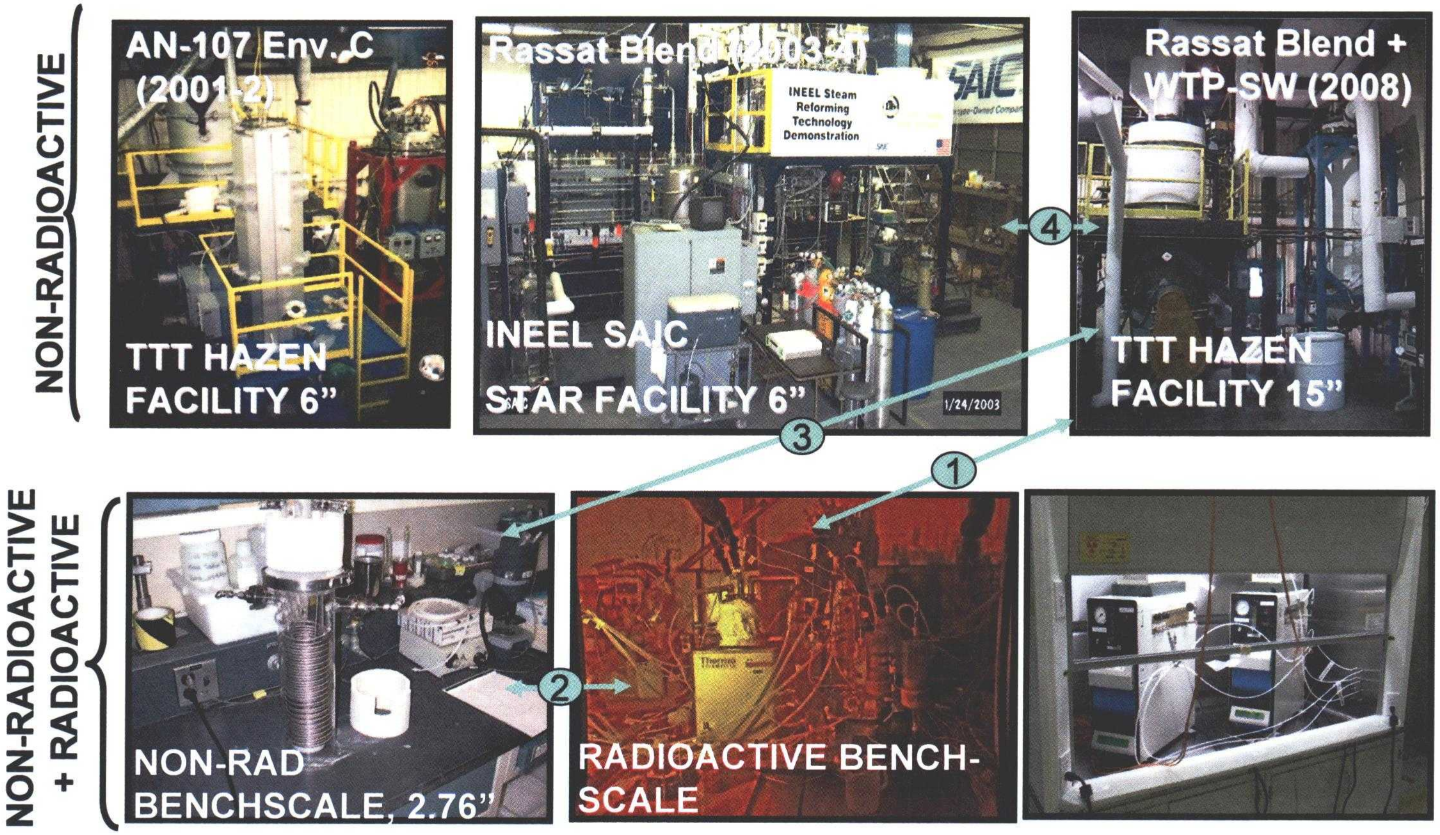

Figure 2-1. Tie-back strategy between engineering scale non-radioactive pilot testing (top row) and BSR non-radioactive and radioactive testing (bottom row).

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.

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 51. These activities were designed to:

1. Characterize the Module B FBSR products from the HRI/ESTD/TTT P-1B runs blended bed and fines products made from the Hanford Rassat (68 tank blend) simulant. Documented in detail in Reference 32 and summarized in this study.

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.

3. Receive three Hanford LAW samples (Modules C, D, and E): one with low anion content, one with high anion content, and 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.

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.

8. Perform XRD analysis on monolithic waste forms.

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.

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.

11. Synthesize phase pure minerals (nepheline and sodalites) [73] 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 51 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.[86]

13. Thermodynamic parameters of the phase pure minerals were measured at University of California, Davis.[86]

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 [51,86]

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. A modified waste form release/radionuclide source term model must be developed and validated for inclusion in the IDF performance assessment code. This source-term model will start with that developed by McGrail et al. [35,36], 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 anion 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 the same Rassat simulant tested in the ESTD TTT engineering scale FBSR at HRI. 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 with 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) [87,88] with TTT. These demonstrations also provided needed tie backs to previous durability testing of the Rassat simulant FBSR granular and monolithic products as described in Section 1.4.2.

The scope of work addressed in this document also consists of SRNL mineralizing a radioactive SRS salt supernate sample from Tank 50 that was available in SRNL and had already been chemically analyzed for another program. The Tank 50 salt supernate was shimmed to look like the Rassat simulant and processed in the radioactive BSR in the SCF to provide (1) radioactive granular samples for testing the durability response of BSR product compared to the TTT pilot scale product and the non-radioactive granular product produced in the previous monolith testing discussed above, and (2) radioactive granular products to monolith and compare (durability and compressive strength) to the non-radioactive monolithic waste forms described in the WFO scope above.

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.

The work flow discussed in the TDD Task Plan [80] and the SRNL TT&QAP [85] is given in the following order:

1. Prepare Individual Phases of FBSR Products
2. Prepare Non-Radioactive Simulant
3. Prepare Radioactive Waste
4. Prepare Feed for BSR
5. Process SRS Modified LAW
6. Prepare Monolith Process
7. Prepare Granular and Monolithic Waste Forms for Analyses
8. Perform Sample Characterization Methods
9. Perform Regulatory Testing
    a. Perform Compressive Strength Testing— (ASTM C 39/C 39M–01) [89,90]
    b. ASTM C1308/ANSI/ANS 16.1 [91,70]
    c. TCLP [92]
10. Perform Waste Form Performance Testing

a. PCT (ASTM C 1285-02) [93]
   - Short Term Testing (7 day)
   - Long Term Testing (up to 1 year)
b. SPFT (ASTM C 1662) [94]
c. PUF Experiments [95]

The 10.b and 10.c tests are being performed at PNNL and ORNL, so discussions of these tests are not included in this document. The remainder of the experimental section in this document follows the outline of work flow given above.

4.1 Preparation of Individual Phases of FBSR Products

In a multiphase ceramic the durability response is complex as Na release comes from multiple phases, while release of Re, I, F, SO_4 may only come from one of several isostructural sodalite phases. In order to understand the durability response of the individual mineral phases in the FBSR product, e.g. nepheline ($NaAlSiO_4$), sodalites [nominally $Na_6Al_6Si_6O_{24}(2NaCl)$, $Na_6Al_6Si_6O_{24}(2NaI)$, $Na_6Al_6Si_6O_{24}(2NaF)$, $Na_6Al_6Si_6O_{24}(NaRe^{7+}O_4)$, $Na_6Al_6Si_6O_{24}(NaTc^{7+}O_4)$, and nosean $Na_6Al_6Si_6O_{24}(Na_2S^{4+}O_4)$, phase pure standards were made at SRNL for SPFT testing at ORNL and for the determination of thermodynamic parameters at the University of California at Davis. The SPFT testing generates single phase forward rates that are used during Performance Assessments (PA). The thermodynamic parameters are also used during PA analyses. The fabrication of these phase pure materials is documented elsewhere [73] but was part of the TT&QAP for Module B.

4.2 Prepare Non-Radioactive Simulant and Radioactive

For the testing, both a non-radioactive simulant and an actual radioactive waste sample were used. Section 4.2.1 discusses the simulant make-up and characterization, while Section 4.2.2 discusses the radioactive sample used in testing.

4.2.1 *Rassat Simulant*

A non-radioactive simulant was tested in the SRNL non-radioactive BSR in order to provide (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the BSR product in comparison with the TTT engineering scale and the INL pilot scale products, and (3) granular product to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from the ESTD TTT program.

Table 4-1 provides the Rassat recipe both as prepared at the INL pilot scale FBSR [43] without elevated RCRA metal ions and as prepared at HRI/TTT at the engineering scale FBSR [28] with elevated RCRA metal ions. The Rassat simulant for this testing was made using the formulation given in Table 4-1. The target concentration for the LAW was increased by a factor of 10 for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs as done in the TTT engineering scale demonstrations of the Rassat simulant[28] in order to observe their behavior during mass balance of the process. The HRI/TTT levels were chosen to achieve reliable detection in the off-gas sampling without regard to potential results of those determinations or impacts on product durability response such as TCLP. Ferric nitrate nona-hydrate was added to have ≥1.5 wt% Fe in the final BSR product as a REDuction/Oxidation (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} from an Electro-Motive Force (EMF) series developed for FBSR products by Schreiber. [96]

The simulant for Module B had been specified to be exactly the same as that processed in the ESTD with the increased RCRA metals discussed above. When it was made in the laboratory, some of the RCRA metals precipitated and were filtered. They were filtered in case the precipitates were soluble precipitates that could give erroneous TCLP responses when the FBSR product was tested. Since the HRI/TTT simulants had not been filtered, comparison of the BSR FBSR product to the ESTD FBSR product this would also give a comparison as to how well any precipitates in the simulant were incorporated into the FBSR mineral phases.

The Rassat simulant was made with Re as a surrogate for Tc-99 and non-radioactive isotopes of I and Cs. Two batches of the filtrate were needed to make the required mass of FBSR product for all the "tie back" testing. The measured simulant composition given in Table 4-1 was obtained following addition of Re, but prior to addition of clay, coal, or Fe used to measure REDOX in the final BSR product. The simulant compositions in Table 4-1 labeled as B1 and B2 were measured following removal of any precipitated solids from the simulant. The granular product produced in the Module B simulant runs was roughly an equal mixture of these two simulants. Analyses 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.

4.2.2 *Radioactive Sample Shimmed to Match Rassat Composition*

Radioactive Module B was made starting with a composite of SRS Tank 50 radioactive LAW. Samples labeled A, B, D, F, and R were each filtered and the filtrates composited. The total composite was 2.4 L in a 4-L wide mouth poly bottle. The 2.4 L of Tank 50 material was trimmed with Rassat reagents to levels given in Table 4-1. The batch was heated to between 50°C and 70°C and agitated overnight so that reagents would have time to dissolve. As expected the batch contained significant solids since the solubility of the RCRA species were exceeded in the Tank 50 sample. The precipitates were sampled and identified by XRD (see Figure 4-1) as enriched in sodium antimony (+5) hydroxide, lead phosphate, lead carbonate, and barium nitrate. Since the precipitates were primarily RCRA species which had exceeded their solubility, they were filtered out causing the analyzed compositions shown in Table 4-1 to be lower than the RCRA species added initially.

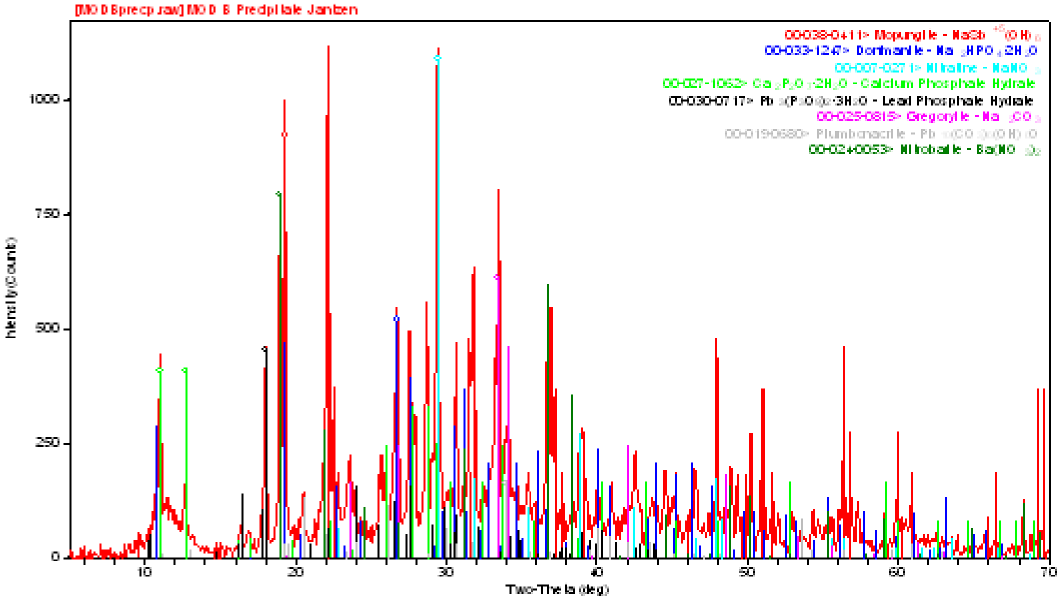

Figure 4-1. XRD of the Filtered Precipitates Showing that Antimony, Lead, and Barium had Exceeded their Solubility in the Rassat Simulant when Concentrations as high as the ESTD Concentrations were Doped into the Simulant.

The Tank 50 sample was then shimmed with I-125, I-129, Tc-99, and Re. The Re and Tc-99 spikes were to determine the suitability of Re as a surrogate for Tc-99 in these minerals as the oxyanion.[§] The Tank 50 sample had sufficient Cs-137 that it did not require additional shimming. I -125 and I-129 were added to the radioactive feed in order to detect these elements radiometrically during leach testing.

Filtrate analyses included elemental composition as determined by ICP-AES and ICP-MS measurements on supernate samples; separation and counting techniques for Cs-137, Tc-99, I-125 (where applicable), and I-129; IC anion measurements on filtered, weighted dilutions of supernate; total base, free OH^-, and other base excluding CO_3^{2-} titration of unfiltered, weighted dilutions of supernate; TIC measurement for carbonate.

The data in Table 4-1 indicated that there is good agreement between the composition of the shimmed Tank 50 salt supernates and the target Rassat simulants except that the Tank 50 composition was 4X higher in aluminum than the Rassat simulant waste. In terms of the FBSR minerals formed this was compensated for by the mineral stoichiometry (variable x and y in the minerals listed in, Table 1-1) and the choice of clay which can be chosen to have variable Si:Al ratios.

[§] similar oxyanion size in the VII oxidation state, i.e. 1.702 (TcO_4^-) and 1.719 (ReO_4^-)

4.3 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 non-volatile 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 in Equation 1 forming from NaOH in the LAW.

Table 4-1. Compositions for Module B Target, Simulants, and SRS LAW Shimmed to Match the Rassat Simulant

Species	SRNL Analysis Radioactive B	SRNL Analysis Simulant B2	SRNL Analysis Simulant B1	Rassat Recipe HRI/ TTT	Rassat Recipe INL	Rassat Recipe [25]
	Molar	**Molar**	**Molar**	**Molar**	**Molar**	**Molar**
Ag	<1.74E-05	<1.97E-04	5.56E-04	1.61E-03		
Al	2.57E-01	6.28E-02	7.64E-02	6.37E-02		
As	6.94E-04	<1.11E-06	1.25E-03	1.37E-03		
B	5.80E-03					
Ba	1.08E-05	<2.23-04	1.15E-03	7.51E-03		
Cd	4.72E-06	<9.98E-04	<9.98E-04	4.20E-03		
Cr	8.90E-03	5.87E-03	1.01E-02	1.04E-02		
Cs-133	4.67E-06	1.41E-02	1.41E-02	1.30E-02	5.10E-07	5.10E-07
Fe	<1.02E-05					
Hg	6.26E-05					
K	1.40E-02	1.59E-02	4.08E-02	1.24E-02		
Li	<2.49E-04					
Mg	<1.03E-05					
Mn	<2.00E-05					
Na	5.36E+00	5.05E+00	5.05E+00	5.02E+00		
Ni	<3.27E-05	<6.60E-03	<6.60E-03	1.06E-02		
P	5.10E-02			4.92E-02		
Pb	5.60E-03	1.90E-03	5.00E-03	6.06E-03		
Re	1.60E-03	1.83E-03	1.83E-03	1.70E-03	3.95E-04	
Sb	2.00E-04	1.53E-04	3.58E-03	4.34E-03		
Se	1.04E-06	9.54E-04	7.91E-04	1.23E-03		
Si	5.00E-04					
Sr	<9.13E-07					
Ti	<1.55E-05	NA*	NA*			
Tl	NA	3.02E-04	6.37E-03	2.02E-03		
U	<3.15E-04					
Zn	1.00E-04					
Cs-137	3.44E-08					
Tc-99	6.69E-06					
I-125	2.99E-12					
I-129	2.04E-04					
$CH_3CO_2^-$	NA	NA	NA	1.32E-01		
CO_3^{2-}	3.40E-01	NA	NA	4.75E-01		
Cl^-	5.82E-02	4.40E-02	4.25E-02	4.38E-02		
F^-	1.95E-02	<5.26E-03	<5.26E-03	3.16E-02		
HCO_2^-	5.60E-03	NA*	NA*			
OH^-	8.53E-01	NA	NA	7.40E-01		
I^--127	7.84E-03	7.13E-03	NA	1.30E-02	1.34E-04	
NO_3^-	3.80E+00	2.69E+00	3.00E+00	2.51E+00		
NO_2^-	3.12E-02	4.23E-01	5.34E-01	4.24E-01		
$C_2O_4^{2-}$	1.01E-02	1.06E-02	8.50E-03	1.18E-02		
SO_4^{2-}	1.13E-01	8.93E-02	9.08E-02	9.00E-02		
	Wt%	**Wt%**	**Wt%**	**Wt%**	**Wt%**	**Wt%**
Insoluble Solids	removed	removed	removed	not removed	not removed	Not Applicable
	g/mL	**g/mL**	**g/mL**	**g/mL**	**g/mL**	**g/mL**
Density	1.32	1.25	1.26	N/A	N/A	1.24

NA not analyzed but was in simulant; NA* not part of simulant

Equation 1

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

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

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

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

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

These reactions 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 4-2). Once the hydroxides are lost, the clay becomes amorphous (loses its crystalline structure) and very reactive at the FBSR temperatures. This amorphous clay is called meta-kaolin. Stable crystalline clays (kaolin) are known [97] 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 4-2). 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.[8] 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.[39] In section 4.8.3 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 4-3). MINCALC™ was used during the 2004 INL pilot scale tests [43], the 2008 TTT/HRI ESTD campaigns [28], and the BSR campaigns in 2004 [98] and this study.

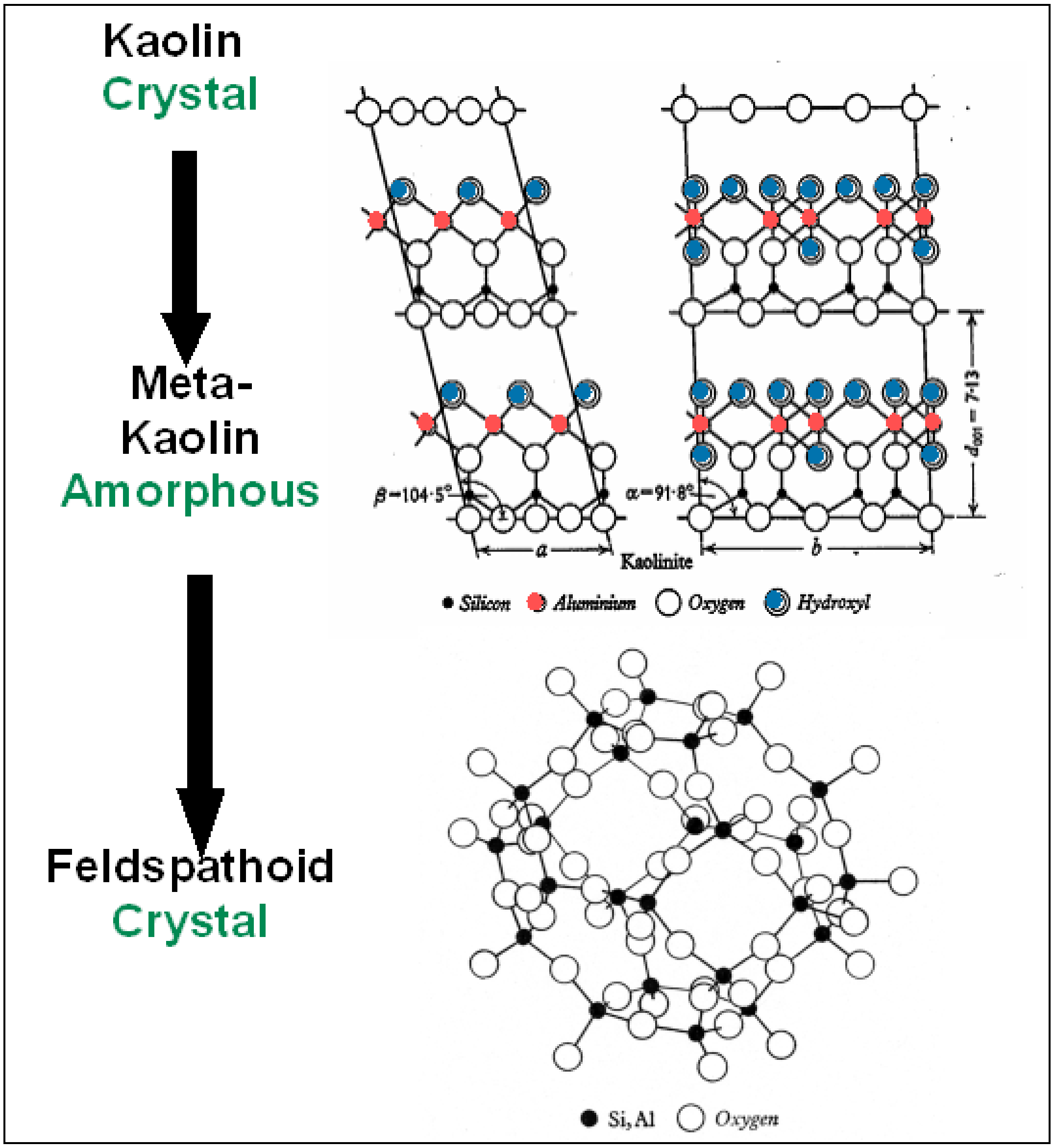

Figure 4-2. Kaolin transformation to meta-kaolin to Feldspathoid (Sodalite) Crystal by loss of hydroxyls and alkali activation as a function of increasing temperature (after reference 97).

MINCALC™ controls the simulant (✭) or radioactive (⬢) B LAW FBSR product in the region of nepheline/sodalite formation (region in Figure 4-3 where the blue rectangle for AN-107 lies). MINCALC™ can also be used to calculate the theoretical weight percent of each of the mineral phases. All campaigns are run with excess clay and hence excess Al_2O_3 and SiO_2 appear in the species predictions (Table 4-2) and in the products. The sum of all predicted phases has not been normalized to 100%, so sums shown at the bottom of Table 4-2 do not add completely to 100% but show how accurate MINCALC™ is in accounting for the major mineral species which, for Module B, are primarily nepheline and nosean which are shaded in Table 4-2.

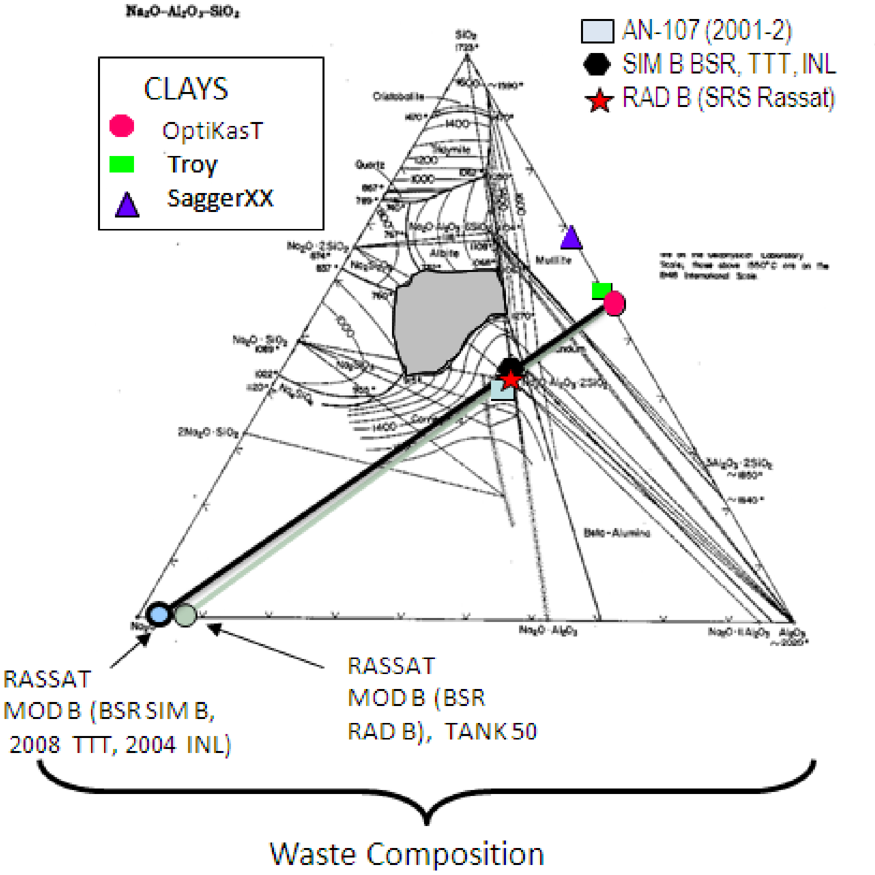

Figure 4-3. Na_2O-Al_2O_3-SiO_2 (NAS) ternary phase diagram

Note: The composition of the Rassat simulant (Module B) waste composition is shown along the base of the triangle (Na_2O-Al_2O_3 binary) for the non-radioactive BSR tests discussed in this study, the 2004 INL FBSR tests with the same simulant and the 2008 TTT/HRI FBSR tests with the same simulant. The radioactive BSR tests with Tank 50 had 0.25 M Al instead of 0.06 M Al and the position of the radioactive material is shifted slightly from the non-radioactive species 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 28.

Table 4-2. Mineral Speciation for Non-Radioactive and Radioactive Module B LAW (Rassat Simulant) Predicted from MINCALC™-Version 3

Mineral Component	Chemical Component	Non-radioactive				Radio-active
		[b]Rassat simulant Wt%	[b]Rassat Simulant from INL Testing (wt%)	[a,b]Rassat Simulant from HRI/TTT Testing (wt%)	[a,b]LAW Rassat simulant (MOD B SIM) Wt%	[a,b]LAW Rassat Tank 50 (MOD B RAD) Wt%
Na Nepheline	$Na_2Al_2Si_2O_8$	67.58	67.58	63.75	63.75	65.01
K Nepheline	$K_{0.5}Na_{1.5}Al_2Si_2O_8$ or $K_2Na_6Al_8Si_8O_{32}$	2.43	2.43	2.38	2.38	2.5
Cl Sodalite	$Na_8Al_6Si_6O_{24}(Cl_2)$	2.83	2.83	2.69	2.69	3.56
F Sodalite	$Na_8Al_6Si_6O_{24}(F_2)$	1.97	1.97	1.87	1.87	1.15
I Sodalite	$Na_8Al_6Si_6O_{24}(I_2)$	1.31	1.31	1.25	1.25	1.65
Nosean	$Na_8Al_6Si_6O_{24}(SO_4)$	11.93	11.93	11.33	11.33	14.20
Re Sodalite	$Na_8Al_6Si_6O_{24}(ReO_4)_2$	0.04	0.04	0.15	0.15	0.14
Tc Sodalite	$Na_8Al_6Si_6O_{24}(TcO_4)_2$	---	---	---	---	0.0005
Free Silica	SiO_2	5.32	5.32	7.30	7.30	4.38
Free Alumina	Al_2O_3	3.49	3.49	5.15	5.15	3.94
	SUM	96.89	96.89	95.85	95.85	96.52

[a]RCRA metals (Sb, As, Ag, Cd, Ba, and Tl) and radionuclide surrogates (Re, I, Cs) were doped in at elevated concentrations

[b]LAW simulant used to produce the FBSR samples were based on Rassat et al. [25]

Because the Module B feed was primarily Na_2O species, OptiKasT® clay was the only clay that had to be added (Table 4-3) to drive the clay-waste mixture into the nepheline forming region of the NAS ternary shown in Figure 4-3. Note that MINCALC™ predicts that the high Na_2O concentration will make ~ 66-67% nepheline (combined sodium nepheline and sodium/potassium nepheline) and high concentrations of the sulfate host nosean. These primary phases are highlighted in Table 4-2.

In all 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. The same Bestac® coal as was used by the ESTD FBSR was added to the BSR feeds 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 much larger and was added as a separate stream in the FBSR. This was necessary due to the small orifice on the BSR feed pump.

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. 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. Two Simulant B runs had 3 wt% Fe to check the effect of extra ferric nitrate; both runs were found to make good product but were not included in subsequent analyses and monolith formation.

Table 4-3. Feed Slurry Composition from MINCALC™

Module	Target Clay g/L of Initial Solution	Target Coal g/L of Initial Solution	$Fe(NO_3)_3 \cdot 9H_2O$
Sim B	640 OptiKasT®	139.0 for 1x	64.5
Rad B	652 OptiKasT®	139.0 for 1x 180.7 for 1.3x[*]	57.14

4.4 Bench Scale Reactor Description: Processing Module B LAW

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. 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 as the ESTD mineralogy
- the REDOX measured after each campaign had 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) had to be in the range of 0-2 percent to match that of the ESTD DMR bed product.

4.4.1 *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 reactions but only impacts particle nucleation and growth.

Steam, the fluidizing media, does flow freely though 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 4-4). Only the first reformer, the DMR, was used for this study. A schematic of the single

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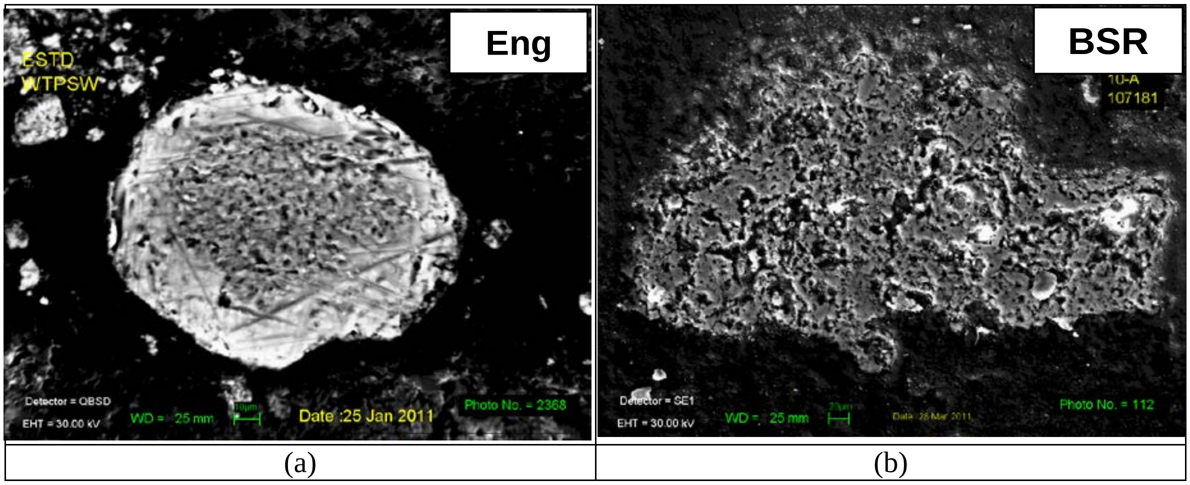
[*] After five runs of radioactive MOD B at 1x coal, where the 1X is the amount calculated to force all the nitrates and nitrites to N_2, it was found that REDOX could not be increased from near zero. The coal content was raised from 1.0x to 1.3x the stoichiometric MINCALC™ value in order to adjust the "Gas REDOX" discussed in Section 4.4.2. Radioactive Module B provided good product consistently at the 1.3x coal level. It is noted that the calculation for the coal addition considers reduction of the nitrate added as the ferric salt, since this has significant oxidizing capacity that must also be reduced. The slurry was diluted as needed in further runs when viscosity was found to be too high for feeding.

[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.

reformer unit as used is shown in Figure 4-5, while the details of the DMR are shown in Figure 4-6.



(a) (b)

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

Note the similarity of the reaction textures and how completely reacted each granule is.

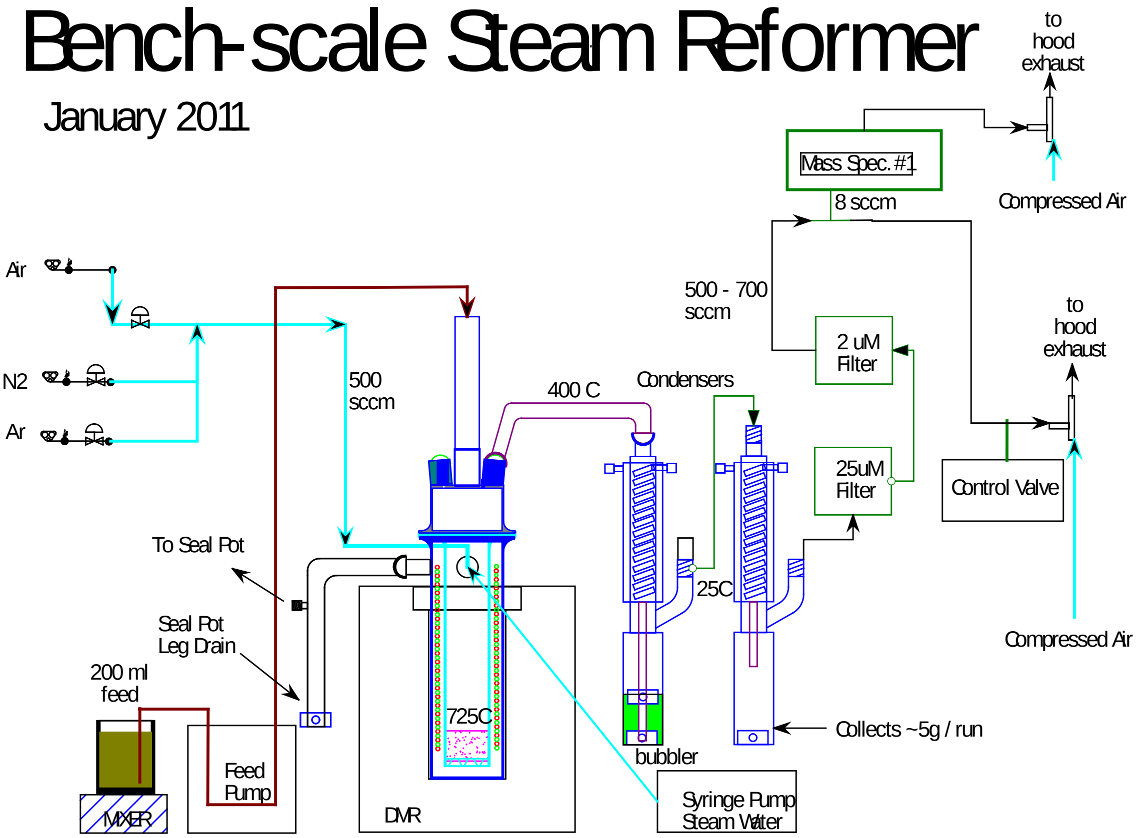


Figure 4-5. Schematic of the Bench-Scale Steam Reformer (BSR)

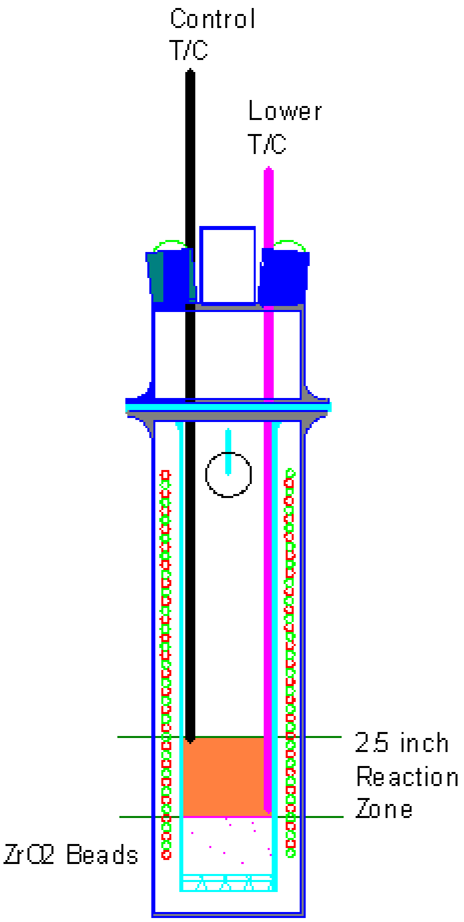


Figure 4-6. The BSR Denitration Mineralization Reformer (DMR)

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 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 um 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 to improve operational control.

4.4.2 *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. For non-rad runs, the DMR reaction zone held from 25.5 to 46.7 grams of solid product that was converted from 80 to 141 grams of Rassat waste with clay and coal added. For radioactive runs, the DMR reaction zone held from 16.6 to 42.8 grams of solid product that was converted from 47 to 136 grams of Rassat waste with clay and coal added. The control temperature ranged from 700°C to 750°C in the DMR for all of these runs.

The DMR off-gas treatment system consisted of the crossover bar (see Figure 4-7) 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.

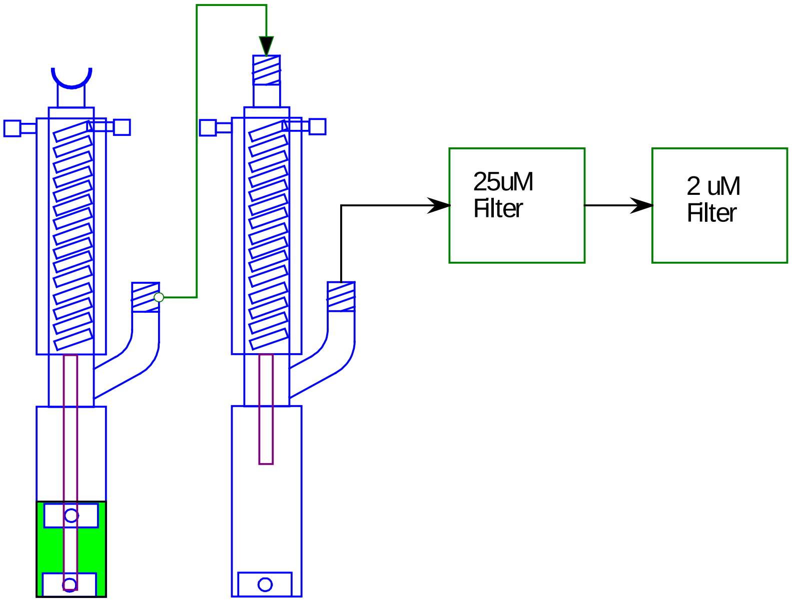


Figure 4-7. BSR DMR Off-Gas Treatment

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^{o}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 BSR used a Monitor Instruments LAB 3000 Cycloidal MS for the reformer real time off-gas analysis, see Figure 4-8 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 with Monitor Instruments proprietary software loaded. Data from the MS computer was transferred to the control computer in real time via a serial connection.

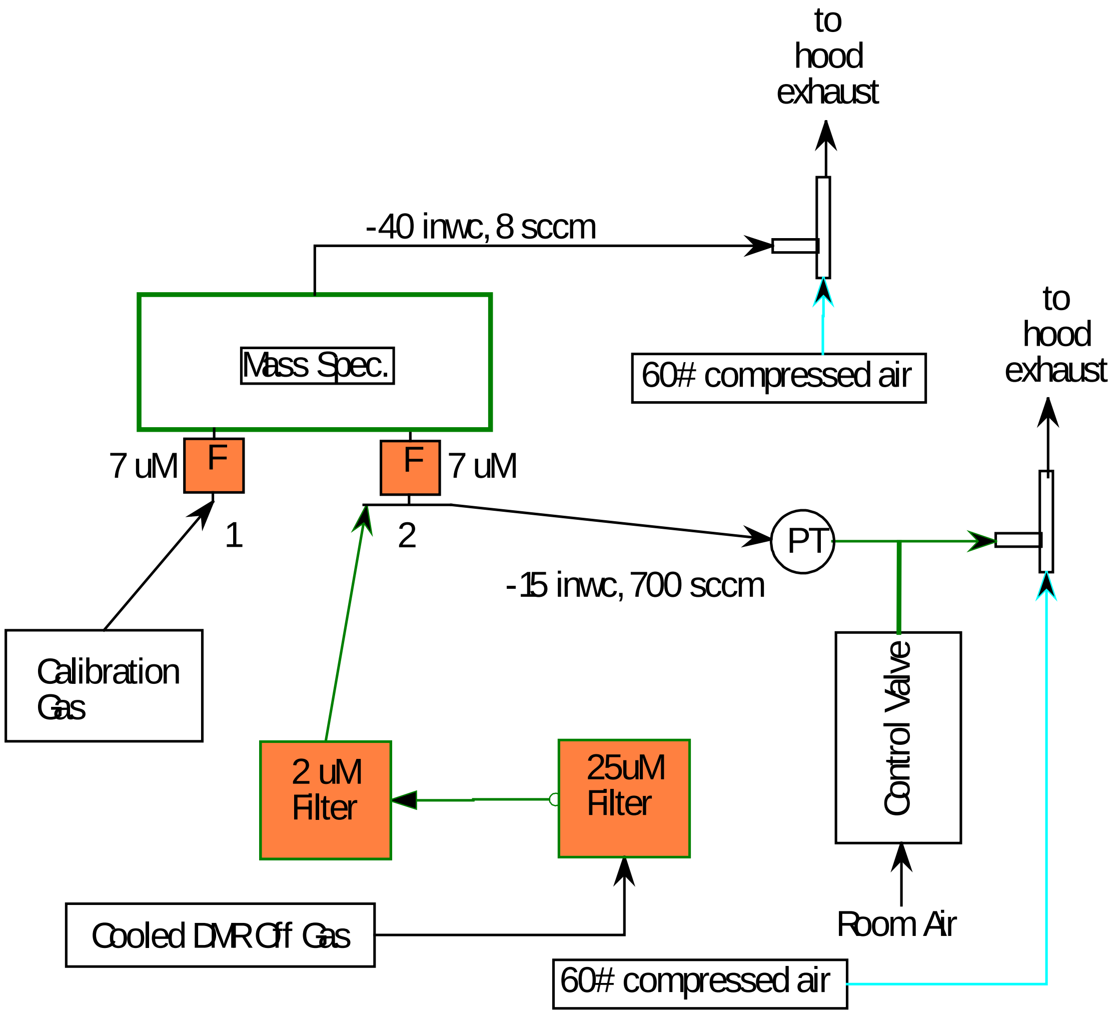


Figure 4-8. The BSR Mass Spectrometer

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.

From 10/19/10 forward, 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.

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 personal computer (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 4-9.

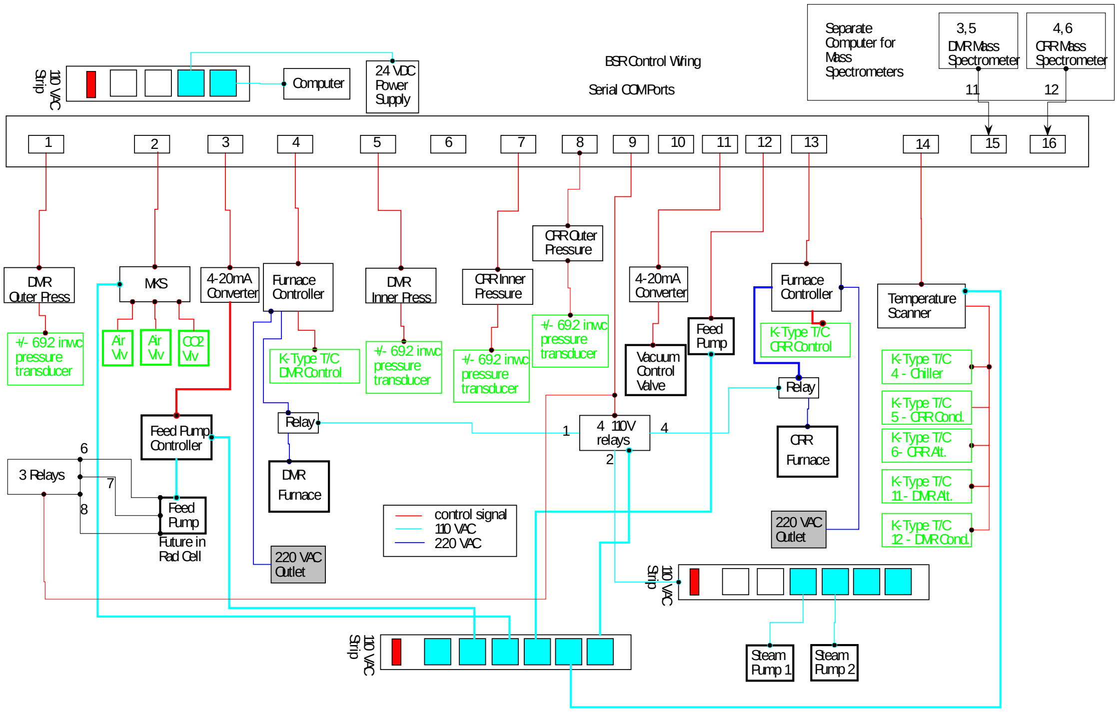


Figure 4-9. BSR Process Controller Diagram

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.

Process parameters controlled were:

- Slurry Feed Rate,
- DMR Control Temperature,
- DMR outer pressure, and
- the DMR Air flow-rate coupled to the N_2 and Ar flowrates.

4.5 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 4.6. The BSR granular bed product also needed to be analyzed to normalize leach test results for the performance testing (see Section 4.8).

The BSR product samples were digested by both closed Teflon® vessel aqua regia (AR) and short duration alkali [Na_2O_2/NaOH] 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. 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.[39,40] Comparative studies have been performed at PNNL of roasted and unroasted samples and the same compositions were also achieved.[99] 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.[39,40]

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 [100] 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.[101] 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. For Module B the coal as measured by the LOI was <2 wt%.

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 51). 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 the REDOX is not overly oxidizing forcing the chromium to soluble +6 state. To prevent the chromium oxidation, often the Iron Oxide Catalyst (IOC) is added.[33,39,40] 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 was between 0.2-0.6 $Fe^{+2}/\Sigma Fe$ to match the measured REDOX of the ESTD FBSR product receipt (see Table 4-4). 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. During processing, it was determined that an $Fe^{+2}/\Sigma Fe$ exceeding 0.5 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 limit was lowered to 0.5 for radioactive Module C (SX-105) and simulant/radioactive Module D (AN-103) [27] to ensure a high percentage of the Re was present as Re^{+7} for the sodalite cage (Table 1-1).

Table 4-4. REDOX Targets for Hanford Rassat Simulant

	Module B (Rassat Simulant)	
	Measured REDOX	**Target REDOX**
BSR Simulant		0.4-0.6
BSR Radioactive		0.4-0.6
ESTD Product Receipt (PR)	0.41-0.58	
Iron Oxide Catalyst (IOC)	0.567	

4.6 <u>BSR Mass Balance</u>

The BSR is a simpler design than the ESTD facility in Golden, CO and so it is easier to perform a mass balance. For the Rassat 68 tank blend (Module B), there were five mass balance product vectors and one feed vector. The product vectors were composed of the product solids, the solids in a cross bar that provided a pathway to a condenser, the solids in the condenser, cross bar rinses to determine if any species adhered to the crossbar, and the condenser solution.

The mass balance calculational approach for the Rassat 68 tank blend (Module B) 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 for the Module C and D campaigns due to the limitations of the radioactive systems, i.e., accessibility to various streams given the physical constraints of the cells operations. For the simulant and radioactive runs in the Module B campaign the same number of streams were analyzed.

The key input and output streams for which mass balance calculations were performed are shown in Table 4-5 and Table 4-6, respectively.

Table 4-5. Key Input Streams for Simulant and Radioactive Module B

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

Table 4-6. Key Output Streams for Simulant and Radioactive Module B

Output Stream	Simulant Runs	Radioactive Runs
Granular Product	Yes	Yes
DMR Condensate Filtrate	Yes	Yes
DMR Condensate Solids	Yes	Yes
Crossbar Filtrate	Yes	Yes
Crossbar Solids	Yes	Yes
Seal Pot Filtrate	No	No
Seal Pot Solids	No	No

The key input and output streams for the simulant mass balances are shown pictorially in Figure 4-10 and Figure 4-11. Note that the mass balance input and output streams are in yellow boxes.

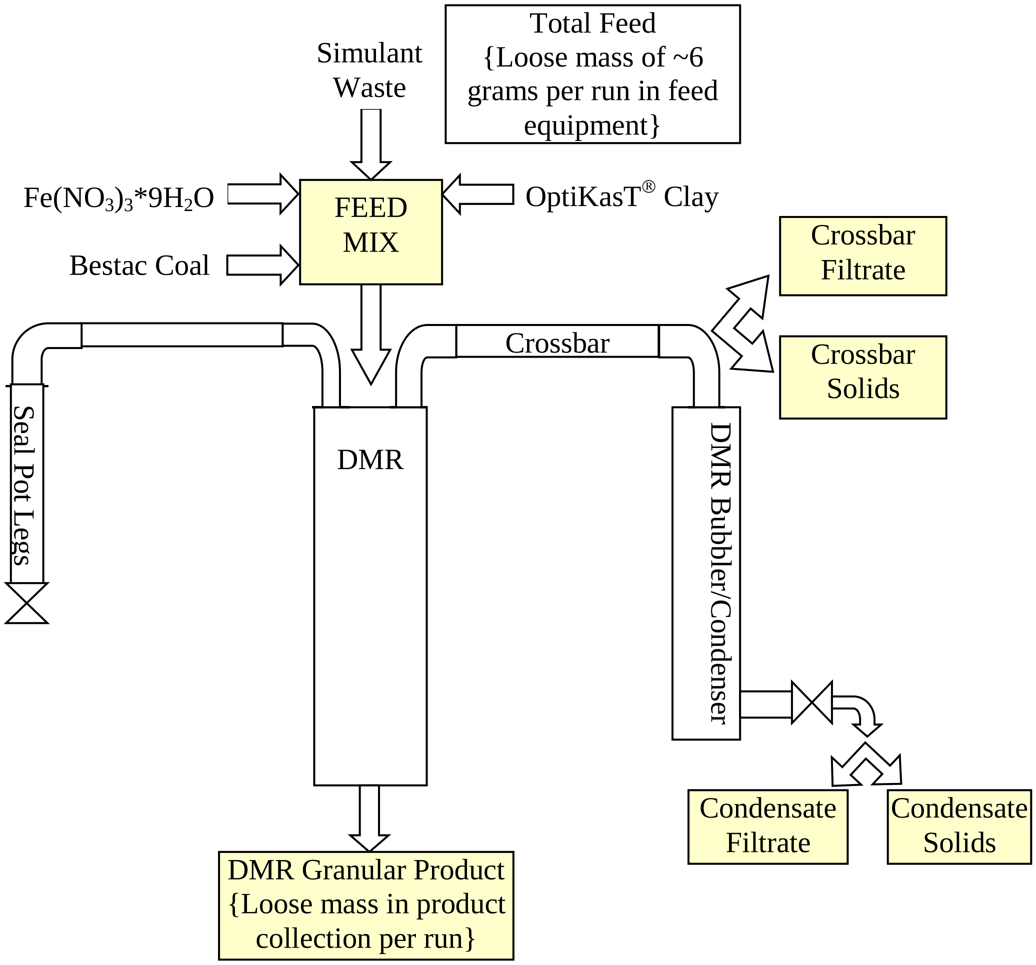


Figure 4-10. Mass Balance Input and Output Streams for Simulant Module B

The key input and output streams for the radioactive mass balances are shown pictorially in Figure 4-11. Due to the timing of the radioactive experiments and the limitations in the SCF, no seal pot samples were collected.

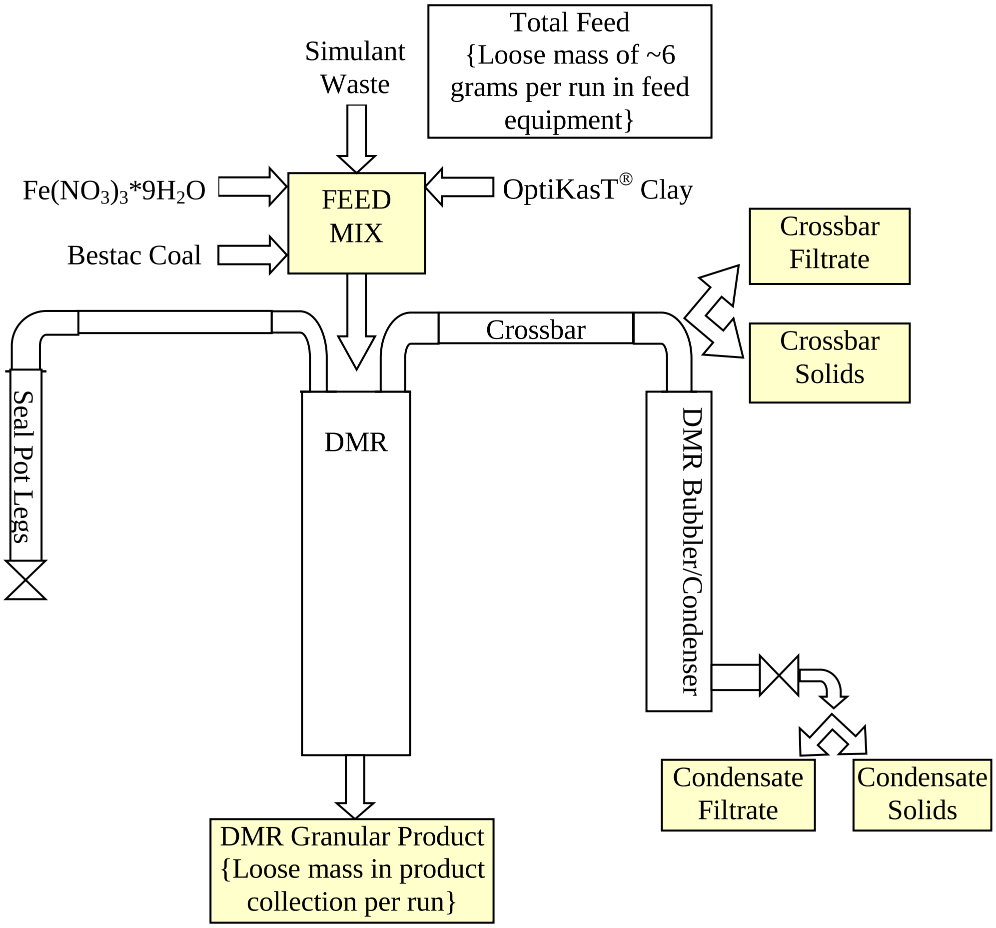


Figure 4-11. Input and Output Streams for Radioactive Module B

The key species examined in the simulant and radioactive campaigns for the mass balance are shown in Table 4-7.

Table 4-7. 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 can be described as shown in Equation 2 below:

Equation 2

$$\text{Waste}*w_i + \text{Fe}*f_i + \text{Coal}_{ash}*ca_i + \text{Coal}_{un}*cu_i + \text{O\_Clay}*o_i = \text{Product}*p_i + \text{CD\_fil}*cf_i + \text{CD\_sol}*cs_i + \text{XR\_fil}*xf_i + \text{XR\_sol}*xs_i$$

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 = mass of OptiKasT® Clay added to waste stream

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

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

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

Due to feed remaining in the feed containers and the feed lines, a special BSR run was performed [27]. This special run was performed to better quantify the masses of the input and output streams for the BSR system. For this special run, an Oxidizing Solution was used in the DMR Condenser/Bubbler instead of deionized water as used in the normal runs. A 5-wt% Spectrosol 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 run as shown in Table 4-8 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 Table 4-1. Note that the mass balance input and output streams are in yellow boxes.

Table 4-8. 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

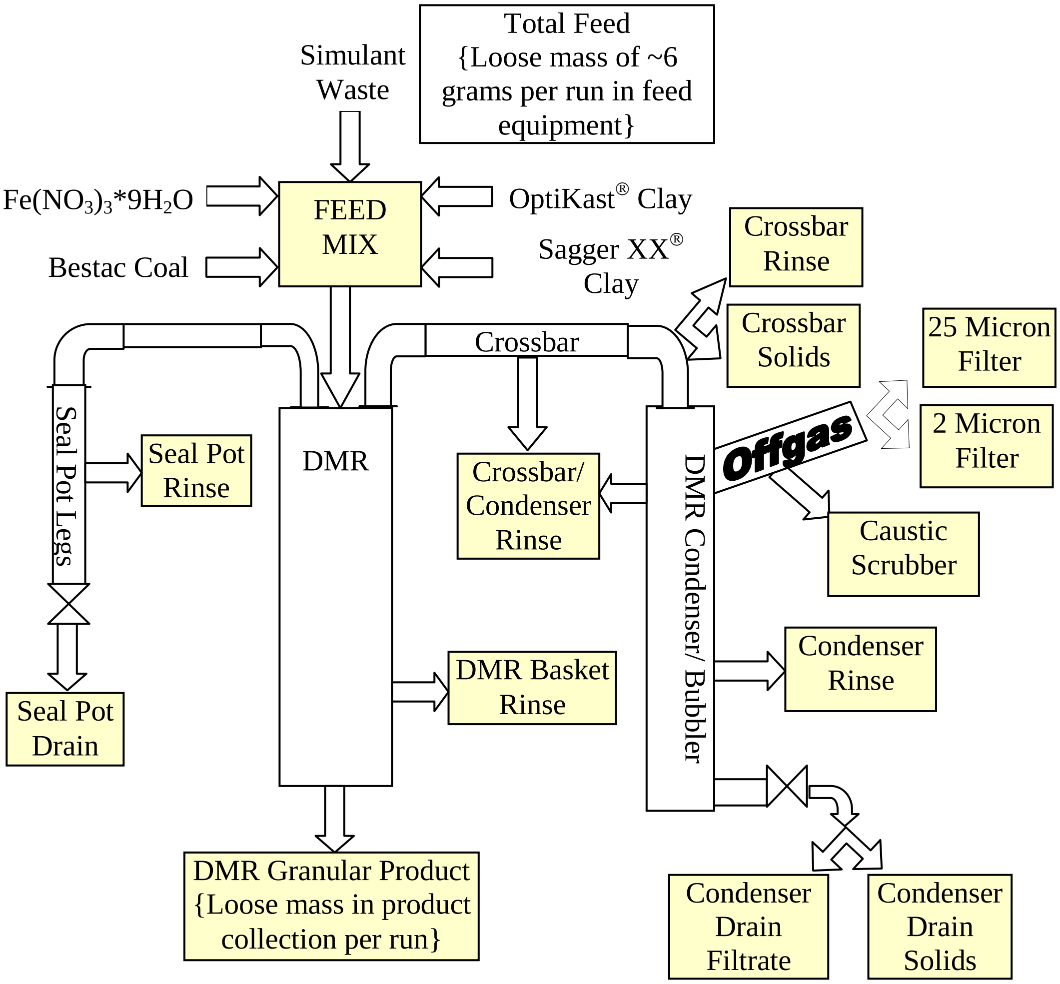


Figure 4-12. Mass Balance Input and Output Streams for Special BSR Run

For the special BSR run, the mass balance uses similar logic shown above and in Equation 2 but the terms are slightly different as shown below in
Equation 3**:**

Equation 3

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*cr_i + XR*xr_i + XR_sol*xs_i + SP*sp_i + SPR*sr_i + BR*br_i + XRCD*$xrcd_i$ + F25_sol*$f25_i$ + F2_sol*$f2_i$ + 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 offgas caustic scrubber drains
cas_i = concentration of species i in offgas caustic scrubber drains

During the special BSR run, masses of various components 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.

Based on the special BSR run, the Module B simulant testing consisted of 18 runs so the total measured feed (2064 g) had to be decreased by 108 grams to 1956 g. The radioactive campaign had 23 runs so the total measured feed of about 1981 g was decreased by 138 grams to 1843 g. It was also shown [27] 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 4-9. The average across all campaigns was 0.40 with a standard deviation of 0.03.

Table 4-9. Product to Feed Mass Ratios for BSR Runs

Run	Module				
	SIM B	**RAD B**	**SIM C**	**RAD C**	**RAD D**
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**	**0.40**	**0.40**
Standard Deviation	0.01	0.02	0.04	0.03	0.04

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

Equation 4

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

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 = mass of OptiKasT® Clay fed

S_Clay = mass of Sagger XX® Clay fed

$Coal_{ash}$ = 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 as follows:

Equation 5

$$c_{wt}\% = \text{LOI} - \text{LOD}$$

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 as follows:

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 as follows:

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 as follows:

Equation 8

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

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

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

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

Equation 10

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

Where:

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

$\mathrm{Out}_{i,j}$ = 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

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

Equation 11

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

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:

Equation 12

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

Where:

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

4.7 Monolith Preparation and Characterization

Monolithing of the granular FBSR product was investigated to prevent dispersion during transport or burial/storage (the 500 psi strength criteria). The granular product has a comparable durability to glass and could be disposed of in a HIC. Monolithing in an inorganic geopolymer binder, which is an amorphous aluminosilicate material, macro-encapsulates the granules (Figure 4-13). Geopolymers have an amorphous cross-linked three dimensional aluminosilicate structure: geopolymers remain amorphous because they contain insufficient water to crystallize zeolite phases like the hydroceramics

The aluminosilicate geopolymers were chosen as a binder after a downselect of various types of binders [32] and because they are inorganic. They can be made of fly ash or kaolin clay as a source of the aluminosilicate, sodium hydroxide, and sodium silicate and so are rich in Al_2O_3, SiO_2 and Na_2O, the same chemistry as the NAS FBSR product. The synergy in chemistry means that if the geopolymer binder leaches into a solution or the groundwater that it will saturate the immediate solution with Na, Al, and Si and slow down the leaching of the macro-encapsulated particles. This is known as the “common-ion effect.”

(a) (b)

Figure 4-13. (a) Granules of FBSR product from the TTT/HRI 2001 campaign on a mm ruler and (b) how these granules which sequester COC's indicated by the small symbols inside the grains are micro-encapsulated in the gray amorphous geopolymer binder which contain no COC's.

4.7.1 *Geopolymers*

Monolithing Hanford LAW FBSR products using various cements, hydroceramics, Ceramicrete, and geopolymers began in 2005 and continued into 2006.[30,31 ,84] These experiments used the granular FBSR product produced from the SAIC-STAR test program on FBSR product that had the coal roasted out.[43,47] The monolith test work began again in the 2008-2009 [32] timeframe and this program used the granular FBSR product produced from the engineering scale HRI/TTT campaigns that included the residual coal component.[28] A downselect amongst various cements, Ceramicrete, Nucap, and various geopolymers was performed and documented.[29,30,31,32] The details of these monolith activities are summarized in this section and in Table 4-10.

In 2006-2007, SRNL funded a Laboratory Directed Research & Development (LDRD) project directed at developing geopolymers as low temperature (green technology[f]) waste forms and this provided funding for the SRNL FBSR team to investigate geopolymers for various applications. During the LDRD project, two geopolymer matrices (tested in triplicate by ASTM C1285) performed better than other matrices tested such as OPC, Ceramicrete, and hydroceramic binders tested in References 30 and 31. The two geopolymer formulations studied during the LDRD project [84] were selected in the region of the Na_2O-Al_2O_3-SiO_2 ternary (Figure 4-14) designated as G1 (parameters from the literature). Geopolymers made in region G1 (atomic Si:Al = 1:1) are often used as applications for bricks, ceramics and fire products, while geopolymers made in region G2 (atomic Si:Al = 2:1) are often used as cements and concretes. Of the two formulations, formulation B from Figure 4-14 exhibited the overall superior performance. The region of formation of hydroceramics is given on Figure 4-14 for reference and it is clear that these formulations lie along a line that crosses the ternary diagram between the kaolin clay compositions and Na_2O which is added as NaOH and/or sodium silicate solution. In Figure 4-14, the G1 region is defined to be bounded by the following ratios Na_2O/SiO_2 = 0.20-0.48,

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[f] The raw material, kaolin, only requires roasting at ~700°C with no off-gas except steam compared to the high temperature kilning of cement raw materials and the formation of greenhouse gases.

Table 4-10. Target Geopolymer Compositions from the Literature and Compositions Achieved without FBSR Excess Alumino-silicate Participation in Geopolymerization

Waste Type	Identifier	Identifier	Na_2O/SiO_2	SiO_2/Al_2O_3	H_2O/Na_2O	Na_2O (mol%)	Al_2O_3 (mol%)	SiO_2 (mol%)	FBSR Loading (Wt%)
Targets	Target G1	Blackford, et.al.,[102], Curtin University,[103,104] Davidos,[105,106]	0.20-0.48	3.3-4.5	10-25	Range	Range	Range	Range
	Target G1	Kriven[107]	0.25-0.3	4	12				
	Target G2	Van Jaarsveld et.al.[109]	0.15-0.25	5.5-6.5	10-25				
STAR Rassat LAW & SBW	LDRD A (Troy)		0.25	3.99	13	16.64	16.71	66.65	33-44
	LDRD B (Troy)		0.25-0.278	3.3-3.55	13	16.09	19.52	64.39	33-44
HRI Rassat LAW	GEO-1 (Troy)	2” x 2”	0.396	5.299	17.168	25	12	63	67.44
	GEO-2 (Troy)	2” x 2”	0.43	6.205	18.083	27	10	63	72.09
	GEO-3 (Troy)	2” x 2”	0.469	7.604	13.973	29	8	63	67.51
	GEO-4 (Troy)	2” x 2”	0.537	12.786	13.965	33	5	62	71.72
	GEO-5 (Barden)	2” x 2”	0.418	8.081	13.342	27	8	65	62.72
	GEO-6 (Barden)	2” x 2”	0.391	6.768	17.221	25.5	9.5	65	66.61
	GEO-7 (Fly Ash)	2” x 2”	0.618	4.424	11.223	33.5	12.26	54	67.16
	GEO-1 (Troy)	3” x 6”	0.396	5.299	16.048	24.968	11.912	63	67.46
	GEO-7 (Fly Ash)	3” x 6”	0.618	4.425	11.603	33.5	12.26	54	67.17
	GEO-1 (Troy)	6” x 12”	0.396	5.304	18.476	24.975	11.902	63	67.44
	GEO-7 (Fly Ash)	6” x 12”	0.618	4.424	11.676	33.511	12.257	54	67.17
BSR Rassat LAW	BSR GEO-7 (Fly Ash)	1” x 2”	0.542	4.445	14.89	30.692	12.73	56.6	67.95
Hanford WTP-SW	GEO-1 (Troy)	3” x 6”	0.394	5.284	17.546	24.881	11.954	63	67.45
	GEO-7 (Fly Ash)	3” x 6”	0.62	4.447	11.751	33.616	12.187	54	67.05
	GEO-1 (Troy)	6” x 12”	0.396	5.304	16.639	24.977	11.902	63	67.44
	GEO-7 (Fly Ash)	6” x 12”	0.618	4.424	11.676	33.511	12.257	54	67.17
	GEO-7 (Fly Ash)	2” x 4”	0.618	4.424	11.862	33.512	12.257	54	67.16

SiO_2/Al_2O_3 = 3.3-4.5, and H_2O/Na_2O = 10-25 from references by Blackford, et al. (ANSTO), [102] Rowles and O'Connor (Curtin University),[103] Hardjito (Curtin University),[104] Davidos (Geopolymer Institute, France),[105, 106] and Kriven (University of Illinois).[107] The LDRD formulations were based on the work of Blackford, et al. but are most similar to those of Kriven. The LDRD monolith FBSR loadings were in the 33-44 wt% range and used a 16-16-66 and 16-19-64 formulation of $Na_2O:Al_2O_3:SiO_2$ mol%, which is in the composition region that Kriven [108] maintains is 1:1:4 and the most durable of all geopolymers. The G2 region in Figure 4-14 comes from the work of van Jaarsveld et. al (University of S. Africa)[109] with Na_2O/SiO_2 = 0.15-0.25, SiO_2/Al_2O_3 = 5.5-6.5, and H_2O/Na_2O = 10-25. This range was neither targeted in the LDRD nor subsequent studies and is shown for reference only.

Since unreacted clay cores had been observed in all of the FBSR products produced from 2001 to 2004, it was also assumed that ~10% unreacted clay existed in the FBSR product and ~ 20% fly ash from the coal that is used during FBSR processing. Geopolymer formulations for Mod B granular BSR products were targeted close to the LDRD A and B formulations assuming that 30% more free aluminosilicate was available in the FBSR product to participate in the geopolymerization. This also facilitated getting more FBSR product into the monoliths, e.g. higher FBSR loadings. The availability of the excess clay and fly ash was found to be an incorrect assumption in 2011 when SEM was performed on the 2008 ESTD LAW and BSR LAW (see Figure 4-4). The 2008 granular products do not have the unreacted clay cores that were found in the 2001 TTT/HRI samples and the 2003-2004 STAR samples. This is attributed to design and process improvements that were made by TTT/HRI since 2006 which have increased bed reactivity and the improved reactivity in the BSR due to its small size and the fact that it is both internally and externally heated (Table 1-2).

During the downselect, various types of geopolymer binders were tested [32], those that were fly ash based and several clay based geopolymers (Table 4-10). The best geopolymers during the downselect, for the Module B Rassat FBSR material appeared to be a fly ash based geopolymer. The formulations given in Table 4-10 were recalculated assuming no unreacted clay cores in the ESTD and BSR FBSR granules. The boxes shaded in Table 4-10 are the formulations that fall outside the desired G1 ranges defined at the top of the table. The downselect criteria were (1) compressive strength, (2) short term durability measured by the PCT (ASTM C1285), (3) TCLP response at the UTS since the Hanford wastes are RCRA listed wastes, and (4) FBSR loading in the monolith. The GEO-7 monolith performed the best with the ESTD P-1B material but when an identical formulation was tried with FBSR product made from WTP-SW FBSR product, which contained high concentrations of fluoride, the fly ash based geopolymer did not perform as well as expected.

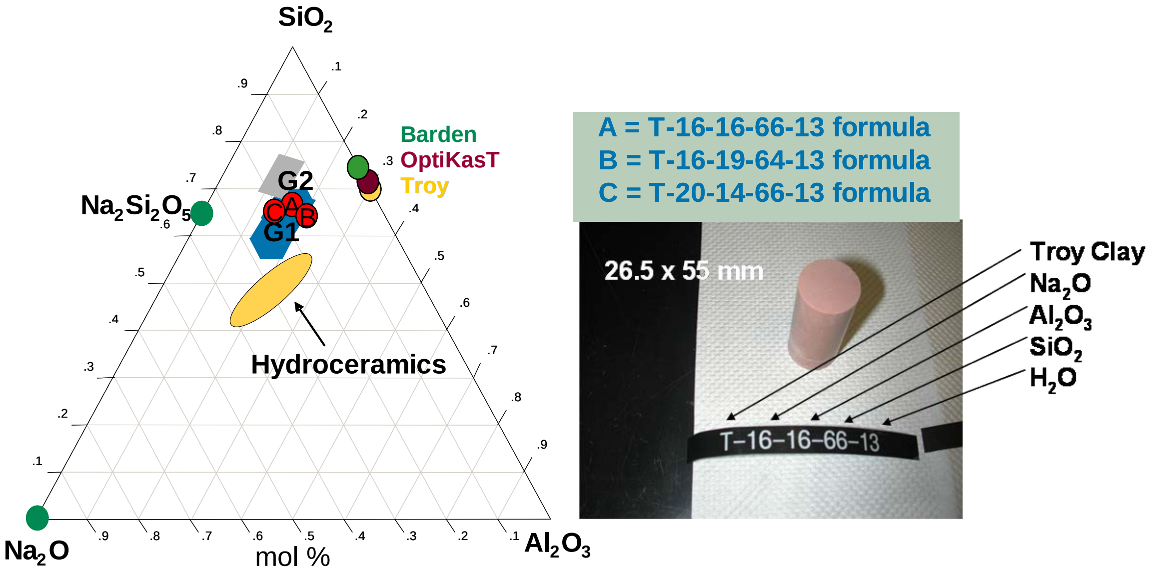

Figure 4-14. Formulation region for geopolymers compared to hydroceramics in the Na_2O-SiO_2-Al_2O_3 (mol%) ternary

Note that the fourth dimension is water content. G1 is the target range. Optimum formulations from LDRD testing are designated as A,B,C and a 1” x 2” cylindrical monolith made with composition A is shown in the photograph.

Therefore, in the Module B monolithing a two-fold approach was taken to compare fly ash based geopolymers to geopolymers made with reactive clay. Formulations made with fly ash were made with minimal NaOH and in the G1 region. Other formulations were made with the reactive clays determined from the LDRD program also in the G1 region. The fly ash based geopolymers were made first since the FBSR product contains some fly ash residue from coal degradation.

However, there are three primary reasons for preferring kaolin over fly ash:

(1) the unreactive nature of some of the components found in fly ash, e.g. the minerals mullite and quartz,
(2) the variable nature of fly ash compositions from various coal production facilities, and
(3) fluoride, if present as it was in the WTP-SW FBSR products [26], should not attack clay based binders as readily as those made from fly ash.

Formulations with clays are preferred since clays are less variable in composition than fly ash and the clays can be chosen, as done in the LDRD study [84], to have minimal unreactive components such as quartz and muscovite micas. Clays such as Troy®, Barden® and OptiKasT® were found to have good reactivity during the LDRD study. In addition, clays will continue to react with any excess alkali in the formulation as a function of time, while this is less likely in fly ash based geopolymers due to unreactive components such as mullite.

In addition, for the latter formulations made with clay, a different mixing strategy was used than was used with the fly ash geopolymers. The liquids were premixed then blended with the dry clay powders to get a smooth consistent ‘slurry’ representing all the ‘binder’ components. To this slurry, the final dry BSR granular powders were then added with final mixing.

4.7.2 *Preparation of ESTD LAW P-1B Geopolymers Made with Fly Ash*

A geopolymer was made using the ESTD LAW simulant Rassat blend from the TTT/HRI P-1B run. The blend was similar to the development of the geopolymer for the FBSR waste form given in reference 32 with a 65% dry basis waste loading. The FBSR product and Class F fly ash were combined in the mixing bowl of a planetary mixer. The sodium silicate solution was added and mixed. After the sodium silicate was incorporated into the dry powders, the sodium hydroxide solution was added while mixing and mixed to resemble coarse granules. Water was then added during mixing. With continued mixing, the granules coalesced into a "dough-like" ball. The ball transformed into a paste after approximately thirty seconds of additional mixing. Mixing continued for an additional thirty seconds. The paste then was transferred into two plastic cylinders and capped. Typical curing times were 28 days at ambient conditions on the benchtop. The monoliths were typically removed from the curing molds within about 1 week of planned compression testing and allowed to final cure open to the atmosphere.

Table 4-11. Composition of GEO-7 Geopolymer for Monoliths Prepared with ESTD LAW P-1B and Fly Ash

Component	Wet Basis Mass (g)	Wet Basis Mass %	Dry Basis Mass %
ESTD LAW P-1B	54.76	48.42	67
Class F fly ash	14.80	12.47	
Silica D (44.1 wt% $Na_2O \bullet SiO_2$)	20.60	17.36	
Caustic (50 wt% NaOH)	13.71	11.55	
Water (H_2O)	12.11	10.20	
Geopolymer Components			Mol%[f]
Geopolymer Na_2O			30
Geopolymer Al_2O_3			13
Geopolymer SiO_2			57
Total Mass	118.68	100.00	100.00
Geopolymer Water Content			Mol% Ratio
Geopolymer H_2O/Na_2O			15

[f] when the geopolymer program was initiated all FBSR products had contained some unreacted kaolin clay and coal fly ash. It was assumed that between 10-20% of this excess clay would be available as a geopolymer formulation component. This gave a geopolymer $Na_2O/Al_2O_3/SiO_2$ ratio of 23/17/60 in the G1 region of Figure 4-14. SEM (Figure 5-14) showed no unreacted kaolin cores in the FBSR granules and so the composition was adjusted to that shown in this table which assumes no excess kaolin or fly ash in the FBSR product.

4.7.3 *Preparation of BSR Module B Simulant Geopolymers Made with Fly Ash*

The Module B simulant geopolymer was made using a similar methodology to the ESTD LAW simulant blend described above in Section 4.7.2. The composition of the geopolymer mixture, which made two cylinders is shown in Table 4-12. This formulation results in a 68% dry basis FBSR loading. Initial testing was performed using BSR product that did not meet REDOX and LOI requirements to confirm the mixing process and formulation. Results indicated that product from the BSR was coarser than that of the ESTD LAW blend (80% HTF and 20% PRB) used to develop the Rassat P-1B ESTD geopolymer. To obtain a similar particle size distribution, the Module B simulant BSR powders were milled in a high density polyethylene bottle with 6 mm partially stabilized zirconia grinding media for approximately one hour. Twelve one-inch by two-inch cylinders were prepared in six batches using the GEO-7 composition described in Reference 32.

The BSR product and Class F fly ash were combined in the mixing bowl of a planetary mixer. The sodium silicate solution was added and mixed. After the sodium silicate was incorporated into the dry powders, the sodium hydroxide solution was added while mixing and resembled coarse granules. Water was then added during mixing. In these tests, the water was partitioned in half, with the second half added drop wise until the mix had the same consistency as the mixes made with the ESTD LAW. With continued mixing, the granules coalesced into a "dough-like" ball. The ball transformed into a paste after approximately thirty seconds of additional mixing. Mixing continued for an additional thirty seconds. The paste then was transferred into two cylinders, capped, and set aside to cure for 28 days prior to testing. The monoliths were typically removed from the curing molds within about 1 week of planned compression testing and allowed to final cure open to the atmosphere.

Table 4-12. Composition of GEO-7 Geopolymer for Monoliths Prepared with BSR Module B Simulant and Fly Ash

Component	**Wet Basis Mass (g)**	**Wet Basis Mass %**	**Dry Basis Mass %**
BSR Module B Simulant	51.13	47.35	68
Class F fly ash	13.82	12.80	
Silica D (44.1 wt% $Na_2O \bullet SiO_2$)	20.26	18.76	
Caustic (50 wt% NaOH)	13.48	12.48	
Water (H_2O)	9.30	8.61	
Geopolymer Components			Mol%[f]
Geopolymer Na_2O			31
Geopolymer Al_2O_3			13
Geopolymer SiO_2			56
Total Mass	107.99	100.00	100.00
Geopolymer Water Content			Mol% Ratio
Geopolymer H_2O/Na_2O			14

[f] when the geopolymer program was initiated all FBSR products had contained some unreacted kaolin clay and some coal fly ash. It was assumed that between 10-20% of this excess clay and fly ash would be available as a geopolymer formulation component. This gave a geopolymer $Na_2O/Al_2O_3/SiO_2$ ratio of 24/16/60 in the G1 region of Figure 4-14. SEM (Figure 5-14) showed no unreacted kaolin cores in the FBSR granules and so the composition was adjusted to that shown in this table which assumes no excess kaolin or fly ash in the FBSR product.

4.7.4 *Preparation of ESTD LAW P-1B and Module B Simulant Geopolymers Made with Metakaolin Clay*

Another approach for successful monolithing of the BSR granular product involved using a clay-based geopolymer monolith with lower dry-basis waste loading. Ultimately it was decided through review of past monolith testing [51] to pursue the lower waste loading 'centroid' in the G1 region of Figure 4-14 formulation involving clay.

Although this approach would use a lower waste loading than the GEO-7 recipe, scoping testing indicated that it would not require milling of the BSR granular product prior to monolithing. Apparently the coarser BSR mineral could be successfully monolithed using the lower waste loading and clay vs. the milling requirement discussed in Section 4.7.3 for the BSR mineral in the GEO-7 Fly Ash recipe.

Table 4-13 shows the centroid formulation recipe giving a maximum dry basis waste loading of 42% to make two 1”x 2” cylinders. This same recipe was used to make three different sets of clay centroid geopolymer monoliths containing either ESTD LAW P-1B, ESTD LAW P-1A or the BSR Simulant B. This recipe is labeled as ‘T-22-16-62-13’ using the nomenclature previously used by SRNL geopolymer researchers.[84] ‘T-22-16-62-13’ represents the molar composition of 22% Na_2O, 16% Al_2O_3 and 62% SiO_2 (see Figure 4-14). The last number in the label indicates a literature-based suggested molar ratio of H_2O:Na_2O of 13.

Latter formulations involving clay used a different mixing strategy from the fly ash geopolymers discussed above. The liquids were premixed then blended with the dry clay powders to get a smooth consistent ‘slurry’ representing all the ‘binder’ components. To this slurry, the final dry BSR granular powders were then added with final mixing.

Table 4-13. Centroid 42% Waste Load Geopolymer ESTD LAW P-1B Simulant Monolith Recipe Made with Clay

T-22-16-62-13 Component Makeup	Wet Basis Mass (g)	Wet Basis Mass %	Dry Basis Mass %
FBSR ESTD LAW P-1B	28.2	28.98	42
Troy (Helmer) Kaolin (HT@650 °C)	24.4	25.08	
Silica D (44.1 wt% $Na_2O \bullet SiO_2$)	23.8	24.46	
Caustic (50 wt% NaOH)	10.8	11.10	
Water (H_2O)	10.1	10.38	
Geopolymer Components			Mol%
Geopolymer Na_2O			22
Geopolymer Al_2O_3			16
Geopolymer SiO_2			62
Total Mass	97.3	100.00	100.00
Geopolymer Water Content			Mol% Ratio
Geopolymer H_2O/Na_2O			13

Further development of the G1 centroid recipe with 42% dry basis FBSR loading and H_2O:Na_2O ratio of 13 was pursued in order to fabricate geopolymer clay centroid monoliths with waste loadings approaching the previous nominal 65% dry basis FBSR loading of the fly ash GEO-7 monoliths. It was determined through scoping trials using the ESTD LAW P-1B that a 65% loading could be achieved by increasing the content up to the range of H_2O:Na_2O of 20. This higher waste loading clay centroid recipe is shown in Table 4-14 and was used to make two 1” x 2” cylinders.

Table 4-14. Centroid 65% Waste Load Geopolymer ESTD LAW P-1B Simulant Monolith Recipe Made with Clay

T-22-16-62-20 Component	Wet Basis Mass (g)	Wet Basis Mass %	DryBasis Mass %
FBSR ESTD LAW P-1B	44.8	46.52	65
Troy (Helmer) Kaolin (HT@650 °C)	14.9	15.47	
Silica D (44.1 wt% $Na_2O•SiO_2$)	14.6	15.16	
Caustic (50 wt% NaOH)	6.7	6.96	
Water (H_2O)	15.3	15.89	
Geopolymer Components			Mol%
Geopolymer Na_2O			22
Geopolymer Al_2O_3			16
Geopolymer SiO_2			62
Total Mass	96.3	100.00	100.00
Geopolymer Water Content			Mol% Ratio
Geopolymer H_2O/Na_2O			20

4.7.5 *Preparation of BSR Module B Radioactive Monoliths*

The Module B radioactive geopolymers were made using similar recipes and methodology to the BSR Module B simulant metakaolin clay geopolymers in Section 4.7.4. The composition of the geopolymer to make two cylinders is shown in Table 4-15 for the 42% waste loading which indicates that slightly higher water content was required to get the Module B radioactive granular product to set. The calculated molar ratio of $H_2O:Na_2O$ in the binder is 16.2%. The same recipe as was shown in Table 4-14 for simulant monolith formation at 65% waste loading was successful in making the Module B radioactive geopolymers at 65% waste loading.

Table 4-15. Centroid 42% Waste Load Geopolymer Module B Radioactive Monolith Recipe Made with Clay Composition

T-22-16-62-16 Component	Wet Basis Mass (g)	Wet Basis Mass %	Dry Basis Mass %
BSR Module B Radioactive	26.5	27.24	42
Troy (Helmer) Kaolin (HT@650°C)	22.9	23.54	
Silica D (44.1 wt% $Na_2O \bullet SiO_2$)	22.4	23.02	
Caustic (50 wt% NaOH)	10.2	10.48	
Water (H_2O)	15.3	15.72	
Geopolymer Components			Mol%
Geopolymer Na_2O			22
Geopolymer Al_2O_3			16
Geopolymer SiO_2			62
Total Mass	97.3	100.00	100.00
Geopolymer Water Content			Mol% Ratio
Geopolymer H_2O/Na_2O			16

4.7.6 *Monolith Characterization*

Monoliths prepared above were all tested for compressive strength and for phase mineralogy by XRD. Some of the monoliths were also tested for durability via the PCT [93], and leachability using the ASTM C 1308-10.[91] The monolith samples used in all tests following compressive strength testing were generally obtained by using the post-compressive strength fragments derived from running the compressive strength test to past failure resulting in cracked and/or fractured monoliths. A portion of some of the post-compression tested samples prepared for PCT were analyzed for surface area and this is described in Section 4.8.1 and for loss on ignition as described in Section 4.5.

Table 4-16 summarizes the various monolith testing and characterization methods used to test the geopolymers in this study to support waste form performance and PCT calculations.

Table 4-16. Monolith Testing and Characterization Performed

Monolith	As Made Composition	Dry Basis FBSR Loading (%)	Compression Tested [89,90]	XRD Phases	PCT [93]	Analyzed Chemical Composition	TCLP Testing [92]	Bulk Density (g/cc)	ANSI/ANS 16.1/ ASTM C1308 Leaching [70,91]
Fly Ash GEO-7 ESTD LAW P-1B	Table 4-11	67	Yes	Yes	Short Term and Long Term	Yes	Yes	Yes	Yes
Fly Ash GEO-7 Mod B Sim	Table 4-12	68	Yes	Yes	Short Term and Long Term	Yes	Yes	Yes	Yes
Clay ESTD LAW P-1B	Table 4-13	42	Yes	Yes	No	No[b]	No	Yes	Yes
	Table 4-14	65				No[b]	No	No	No
Clay Mod B Sim	Table 4-13	42	Yes	Yes	No	No[b]	No	Yes	Yes
Clay Mod B Rad	Table 4-15	42	Yes	Yes	Short Term[a]	No[b]	Yes	No	No
	Table 4-14	65				No[b]	Yes	No	No

a) Both the 42% WL and the 65% WL Mod B radioactive monoliths made with clay were tested with PCT. The lower 42% WL PCT leachates were archived and the 65% WL PCT leachates were analyzed and reported in this work.

b) Chemical compositions calculated from analyzed granular products and known Na, Al and Si oxide compositions of the binder additives.

After the monoliths were cured for 28 days, the compressive strength was measured using the ASTM procedure for compressive strength of cylinders see Table 4-16.

Compression testing of the ESTD LAW P-1B monoliths was performed at the URS 717-5N Civil Test Laboratory at SRS. Compression testing of the radioactive and simulant Module B monoliths were performed at SRNL with the same modifications to the ASTM compression test procedure as the ESTD LAW P-1B monoliths. Testing at SRNL used unbounded caps.

The broken pieces of monolith from compression testing were used for composition analysis and PCT testing (Table 4-16). Monoliths prepared from Module B simulant were dissolved for analysis using the same AR dissolution used for the granular products. Using the AR dissolution allowed the measurement of arsenic, manganese, and sulfur. A lithium tetraborate dissolution was used to obtain the balance of the cations. A KOH fusion with a water uptake was used for the anion analysis.

4.8 Performance Testing

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

The PCT was conducted on granular mineral and geopolymer monolith samples following the procedures described in ASTM C 1285-08.[93] 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 (BET) 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.[37] When the durability of the FBSR product is calculated using the BET surface area, 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 surface area but the appendices contain the necessary data to calculate the durability from 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 either stainless steel or Teflon® 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 $_{(waste\ form)}$ /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.

For the monolith samples, the surface area measurements were made on sieved and washed samples for PCT that were also roasted at 525°C to remove residual water and unreacted carbon. If the carbon is not removed, the carbon contributes to the surface area.[39] A particle size distribution analysis was performed to confirm that the wet sieving and washing resulted in the particle distribution expected by the PCT procedure.

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

The long term PCTs were conducted on granular mineral and geopolymer monolith samples that had been crushed following the procedures described in ASTM C 1285-08.[93] The samples were prepared in the same manner as samples in Section 4.8.1. 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 4.8.1. 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 4.8.1. The leached solids were analyzed for phase mineralogy using x-ray diffraction.

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

The TCLP [92] was used to assess the release of RCRA metals from the granular BSR product. 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 will meet the requirements of the RCRA Land Disposal Restrictions (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. For the monoliths, remnants from samples that were compression tested in Section 4.7.6 were size reduced, if necessary, to meet the TCLP procedure.

Samples were submitted by SRNL to General Engineering Laboratories (GEL) in Charleston, SC or Davis & Floyd, Inc., Greenwood, SC. Both GEL and Davis & Floyd are South Carolina Department of Health and Environmental Control (SCDHEC) certified EPA laboratories. Figure 4-15 shows the flowchart of the TCLP analytical process that were performed in the samples.

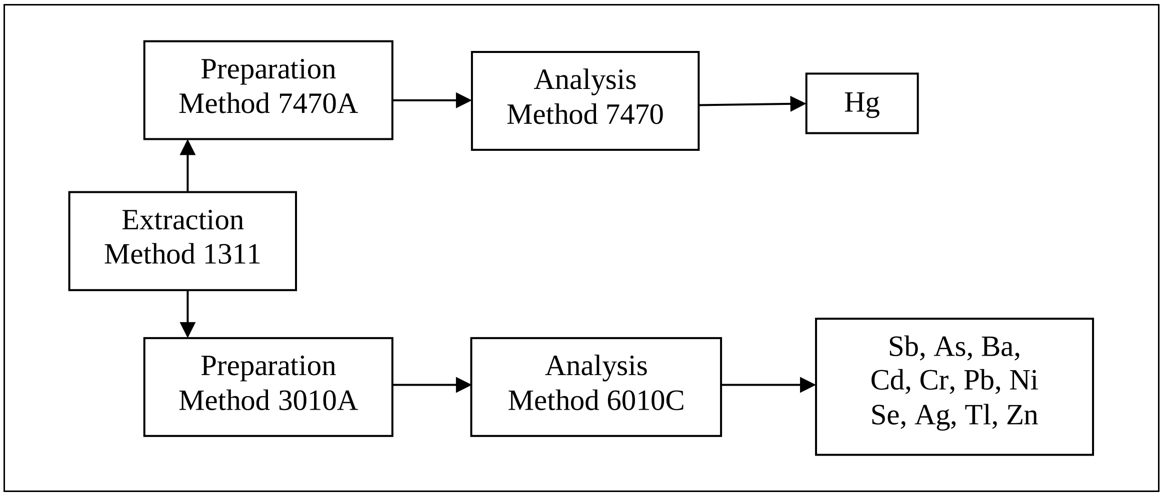

Figure 4-15. TCLP Analysis Sample Flow

4.8.4 *ASTM 1308 on Monoliths*

The monolith was leach tested using the ASTM 1308 'Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste'.[91] This test is similar to the ANS 16.1 Leach Test.[70] Leaching intervals were chosen to satisfy both the ASTM 1308 test protocol and the ANSI/ANS 16.1 test protocol (Figure 4-16). The ASTM 1308 protocol was also chosen as it has more frequent exchange intervals at the beginning of the test when the leachate concentrations are rapidly changing (Figure 4-16 and Table 4-17). The semi-dynamic test used successive batch contacts with ASTM-I water per Figure

4-17. The liquid to solid ratio was 10X the volume (mL) to monolith surface area (cm^2). This study used 1" x 2" monoliths with total surface areas of 50.65 cm^2 which required use of 506 mL leachate volume. Leaching intervals consisted of 2 hours, 5 hours, 17 hours, and 24 hours, and then daily for the next 10 days. Additional leaching intervals of 19, 47, 77 and 90 days were also included in this work. The specimen was suspended from the top of the polybottle container lid and the specimen support contacted no more than 1% of the surface area so as to not impede leaching. All tests were performed in duplicate which is required by ANSI/ANS 16.1 but not ASTM C1308.

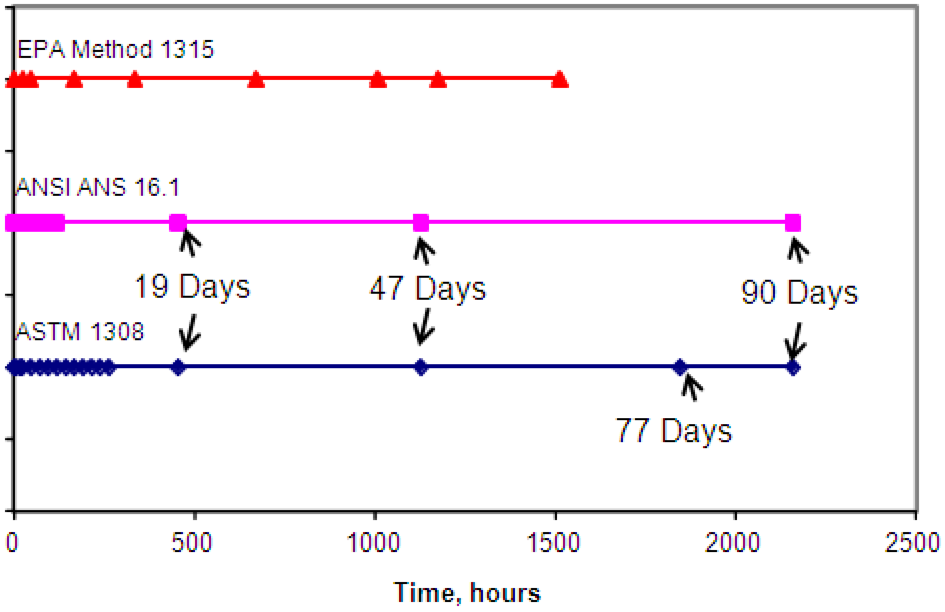

Figure 4-16. Leach exchange intervals for ANSI/ANS 16.1 versus ASTM C1308 versus EPA 1315.

Table 4-17. Comparison of Leach Exchange Intervals for ANSI/ANS 16.1, ASTM C1308, EPA 1315 and the Leach Intervals Used in This Study

Cumulative Time ANSI/ANS 16.1		Cumulative Time ASTM 1308		Cumulative Time EPA 1315		Cumulative Time This Study	
Hours	Days	Hours	Days	Hours	Days	Hours	Days
2	0.083	2	0.083	2	0.083	2	0.0833
		5	0.208333			5	0.208
7	0.291667						
		17	0.708333			17	0.708
24	1	24	1	25	1.04	24	1
48	2	48	2	48	2	48	2
72	3	72	3			72	3
96	4	96	4			96	4
120	5	120	5			120	5
		144	6			144	6
		168	7	168	7	168	7
		192	8			192	8
		216	9			216	9
		240	10			240	10
		264	11			264	11
				336	14		
456	19	456	19			456	19
				672	28		
				1008	42		
1128	47	1128	47				
				1176	49	1176	47/49
				1512	63		
		1848	77			1848/1896	77
2160	90	2160	90			2160/2184	90/91
2880	120					2568	107

Leachate concentrations were converted to cumulative amounts of constituents leached using the leachate volume and mass of monolith and measured elemental compositions. Leachates were analyzed for metals by ICP-AES except that Cs and Re were analzyed by ICP-MS. Iodide anion was analyzed by a separate ICP-MS method and chloride, sulfate, and phosphate anions were measured by IC. The pH of each leach interval leachate was also measured.

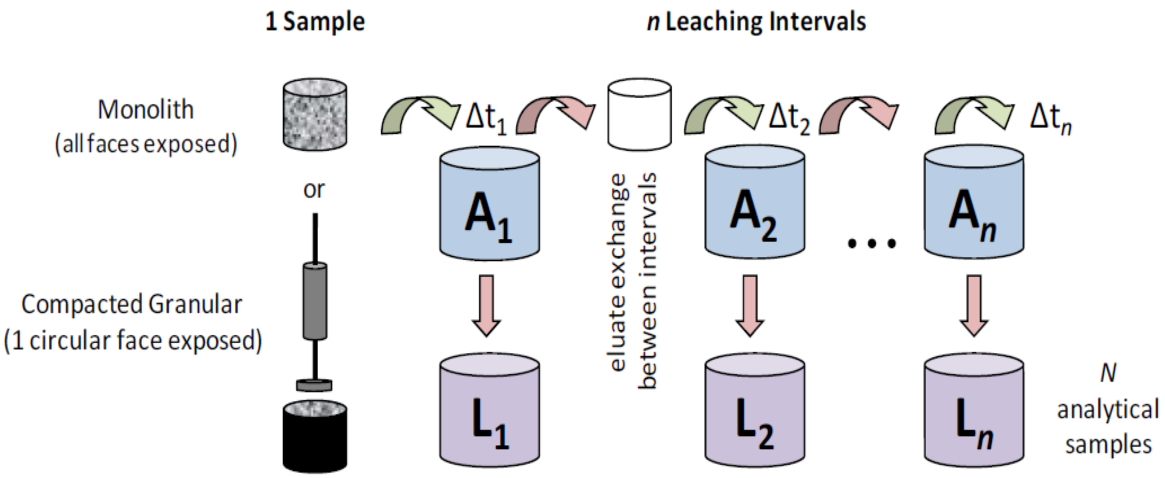

Figure 4-17. Schematic of the Semi-dynamic Monolith Leach Test

The observed diffusivity for each constituent is calculated using the analytical solution shown below, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank. [110]

Equation 14

$$D_i = \pi \left[\frac{M_{t_i}}{2\rho C_0 (\sqrt{t_i} - \sqrt{t_{i-1}})} \right]^2$$

where

D_i = observed diffusivity of a specific constituent for leaching interval, *i* [m^2/s]

i = Leaching interval

M_{ti} = mass released during leaching interval *i* [mg/m^2]

t_i = cumulative contact time after leaching interval, *i*[s]

t_{i-1} = cumulative contact time after leaching interval, *i-1*[s]

C_o = initial leachable content [mg/Kg-dry]

ρ = sample density [$kg\text{-}dry/m^3$].

The mean observed diffusivity for each constituent can be determined by taking the average of the interval-observed diffusivity with the standard deviation.

The leach index (LI), the parameter derived directly from immersion test results, evaluates diffusion-controlled contaminant release with respect to time. The LI is used as a criterion to assess whether solidified/stabilized waste will likely be acceptable for subsurface land disposal. In most cases, the solidified waste is considered effectively treated when the LI value is equal to or greater than 9. The LI is calculated from the D_i above with the following equation:

Equation 15

$$LI = -\log [D_n / cm^2/s]$$

where LI is the leach index, and D_n is the effective diffusivity for the elements of interest (cm^2/s) during the leach interval *n*.

5.0 Results and Discussion

5.1 BSR Run Results

This section describes the runs performed for testing Module B, the Rassat simulant and the SRS Tank 50 radioactive runs shimmed to match the Rassat formulation. 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 given in Table 5-1. The change in product REDOX and LOI control occurred on October 19, 2010 and all subsequent runs used these improved controls as described in Section 4.4.2.

Table 5-1. Timing of Module B Campaigns and Location of Run Data Details

Module	Simulant or Radioactive	Start Date	End Date	Run Data Details
B (Rassat LAW-68 Tank Blend)	Simulant (H_2 Controlled)	10-01-2010	10-18-2010	Appendix B
	Simulant (Gas REDOX Controlled)	10-19-2010	10-28-2010	Appendix C
	Radioactive	11-09-2010	12-09-2010	Appendix D
	Radioactive Tc-99 Spike	12-10-2010	12-10-2010	

5.1.1 *Simulant Module B Campaign with H_2 Concentration Control*

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. 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 relies on the coal used to auto-thermally heat the DMR. In addition, excess unreacted coal in the product is undesirable because it adds unnecessary volume to the product and causes REDOX measurement problems when present in excess. Total gas flow 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. Table 5-2 shows a comparison of the BSR and ESTD FBSR parameters.

Table 5-2. Relative Scaling of Process Operating Parameters, FBSR vs BSR

Property	ESTD FBSR	ESTD FBSR	Scaled BSR	Actual BSR
Feed Rate	0.2 gpm	757 ml/min	0.9 ml/min	1 ml/min
Coal Rate	35 lbs/hr	265 g/min	0.32 g/min	0.12 g/min
Gas Rate	101.9 scfm	2885 SLM	3.4 SLM	0.5 SLM
Steam Rate				24 ml/hr
H_2 Conc.	1% - 2%			1.5% - 3%
DMR Temp.	720°C			720°C
Pressure	Positive 2-3 psig			-4 inwc

The actual BSR process operating conditions for the simulant runs using hydrogen concentration control as done in the ESTD FBSR are shown in Table 5-3.

Initially, no process control conditions for LOI were developed for the BSR. To help lower the LOI, initial attempts included allowing the DMR to operate longer after the feeding completed. To complement this effort, the coal was reduced from 0.16 g/min to 0.12 g/min (with TTT approval).

Initially, the targeted product REDOX was between 0.40 and 0.60 for the hydrogen concentration controlled simulant runs. However, it was found that there was no effective control of the REDOX. Later in the Module B campaign, the target REDOX was changed to between 0.15 and 0.5 as it was learned that a more oxidizing product mineralized more of the Re and Tc-99. Thus, runs that had a REDOX from 0.176 to 0.437 were considered acceptable.

A typical process trend is shown in Figure 5-2 from the 10/08/10 night run. The process trends for all of the hydrogen controlled simulant runs are shown in Appendix B.

Note on the 10/08/10 temperature trend (Figure 5-2), where the bed temperature quickly rises from 740°C to 755°C. This typically happens because the control system cannot offset the loss of cooling that occurs when the feed slurry is stopped. Notice that the control temperature 2 ½ inches above the bed was still at 710°C. In later campaigns, the control temperature was lowered just before the feed was to be shut off to reduce the amount of temperature rise.

The task plan did require a mass balance on the process operation. There was no quartz wool in the crossover tube from the DMR to the condenser during this campaign. Quite a noticeable amount of solids from process carryover were collected in the condenser bubbler, which led to the future use of quartz wool in the crossover tube (beginning with the Module C runs). Concerns were expressed that some species may leach out of the unreacted carry-over into the bubbler water, which could then be mistakenly interpreted as losses via the off-gas.

Table 5-3. BSR Process Operation Conditions & Results for H_2 Controlled Simulant Runs 2010

Run Date	**10/01/10 am**	**10/06/10 pm**	**10/08/10 pm**	**10/09/10 am**	**10/09/10 pm**	**10/10/10 pm**	**10/11/10 am**
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 (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 (stoich)	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
H_2 Concentration Control	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %
Post Feed Run Time (min)	95	45	187	130	150	73	93
Product REDOX	0.176	0.182	0.437	0.254	0.352	0.191	0.223
Product LOI	0.96%	0.23%	0.87%	0.31%	1.22%	0.67%	0.98%
Product Quantity (g) before sampling	37.90	48.75	45.68	41.95	46.49	32.69	43.23
Feed Quantity (g)	109	115	141	128	138	101	131

Run Date	**10/12/10 am**	**10/12/10 pm**	**10/13/10 am**	**10/14/10 pm**	**10/16/10 pm**	**10/17/10 pm**	**10/18/10 pm**
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 (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
H_2 Concentration Control	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %
Post Feed Run Time (min)	165	150	150	142	200	130	156
Product REDOX	0.366	0.389	0.282	0.434	0.211	0.177	0.181
Product LOI	0.69%	0.74%	1.53%	1.57%	1.48%	1.77%	1.15%
Product Quantity (g) before sampling	38.70	40.45	43.96	36.06	43.08	31.09	25.48
Feed Quantity (g)	118	124	138	109	128	97	80

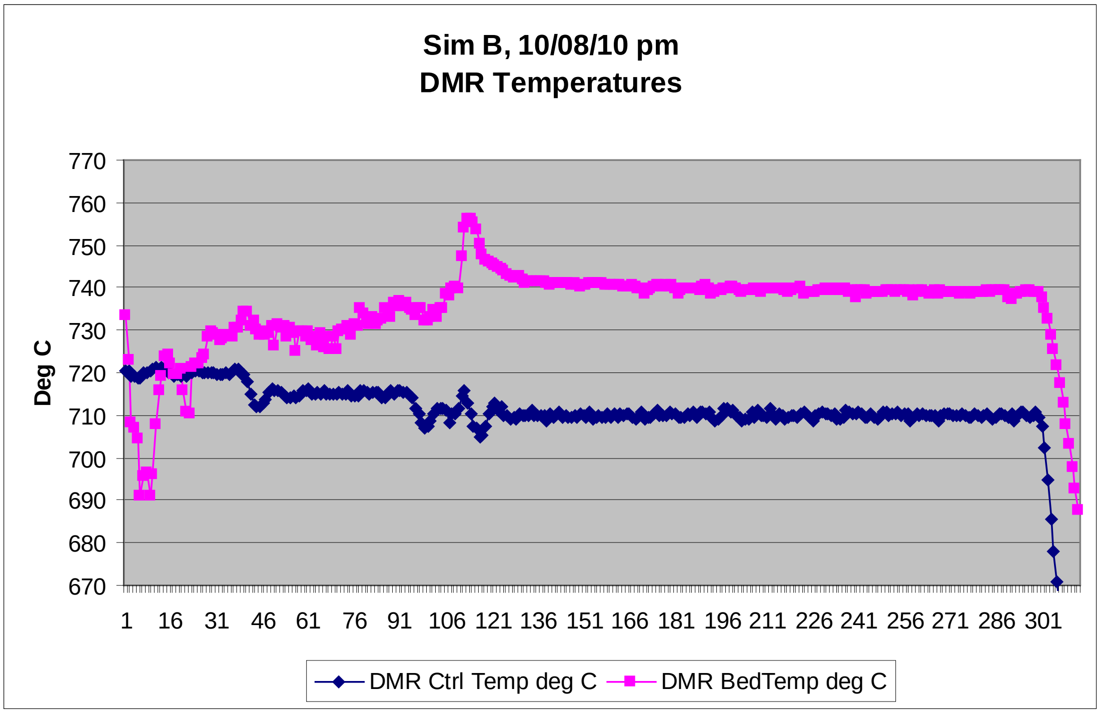

Figure 5-1. Run 10/08/10 pm Temperatures in DMR

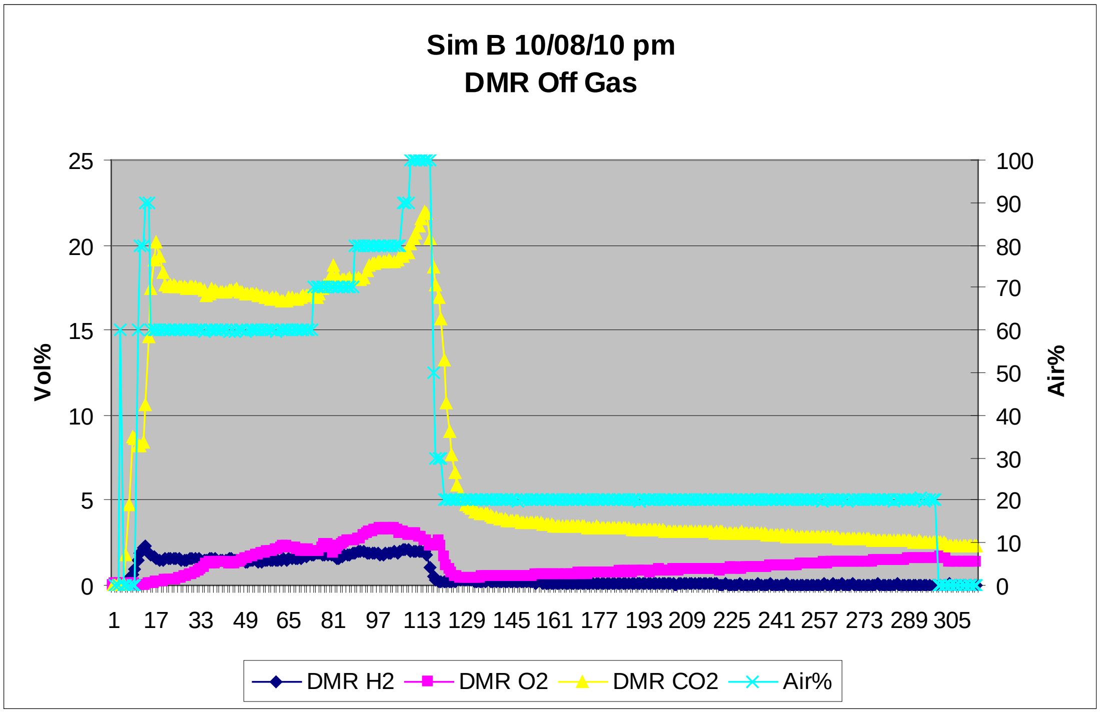

Figure 5-2. Run 10/08/10 pm Off-gas Concentrations and Air% Fed

5.1.2 *Simulant Module B Campaign with Gas REDOX and LOI Control*

The REDOX controlled simulant runs consisted of six accepted runs using the newly developed REDOX and LOI control scheme discussed in Section4.4.2. The actual BSR process operating conditions for the runs are shown in Table 5-4.

Only the process data from the 10/21/10 run will be shown in the body of this text (see Figure 5-3 and Figure 5-4). The process trends for all of the runs are shown in Appendix C. Notice in the 10/21/10 Off-gas trend how the Air% (cyan line) is fairly constant between 60 and 72%.

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 an imperfect mass balance of carbon since the MS did not measure CO.

Equation 16

$$\text{(Carbon fed into DMR)} - \text{(Carbon Leaving as } CO_2\text{)} = \text{Unreacted carbon in product}$$

The CO_2/ml fed endpoint was determined experimentally in the simulant BSR after REDOX control was established. Since the CO_2/ml fed vs. product LOI was a linear relationship, two runs were performed at different endpoints. A line was drawn between the two CO_2/ml fed vs product LOI points and the CO_2/ml fed was determined for the desired product LOI.

MINCALC™–Version 3 calculates the stoichiometric (1x) amount of carbon required to complete the denitration processes. This stoichiometric amount of carbon is then converted to an amount of the actual type of coal that is being used. However, some of the carbon goes into making heat, some doesn't completely react, and some is lost as off-gas carryover (CO and CO_2). Because the BSR is externally heated, and coal consumption is not as efficient, often more coal is needed than is calculated. The required amount of coal was therefore determined experimentally and it was finally shown that 1.3X the stoichiometric amount worked sufficiently for the Module B feeds (Table 4-3).

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 (700^{n}– 740°C)
- 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 non-condensable gases fed to DMR
- O_2 concentration (controlled by air% fed, determined experimentally from product REDOX, not measurable by the MS, $\sim log\,(f_{O_2}) =$ -21 to -18 atm)[f]
- 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.

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[f] Having an oxygen fugacity probe would have greatly improved the control of this parameter and is intended to be incorporated into the design for any future work in the BSR.

Near the end of the simulant Module B runs in October 2010, the first attempts were made to control the product REDOX. The FBSR and hence the BSR were run by H_2 concentration control per TTT. However, H_2 concentration control does not control product REDOX.

Thirty-three simulant Mod B runs were performed using H_2 concentration control and the product REDOX from these runs was fairly random. Fifteen of the runs had a product REDOX in the desired range, so the data from eight of these runs was studied to find a correlation. A roughly linear correlation was found and called the "Gas REDOX" which relied on the concentrations of CO_2 and H_2.

Equation 17

$$\text{Gas REDOX} = [CO_2] - (0.45 \times [H_2])$$

Its derivation was purely empirical but strives to balance CO_2 vs H_2 which is the manner in which the steel industry controls the REDOX during production.[111] This type of control is being pursued for the BSR and includes direct measurement of oxygen fugacity with commercially available REDOX probes.

The "Gas REDOX" control doubled the success rate of making good product from 48% to 100% for the remainder of the Module B runs. During the Module C scoping runs in December 2010, and upon review of the Mod B runs performed, it was observed that getting good Gas REDOX control required a nearly constant Air% being fed to the DMR during feeding. So REDOX control was based on Air% from then on.

Table 5-4. BSR Process Operation Conditions & Results for Simulant Module B REDOX Controlled Runs

Run Date	**10/19/10 pm**	**10/21/10 am**	**10/21/10 pm**	**10/22/10 am**	**10/27/10 am**	**10/28/10 am**
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 (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.	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.1	16.4	16	15.7	16.6	16.0
Post Feed Run Time (hrs)	96	94	131	131	113	124
Product REDOX	0.295	0.250	0.345	0.343	0..224	0..224
Product LOI	1.40%	1.58%	0.99%	1.17%	1.08%	0.93%
Product Quantity (g) before sampling	29.94	40.95	31.29	32.57	32	30.84
Feed Quantity (g)	91	124	96	96	98	96

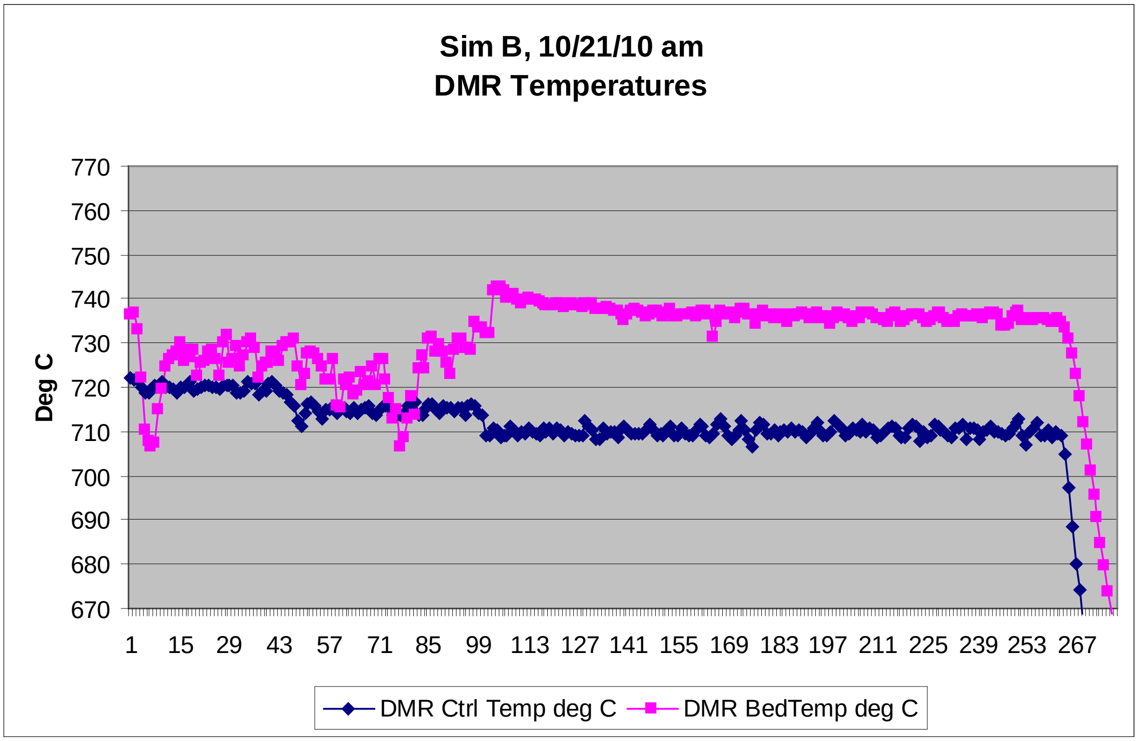


Figure 5-3. Run 10/21/10 am Temperatures in DMR

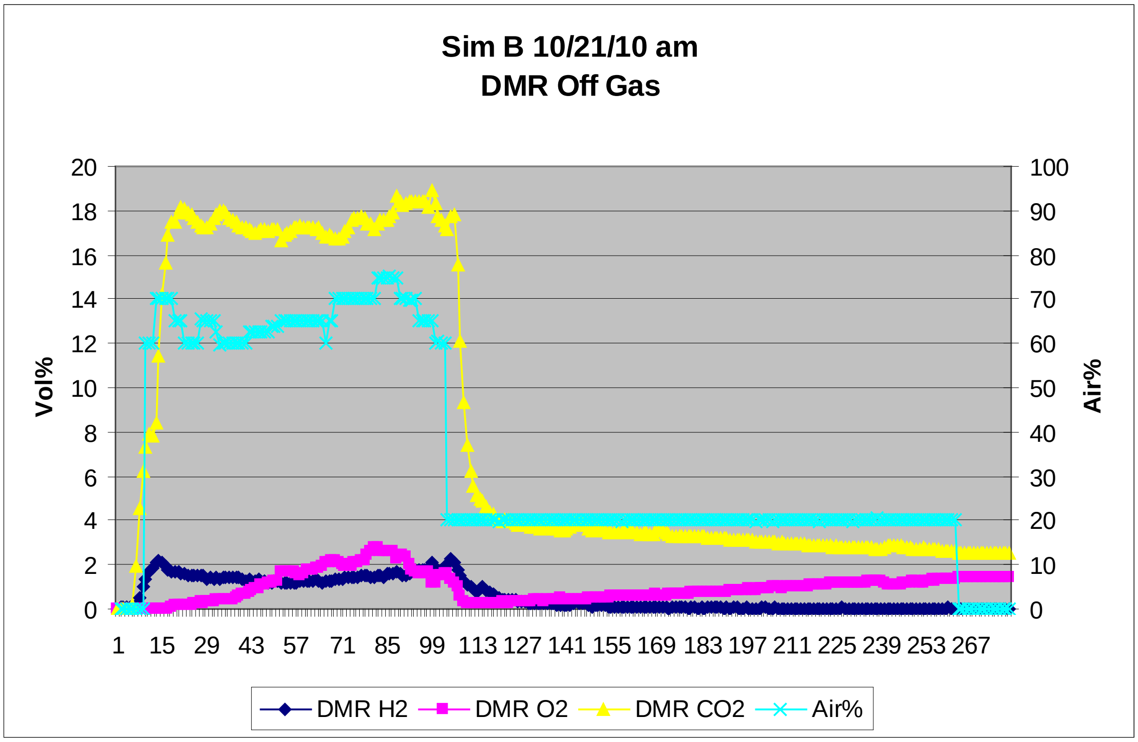


Figure 5-4. Run 10/21/10 am Off-gas Concentrations and Air% Fed

5.1.3 *Radioactive Module B Campaign Runs*

The radioactive Module B campaign consisted of 24 acceptable runs using radioactive Rassat simulant (shimmed SRS Tank 50) with emphasis on using the developed product LOI control and product REDOX control.

The actual BSR process operating conditions for the 24 acceptable runs are shown in Table 5-5. These operating parameters include Air% and CO_2/ml to control REDOX and LOI-LOD respectively.

The operating graphs from the 11/12/10 run are included in Figure 5-5 and Figure 5-6. Notice how the Air% is nearly a constant at about 70% during feeding. The graphs from all the acceptable runs are in Appendix D.

Table 5-5. BSR Process Operation Conditions & Results for Radioactive Module B REDOX Controlled Runs

Run Date	**11/9/10**	**11/10/10**	**11/11/10**	**11/12/10**	**11/13/10**	**11/14/10**
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 (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.	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16	17.2	17.3	16.7	16.8	17
CO_2/ml	26.4	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	156	192	144	192	212	92
Product REDOX	0.190	0.325	0.326	0.500	0.455	0.500
Product LOI	0%	.27%	1.17%	1.00%	0%	1.66%
Product Quantity (g) before sampling	30.90	33.08	32.27	32.91	31.64	17.82
Feed Quantity (g)	97.2	106.1	107.06	103.1	103.22	85.61
Run Date	**11/17/10**	**11/18/10**	**11/20/10**	**11/21/10**	**11/22/10**	**11/23/10**
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 (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.	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.5	17	17	17	17	17
CO_2/ml	27.8	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	56	62	76	162	151	124
Product REDOX	0.472	0.240	0.376	0.511	0.356	0.537
Product LOI	0%	0%	0%	1.68%	1.38%	0%
Product Quantity (g) before sampling	35.31	24.34	19.63	34.31	15.03	36.52
Feed Quantity (g)	108.81	91.57	49.71	104.22	92.04	104.15

*Tc-99 spike campaign

Table 5-5. BSR Process Operation Conditions & Results for Radioactive Module B REDOX Controlled Runs (continued)

Run Date	**11/24/10**	**11/27/10**	**11/28/10**	**11/29/10**	**11/30/10**	**12/1/10**
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 (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.	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.9	16.8	16.8	17	17	17
CO_2/ml	27.8	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	136	206	159	150	120	168
Product REDOX	0.479	0.503	0.376	0.175	0.287	0.210
Product LOI	0%	0.4%	0%	0%	0%	0.09%
Product Quantity (g) before sampling	21.72	30.61	29.90	38.88	24.87	42.80
Feed Quantity (g)	76.49	100.35	103.71	110.79	75.75	136.58
Run Date	**12/2/10**	**12/3/10**	**12/5/10**	**12/7/10**	**12/9/10**	**12/10/10**
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 (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.	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.4	17	17	17	17	17
CO_2/ml	27.8	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	150	150	126	145	177	97
Product REDOX	0.164	0.519	0.185	0.332	0.318	0.370
Product LOI	0.28%	1.64%	0%	0.59%	0.18%	0.49%
Product Quantity (g) before sampling	21.91	26.88	16.56	17.34	25.93	23.45
Feed Quantity (g)	81.55	91.7	47.21	73.97	95.36	82.38

*Tc-99 spike campaign

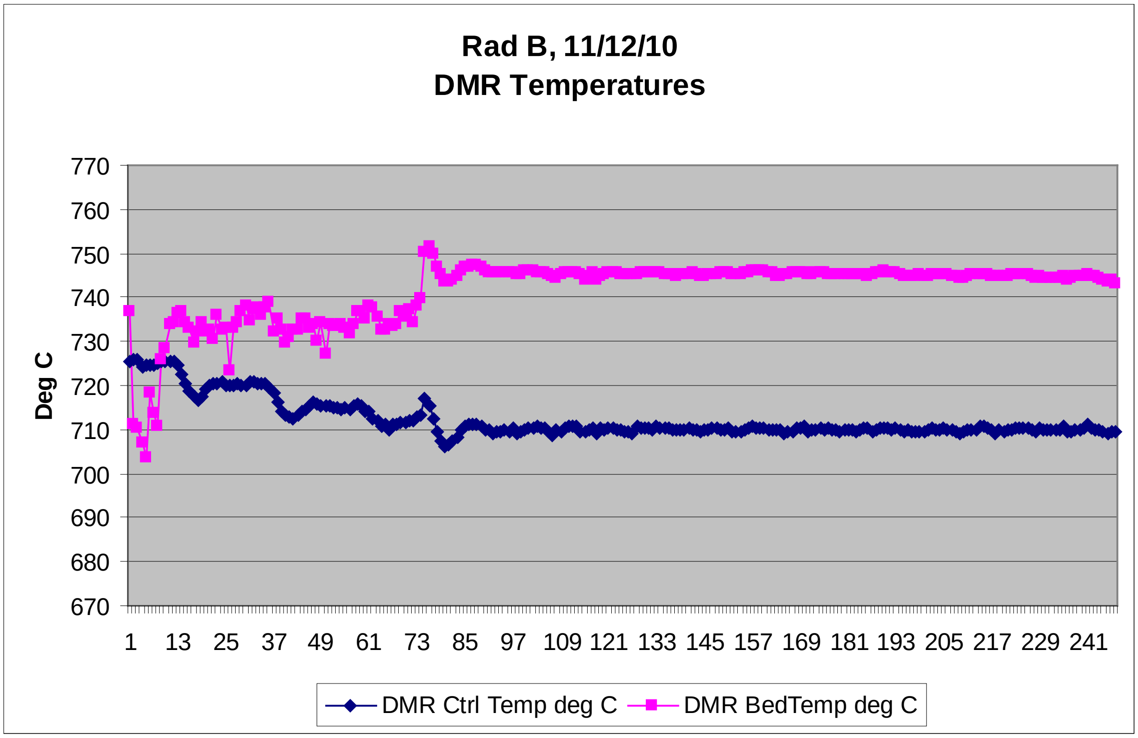


Figure 5-5. Run 11/12/10 Temperatures in DMR

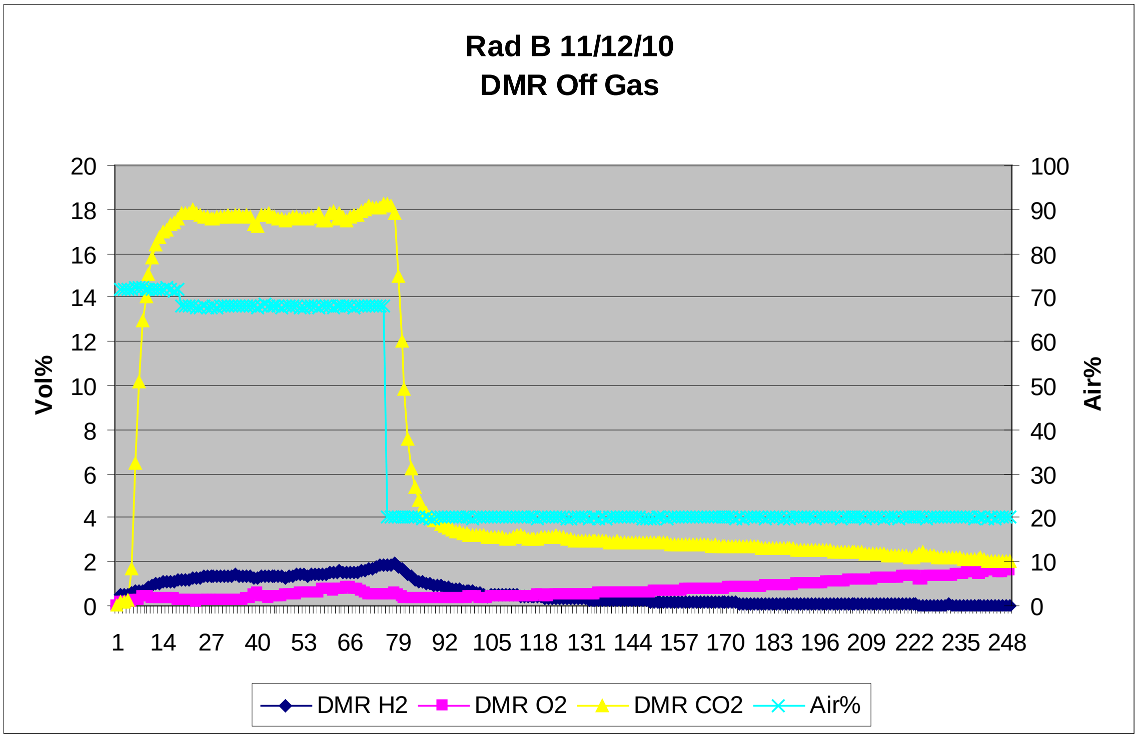


Figure 5-6. Run 11/12/10 Off-gas Concentrations and Air% Fed

5.2 Granular Product Characterization

5.2.1 *Constituent Analyses of ESTD FBSR Simulant Granular Products*

The chemical analyses, REDOX analyses, product skeletal density, particle size distribution, and mineralogy by XRD, of the ESTD FBSR products made from the Rassat simulant are given elsewhere. [32] Since the BSR campaigns were designed to reproduce the ESTD FBSR products as closely as possible and the monoliths in this study were made from both the ESTD FBSR LAW P-1A and P-1B samples, a summary of the composition, density, and REDOX from Reference 32 are provided in Table 5-6. The P-1B sample is a blend of 80% HTF fines and 20% DMR bed product. The P-1A sample is a blend of 84% HTF product and 16% DMR bed product. The P-1B was made with 640 g wet clay per Rassat simulant and the P-1A was made with 675 g wet clay per Rassat simulant in the DMR feed. During the BSR campaigns in this study, the 640 g wet clay per Rassat simulant recipe was used. This amount of clay provided excess SiO_2 and Al_2O_3 in the range of 12.5 wt% for simulant Module B (Table 4-2) and 8.3 wt% for radioactive Module B (Table 4-2).

Table 5-6. Analyses of ESTD FBSR Granular Products from Reference 32

Form	**7-kg bag (08-1712)**			**7-kg bag (08-1713)**			**Bucket (08-1714)**		
Sample	**P-1A (A)**	**P-1A (B)**	**Average**	**P-1B (A)**	**P-1B (B)**	**Average**	**P-1B Bucket 1/5 (A)**	**P-1B Bucket 1/5 (B)**	**Average**
	(wt%)	**(wt%)**	**(wt%)**	**(wt%)**	**(wt%)**	**(wt%)**	**(wt%)**	**(wt%)**	**(wt%)**
Ag_2O	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.04
Al_2O_3	31.56	31.37	31.46	34.39	34.58	34.48	34.77	34.96	34.86
As_2O_3	<0.26	<0.26	<0.26	<0.26	<0.26	<0.26	<0.26	<0.26	<0.26
B_2O_3	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
BaO	0.11	0.11	0.11	0.13	0.13	0.13	0.13	0.13	0.13
CaO	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06
CdO	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.05
Cl	0.18	0.19	0.18	0.23	0.2	0.22	0.21	0.22	0.21
Cr_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cs_2O	0.27	0.24	0.26	0.24	0.22	0.23	0.18	0.18	0.18
F	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Fe_2O_3	1.29	1.5	1.39	1.72	1.57	1.64	2.29	2.3	2.29
I	0.16	0.16	0.16	0.18	0.18	0.18	0.18	0.18	0.18
K_2O	0.2	0.2	0.2	0.23	0.22	0.23	0.22	0.23	0.22
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03
MnO_2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Na_2O	19.28	18.87	19.07	19.95	20.49	20.22	20.89	20.62	20.76
NiO	0.08	0.07	0.08	0.1	0.09	0.09	0.1	0.1	0.1
PO_4	0.72	0.72	0.72	0.81	0.81	0.81	0.81	0.83	0.82
PbO	0.12	0.12	0.12	0.16	0.15	0.16	0.16	0.17	0.17
ReO_2	0.07	0.07	0.07	0.05	0.05	0.05	0.04	0.04	0.04
SO_4	0.91	0.91	0.91	1.55	1.5	1.53	1.47	1.46	1.47
Sb_2O_3	0.06	0.07	0.06	0.08	0.08	0.08	0.08	0.08	0.08
SeO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SiO_2	37.01	37.05	37.03	39.58	40	39.79	40	40.43	40.22
SrO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
TiO_2	<1.05	<1.04	<1.05	<1.14	<1.11	<1.12	<1.12	<1.15	<1.13
Tl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ZnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total	93.51	93.15	93.33	100.99	101.87	101.43	103.12	103.57	103.34
Coal	9.11 wt%			0.79 wt%			1.72 wt%		
Skeletal Density	Not Measured			2.39 g/cc			2.39 g/cc		
$Fe^{2+}/\Sigma Fe$	0.41-0.58			0.50			0.50		

5.2.2 *Constituent Analyses of BSR 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. During Module B, there was an effort to keep the coal content (LOI-LOD) below 2 wt%. The “on-spec” target REDOX ratio was maintained in the 0.1 – 0.5 range for Module B testing as shown in Table 4-4. 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 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 as they were not in the REDOX range of the ESTD tests that the BSR was emulating. 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 the calculated speciation of Re and SO_4 from Reference 96 are summarized in Table 5-7.

Table 5-7 LOI, REDOX and Speciation of Re and SO_4

Waste	**Sample**	**LOI (%)**	**$Fe^{+2}/\Sigma Fe$**	**Re^{+7} (%)**	**SO_4 (%)**
Module B HRI/TTT P-1B (Rassat Simulant)	PR	0-2.0	0.41-0.6	94	86
Module B (Rassat Simulant)	Simulant	1.14	0.36	98	99
	Radioactive	1.03	0.41	96	96
	Radioactive Tc-99 Spike “on-spec”	0.49	0.37	98	99
	Radioactive Tc-99 Spike “off-spec”	1.72	0.64	67	5

Table 5-8 provides the analyses for Module B 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 Many of the simulant constituents are listed as not present (NP) in the table and were not part of the simulant feed to the BSR. 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 present at trace levels in the added clay.[28] The Ti constituent in the simulant product was not analyzed for in the suite of metals from ICP-AES on dissolved simulant product but is present derived from trace levels in the added clay.[28]

Table 5-8. BSR Granular Product Analyses for Simulant and Radioactive Module B Samples

Species	Granular Product Simulant B	Granular Product Radioactive B
	Wt%	Wt%
Al	1.77E+01	1.86E+01
As	1.37E-02	<9.92E-04
B	NP	1.18E-02
Ba	2.74E-03	6.94E-03
Ca	NP	1.63E-01
Cd	<2.00E-04	<9.24E-04
Ce	NP	<9.46E-03
Co	NP	9.16E-04
Cr	6.83E-02	6.77E-02
Cs	2.23E-01	1.01E-03
Cu	NP	2.26E-03
Fe	7.32E-01*	1.28E+00
K	1.34E-01	1.36E-01
La	NP	2.29E-03
Li	NP	<5.45E-03
Mg	NP	3.83E-02
Mn	<2.00E-04	1.09E-03
Mo	NP	<4.52E-03
Na	1.50E+01	1.56E+01
Ni	<2.00E-03	5.17E-03
P	2.44E-01	2.08E-01
Pb	5.04E-02	1.32E-01
Re	3.64E-02	3.62E-02
S	3.61E-01	4.35E-01
Sb	<2.00E-04	6.05E-03
Se	<2.00E-03	7.85E-03
Si	1.82E+01	1.87E+01
Sn	NP	<3.10E-03
Sr	NP	3.50E-03
Th	NP	1.73E-03
Ti	NP/NA	7.81E-01
U	NP	<9.02E-04
Zn	<2.00E-04	2.39E-03
Zr	2.26E-02	2.31E-03
Cs-137	NP	7.04E-07
Tc-99	NP	2.79E-05
I-129	NP	8.70E-04
Cl^-	2.10E-01	1.97E-01
Br^-	NP	NA
F^-	<5.00E-02	<9.84E-02
HCO_2^-	NP	NA
I^-	1.18E-01	6.32E-02
NO_3^-	<1.00E-01	<9.84E-02
NO_2^-	<1.00E-01	<9.48E-02
$C_2O_4^{2-}$	NA	<9.84E-02
PO_4^{3-}	4.34E-01	4.46E-01
SO_4^{2-}	1.31E+00	1.17E+00
	g/cc	**g/cc**
Density	2.39	2.59

NP – Constituents not added to simulant feed, NA – Not Analyzed
NP/NA – Ti was not added to simulant feed but is present in the simulant granular product from the added clay, *Fe – Fe 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

Table 5-9 provides a summary of the measured $\mathrm{Fe}^{2+}/\sum\mathrm{Fe}$ REDOX ratio, the difference between the LOI and LOD, which is a measure of the coal content, and the mineral phases measured.

Table 5-9. Summary of On-Spec and Off-Spec Granular Product Redox ($\mathrm{Fe}^{2+}/\sum\mathrm{Fe}$), LOI-LOD, and Mineralogy for Module B

Module	Type	Composite $\mathrm{Fe}^{2+}/\sum\mathrm{Fe}$	Range of $\mathrm{Fe}^{2+}/\sum\mathrm{Fe}$	Composite LOI-LOD	Range of LOI-LOD	Composite Mineralogy	Range of Mineralogy
Simulant Module B (Rassat)	*On-Spec*	0.36	0.176 – 0.437	1.14%	0.23 – 1.77%	Nepheline (H) Nepheline (O) Nosean Anatase	Nosean, Nepheline (H) Nepheline (O) Sodalite Anatase Quartz
	Off-Spec	*NA*	0.000 – 0.846	NA	0.05 – 3.59%	NA	Nepheline (H) Nepheline (O) Nosean Sodalite Anatase Quartz
Radioactive Module B (SRS LAW)	*On-Spec*	0.41	0.164 – 0.537	1.03%	0.00 – 1.68%	Nepheline (H) Nepheline (O) Nosean Anatase	Nepheline (H) Nepheline (O) Sodalite Nosean Anatase
	Off-Spec	*NA*	0.356 – 0.707	NA	0.70 – 2.38%	NA	Nepheline (H) Nepheline (O) Sodalite Nosean Anatase

Where Nepheline (H) is hexagonal $NaAlSiO_4$ (PDF 00-035-0424)
Nepheline (O) is orthorhombic $NaAlSiO_4$ which “may be synthetic low-carnegieite” [112] (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)

5.2.3 *Mineralogy Targeted vs. Analyzed*

The mineralogy observed for the BSR non-radioactive and radioactive samples for Module B (Rassat simulant) are the same as those of the ESTD bed products (see Table 5-9 and Figure 5-8). 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 peaks are weaker than the nosean peaks and 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 ($Na_8(AlSiO_4)_6SO_4$ [21,113] as shown in Figure 5-7 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 5-9 and Figure 5-8. 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.[112]

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.

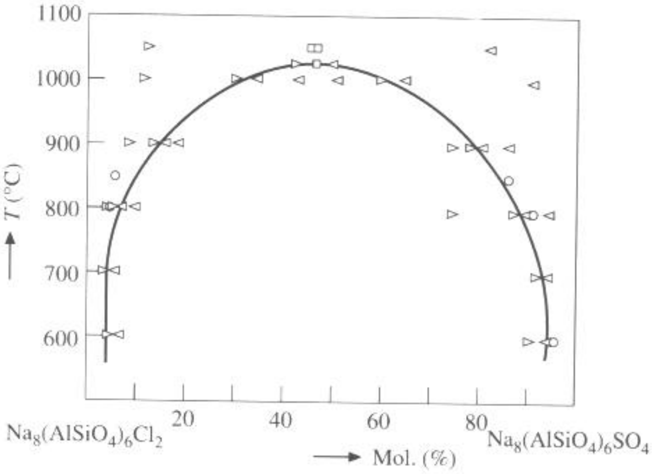


Figure 5-7. Experimentally Determined Sodalite-Nosean Solid Solution[113]

The phases found in the non-radioactive and radioactive BSR products agreed with the predicted mineralogy from MINCALC™ of more nosean (stronger Bragg reflections) than sodalite (weaker Bragg reflections) and quantities of 65-70 wt% of Na-K-Cs nepheline (see Section 4.3 and Table 4-2).

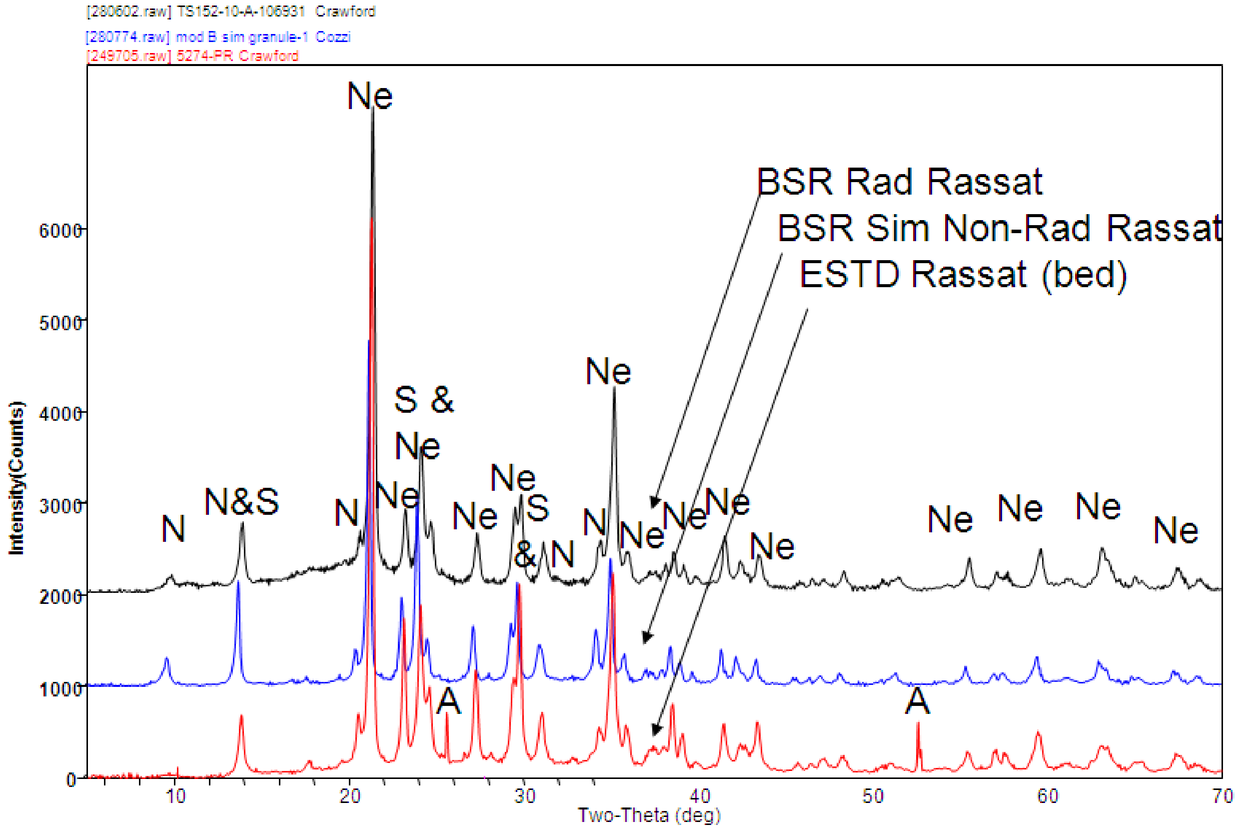


Figure 5-8. Overlay of X-ray Spectra for Module B (Rassat Formulation) for ESTD Engineering-scale DMR Products (P-1B), BSR Bench-scale Simulant and Radioactive Products

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 Corundum, Al_2O_3 (PDF 01-089-3072)
Quartz is SiO_2 (PDF 00-046-1045)
Original XRD spectra fits are in Appendix I

5.3 Mass Balance

The input and output masses for the various campaigns are shown in Table 5-10 and Table 5-11.

Table 5-10. Input Stream Masses for Module B Campaigns

Input Stream	Simulant Campaign (g)	Radioactive Campaign (g)
Feed-Supernate	1174.69	1099.49
Feed-$Fe(NO_3)_3$*$9H_2O$	28.05	48.02
Feed-Coal (Coal$_{un}$)	9.34	3.63
Feed-Coal Ash (Coal$_{ash}$)	7.33	7.53
Feed-Clay-OptiKasT®	600.39	544.91

Table 5-11. Output Stream Masses for Module B Campaigns

Output Stream	Simulant Campaign (g)	Radioactive Campaign (g)
Granular Product	724.37	680.05
DMR Condensate Filtrate	5262.56	6472.15
DMR Condensate Solids	3.846	3.397[&]
Crossbar Filtrate	2882.05	2538
Crossbar Solids	0.769	1.034[&]
Seal Pot Filtrate	None	None
Seal Pot Solids	None	None

[&] The Radioactive B condensate and crossbar solids masses were estimated based on the filters with solids being dissolved in 100 mL or g of solution and then analyzed. The concentration values were then based on the estimated masses.

The concentrations of key species in the input and output streams are shown in Table 5-12 through Table 5-14. Some cells are marked as ‘BDL’ for below detection limits.

Table 5-12. Key Species Concentrations for Module B 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%]*
ICP-MS	Cs-133	1.87E+06	0.00	0.00	0.00	0.00	0.22	1.07E+03	0.10	1.98E+01	0.16
	Re	3.40E+05	0.00	0.00	0.00	0.00	0.04	7.94E+02	0.02	2.26E+01	0.01
	I-127	9.04E+05	0.00	0.00	0.00	0.00	0.12	5.49E+03	0.07	4.99E+02	0.03
ICP-ES	Al	1.89E+06	0.71	13.81	19.98	16.66	17.65	3.21E+02	14.10	1.77E+02	16.48
	Cr	3.45E+05	0.00	0.00	0.00	0.00	0.07	8.60E+01	0.05	< 2.00E+01	0.05
	Na	1.16E+08	0.02	0.36	0.01	0.07	14.95	6.73E+04	9.03	1.06E+04	7.91
	Si	0.00E+00	1.45	28.40	20.88	25.75	18.15	4.41E+03	0.13	2.04E+03	0.12
IC	Cl	1.56E+06	0.00	0.00	0.00	0.00	0.21	6.32E+03	0.00	2.92E+02	0.00
	SO_4^{2-}	8.69E+06	1.40	1.02	0.00	0.00	1.31	2.52E+04	0.34	3.74E+02	0.31

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.
$^+Fe(NO_3)_3*9H_2O$ was analyzed and none of these species were present.

Table 5-13. Key Species Concentrations for Module B 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]*	Condensate Solids [wt%]*	Crossbar Filtrate [ug/L]*	Crossbar Solids [wt%]*
ICP-MS	Cs-133	6.17E+02	0.00	0.00	0.00	0.00	< 0.0004	2.02E+00	0.0001	1.24E+00	0.00
	Re	3.06E+05	0.00	0.00	0.00	0.00	0.04	8.21E+02	0.00007	1.33E+01	0.00
	I-127	9.95E+05	0.00	0.00	0.00	0.00	0.11	5.95E+03	0.03	3.25E+02	0.03
ICP-ES	Al	6.93E+06	0.71	13.81	19.98	16.66	18.55	5.58E+02	13.48	8.57E+02	16.10
	Cr	4.63E+05	0.00	0.00	0.00	0.00	0.07	4.21E+01	0.05	< 1.10E+01	0.07
	Na	1.23E+08	0.02	0.36	0.01	0.07	15.63	8.29E+04	8.15	1.06E+04	0.00
	Si	1.32E+04	1.45	28.40	20.88	25.75	18.67	6.21E+03	14.20	3.48E+03	16.90
IC	Cl	2.06E+06	0.00	0.00	0.00	0.00	0.20	1.30E+04	< 0.08	< 5.00E+03	< 0.41
	SO_4^{2-}	8.66E+06	1.40	1.02	0.00	0.00	1.17	5.47E+04	0.17	< 5.00E+03	0.41

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream.
$^+Fe(NO_3)_3*9H_2O$ was analyzed and none of these species were present.

Table 5-14. Key Radioactive Species Concentrations for Module B Radioactive Run Input and Output Streams

Method	Radioactive Species	Feed-Supernate [dpm/mL]	Granular Product [dpm/g]	Condensate Filtrate [dpm/mL]*	Condensate Solids [dpm/g]*	Crossbar Filtrate [dpm/mL]*	Crossbar Solids [dpm/g]*
Radiochem	Cs-137	9.06E+05	1.36E+06	1.20E+03	4.91E+05	2.39E+01	6.29E+05
	Tc-99	1.13E+04	1.05E+04	1.48E+02	2.37E-02	< 7.54E+00	0.00E+00
	I-129	4.25E+03	3.41E+03 (3.73E+03)[&]	2.04E+01	1.00E+03	1.13E+00	0.00E+00
	I-125	6.50E+03	6.38E+03	3.29E+01	1.70E+03	1.66E+00	2.39E+03

*Condensate and crossbar concentrations are based on individual sample analyses and quantities that were combined based on the total masses for each stream, [&]First Concentration is average of 2 values leaving out 1 replicate and second concentration in parentheses is average of all 3 values

The total recoveries of the key species for the key streams were calculated for the Module B campaigns using the logic presented in Section 4.6. The recoveries for Module B simulant from the BSR processing campaign are shown in Table 5-15. The recoveries for the Module B radioactive campaign are shown in Table 5-16.

Table 5-15. Recoveries for Key Streams and Species for Simulant Module B

Method	Element	Total Recovery (%)	Normalized Recoveries				
			Product %	Condensate Filtrate %	Condensate Solids %	Crossbar Filtrates %	Crossbar Solids %
ICP-MS	Cs-133	92	99.3	0.3	0.2	0.004	0.1
	Re	83	98.1	1.6	0.2	0.02	0.03
	I-127	103	96.2	3.3	0.3	0.2	0.03
ICP-ES	Al	105	99.5	0.00	0.4	0.00	0.1
	Cr	152	99.5	0.1	0.4	BDL	0.1
	Na	99	99.3	0.3	0.3	0.03	0.1
	Si	103	100.0	0.02	0.0	0.00	0.00
IC	Cl	106	97.8	2.1	0.0	0.05	0.00
	SO_4^{2-}	114	98.5	1.4	0.1	0.01	0.02

Table 5-16. Recoveries for Key Streams and Species for the Module B Radioactive Campaign

Method	Element	Total Recovery (%)	Normalized Recoveries				
			Product %	Condensate Filtrate %	Condensate Solids %	Crossbar Filtrates %	Crossbar Solids %
Radiochem	Cs-137	124	98.9	0.8	0.2	0.01	0.1
	I-125*	84	95.0	4.7	0.1	0.1	0.1
	I-129[&]	69	94.3	5.4	0.1	0.1	0.00
		75	94.8	5.0	0.1	0.1	0.00
	Tc-99	87	87.9	11.8	0.0	0.2	0.00
ICP-MS	Tc-99	Not performed					
	Re	98	97.8	2.1	0.1	BDL	0.00
	I-127	94	94.8	5.0	0.1	0.1	0.04
ICP-ES	Al	110	99.5	0.0	0.4	0.00	0.1
	Cr	120	99.4	0.1	0.3	BDL	0.2
	Na	104	99.2	0.5	0.3	0.03	0.00
	Si	110	99.4	0.03	0.4	0.01	0.1
IC	Cl	83	94.1	5.9	BDL	BDL	BDL
	SO_4^{2-}	113	95.6	4.3	0.1	BDL	0.1

*****I-125 values based on half-life decay from when sample pulled and actually analyzed. I-125 analytical more accurate than I-129. [&]First row of I-129 recoveries use 3.41E+03 dpm/g for product concentration, while second row uses 3.73E+03 dpm/g.

The non-radioactive Cs-133 recovery was 92% for the simulant campaign. This recovery was good since the concentration of Cs-133 in the feed was about 1,874,000 ug/L with a total Cs mass fed of about 1.78 grams over 18 runs. The Re recovery was 83% and the I-127 recovery was 103% for the simulant campaign. The SO_4 recovery was about 114%. The SO_4 recovery was very dependent on the SO_4 coming in from the coal in the feed mix and how much of the coal in the feed became ash. The approach on how to handle the feed coal SO_4 and other species was discussed in Section 4.6. More details of the mass balance are shown in Appendix E.

The Re recovery was 98% for the Module B radioactive campaign. The I-127 recovery was 94%. More details of the mass balance are shown in Appendix F. Most recoveries for the radionuclides in the Module B radioactive campaign were in the range of 84% to 124% except for I-129. The I-129 value had higher variability in the granular product, which gave a range of 69-75% recovery using the average values. The 95% confidence interval for the 3.73E+03 dpm/g concentration is 627 dpm/g or the concentration could vary as high as 4,357 dpm/g giving a total recovery of I-129 of 87%. The Cs-137 and Tc-99 recoveries were 124% and 87%, respectively. Comparison of the total recoveries shown in Table 5-16 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.

5.4 Monolith Product Characterization

5.4.1 *Chemical and Phase Analyses of Monolith Waste Forms*

The chemical compositions of the GEO-7 monoliths prepared from BSR simulant granular product were measured as described in Section 4.7.6 and are reported in Table 5-17. The elemental concentrations were converted to oxides and the measured LOI was taken into account to demonstrate full recovery of the sample. The LOI was then subtracted out and the oxides renormalized to 100% for PCT calculations. The difference in the sodium and silica values between the ESTD and BSR monoliths are attributed to the small change in the geopolymer composition that resulted from formulation and preparation work performed. This testing resulted in a slightly higher sodium hydroxide addition in the batch sheet.

Table 5-17. Chemical Composition of Simulant Monoliths Fabricated with Fly Ash

Component	**ESTD Rassat Simulant Monolith GEO-7 SRNL**	**BSR Rassat Simulant Monolith GEO-7**
	wt%	**wt%**
Al_2O_3	27.23	26.54
CaO	0.37	0.72
Cr_2O_3	0.07	0.08
Fe_2O_3	2.50	3.31
K_2O	0.99	0.59
Na_2O	21.07	24.51
P_2O_5	0.33	0.38
PbO	0.10	0.05
SO_4	0.99	1.26
SiO_2	44.95	40.78
TiO_2	0.99	0.99
ZrO_2	0.00	0.05
Cl	0.10	0.33
F	<0.06	<0.12
I	0.07	0.07
Cs_2O	0.14	0.18
Re_2O_7	0.03	0.03
Total	99.99	99.99
LOI	19.82%	18.67%

The chemical compositions of the centroid clay monoliths prepared from BSR simulant granular product were calculated from the simulant granular product analyses from rom Table 4-13 for the 42% waste loading. The centroid clay monolith oxide composition is shown in Table 5-18

Table 5-18. Chemical Composition of BSR Simulant Monolith's Fabricated with Clay

Component	BSR Rassat Simulant - Centroid with Clay (wt%)
Al_2O_3	30.69
Cr_2O_3	0.04
Fe_2O_3	0.44
K_2O	0.07
Na_2O	19.86
P_2O_5	0.23
PbO	0.02
SO_4	0.45
SiO_2	46.35
ZrO_2	0.01
Cl	0.09
F	<0.02
I	0.05
Cs_2O	0.10
Re_2O_7	0.02
Total	98.45

The chemical compositions of the centroid clay monoliths prepared from ESTD P-1A and P-1B simulant granular product were calculated from the simulant granular product analyses from Reference 32 and the known Na, Al, and Si oxide chemical compositions of the binder additives from Table 4-13 for the 42% waste loading. These monolith oxide compositions are shown in Table 5-19.

Table 5-19. Chemical Composition of ESTD Simulant Monolith's Fabricated with Clay

Component	ESTD P-1A (wt%)	ESTD P-1B (wt%)
Ag_2O	0.02	0.02
Al_2O_3	31.18	31.54
As_2O_3	<0.11	<0.11
B_2O_3	<0.15	<0.14
BaO	0.05	0.05
CaO	0.03	0.03
CdO	0.02	0.02
Cl	0.08	0.09
Cr_2O_3	0.05	0.04
Cs_2O	0.12	0.08
F	<0.09	<0.08
Fe_2O_3	0.64	0.98
I	0.08	0.08
K_2O	0.09	0.10
MgO	0.01	0.01
MnO_2	<0.01	<0.01
Na_2O	20.18	20.24
NiO	0.03	0.04
PO_4	0.33	0.35
PbO	0.05	0.07
Re_2O_7	0.03	0.02
SO_4	0.42	0.62
Sb_2O_3	0.03	0.03
SeO_2	<0.004	<0.004
SiO_2	47.11	47.18
SrO	<0.004	<0.004
TiO_2	0.55	0.55
ZnO	<0.004	<0.004
Total	101.10	102.13

The chemical compositions of the centroid clay monoliths prepared from BSR radioactive granular product were calculated from the radioactive granular product analyses and the known Na, Al, and Si oxide chemical compositions of the binder additives from Table 4-15 for the 42% waste loading and Table 4-14 for the 65% waste loading. These monolith oxide compositions are shown in Table 5-20.

Table 5-20. Chemical Composition of Radioactive Monolith's Fabricated with Clay

Component	BSR Radioactive Module B (Rassat)	
	Centroid with Clay at 42% WL (wt%)	Centroid with Clay at 65% WL (wt%)
Al_2O_3	31.38	32.88
CaO	0.10	0.15
Cr_2O_3	0.04	0.06
Fe_2O_3	0.77	1.19
K_2O	0.07	0.11
Na_2O	20.24	20.55
P_2O_5	0.20	0.31
PbO	0.06	0.09
Re_2O_7	0.02	0.03
SO_4	0.55	0.85
SiO_2	46.79	44.07
TiO_2	0.55	0.85
ZrO_2	0.001	0.002
Cl	0.08	0.13
F	<0.04	<0.06
I	0.03	0.04
Cs-137	2.9E-07	4.6E-07
Tc-99	1.2E-05	1.8E-05
I-129	3.6E-04	5.7E-04
Total	100.89	101.38

Figure 5-9 and Figure 5-10 demonstrate that the phase assemblages of the granular products are not compromised when monolithed. Figure 5-9 shows the ESTD FBSR product monolithed at 42 wt% FBSR loading in Troy (Helmer) clay (see Table 4-16 as both 42 wt % and 65 wt% FBSR loaded monoliths were made from the ESTD material but only the 42 wt% loaded samples was submitted for XRD analyses). Figure 5-10 demonstrates that the phase assemblages are not compromised when the BSR radioactive Module B material was bound in a geopolymer made with Troy (Helmer) clay at a FBSR loading of either 42 wt% (top) or 65 wt% (bottom). See Table 4-16 for reference.

Figure 5-11 demonstrates that the phase assemblages are not compromised when the BSR simulant B material is bound in a geopolymer made with fly ash at an FBSR loading of 65 wt%. Figure 5-12 demonstrates that the phase assemblages are not compromised when the BSR FBSR material is made into a clay based geopolymer at an FBSR loading of 42 wt% either. Figure 5-12 shows the original spectra of the BSR minerals, a spectra of the monolithed BSR minerals, and an overlay of a geopolymer made with the Troy (Helmer) clay that does not contain any FBSR product. In Figure 5-12, Na_5FeO_4 and quartz are identified as impurities in the geopolymer clay and anatase (TiO_2) is an impurity in the OptiKasT® clay used for FBSR processing.

However, it should be noted that the individual Bragg reflections in Figure 5-11 and Figure 5-12 are less intense in the monolith patterns due to the dilution with the amorphous geopolymer matrix. The monolith peak intensities could also be lower if the granular FBSR product was being degraded by the geopolymer additives, specifically the NaOH additive, but the SEM shown in Figure 5-14 demonstrates that the individual FBSR granules have sharp grain boundaries in contact with the geopolymer matrix.

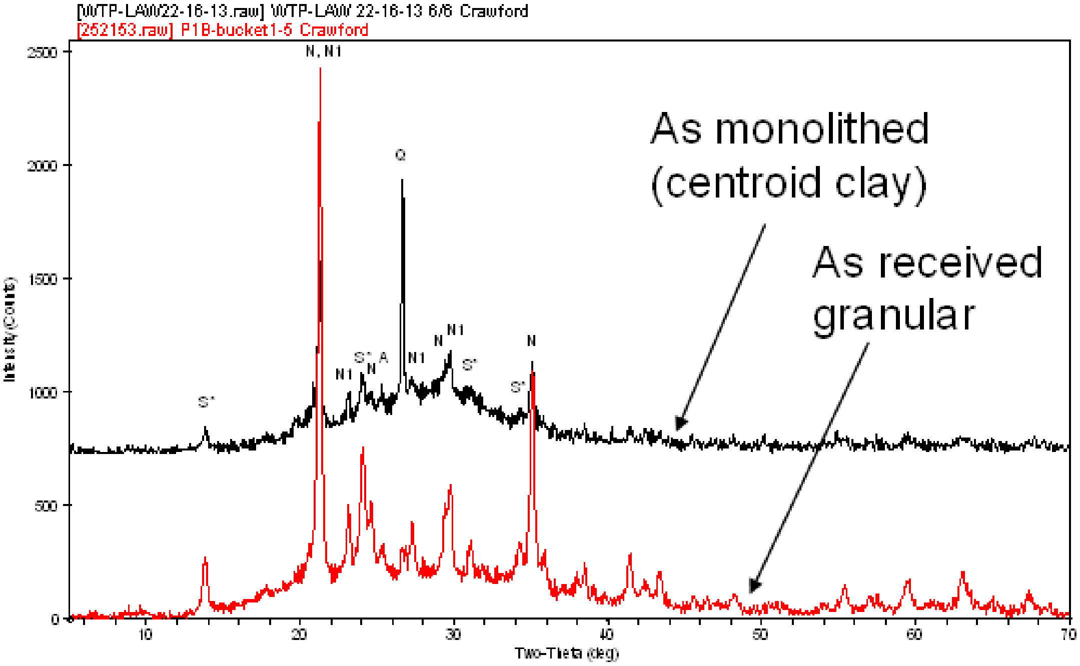


Figure 5-9. Overlay of As-received Engineering Scale Granular Product (P-1B) and Monolithed Geopolymer Made with Clay

Note that all the original phases survive in the XRD but are present at less intensity in the monolith pattern due to the dilution with the amorphous geopolymer matrix.

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)

N is Nepheline (H) either $NaAlSiO_4$ (PDF 00-035-0424 top spectra) or $K_{0.17}Na_{0.75}AlSiO_4$ (PDF 01-072-7408 bottom spectra from TTT/HRI ESTD campaigns – high K containing wastes from INL had been processed recently and may have provided some K to the nepheline)

S* is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)

A is Anatase, TiO_2 (PDF 00-021-1272)

Q is Quartz, SiO_2 (PDF 00-046-1045)

Original XRD spectra fits are in Appendix I

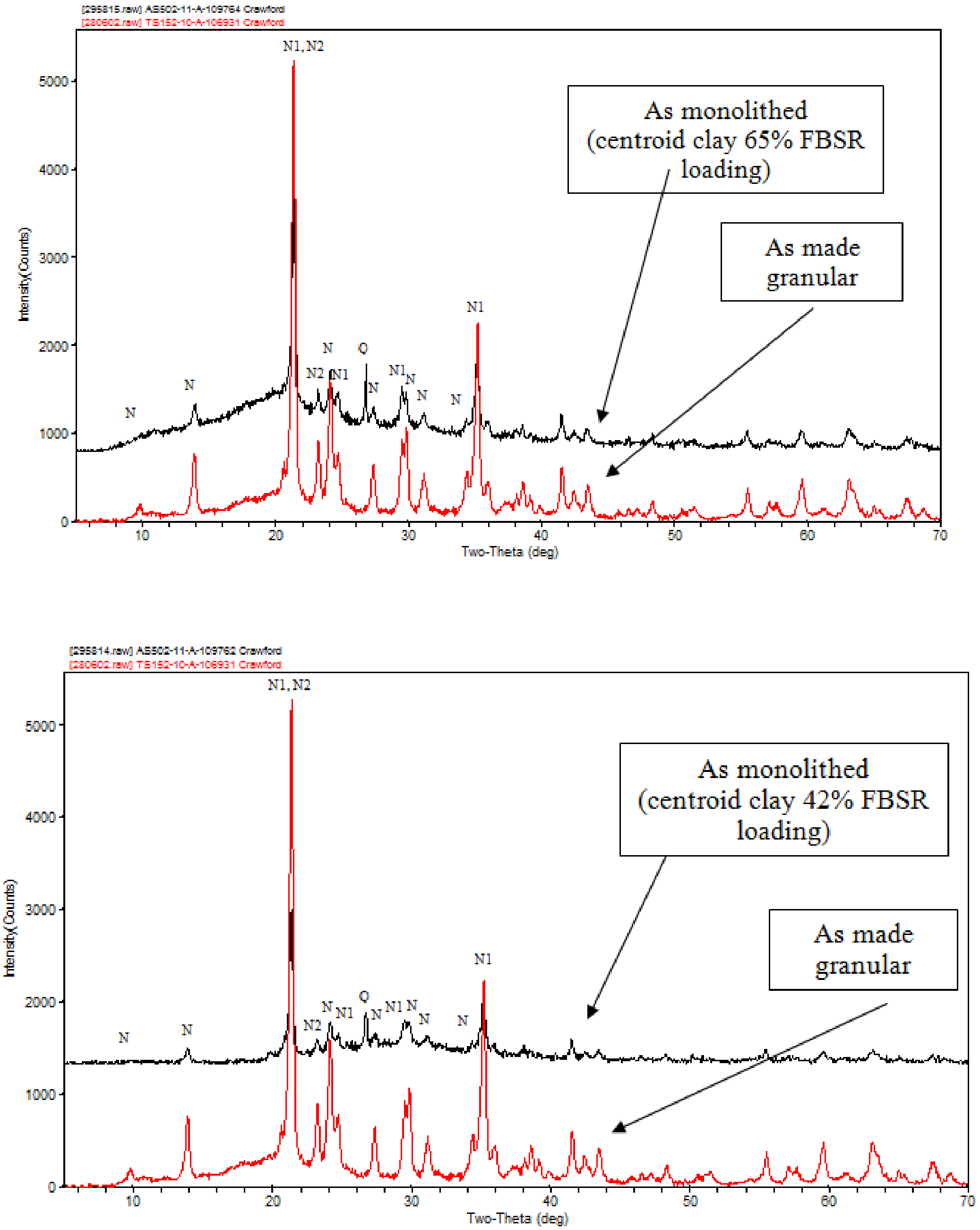


Figure 5-10. Overlay of As-made BSR Radioactive B Granular Product and Radioactive Monolithed Geopolymers Made with Clay at 42% and 65% FBSR Loading

Note that all the original phases survive in the XRD but are present at less intensity in the monolith pattern due to the dilution with the amorphous geopolymer matrix.

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
N is Nosean (cubic) $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
Q is Quartz, SiO_2 (PDF 00-046-1045)
Original XRD spectra fits are in Appendix I

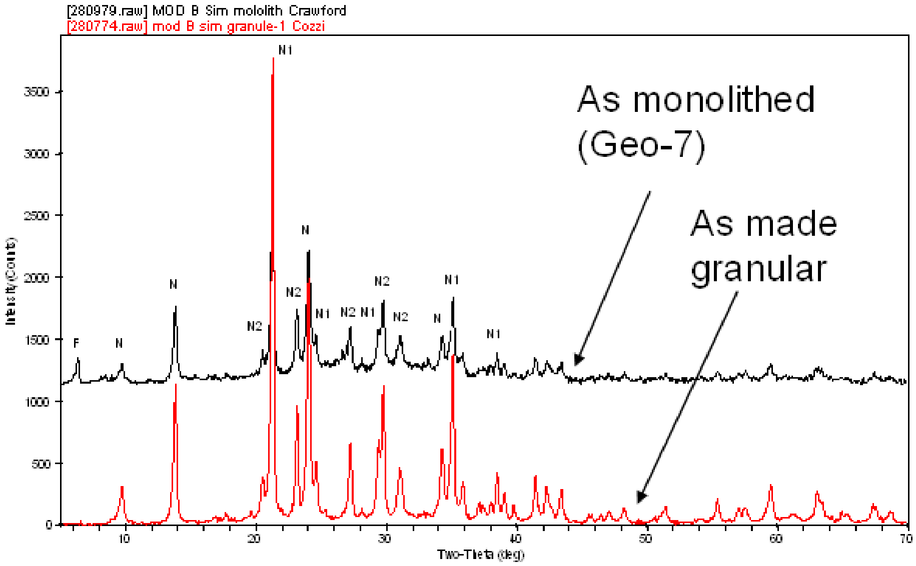


Figure 5-11. **Overlay of As-made BSR Non-radioactive Granular Product and Monolithed Geopolymer Made with Fly Ash (GEO-7).**

Note that all the original phases appear in the XRD of the monolith.

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
N is Nosean (cubic) $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
Q is Quartz, SiO_2 (PDF 00-046-1045)
F is faujasite, $Na_2Al_2Si_40_{12}$•$8H_2O$ (PDF 00-039-1380) a geopolymer reaction product [51, 118]
Original XRD spectra fits are in Appendix I

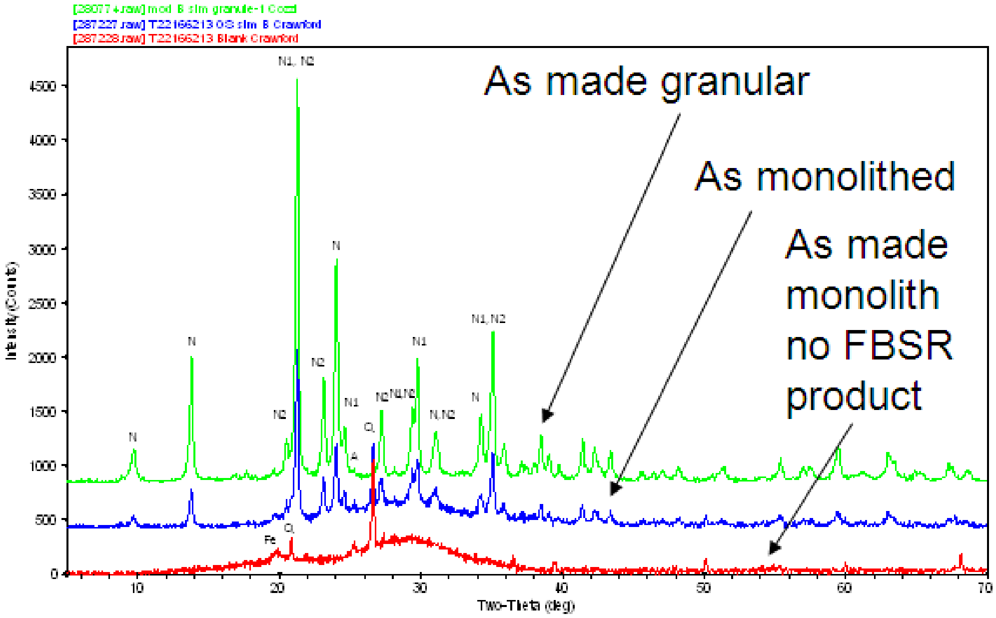


Figure 5-12. Overlay of As-made BSR Non-radioactive Granular Product, a Monolithed Geopolymer with the BSR product, and a Geopolymer with no FBSR product. The monolith with the BSR product contained 42 wt% FBSR product.

Note - all the original phases appear in the XRD of the monolith. The anatase is TiO_2 from impurities in the clay used in the FBSR process, but anatase is also an impurity in the geopolymer clay. In the geopolymer spectra, Na_5FeO_4, quartz, and anatase are present from the clay binder where the sodium iron phase is likely formed from the muscovite impurities in the clay (see Figure 5-13).
N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
N is Nosean (cubic) $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
Q is Quartz, SiO_2 (PDF 00-046-1045)
A is Anatase, TiO_2, (PDF 00-021-1272)
Fe is Na_5FeO_4 (PDF 00-036-0874)
Original XRD spectra fits are in Appendix I

During the mixing of the fly ash monolith formulations, all the ingredients were mixed together, i.e. the FBSR product, the metakaolin, the sodium hydroxide and the sodium silicate. This gave a less homogeneous monolith than desired. When the monolith formulations were made with clay, the geopolymer was made first from the metakaolin, the sodium hydroxide, and the sodium silicate to the desired composition in the G1 region shown in Figure 4-14. After the mixture reached the desired consistency, the FBSR granular product was added to ensure that the granules were macro-encapsulated.

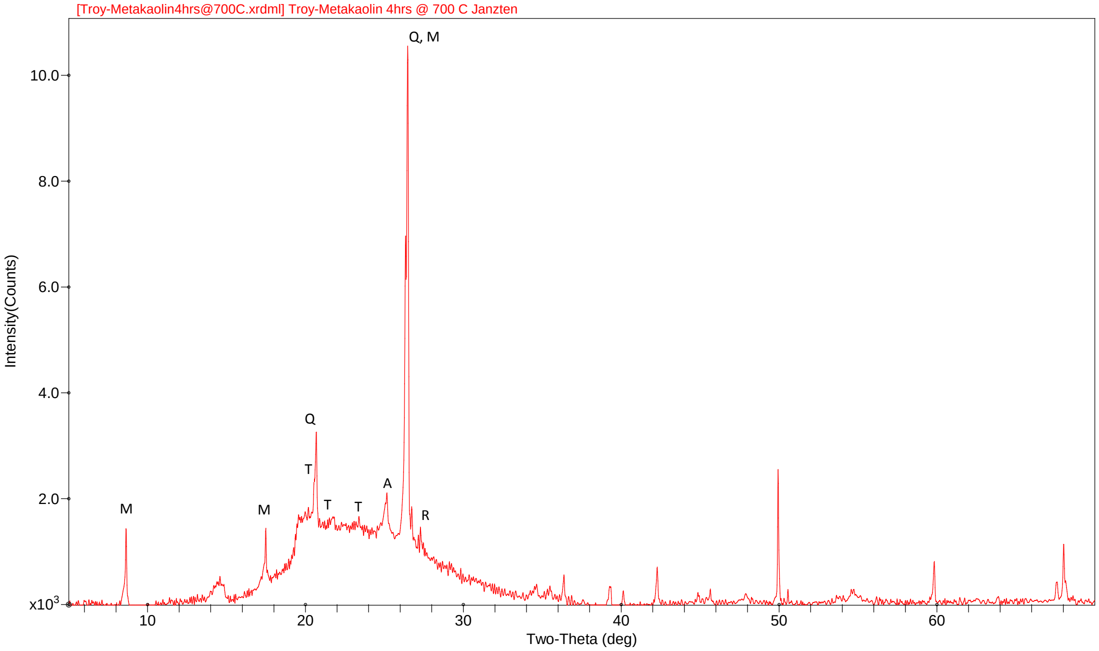


Figure 5-13. X-ray Diffraction Pattern of the Troy (Helmer) metakaolin after roasting at 700°C for 4 hours.

M is muscovite $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ (PDF 00-007-0042)
Q is Quartz, SiO_2 (PDF 00-046-1045)
T is Tridymite, SiO_2 (PDF 01-088-1535)
A is Anatase, TiO_2, (PDF 00-021-1272)
R is Rutile, TiO_2, (PDF 00-021-1276)
Original XRD spectra fits are in Appendix I

Figure 5-14 shows the ESTD engineering scale P-1B FBSR product embedded in a geopolymer made from fly-ash. The coal and Fe in the image come from the fly ash and the observed cracking in the geopolymer is due to SEM preparation. Note the three circular granules at the tips of the dashed triangles. They are rich in Cl, S, Al and Na and are sodalite/nosean solid solution FBSR minerals. The edges of the FBSR sodalite/nosean minerals are sharp and show no degradation or attack, which would cause irregular grain boundaries, from being embedded in the geopolymer (GEO-7).

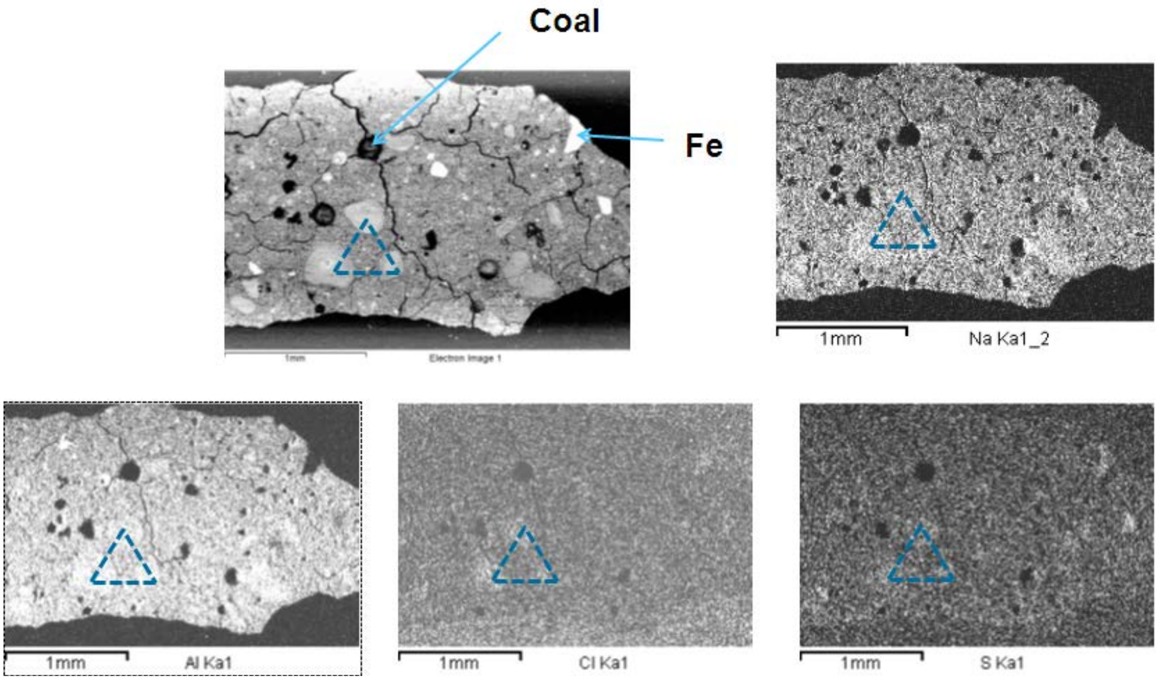
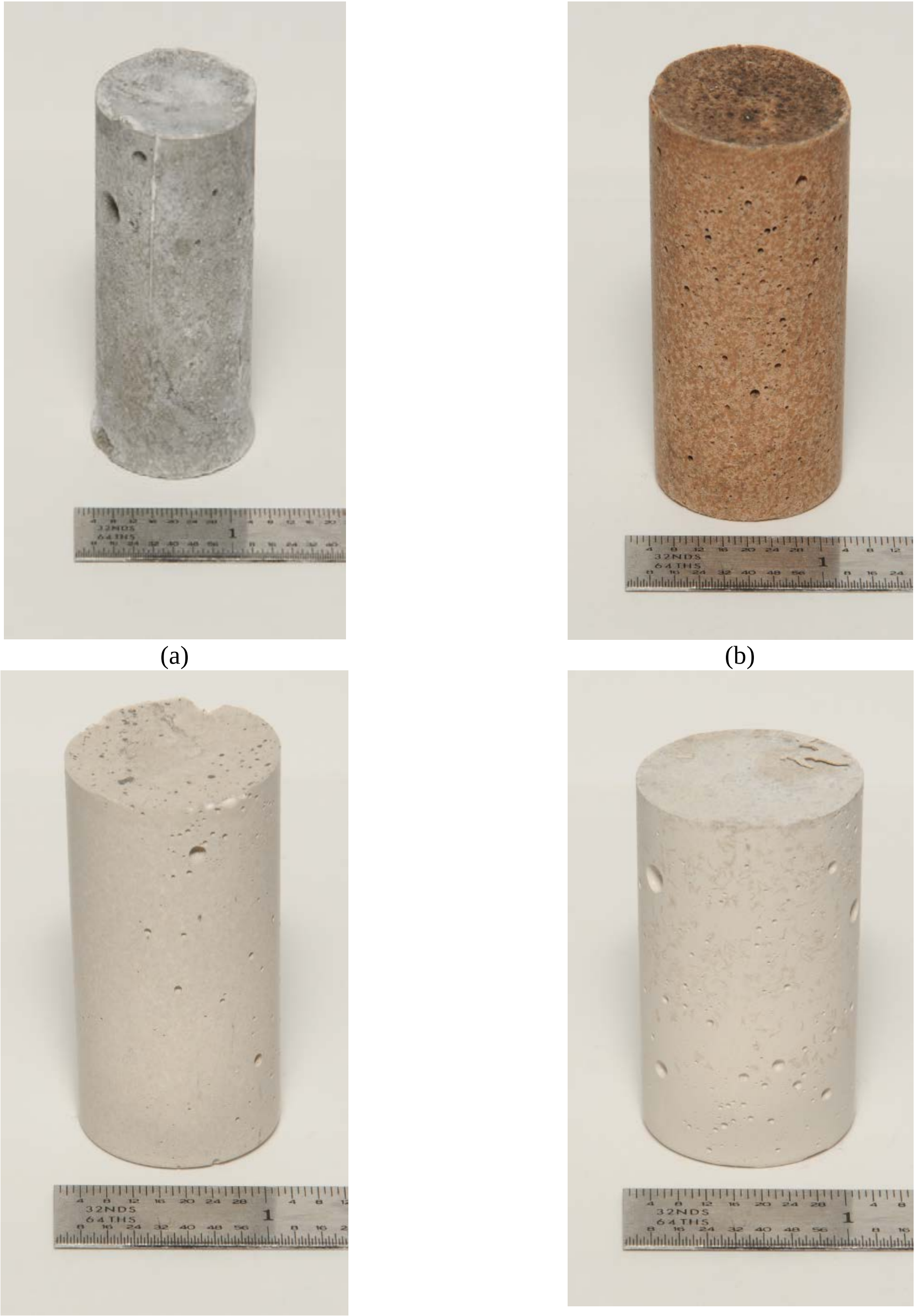


Figure 5-14. Scanning Electron Microscopy of ESTD FBSR Granular Product P-1B Embedded in a Fly Ash Geopolymer

Photographs of representative 1” diameter x 2” high right circular cylinder monoliths made during this study are shown in Figure 5-15. The Figure 5-15a shows ESTD GEO-7 made with fly ash at 65% FBSR loading and Figure 5-15b shows a Troy clay monolith made with BSR Module B at 42% BSR loading with the recipe of T-22-16-62-13. Figure 5-15c and Figure 5-15d photographs show Troy clay monoliths made with ESTD P-1B at two similar recipes of T-16-16-66-20 and T-20-20-60-20, respectively, each containing 60% FBSR loading. All four monoliths are shown in Figure 5-16 for side by side comparison. All of these monoliths show various small-sized indentions or craters that derive from trapped air pockets that form during initial loading of the monolith material into the plastic curing molds. The embedded coal may be from the FBSR product or the fly ash. The metallic Fe is an impurity in the fly ash.



(a) (b)

(c) (d)

Figure 5-15. (a) ESTD GEO-7 made with fly ash at 65% FBSR loading; (b) Troy Clay Monolith made with BSR Module B at 42% BSR loading and T-22-16-62-13 recipe; (c) and (d) Troy Clay Monoliths made with ESTD P-1B at 60% FBSR loading and two similar recipes of T-16-16-66-20 and T-20-20-60-20, respectively

Note the difference in color between the fly ash and clay based geopolymer monoliths. Note: Bubbles are due to setting without vibration to remove air pockets and dark coloration of GEO-7 made with fly ash is from the ESTD PR/HTF mixture and the fly ash binder.

Figure 5-16. Side by Side Comparison of the Monoliths Shown in Figure 5-15

5.5 Regulatory Testing of Monoliths and Granular Product

Regulatory testing includes the compressive strength measurements [89,90], the ASTM 1308/ANSI/ANS 16.1 testing [70,91], and the TCLP testing [92]. While the compressive strength measurement and the ASTM 1308/ANSI/ANS 16.1 testing are on the monolith, the TCLP testing will compare the granular releases to the monolith releases. These regulatory tests will be discussed in this order.

5.5.1 *Compression Testing of Monoliths*

One replicate from each of the six batches of geopolymer monoliths prepared in Section 4.7 were tested for compressive strength at the URS 717-5N Civil Test Laboratory at SRS as noted in Section 4.7.6 after 28 days of curing. The remainder of the samples were either transferred to PNNL for further durability testing or reserved for leach testing. Table 5-21 provides data from the compressive strength measurements of the samples representing each of the six batches produced. The geopolymers made with fly-ash had an average strength of 905.1 psi.

Table 5-21. Compressive Strength of the ESTD P-1B GEO-7 Monoliths Made with Fly Ash After 28 Days of Curing

ID	ESTD Rassat Simulant Monolith GEO-7 Compressive Strength (psi)
P-1B GEO-7 1-1	946.8
P-1B GEO-7 2-1	846.6
P-1B GEO-7 3-1	899.5
P-1B GEO-7 4-1	957.1
P-1B GEO-7 5-1	681.6
P-1B GEO-7 6-1	1099.4
Average	905.1
RSD	15.3%

Geopolymers prepared in Section 4.7 were tested for compressive strength at SRNL as noted in Section 4.7.6 after 28 days of curing. The first two samples were demolded, the ends were ground flat using 240 grit silicon carbide paper, and tested. Both of the samples failed before the instrument began recording data —1000 psi. It was noted that the samples were moist. The remainder of the samples identified for compression testing were demolded and stored in closed, zip-top bags for an additional seven days. Results of the compression tests are in Table 5-22. Note that the average compressive strength is 1134 psi considering the two failed samples are counted as 0 psi—visual observation of the instantaneous compressive stress for both samples was >300 psi at the time of failure. Figure 5-17 is a representative compressive stress versus time plot for geopolymers made with steam reformed product. Jaggedness of the curve is due to the frequency of data sampling and the use of rubber end caps. It does not affect the test or the strength values.

Table 5-22. Compression Testing of Simulant BSR Module B GEO-7 Monolith After 28 Days Curing

Sample ID	Monolith GEO-7 Curing History	BSR Rassat Simulant Monolith GEO-7 Compressive Strength (psi)
Sim Mod B GEO-7 1-1	28 days in sealed mold; samples still moist when demolded	>300
Sim Mod B GEO-7 2-1		
Sim Mod B GEO-7 1-2	cured an additional 7 days out of mold but in a sealed zip top bag for more access to air/drying	750
Sim Mod B GEO-7 3-1		1098
Sim Mod B GEO-7 4-1		1404
Sim Mod B GEO-7 5-1		3550
Average	35 day cured samples	1700
RSD		74.2%

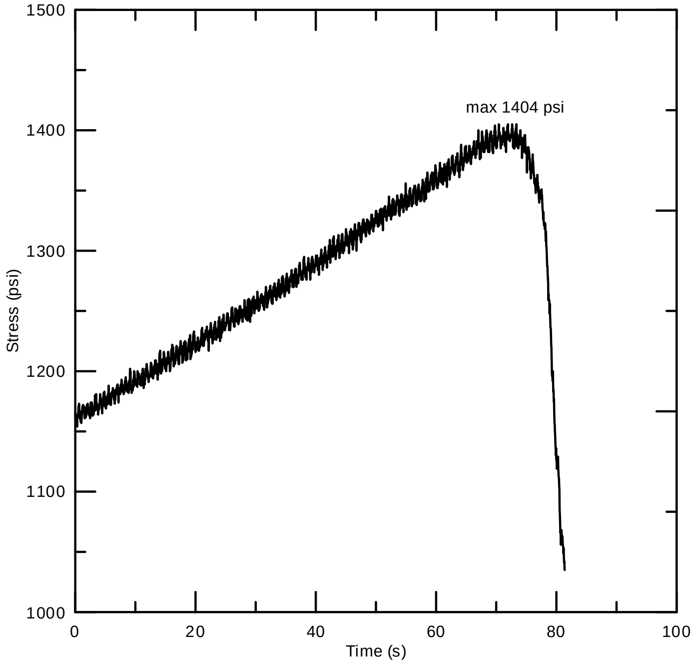
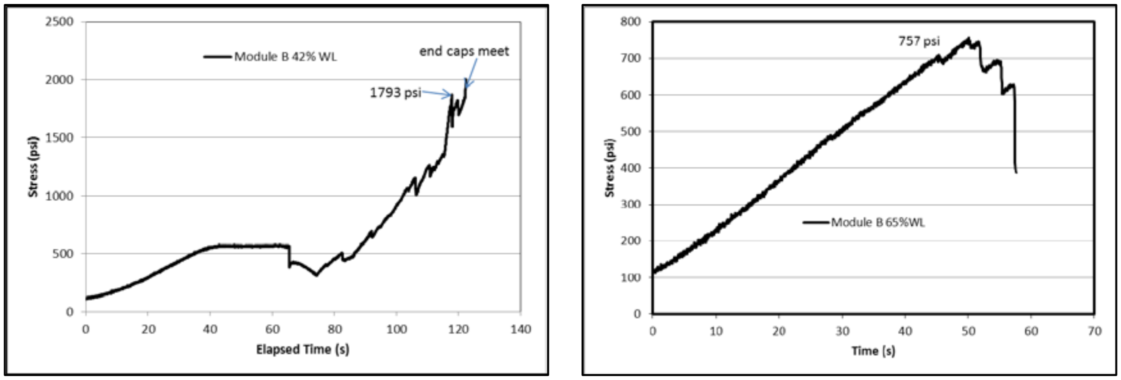


Figure 5-17. Typical Stress versus Time Plot for Geopolymers Made with Fly Ash and FBSR Product; Plot is for Simulant Module B GEO-7 4-1

Geopolymers prepared in Section 4.7.5 were tested for compressive strength at SRNL as noted in Section 4.7.6 after 28 days of curing. Based on the observed behavior of freshly demolded samples in Section 5.4.1, the samples were demolded, and stored in closed, zip-top bags for an additional seven days. The ends were ground flat using 240 grit silicon carbide paper, and tested. The first replicate of the 42%WL sample was too elastic and the steel end caps contacted, causing the test to be aborted. Since the equipment did not record a break, the data was not saved. It was noted that the stress on the display had exceeded 1500 psi prior to the excursion to much higher stresses associated with steel on steel. When the sample was removed from the equipment, it was apparent that the sample had failed, but the failure was not recorded by the equipment. The second sample of the 42%WL was tested, Figure 5-18. Again the sample was elastic enough that the steel end caps met, however, the data was recoverable and the plot was annotated with the assumed break point and instant when the end caps met. The 65%WL samples was more brittle due to the reduced volume of geopolymer matrix and performed comparable to the monoliths prepared with either ESTD or BSR simulant granular FBSR product. The 65%WL sample, Figure 5-18, resulted in a compressive strength of 757 psi.



42% WL 65% WL

Figure 5-18. Compressive Stress/Time Plots for Radioactive Module B Geopolymers Prepared with Clay

An overall comparison can be made between compressive strengths of fly ash and clay monoliths using data presented above from this study, previous work on ESTD monoliths (Reference 32), and monoliths prepared with ESTD WTP-SW simulants (Reference 26). These data are shown in Table 5-23 with the first four rows of data from Reference 32 and the last row of data from Reference 26. Examination of the ESTD monoliths in the first five rows indicates that all of the 65%WL monoliths regardless of size and curing time have compressive strengths of about 1,000 psi or higher. Lowering the waste loading in the two Troy Clay monoliths in the sixth and seventh row of data shows a noticeable increase in compressive strength up to the range of 4600 to 5800 psi. This same trend of increased compressive strength with lower waste loading is noticed in comparing the Sim B 65% WL GEO-7 fly ash monolith (avg. 1700 psi) with the Sim B 42% WL centroid clay monolith (3300 psi). The final row of Table 5-23 shows that both the BSR Simulant Module B granular material and the BSR Simulant Module A granular material from the previous study when fabricated into the 42% WL centroid clay monolith give very high compressive strengths in the range of 3300 to 4356 psi.

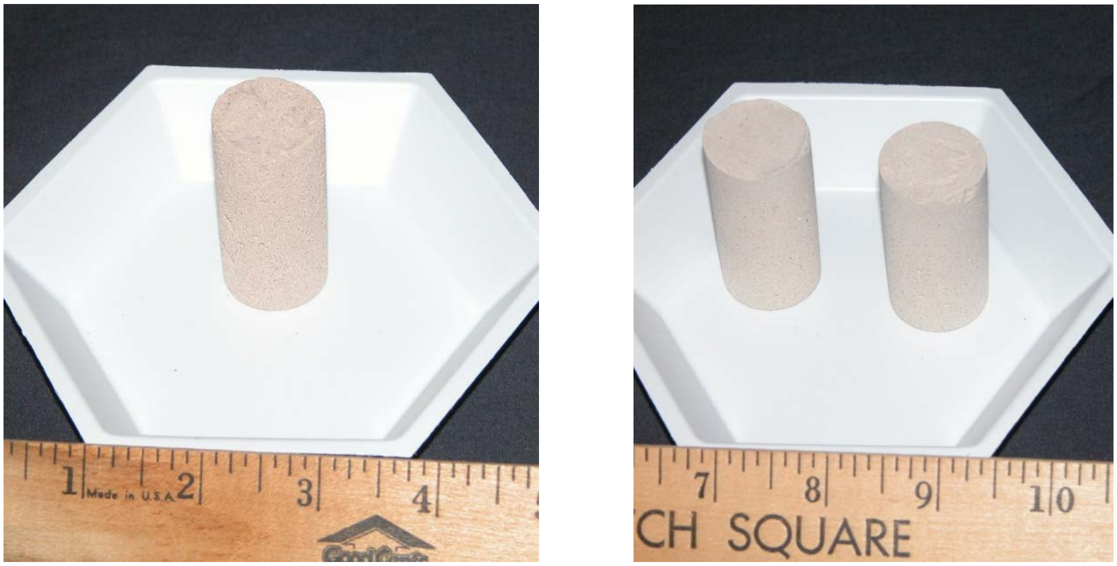
Table 5-23. Compressive Strengths of Geopolymer Monoliths Made with Fly Ash Vs. Clay

Size	Matrix	FBSR Loading (wt%)	Compressive Strength (psi)	Cure Time (days)	Bulk Density (g/cc)
Module B Engineering Scale					
3” x 6” (P-1B GEO-7)	Fly Ash	65	2500	14	1.90
3” x 6” (P-1B GEO-1)	Troy Clay	67	1690	14	1.85
6” x 12” (P-1B GEO-7)	Fly Ash	65	1920	18	NM
6” x 12” (P-1B GEO-1)	Troy Clay	67	1530	14	1.82
1” x 2” (P-1B GEO-7) (See Table 5-21)	Fly Ash	67	681-1099 905 (average of 6)	28	NM
1” x 2” (P-1B Centroid)	Troy Clay	42	4652	7	1.71
1” x 2” (P-1A Centroid)	Troy Clay	42	5844	7	1.72
Module B Bench-Scale Reformer (BSR) Simulant					
1” x 2” (SIM B GEO-7) (See Table 5-22)	Fly Ash	68	750-3550 1700 (average of 4)	29-35	1.88
1” x 2” (SIM B Centroid)	Troy Clay	42	3300	7	1.68
Module A Bench-Scale Reformer (BSR) Simulant (WTP-SW)					
1” x 2” (SIM A Centroid)	Troy Clay	42	4356	7	1.75

NM – Not measured

5.5.2 *ASTM C1308/ANSI/ANS 16.1 Monolith Testing*

Monolith leach testing was performed as given in Table 4-16 and included GEO-7 fly ash formulations with both ESTD and BSR simulants and centroid clay monoliths with both ESTD and BSR simulants. The monoliths were leached at ambient room temperature for the specified intervals and leachate data and cumulative mass fraction leached of the various analytes are shown in Appendix G. Pictures of the monoliths after leaching are provided in Figure 5-19. Mis-formulation of the fly-ash geopolymers is discussed in Section 5.6.4 when the long term PCT testing of these formulations are compared to the centroid clay monolith durability which was correctly formulated (did not contain excess Na_2O).



(a) BSR Module B Clay Monolith at 42% Loading (b) ESTD P-1b Clay Monolith at 42% Loading

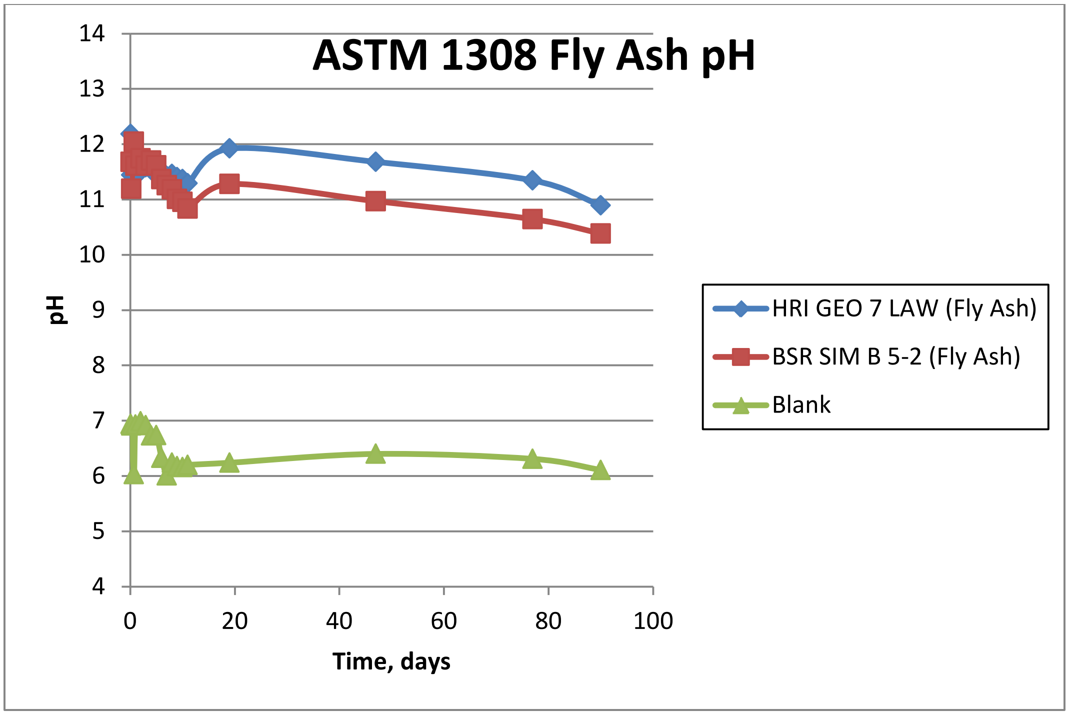
(c) BSR Module B Fly Ash Monolith at 65% Loading

Figure 5-19. Monoliths after ASTM C1308/ANSI/ANS 16.1 Testing

The pH values measured after each leaching interval are shown in Figure 5-20 for the HRI ESTD fly ash (top) and BSR Simulant Module B fly ash (bottom) monoliths. Data for the fly ash pH shown in the top plot of Figure 5-20 indicate that the ESTD fly ash monoliths gave slightly higher leachate pH values and attained a maximum pH of 12 at 19 days versus the fly ash monoliths made with BSR Simulant Module B that are only slightly above a pH of 11 at 19 days. The centroid clay monolith leachate pH data show that the pH initially decreased from starting values of 11.5 down to 10.7 during the first 11 days, then slightly increased during the longer leach interval ending at 19 days, followed by a slight decrease to 11 and finally 10.7 for the 47 day and 91 day cumulative leach intervals. The pH values are also shown for blank solutions of the ASTM Type-I ultrapure water used in these tests which indicate that all blank solutions maintained a pH in the range of 6 to 7.

Representative cumulative leach fraction plots are shown in Figure 5-21 for the fly ash monoliths and Figure 5-22 for the centroid clay monoliths where each plot is plotted on the same scale for ease of interpretation. It is apparent from the Figure 5-21 and Figure 5-22 that P and S are released faster than Na for the ESTD geopolymers made from P-1B and P-1A where the unreacted coal concentrations were higher than in the BSR FBSR products. This indicates that the S released may be coming from the sulfur in the coal. For the BSR simulant monoliths made with fly ash the S comes out slower than the Na (Figure 5-21) and for the BSR simulant monoliths made with clay (Figure 5-22) the S and Na are released at the same concentrations.

Re, Cs, and I are released at about the same concentrations as Si and Al in all monoliths irregardless of FBSR loading or whether the monoliths were made with clay or fly ash (Figure 5-21 and Figure 5-22). This indicates that the Cs is likely tied up in $CsAlSiO_4$ the Cs analog of nepheline and/or in a $(Na,Cs)_6Al_6Si_6O_{24}(NaI)_2$-$(Na,Cs)_6Al_6Si_6O_{24}(NaReO_4)_2$ sodalite solid solution so that the Cs, Re, and I are not released until the aluminosilicate framework structure of the minerals begins to degrade. All of the cumulative fraction leached plots in Figure 5-21 and Figure 5-22 show that steady state releases are reached after about 20 days during ASTM C1308 testing except for the HRI P-1B Geo-7 monolith made with fly ash (Figure 5-21 top).



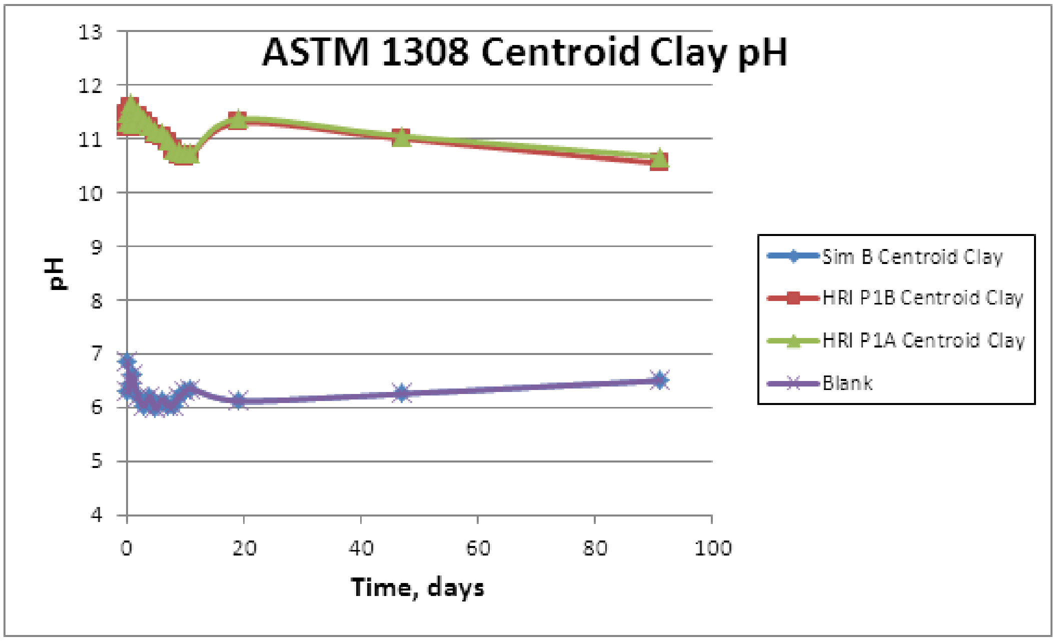
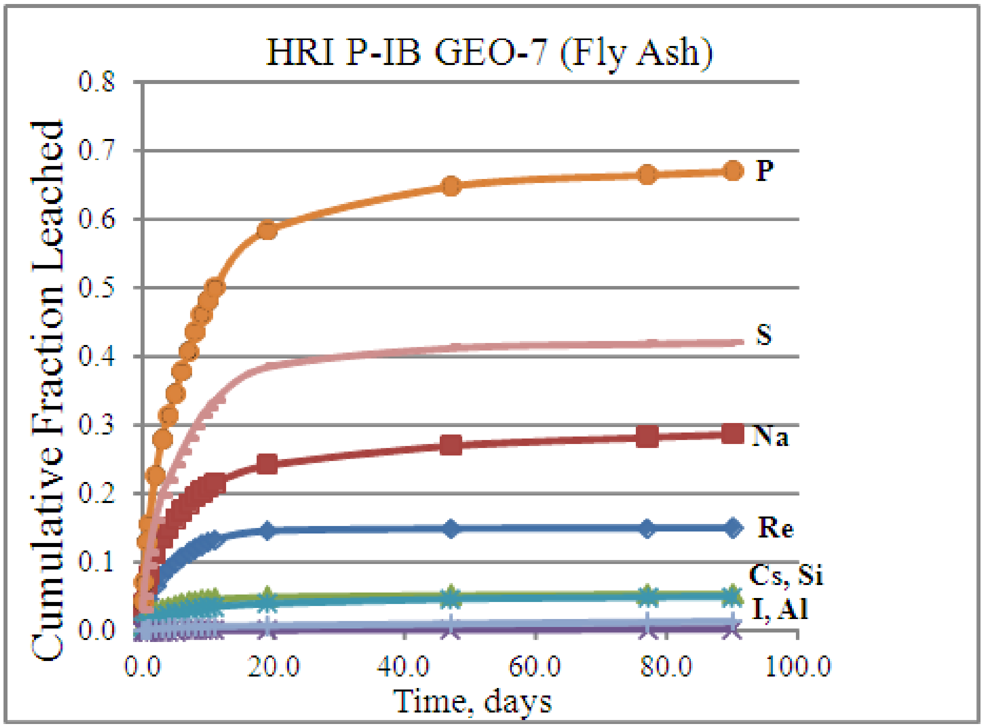


Figure 5-20. Measured pH for ASTM 1308 Leachates



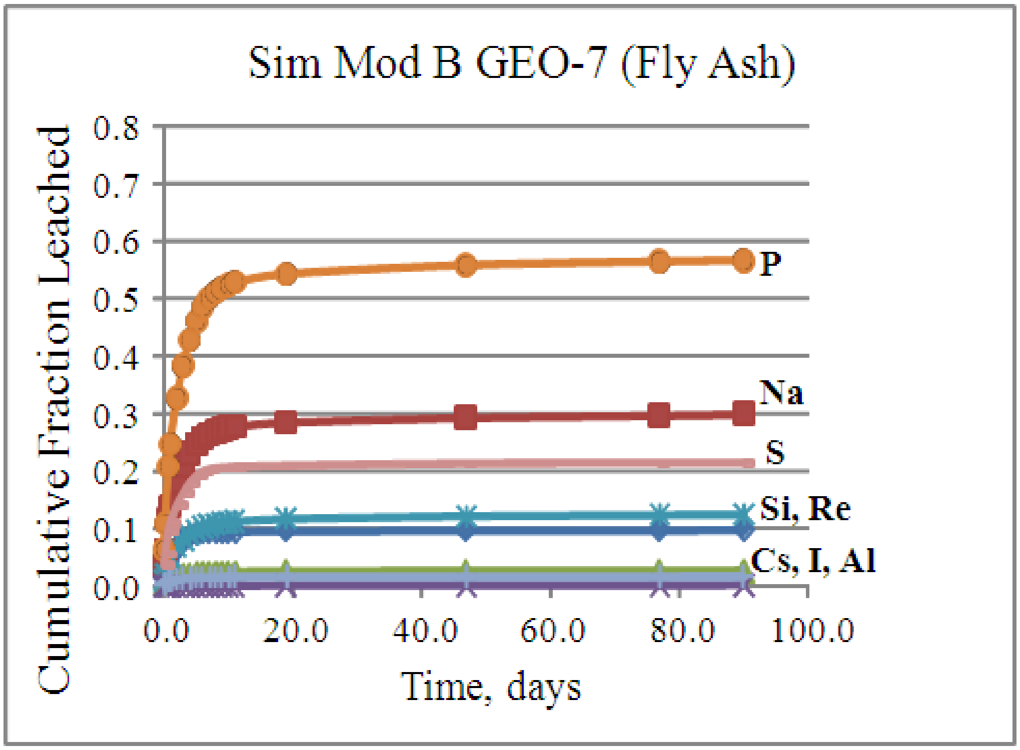


Figure 5-21. Cumulative Fraction Leached for Fly Ash Monoliths

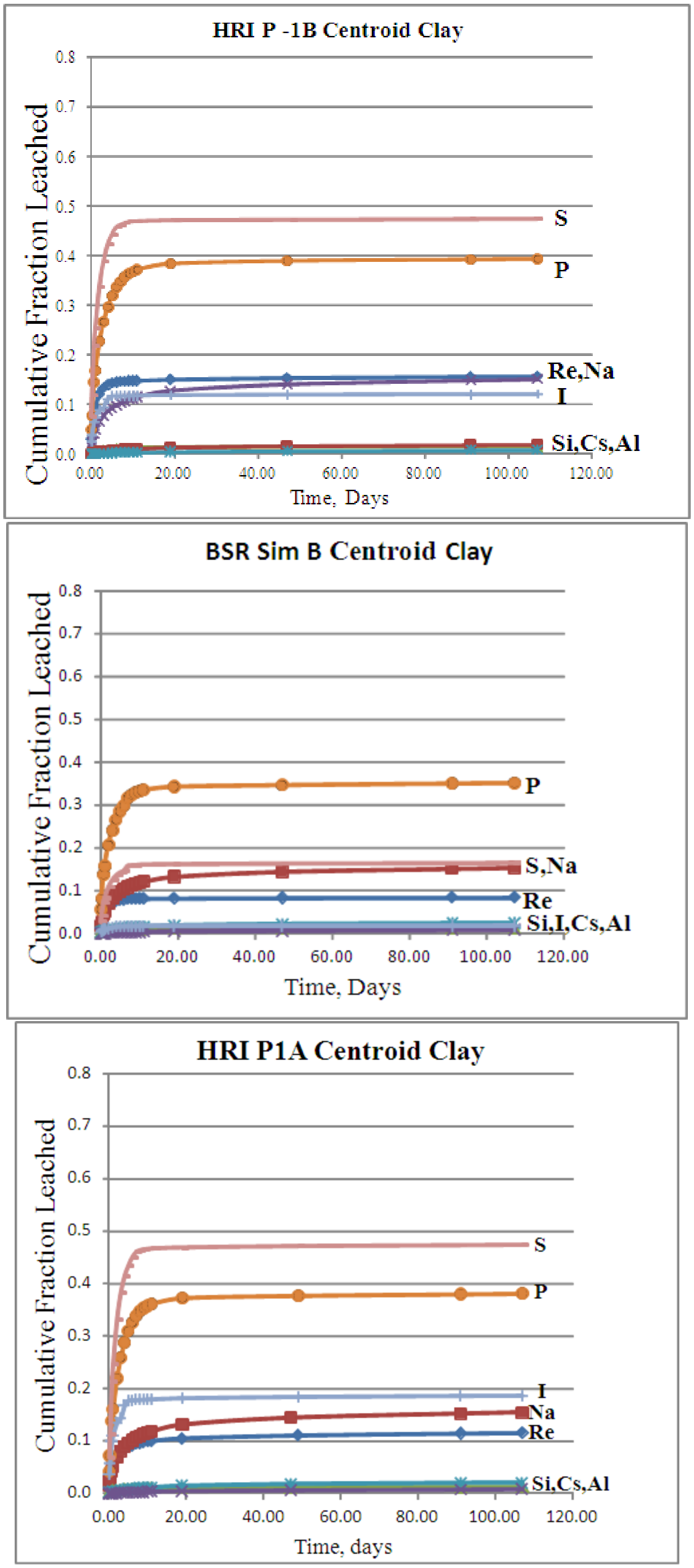


Figure 5-22. Cumulative Fraction Leached for Centroid Clay Monoliths

All of the ASTM 1308 leachate data from the initial testing on the fly ash monoliths (67-68 wt% FBSR loading) and the latter testing on the centroid clay monoliths (42 wt% FBSR loading) were used along with the various C_0 values and monolith densities to calculate the diffusivities using Equation 14 and Equation 15. Details are given in Appendix G and a summary of the calculated Leach Indices (LIs) for Re, Cs, I, and Na are given in Table 5-24.

Table 5-24. Summary Table of Leach Indices for Re, Cs, I, and Na from ASTM C1308 Testing

Monolith	**Geopolymer Binder and FBSR Loading**	**Cumulative Time Days**	**Duplicate Diffusivities Converted to Leach Index (see Equation 14 and Equation 15)**			
			Re	**Cs**	**I**	**Na**
ESTD GEO- 7	**Fly Ash 67% FBSR Loading**	0.0833	8.37	8.87	10.9	7.77
		0.208	8.25	8.82	10.8	7.71
		0.708	8.27	9.08	10.9	7.81
		1	8.25	9.01	11.1	7.79
		2	8.23	9.17	10.8	7.86
		3	8.24	9.23	10.9	7.90
		4	8.49	9.47	11.2	8.08
		5	8.48	9.53	11.2	8.13
		6	8.45	9.56	11.2	8.10
		7	8.52	9.65	11.2	8.16
		8	8.54	9.68	11.1	8.17
		9	8.63	9.81	11.2	8.26
		10	8.76	9.95	11.3	8.35
		11	8.86	10.1	11.2	8.41
		19	9.44	10.7	11.6	8.80
		47	11.4	11.6	11.5	9.48
		77	12.4	12.1	11.4	10.0
		90	12.4	12.1	11.1	10.0
BSR SIM Module B	**Fly Ash 68% BSR Loading**	0.0833	8.22	9.50	9.62	7.40
		0.208	8.10	9.34	9.56	7.26
		0.708	8.19	9.57	9.79	7.33
		1	8.29	9.49	9.95	7.35
		2	8.47	9.73	10.0	7.60
		3	8.44	9.75	10.1	7.72
		4	8.78	9.97	10.4	7.81
		5	9.06	10.2	11.0	7.99
		6	9.49	10.4	11.5	8.25
		7	10.1	10.6	11.5	8.52
		8	10.7	10.8	11.8	8.77
		9	11.2	11.0	11.7	8.97
		10	11.3	11.2	12.0	9.13
		11	11.6	11.3	12.0	9.27
		19	12.0	12.0	13.3	9.89
		47	12.5	12.8	13.8	10.6
		77	13.0	13.1	13.9	11.0
		90	13.1	12.9	13.6	10.7

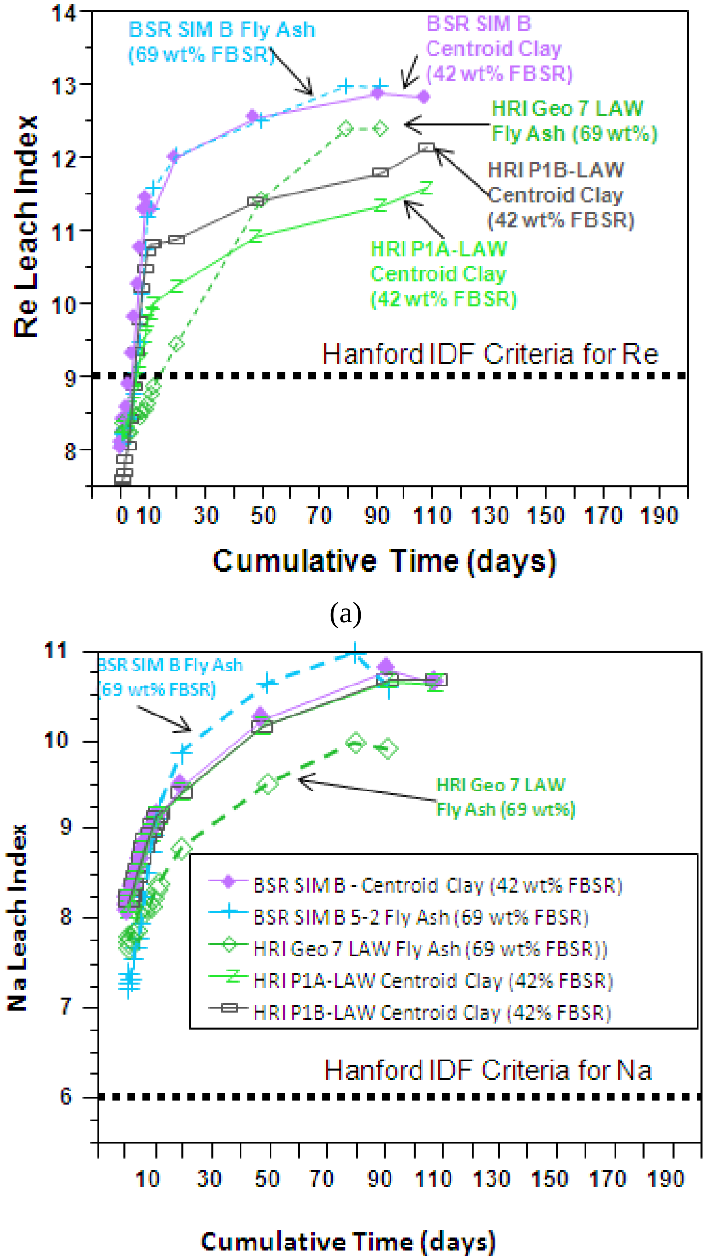
Table 5-24. Summary Table of Leach Indices for Re, Cs, I, and Na from ASTM C1308 Testing (Continued)

Monolith	Geopolymer Binder and FBSR Loading	Cumulative Time Days	Duplicate Diffusivities Converted to Leach Index (see Equation 14 and Equation 15)			
			Re	Cs	I	Na
BSR SIM Module B Centroid Clay	Troy Clay 42% BSR Loading	0.0833	8.04	10.1	9.49	8.10
		0.208	8.12	10.2	9.62	8.16
		0.708	8.24	10.4	9.73	8.25
		1	8.42	10.4	10.0	8.27
		2	8.58	10.7	10.1	8.38
		3	8.89	10.7	10.8	8.44
		4	9.32	10.8	9.76	8.56
		5	9.82	10.9	10.5	8.67
		6	10.3	10.9	11.5	8.76
		7	10.8	11.0	11.4	8.87
		8	11.3	11.1	11.3	8.97
		9	11.4	11.1	11.3	9.04
		10	11.3	11.2	12.0	9.15
		11	11.3	11.3	11.9	9.16
		19	12.0	11.8	13.4	9.51
		47	12.5	12.6	14.2	10.3
		91	12.9	13.2	14.2	10.8
		107	12.8	12.6	13.5	10.7
HRI P-1B Centroid	Troy Clay 42% FBSR Loading	0.0833	7.60	10.2	7.80	8.22
		0.208	7.62	10.2	7.80	8.22
		0.708	7.69	10.3	7.96	8.29
		1	7.87	10.4	8.21	8.30
		2	8.06	10.5	8.48	8.41
		3	8.44	10.7	9.12	8.51
		4	8.87	10.7	8.06	8.60
		5	9.36	10.8	8.84	8.71
		6	9.77	10.7	11.1	8.83
		7	10.2	10.7	11.4	8.93
		8	10.5	10.9	11.6	9.01
		9	10.7	10.9	11.6	9.10
		10	10.8	10.8	11.6	9.20
		11	10.8	11.1	11.7	9.21
		19	10.9	11.6	11.8	9.45
		47	11.4	12.4	12.3	10.2
		91	11.8	13.0	12.7	10.7
		107	12.1	12.5	13.0	10.7

Table 5-24. Summary Table of Leach Indices for Re, Cs, I, and Na from ASTM C1308 Testing (Continued)

Monolith	Geopolymer Binder and FBSR Loading	Cumulative Time Days	Duplicate Diffusivities Converted to Leach Index (see Equation 14 and Equation 15)			
			Re	Cs	I	Na
HRI P-1A Centroid Clay	Troy Clay 42% FBSR Loading	0.0833	8.32	10.3	7.42	8.21
		0.208	8.14	10.2	7.42	8.13
		0.708	8.17	10.4	7.53	8.25
		1	8.33	10.0	8.03	8.25
		2	8.41	10.7	8.10	8.36
		3	8.57	10.8	8.74	8.47
		4	8.79	10.8	7.69	8.57
		5	8.98	10.9	8.44	8.68
		6	9.21	10.9	10.5	8.79
		7	9.40	11.0	10.5	8.90
		8	9.56	11.1	10.9	9.00
		9	9.77	11.2	10.9	9.07
		10	9.87	11.3	10.9	9.17
		11	10.0	11.3	10.9	9.18
		19	10.2	11.8	11.0	9.44
		47	11.0	12.6	11.6	10.2
		91	11.3	13.1	12.0	10.7
		107	11.6	12.9	12.2	10.7

The leach indices for Re and Na are plotted in Figure 5-23. The data in Figure 5-23a show that all the Re leach indices are ≥ 9 after ~5 days for both the fly ash based and the clay based geopolymer monoliths. The ESTD GEO-7 fly ash monolith, which contained excess Na_2O (see Table 4-10) eventually goes to ≥ 9 Re release within ~19 days. The data in Figure 5-23b show that the Na leach indices are >7.75 even after 2 hours of leaching for all the geopolymers whether they are fly ash or clay based geopolymers. The formulations that meet Re>9 and Na>6 are the preferred formulations to meet the performance criteria for the Hanford IDF [75]. More testing with clay based geopolymers at higher FBSR loadings are needed to make a final comparison between using clay based versus fly ash based geopolymers.



(a)

(b)

Figure 5-23. **Log Diffusivity Plots for Re (surrogate for Tc-99) and Na in ASTM C1308 Testing**

Note: Fly ash based geopolymers are fitted with the dashed line and clay based geopolymers are fit with the solid lines.

5.5.3 *Toxicity Characteristic Leaching Procedure (TCLP) for Granular and Monolith Module B (Rassat Simulant)*

Table 5-25 contains the TCLP results for the Module B granular products for all sets of testing with the Rassat material. For comparison, results from granular product reported in Reference

32 for material produced from the HRI/TTT engineering-scale tests and for products from the SAIC-STAR facility are given. The results from the SAIC-STAR facility are provided since they had no IOC versus the HRI/TTT ESTD runs with IOC. The table also includes TCLP analysis performed on the Module B samples by PNNL, including the radioactive Module B granules. Green shaded elements were shimmed in at 10X and yellow shaded elements were shimmed in at 100X the concentrations given in the Rassat simulant recipe (see Table 4-1). All elements failing TCLP at the UTS limits are shown in bold italic print in Table 5-25 and Table 5-26.

Table 5-25. TCLP Results for Granular Product Prepared from Rassat Simulants and Shimmed Tank 50 Radioactive LAW Solutions

Constituent	ESTD Simulant Granular with IOC		BSR Simulant Module B Granular		BSR Radioactive Module B Granular		SAIC-STAR Rassat Simulant Granular		HRI/TTT AN-107 Simulant Granular HRI/TTT [33] with IOC	Reporting Limit (RL)	UTS 40CFR 268.48 (Non-waste water std)
	SRNL[c]	PNNL[b]	SRNL[c]	PNNL[b]	SRNL[c]	PNNL[b]	SRNL[c] [39,40] Bed	SRNL[c] [39,40] Fines			
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sb	***2.13***	0.309 0.334	<MDL	0.009	0.0336 <MDL	0.0394	NM	NM	NM	0.1	1.15
As	<MDL	0.02 0.07	<MDL	0.009	0.00908 <MDL	0.0077 0.0085	NM	NM	NM	0.15	5
Ba	0.283	0.20 0.23	0.0394[J]	0.246 0.263	0.059 <MDL	0.066 0.142	0.069[a]	0.17[a]	NM	0.05	21
Cd	***1.02***	3.040 3.240	<MDL	<MDL	<MDL	0.00107	NM	NM	NM	0.05	0.11
Cr	<MDL	0.048 0.078	***1.35***	***1.09*** ***1.30***	0.310	0.074 0.083	***9.2***	***8.4***	0.015 0.06	0.05	0.6
Pb	<MDL	0.064 0.108	0.0475[J]	0.0076 0.05	0.0888[J]	0.01315	0.046[a]	<0.0310	0.002 0.067	0.1	0.75
Se	0.373	0.341 0.427	1.12	1.14 1.29	0.508	0.192 0.195	NM	NM	NM	0.15	5.7
Ag	<MDL	<MDL	0.0115[J]	0.0003 0.001	0.00339 <MDL	0.000389	NM	NM	NM	0.05	0.14
Hg	<MDL	0.000012 0.000026[J]	<MDL	<MDL	<MDL	0.004 0.013	NM	NM	NM	0.002	0.025
Ni	0.567	1.57 1.61	0.0249[J]	0.0229 0.0278	0.0083 <MDL	<MDL	NM	NM	NM	0.05	11
Tl	<MDL	NM	<MDL	NM	<MDL	<MDL	NM	NM	NM	0.2	0.2
Zn	0.0379[J]	0.151 0.183	0.0957[J]	0.272 0.325	0.0662[J]	<MDL	NM	NM	NM	0.1	4.3

Notes: Green shaded boxes were shimmed 10X and yellow shaded were shimmed 100X. MDL is the Method Detection Limit; NM is not measured. J indicates a detected value that was below quantitative limit. Where duplicate measurements were different, both values are reported. [a] Result is above method detection limit, but below reporting limit (reporting limit is 0.02 mg/L for Hg, and 1.0 g/L for the other metals). [b] PNNL performed the TCLP in Washington at the Coastal Biogeochemistry Group at the MSL maintains national accreditation for its analytical services work with NTI (formerly called NELAC) (http://www.nelac-institute.org/index.php). MSL's accreditation is through the State of new Jersey, Department of Environmental Protection (Laboratory Certification ID# WA004). Among the analyses that MSL has accreditation for is the TCLP of wastes and soils for the analysis of metals. [c] SRNL performed TCLP in South Carolina with the General Engineering Laboratory in Charleston.

Analytes detected but at concentrations too low to determine quantitatively have been flagged with the "J" qualifier. The engineering-scale ESTD samples were found to be above the Universal Treatment Standards (UTS) limits for Sb and Cd by the South Carolina GEL laboratory but below the UTS by the PNNL laboratory.[ii] In the salt solution used to make these samples, these elements had been shimmed into the HRI/TTT simulant at 10X the concentration anticipated. During the engineering-scale experiments, the excess precipitates that were formed when the solubility for these RCRA elements were exceeded, were not filtered out as was done in the BSR simulants when the precipitates were observed (see Section 4.2.1). Recall that the Sb precipitated as insoluble sodium antimony (+5) hydroxide (see Section 4.2.1) in the BSR simulants and was removed through filtration. The BSR granular products all passed TCLP below the UTS for Sb and Cd as these species are below their solubility limit in the granular FBSR products. Since antimony will not be present in the excessive amounts in LAW that they were in the engineering-scale ESTD TCLP results, these observations are considered not applicable.

The only remaining element that failed the TCLP at or below the UTS was Cr. SRNL and PNNL analyses identified a chromium concentration greater than the UTS limit. However, the granular product made using radioactive waste (Module B) passed TCLP for all contaminants of concern including chromium. It should be noted that in the engineering-scale tests IOC was used and this provided an insoluble spinel host phase for the Cr but the IOC was not used in the BSR Module B testing. It is apparent in Table 5-25 that when the IOC is present that elements such as Cr and Pb are sequestered in the spinel structure of the IOC. Conversely, for the columns of data tabulated for the granular product when IOC was not added to the process, almost all do not meet the UTS for Cr. Since the IOC is a process additive to enhance denitration, it can easily be added as a co-reactant. The IOC should be added to sequester all RCRA metals in future studies.

Table 5-26 contains the TCLP results for the monolith prepared with the engineering scale P-1B LAW and the SRS Module B simulant FBSR granular product. In monolith testing of these geopolymers the Sb and Cd are still released at greater than the UTS for the ESTD samples, i.e. only when they were shimmed into the FBSR product in excess of their solubility limit. When the granular sample was tested after monolithing, the chromium release was reduced by greater than 10x and is now 10x below the UTS limit. Therefore, monolithing appears to help minimize Cr release in samples that were not processed with the IOC where the IOC would have provided a host mineral phase for these species.

[ii] Note that PNNL performed the TCLP in Washington at the Coastal Biogeochemistry Group at the Marine Science Laboratory (MSL). The MSL maintains national accreditation for its analytical services work with NTI (formerly called NELAC) (http://www.nelac-institute.org/index.php). MSL's accreditation is through the State of New Jersey, Department of Environmental Protection (Laboratory Certification ID# WA004). Among the analyses that MSL has accreditation for is the Toxicity Characteristic Leaching Procedure (TCLP) of wastes and soils for the analysis of metals.

Table 5-26. TCLP Results for Monoliths Prepared with Simulant Rassat FBSR Product and Fly Ash

Constituent	ESTD Simulant Monolith GEO-7 (67% FBSR loading with Fly Ash)		BSR Simulant Module B Monolith GEO-7 (68% FBSR loading with Fly Ash)		BSR Radioactive Module B Monolith (42% FBSR loading with Kaolin)	BSR Radioactive Module B Monolith (65% FBSR loading with Kaolin)	Reporting Limit (RI)	UTS 40CFR 268.48 (Non-waste water standard)
	SRNL	PNNL	SRNL	PNNL	SRNL	SRNL		
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sb	***2.32***	0.88 1.13	<MDL	0.0165 0.019	0.046^J	0.0298 <MDL	0.1	1.15
As	3.07	1.89 2.05	2.48	2.16 2.32	0.00117 <MDL	0.059^J	0.15	5
Ba	0.601	0.081 0.091	<MDL	0.132 0.179	0.278	0.257	0.05	21
Cd	***0.134***	0.009 0.027	<MDL	0.0005 0.0006	<MDL	0.00126 <MDL	0.05	0.11
Cr	0.112	0.035 0.056	<MDL	0.055 0.075	0.106	0.256	0.05	0.6
Pb	0.703	0.135 0.171	0.0473^J	0.109 0.189	0.052^J	0.0697^J	0.1	0.75
Se	0.692	0.99 1.20	<MDL	0.443 0.473	0.207^J	0.263^J	0.15	5.7
Ag	<MDL	<MDL	0.0133^J	0.0003 0.0004	0.00041 <MDL	0.00907 <MDL	0.05	0.14
Hg	NM	<MDL	<MDL	0.00005	<MDL	<MDL	0.002	0.025
Ni	0.0845	0.023 0.033	<MDL	0.0105 0.0139	0.00598 <MDL	0.0142 <MDL	0.05	11
Tl	<MDL	NM	<MDL	NM	<MDL	0.0067 <MDL	0.2	0.2
Zn	0.0694	0.024 0.113	<MDL	0.08 0.0989	0.0277 <MDL	0.111	0.1	4.3

Green shaded boxes were shimmed 10X and yellow shaded were shimmed 100X. MDL is the Method Detection Limit; NM is not measured. J indicates a detected value that was below quantitative limit. Where duplicate measurements were different, both values are reported.

5.6 Wasteform Performance Testing Results

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

The 7-day PCT was conducted on the ESTD LAW P-1B Rassat FBSR granular product and BSR Module B Rassat simulant and radioactive Tank 50 Rassat BSR products as described in Section 4.8.1. Data from Module B provides a comparison with PCT results from prior pilot-scale tests at INL and engineering-scale tests at TTT/HRI (ESTD) with simulants. All data is provided in Table 5-27 and the raw data for the short term PCT tests on the FBSR granular products are given in Appendix H. All the release rates are below 2 g/m^2. Rhenium was added to the Module B radioactive Tank 50 salt solution 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 5-27, the release of rhenium is consistent among the three granular products made from similar salt solutions using the ESTD FBSR, the non-radioactive BSR, and the radioactive BSR as well as with Tc-99. 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.[86]

Table 5-27. 7-Day PCT Results for Granular Product Prepared from FBSR Product Made from the Rassat Simulant and Tank 50 Shimmed Radioactive Waste

Normalized Elemental Release	ESTD P-1B Granular		BSR Module B Simulant Granular		BSR Module B Radioactive Granular	
	(g/m^2)	Std. Dev.	(g/m^2)	Std. Dev.	(g/m^2)	Std. Dev.
Al	2.12E-03	2.01E-06	2.34E-03	7.09E-05	3.97E-03	1.33E-04
S	3.42E-01	2.17E-03	4.34E-02	1.59E-03	7.72E-02	1.47E-03
Cs-133	9.31E-03	8.78E-05	1.09E-02	2.36E-04		
Cs-137					2.29E-03	1.71E-04
Re	4.10E-03	4.07E-04	8.83E-03	3.45E-04	1.13E-02	1.22E-03
Tc-99					2.42E-02	5.86E-03
Na	2.15E-02	2.40E-04	1.14E-02	4.73E-04	1.24E-02	3.96E-04
Si	7.82E-04	2.50E-05	9.86E-04	4.71E-05	6.17E-04	4.83E-05
I-127	1.51E-02	4.13E-04	9.82E-04	1.06E-03	1.69E-03	8.04E-05
I-129					<3.61E-03	N/A
pH	11.63 (Blend)		11.4		11.25	

N/A = Not Applicable

The short term PCT leachate data are shown graphically in Figure 5-24. These short-term PCT data are in agreement with the data generated in 2001 on AN-107, the 2004 SAIC-STAR facility samples with the Rassat simulant. The correlations shown in Figure 5-24 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 Product Receipt, PR, 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 (PR and HTF) 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 5-24 are plotted as the log of the release rates shown in Table 5-27.

As with the 2001 and 2004 data, the pH increases (becomes more caustic) as the surface area of the material is decreased (see Figure 5-24a). For glass waste forms, pH usually increases with increasing surface area. This indicates that a buffering mechanism is occurring. Based on the trend of alkali (Na) release being co-linear with Al release (Figure 5-24b) 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 5-24b and f. All the other cations appear to be released as a function of the solution pH (Figure 5-24c, 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.[52,75,86,114]

The Re release plot for the BSR (radioactive and simulant Module B), the 2008 engineering scale, and the historic data appear in Figure 5-24d. Due to the low concentrations of rhenium, it is a difficult element to measure. It is noteworthy that the Re release from the Module B simulant PCT tracks close to the Re release measured at SRNL for the radioactive Module B granular product. Note that the simulant Module B Re release tracks with the radioactive Tc-99 release. This demonstrates that Re and Tc-99 release is within experimental error of one another. 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.

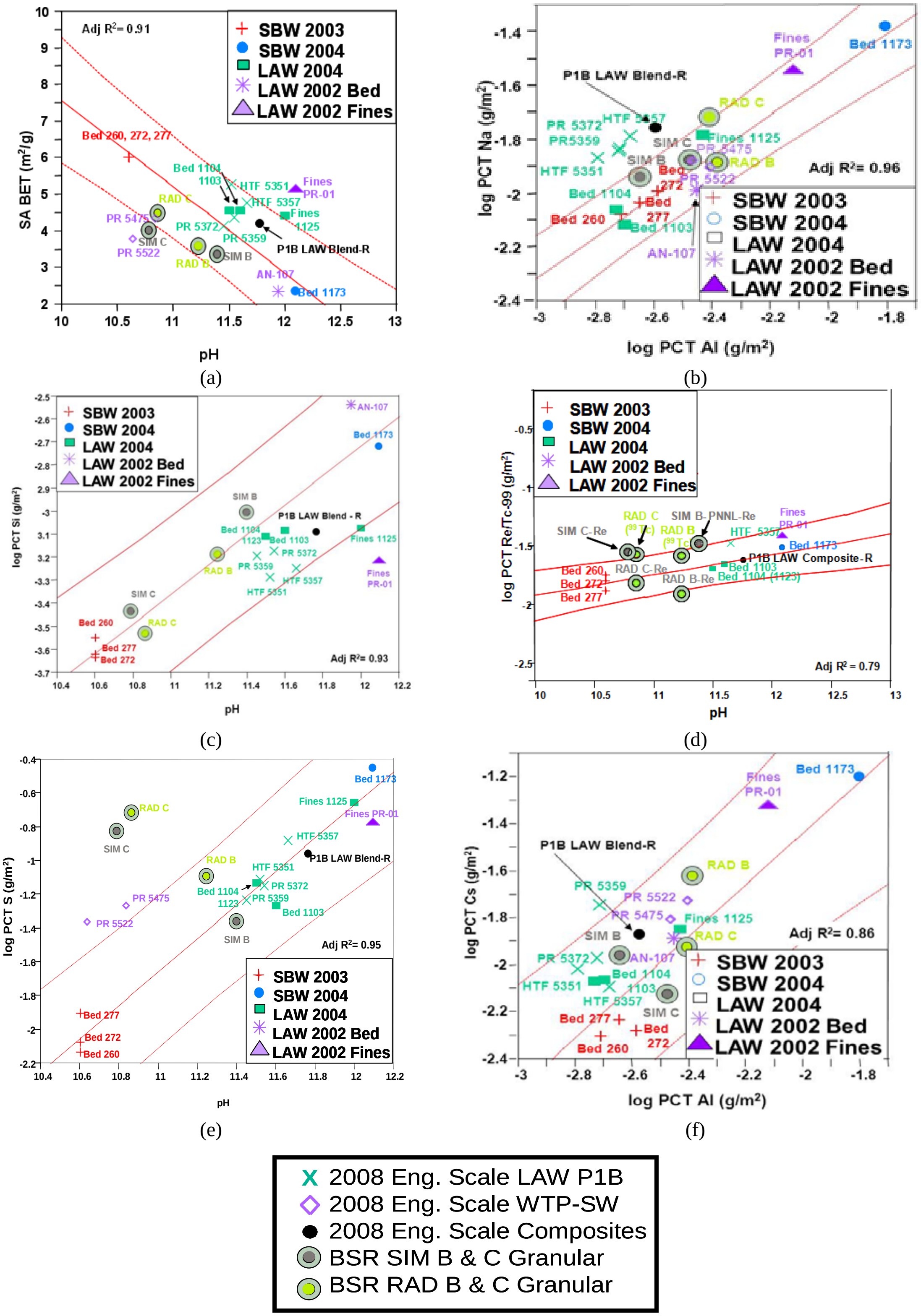


Figure 5-24. Short Term PCT Testing (ASTM C1285) Correlation Developed with INL Pilot-scale Test Results with Rassat Simulant from 2003-2004, and HRI/TTT Testing of LAW AN-107 Samples from 2001-2002 Testing with Current Module B PCT data from Engineering Scale ESTD samples and BSR samples Modules B and C (non-radioactive and radioactive).

5.6.2 *Product Consistency Test (PCT) – Short Term on FBSR Monoliths*

The 7-day PCT was conducted on the Engineering scale LAW P-1B GEO-7 and the Module B simulant GEO-7 monoliths made with Fly Ash at 67-68 wt% FBSR loading and on the radioactive monoliths made at 42 wt% waste loading and 65% FBSR loading. The leachates were only analyzed for the 65 wt% FBSR loaded monolith and the leachates from the 42 wt% FBSR loaded monolith were archived (see footnote to Table 4-16). The results for the PCT of the engineering scale P-1B and Module B simulant monolith are shown in Table 5-28, and the raw data for the short term PCT monolith tests are given in Appendix H. The granular PCT results from Table 5-27 are repeated in Table 5-28 for comparison. As can be seen from the data in Table 5-28, the release of rhenium is consistent among the monolith and granular products made from similar salt solutions.

Table 5-28. 7-Day PCT Results for Monoliths and Granules Prepared from Engineering Scale FBSR and Module B Simulants

Normalized Elemental Release (g/m^2)	Non-Radioactive				Radioactive	
	Fly Ash ESTD P-1B* GEO-7 Monolith (67% FBSR loading)	Fly Ash BSR Mod B GEO-7 Monolith (68% FBSR loading)	ESTD P-1B Granular	BSR Mod B Granular	BSR Mod B Clay Monolith (65% FBSR loading)	BSR Mod B Granular
Al	4.30E-05	4.47E-04	2.12E-03	2.34E-03	2.60E-04	3.97E-03
S	4.78E-02	1.02E-01	1.41E-01	4.34E-02	3.20E-02	7.72E-02
Cs-133	2.01E-03	4.60E-03	9.31E-03	1.09E-02		
Cs-137					7.00E-05[**]	2.29E-03
Re	1.05E-02	1.99E-02	1.87E-02	8.83E-03	3.96E-03	1.13E-02
Tc-99					<8.35E-03	2.42E-02
Na	2.15E-02	7.30E-02	1.74E-02	1.14E-02	1.81E-02	1.24E-02
Si	2.70E-03	7.02E-03	7.82E-04	9.86E-04	2.40E-04	6.17E-04
I-127	5.27E-03	3.61E-03	1.51E-02	9.82E-04	5.00-E-04	1.69E-03
I-129					<3.23E-03	<3.61E-03
pH	12.39	12.56	11.63	11.40	10.33	11.25

* The elemental composition of the ESTD LAW P-1B monolith made with fly ash was reported in Table 37 of Reference 32.

** The Cs-137 value is result of only single detectable value from triplicate PCT leachates.

5.6.3 *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. All of the raw data for the long term PCT testing of the granular products are given in Appendix H.

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.

Table 5-29 contains the PCT results for the engineering scale FBSR product of the LAW P-1B run at HRI and tracks the release rate of analytes as a function of time. PCT samples of the P-1B simulant granular product were leached for extended times. The 7-day results from Table 5-29 are shown with release results from samples leached for 1, 3, 6 and 12 months in Figure 5-25. For each of the elements analyzed, the release was consistent over the 1 year of testing. Silicon release was decreasing indicating solution saturation. Cesium release was decreasing as the silicon release was decreasing. Releases of other species held constant over the one year of testing indicating that the FBSR granular product was not undergoing a significant degradation. Re, I and Na were all released at about the same rate.

Table 5-29. Long Term PCT Results for the Engineering Scale LAW P-1B Granular Product

Normalized Elemental Release (g/m^2)	Eng. Scale P-1B granular Test Interval				
	7 Days	1 Month	3 Month	6 Month	1 Year
Al	2.12E-03	2.86E-03	2.86E-03	2.93E-03	2.08E-03
S	1.41E-01	1.91E-01	1.42E-01	1.85E-01	1.61E-01
Cs	9.31E-03	1.66E-02	1.21E-02	1.58E-02	4.09E-03
Re	1.87E-02	3.56E-02	3.22E-02	3.92E-02	3.57E-02
Na	1.74E-02	2.53E-02	2.52E-02	2.94E-02	3.64E-02
Si	7.82E-04	6.84E-04	4.75E-04	3.39E-04	1.10E-04
I	1.51E-02	2.71E-02	2.59E-02	2.92E-02	2.79E-02
pH	11.63	11.65	11.50	11.43	10.29

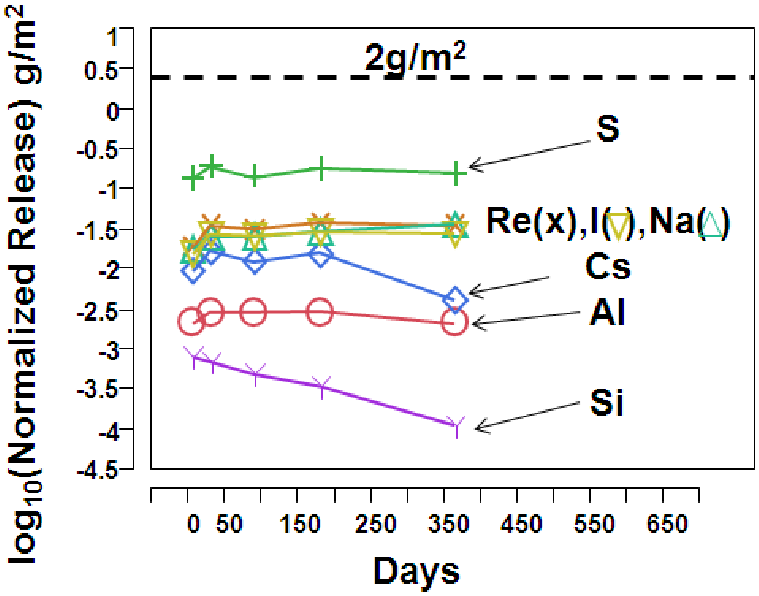


Figure 5-25. Release of Elements from P-1B ESTD Non-radioactive Rassat Simulant during 7 day, 1 month, 3 month, 6 month and 12 month Long Term PCT Testing

Figure 5-26 is an overlay of the XRD patterns of the ESTD FBSR LAW granules as received and after each 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 5-25.

Only one reaction product was noted in the XRD pattern, halloysite, indicated by the circle in Figure 5-26. Halloysite can form from many aluminosilicates and is the metastable reaction product that eventually forms kaolin clay. In other words, halloysite is the main metastable reaction product that on geologic time scales converts to a kaolin clay reaction product.[115,116] This indicates that excess and/or unreacted clay in the FBSR granular product may be degrading with time rather than the mineral phases formed during the FBSR processing or the aluminosilicates are degrading and forming halloysite, which on geologic time scales will revert back to kaolin clay as a reaction product. However, since halloysite is only seen in the ESTD leaching experiments when >10% excess kaolin was present and not in the BSR experiments where <5 wt% excess kaolin was present, it is most likely that the halloysite formed from the excess clay. The diaoyudaoite seen in only one spectra is a mineral previously found in the ESTD FBSR products.[39,40]

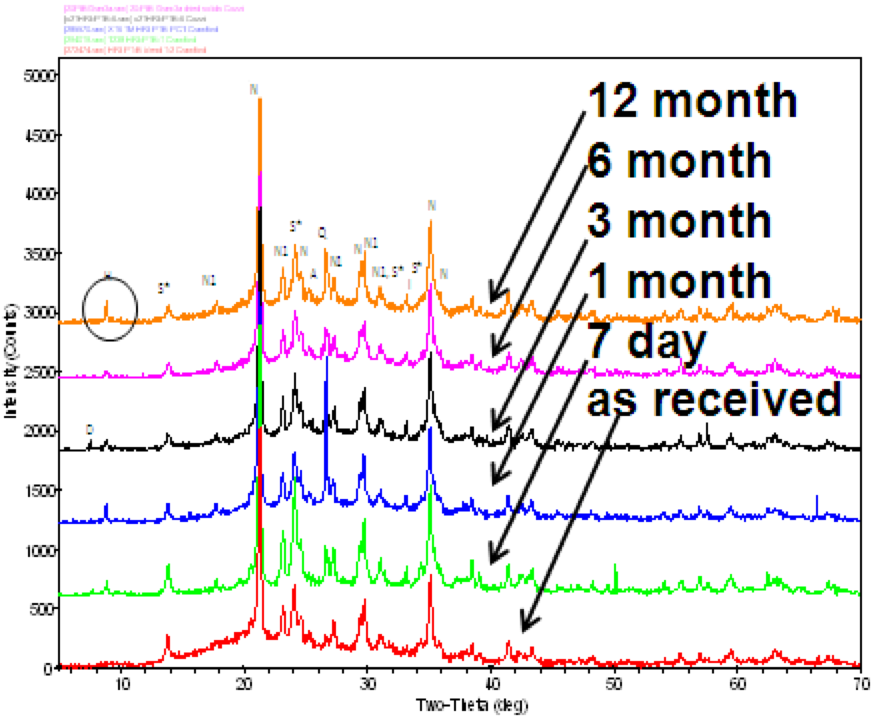


Figure 5-26. XRD Patterns of FBSR LAW P-1B Granules As-Received and After PCT Leaching

N1 is Nepheline (O) $NaAlSiO_4$ (PDF 00-052-1342)
N is Nepheline (H) either $NaAlSiO_4$ (PDF 00-035-0424 top spectra)
S* is Sodalite (cubic) $Na_6Al_6Si_6O_{24}$ (PDF 00-042-0217)
A is Anatase, TiO_2 (PDF 00-021-1272)
Q is Quartz, SiO_2 (PDF 00-046-1045)
H is Halloysite, $Al_2Si_2O_5(OH)_4 \bullet 2H_2O$ (PDF 00-029-1489)
D is Diaoyudaoite, $NaAlO_{17}$, (PDF 00-021-1096)
Original XRD spectra fits are in Appendix I

For the BSR Module B granular product, the 7-day results are shown with release results from samples leached for 1, 3, 6 and 12 months in Table 5-30 and Figure 5-27. For each of the elements analyzed, the release was consistent over the 1 year of testing. Silicon release was decreasing, while the other releases have held constant over the one year of testing indicating that the FBSR granular product was not undergoing significant degradation of the mineral species. Re, Cs and Na were all released at about the same rate with Na bounding the other releases. The sample REDOX was >0.36 $Fe^{2+}/\Sigma Fe$ and indicates that iodine from more oxidized samples leaches less than in the more reduced P-1B sample.

Table 5-30. Long Term PCT Results for the Bench Scale Module B Simulant Granular Product

Normalized Elemental Release (g/m^2)	Bench-Scale B Simulant Granular Test Interval				
	7 Days	**1 Month**	**3 Month**	**6 Month**	**1 Year**
Al	2.34E-03	2.32E-03	2.19E-03	2.30E-03	2.10E-03
S	4.34E-02	4.74E-02	5.04E-02	5.36E-02	6.00E-02
Cs	1.09E-02	NM	9.84E-03	8.05E-03	1.11E-02
Re	8.83E-03	8.65E-03	9.23E-03	9.86E-03	1.06E-02
Na	1.14E-02	1.22E-02	1.45E-02	1.66E-02	1.91E-02
Si	9.86E-04	8.24E-04	5.52E-04	3.32E-04	2.00E-04
I	9.82E-04	2.18E-03	2.19E-03	2.34E-03	2.10E-03
pH	11.40	11.10	10.48	10.01	10.30

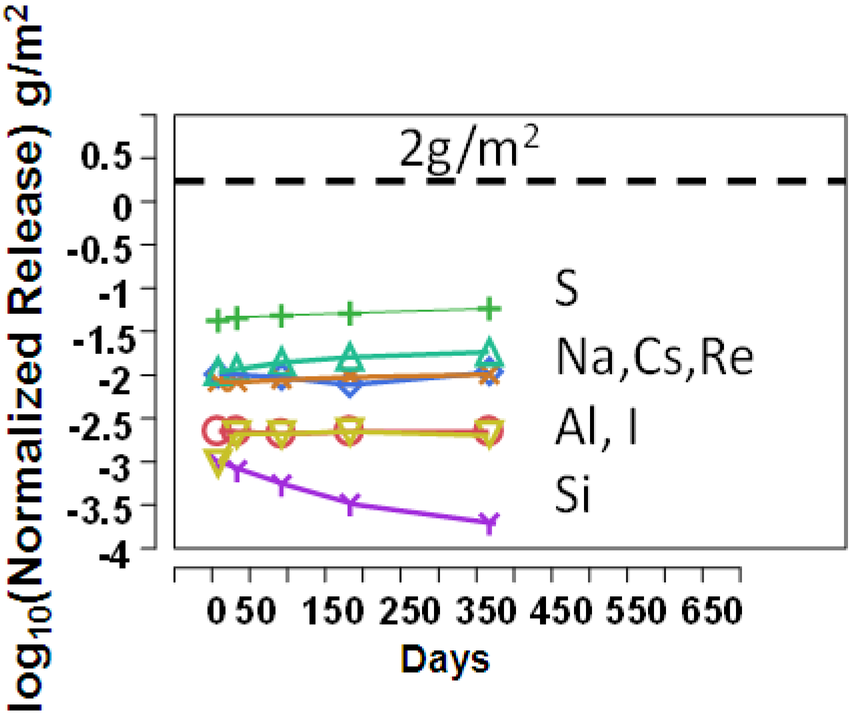


Figure 5-27. Release of Elements from BSR Simulant Module B during 7 day, 1 month, 3 month, 6 month and 12 month Long Term PCT Testing

Figure 5-28 is an overlay of the XRD patterns of the Module B simulant BSR product granules as prepared for PCT and after each 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. As with the FBSR LAW P-1B waste forms, the intensity and width of the major phases persist through all the leach intervals, indicating minimal degradation of the minerals. No reaction products were observed in any of the powders after the long leaching intervals as with the 1 year ESTD P-1B sample. This is likely because the BSR granules are completely reacted in the small chamber of the BSR.

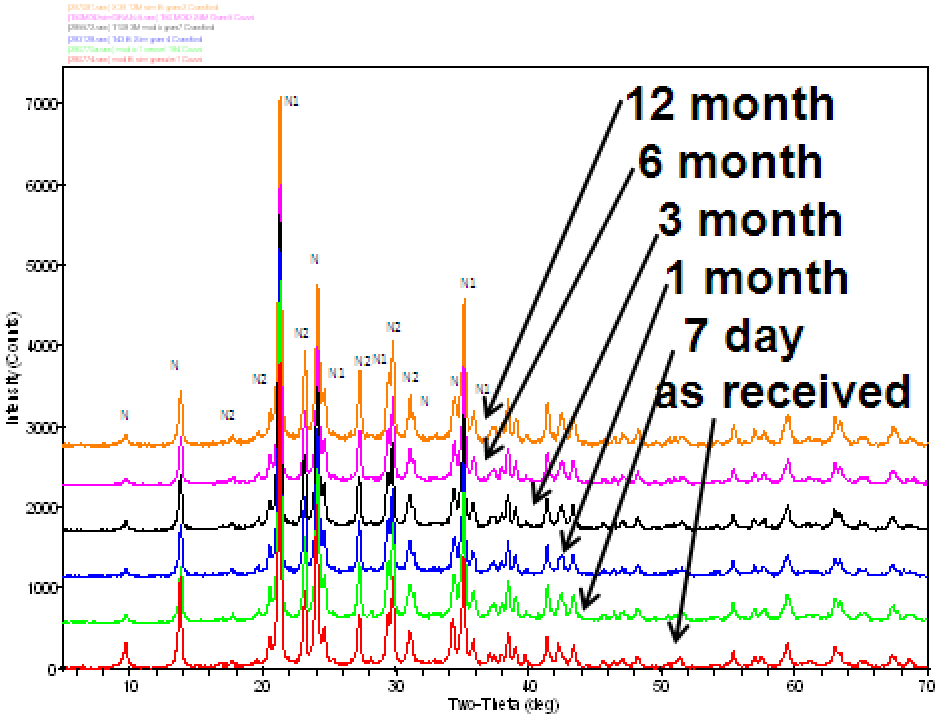


Figure 5-28. XRD Patterns of BSR Simulant Module B Granules As-Made and After PCT Leaching

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

For the Module B 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 and Figure 5-29. 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 consistent over the 1 year of testing. 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 and Na were released at the same rate, which is similar to their congruent release with each other in glass. The sample REDOX was >0.41 $Fe^{2+}/\Sigma Fe$, which was similar to the 0.36 of the non-radioactive BSR samples. Iodine release rates were again lower than in the engineering scale P-1B sample, which was more reduced indicating that iodine release may be lower from more oxidized samples.

Table 5-31. Long Term PCT Results for the Module B Radioactive Granular Product

Normalized Elemental Release (g/m^2)	BSR Rad B granular Test Interval			
	7 Days	**1 Month**	**3 Month**	**1 Year**
Al	3.97E-03	4.32E-03	4.39E-03	5.04E-03
S	7.72E-02	7.96E-02	9.14E-02	9.41E-02
Cs-137	2.29E-03	4.89E-03	4.18E-03	3.61E-03
Re	1.13E-02	9.26E-03	9.66E-03	1.12E-02
Na	1.24E-02	1.59E-02	1.76E-02	2.36E-02
Si	6.17E-04	6.39E-04	4.82E-04	3.30E-04
I-127	1.69E-03	1.61E-03	1.77E-03	2.16E-03
Tc-99	2.42E-02	<1.56E-02	1.96E-02	2.73E-02
I-125	<1.01E-01	<1.43E-02	<1.30E-02	<9.40E-01*
I-129	<3.61E-03	<2.92E-03	1.77E-03	<3.79E-03
pH	11.25	11.45	10.79	10.16

*Due to 60-day half life of I-125, the concentration at the 1-year interval had undergone numerous half lifes and is a very small concentration for the normalization [f_i – see section 4.8.1]

Figure 5-30 is an overlay of the XRD patterns of the Module B radioactive granular product as received and after each 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 (nosean/sodalite, the two varieties of nepheline) from the BSR campaigns (radioactive Module B and non-radioactive Module B) appear in the XRD spectra and there are no reaction products present. The sodalite is reported as 42-0217 as in Figure 5-28 and is anhydrous. A hydrous sodalite pattern exists (42-0216) and the two structures are related and reported in the same reference by the same researchers. The sodalite in PDF 42-0217 states that the anhydrous sodalite was prepared from a hydrated sodalite with 8 waters of hydration but that the sodalite prepared in PDF 42-0216 cannot be made that way and had to be prepared by slow rehydration of the anhydrous sodalite over a $NaNO_2$ solution at 65% relative humidity. Given that the sodalite formed over the $NaNO_2$ solution is not relative to the leaching scenario of the BSR product in deionized water, it is unlikely that the hydrated sodalite (PDF 42-0216) forms, otherwise it would contain 8 waters of hydration, which the XRD pattern fit does not support.

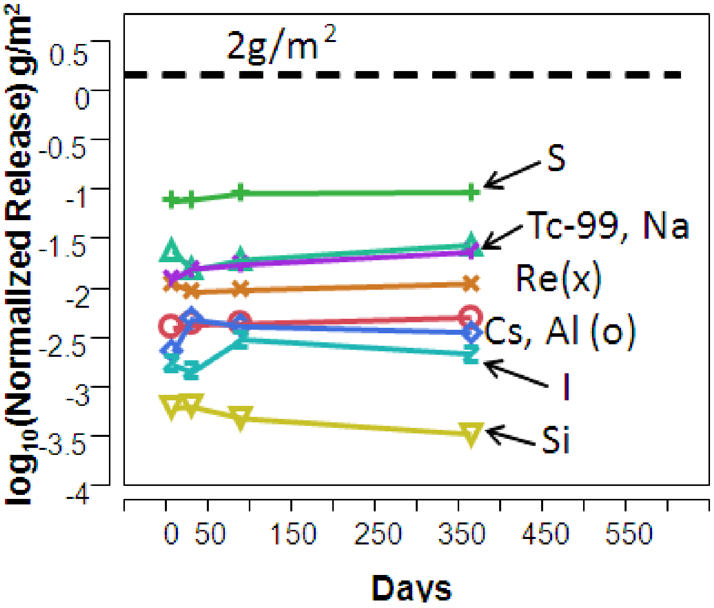


Figure 5-29. Release of Elements from BSR Radioactive Module B Granular Product during 7 day, 1 month, 3 month and 12 month Long Term PCT Testing

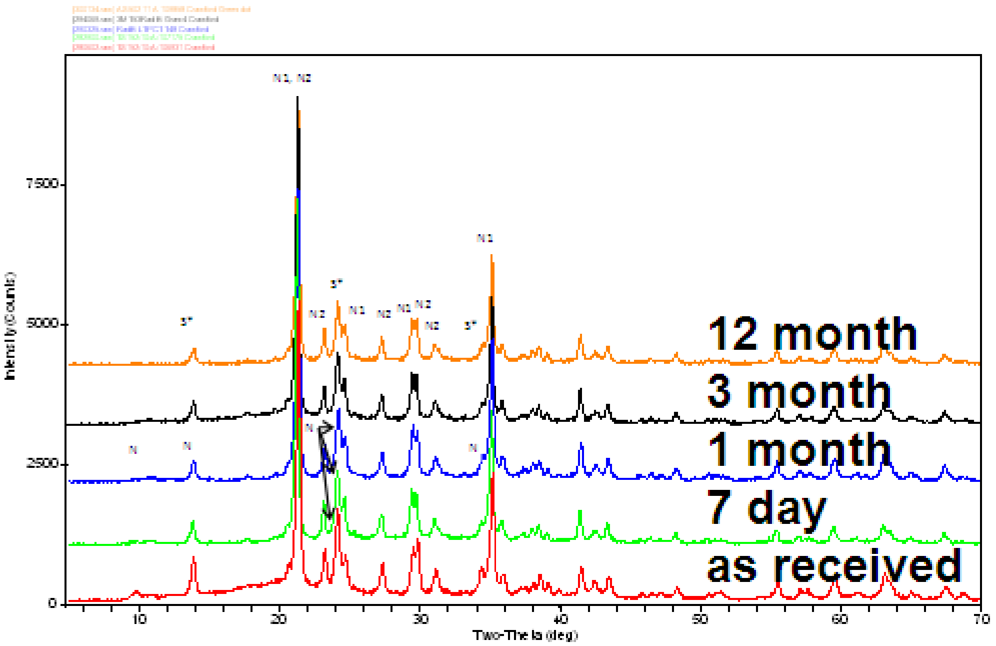


Figure 5-30. XRD patterns of Module B Radioactive Granules As-Made and After Long – Term PCT Leaching

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
N is Nosean (cubic) $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
S* is Sodalite $Na_6(AlSiO_4)_6$ (PDF 00-042-0217)
Original XRD spectra fits are in Appendix I

Nephelines are known to have survived anywhere from 879-1169 million years in nature as measured by K-Ar dating.[117] Weathering products from natural nepheline include but are not limited to analcite ($NaAlSi_2O_6$), boehmite (AlOOH), hydronepheline (nepheline with attached water molecules), kaolinite, muscovite, natrolite, and/or sodalite.[117] Thus, 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.

5.6.4 *Product Consistency Test (PCT) – Long Term on FBSR Monoliths*

Long term PCT-B testing was also performed on GEO-7 monoliths made from the ESTD granular non-radioactive product and the BSR granular non-radioactive product. Samples were collected at one month, three month, six month, and one year intervals. All of the raw data for the long term PCT tests on the monoliths are given in Appendix H.

As with the long term PCT-B tests on the granular products, the long term PCT tests on the monolithic products 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.

Table 5-32 provides the PCT results over the PCT duration for the GEO-7 monolith prepared with the engineering scale FBSR product of the LAW P-1B run at HRI using the fly ash formulation. For each of the elements analyzed, the release was consistent over the duration of testing. Comparisons of the one year releases from the monolith samples (Table 5-32) to the granular product releases (Table 5-29) shows that the monolith releases are about an order of magnitude lower for S, R, I, Cs, Na, Al, and Si than the granular product releases due to the encapsulation of the granules by the monolith binder. The order of elemental release, i.e. which are slower vs. which are more rapid, is the same as the order in the granular P-1B (see Figure 5-25).

Table 5-32. Long Term PCT Results for the GEO-7 Fly Ash Monolith Prepared with the Engineering Scale P-1B LAW Granules

Normalized Elemental Release (g/m^2)	Eng. Scale P-1B GEO-7 Monolith Test Interval				
	7 Days	1 Month	3 Month	6 Month	1 Year
Al	4.30E-05	2.98E-04	4.71E-04	1.30E-04	7.80E-04
S	3.42E-02	4.93E-02	6.30E-02	7.85E-02	6.26E-02
Cs	2.01E-03	2.70E-03	2.59E-03	3.58E-03	3.00E-03
Re	4.10E-03	9.24E-03	3.67E-02	4.70E-02	8.72E-02
Na	2.15E-02	3.12E-02	2.61E-02	2.31E-02	7.23E-03
Si	2.70E-03	1.89E-03	1.90E-04	2.80E-04	4.00E-05
I	5.27E-03	1.28E-02	6.31E-02	7.85E-02	1.20E-01
pH	12.39	12.45	12.49	12.79	11.94

The PCT results are shown in Table 5-32 and Figure 5-31. Silicon release decreases with time indicating solution saturation. 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. Sodium release also decreased compared to the other elements. Aluminum release appeared erratic while S, Re, and I release increased slightly with time. No reaction products were identified that were from reaction of the granular product with the leachant.

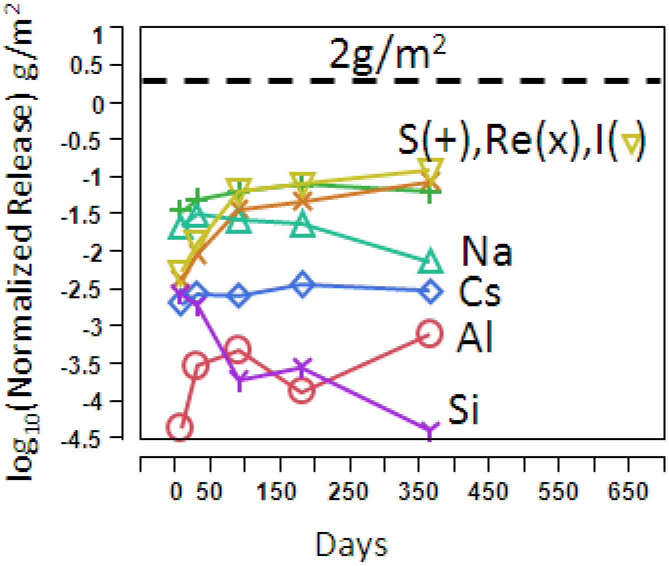


Figure 5-31. Release of Elements from ESTD P-1B Rassat GEO-7 Fly Ash Monoliths during 7 day, 1 month, 3 month, 6 month and 12 month Long Term PCT Testing.

Figure 5-32 is an overlay of the XRD patterns of the ESTD B non-radioactive monolith product as received and after each 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 granular phases persists through all the leach intervals, indicating minimal degradation of the mineral species.

The mineral faujasite was observed in XRD analysis (Figure 5-32) but that phase was present in the "as made" geopolymer. It is a zeolite that can form during geopolymerization in the presence of fly ash. Synchrotron radiation-based infrared microscopy (SR-FTIR) data processed via hierarchical clustering analysis was performed by researchers in Australia on geopolymers made from various fly ash compositions.[118] In general, fly ash was found to be composed of reactive components such as 36.6% amorphous SiO_2, and 15.3% amorphous Al_2O_3 and the remainder is unreactive crystalline mullite, quartz, and iron oxide phases. This was verified for the SEFA fly ash used by SRNL, which was found to contain crystalline mullite and quartz.[32]

In the Australian study[118], the formation of higher Si/Al ratio crystals such as faujesite occurred in samples with a slower alumina release rate, e.g. a lower availability of aluminum since the generally accepted reaction sequence of geopolymerization is that the first stage of reaction is the release of aluminate and silicate monomers by alkali attack on the solid aluminosilicate source (clay or fly ash), which is required for the conversion of solid particles to geopolymer gel. Hydrolysis reactions occur on the surface of the solid clay or fly ash particles, followed by the formation of dissolved species that cross-link to form oligomers, and then set and harden by polycondensation and the formation of a three-dimensional aluminosilicate network.

While the formation of faujasite has been well studied in fly ash based geopolymers [118], it is not a desired phase due to the 7 or 8 waters of hydration bound to its structure. However, faujesite, Zeolite X, and Zeolite P, all have the identical cage structure as sodalite.[119] So while the sodalite in the FBSR mineral phases may be attracting structural waters of hydration to its structure the sodalite cage structure appears to remain in tact. Another zeolite, known as N3 or Zeolite Na-P1, was also observed but also forms from the alteration of fly ash according to the Australian study [118]. The fly ash is a geopolymer additive and not an FBSR mineral phase. Therefore, no reaction products were identified that were associated with the degradation of the granular FBSR phases.

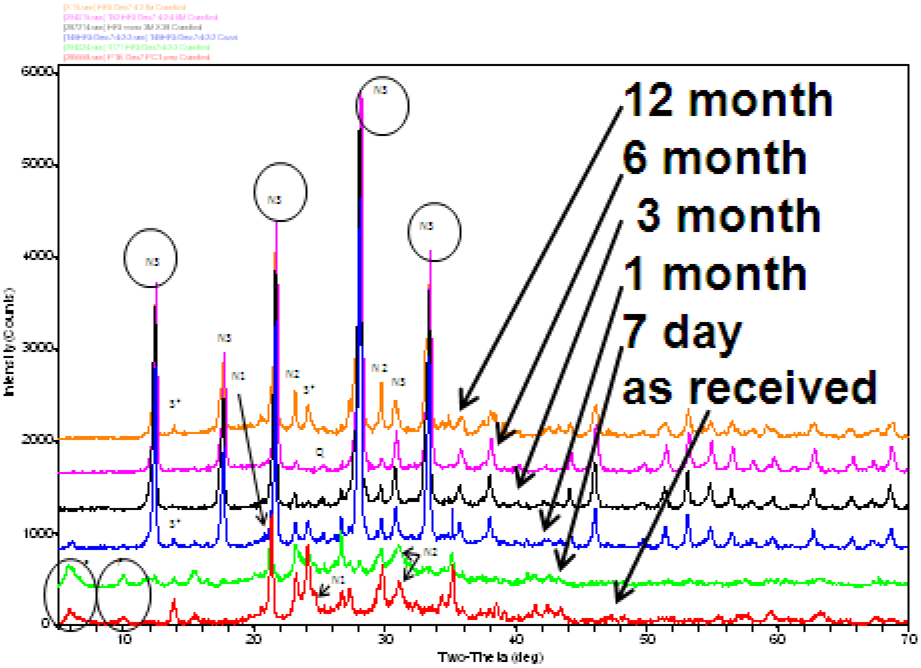


Figure 5-32. XRD patterns of Module B ESTD GEO-7 Fly Ash Monolith As-Made and After Long –Term PCT Leaching

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
S* is Sodalite $Na_6(AlSiO_4)_6$ (PDF 00-042-0217)
N3 is Zeolite Na-P1, $NaAl_6Si_{10}O_{32}{\bullet}12H_2O$ (PDF 00-039-0219)
F is Faujasite-K, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}{\bullet}243H_2O$ (PDF 00-026-0896)
Q is Quartz, SiO_2 (PDF 00-046-1045)
Original XRD spectra fits are in Appendix I

Table 5-33 contains the PCT results for the GEO-7 monolith prepared with the Module B simulant BSR product. As with the engineering scale long term PCT, the release of the elements analyzed was consistent throughout the duration of the test.

The 7-day results from Table 5-33 are shown with release results from samples leached for 1, 3, 6, and 12 months in Figure 5-33. Silicon release is decreasing indicating solution saturation and so is aluminum in solution. The other releases are about constant over the one year of testing which indicates that the FBSR granular product is not undergoing significant degradation of the mineral species.

Table 5-33. Long Term PCT Results for the GEO-7 Fly Ash Monolith Prepared with the Module B BSR Simulant Granules

Normalized Elemental Release (g/m^2)	**BSR Module B Simulant GEO-7 Test Interval**				
	7 Days	**1 Month**	**3 Month**	**6 Month**	**1 Year**
Al	4.47E-04	1.21E-03	1.74E-03	1.99E-03	1.00E-04
S	1.02E-01	1.89E-01	1.86E-01	2.40E-01	3.11E-01
Cs	4.60E-03	NM	7.64E-03	5.93E-03	1.13E-02
Re	1.99E-02	8.51E-02	1.60E-01	2.16E-01	2.84E-01
Na	7.30E-02	7.48E-02	7.69E-02	7.94E-02	8.86E-02
Si	7.02E-03	2.28E-03	9.60E-04	5.80E-04	3.00E-04
I	3.61E-03	6.35E-02	1.48E-01	2.12E-01	2.22E-01
pH	12.56	12.64	12.56	12.48	13.07

NM – not measured

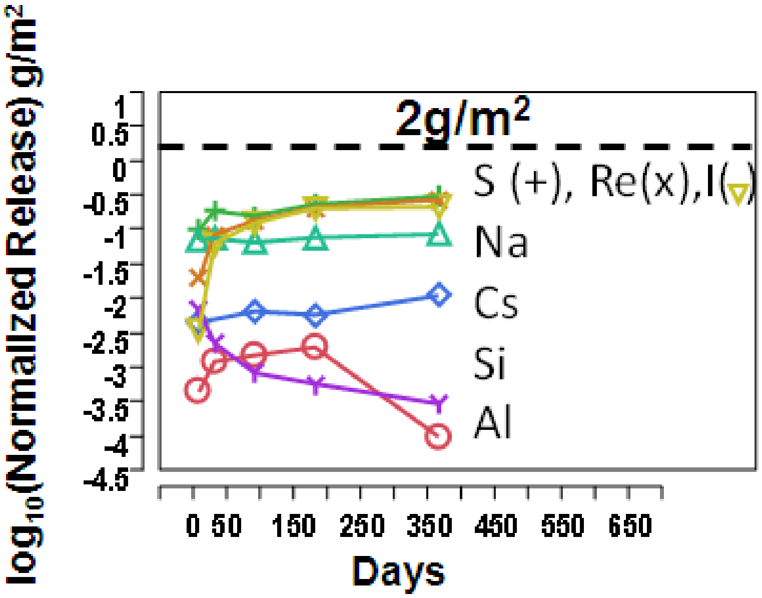


Figure 5-33. Release of Elements from BSR Module B GEO-7 Fly Ash Monolith Made from Rassat Simulant during 7 day, 1 month, 3 month, 6 month and 12 month Long Term PCT Testing

Figure 5-34 is an overlay of the XRD patterns of the Module B simulant BSR monolith product as prepared for PCT and after each leach interval. The same secondary phases were found in the fly ash based BSR monolith as in the fly ash based ESTD monolith. Both contained faujasite in the as made monoliths, which is a reaction product of fly ash and NaOH. Both contained Zeolite

N3, which is also a degradation product of fly ash. Halloysite was also found, which is the main reaction product of unreacted kaolin clay. No reaction products were identified that could have formed from the FBSR minerals, nepheline, sodalite, or nosean.

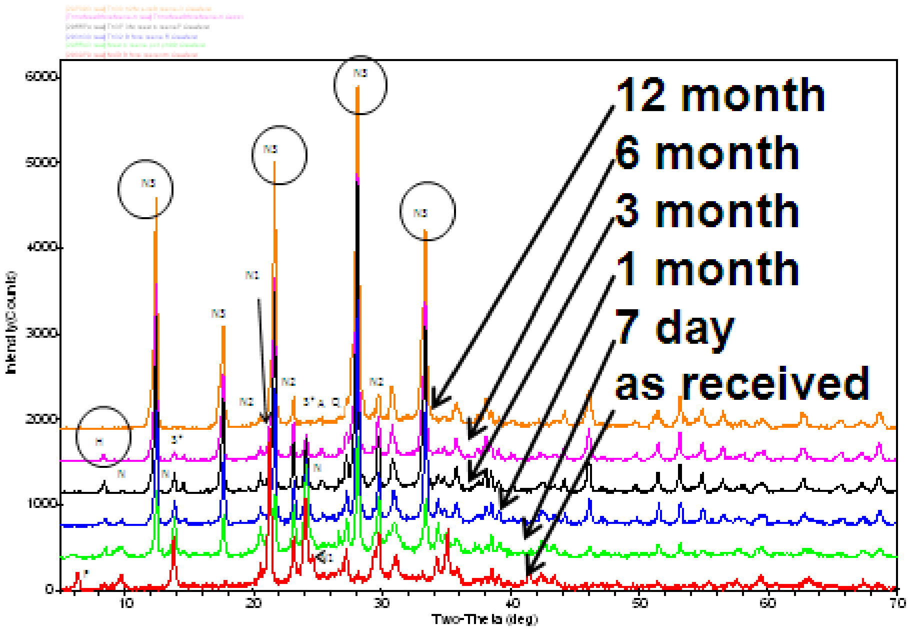


Figure 5-34. XRD Overlay for the GEO-7 Fly Ash Monolith Made from BSR Simulant Module B Rassat Granular Product

N1 is Nepheline (O) $NaAlSiO_4$ (PDF00-052-1342)
N2 is Nepheline (H) $NaAlSiO_4$ (PDF 00-035-0424)
S* is Sodalite $Na_6(AlSiO_4)_6$ (PDF 00-042-0217)
N is Nosean (cubic) $Na_8Al_6Si_6O_{24}SO_4$ (PDF 01-072-1614)
N3 is Zeolite Na-P1, $NaAl_6Si_{10}O_{32}\bullet12H_2O$ (PDF 00-039-0219)
F is Faujasite-K, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet243H_2O$ (PDF 00-026-0896)
Q is Quartz, SiO_2 (PDF 00-046-1045)
H is Halloysite, $AlSi_2O_5(OH)_4\bullet2H_2O$
Original XRD spectra fits are in Appendix I

Geopolymers were chosen as the FBSR binder due to the similarity of the Na-Al-Si (NAS) chemistry of the binder to that of the FBSR product (Figure 4-14). It was also anticipated based on the previous binder studies with hydroceramics [30,31], that any ash from the Erwin/Bestac or other coals used in the FBSR process would be available to participate in the alkali reactions. Since unreacted clay cores had been observed in all of the FBSR products produced from 2001 to 2004, it was also anticipated that ~10% unreacted clay existed in the FBSR product and ~ 10% fly ash from the coal that is used during FBSR processing. Geopolymer formulations were targeted close to the G1 regions in Figure 4-14 assuming that 20-30% more free aluminosilicate (coal ash and unreacted clay) was available in the FBSR product to participate in the geopolymerization. This also facilitated getting more FBSR product into the monoliths, i.e. higher FBSR loadings.

As explained previously, during the monolith formulation and after the long term durability testing had been initiated, SEM was performed (Figure 5-14) and unreacted cores were not found in either the FBSR products from the ESTD or BSR testing. Therefore, new formulations were made without including any interactions with the kaolin or fly ash in the FBSR product. A clay geopolymer formulation was used instead of fly ash and the old fly ash formulations were recalculated (see Table 4-11 and Table 4-12) based on zero extra aluminosilicate in the FBSR product. The position of the three final monoliths that were durability tested are shown in Figure 5-35 relative to the desired G1 geopolymerization region.

The GEO-7 fly ash Module B monoliths made with fly ash and the ESTD and BSR non-radioactive FBSR products are barely outside the preferred G1 region of geopolymer formation (Figure 5-35). Since the long term durability testing had already begun and the geopolymer formulations were close to the G1 region, the long term testing was completed.

Geopolymers made with clay at 42 and 65 wt% FBSR loading were also formulated (see Table 4-13, Table 4-14, and Table 4-15) and both radioactive geopolymer formulations (Table 4-15) were leach tested. Only short term PCT testing was performed on this sample due to lack of funding and only the 65 wt% FBSR loaded monolith leachates were analyzed but the results of this short term PCT testing will be discussed relative to the PCT long term testing of the fly ash monoliths at 67-68 wt% FBSR loading.

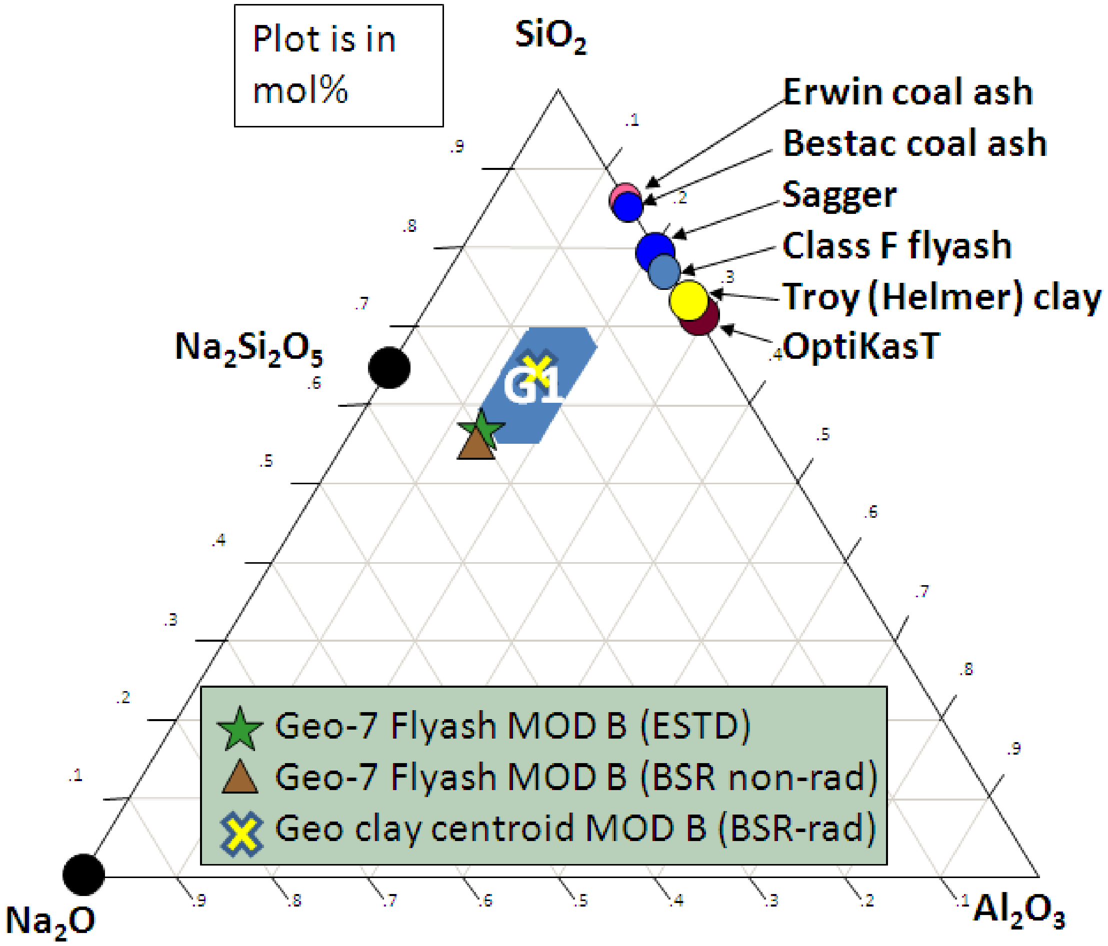


Figure 5-35. Position of the Two Fly Ash and One Clay Based Geopolymers that Underwent Long Term PCT Testing

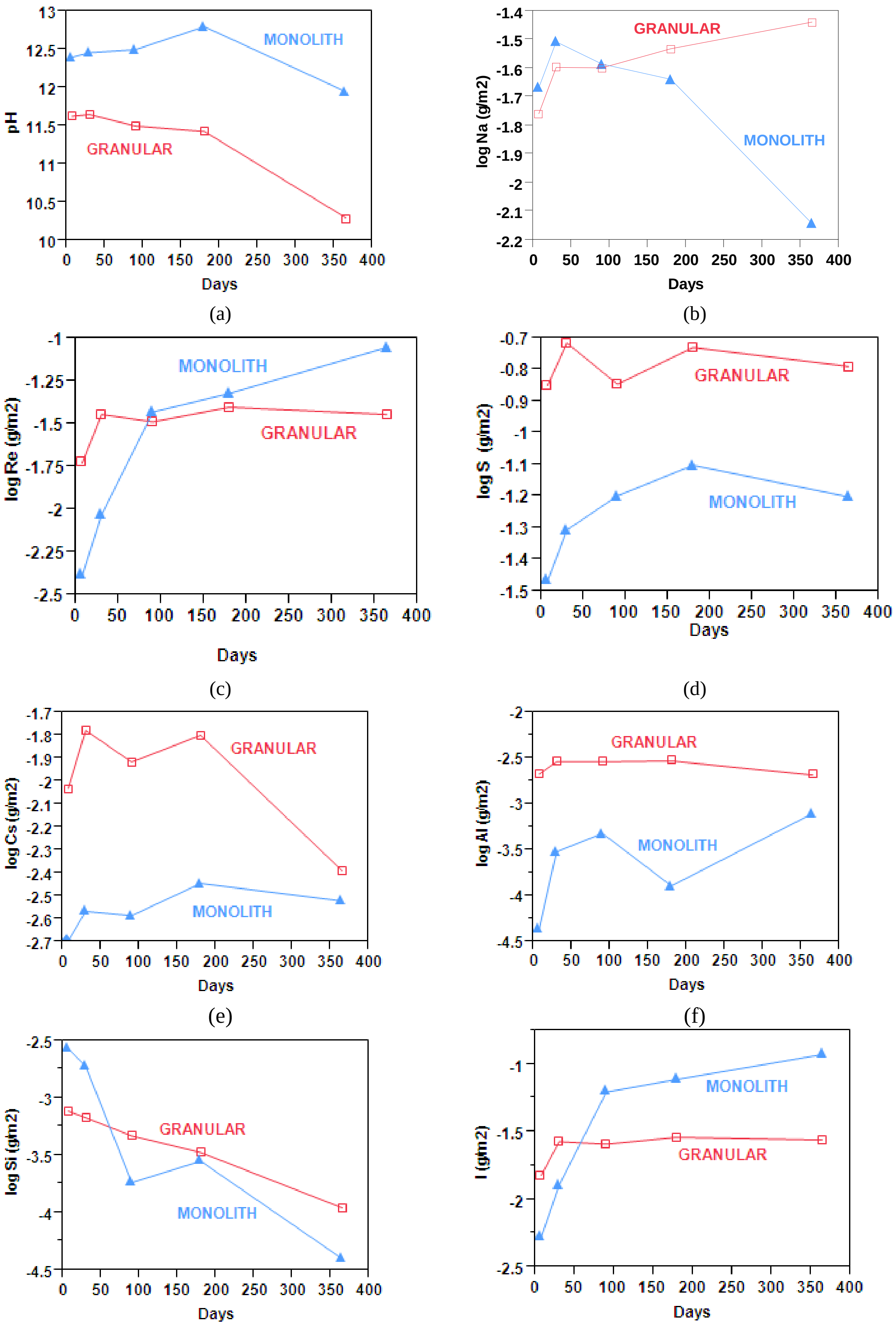
In Figure 5-36, the long term releases from the granular and monolith PCT tests are compared for the mis-formulated GEO-7 fly ash monoliths made from the ESTD simulant. Of note is that the pH of the leachate is always higher for the monolith, likely due to the NaOH and/or Na silicate in the pore water due to the compounds used to form the geopolymers (Figure 5-36a). Even with the mis-formulation in the geopolymer binder and the high H_2O/Na_2O ratio used in this formulation, the monolith actually leached less than the granular product for all elements except Re and I.

In Figure 5-37, the long term releases from the granular and monolith PCT tests are compared for the mis-formulated GEO-7 fly ash monoliths made with too much Na_2O and made from the BSR simulant. Note that the GEO-7 monolith for the simulated BSR sample is more outside the G1 geopolymer region than the GEO-7 ESTD monolith. For the BSR GEO-7 monolith the leachate pH values are higher than that of the FBSR granular products (Figure 5-37). For most elements, the leaching was higher from the GEO-7 fly ash monolith than from the granular product except for Cs and Al.

In Figure 5-38, the long term releases from the radioactive BSR granular and monolith PCT tests are compared for the correctly formulated clay based 65 wt% FBSR loaded centroid geopolymer composition. A 42 wt% FBSR loaded centroid geopolymer composition was also made with clay but was not durability tested due to lack of funding. Note that only short term PCT testing was available for the radioactive clay based geopolymer.

For the clay monolith, the pH values are lower for the monolith than for the granular product (Figure 5-38a), which is due to better formulations in the G1 polyhedra of Figure 5-35. The Na releases of the leachate from the monolith are the only element that leaches more from the monolith than from the granular product (Figure 5-38b). However, all the other elements, including Tc-99, Re and I are released over an order of magnitude more slowly from a correctly formulated geopolymer than the granular product as the granular product is macro-encapsulated (see Figure 5-14). It should be noted that Figure 5-38g and h show comparable releases of Re and Tc-99 from the granular products and the monolith. It should also be noted that the releases of all elements, except Na from the monolith, follow the pH as noted in Section 5.6.1 on the short term testing of the FBSR granular product. This trend with pH was also observed in the historical short term PCT data (Figure 5-24) and data from other leach testing and thermodynamic modeling.[52,75,86,114]

In general, for a correctly formulated monolith, COC releases are an order of magnitude lower than the releases from the granular product due to the way in which the geopolymer encapsulates the granular product. It also demonstrates that the geopolymer matrix does not attack the FBSR granular product and cause any adverse reactions or releases from the FBSR granular product. Finally, the data demonstrate that the reaction products formed from the fly ash or kaolin clay (binder or FBSR additives) do not diminish the capacity of the FBSR granular product from retaining the COC.



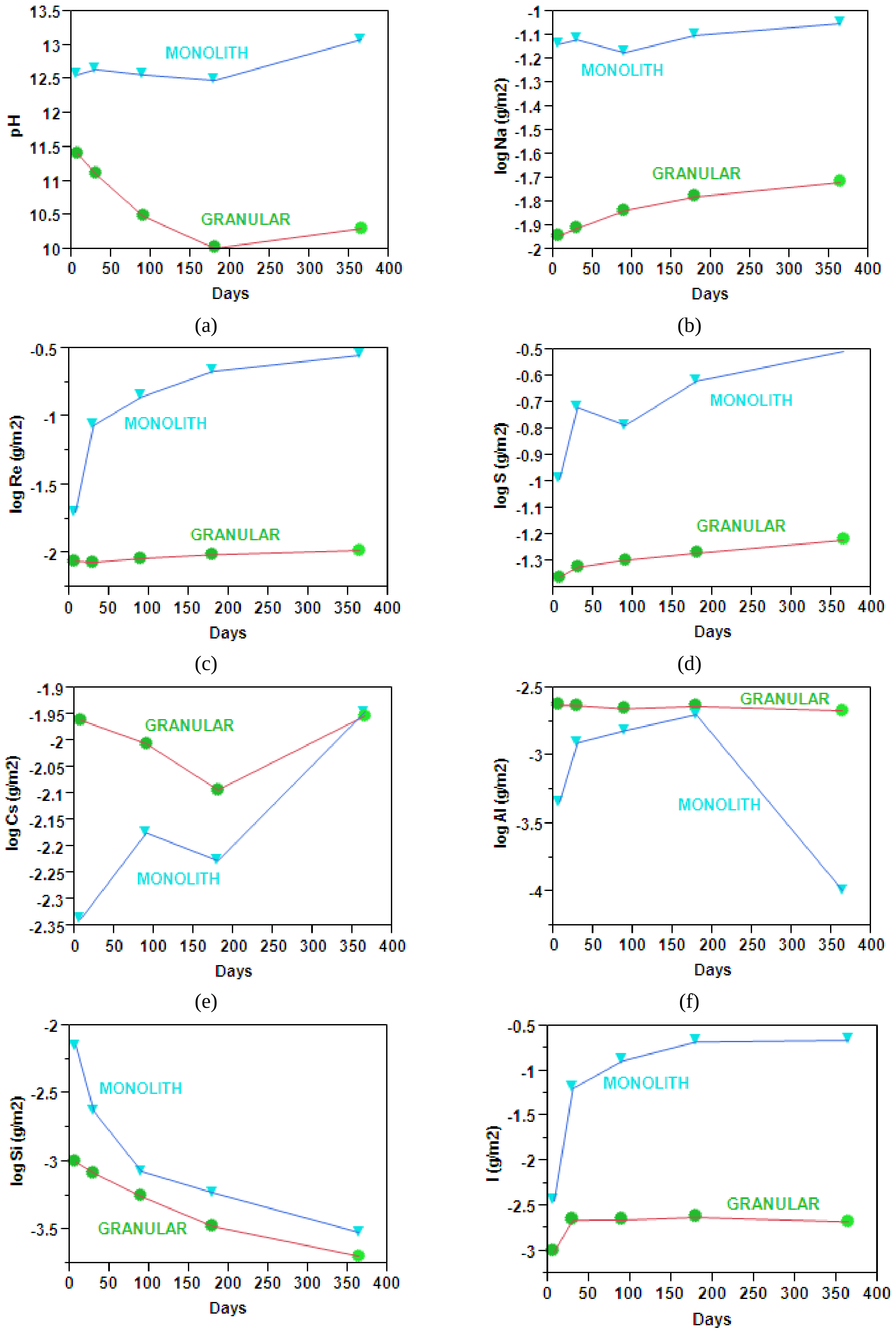
(a) (b)

(c) (d)

(e) (f)

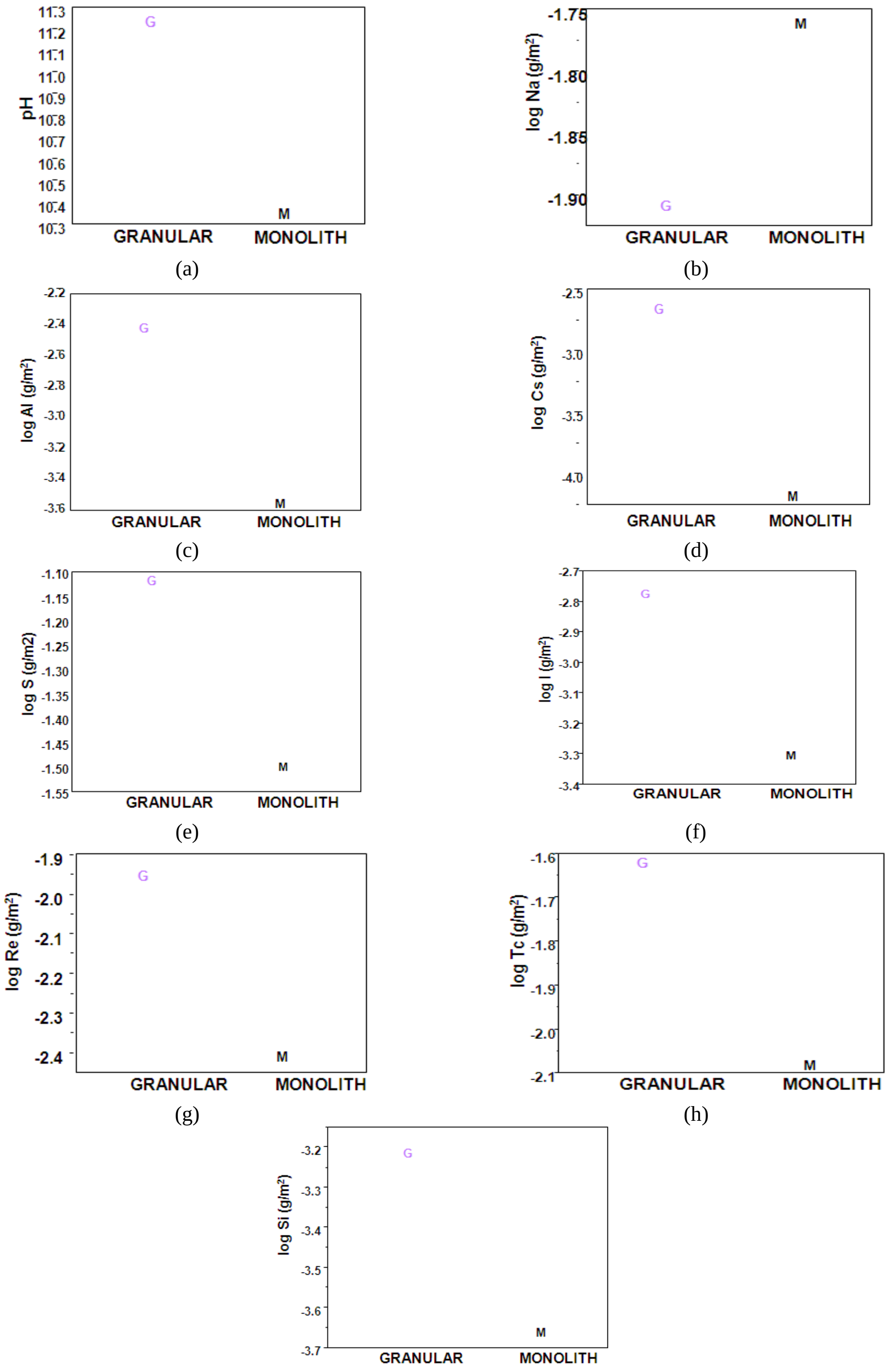
(g) (h)

Figure 5-36. Overlay of the Simulated ESTD FBSR Granular Product Releases Compared to the Monolithed Product Releases for the GEO-7 Fly Ash Based Geopolymer at 67% FBSR Loading for PCT tests up to one year in duration.



(a) (b) (c) (d) (e) (f) (g) (h)

Figure 5-37. Overlay of the Simulated BSR Granular Product Releases Compared to the Monolithed Product Releases for the GEO-7 Fly Ash Based Geopolymer at 68% FBSR Loading for PCT testing up to one year in duration.



(a) (b)

(c) (d)

(e) (f)

(g) (h)

(i)

Figure 5-38. Overlay of the Radioactive BSR Granular Versus Monolithed Product Releases for a Clay Based Geopolymer at 65% FBSR Loading (that was correctly formulated) for 7-day PCT testing.

The Tc-99 release for the monolith is a less than number so the actual concentration of Tc-99 released is lower than shown from the monolith.

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 glass. Monolithing of the granular product has been shown to be feasible and 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 of this study are given below and generally follow the order of the success criteria given in Section 3.0:

- The Module B FBSR products from the HRI/ESTD/TTT P-1B runs blended bed and fines products made from the Hanford Rassat (68 tank blend) simulant were analyzed and the details are given in Reference 32 and summarized in Section 5.2.1 and throughout the remainder of Section 5.0 where the ESTD and BSR products are compared.
    - The mineralogy of the radioactive and simulant products from the BSR and Engineering-scale Test Demonstration (ESTD) and the 2001 and 2004 pilot studies are the same.
    - The skeletal density of the radioactive and simulant products from the BSR were 2.59 g/cc and 2.39 g/cc, respectively, which is similar to the ESTD and the 2001 and 2004 pilot studies where the product density was 2.39 g/cc.
    - The $Fe^{2+}/\Sigma Fe$ REDOX ratio of the radioactive and simulant products from the BSR were 0.41 and 0.36, respectively, and ESTD were 0.50.
    - The coal content of the radioactive and simulant products from the BSR were 1.03 wt% and 1.14 wt%, respectively, within range of the ESTD 0.79 to 1.72 wt% coal content.
- A Hanford Rassat radioactive LAW was made from SRS Tank 50 LAW. Tc-99, I-129/I-125, Cs-137, and Re were shimmed into the simulant to determine how well Re tracks Tc-99 in the off-gas versus the mineral product and the fate of I-129/I-125 and Cs in the off-gas vs. the mineral product.
    - 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 and Tc-99 depending on the REDOX conditions.
- 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 obtained on all radioactive and non-radioactive species including halides.

  - Good mass balance closure was obtained on Tc, Re, Cs, I, and Cl in all BSR tests (radioactive and non-Radioactive) with Rassat simulant and SRS radioactive LAW shimmed to match Hanford LAW.
    - 83-98% recovery of Re in the product streams for simulant and radioactive campaigns
    - 87% recovery of Tc-99 in the product streams for radioactive campaign
    - 103% recovery of non-radioactive I-127 and 106% recovery for chloride (Cl) in the product streams for simulant campaign
    - 94% recovery of I-129 in the product streams for radioactive campaign and 84% recovery of I-125 in the radioactive campaign
- The FBSR granular and monolith products made with non-radioactive and radioactive Hanford (68 tank blend) recipes were tested by TCLP.
  - TCLP data are acceptable when RCRA metals are not shimmed in excess and REDOX is controlled or an IOC is present as a spinel host for Cr.
- Process control calculations (MINCALC™) were used to determine the fractions and compositions of the minerals formed by FBSR.
  - Phase pure standards were made for qualitative XRD [73].
  - SEM analyses showed that an individual grain of FBSR product had regions of each type of sodalite anion phase in micro-domains making qualitative XRD difficult.
    - Tc-99, Re, SO_4, and Cr behavior were found to be controlled by the oxygen fugacity in the FBSR/BSR process, i.e. control of the REDuction/OXidation (REDOX) equilibrium.
- Granular waste form performance testing using ASTM C1285 (short term 7 day) was completed.
  - ASTM C1285 (Product Consistency Test) testing of the ESTD/BSR granular product 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.
  - Re is a good surrogate for Tc-99 during short 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 and also prove the “tie back” strategy.
  - 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 B (non-radioactive and radioactive) are in agreement with the data from the non-radioactive ESTD testing in 2008 and pilot scale testing from 2001 and 2004
    - 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.
    - This is the same conclusions reached by SPFT and PUF testing of the Rassat FBSR ESTD and BSR products.
- Granular waste form performance testing using ASTM C1285 (long term 1, 3, 6, and 12 month) was also completed.
  - Long term testing (1, 3, 6 month and/or 1 year) at 90°C by ASTM C1285 did not show any significant change in the mineral assemblages as analyzed by X-Ray Diffraction (XRD) for BSR Rassat simulant and radioactive samples.

    - Silica concentrations in solution are decreasing with time indicating solution supersaturation: if reaction products were going to form, they will form when the solution saturates or supersaturates.
        - Long term testing of the ESTD FBSR products tested up to 1 year did contain small amounts of halloysite ($Al_2Si_2O_5(OH)_4$), which can form from aluminosilicate weathering or from unreacted clay since the Al:Si ratio is 1:1 as in the parent kaolin clay.
      - Halloysite is the primary reaction product of kaolin clay [115], which was present in ~ 10% excess in the ESTD testing but only ~ 2 wt% excess in the BSR testing.
      - The halloysite found did not increase in amount with time of leaching indicating that it is forming from a minor component, likely excess kaolin clay, in the FBSR mineral waste 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, and also proves the "tie back" strategy.
- Monolithic waste forms containing mineralized FBSR products were made.
    - Geopolymer waste form made with fly ash were less durable than those made with clay.
    - Monoliths with FBSR loadings of 65-68 wt% FBSR loading were made and durability tested (short and long term) for non-radioactive and radioactive FBSR products.
    - The clay based monolith (radioactive) performed better than the fly ash based monoliths (non-radioactive) at equivalent FBSR loadings (65 vs. 68 wt%) based on a short term (7-day) PCT test
    - Geopolymers made with fly ash at 67-68 wt% FBSR loading performed equivalent to clay based geopolymers at 42 wt% waste loading in extended (90-107 day) ASTM C1308 testing. No conclusions can be made regarding whether clay or fly ash geopolymers are better for FBSR macro-encapsulation until higher FBSR loaded clay monoliths can be tested.
    - The geopolymer binder macro-encapsulates the FBSR granular product and slows the dissolution by one to two orders of magnitude.
- XRD, SEM, compression testing, short term and long term ASTM C1285 tests were performed on the monolithic waste forms.
    - Upon fabrication, XRD analysis of geopolymers made with fly ash and clay showed no other phases present other than those phases that constituted the FBSR granular minerals (nepheline, sodalite, nosean).
    - SEM analysis showed the macro-encapsulation of the FBSR granular minerals and showed that the geopolymer binder was not selectively degrading, as in eroding the FBSR mineral particles, at the grain boundaries.
    - After long term leaching, monoliths made with fly ash contained faujasite in the as made monoliths, which is a reaction product of fly ash and NaOH.
    - After long term leaching, monoliths made with fly ash also contained Zeolite N3, which is a reaction product of fly ash and the other geopolymer making components.
    - After long term leaching, monoliths made with fly ash also contained halloysite, which is the main reaction product of unreacted kaolin clay.
    - No reaction products were identified that could have formed from the FBSR minerals, nepheline, sodalite, or nosean over a one year duration as determined by XRD but XRD has limited sensitivity for minor components.

  - ➢ All radioactive and non-radioactive (BSR Module A, BSR Module B, and the ESTD engineering-scale) monolith products pass compression testing at >500 psi.
  - ➢ Radioactive and non-radioactive (BSR Module A, BSR Module B, and the ESTD engineering-scale) monolith products maintain short term PCT leach rates <2 g/m^2.
- Diffusion tests such as ASTM C1308/ANSI/ANS 16.1 were performed up to 90 days for a number of samples including Re-loaded simulants to determine the transport properties of the monolithed waste form.
  - ➢ The Re diffusivities plotted as the negative log of the diffusivity vs. time gives the leach index (LI).
    - o All the Re leach indices are >9 and all the Na leach indices are >6 (Hanford IDF criteria)
      - The excess Na_2O containing ESTD GEO-7 fly ash monolith goes above a leach index of 9 within 19 days, all the other geopolymers reach an LI >9 in a few days
    - o Kaolin clay geopolymers and one of the two fly ash geopolymers reached the targeted ≥9 leach index values more rapidly than the fly ash based geopolymers.
      - Kaolin clay geopolymers have advantages due to the high compositional variability of fly ash and presence of unreactive refractory components in the fly ash such as mullite.

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 (>90%) 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.

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.

6. Qualitative XRD should be completed.

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8.0 References

1. P.J. Certa and M.N. Wells, **"River Protection Project System Plan,"** ORP-11242, Rev. 5, DOE Office of River Protection, Richland, WA (November 2010).

2. Jantzen, C.M., **"Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Comparisons to Vitreous Waste Forms and Pertinent Durability Testing"**, U.S. DOE Report, WSRC-STI-2008-00268, Savannah River National Laboratory, Aiken, SC (2008).

3. Lutze, W. and R.C. Ewing, **"Radioactive Waste Forms for the Future"**, Elsevier Science Publishers, Amsterdam, The Netherlands, 778pp (1988).

4. Hatch, L.P., **"Ultimate Disposal of Radioactive Wastes"**, Am. Scientist, 41, 410-421 (1953).

5. Roy, R., **"Hydroxylated Ceramic Waste Forms and the Absurdity of Leach Tests",** Proc. Int. Sem. on Chem. and Process Eng. for High-Level Liquid Waste Solidification, Vol. 2, Julich, JUL-Conf-42, eds. R. Odoj and E. Merz, 576-602 (1981).

6. Mason, J.B., T.W. Oliver, M.P. Carson, and G.M. Hill, **"Studsvik Processing Facility Pyrolysis/Steam Reforming Technology for Volume and Weight Reduction and Stabilization of LLRW and Mixed Wastes"**, Waste Management 99, Tucson, AZ (1999).

7. Mason, J.B., J. McKibben, K. Ryan, and D. Schmoker, **"Steam Reforming Technology for Denitration and Immobilization of DOE Tank Wastes"**, Waste Management 03, Phoenix, AZ (2003).

8. Jantzen, C.M., M.R. Williams, N.E. Bibler, C.L. Crawford, and A.R. Jurgensen, **"Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Application to Cs-137/Sr-90 Wastes for the Global Nuclear Energy Partnership (GNEP)"**, U.S. DOE Report, WSRC-MS-2008-00013, Savannah River National Laboratory, Aiken, SC (2008).

9. Klingenberg, R. and J. Felsche, **"Interstitial Cristobalite-type Compounds $(Na_2O)_{0.33}Na[AlSiO_4]$"**, *J. Solid State Chemistry*, 61, 40-46 (1986).

10. Buhl, J.Ch., G. Englehardt, and J. Felsche, **"Synthesis, X-ray Diffraction, and MAS N.M.R. Characteristics of Tetrahydroxoborate Sodalite"**, *Zeolites*, 9, 40-44 (1989).

11. Tobbens, D.M. and J.C. Buhl, **"Superstructure of Sodiumborate Sodalite"**, Berline Neutron Scattering Center (BENSC) Experimental Report E9, Helmholtz Zentrum fur Materialiene und Energie (formally the Hahn-Meitner Institute), Berlin, Germany (2000).

12. Fleet, M.E., **"Structures of Sodium Alumino-Germanate Sodalites"**, *Acta Cryst.* C45, 843-847 (1989).

13. Sinkler, W., T.P. O'Holleran, S.M. Frank, M.K. Richmann, and S.G. Johnson, **"Characterization of a Glass-Bonded Ceramic Waste Form Loaded with U and Pu"**,

Scientific Basis for Nuclear Waste Management, XXIII, Mat. Res. Soc.: Pittsburgh, PA, 423-429 (2000).

14. Moschetti, T.L., W. Sinkler, T. DiSanto, M.H. Novy, A.R. Warren, D. Cummings, S.G. Johnson, K.M. Goff, K.J. Bateman, and S.M. Frank, **"Characterization of a Ceramic Waste Form Encapsulating Radioactive Electrorefiner Salt"**, *Scientific Basis for Nuclear Waste Management*, XXIII, Mat. Res. Soc.: Pittsburgh, PA, 577-582 (2000).

15. Babad, H. and D.M. Strachan, **"Method for Immobilizing Radioactive Iodine"**, U.S. Patent #4,229,317 (October 1980).

16. Brookins, D.G., **"Geochemical Aspects of Radioactive Waste Disposal"**, Springer-Verlag: NY, 347pp (1984).

17. Deer, W.A., R.A. Howie, and J. Zussman, "**Rock-Forming Minerals, V. 4"**, John Wiley & Sons, Inc., NY, 435pp (1963).

18. Dana, E.S., **"A Textbook of Mineralogy"**, John Wiley & Sons, Inc., New York, 851pp (1932).

19. Mattigod, S.V., B.P. McGrail, D.E. McCready, L. Wang, K.E. Parker, and J.S. Young, **"Synthesis and Structure of Perrhenate Sodalite"**, *J. Microporous & Mesopourous Materials*, 91 (1-3), 139-144 (2006).

20. Barrer, R.M. **"Hydrothermal Chemistry of Zeolites"**, Academic Press, New York, 360pp (1982): see references by St. J. Thugutt, Z. Anorg. Chem, 2, 65 (1892) and E. Flint, W. Clarke, E.S. Newman, L. Shartsis, D. Bishop and L.S. Wells, J. Res. Natl. Bur. Stds, 36, 63 (1945).

21. Deer, W.A. R.A. Howie, W.S. Wise, and J. Zussman, **"Rock-Forming Minerals, Vol. 4B, Framework Silicates: Silica Minerals, Feldspathoids and the Zeolites"**, The Geological Society, London, UK, 982pp (2004).

22. F. Liebau, **"Zeolites and Clathrasils – Two Distinct Classes of Framework Silicates"**, Zeolites, 3[7] 191-92 (1983).

23. Soelberg, N.R., D.M. Marshall, S.O. Bates, and D.D. Siemer, **"SRS Tank 48H Steam Reforming Proof-of-Concept Test Report"**, INEEL/EXT-03-01118, Rev 1, Idaho National Laboratory, Idaho Falls, ID, (2004).

24. Jantzen, C.M., **"Disposition of Tank 48H Organics by Fluidized Bed Steam Reforming (FBSR)"**, U.S. DOE Report, WSRC-TR-2003-00352, Savannah River National Laboratory, Aiken, SC (2003).

25. Rassat, S.D., L.A. Mahoney, R.L. Russell, S.A. Bryan, and R.L. Sell, **"Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis"**, PNNL-14194 Revision 1, Pacific Northwest National Laboratory, Hanford, WA, (2003).

26. Crawford, C.L., P.B. Burket, A.D. Cozzi, W.E. Daniel, C.M. Jantzen, and D.M. Missimer, **“Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Waste Treatment Plant Secondary Waste (WTP-SW) by Fluidized Bed Steam Reformation (FBSR)”**, U.S. DOE Report, SRNL-STI-2011-00331, Savannah River National Laboratory, Aiken, SC (September 1, 2011).

27. Jantzen, C.M., C.L. Crawford, C.J. Bannochie, P.R. Burket, A.D. Cozzi, Daniel, W.E., Hall H.K., Miller, D.H., Missimer, D.M., Nash, C.A. and Williams, M.F., **“Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Low Activity Waste (Tank SX-105, AN-103, and Blended AZ-101/AZ-102) by Fluidized Bed Steam Reformation”**, U.S. DOE Report, SRNL-STI-2011-00384, Savannah River National Laboratory, Aiken, SC (July 2013).

28. THOR® Treatment Technologies, Project Number 29387, **“Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet,”** Document Number RT-21-002, Rev. 1 (April 2009).

29. Jantzen, C.M., and C.L. Crawford, **"Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Radionuclide Incorporation, Monolith Formation, and Durability Testing"**, WM'10, Phoenix, AZ (2010).

30. Jantzen, C.M., "**Fluidized Bed Steam Reformer (FBSR) Product: Monolith Formation and Characterization**," Savannah River National Laboratory, Aiken, SC, WSRC-STI-2006-00033 (2006).

31. Jantzen, C.M., **“Fluidized Bed Steam Reformer (FBSR) Monolith Formation”**, WM'07, Paper 7075, Tucson, AZ (2007).

32. Crawford, C.L. and C.M. and Jantzen, **“Evaluation of THOR^{TM} Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project”**, U.S. DOE Report SRNL-STI-2009-00505, Rev.0, Savannah River Technology Center, Aiken, SC (December 2011).

33. Jantzen, C.M., **“Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process”**, U.S. DOE Report WSRC-TR-2002-00317, Savannah River Technology Center, Aiken, SC (2002).

34. Jantzen, C.M., **“Characterization and Performance of Fluidized Bed Steam Reforming (FBSR) Product as a Final Waste Form”**, Ceramic Transactions, Vol. 155, 319-29, J. D. Vienna, and D.R. Spearing (Eds) (2004).

35. McGrail, B.P., H.T. Schaef, P.F. Martin, D.H. Bacon, E.A. Rodriquez, D.E. McReady, A.N. Primak, and R.D. Orr, **“Initial Evaluation of Steam-Reformed Low Activity Waste for Direct Land Disposal”**, Pacific Northwest National Laboratory, Hanford, WA, U.S. DOE Report PNWD-3288 (2003).

36. McGrail, B.P., E.M. Pierce, H.T. Schaef, E.A. Rodriques, J.L. Steele, A.T. Owen, and D.M. Wellman, **“Laboratory Testing of Bulk Vitrified and Steam-Reformed Low-**

Activity Forms to Support a Preliminary Assessment for an Integrated Disposal Facility", Pacific Northwest National Laboratory, Hanford, WA, PNNL-14414 (2003).

37. Pierce, E.M., **"Accelerated Weathering of Fluidized Bed Steam Reformation Material under Hydraulically Unsaturated Conditions"**, Materials Science & Technology, September 16-20, 2007, Detroit, Michigan, electronic file (2007).

38. Mann, F.M., R.J. Puigh, R. Khaleel, S. Finfrock, B.P. McGrail, D.H. Bacon, and R.J. Serne, **"Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies"**, Pacific Northwest National Laboratory, Hanford, WA, RPP-17675 (2003).

39. Pareizs, J.M., C.M. Jantzen, and T.H. Lorier, **"Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for High Sodium Wastes at Hanford and Idaho"**, U.S. DOE Report, WSRC-TR-2005-00102, Savannah River National Laboratory, Aiken, SC (2005).

40. Jantzen, C.M., J.M. Pareizs, T.H. Lorier, and J.C. Marra, **"Durability Testing of Fluidized Bed Steam Reforming (FBSR) Products"**, *Ceramic Transactions*, V. 176, C. C. Herman, S.L. Marra, D.R. Spearing, L. Vance, and J.D. Vienna, p. 121-37 (Eds) (2006).

41. Jantzen, C.M., T.H. Lorier, J.C. Marra, and J.M. Pareizs, **"Durability Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms"**, WM'06, Tucson, AZ (2006)

42. Marshall, D.W., N.R. Soelberg, and K.M. Shaber, **"THOR^{sm} Bench-Scale Steam Reforming Demonstration"**, Idaho National Laboratory, Idaho Falls, ID, INEEL/EXT.03-00437 (2003).

43. Olson, A.L., N.R. Soelberg, D.W. Marshall, and G.L. Anderson, **"Fluidized Bed Steam Reforming of Hanford LAW Using THOR^{sm} Mineralizing Technology"**, Idaho National Laboratory, Idaho Falls, ID, INEEL/EXT-04-02492 (2004).

44. Lorier, T.H., J.M. Pareizs, and C.M. Jantzen, **"Single Pass Flow through (SPFT) Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms"**, U.S. DOE Report WSRC-TR-2005-00124, Savannah River National Laboratory, Aiken, SC (2005).

45. Jantzen, C.M., T.H. Lorier, J.M. Pareizs, and J.C. Marra, **"Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Characterization and Durability Testing"**, *Scientific Basis for Nuclear Waste Management XXX*. Edited by D. S. Dunn, C. Poinssot, B. Begg. pp. 379-86 (2007).

46. Pierce, E.M., W.W. Lukens, J. Fitts, G. Tang, and C.M. Jantzen, **"Multiphase Ceramic Waste Form Corrosion: Perrhenate Partitioning and Release as a Chemical Analogue for Pertechnetate"**, Applied Geochemistry (in preparation).

47. Olson, A.L., N.R. Soelberg, D.W. Marshall, and G.L. Anderson, **"Fluidized Bed Steam Reforming of INEEL SBW Using THOR^{sm} Mineralizing Technology"**, INL, Idaho Falls, ID, INEEL/EXT-04-02564, (2004).

48. Crawford, C.L. and C.M. Jantzen, **"Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for Sodium Bearing Waste (SBW) at INL"**, U.S. DOE Report WSRC-STI-2007-00319, Savannah River National Laboratory, Aiken, SC (2007).

49. Jantzen, C.M., C.L. Crawford, P.R. Burket, W.E. Daniel, A.D. Cozzi, and C.J. Bannochie, **"Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) as a Supplementary Treatment for Hanford's Low Activity Waste (LAW) and Secondary Wastes (SW)"** , WM'11, Paper #11593 (2011).

50. Evans, B., A. Olson, J.B. Mason, K. Ryan, C.M. Jantzen, and C.L. Crawford, **"Radioactive Bench Scale Reformer Demonstration of a Monolithic Steam Reformed Mineralized Waste Form for Hanford Waste Treatment Plant Secondary Waste"** , WM'12 Paper #12306 (February 2012).

51. Jantzen, C.M., E.M. Pierce, C.J. Bannochie, P.R. Burket, A.D. Cozzi, C.L. Crawford, W.E. Daniel, K.M. Fox, C.C. Herman, D.H. Miller, D.M. Missimer, C.A. Nash, M.F. Williams, C.F. Brown, N.P. Qafoku, M.M. Valenta, G.A. Gill, D.J. Swanberg, R.A. Robbins, L.E. Thompson, **"Fluidized Bed Steam Reforming Waste Form Performance Testing to Support Hanford Supplemental Low Activity Waste Immobilization Technology Selection"**, U.S. DOE Report SRNL-STI-2011-00387, Savannah River National Laboratory, Aiken, SC (in revision).

52. Neeway, J.J., N.P. Qafoku, B.D. Williams, M.M. Valenta, E.A. Cordova, S.C. Strandquist, D.C. Dage, and C.F. Brown, **"Single Pass Flow-Through (SPFT) Test Results of Fluidized Bed Steam Reforming (FBSR) Waste Forms used for LAW Immobilization"**, WM'12, Paper #12252 (2012).

53. Pires, R.P., J.H. Westsick, R.J. Serene, E.C. Golovich, M.M. Valenta, and K.E. Parker, **"Secondary Waste Form Screening Test Results - THOR® Fluidized Bed Steam Reforming Product in a Geopolymer Matrix"**, PNNL- 20551 (July 2011).

54. Jantzen, C.M., C.L. Crawford, P.R. Burket, C.J. Bannochie, W.G. Daniel, C.A. Nash, A.D. Cozzi, and C.C. Herman, **"Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) with Actual Hanford Low Activity Wastes: Verifying FBSR as a Supplemental Treatment"**, WM12 Paper #12317 (February 2012).

55. U.S. DOE Office of Environmental Restoration and Waste Management, **"Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms"**, U.S. DOE Document EM-WAPS, Rev.0, Washington, DC (February 2003).

56. Borders, M.N., **"DWPF Waste Form Compliance Plan"**, U.S. DOE Report WSRC-IM-91-116-0, Rev. 9, Savannah River Remediation, Savannah River Site, Aiken, SC, (June 2012).

57. Burbank, D.A., **"Waste Acceptance Criteria for the Immobilized Low-Activity Waste Disposal Facility"**, US DOE Report RPP-8401, Rev. 0, CH2M HILL Hanford Group, Richland, WA (May 2002).

58. Jantzen, C.M., N.E. Bibler, D.C. Beam, and M.A. Pickett, **"Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material"**, U.S. DOE Report WSRC-TR-92-346, Rev. 1, Westinghouse Savannah River Company, Aiken, SC (February 1993).

59. U.S. Department of Energy, **"Environmental Assessment-Waste Form Selection for SRP High-Level Waste"**, U.S. DOE Report DOE/EA-0179, Washington, DC (1982).

60. Bibler, N.E., and J.K. Bates, **"Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glasses"**, *Scientific Basis for Nuclear Waste Management*, XIII, Oversby, V. M. and Brown, P. W., eds., Materials Research Society, Pittsburgh, PA, 327–338 (1990).

61. Bates, J.K., D.J. Lam, and M. J. Steindler, **"Extended Leach Studies of Actinide-Doped SRL 131 Glass"**, *Scientific Basis for Nuclear Waste Management*, VI, D. G. Brookins (Ed.), North-Holland, NY, 183–190 (1983).

62. Bibler, N.E. and A.R. Jurgensen, **"Leaching Tc-99 from SRP Glass in Simulated Tuff and Salt Groundwaters"**, *Scientific Basis for Nuclear Waste Management*, XI, M.J. Apted and R.E. Westerman (eds.), Mat. Res. Soc., Pittsburgh, PA, 585–593 (1988).

63. Bradley, D.J., C.O. Harvey, and R.P. Turcotte, **"Leaching of Actinides and Technetium from Simulated High-Level Waste Glass"**, U.S. DOE Report PNL-3152, Pacific Northwest Laboratory, Richland, WA (1979).

64. Fillet, S., J. Nogues, E. Vernaz, and N. Jacquet-Francillon, **"Leaching of Actinides from the French LWR Reference Glass"**, *Scientific Basis for Nuclear Waste Management*, IX, L. O. Werme, Mat. Res. Soc., Pittsburgh, PA, 211–218 (1985).

65. Bazan, F., J. Rego, and R.D. Aines, **"Leaching of Actinide-doped Nuclear Waste Glass in a Tuff-Dominated System"**, *Scientific Basis for Nuclear Waste Management*, X, J. K. Bates and W. B. Seefeldt (eds.), Mat. Res. Soc., Pittsburgh, PA, 447–458 (1987).

66. Vernaz, E.Y. and N. Godon, **"Leaching of Actinides from Nuclear Waste Glass: French Experience"**, *Scientific Basis for Nuclear Waste Management*, XV, C. G. Sombret (ed.), Mat. Res. Soc., Pittsburgh, PA, 37–48 (1992).

67. Ebert, W.L., S.F. Wolf, and J.K. Bates, **"The Release of Technetium from Defense Waste Processing Facility Glasses"**, *Scientific Basis for Nuclear Waste Management*, XIX, W. M. Murphy and D. A. Knecht (eds.), Mat. Res. Soc., Pittsburgh, PA, 221–227 (1996).

68. McGrail, B.P., **"Waste Package Component Interactions with Savannah River Defense Waste Glass in a Low-Magnesium Salt Brine"**, Nuclear Technology, 168–186 (1986).

69. Burbank, D.A., **"Waste Acceptance Criteria for the Immobilized Low-Activity Waste Disposal Facility"**, US DOE Report RPP-8401, Rev. 0, CH2M HILL Hanford Group, Richland, WA (May 2002).

70. ANSI/ANS/ANS-16.1, **“Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short Term Test Procedure”**, American National Standards Institute/American Nuclear Society, La Grange Park, IL

71. DOE/ORP Contract with Bechtel National, Inc., **“Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant”**, Contract Number DE-AC27-01RV14136, U.S. Department of Energy, Office of River Protection, Richland, WA (December 2000).

72. ASTM 1663-09, “**Standard Test Method for Measuring Waste Glass Durability by Vapor Hydration Test”**, ASTM International, West Conshohocken, PA (2010).

73. Missimer, D.M. and R.L. Rutherford, **“Preparation and Initial Characterization of Fluidized Bed Steam Reforming Pure-Phase Standards”**, U.S. DOE Report SRNL-STI-2013-00111, Savannah River National Laboratory, Aiken, SC (Febuary 2013).

74. River Protection Project, **“Integrated Disposal Facility Waste Acceptance Criteria”**, RPP-8402, Revision 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2005).

75. Qafoku, N.P., J.H. Westsik, D.M. Strachan, M.M. Valenta, and R.P. Pires, **“Secondary Waste Form Down-Selection Data Package- Fluidized Bed Steam Reforming Waste Form”**, U.S. DOE Report PNNL-20704, Pacific Northwest National Laboratory, Richland, WA (September 2011).

76. Environmental Protection Agency, **“Paint Filters Liquids Test – Physical and Chemical Methods”**, *SW-846*. Method 9095B, Rev. 2. U.S. Environmental Protection Agency, Washington, D.C. (2004)

77. U.S. Nuclear Regulatory Commission, **“Technical Position on Waste Form (Revision 1)”**, U.S. NRC Low-Level Waste Management Branch Division of Low-Level Waste management and Decommissioning (January 1991).

78. U.S. Nuclear Regulatory Commission, **“Radionuclide Release from Slag and Concrete Waste Materials, Part I. Conceptual Models of Leaching from Complex Materials and Laboratory Test Methods”**, U.S. NRC Document No. NUREG/CR-7025 (March 2010).

79. Lea, F.M., “**The Chemistry of Cement and Concrete”**, Edward Arnold Publishers, Ltd., 727 pp (1970).

80. DOE EM-31 Technology Development & Deployment (TDD) Program Task Plan, **“Fluidized Bed Steam Reformer Low-Level Waste Form Qualification,”** U.S. DOE Document No.: WP-5.2.1-2010-001 (October 2010).

81. Pierce, E.M., “Review of Existing Fluidized-Bed Steam Reformer Sodium Aluminosilicate Waste Form Performance Data,”ORNL/TM-2012/19. Oak Ridge National Laboratory, Oak Ridge, TN (2012).

82. Burket, P.R., W.E. Daniel, C.A. Nash, C.M. Jantzen, and M.R. Williams, **“Bench-Scale Steam Reforming of Actual Tank 48 Waste”**, US DOE Report SRNL-STI-2008-00105, Savannah River National Laboratory, Aiken, SC (September 2008)

83. Burket, P.R., W.E. Daniel, C.M. Jantzen, C.A. Nash, C.L. Crawford, M.R. Williams, and A.B. Barnes, **“Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste”**, WM’09, Paper #9138 (2009).

84. Jantzen, C.M., P.R. Burket, A.R. Jurgensen, D.M. Misimer, and C.L. Crawford, **“Geopolymers: Low Temperature Waste Forms for Hazardous Wastes and Thermal Treatment”**, U.S. DOE Report SRNS-STI-2008-00127, Journal Am. Ceram. Soc. (in preparation) also U.S. DOE Slide Presentation WSRC-STI-2007-00584S (2007).

85. Jantzen, C.M. and C.J. Bannochie, **“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 68 Tank Blend Study”**, U.S. DOE Report SRNL-RP-2010-01363, Savannah River National Laboratory, Aiken, SC (September 2010).

86. Pierce, E.M., W.W. Lukens, K. Lilova, J. Fitts, and A. Navrosky, **“Summary Report of Fluidized Bed Steam Reformer Performance Testing”**, U.S. DOE Report, Oak Ridge National Laboratory, Oak Ridge, TN (in preparation).

87. Work For Others Request WFO-09-003, **“Evaluation of Radioactive THOR® Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project”**, (April 2, 2009).

88. Work For Others Request WFO-08-003, **“Technical Consulting and Evaluation of THOR® Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project”**, (2008).

89. ASTM C39/C39M-10, **“Compressive Strength of Cylindrical Concrete Specimens”**, ASTM International, West Conshohocken, PA (2010).

90. ASTM C1231/C1231M-10a, **“Use of Unbonded Caps in Determination of Compressive Strength of Hardened Concrete Cylinders”**, ASTM International, West Conshohocken, PA (2010).

91. ASTM C1308-10. **“Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms”**, ASTM International, West Conshohocken, PA (2010).

92. EPA Test Method 1311, **“ Toxicity Characteristic Leaching Procedure, TCLP,” U.S. Environmental Protection Agency (EPA),**” Washington, DC (2008).

93. ASTM C1285-08, **“Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)”**, ASTM International, West Conshohocken, PA (2008).

94. ASTM 1662-10. **“Standard Practice for For Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method”**, ASTM International, West Conshohocken, PA (2010).

95. McGrail, B.P., P.F. Martin, and C.W. Lindenmeier, **“Accelerated Testing of Waste Forms Using a Novel Pressurized Unsaturated Flow (PUF) Method”**, Materials Research Society Symposium Proceedings, 465, 253-260 (1997).

96. Schreiber, H.D., **“Redox State of Model Fluidized Bed Steam Reforming Systems Final Report Subcontract AC59529T”**, VMI Research Laboratories, VMI, Lexington, VA (December 2007).

97. Grimm, R.E., **“Clay Mineralogy”**, McGraw Hill Book Co., New York, 384pp (1953).

98. P.R. Burket, J.C. Marra, J.P. Pareizs, and C.M. Jantzen, **“Evaluation of Fluidized Bed Steam Reforming (FBSR) Technology for Sodium Bearing Wastes From Idaho and Hanford Using the Bench-Top Steam Reformer (BSR),**” U.S. DOE Report WSRC-TR-2004-00560 (Jan 2005).

99. Christopher Brown of PNNL personal communication.

100. Bullock, J.H., Jr., J.D. Cathcart, and W.J. Betterton, **“Analytical Methods Utilized by the United States Geological Survey for the Analysis of Coal and Coal Combustion By-products”**, US Geological Survey,Denver, CO (2002).

101. Baumann, E.W., **“Colorimetric Determination of Iron(II) and Iron(III) in Glass”**, Analyst,117, 913-916 (1992).

102. Blackford, M.G., J.V. Hanna, K.J. Pike, E.R. Vance, and D.S. Perera, **“Transmission Electron Microscopy and Nuclear Magnetic Resonance Studies of Geopolymers for Radioactive Waste Immobilization”**, *J. Am. Ceram. Soc.*, 90 [4], 1193-1199 (2007).

103. Rowles, M.R. and B.H. O’Connor, **“Chemical and Physical Micro-scale Character of Aluminosilicate Geopolymers Synthesised by Sodium Silicate Activation of Metakaolinite”**, *J. Am. Ceram. Soc.*, 92 [10], 2354-2361 (2009).

104. Hardjito, D. and B. V. Rangan, **“Development and Properties of Low-Calcium Fly Ash-Based Geopolymer Concrete”**, Faculty of Engineering, Curtin University of Technology, Perth, Australia Report (2005).

105. Davidovits, J., **“Geopolymers: Man-Made Rock Geosynthesis and Resulting Development of Very Early High Strength Cement”**, *J. of Materials Education*, 16 [2&3], 91-139 (1994).

106. Davidovits, J., **“Geopolymers: Inorganic Polymeric New Materials”**, *J. Thermal Analysis*, 37, 1633-1656 (1991).

107. Kriven, W.M., M. Gordon, and J.L. Bell, **"Geopolymers: Nanoparticulate, Nanoporous Ceramics Made Under Ambient Conditions"**, AFOSR STTR Grant F49620-02 C-010.

108. Kriven, W.M., **"Inorganic Polysialates or "Geopolymers"**, *American Ceramic Society Bulletin*, 89 [4] 31-34 (2010).

109. van Jaaarsveld, J.G.S., van Deventer, J.S.J. and Lorenzen, L. **"The Potential Use of Geopolymeric Materials to Immobilise Toxic Metals: Part I. Theory and Applications"**, Minerals Engineering, 10[7], 659-669 (1996).

110. Crank, J., **"The Mathematics of Diffusion"**, Oxford University Press, London (1986).

111. Muan, A. and E.F. Osborn, **"Phase Equilibria among Oxides in Steelmaking"**, Addison-Wesley Publishing Company, Inc., Reading, MA, 236 pp. (1965).

112. Nayak, M. and T.R.N. Kutty, **"Luminescence of Fe^{3+} doped $NaAlSiO_4$ Prepared by Conversion"**, Materials Chemistry and Physics, 57 [2], 138-146 (1998).

113. Tomisaka, T. and H.P. Eugster, **"Synthesis of the Sodalite Group and Subsolidus Equilibria in the Sodalite-Noselite System"**, Min. Japan, 5, 249-275 (1968).

114. Neeway, J.J., N.P. Qafoku, B.D. Williams, K., Rod, M.E. Bowden, C.F. Brown, and E.M. Pierce, "**Performance of the Fluidized Bed Steam Reforming Product Under Hydraulically Unsaturated Conditions"**, submitted to J. of Environmental Radioactivity (in rewrite).

115. Steefel, C.I. and Van Cappellen, P., **"A new kinetic approach to modeling water-rock interaction: The role of nucleation, precursors, and Ostwald ripening,"** Geochimica et Cosmochimica Acta, 54, 2657-2677 (1990).

116. Huang, W.H., **"Stabilities of Kaolinite and Halloysite in Relation to Weathering of Feldspars and Nepheline in Aqueous Solution,"** Am. Min., 59, 365-371 (1974).

117. Haaker, R.F. and R.C. Ewing, **"Naturally Occurring Crystalline Phases: Analogues for Radioactive Waste Forms",** U.S. DOE Report PNL-3505 (January 1981).

118. Hajimohammadi, A., J.L. Provis, and J.S.J. van Devente, **"Effect of Alumina Release Rate on the Mechanism of Geopolymer Gel Formation"**, Chemistry of Materials, 22, 5199–5208 (2010).

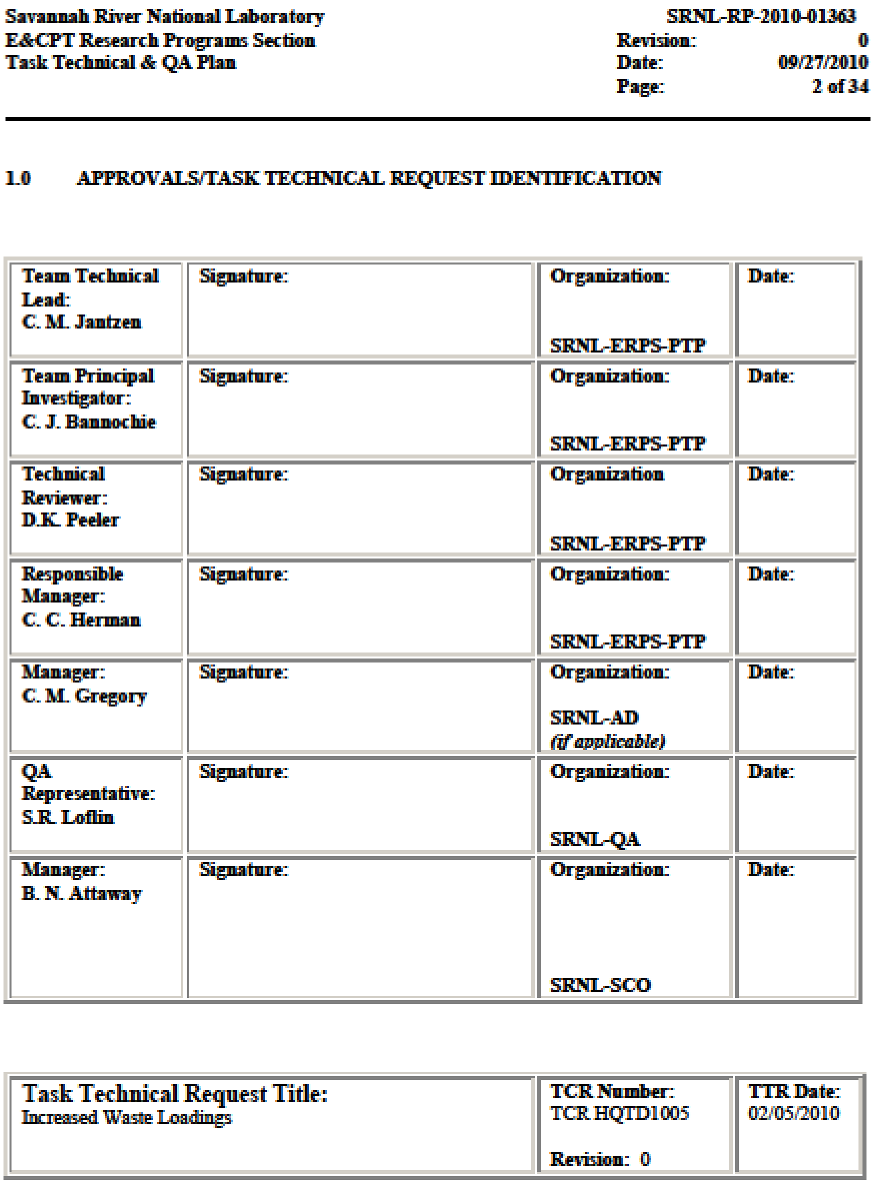
119. Depmeier, W. **"The Sodalite Family – A Simple but Versatile Framework Structure"**, in Review in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C. V. 57, 203-240 (2005).

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

SRNL-RP-2010-01363

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 68 Tank Blend Study

C. M. Jantzen
C. J. Bannochie



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1.0 APPROVALS/TASK TECHNICAL REQUEST IDENTIFICATION

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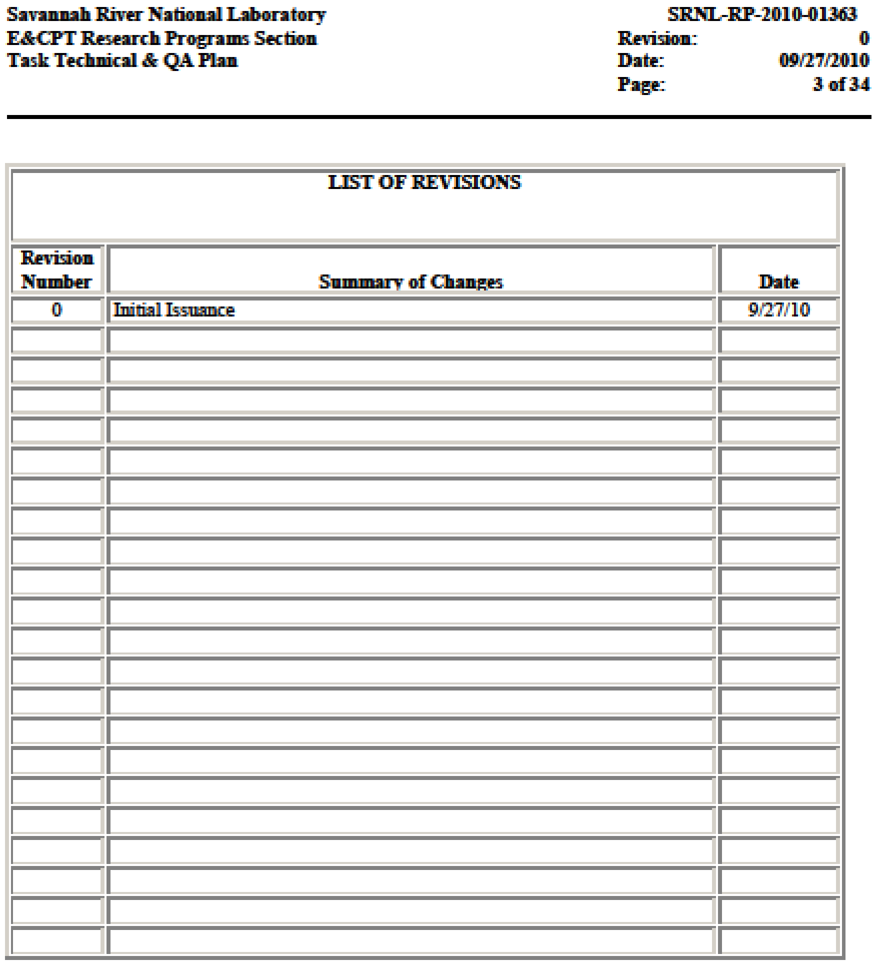
Team Principal Investigator: **C. J. Bannochie**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Technical Reviewer: **D.K. Peeler**	**Signature:**	**Organization** **SRNL-ERPS-PTP**	**Date:**
Responsible Manager: **C. C. Herman**	**Signature:**	**Organization:** **SRNL-ERPS-PTP**	**Date:**
Manager: **C. M. Gregory**	**Signature:**	**Organization:** **SRNL-AD** ***(if applicable)***	**Date:**
QA Representative: **S.R. Loflin**	**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



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LIST OF REVISIONS		
Revision Number	**Summary of Changes**	**Date**
0	Initial Issuance	9/27/10

2.0 INTRODUCTION

2.1 Task Definition

2.1.1 Introduction

The baseline treatment plan is for Hanford 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 Low Activity Waste (LAW). 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 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. The first of which will be a radioactive Savannah River Site (SRS) salt supernate that has been compositionally trimmed to look like the Hanford Rassat simulant that TTT processed.

FBSR treatment offers a low temperature (700-750°C) continuous method by which LAW may be processed into a crystalline ceramic (mineral) waste form irregardless of whether the wastes are high in organics, nitrates, sulfates/sulfides, other anions or components. The FBSR process produces no secondary waste stream. Based on previous testing,[4,5,6,7,8,9,10,11,12,13] 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 (SC).[14,15] 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 SC 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.[16,17]

The scope of work addressed in this task planning document consists of SRNL testing the Rassat simulant tested in the Engineering Scale Technology Demonstration (ESTD) TTT pilot at Hazen Research Inc. (HRI) in the non-radioactive BSR in 735-11A to provide (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the BSR product in comparison with the TTT pilot scale product provided under WFO-09-003[16], and (3) granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared under WFO-09-003[16]. These demonstrations will also provide needed tie backs to previous durability testing of the Rassat simulant FBSR granular and monolithic product[4-13]

The scope of work addressed in this task planning document also consists of SRNL mineralizing a radioactive SRS salt supernate sample from Tank 50 that is available in SRNL and has already been chemically analyzed for a saltstone program. The Tank 50 salt supernate will be shimmed to look like the Rassat simulant and processed in the BSR in the SC to provide (1) radioactive granular samples for testing the durability response of the BSR product compared to the TTT pilot scale product from WFO-09-003[16] and the non radioactive granular product produced in the scope above, and (2) radioactive granular products to monolith and compare (durability and compressive strength) to the non-radioactive monolithic waste forms prepared under WFO-09-003[16] 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. Thus the durability test responses are expected to be comparable when scaled to surface area but the comparison between the durability response from the BSR and the ESTD is actually an objective of the current study.

2.1.2 Non-Radioactive Tests

The Rassat simulant will be fabricated using the formulation given in Table 1 which corresponds to the P1B formulation given in Table 2. The target concentration for the LAW was increased by a factor of 10 for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs as done in the TTT pilot scale demonstrations of the Rassat simulant.[1]

Substitutions for the suggested reagents will be performed for components as necessary based on availability of the chemicals listed in Table 1. Any substitutions will be documented and the concentrations recalculated and independently verified. This simulant, which is intended to be identical to the one used in the TTT pilot scale testing, 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 SC. 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 ten 1"OD x 2"H monoliths and 500 grams of granular product for durability testing at Pacific Northwest National Laboratory (PNNL) and SRNL. Therefore, a total of ~1000 grams) is required. After the 28 day curing, five of the monoliths will be sent to PNNL for future testing and five will be retained at SRNL for testing.

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SRNL will perform analysis 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-ignition (LOI) tests at 110°C to determine moisture content and LOI tests at 525°C to determine the coal fraction in the samples. This temperature removes the carbon as the hydrogen, oxygen and moisture from the coal have been removed by the BSR processing, but this temperature does not vaporize the sulfur in the coal. 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 the temperature recommended by a US Geological Survey procedure developed for coal analyses.[18] 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 Toxicity Characteristic Leaching Procedure (TCLP) will be performed by an Environmental Protection Agency (EPA) certified laboratory.

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[17] matrix or the testing performed as part of EM-31 Task 5.2.1. The monolith will be characterized as described above and using a compression test. Diffusion coefficients for Re, Cs, and I will be determined 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

2.1.3 Radioactive Tests

The Tank 50 SRS salt supernate sample will be analyzed to fully characterize the radioactive constituents after trimming with radioactive Tc^{99}, mixtures of Cs^{137} (radioactive) and Cs^{133} (non-radioactive), and I^{129} (radioactive), I^{125} (radioactive) and/or I^{127} (non-radioactive). The Tc, Cs, and I additions will allow the Tank 50 sample to more closely replicate the constituents of the Rassat 68 tank LAW blend composition from Hanford given in Table 1. Cs^{137} will not be doped into the sample as there is sufficient Cs^{137} in the Tank 50 sample. Resource Conservation and Recovery Act (RCRA) metals will also be added to the levels indicated in Table 1. If precipitates form and cannot be redissolved after either heating or stirring for 48 hours or both, the supernates will be filtered to remove solids that may not react in the BSR or may clog the BSR input feed lines. While this is not prototypic of the TTT pilot scale process this may be necessary due to the effects of scaling. The corresponding column is labeled P1B in Table 2. Finally, non-radioactive Re will be added at the levels given in Table 1 (labeled P1B in Table 2) to determine the effectiveness of Re as a surrogate for Tc^{99} during BSR processing, e.g. 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.

The Rassat simulant, as doped by TTT for the ESTD pilot scale tests were adhered to because the determination of the appropriate metal concentrations was based on an evaluation of the anticipated feed composition (the Rassat Simulant from Reference 2); discussions with the DOE field office; discussions with the environmental regulators, and an evaluation of the Hanford Tank Waste Envelopes A, B, and C.[19] It was determined through the evaluation of the actual tank waste metals concentrations that some metal levels were not sufficient to achieve reliable detection in the off-gas sampling.[1] Therefore, the identified metals concentrations were increased in the simulant feed to ensure detection and enable calculation of system removal efficiencies, product retention efficiencies, and mass balance closure without regard to potential results of those determinations or impacts on product durability response such as TCLP.[1]

During the demonstration, ~90% of the waste will be processed with the Tc, Re, and I levels equivalent to the Rassat simulant given in Table 1 (labeled P1B in Table 2), while the remaining ~10% of the waste will be 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 Synchrotron Accelerator testing at the Stanford Synchrotron Radiation Lightsource (formerly Stanford Synchrotron Radiation Laboratory) to determine the local bonding of the Tc^{99} and I^{125}/I^{129} in the mineral waste form. 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 Synchrotron testing.

Partitioning of the radionuclides (Cs, Tc, and I) and Re and Hg 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 SC, kaolin clay will be added to the modified Tank 50 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 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 SC.

Adequate radioactive granular product must be produced in the BSR in the SC to fabricate ten 1"OD x 2"H monoliths and provide granular product for durability testing at PNNL and SRNL (~1000 grams). After the required 28 day curing, five of the monoliths will be sent to PNNL for future testing and five will be retained at SRNL for testing. In addition, 12 1" OD x 2"H monoliths will be made from the TTT P1B granular product. Granular product (200-300 grams) and 6 of the monoliths will be sent to PNNL for future testing and six will be retained at SRNL for testing.

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 SC. This will include LOI 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 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. 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. TCLP testing will be performed by an EPA certified laboratory.

Both the granular product and the monolith product will be leach-tested using the EPA TCLP procedure performed by a certified offsite laboratory. This activity of packaging and shipping a radioactive sample for off-site TCLP analysis is currently practiced on a quarterly basis at SRS for the saltstone facility support program and similar protocol will be followed for these samples.

Table 1 Rassat Simulant Makeup

Stream Component	Suggested Reagent	Target Component	LAW Target Component Concentration [mol/L]	Reagent Quantity Needed for 1 L	Stoichio-metric Coefficient	Reagent Molecular Weight	Purity [wt%]	Solution Density [g/ml]	Comments
Oxalate	$Na_2(C_2O_4)$	C_2O_4	0.0118	1.58 g	1	134.00	99.90%		
Acetate	$Na(C_2H_3O_2)$	CH_3COO	0.132	10.83 g	1	82.03	99.99%		
Sodium Nitrate	$NaNO_3$	$NaNO_3$	2.308	196.76 g	1	84.99	99.70%		
Potassium Nitrate	KNO_3	K	0.0124	1.26 g	1	101.10	99.80%		
Hydroxide	NaOH	OH	0.74	29.86 g	1	40.00	99.13%		
Aluminum nitrate 60% solution	$Al(NO_3)_3{*}9H_2O$	Al	0.0637	39.64 g	1	375.13	60.28%	1.336	
Carbonate	Na_2CO_3	CO_3	0.475	50.34 g	1	105.99	100.00%		
Sulfate	Na_2SO_4	SO_4	0.09	12.81 g	1	142.04	99.80%		
Chloride	NaCl	Cl	0.0438	2.56 g	1	58.44	99.96%		
Fluoride	NaF	F	0.0316	1.35 g	1	41.99	98.18%		
Iodide	NaI	I	0.013	1.95 g	1	149.89	99.70%		
Nitrite	$NaNO_2$	NO_2	0.424	29.64 g	1	69.00	98.70%		
Silver	$AgNO_3$	Ag	0.00161	0.28 g	1	169.87	99.00%		
Barium	$Ba(NO_3)_2$	Ba	0.00751	1.97 g	1	261.34	99.70%		
Cadmium	$Cd(NO_3)_2{*}4H_2O$	Cd	0.0042	1.30 g	1	308.48	99.34%		
Cesium	$CsNO_3$	Cs	0.013	2.53 g	1	194.91	100.00%		Calculated from impurities
Nickel	$Ni(NO_3)_2{*}6H_2O$	Ni	0.0106	3.10 g	1	290.79	99.38%		Calculated from Ni purity = 20.0579%
Lead	$Pb(NO_3)_2$	Pb	0.00606	2.02 g	1	331.21	99.12%		
Thallium	$TlNO_3$	Tl	0.00202	0.54 g	1	266.39	98.95%		Calculated from Tl purity = 75.92%
Arsenic Soln	H_3AsO_4	As	0.00137	0.26 g	1	141.94	75.40%	1.876	Calculated from As purity = 39.8%
Rhenium	$NaReO_4$	Re	0.0017	0.46 g	1	273.19	100.00%		Calculated from Re purity = 68.16%
Selenium	SeO_2	Se	0.00123	0.14 g	1	110.96	99.40%		
Antimony	Sb_2O_3	Sb	0.00434	0.63 g	2	291.51	99.82%		
Chromium	$Na_2Cr_2O_7{*}2H_2O$	Cr	0.0104	1.55 g	2	298.00	100.00%		Reduced from assay value of 101.50%
Phosphate	$Na_3PO_4{*}12H_2O$	PO_4	0.0492	19.96 g	1	380.12	93.70%		
OptiKasT clay	$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$	clay	640 gm/L	640.00 g	1	258.160	100.00%		Clay on wet basis-determined by $LOI_{700°C}$

The target concentration for the LAW was increased by a factor of 10 for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000.000 for Cs as done in the TTT pilot scale demonstrations of the Rassat simulant. [1]

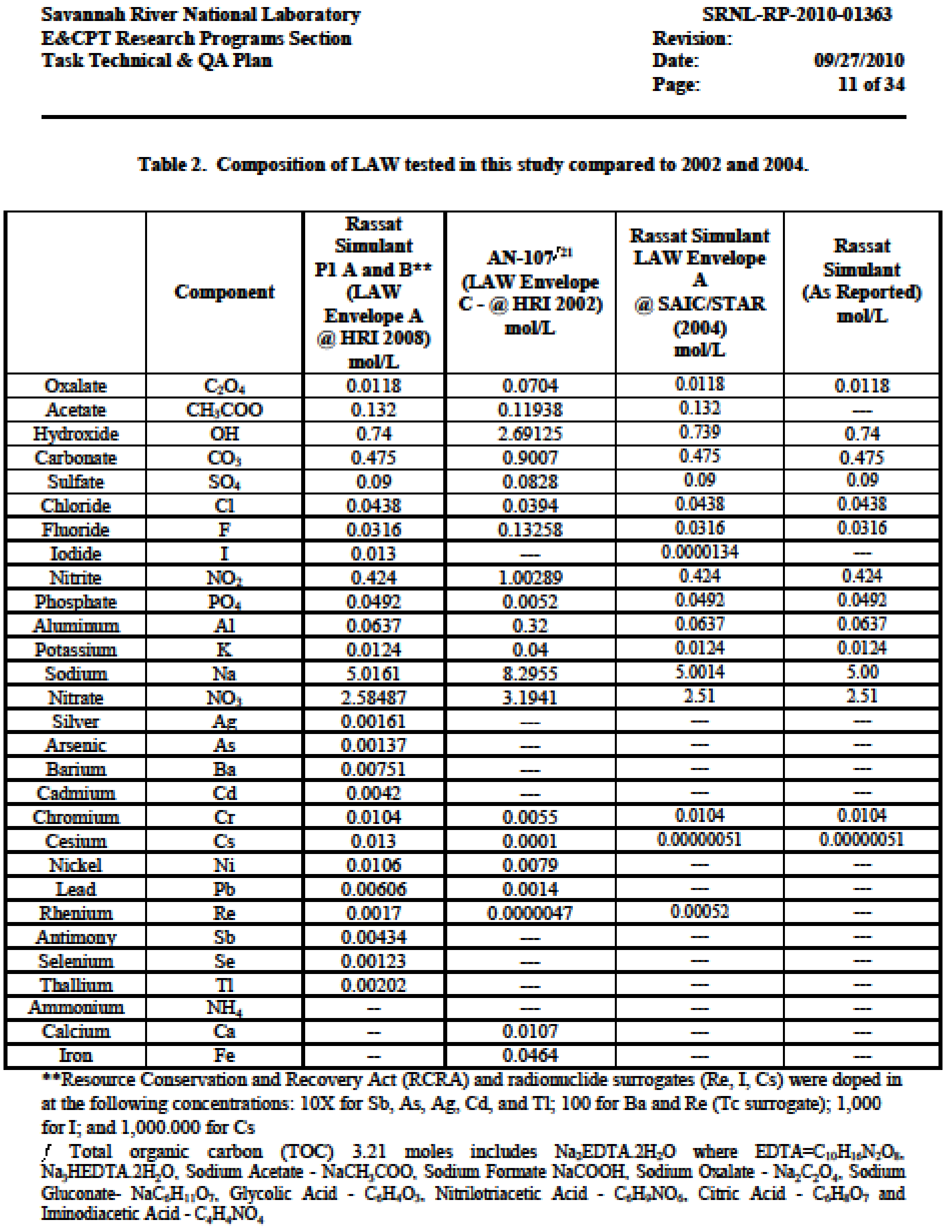

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Table 2. Composition of LAW tested in this study compared to 2002 and 2004.

	Component	Rassat Simulant P1 A and B** (LAW Envelope A @ HRI 2008) mol/L	AN-107[ƒ,21] (LAW Envelope C - @ HRI 2002) mol/L	Rassat Simulant LAW Envelope A @ SAIC/STAR (2004) mol/L	Rassat Simulant (As Reported) mol/L
Oxalate	C_2O_4	0.0118	0.0704	0.0118	0.0118
Acetate	CH_3COO	0.132	0.11938	0.132	---
Hydroxide	OH	0.74	2.69125	0.739	0.74
Carbonate	CO_3	0.475	0.9007	0.475	0.475
Sulfate	SO_4	0.09	0.0828	0.09	0.09
Chloride	Cl	0.0438	0.0394	0.0438	0.0438
Fluoride	F	0.0316	0.13258	0.0316	0.0316
Iodide	I	0.013	---	0.0000134	---
Nitrite	NO_2	0.424	1.00289	0.424	0.424
Phosphate	PO_4	0.0492	0.0052	0.0492	0.0492
Aluminum	Al	0.0637	0.32	0.0637	0.0637
Potassium	K	0.0124	0.04	0.0124	0.0124
Sodium	Na	5.0161	8.2955	5.0014	5.00
Nitrate	NO_3	2.58487	3.1941	2.51	2.51
Silver	Ag	0.00161	---	---	---
Arsenic	As	0.00137	---	---	---
Barium	Ba	0.00751	---	---	---
Cadmium	Cd	0.0042	---	---	---
Chromium	Cr	0.0104	0.0055	0.0104	0.0104
Cesium	Cs	0.013	0.0001	0.00000051	0.00000051
Nickel	Ni	0.0106	0.0079	---	---
Lead	Pb	0.00606	0.0014	---	---
Rhenium	Re	0.0017	0.0000047	0.00052	---
Antimony	Sb	0.00434	---	---	---
Selenium	Se	0.00123	---	---	---
Thallium	Tl	0.00202	---	---	---
Ammonium	NH_4	--	---	---	---
Calcium	Ca	--	0.0107	---	---
Iron	Fe	--	0.0464	---	---

**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

[ƒ] Total organic carbon (TOC) 3.21 moles includes $Na_2EDTA.2H_2O$ where EDTA=$C_{10}H_{16}N_2O_8$, $Na_3HEDTA.2H_2O$, Sodium Acetate - $NaCH_3COO$, Sodium Formate NaCOOH, Sodium Oxalate - $Na_2C_2O_4$, Sodium Gluconate- $NaC_6H_{11}O_7$, Glycolic Acid - $C_2H_4O_3$, Nitrilotriacetic Acid - $C_6H_9NO_6$, Citric Acid - $C_6H_8O_7$ and Iminodiacetic Acid - $C_4H_4NO_4$

2.1.4 Phase Pure Standards

In a multiphase ceramic the durability response is complex as Na release comes from multiple phases while release of Re, I, F, SO_4 may only come from one sodalite phase. In order to understand the durability response of the individual mineral phases in the FBSR product, e.g. nepheline ($NaAlSiO_4$), sodalites [nominally $Na_6Al_6Si_6O_{24}(2NaCl)$, $Na_6Al_6Si_6O_{24}(2NaI)$, $Na_6Al_6Si_6O_{24}(2NaF)$, $Na_6Al_6Si_6O_{24}(Na_2Re_2O_8)$], and nosean $Na_6Al_6Si_6O_{24}(Na_2SO_4)$, phase pure standards need to be fabricated for Single Pass Flow Through (SPFT) testing and for the determination of thermodynamic parameters. The SPFT testing generates single phase forward rates that are used during Performance Assessments (PA). The thermodynamic parameters are also used during PA analyses. In addition, XRD quantitative calibration standards are needed by SRNL to determine the amount of the various phases in the granular FBSR product (see Section 2.1.2). Analytical Development (AD) personnel supported the production of these standards for previous FBSR testing in 2004. They will provide sufficient material to support this testing.

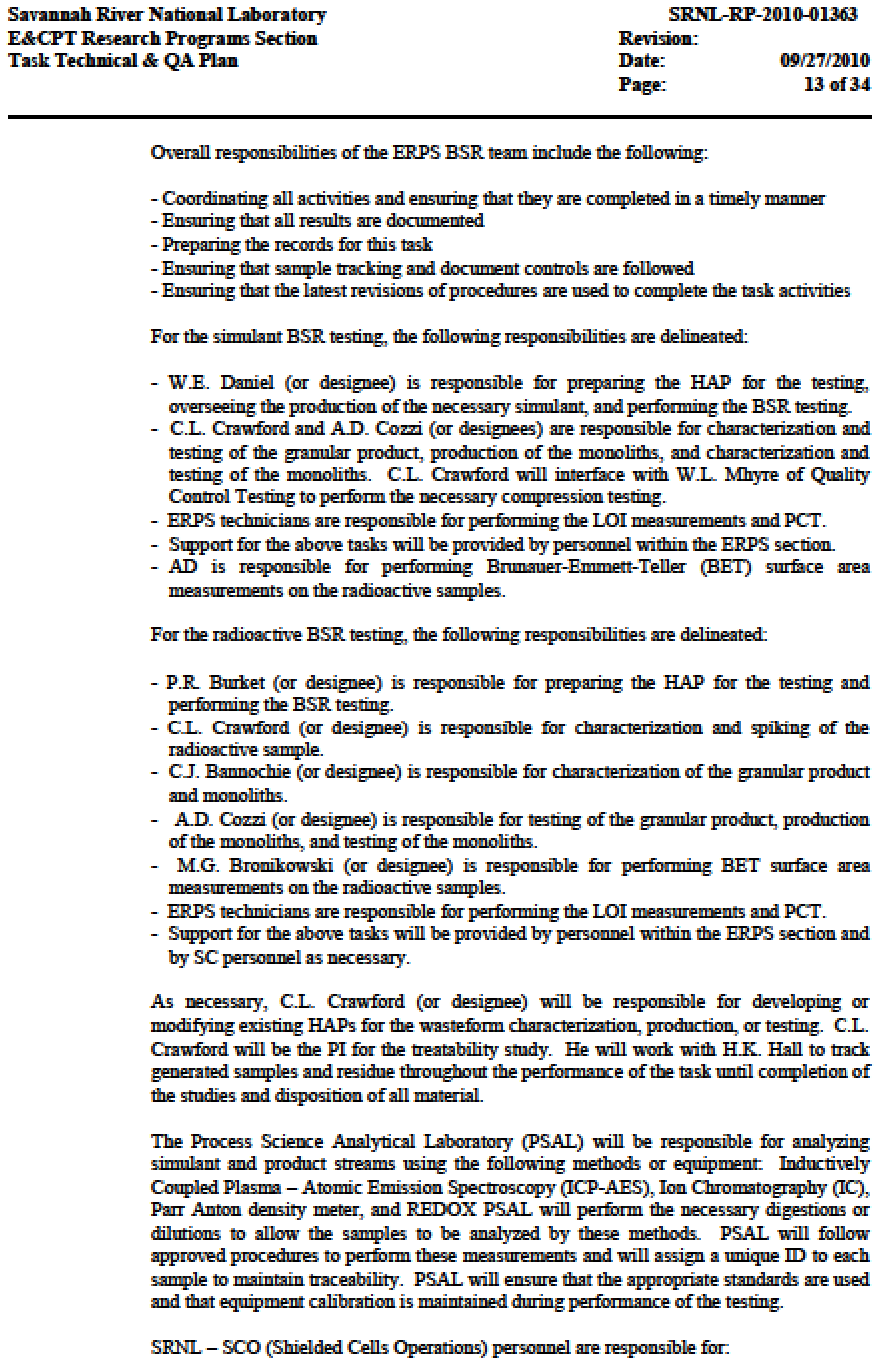
Sufficient quantities must be made for the durability testing, the thermodynamic testing and the SRNL quantitative XRD calibration curves (~200 grams). Of the 200 grams, about 160 grams of each mineral are to be shipped to Oak Ridge National Laboratory (ORNL) for durability measurement and thermodynamic characterization. ORNL will oversee the thermodynamic characterization which may be performed by a third party organization, e.g. PNNL or University of California at Davis. The remaining quantities of each of the phase pure standards will be used to develop quantitative XRD calibration curves at SRNL using a nepheline glass as a matrix. These quantitative XRD standards will be used to evaluate the percentages of each phase in the FBSR product.

2.2 Customer/Requester

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 wasteform 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:

- W.E. Daniel (or designee) is responsible for preparing the HAP for the testing, overseeing the production of the necessary simulant, and performing the BSR testing.
- 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 radioactive 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 performing the BSR testing.
- C.L. Crawford (or designee) is responsible for characterization and spiking of the radioactive sample.
- C.J. Bannochie (or designee) is responsible for characterization of the granular product and monoliths.
- A.D. Cozzi (or designee) is responsible for testing of the granular product, production of the monoliths, and testing of the monoliths.
- M.G. Bronikowski (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.
- Support for the above tasks will be provided by personnel within the ERPS section and by SC personnel as necessary.

As necessary, C.L. Crawford (or designee) will be responsible for developing or modifying existing HAPs for the wasteform characterization, production, or testing. C.L. Crawford will be the PI for the treatability study. He will work with H.K. Hall to track generated samples and residue throughout the performance of the task until completion of the studies and disposition of all material.

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, and REDOX 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.

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
- Fabricating and analyzing the necessary phase pure standards outlined in this TTQAP
- Analyzing radioactive waste samples and simulant and product streams using the following methods or equipment: ICP-AES, ICP-MS, IC, BET, particle size distribution (PSD), XRD, SEM, CSEM, and radiometric analyses
- 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 the simulant recipe and providing the coal and clays to be used by SRNL.

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. Shipment of 5 non-radioactive monoliths and ~250 g granular product to PNNL for further testing.
5. 5 non-radioactive monoliths and ~70 g granular product for further testing for SRNL.
6. Shipment of sufficient quantities (~160 grams) of nepheline, chloride sodalite, iodide sodalite, rhenium sodalite, and nosean to ORNL to support gathering durability and thermodynamic data for Performance Assessment evaluations of the FBSR products.

7. Mass balance of Tc^{99}, I^{129}, and Cs^{137} during radioactive BSR operation.
8. Interim documentation and a final approved report documenting the results of the radioactive BSR mineralized product and subsequent product characterization and testing.
9. Shipment of 5 radioactive monoliths and ~220 g granular product to PNNL for further testing.
10. 5 radioactive monoliths and ~70 grams granular product for SRNL testing.
11. Shipment of granular products made from Tank 50 waste at an elevated solids spiking of 150μg/g Tc^{99} and I^{129} for Synchrotron testing at Stanford Synchrotron Radiation Lightsource.

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 and approval of the Environmental Evaluation Checklist (EEC).
- Conduct R&D/HAP/Safety review for radioactive BSR testing including initiation and 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 initiation and approval of the EEC for simulant and radioactive testing.

4.2 Simulant and BSR Product Formation

- Make ample Rassat simulant (~2 Liters) of the composition provided in Table 1 in the column labeled P1B for non-radioactive testing of the BSR.
- Analyze non-radioactive Rassat 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 (~640g/L on a wet clay basis) and sufficient carbon to provide the necessary reductant (~130.8g/L Bestac carbon) for the non-radioactive BSR campaigns.
- Run the non-radioactive BSR in 735-11A between 650 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each Rassat simulant run will use a minimum of 100 mL and maximum of 250 mL of feed. It is estimated that 20 runs with ~100 mL or 8 runs with 250 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 1000 grams (ten 1" x 2" monolith cylinders and 600 grams of granular product).

4.3 Simulant Product Analysis and Off-Gas Mass Balance

- Analyze the BSR products from several representative BSR campaigns (any time the run parameters change significantly) 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 LOI 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 all elements 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 (7 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 is known.
- Perform long term ASTM C1285 - PCT on the BSR granular products for 6 months with weekly sub-sampling for the first month and bi-monthly sub-sampling thereafter. At the end of each monthly 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)[17].

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[16] 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
- Upon passing the compression test at 500 psi. ship 5 of the monoliths to PNNL along with ~250 grams of granular product.

- 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 (7 day) ASTM C1285 - PCT on the BSR monolith products.
- Perform long term ASTM C1285 - PCT on the BSR monolith products for 6 months with monthly subsampling. 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)[3,16].
- Perform ASTM C1308 (the ASTM variant of ANSI 16.1) on a minimum of two monoliths. This is a 90 day test.

4.6 Preparation of Phase Pure Standards for PNNL Testing and Quantitative XRD Standard Development

- Make ample (~200 grams) nepheline ($NaAlSiO_4$) hydrothermally and confirm acceptability by XRD.
- Make ample (~200 grams) sodalite ($Na_6Al_6Si_6O_{24}(2NaCl)$) and confirm acceptability by XRD.
- Make ample (~200 grams) iodine sodalite ($Na_6Al_6Si_6O_{24}(2NaI)$) and confirm acceptability by XRD.
- Make ample (~200 grams) fluoride sodalite ($Na_6Al_6Si_6O_{24}(2NaF)$) and confirm acceptability by XRD.
- Make ample (~200 grams) rhenium sodalite ($Na_6Al_6Si_6O_{24}(Na_2Re_2O_8)$) and confirm acceptability by XRD.
- Make ample (~200 grams) nosean ($Na_6Al_6Si_6O_{24}(Na_2SO_4)$) and confirm acceptability by XRD.
- Analyze phase pure standards for LOI at 110°C, particle size distribution, and BET surface area.
- Ship requested mass (~160 grams) of each phase pure standard to ORNL for durability and thermodynamic testing.
- Retain remaining phase pure standards at SRNL to develop quantitative XRD calibrations.
- Use quantitative XRD calibrations to re-evaluate all XRD patterns from the radioactive and non-radioactive testing in this task plan. The XRD patterns can be archived electronically for this re-evaluation.

4.7 Radioactive BSR Product Formation

- Obtain the required quantity (~1-1.5L) of Tank 50 SRS salt supernate and transport to the SRNL SC.
- Initiate Treatability Study for radioactive sample handling and processing in the SC in accordance with SRNL Procedure Manual L1, 6.04 'Hazardous/Mixed Waste Treatability Studies'.

- Ensure that enough of the radioactive dopants (Tc^{99}, Cs^{137},I^{129} or I^{125}) have been procured and available.
- Dope the Tank 50 sample with Tc^{99} and I^{125}/I^{129} to the unelevated levels for Re and I in the Rassat simulant (Table 2 column for P1B divided by the correct factor, 10, 1000, etc.). The Cs content of the waste will not be increased by doping as the Cs^{137} level in the Tank 50 sample is already $4.2E^{-8}$ molar which is close to the Rassat simulant level of $5.1E^{-8}$ molar but ~3X the P1B value divided by the million fold increase that was used in the pilot scale studies.
- Analyze the trimmed SRS salt supernate after doping.
- 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 (~640g/L on a wet clay basis) and sufficient carbon to provide the necessary reductant (~130.8g/L Bestac carbon) for the radioactive BSR campaigns if the NO_3 and NO_2 content are in the range of the Rassat simulant. If not, the carbon will have to 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 SC after preliminary testing in the Shielded Cells Mock-up Facility. If already located in the SC, install new glass ware and BSR components to perform the radioactive demonstration.
- Run the radioactive BSR in the SC between 725 - 750°C in the reaction zone for sufficient duration and with enough feed to produce the desired product quantity. Each radioactive doped SRS Tank 50 run will use a minimum of 100 mL of feed. It is estimated that somewhere between 20 runs with ~100 mL each and 8 runs of ~250 mL each of SRS LAW are needed to produce enough granular product to be analyzed and tested. The estimated required granular product mass is 1000 grams (ten 1" x 2" monolith cylinders and 600 grams of granular product).
- 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 LOI 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 and Hg by Cold vapor AA.
- Analyze the off-gas condensate for Cs, I and Tc by ICP-MS and Hg by Cold vapor AA.
- 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 Hg by Cold vapor AA.
- Perform mass balances for Tc, Cs, Hg, 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 (7 day) ASTM C1285 - PCT on the FBSR granular products.
- Perform long term ASTM C1285 - PCT on the FBSR granular products for 6 months with monthly sub-sampling. 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 for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any wastes to SRNL for disposition.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2008-003)[17] 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 non-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 the 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 5 of the radioactive monoliths to PNNL along with ~250 grams 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 (7 day) ASTM C1285 – PCT on the BSR radioactive monolith products.
- Perform long term ASTM C1285 - PCT on the BSR radioactive monolith products for 6 months with monthly subsampling. 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 for TCLP testing by a certified EPA laboratory. The certified laboratory will return the products and any waste to SRNL for disposition.
- Compare results to the analyses performed with the ESTD HRI samples under previous work scope (WFO-2009-003 and WP5-2.1)[3,16] 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 3 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. No acronym after the test method indicates that ERPS personnel will perform these measurements. 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 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 3. 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, P = PSAL, U = E&CPT/PTP)

	No. of Samples†	ICP-AES	ICP-MS	IC ANIONS	CVAA Hg	Se AA	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	COMPRESSION	ASTM 1308*	TCLP*	REDOX	DENSITY	MICROTRAC
Simulant Granular Product (no dissolution)	**3**										5 A	3 U	15 A	10 A	180 A			30 O	3 P	2 P	15 A
Simulant Granular Product (Lithium Metaborate Digest)	**5**	5 P	15 A																		
Simulant Granular Product (KOH/H_2O Digest)	**3**			2 P																	
Simulant Granular Product PCT Leachates	**240**	5 P	15 A																		
Simulant Granular Product LT PCT Solids	**3**										15 A										
Simulant Condensate	**4**	5 P	15 A	5 P																	

	No. of Samples†	ICP-AES	ICP-MS	IC ANIONS	CVAA Hg	Se AA	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	COMPRESSION	ASTM 1308*	TCLP*	REDOX	DENSITY	MICROTRAC
Simulant Rinsed Lines	**4**	5 **P**	15 **A**	5 **P**																	
Simulant Monoliths (no dissolution)	**3**										15 **A**	3 **U**	15 **A**	10 **U**	180 **U**	5 **N**	90 **U**	30 **O**		2 **P**	15 **A**
Simulant Monoliths (Lithium Metaborate Digest)	**9**	5 **P**																			
Simulant Monoliths (KOH/H_2O Digest)	**4**			5 **P**																	
Simulant Monoliths PCT Leachates	**240**	5 **P**	15 **A**																		
Simulant Monoliths LT PCT Solids	**3**										15 **A**										
Radioactive Granular Product (no dissolution)	**3**									15 **A**	15 **A**	3 **U**	15 **C**	10 **U**	90 **U**			30 **O**	15 **C**	15 **U**	15 **A**

	No. of Samples†	ICP-AES	ICP-MS	IC ANIONS	CVAA Hg	Se AA	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	COMPRESSION	ASTM 1308*	TCLP*	REDOX	DENSITY	MICROTRAC
Radioactive Granular Product (AR Digest)	9	15 A	15 A		15 A	15 A			15 A												
Radioactive Granular Product (PF Digest)	9	15 A					15 A	15 A													
Radioactive Granular Product (KOH/H_2O Digest)	4			15 A																	
Radioactive Granular Product PCT Leachates	80	15 A	15 A				15 A	15 A	15 A												
Radioactive Granular Product LT PCT Solids	3										15 A										
Radioactive Condensate	4	15 A	15 A	O	15 A		15 A	15 A	15 A												
Radioactive Rinsed Lines	4	15 A	15 A	O	15 A		15 A	15 A	15 A												

	No. of Samples†	ICP-AES	ICP-MS	IC ANIONS	CVAA Hg	Se AA	GAMMA SCAN	I-129	Tc-99	SEM	XRD	LOI (110°/525°C)	BET	ST PCT	LT PCT*	COMPRESSION	ASTM 1308*	TCLP*	REDOX	DENSITY	MICROTRAC
Radioactive Monolith (no dissolution)	**3**										15 A	3 U	15 C	10 U	90 U	5 U	90 U	30 O		2 U	15 A
Radioactive Monolith (AR Digest)	**9**	15 A	15 A																		
Radioactive Monolith (PF Digest)	**9**	15 A																			
Radioactive Monolith (KOH/H$_2$O Digest)	**4**			15 A																	
Radioactive Monolith PCT Leachates	**80**	15 A	15 A				15 A	15 A	15 A												
Radioactive Monolith LT PCT Solids	**3**										15 A										
Phase Pure Standards	**6**										10 A		10 A								10 A

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 Tank 50 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.

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. Disposition of these solids after analysis will be accomplished through consultation with SRNL Environmental Compliance Authority (ECA) and in compliance with the EEC. An exemption to discharge the remaining solutions (from condensates derived from the BSR process and from the dissolutions of the product for analyses and from PCT leachates) to the High Activity Drain system in the Shielded Cells will be sought. It is expected that all solid radioactive BSR mineralized products (aggregate and monoliths) will pass the TCLP for characteristic metals. These solids could then be dispositioned per ECA guidance, e.g., Nevada Test Site. If the solid radioactive products fail TCLP, then they will be stored in a Satellite Accumulation Area and disposition will be pursued through consultation with SRNL ECA. All job control waste will be disposed of by approved waste streams.

Samples will be sent to an EPA certified laboratory for testing and the sample residues will either be returned to SRNL or will be disposed of by the laboratory within the timeframe of the treatability study. Samples for PNNL will be sent after the treatability study has ended, i.e. once the samples have been archieved, they will be sent to PNNL under the sample exclusion rule rather than as part of the treatability study. Sample residues will be returned to SRNL after their testing is completed. In addition, any samples or waste generated during the testing will also be returned to SRNL for disposition. ERPS will work with the SRNL ECA to disposition these residues.

6.3 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 SC. The simulant BSR will also be used for additional testing and thus will remain set-up until subsequent Hanford testing is completed.

6.4 Exposure of Personnel

The samples are radioactive and 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 4.

Table 4. 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 is maintained but it is currently being used to support simulant testing. Spare parts are available for some of the components. Currently, a spare controller and Mass Spectrometer is not available but both 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 SC, facility support will be required to monitor the SC ventilation system since the BSR system generates appreciable quantities of flammable hydrogen. No physical impacts to the facility are anticipated.

Table 5. Programmatic Risk Review (continued)

Question	Response
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 Tank 50 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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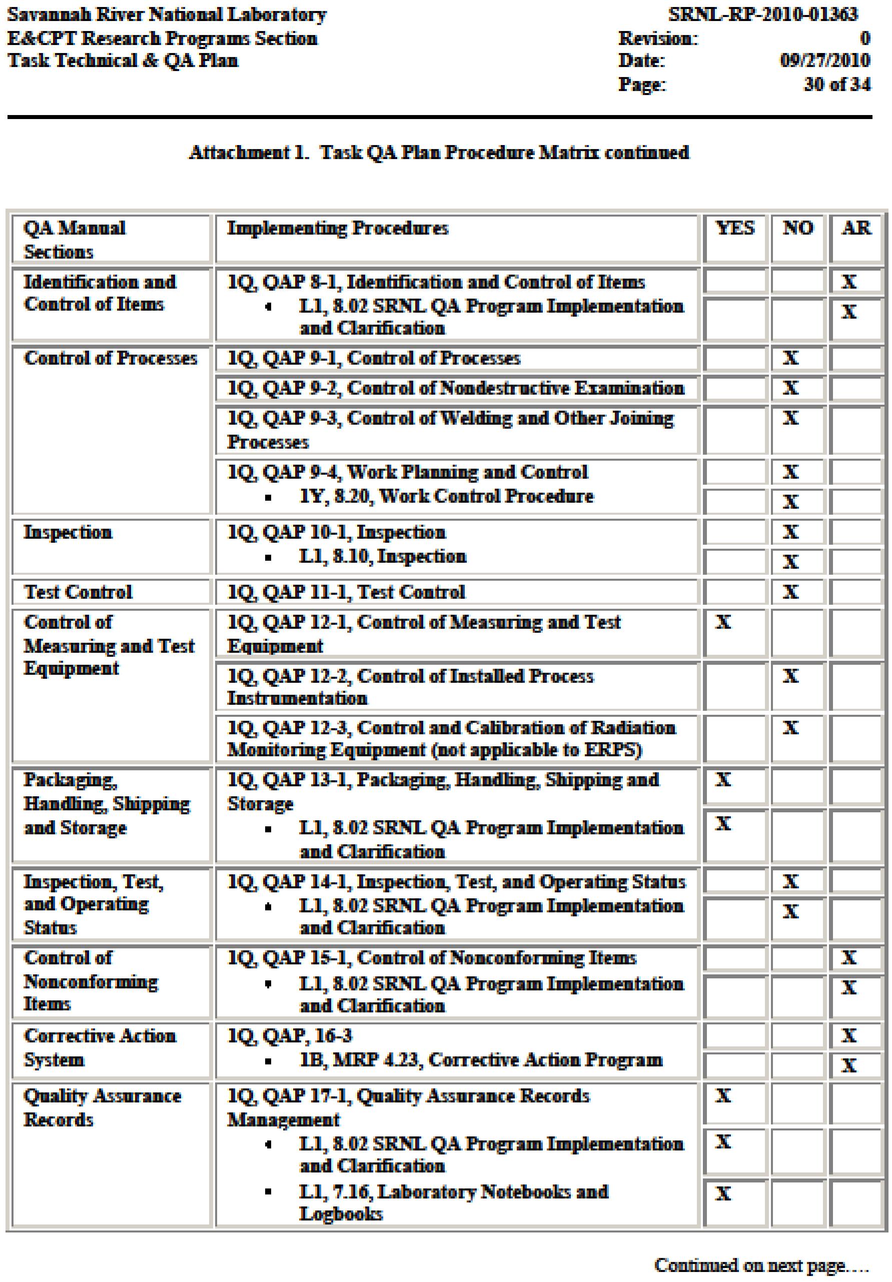

Attachment 1. Task QA Plan Procedure Matrix continued

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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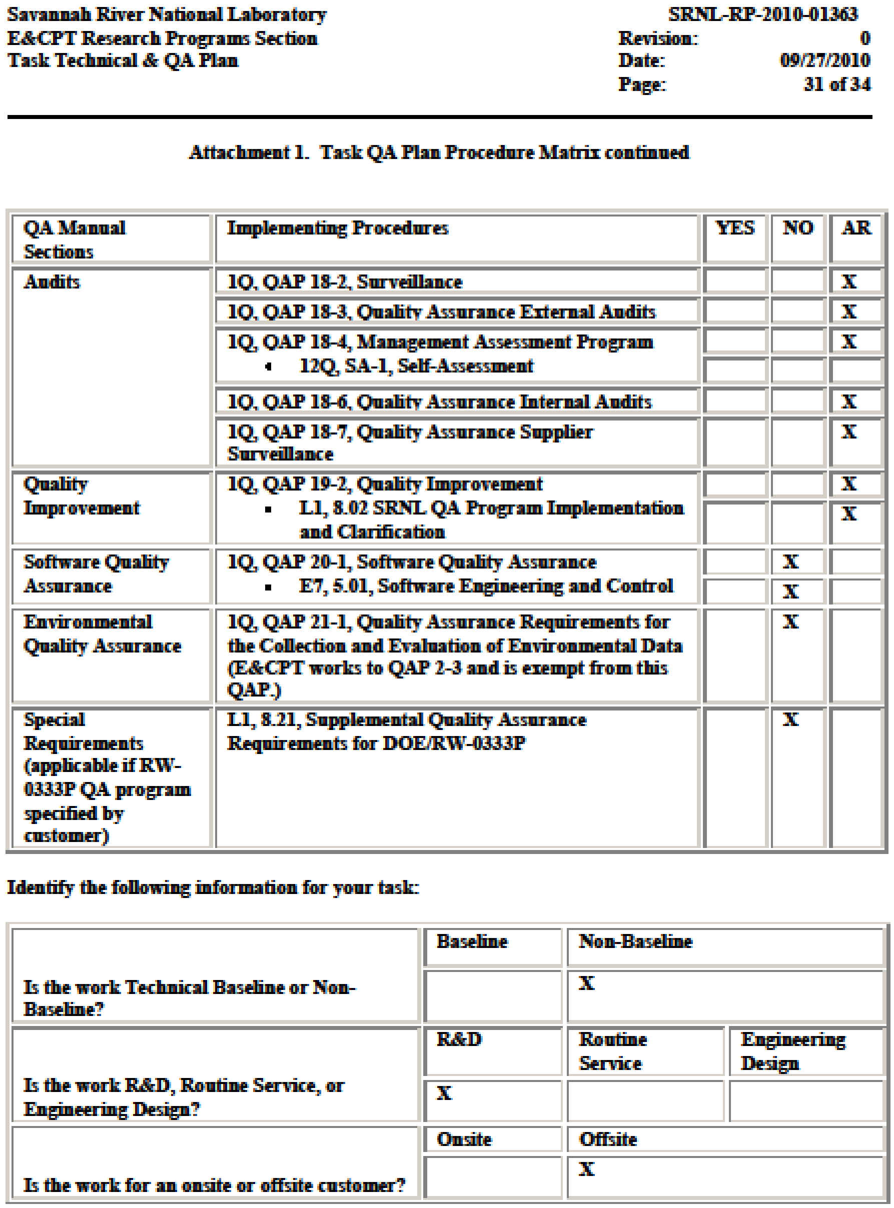

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Attachment 1. Task QA Plan Procedure Matrix continued

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	

10.0 REFERENCES

1. THOR® Treatment Technologies, Project Number 29387, *Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet*, Document Number RT-21-002, Rev. 1, April 2009.

2. Rassat, S.D., Mahoney, L.A., Russell, R.L., Bryan, S.A., Sell, R.L., *Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis*, Pacific Northwest National Laboratory, Hanford, WA, PNNL-14194 Revision 1, (2003).

3. *DOE EM-31 Technology Development & Deployment (TDD) Program Task Plan: Fluidized Bed Steam Reformer Low-level Waste Form Qualification*, Document No. WP-5.2.1-2010-001 (September 2010).

4. Pareizs, J.M., Jantzen, C.M., Lorier, T.H., *Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for High Sodium Wastes at Hanford and Idaho*, Savannah River National Laboratory, Aiken, SC, WSRC-TR-2005-00102, (2005).

5. Jantzen, C.M., Pareizs, J.M., Lorier, T.H., Marra, J.C., *Durability Testing of Fluidized Bed Steam Reforming (FBSR) Products*, pp. 121-37 in Ceramic Transactions, *Environmental Issues and Waste Management Technologies XI* Edited by C. C. Herman, S.L. Marra, D.R. Spearing, L. Vance, and J.D. Vienna. (2005).

6. Jantzen, C.M., Lorier, T.H., Marra, J.C., and Pareizs, J.M., *Durability Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms,* WM06 Paper #6373 (February 2006). .

7. Jantzen, C.M., *Fluidized Bed Steam Reformer (FBSR) Product: Monolith Formation and Characterization*, Savannah River National Laboratory, Aiken, SC, WSRC-STI-2006-00033, (2006).

8. Jantzen, C.M., *Fluidized Bed Steam Reformer (FBSR) Monolith Formation*, WM07, Paper #7075 (2007).

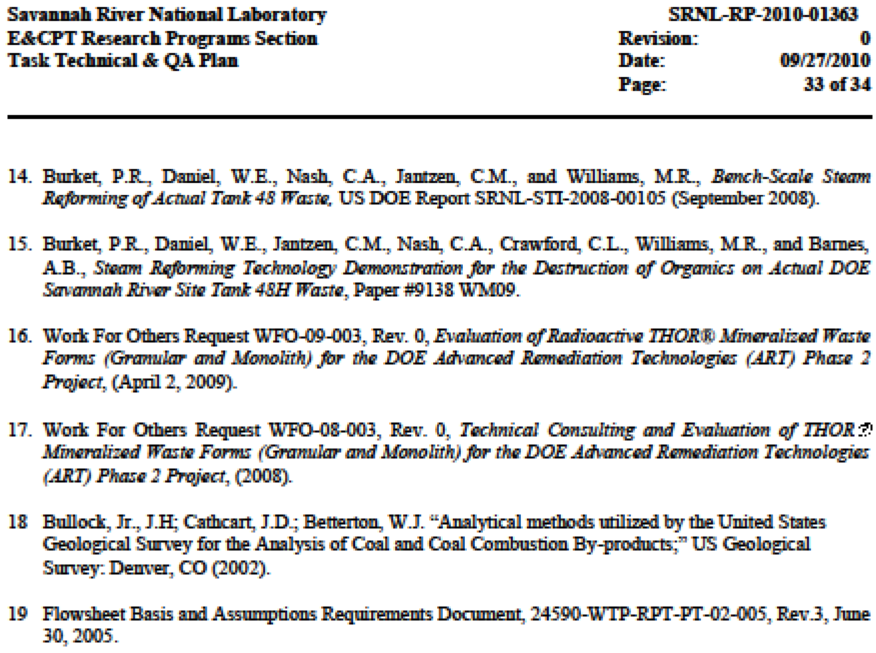
9. Lorier, T.H., Pareizs, J.M., Jantzen, C.M., *Single Pass Flow through (SPFT) Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms*, Savannah River National Laboratory, Aiken, SC, WSRC-TR-2005-00124, (2005).

10. Jantzen, C.M., Lorier, T.H., Pareizs, J.M., Marra, J.C., *Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Characterization and Durability Testing*, pp. 379-86 in *Scientific Basis for Nuclear Waste Management XXX* Edited by D. S. Dunn, C. Poinssot, B. Begg. (2007).

11. Jantzen, C.M., Crawford, C.L., *Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Radionuclide Incorporation, Monolith Formation, and Durability Testing*, WM'10, Phoenix, AZ, (2010).

12. Jantzen, C.M. *Mineralization of Radioactive Wastes By Fluidized Bed Steam Reforming (FBSR): Comparisons to Vitreous Waste Forms and Pertinent Durability Testing,* U.S. DOE Report WSRC-STI-2008-00268 (December 2008).

13 Crawford, C.L and Jantzen, C.M., *Evaluation of THOR™ Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project, SRNL-STI-2009-00505, Rev.0 (in review).*



14. Burket, P.R., Daniel, W.E., Nash, C.A., Jantzen, C.M., and Williams, M.R., *Bench-Scale Steam Reforming of Actual Tank 48 Waste*, US DOE Report SRNL-STI-2008-00105 (September 2008).

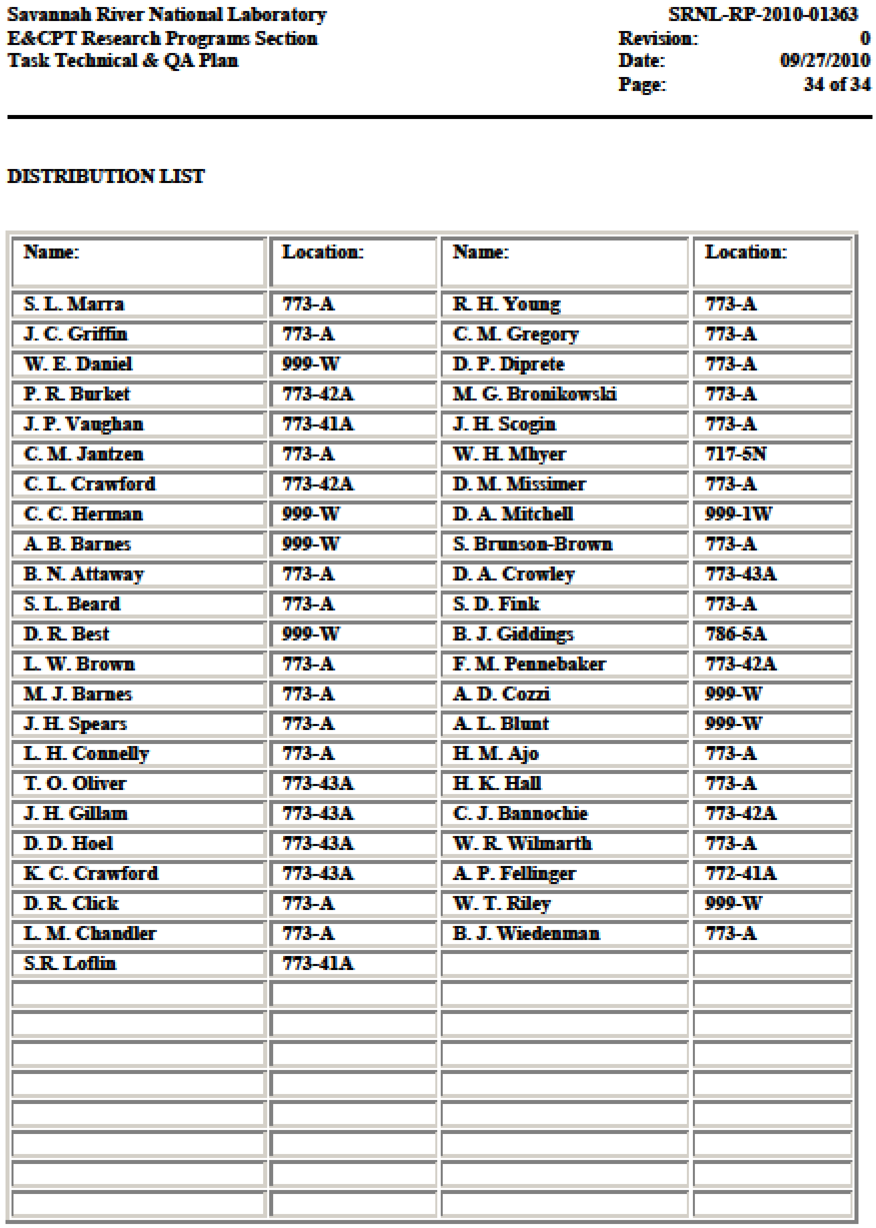
15. Burket, P.R., Daniel, W.E., Jantzen, C.M., Nash, C.A., Crawford, C.L., Williams, M.R., and Barnes, A.B., *Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste*, Paper #9138 WM09.

16. Work For Others Request WFO-09-003, Rev. 0, *Evaluation of Radioactive THOR® Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project*, (April 2, 2009).

17. Work For Others Request WFO-08-003, Rev. 0, *Technical Consulting and Evaluation of THOR® Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project*, (2008).

18 Bullock, Jr., J.H; Cathcart, J.D.; Betterton, W.J. "Analytical methods utilized by the United States Geological Survey for the Analysis of Coal and Coal Combustion By-products;" US Geological Survey: Denver, CO (2002).

19 Flowsheet Basis and Assumptions Requirements Document, 24590-WTP-RPT-PT-02-005, Rev.3, June 30, 2005.



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Appendix B. BSR Process Operation Conditions & Trends for Simulant Module B H_2 Controlled Runs

Table B - 1. BSR Process Operation Conditions & Results for Simulant Module B H_2 Controlled Runs

Run Date	**10/01/10 am**	**10/06/10 pm**	**10/08/10 pm**	**10/09/10 am**	**10/09/10 pm**	**10/10/10 pm**	**10/11/10 am**
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
H_2 Concentration Control	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %	1.5 – 3.0 %
Post Feed Run Time (min)	95	45	187	130	150	73	93
Product REDOX	0.176	0.182	0.437	0.254	0.352	0.191	0.223
Product LOI	0.96%	0.23%	0.87%	0.31%	1.22%	0.67%	0.98%
Product Quantity (g) before sampling	37.90	48.75	45.68	41.95	46.49	32.69	43.23
Feed Quantity (g)	109	115	141	128	138	101	131
Run Date	**10/12/10am**	**10/12/10 pm**	**10/13/10 am**	**10/14/10 pm**	**10/16/10 pm**	**10/17/10 pm**	**10/18/10 pm**
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
Carbon (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
H_2 Concentration Control	1.5 – 3.0%	1.5 – 3.0%	1.5 – 3.0%	1.5 – 3.0%	1.5 – 3.0%	1.5 – 3.0%	1.5 – 3.0%
Post Feed Run Time (hrs)	165	150	150	142	200	130	156
Product REDOX	0.40 – 0.60	0.40 – 0.60	0.40 – 0.60	0.40 – 0.60	0.40 – 0.60	0.40 – 0.60	0.40 – 0.60
Product LOI	<10%	<10%	<10%	<10%	<10%	<10%	<10%
Product Quantity (g)	38.70	40.45	43.96	36.06	43.08	31.09	25.48
Feed Quantity (g)	118	124	138	109	128	97	80

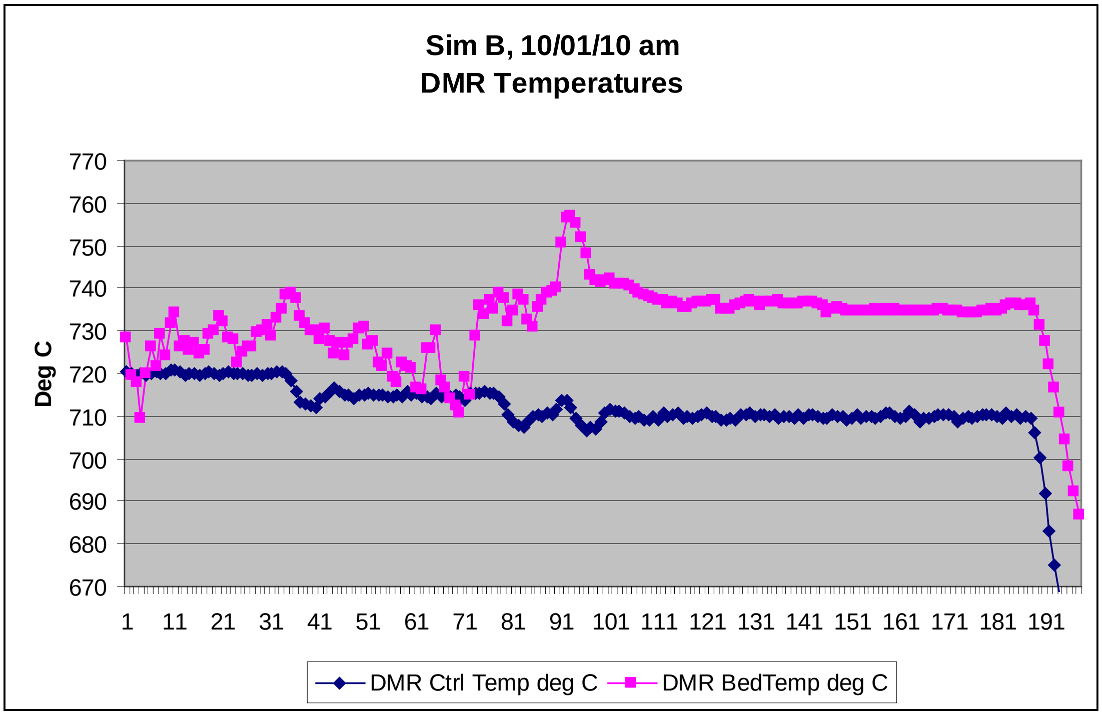

Figure B - 1. Run 10/01/10 Temperatures in DMR

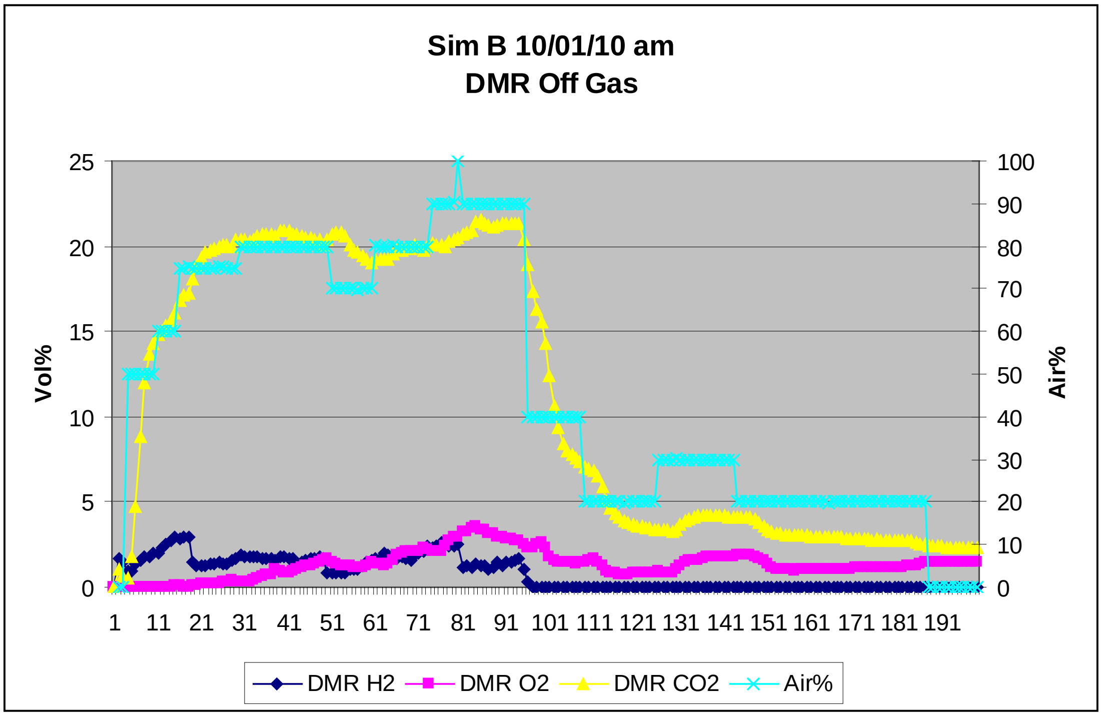

Figure B - 2. Run 10/01/10 Off-Gas Concentrations and Air% Fed

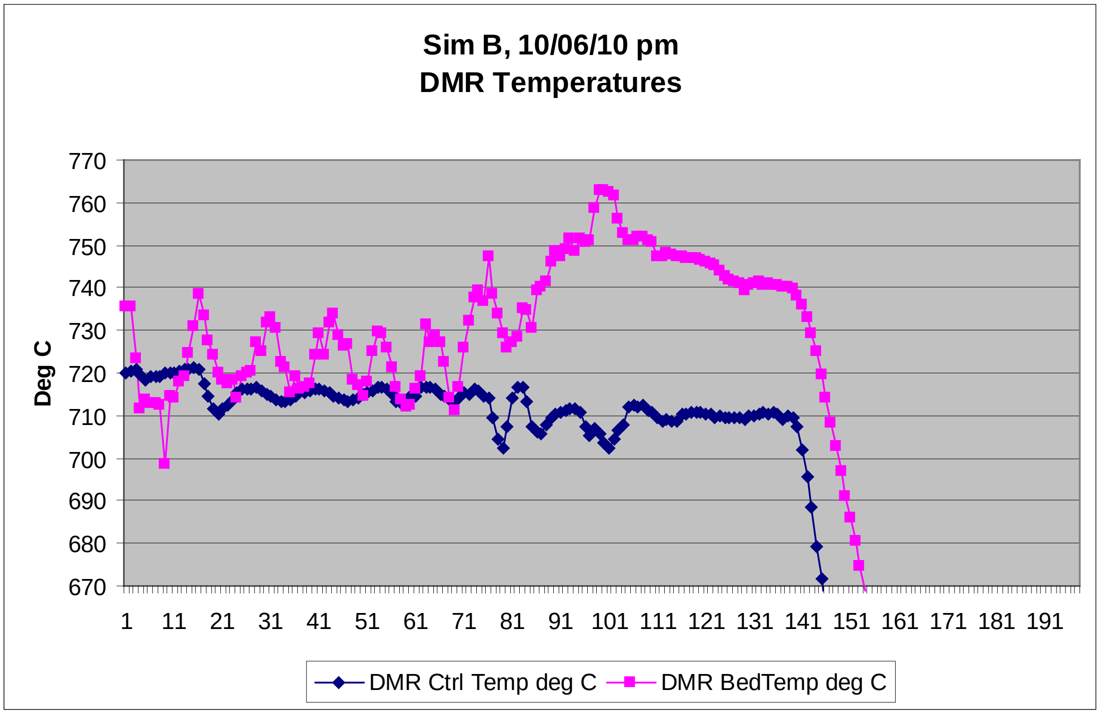

Figure B - 3. Run10/06/10 pm Temperatures in DMR

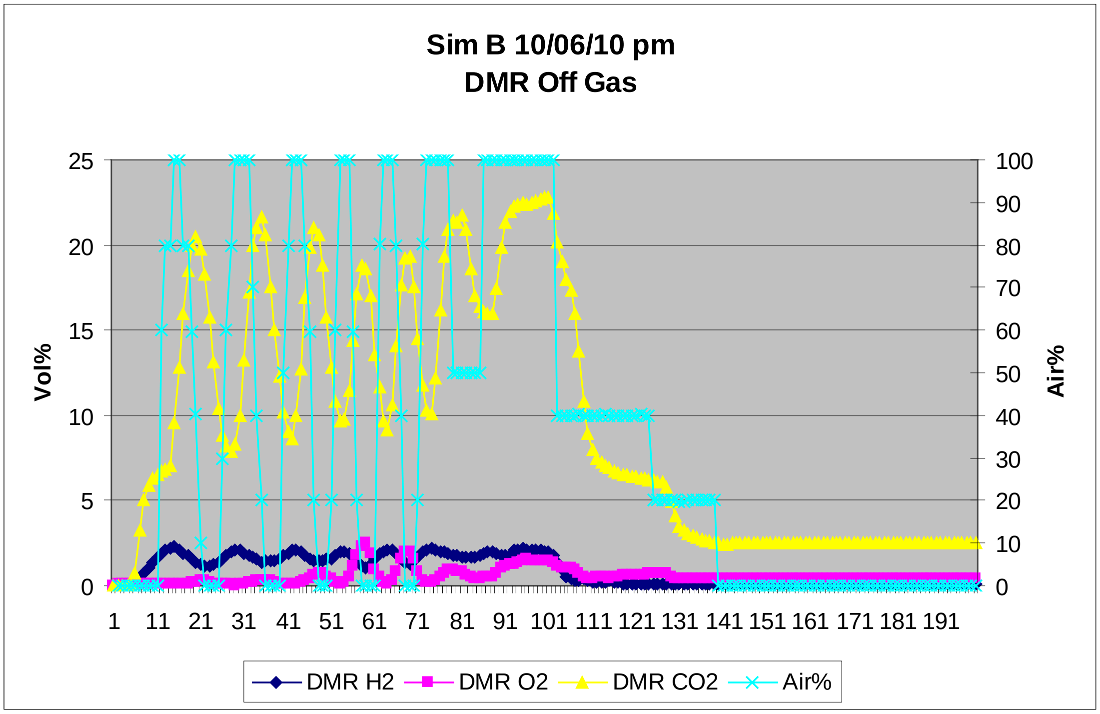

Figure B - 4. Run 10/06/10 pm Off-Gas Concentrations and Air% Fed

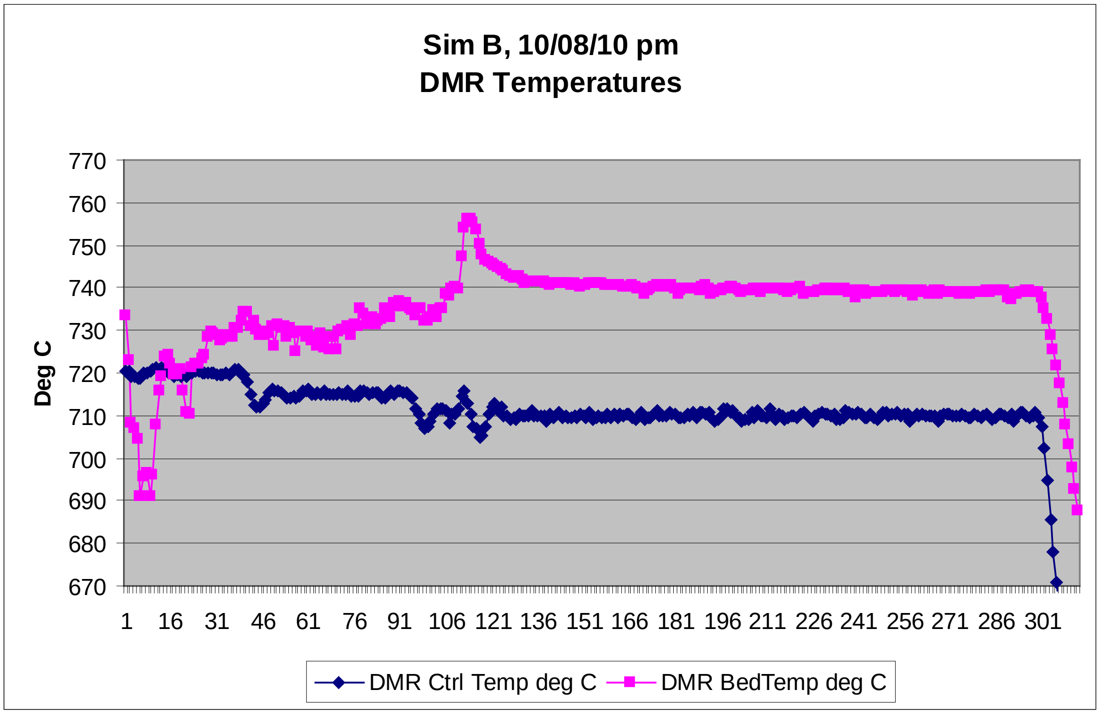

Figure B - 5. Run 10/08/10 pm Temperatures in DMR

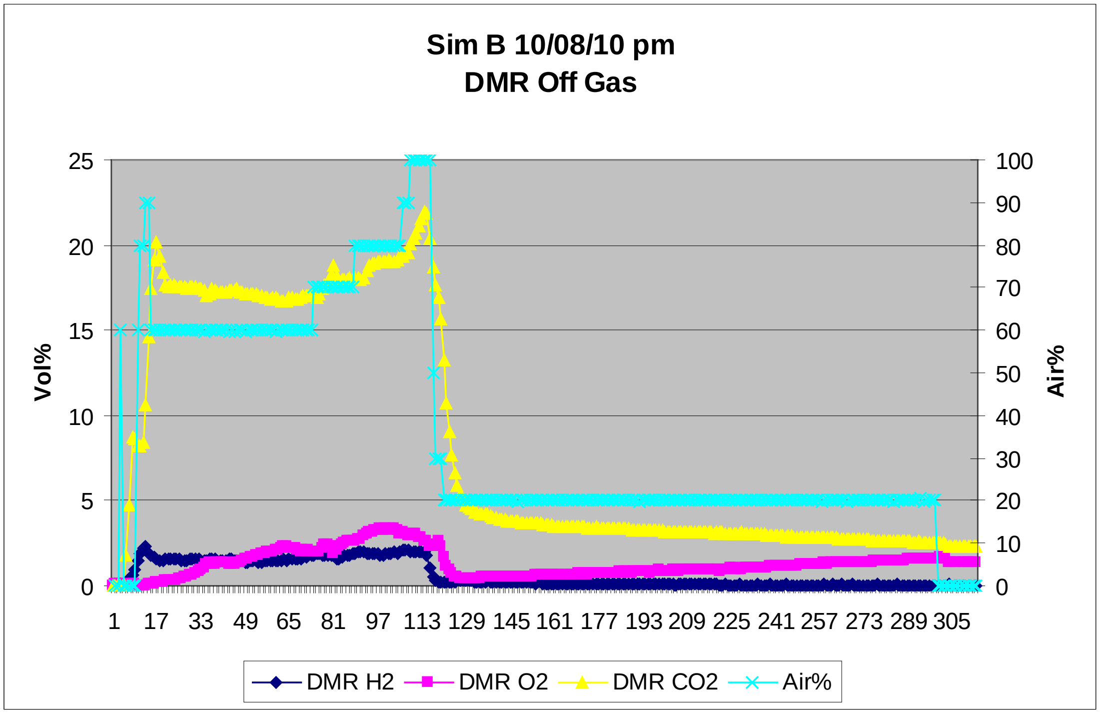

Figure B - 6. Run 10/08/10 pm Off-Gas Concentrations and Air% Fed

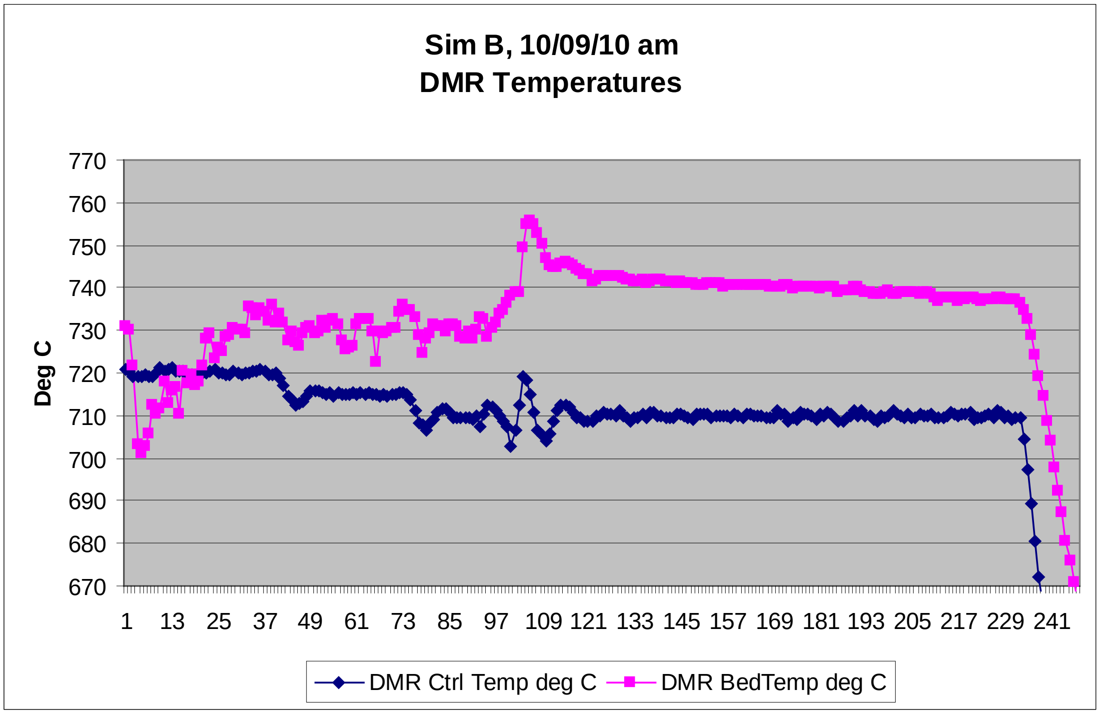

Figure B - 7. Run10/09/10 pm Temperatures in DMR

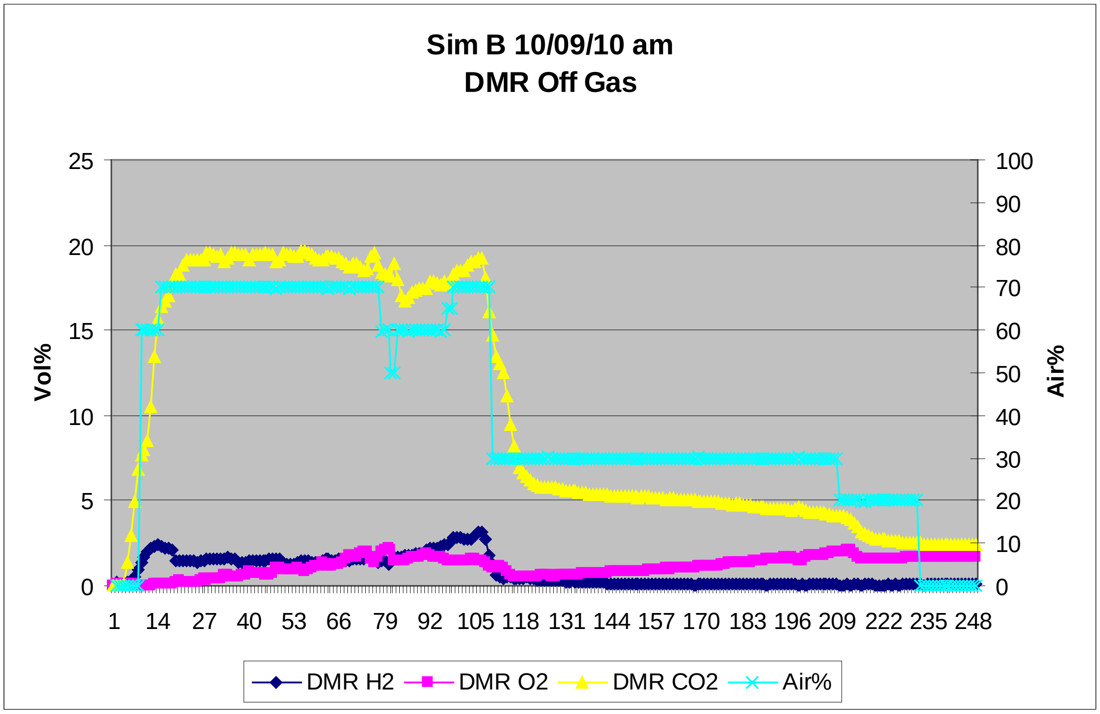

Figure B - 8. Run10/09/10 am Off-Gas Concentrations and Air% Fed

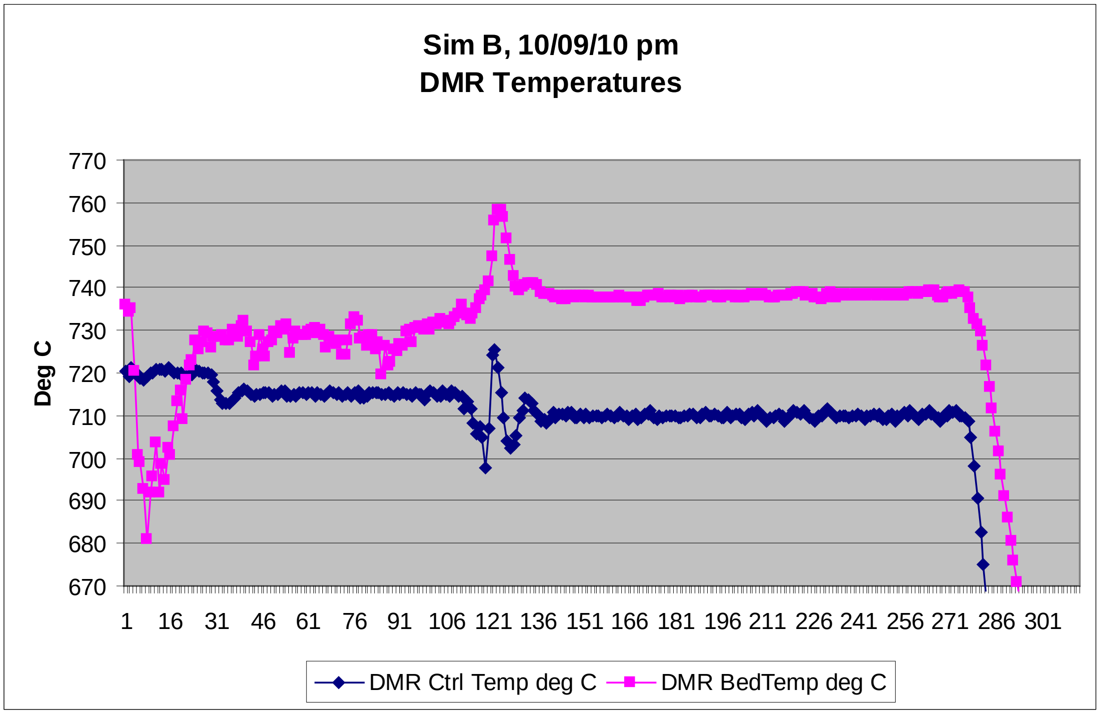

Figure B - 9. Run 10/9/10 pm Temperatures in DMR

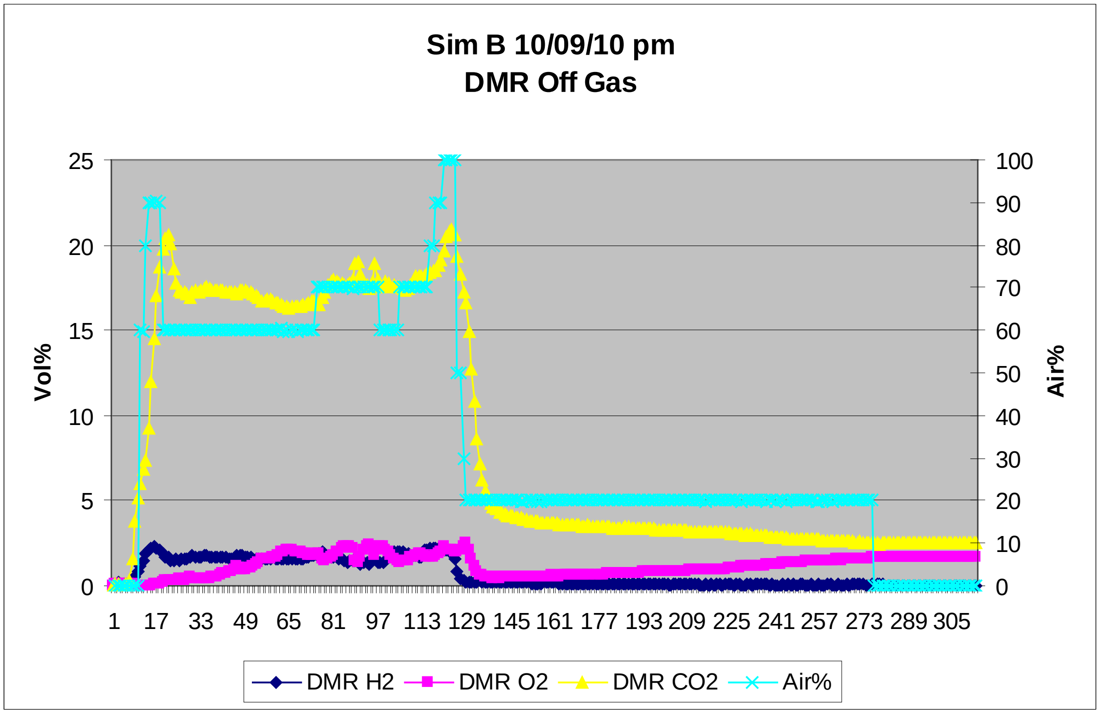

Figure B - 10. Run 10/09/10 pm Off-Gas Concentrations and Air% Fed

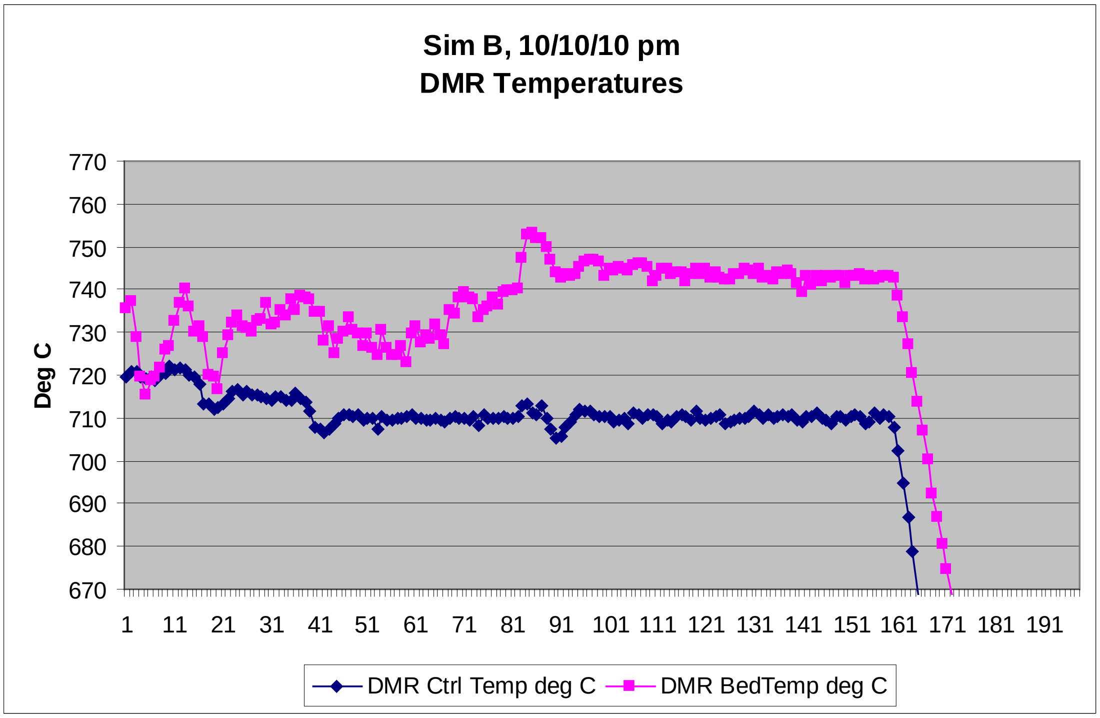

Figure B - 11. Run 10/10/10 pm Temperatures in DMR

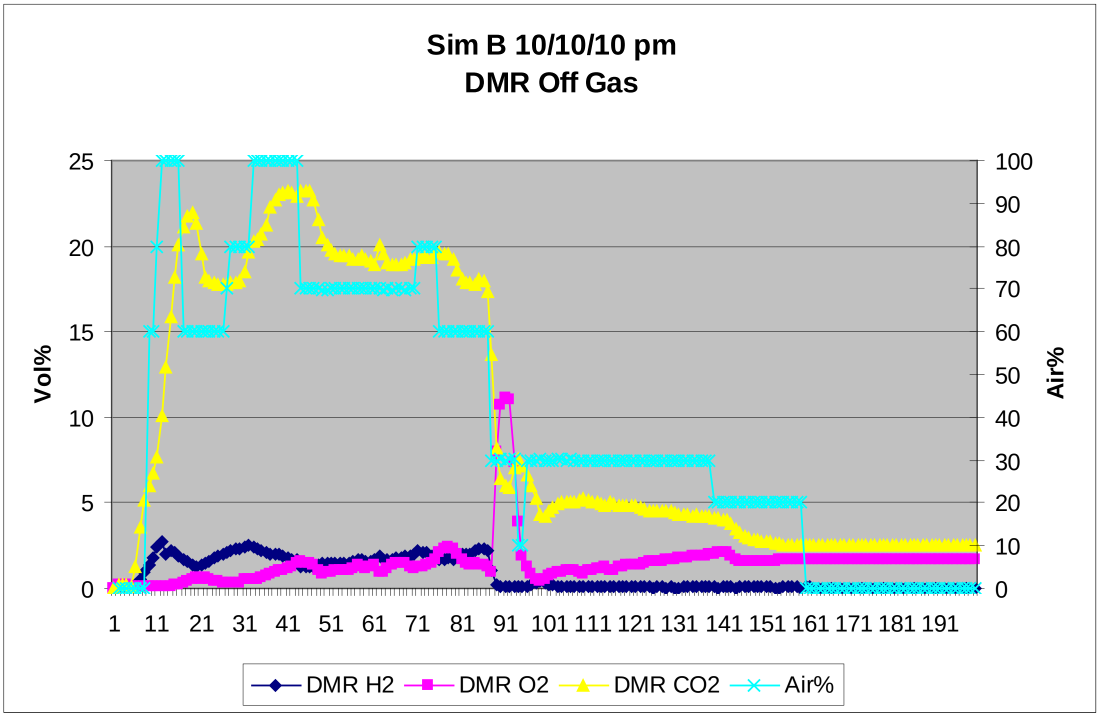

Figure B - 12. Run 10/10/10 pm Off-Gas Concentrations and Air% Fed

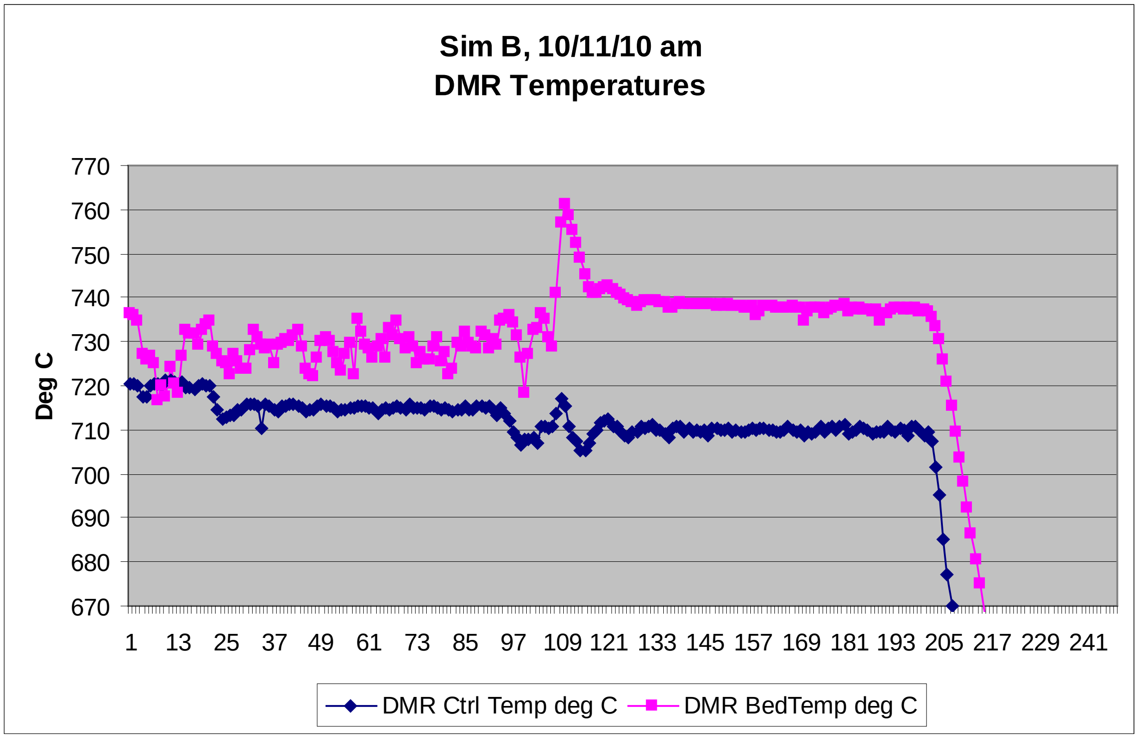

Figure B - 13. Run 10/11/10 am Temperatures in DMR

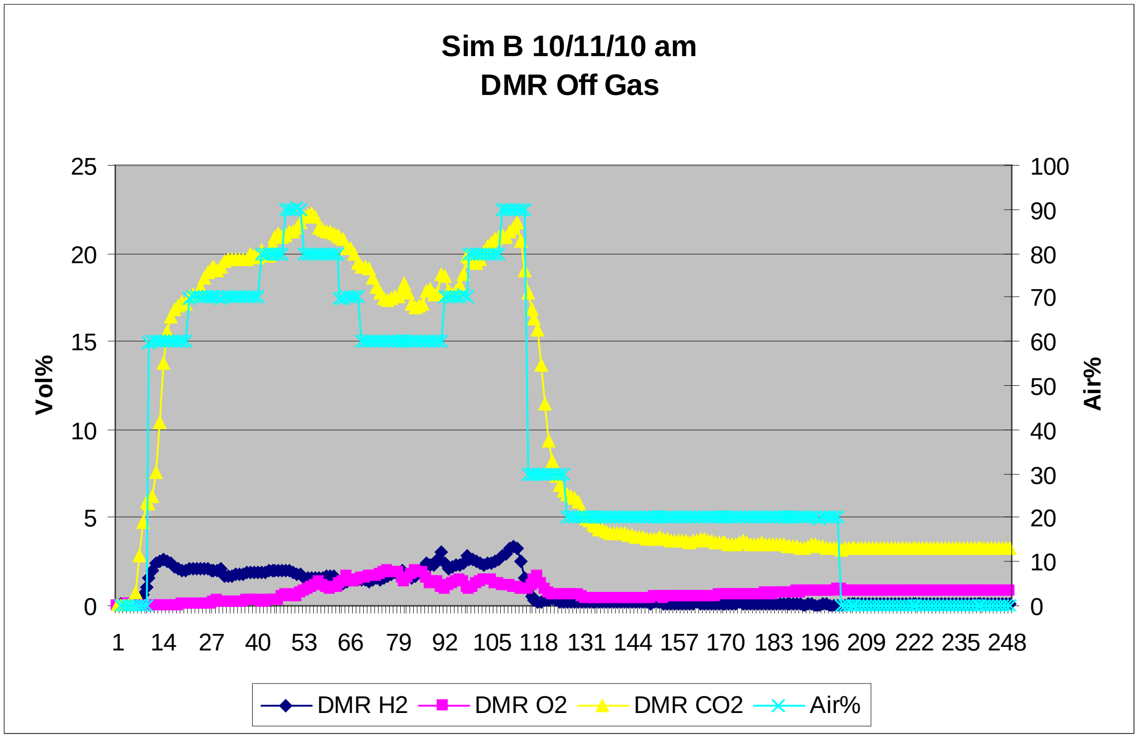

Figure B - 14. Run 10/11/10 am Off-Gas Concentrations and Air% Fed

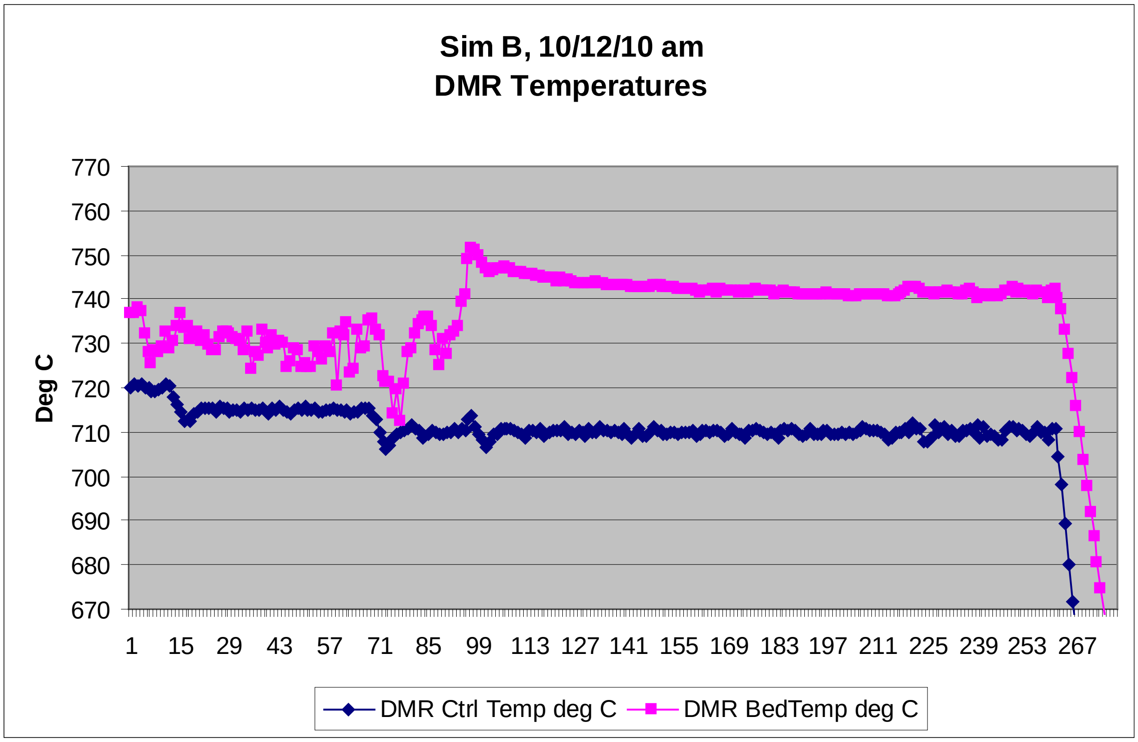

Figure B - 15. Run 10/12/10 am Temperatures in DMR

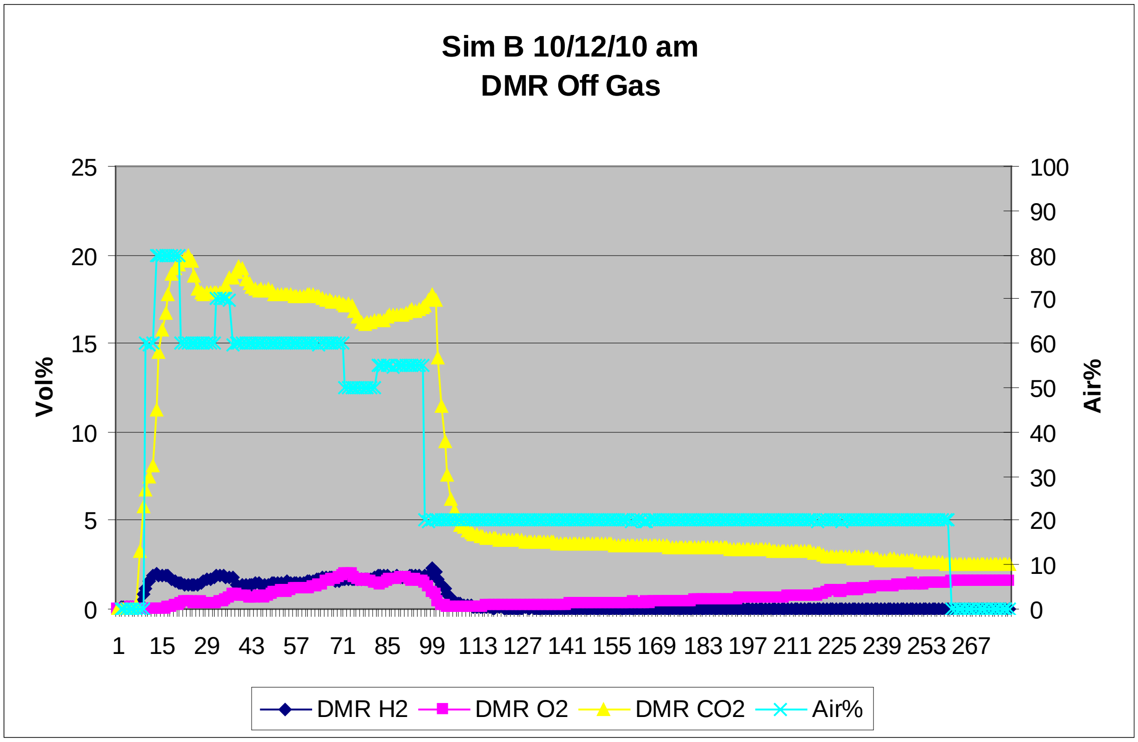

Figure B - 16. Run 10/12/10 am Off-Gas Concentrations and Air% Fed

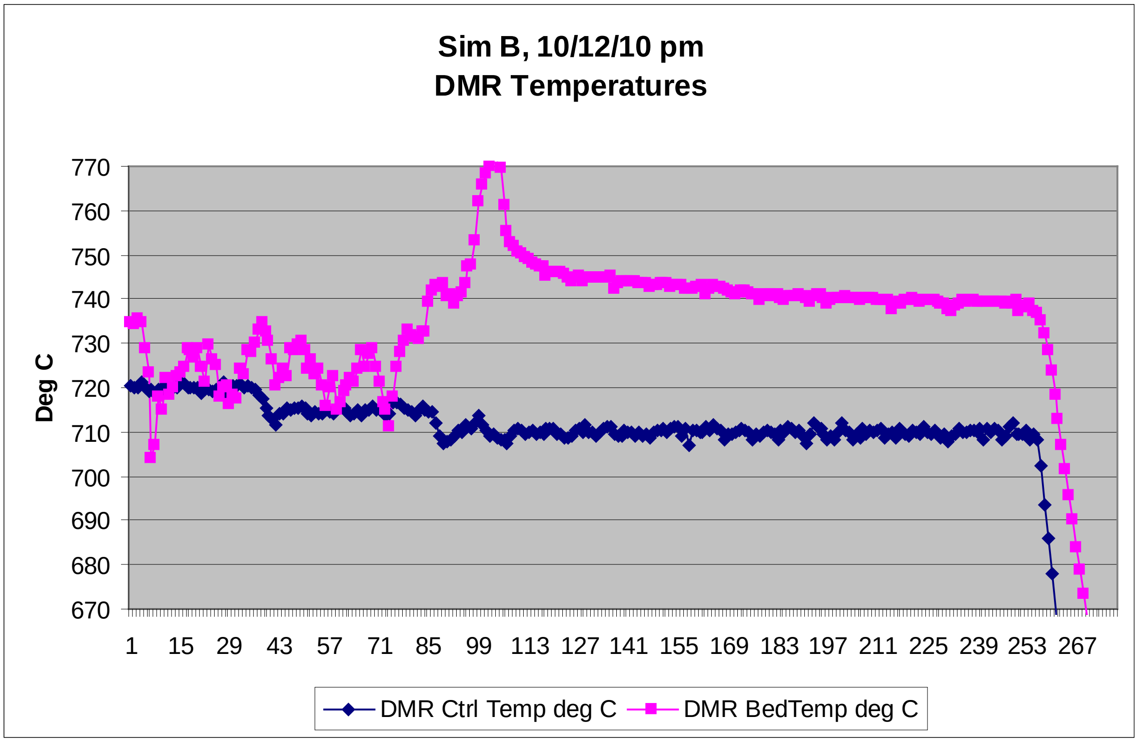

Figure B - 17. Run 10/12/10 pm Temperatures in DMR

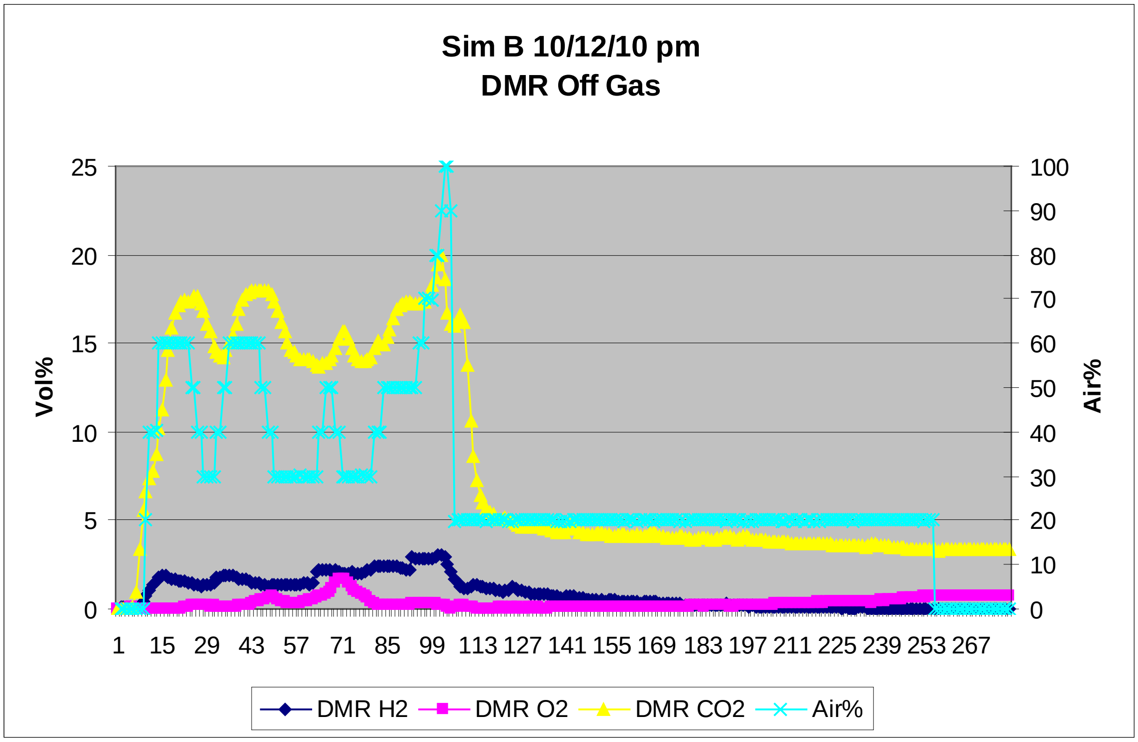

Figure B - 18. Run 10/12/10 pm Off-Gas Concentrations and Air% Fed

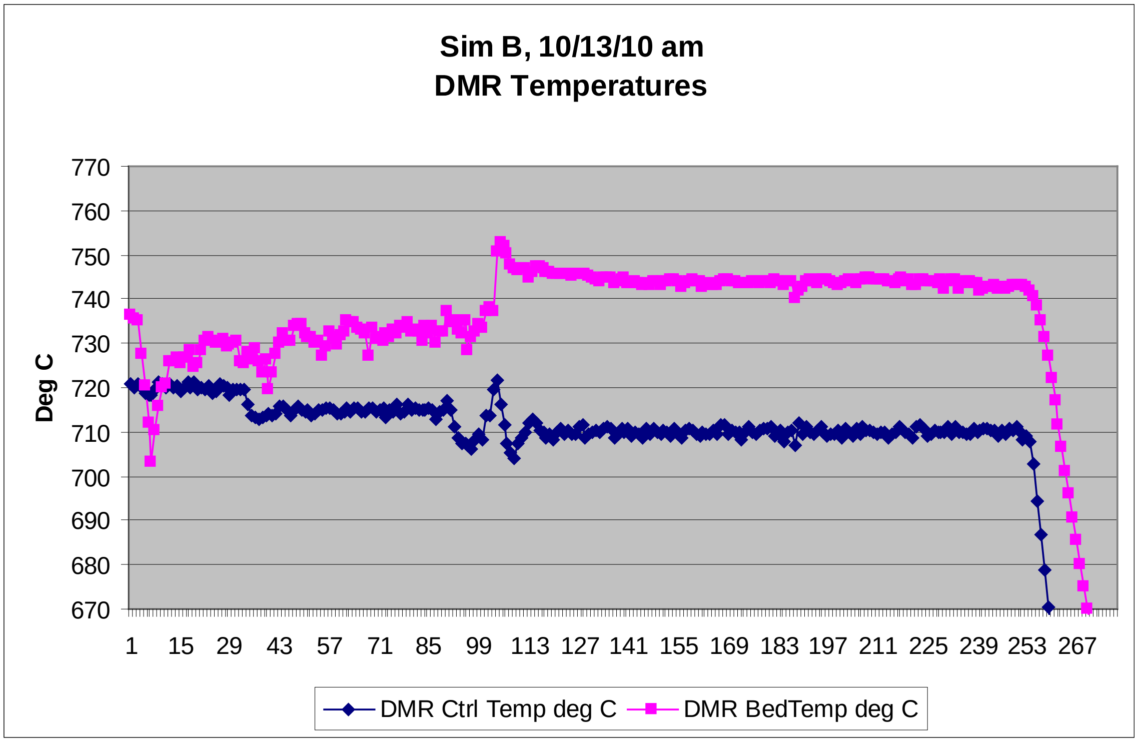

Figure B - 19. Run 10/13/10 am Temperatures in DMR

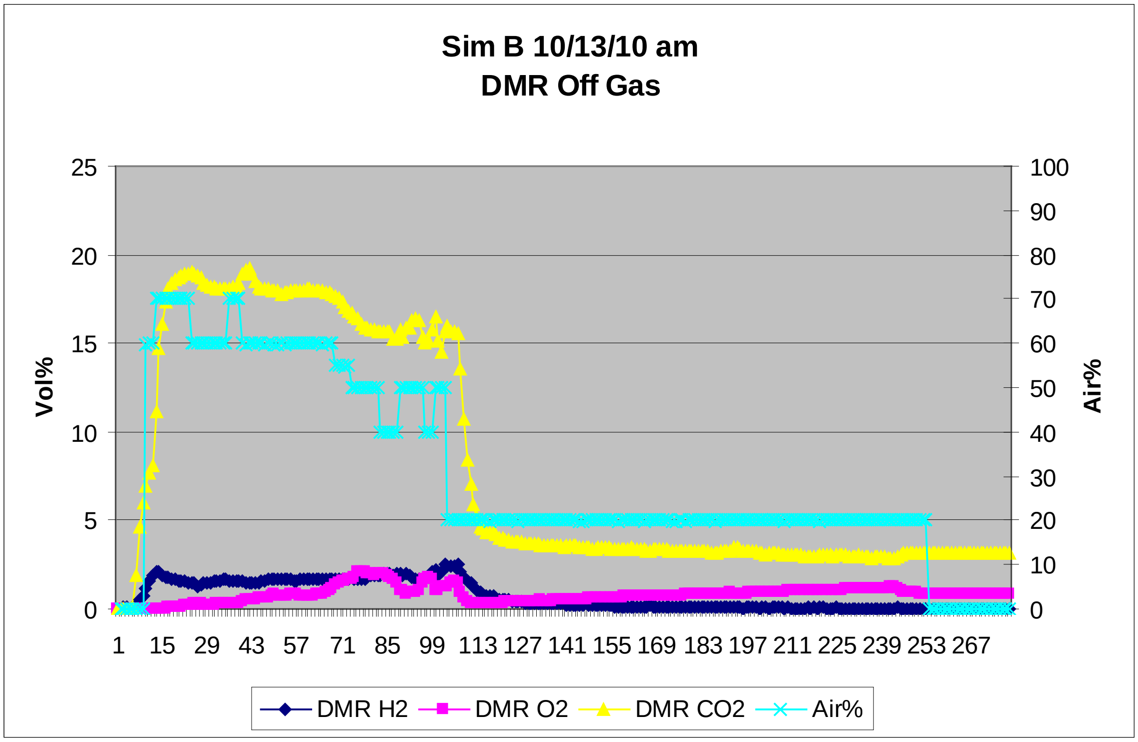

Figure B - 20. Run 10/13/10 am Off-Gas Concentrations and Air% Fed

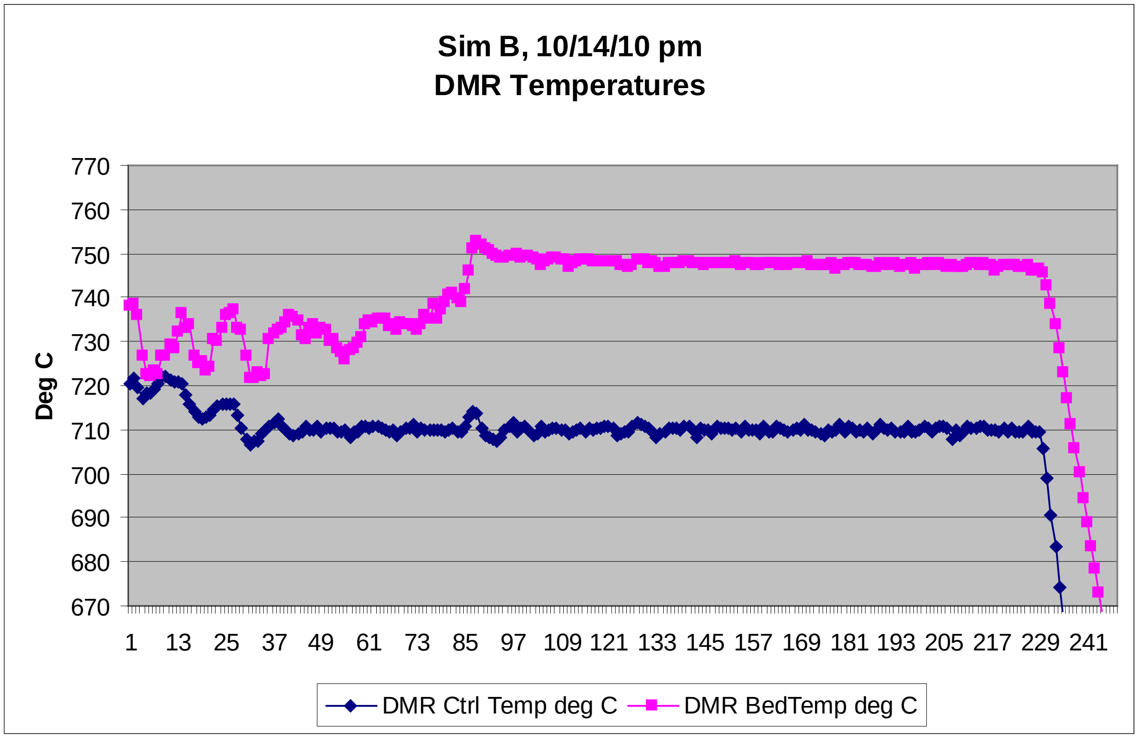

Figure B - 21. Run 10/14/10 pm Temperatures in DMR

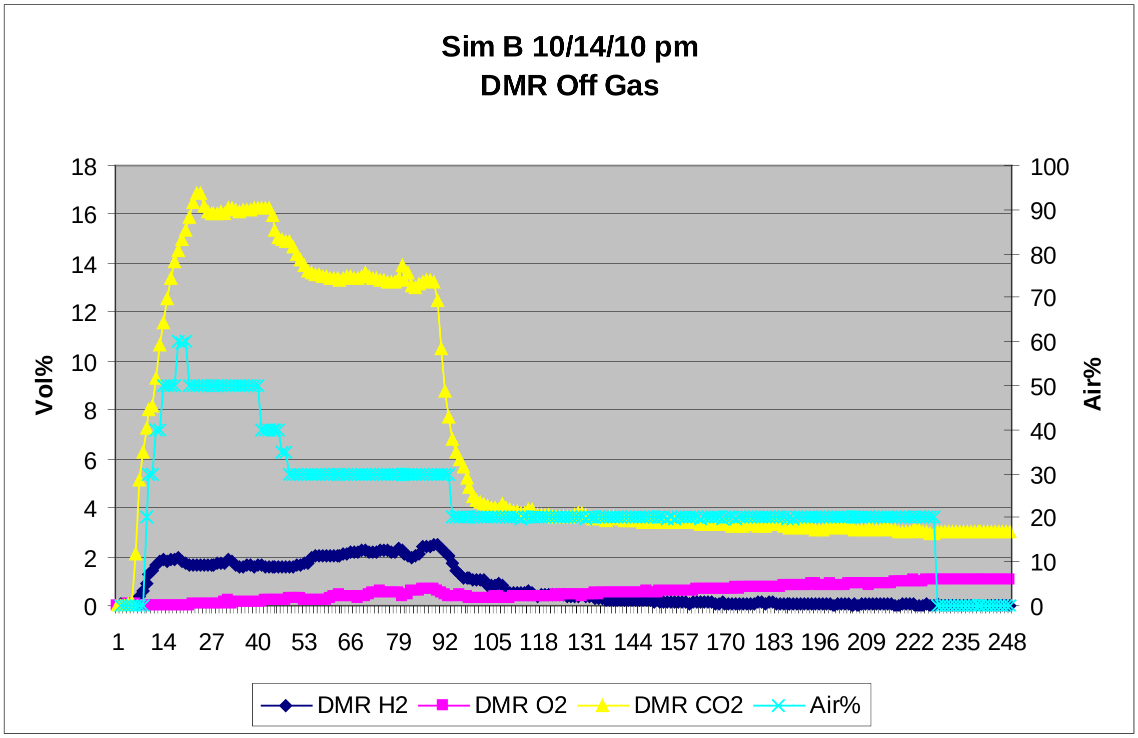

Figure B - 22. Run 10/14/10 pm Off-Gas Concentrations and Air% Fed

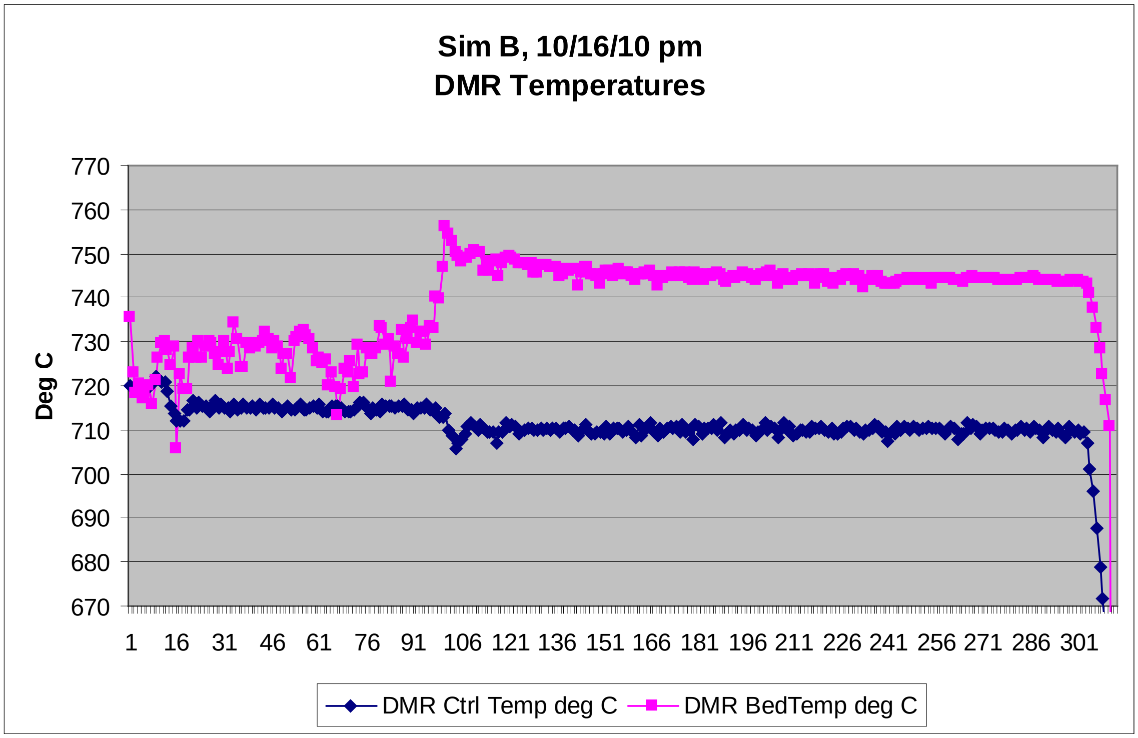

Figure B - 23. Run 10/16/10 pm Temperatures in DMR

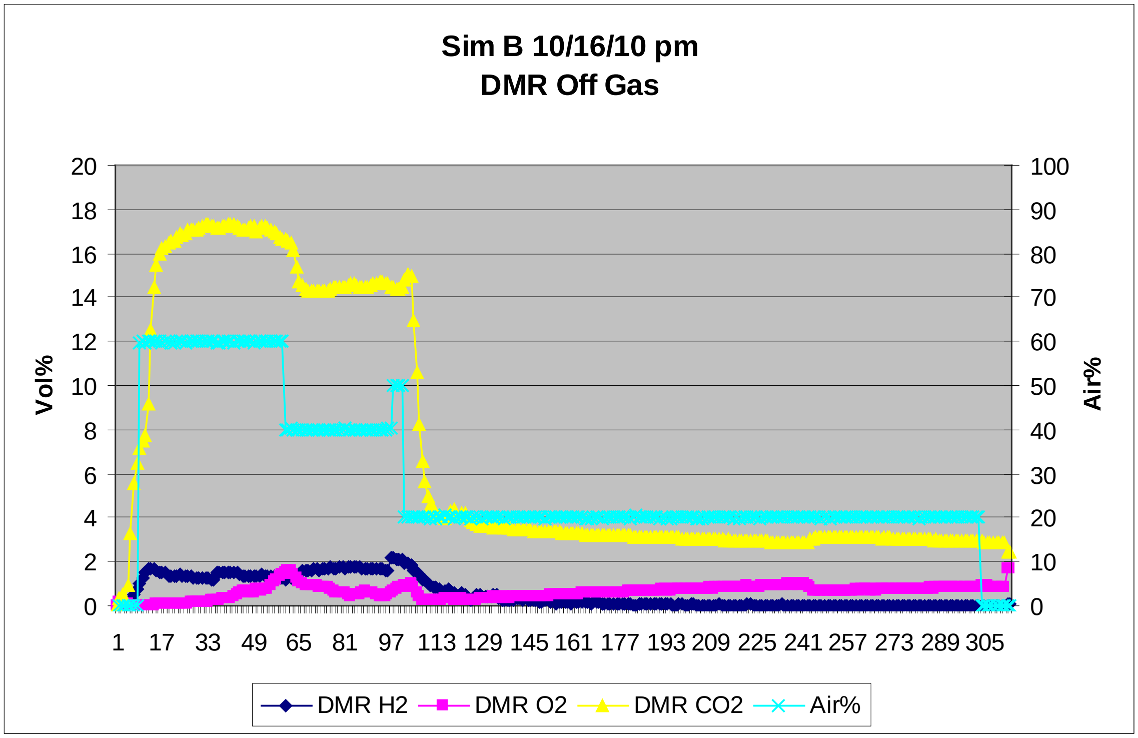

Figure B - 24. Run 10/16/10 pm Off-Gas Concentrations and Air% Fed

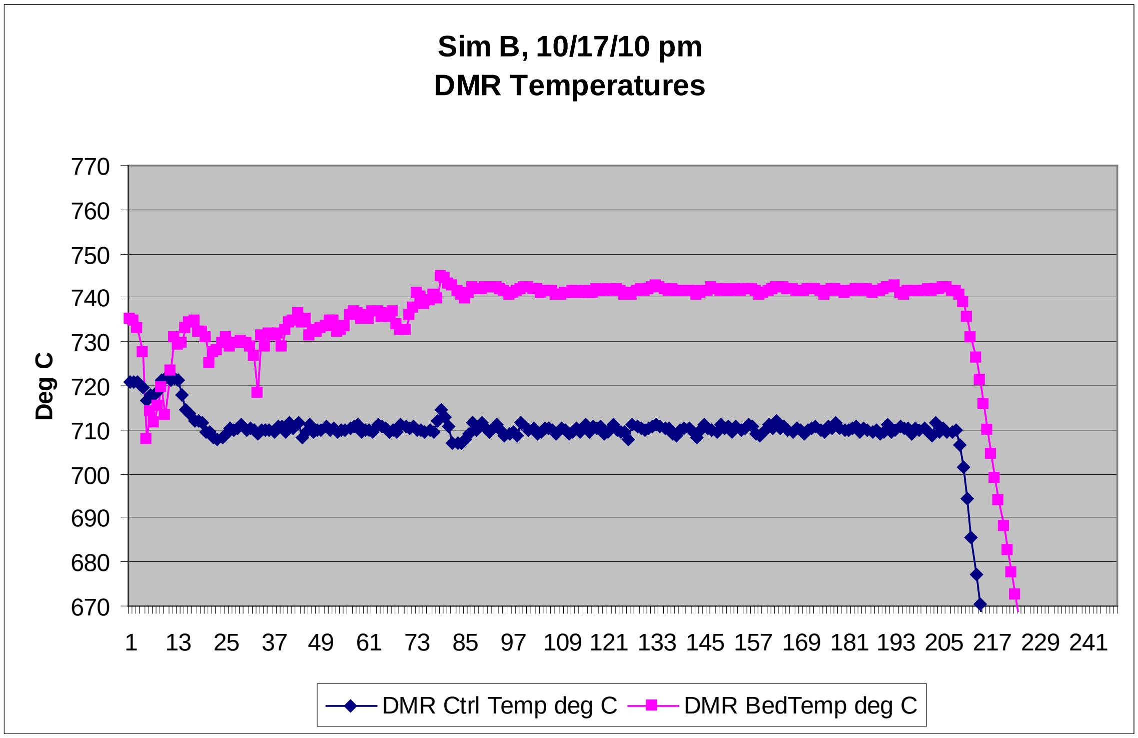

Figure B - 25. Run 10/17/10 pm Temperatures in DMR

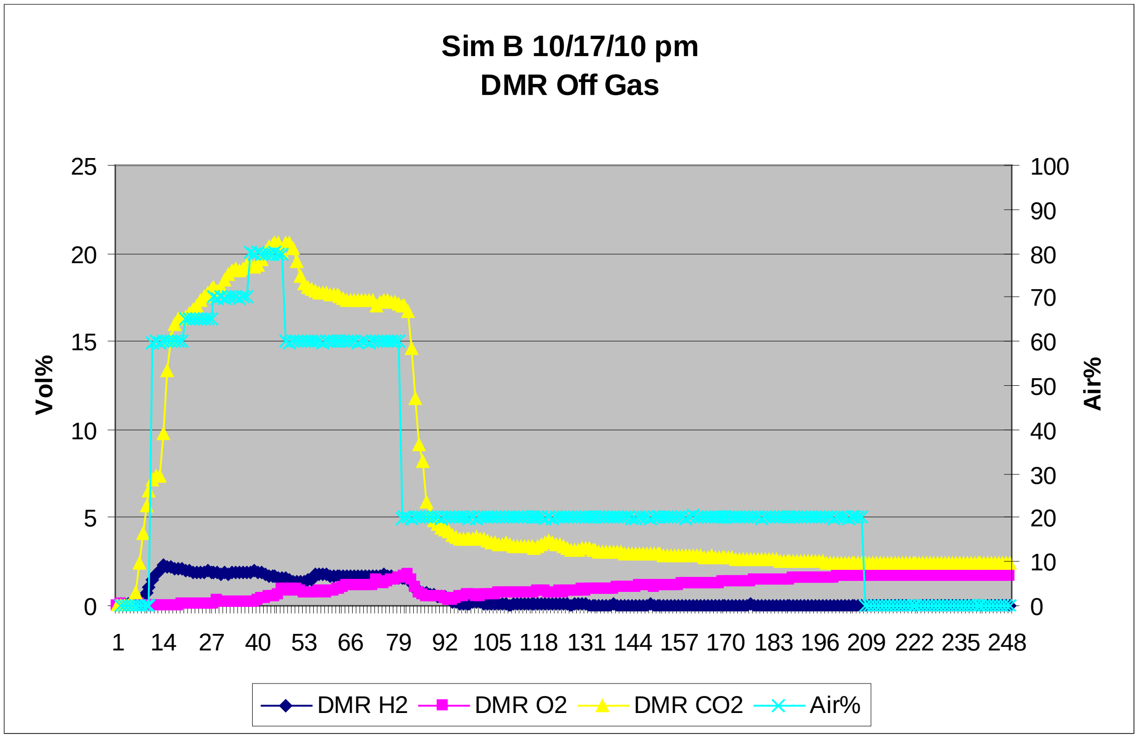

Figure B - 26. Run 10/17/10 pm Off-Gas Concentrations and Air% Fed

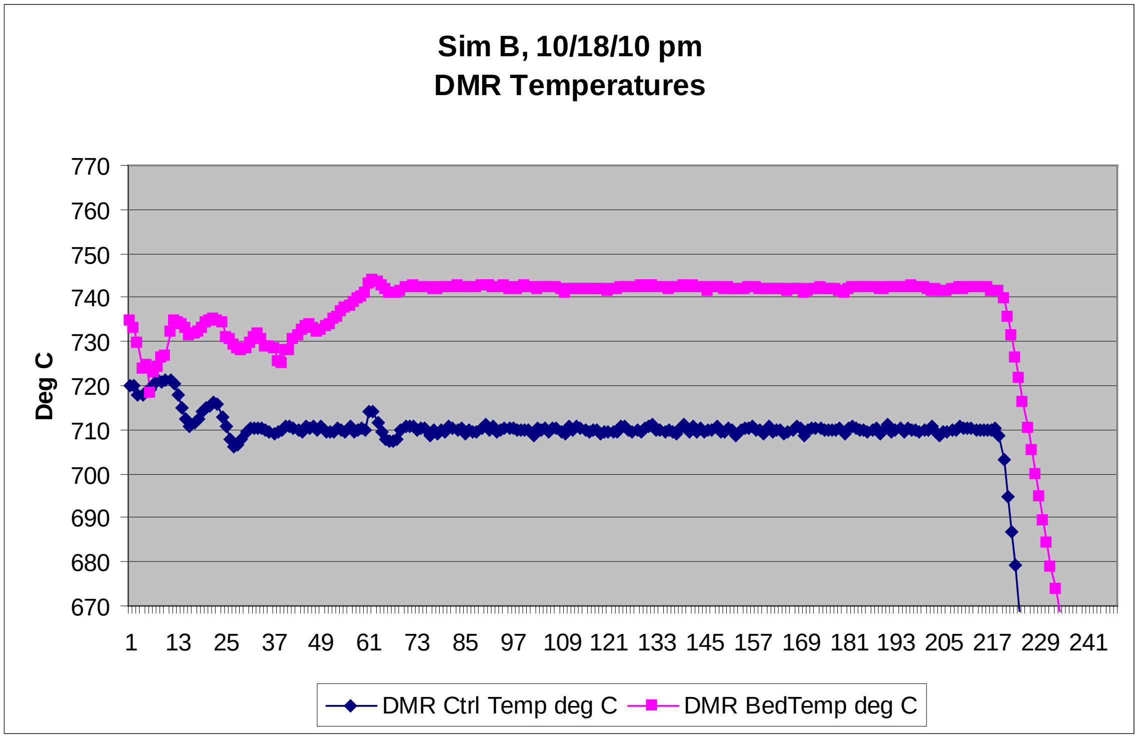

Figure B - 27. Run 10/18/10 pm Temperatures in DMR

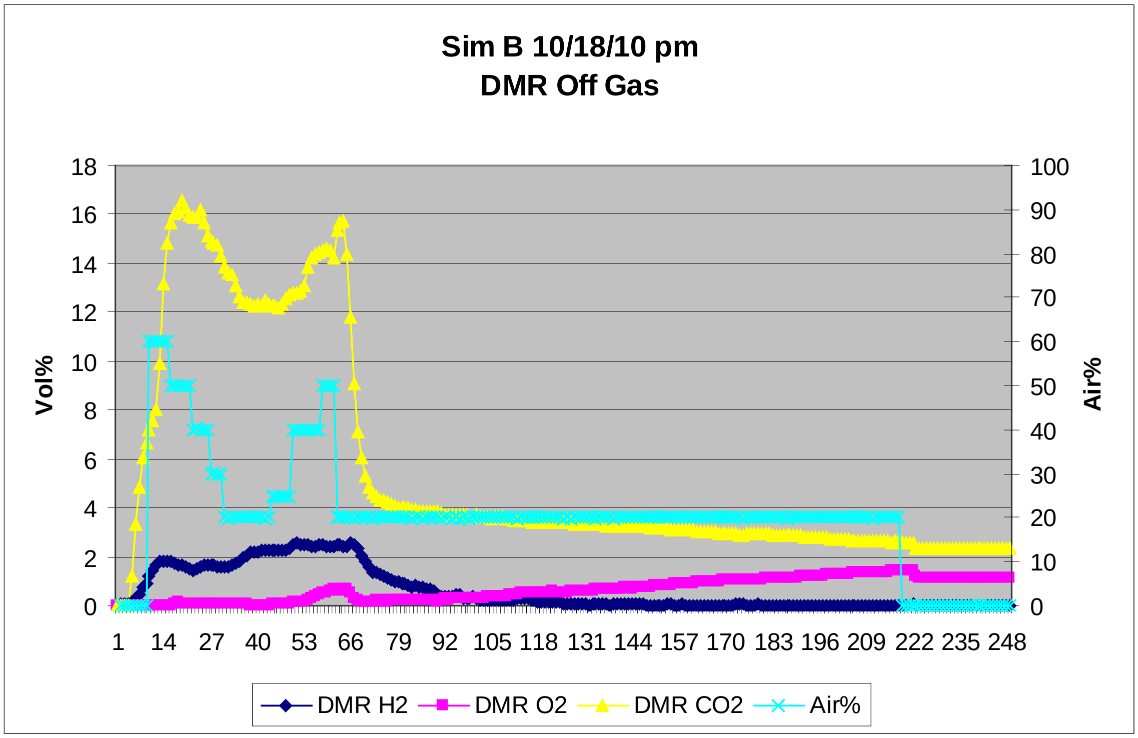

Figure B - 28. Run 10/18/10 pm Off-Gas Concentrations and Air% Fed

Appendix C. BSR Process Operation Conditions & Trends for Simulant Module B Gas REDOX Controlled Runs

Table C - 1. BSR Process Operation Conditions & Results for Simulant Module B REDOX Controlled Runs

Run Date	**10/19/10 pm**	**10/21/10 am**	**10/21/10 pm**	**10/22/10 am**	**10/27/10 am**	**10/28/10 am**
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 (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Carbon (stoichiometry)	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.1	16.4	16	15.7	16.6	16.0
Post Feed Run Time (hrs)	96	94	131	131	113	124
Product REDOX	0.295	0.250	0.345	0.343	0..224	0..224
Product LOI	1.40%	1.58%	0.99%	1.17%	1.08%	0.93%
Product Quantity (g) before sampling	29.94	40.95	31.29	32.57	32	30.84
Feed Quantity (g)	91	124	96	96	98	96

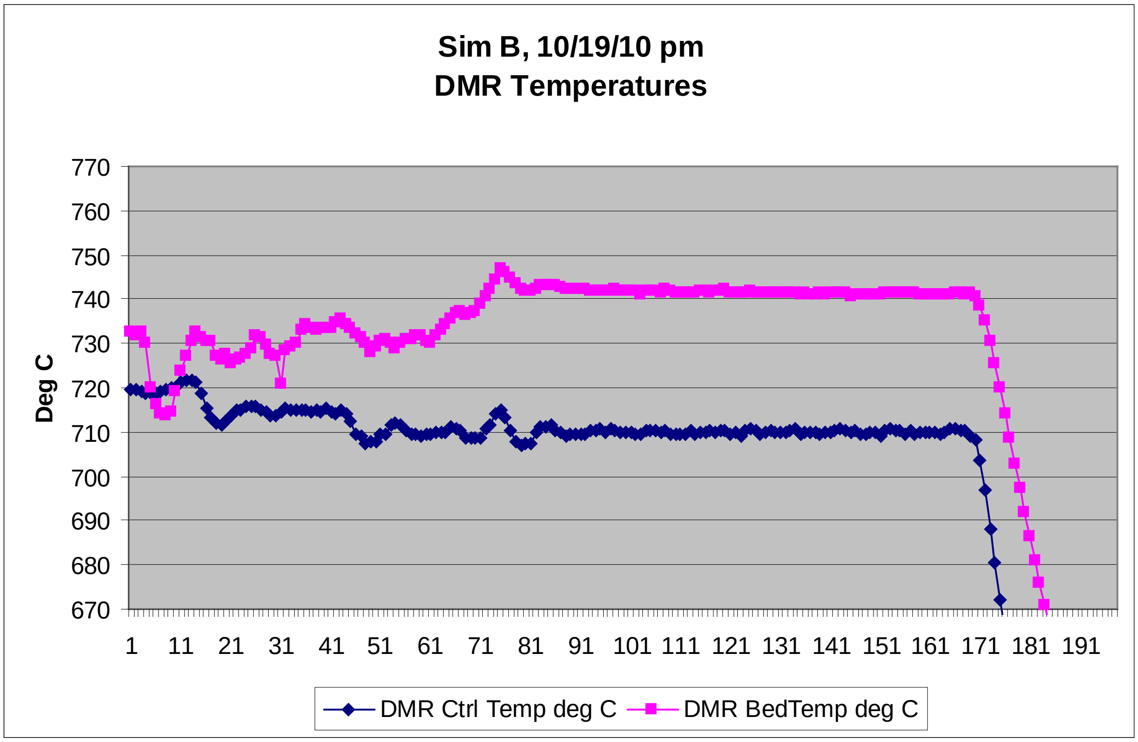

Figure C - 1. Run 10/19/10 pm Temperatures in DMR

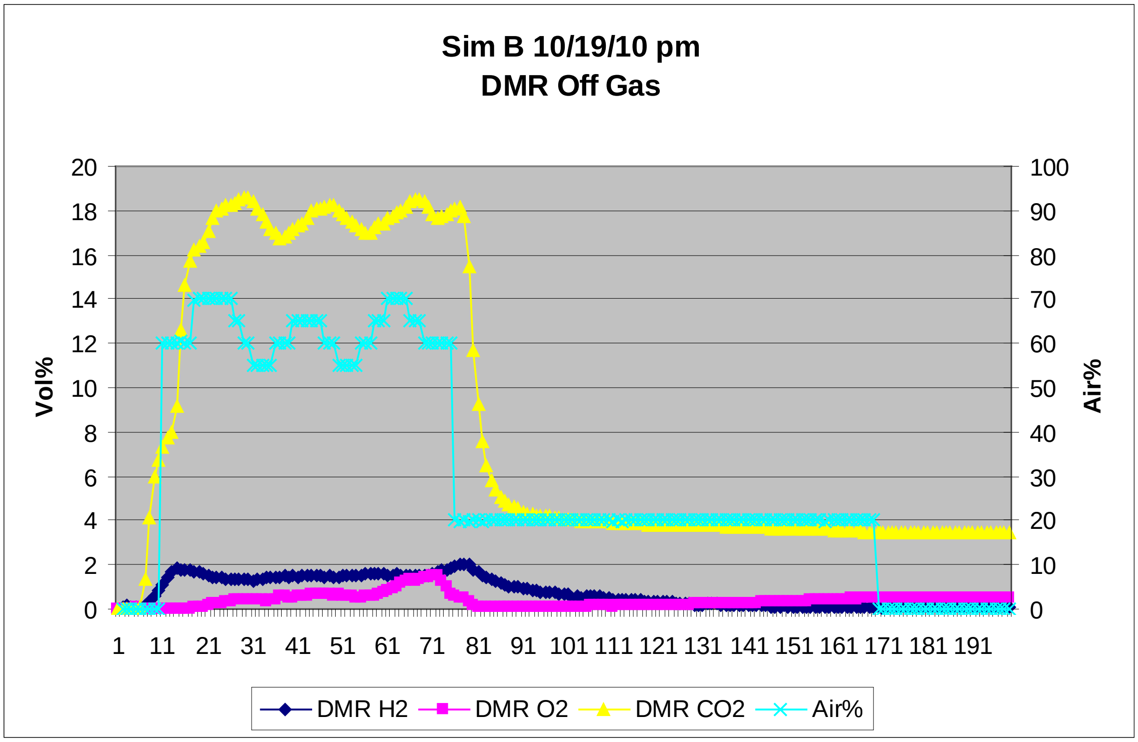

Figure C - 2. Run 10/19/10 pm Off-Gas Concentrations and Air% Fed

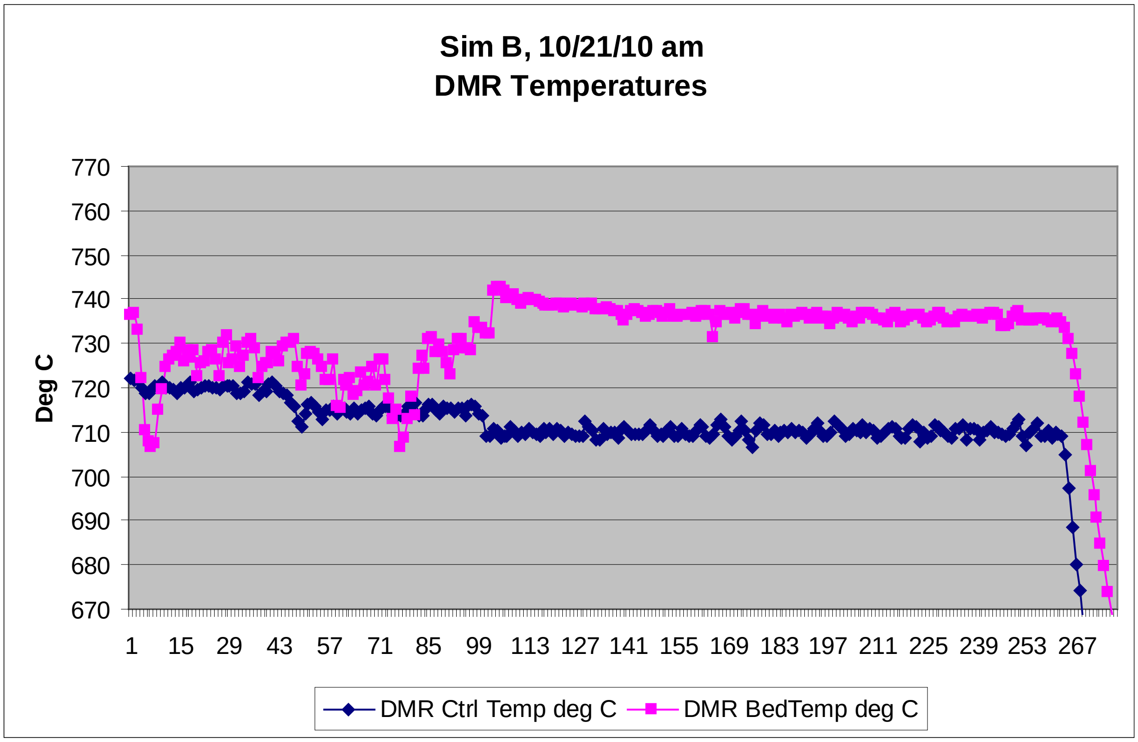

Figure C - 3. Run 10/21/10 am Temperatures in DMR

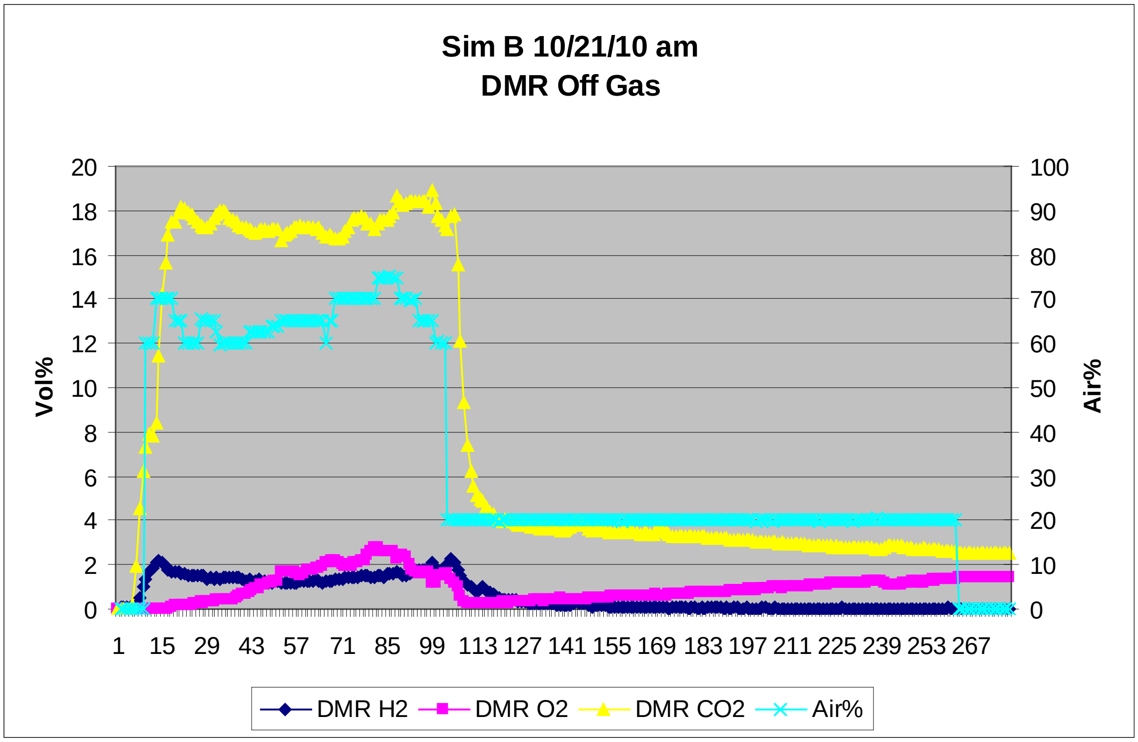

Figure C - 4. Run 10/21/10 am Off-Gas Concentrations and Air% Fed

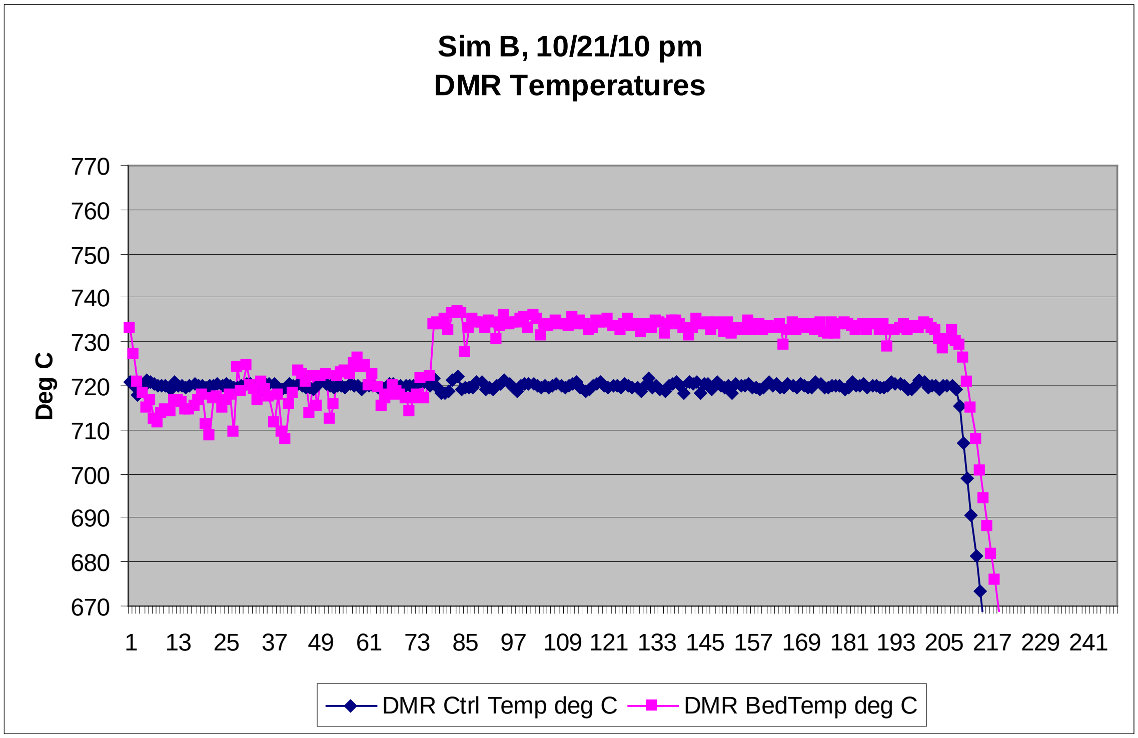

Figure C - 5. Run 10/21/10 pm Temperatures in DMR

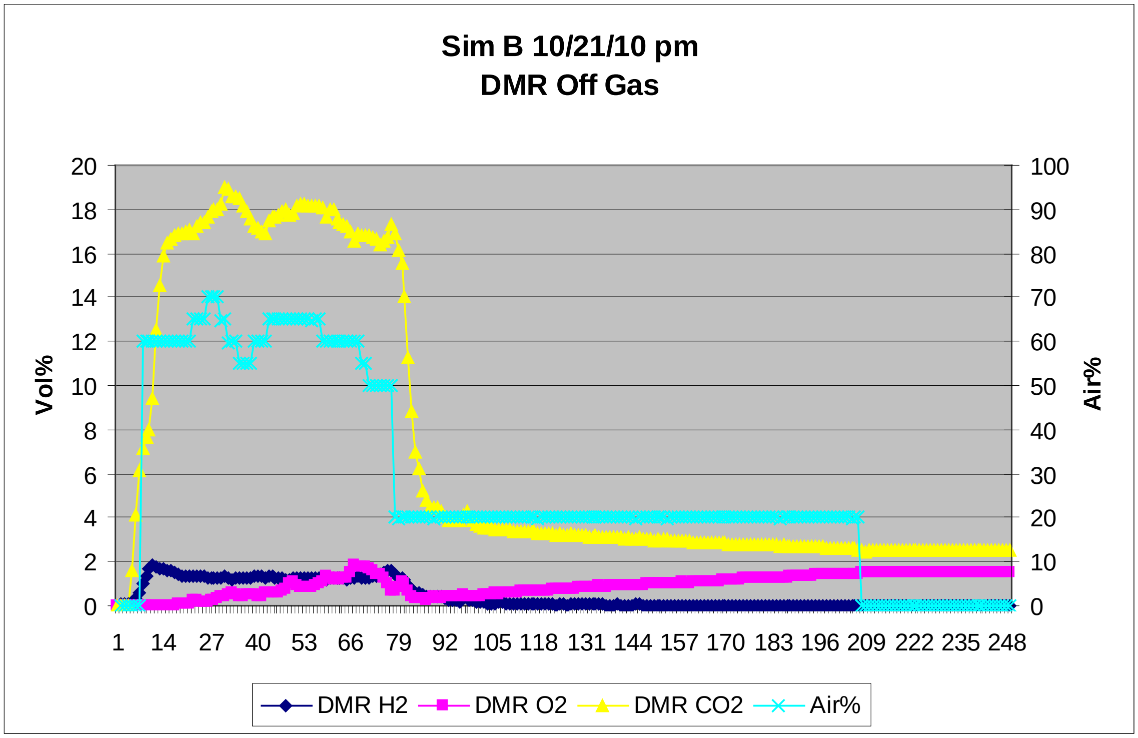

Figure C - 6. Run 10/21/10 pm Off-Gas Concentrations and Air% Fed

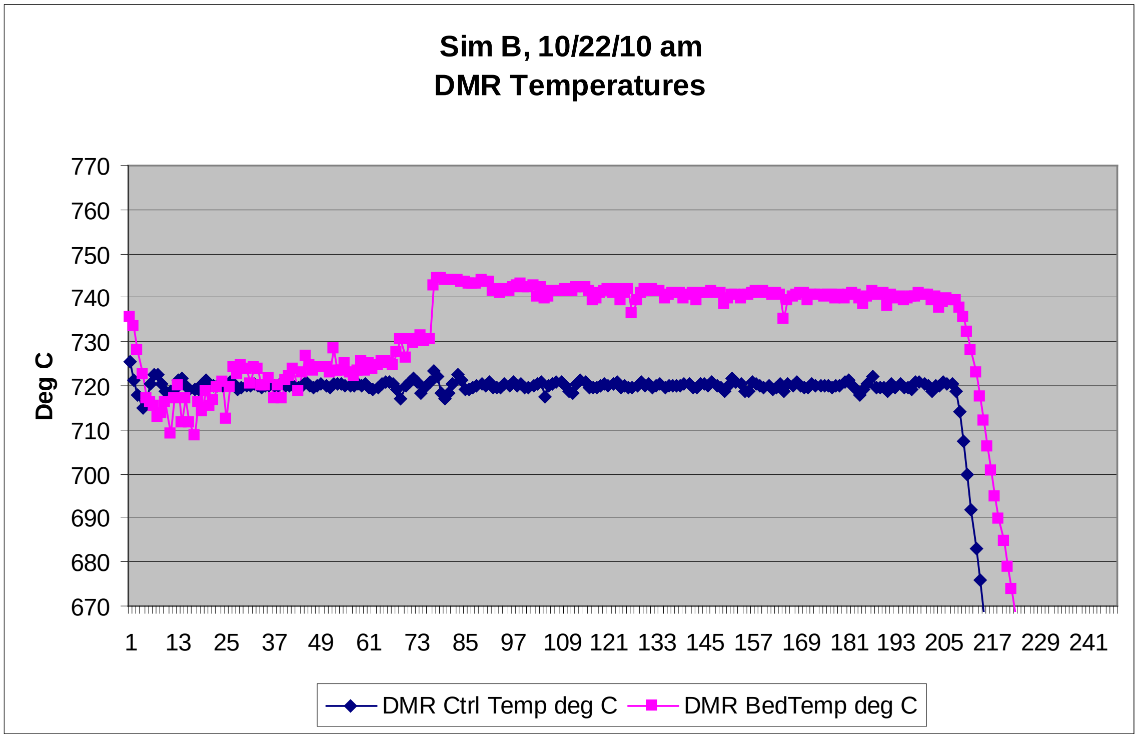

Figure C - 7. Run 10/22/10 am Temperatures in DMR

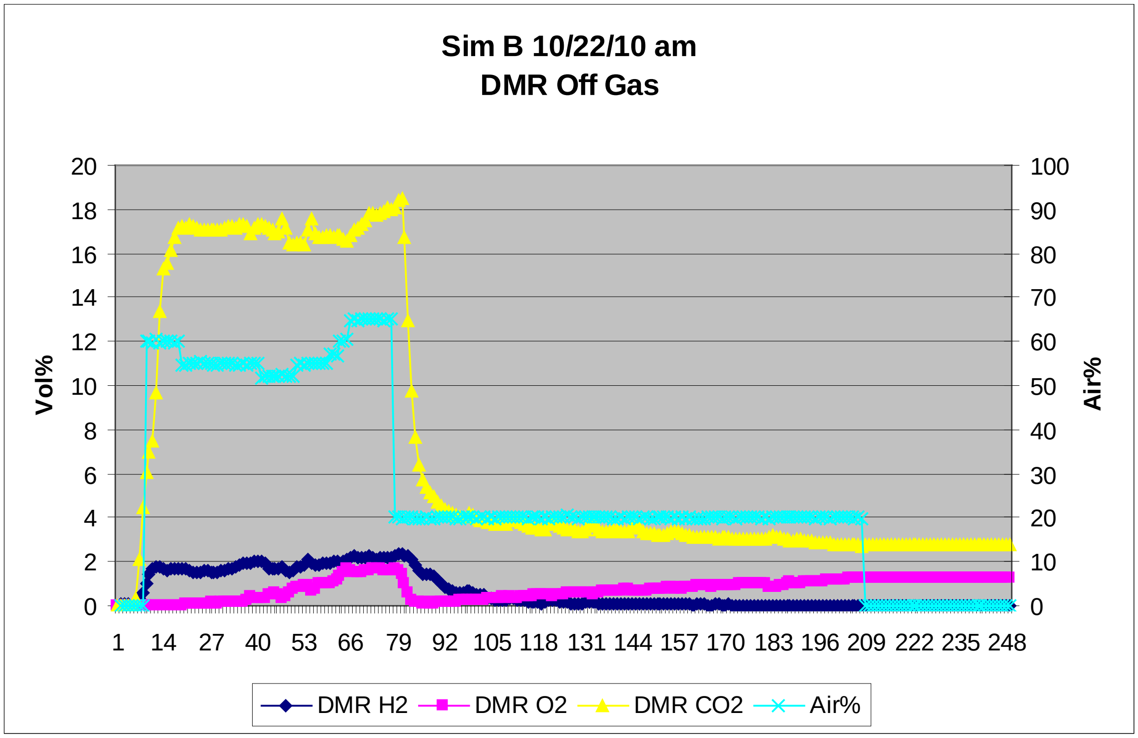

Figure C - 8. Run 10/22/10 am Off-Gas Concentrations and Air% Fed

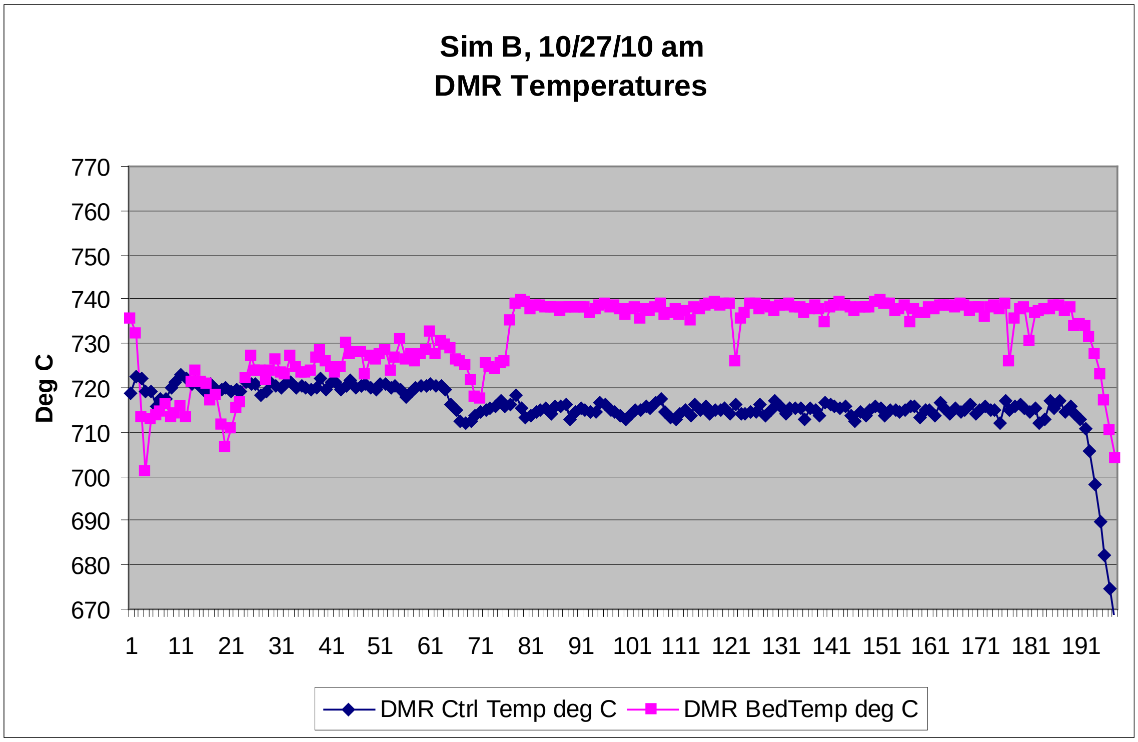

Figure C - 9. Run 10/27/10 am Temperatures in DMR

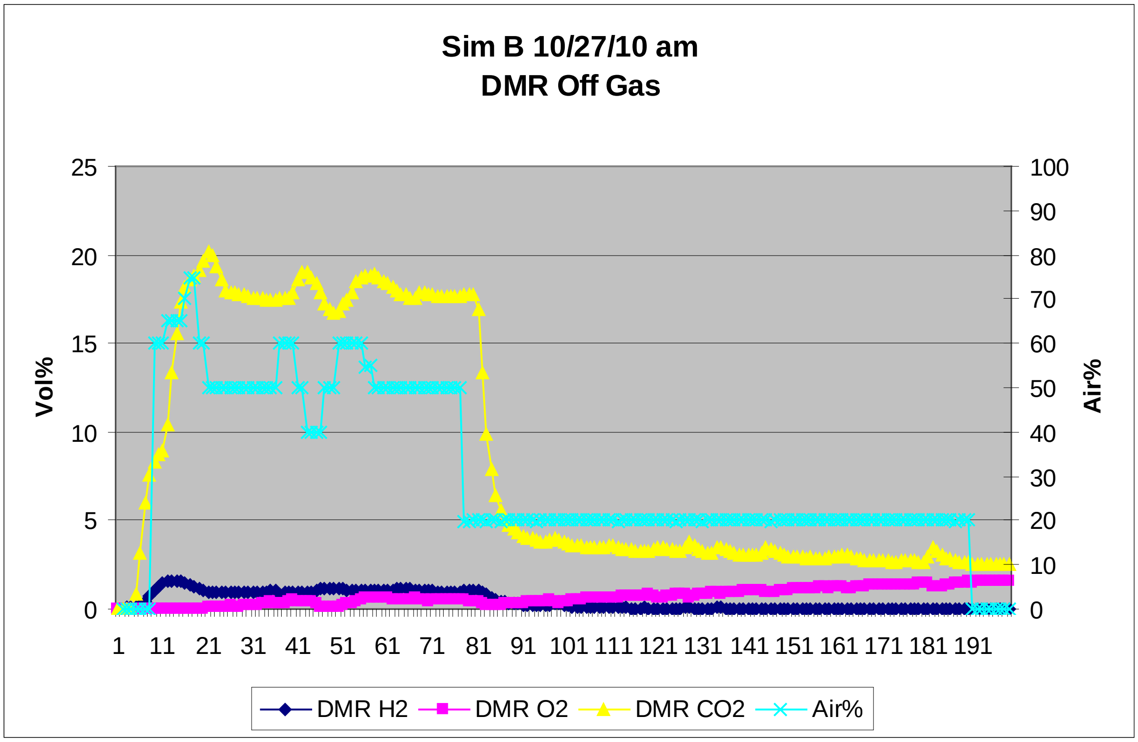

Figure C - 10. Run 10/27/10 am Off-Gas Concentrations and Air% Fed

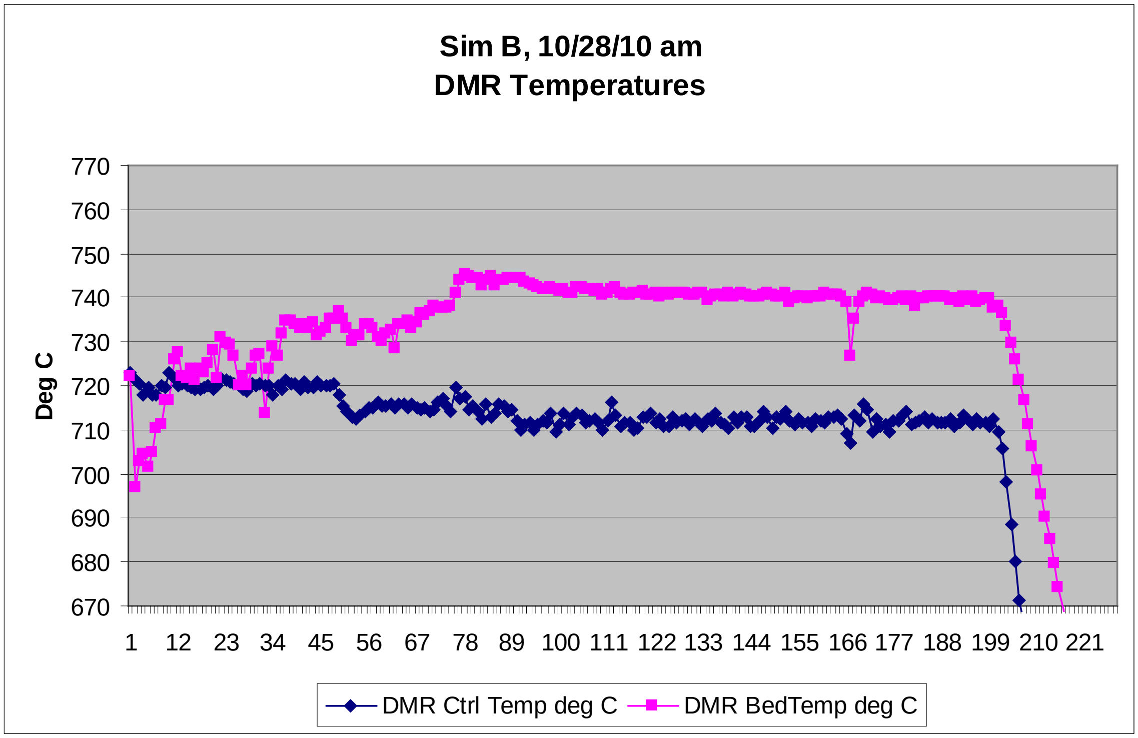

Figure C - 11. Run 10/28/10 am Temperatures in DMR

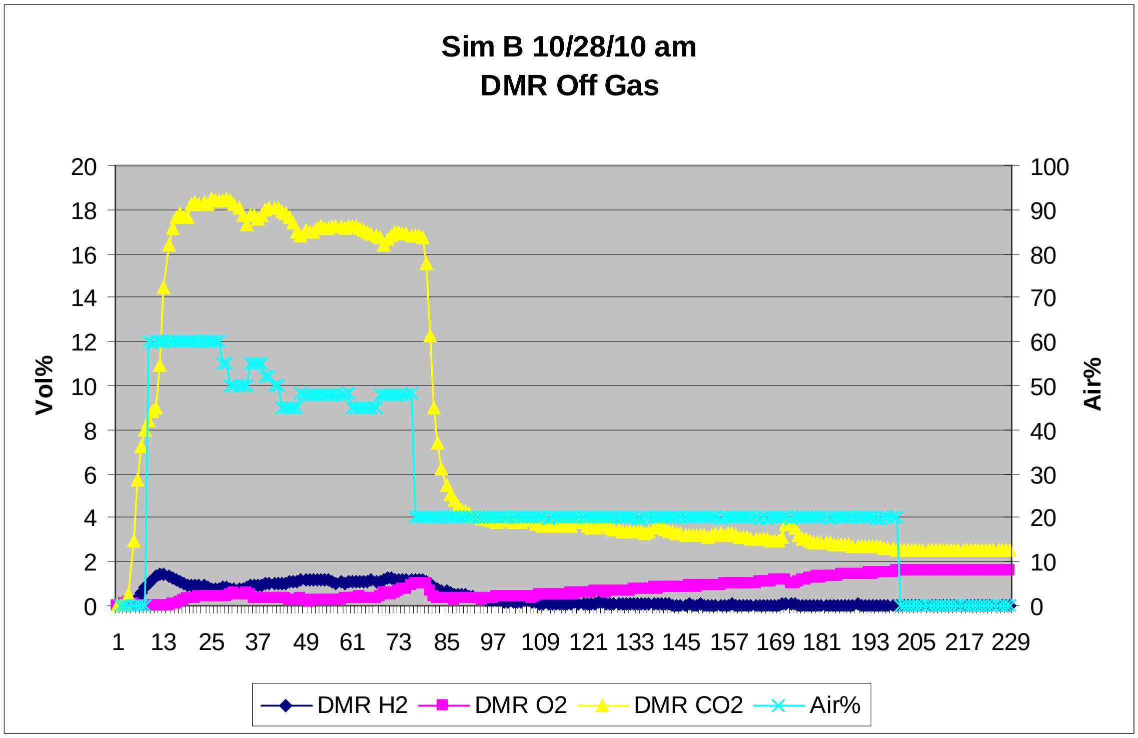

Figure B-12. Run 10/28/10 am Off-Gas Concentrations and Air% Fed

Appendix D. BSR Process Operation Conditions & Trends for Radioactive Module B Gas REDOX Controlled Runs

Table D - 1. BSR Process Operation Conditions & Results for Radioactive Module B REDOX Controlled Runs

Run Date	**11/9/10**	**11/10/10**	**11/11/10**	**11/12/10**	**11/13/10**	**11/14/10**
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 (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Carbon (stoichiometry)	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16	17.2	17.3	16.7	16.8	17
CO_2/ml	26.4	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	156	192	144	192	212	92
Product REDOX	0.190	0.325	0.326	0.500	0.455	0.500
Product LOI	0%	.27%	1.17%	1.00%	0%	1.66%
Product Quantity (g) before sampling	30.90	33.08	32.27	32.91	31.64	17.82
Feed Quantity (g)	97.2	106.1	107.06	103.1	103.22	85.61
Run Date	**11/17/10**	**11/18/10**	**11/20/10**	**11/21/10**	**11/22/10**	**11/23/10**
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 (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Carbon (stoichiometry)	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.5	17	17	17	17	17
CO_2/ml	27.8	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	56	62	76	162	151	124
Product REDOX	0.472	0.240	0.376	0.511	0.356	0.537
Product LOI	0%	0%	0%	1.68%	1.38%	0%
Product Quantity (g) before sampling	35.31	24.34	19.63	34.31	15.03	36.52
Feed Quantity (g)	108.81	91.57	49.71	104.22	92.04	104.15

Table D - 2. BSR Process Operation Conditions & Results for Radioactive Module B REDOX Controlled Runs

Run Date	**12/2/10**	**12/3/10**	**12/5/10**	**12/7/10**	**12/9/10**	**12/10/10***
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 (g/min)	0.40	0.40	0.40	0.40	0.40	0.40
DMR Control Pressure (inwc)	-4	-4	-4	-4	-4	-4
Carbon (stoichiometry)	1.3x	1.3x	1.3x	1.3x	1.3x	1.3x
Total Controlled Gas Flow (sccm)	500	500	500	500	500	500
Gas REDOX	16.4	17	17	17	17	17
CO_2/ml	27.8	27.8	27.8	27.8	27.8	27.8
Post Feed Run Time (hrs)	150	150	126	145	177	97
Product REDOX	.164	.519	.185	.332	.318	.370
Product LOI	0.28%	1.64%	0%	0.59%	0.18%	0.49%
Product Quantity (g) before sampling	21.91	26.88	16.56	17.34	25.93	23.45
Feed Quantity (g)	81.55	91.7	47.21	73.97	95.36	82.38

*Tc-99 spike campaign

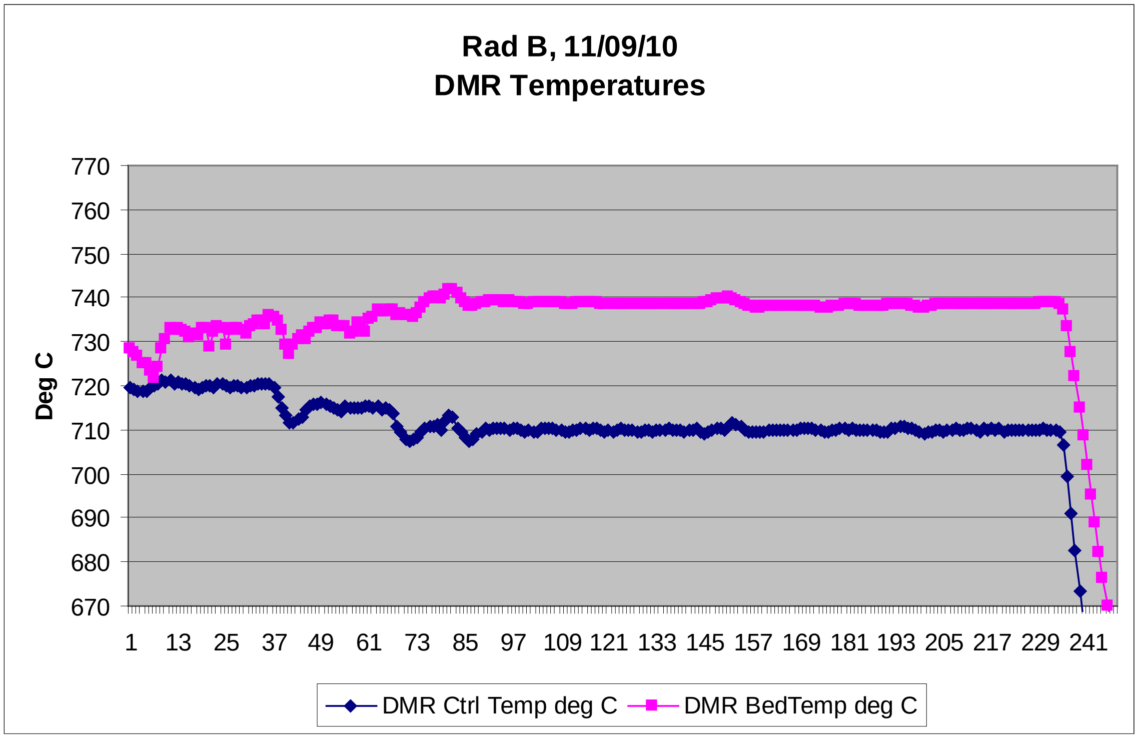

Figure D - 1. Run 11/9/10 Temperatures in DMR

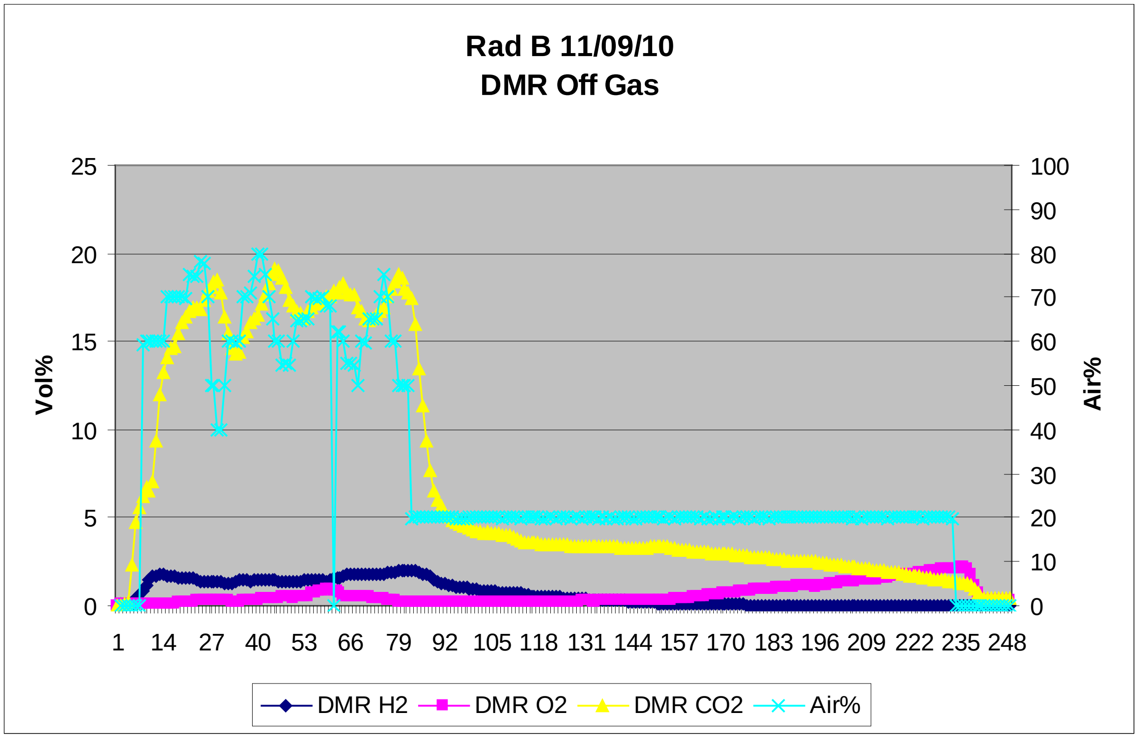

Figure D - 2. Run 11/9/10 Off-Gas Concentrations and Air% Fed

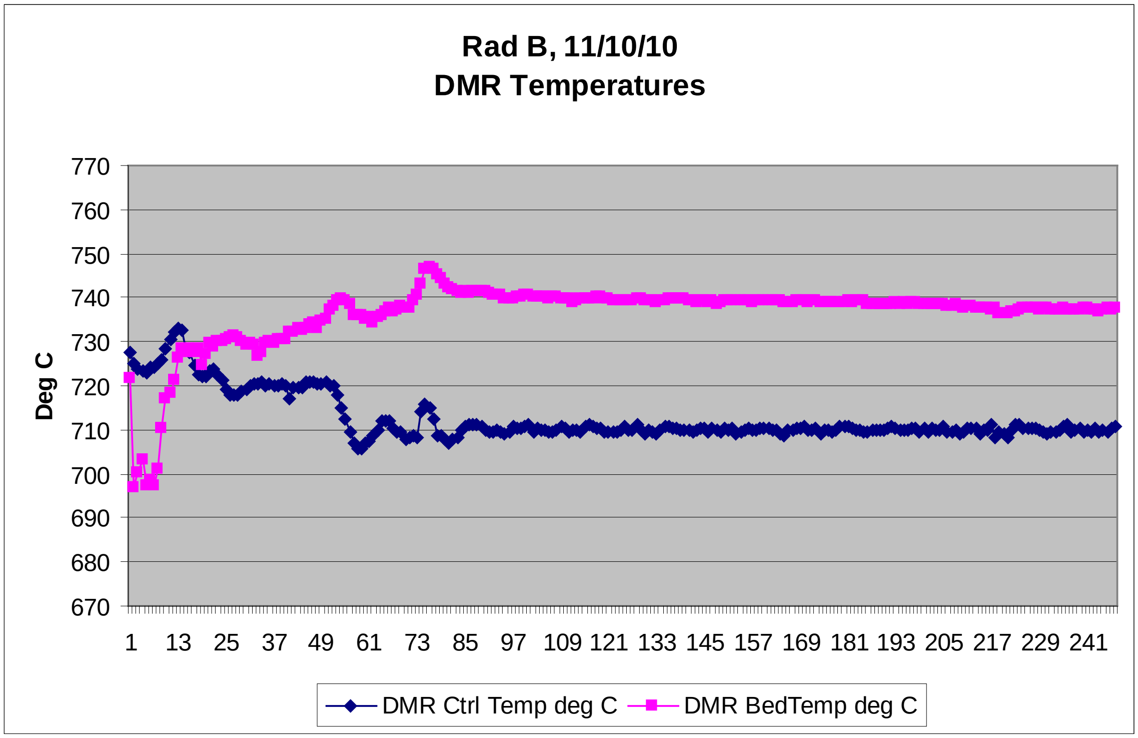

Figure D - 3. Run 11/10/10 Temperatures in DMR

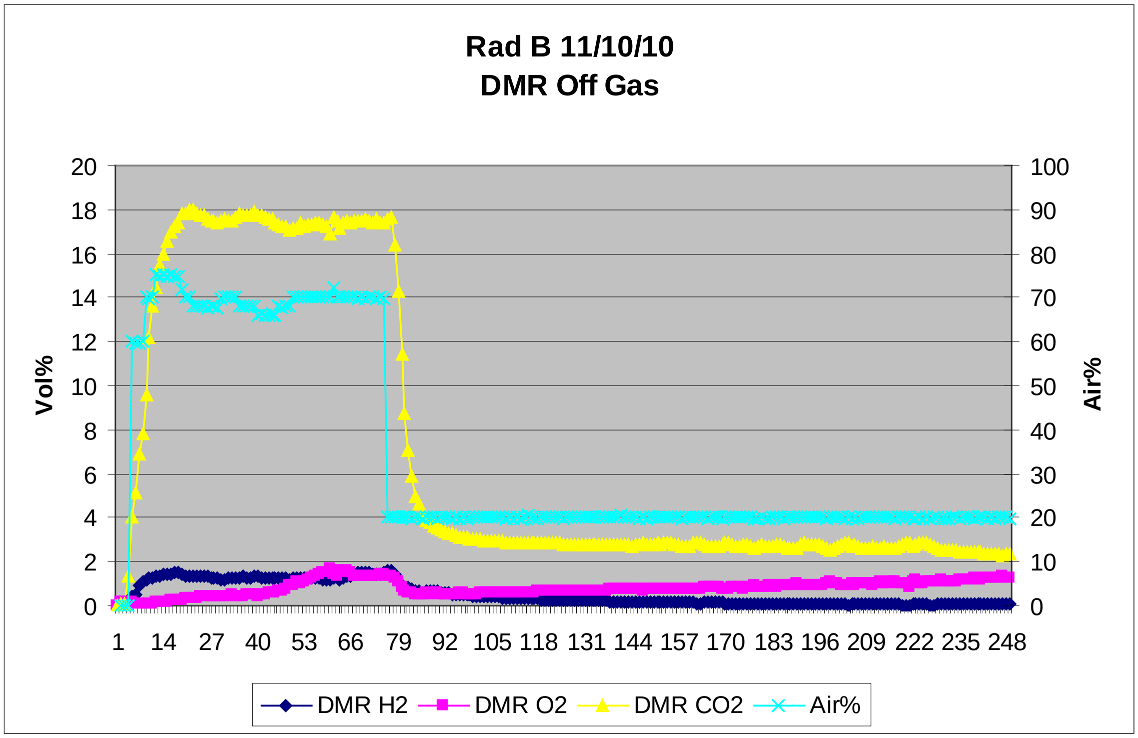

Figure D - 4. Run 11/10/10 Off-Gas Concentrations and Air% Fed

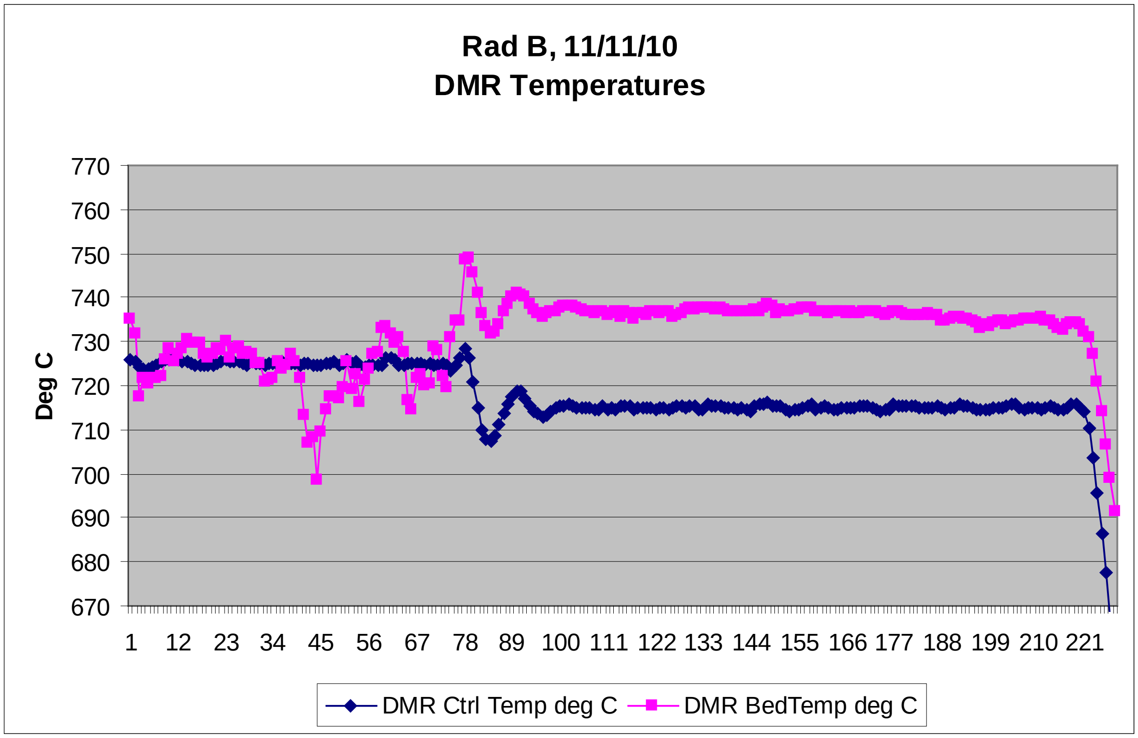

Figure D - 5. Run 11/11/10 Temperatures in DMR

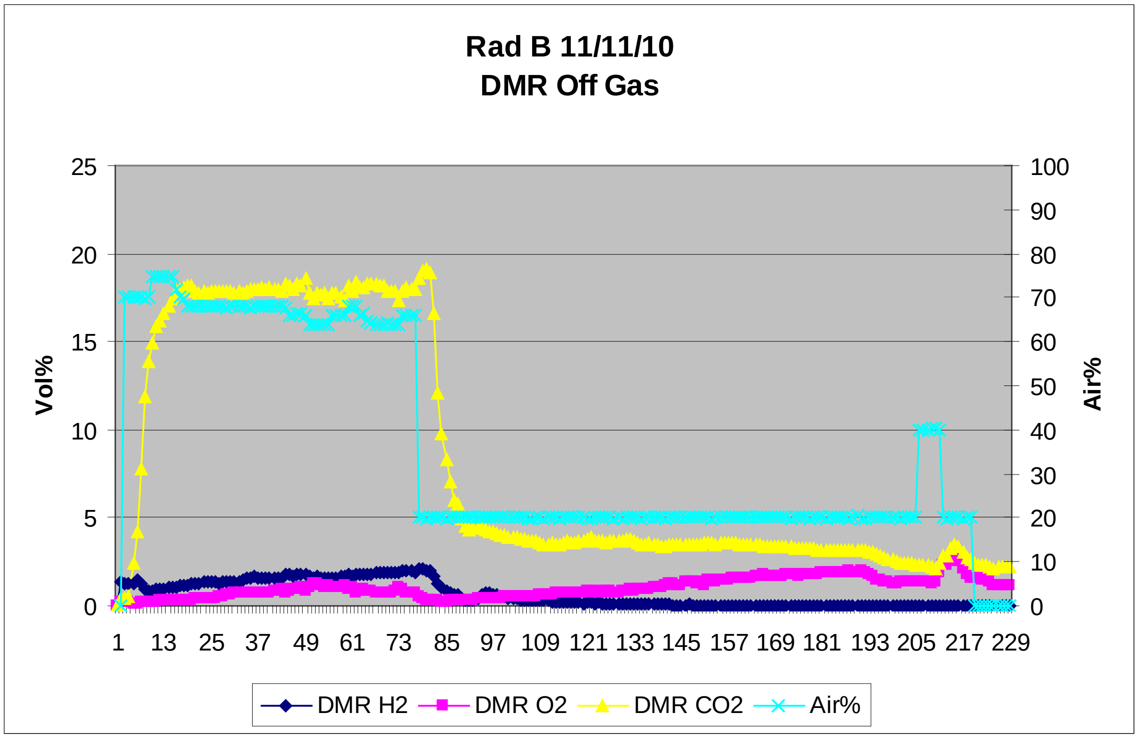

Figure D - 6. Run11/11/10 Off-Gas Concentrations and Air% Fed

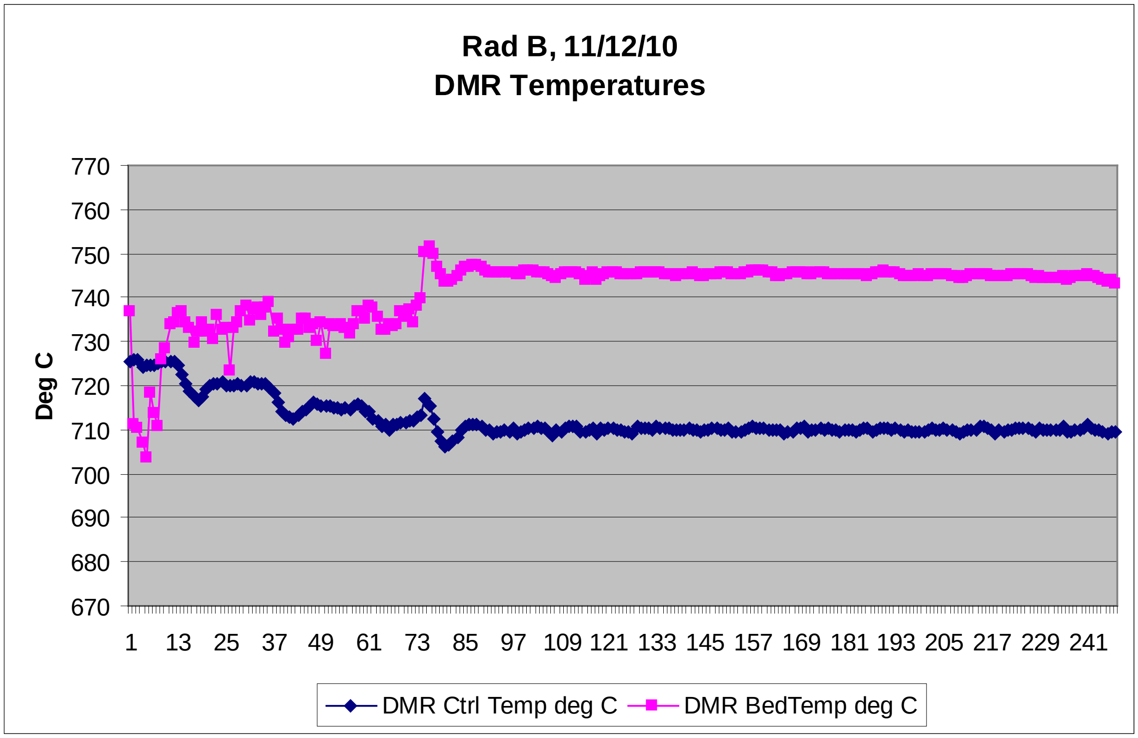

Figure D - 7. Run 11/12/10 Temperatures in DMR

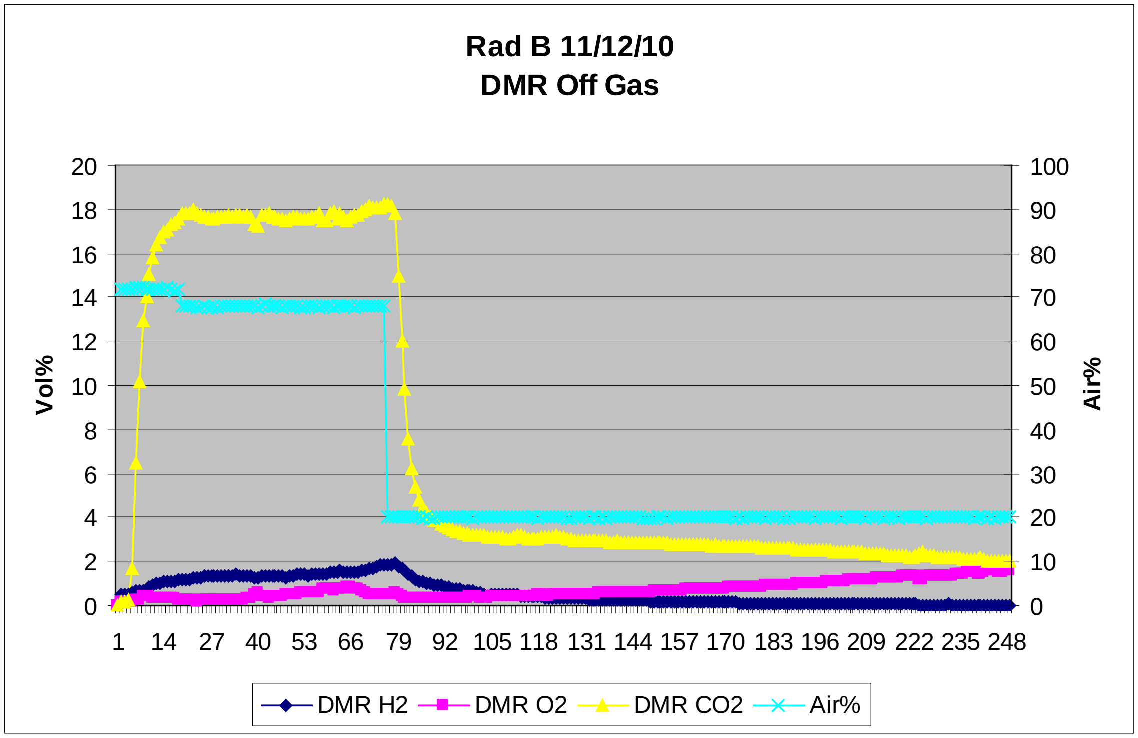

Figure D - 8. Run 11/12/10 Off-Gas Concentrations and Air% Fed

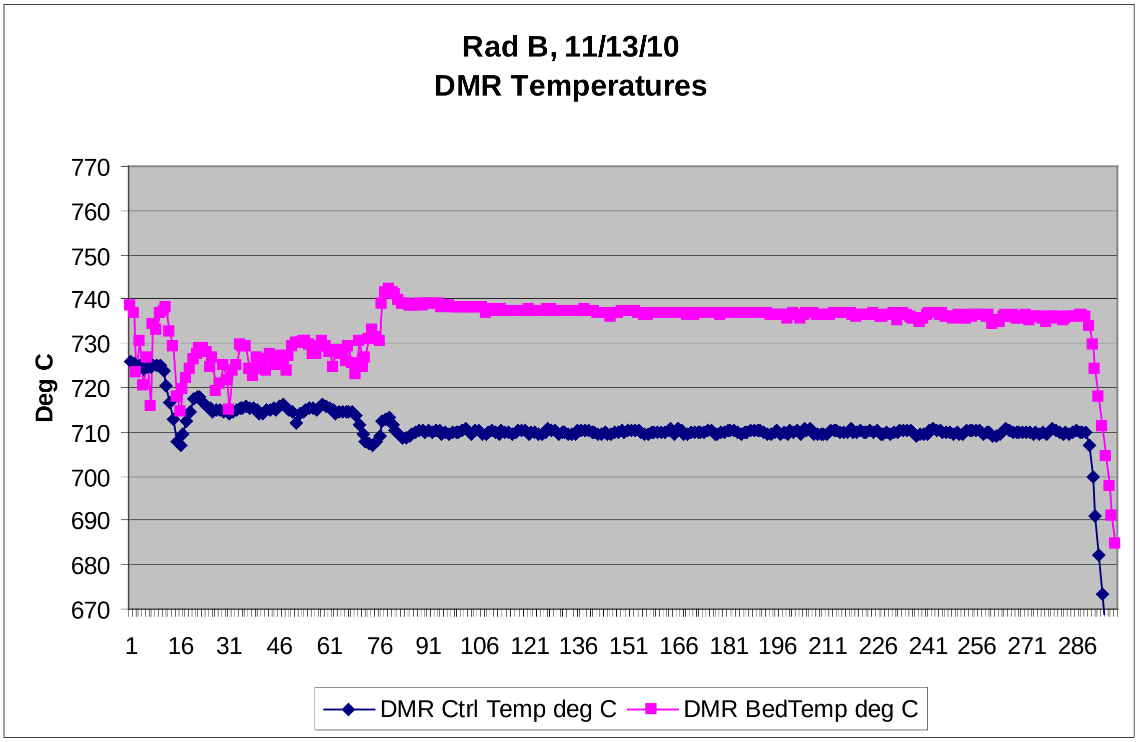

Figure D - 9. Run 11/13/10 Temperatures in DMR

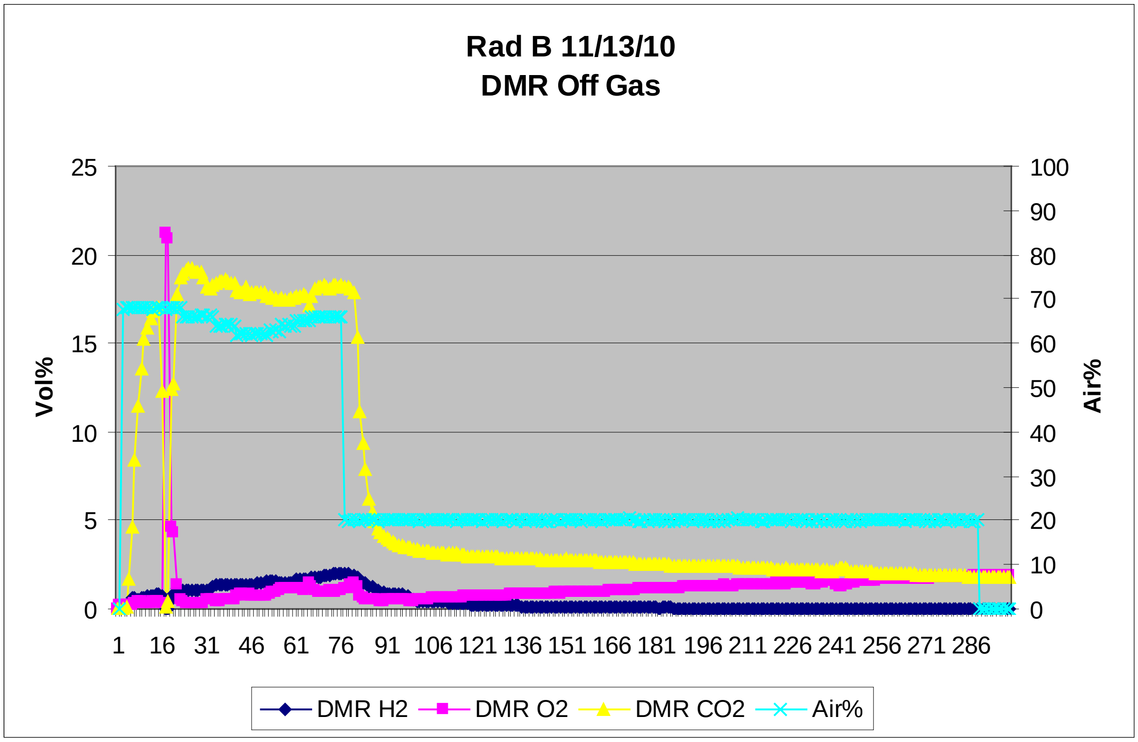

Figure D - 10. Run 11/13/10 Off-Gas Concentrations and Air% Fed

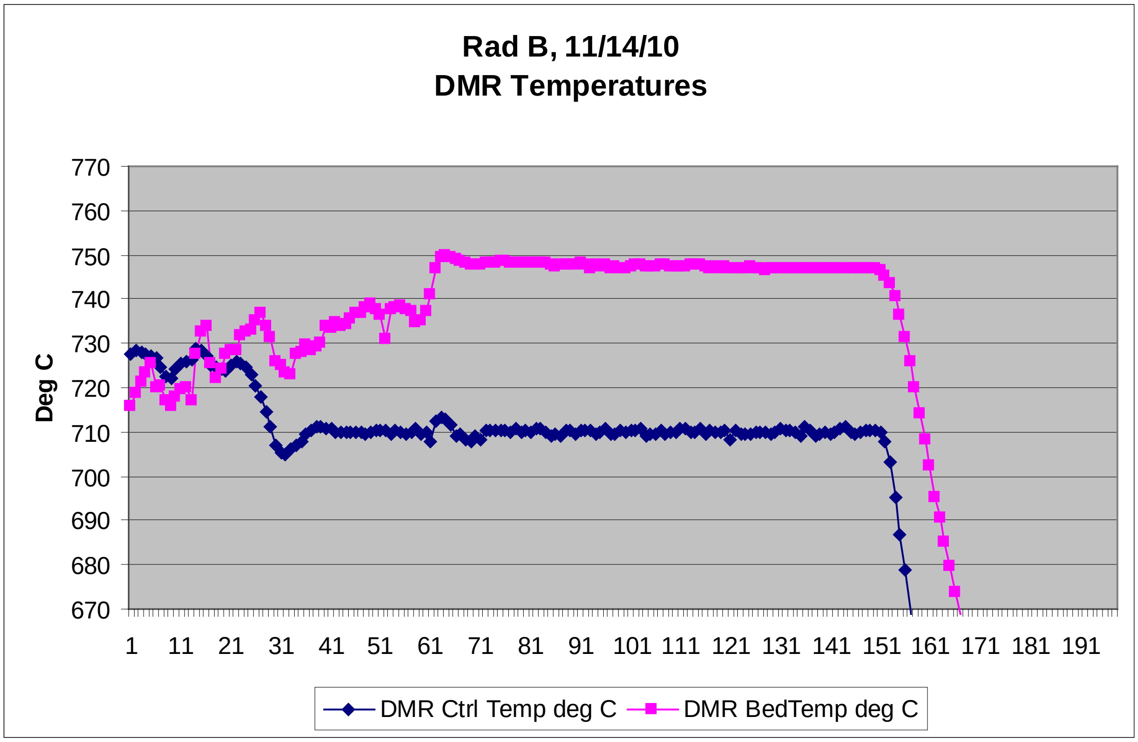

Figure D - 11. Run 11/14/10 Temperatures in DMR

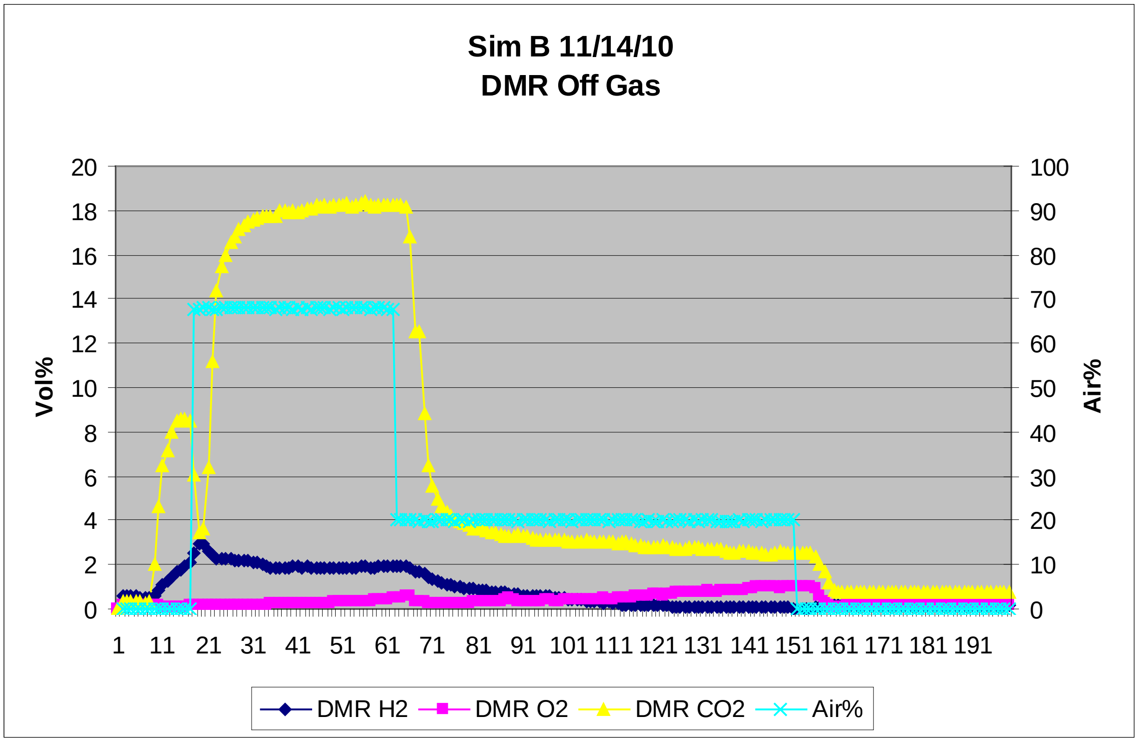

Figure D - 12. Run 11/14/10 Off-Gas Concentrations and Air% Fed

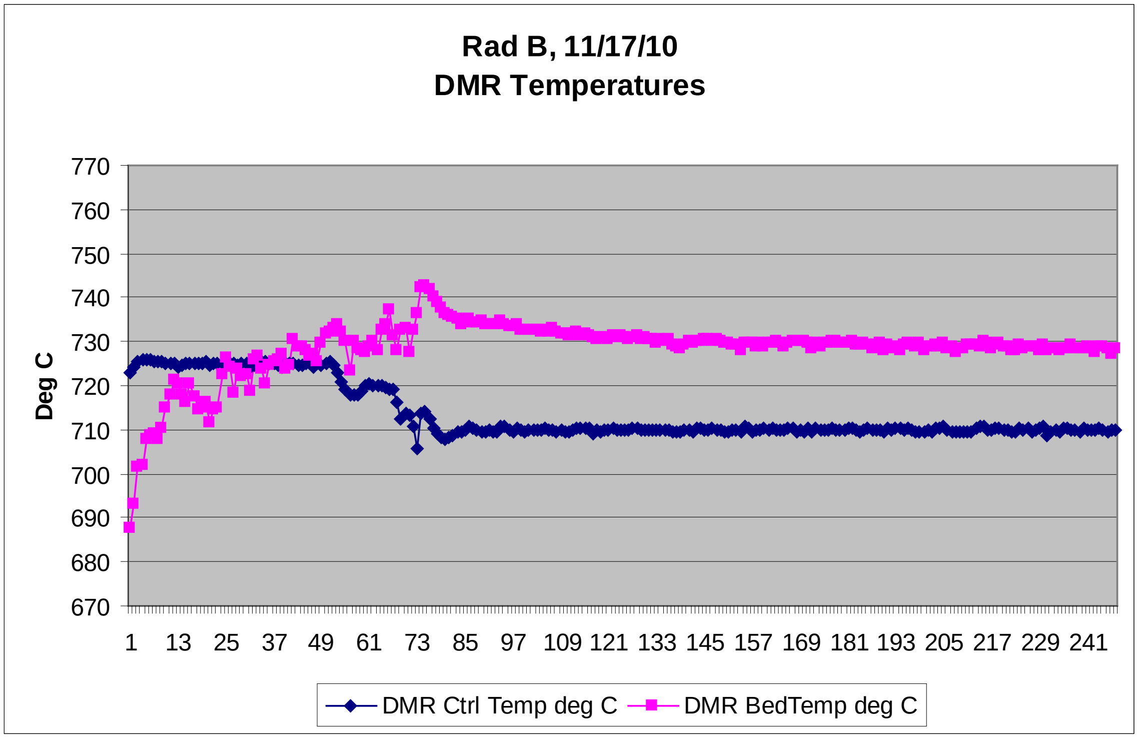

Figure D - 13. Run 11/17/10 Temperatures in DMR

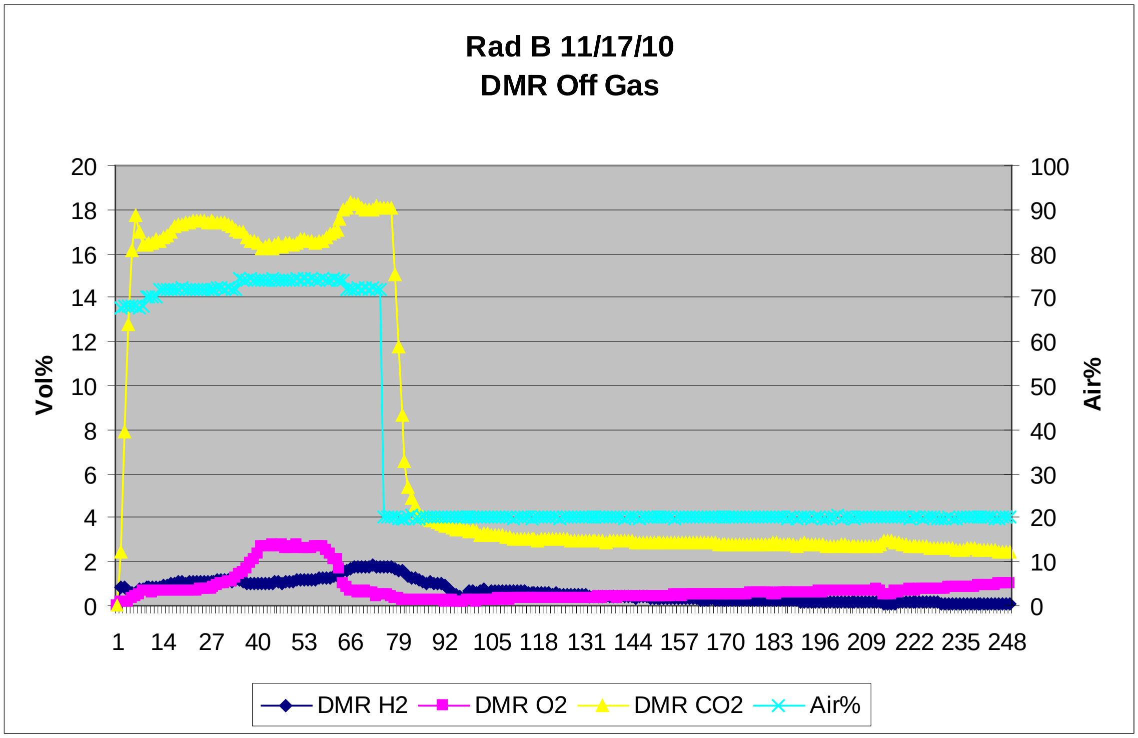

Figure D - 14. Run 11/17/10 Off-Gas Concentrations and Air% Fed

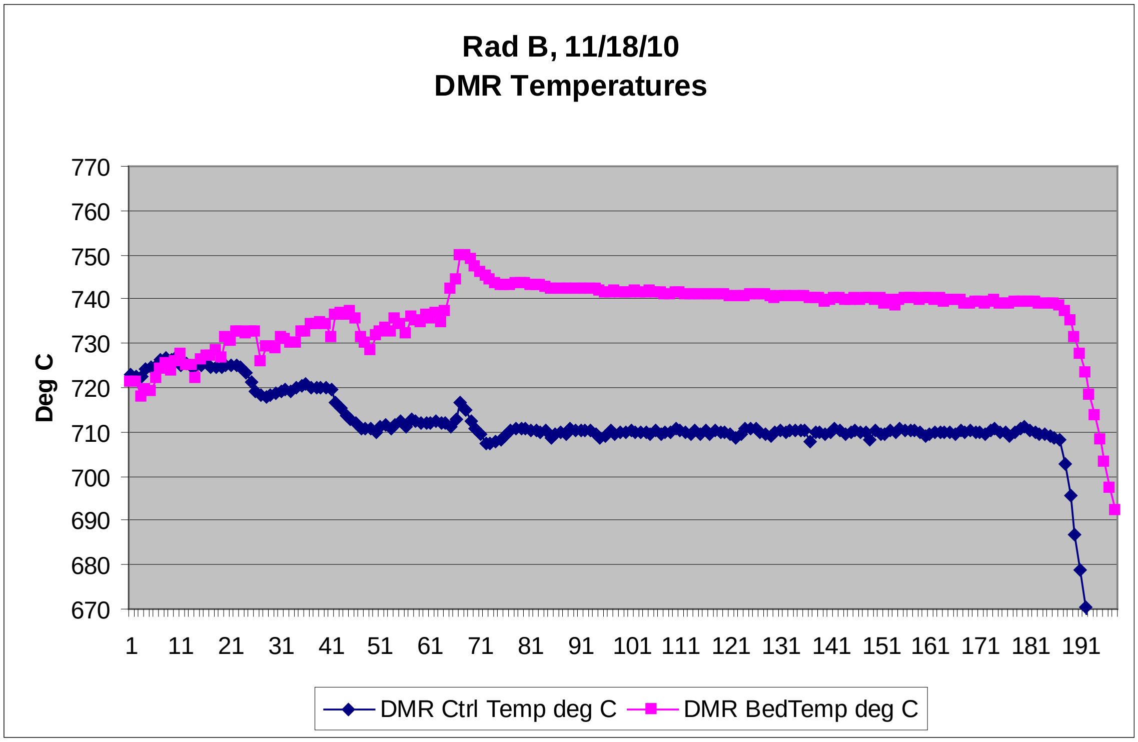

Figure D - 15. Run 11/18/10 Temperatures in DMR

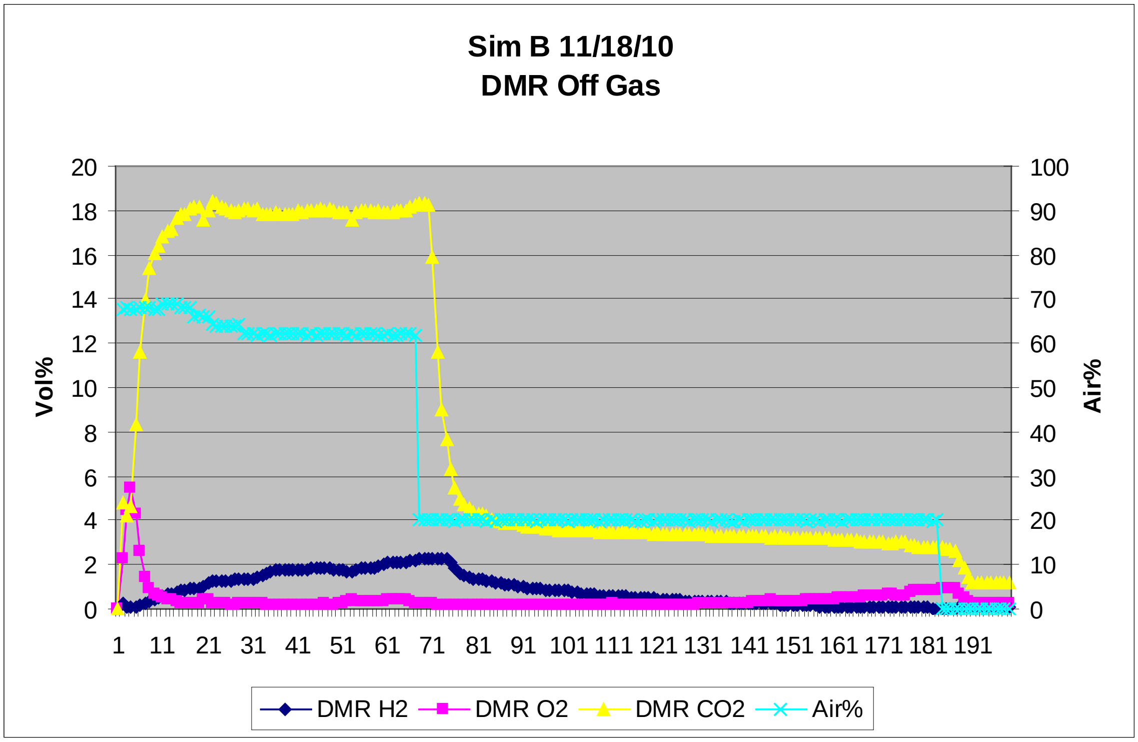

Figure D - 16. Run 11/18/10 Off-Gas Concentrations and Air% Fed

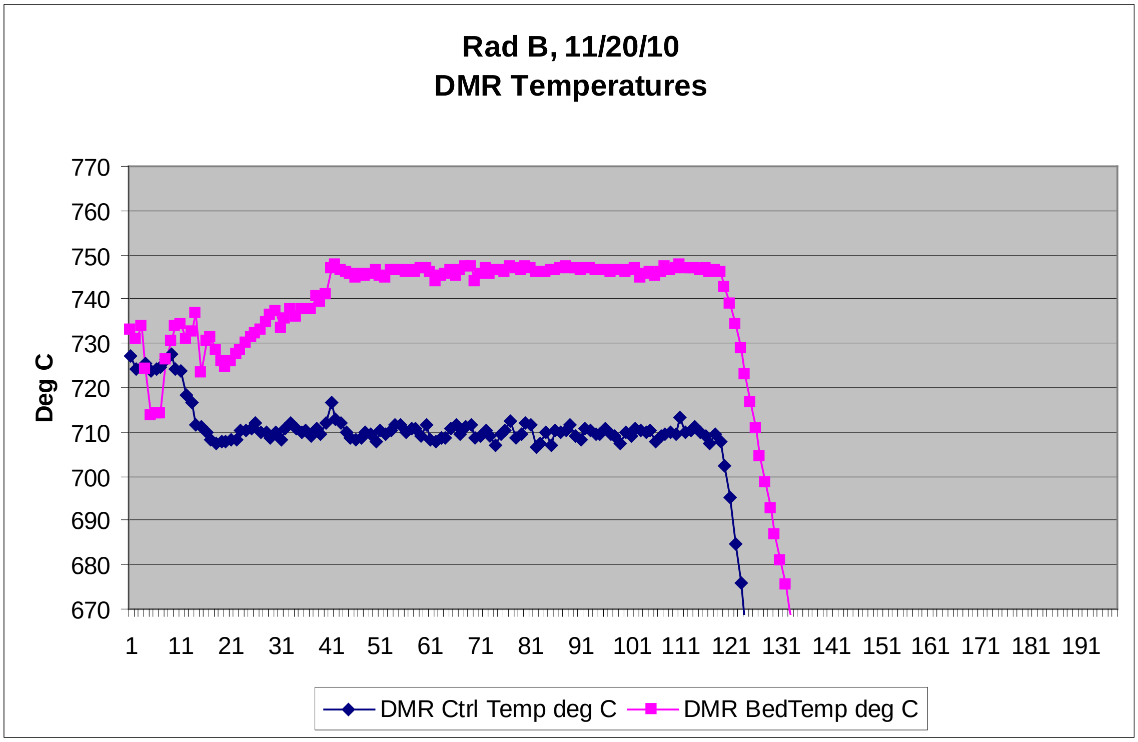

Figure D - 17. Run 11/20/10 Temperatures in DMR

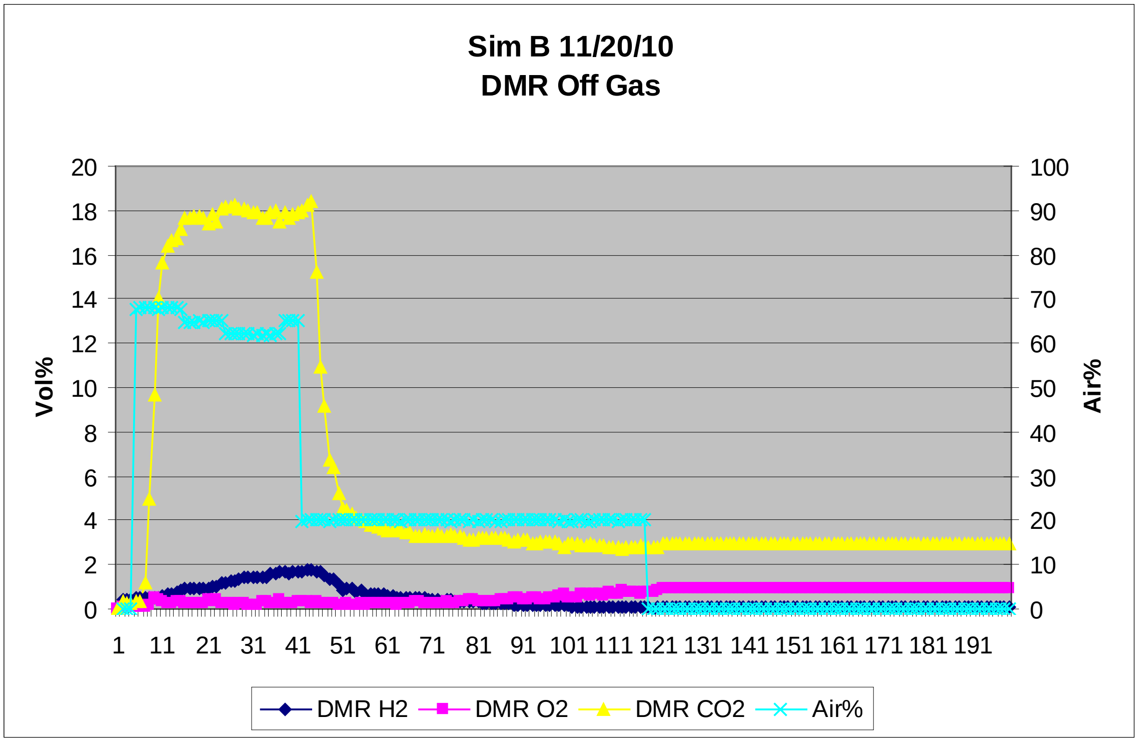

Figure D - 18. Run 11/20/10 Off-Gas Concentrations and Air% Fed

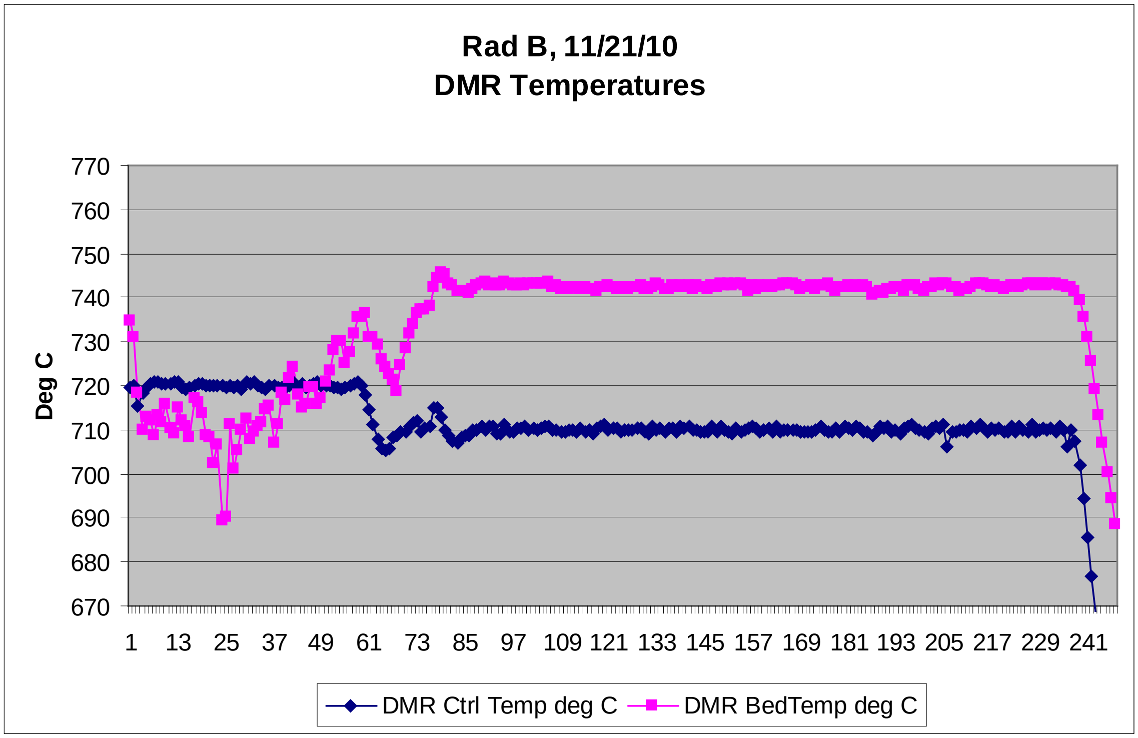

Figure D - 19. Run 11/21/10 Temperatures in DMR

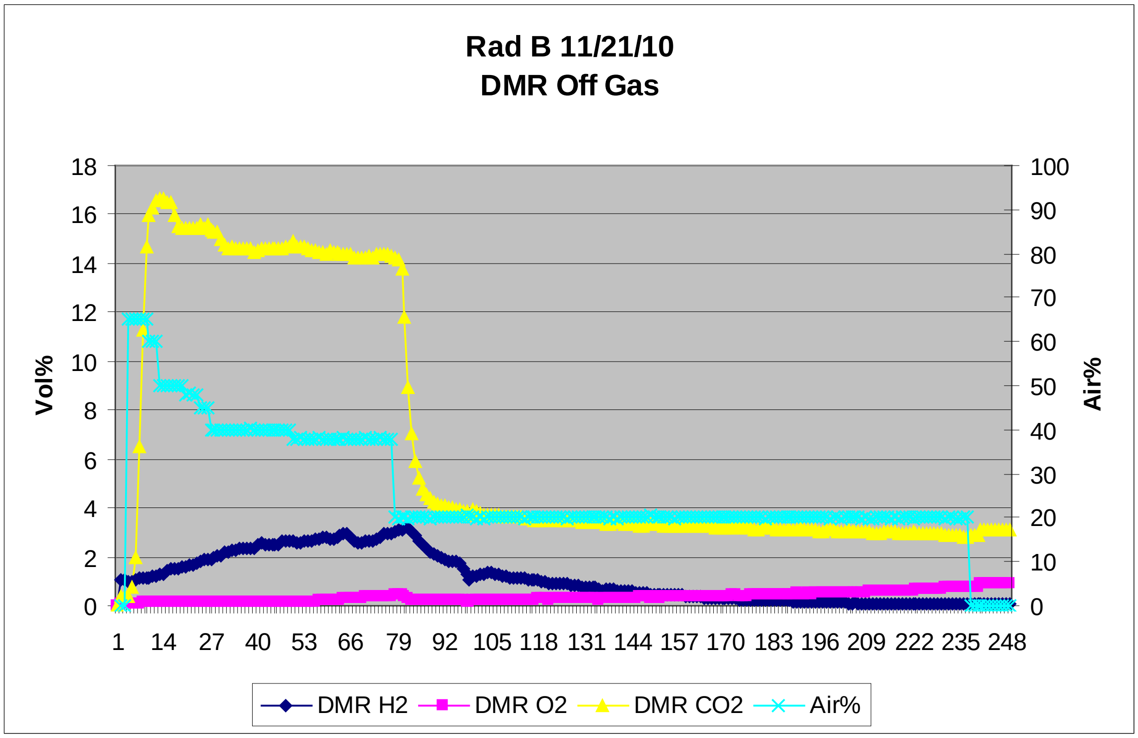

Figure D - 20. Run 11/21/10 Off-Gas Concentrations and Air% Fed

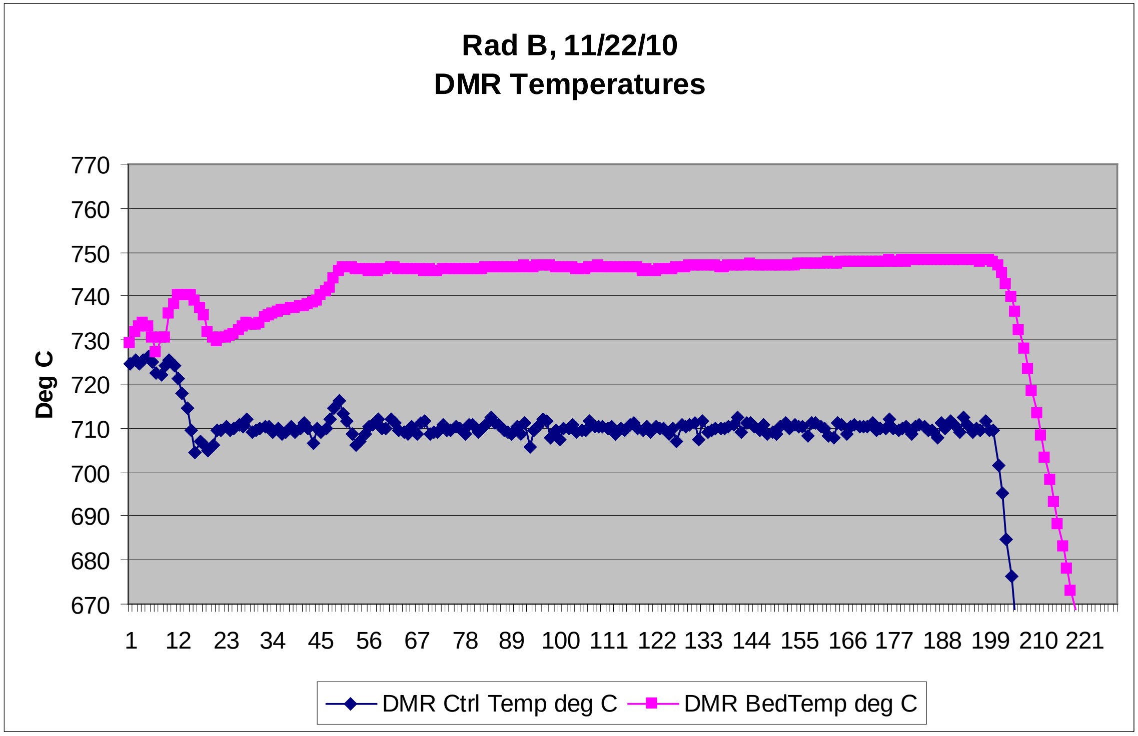

Figure D - 21. Run 11/22/10 Temperatures in DMR

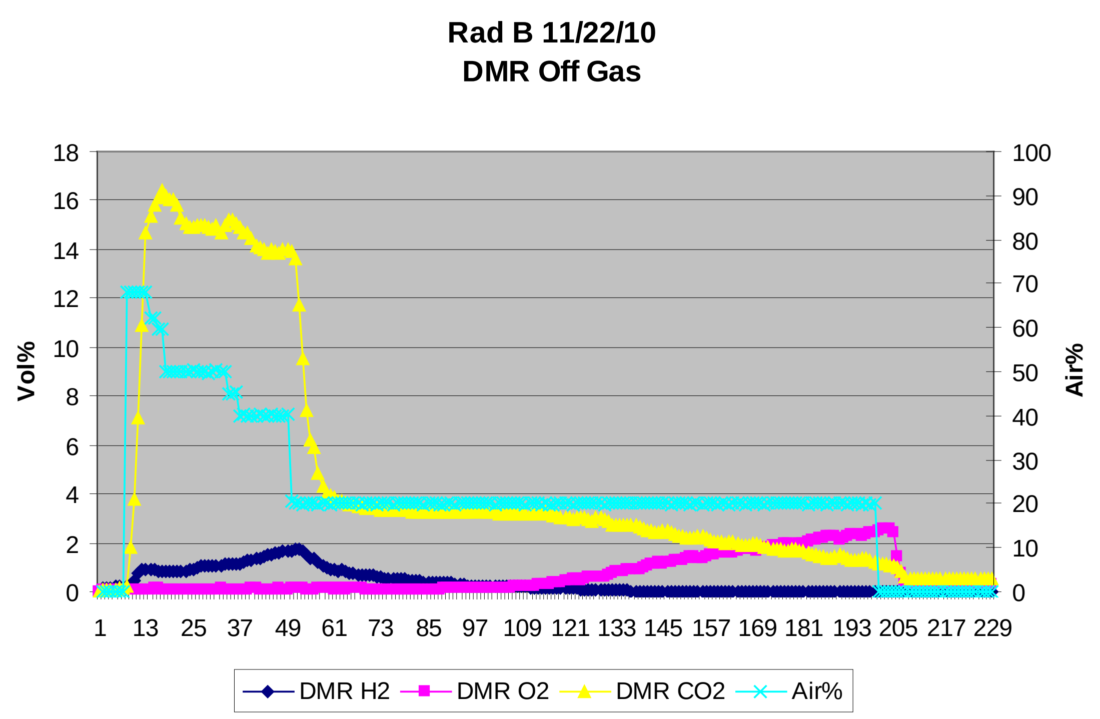

Figure D - 22. Run 11/22/10 Off-Gas Concentrations and Air% Fed

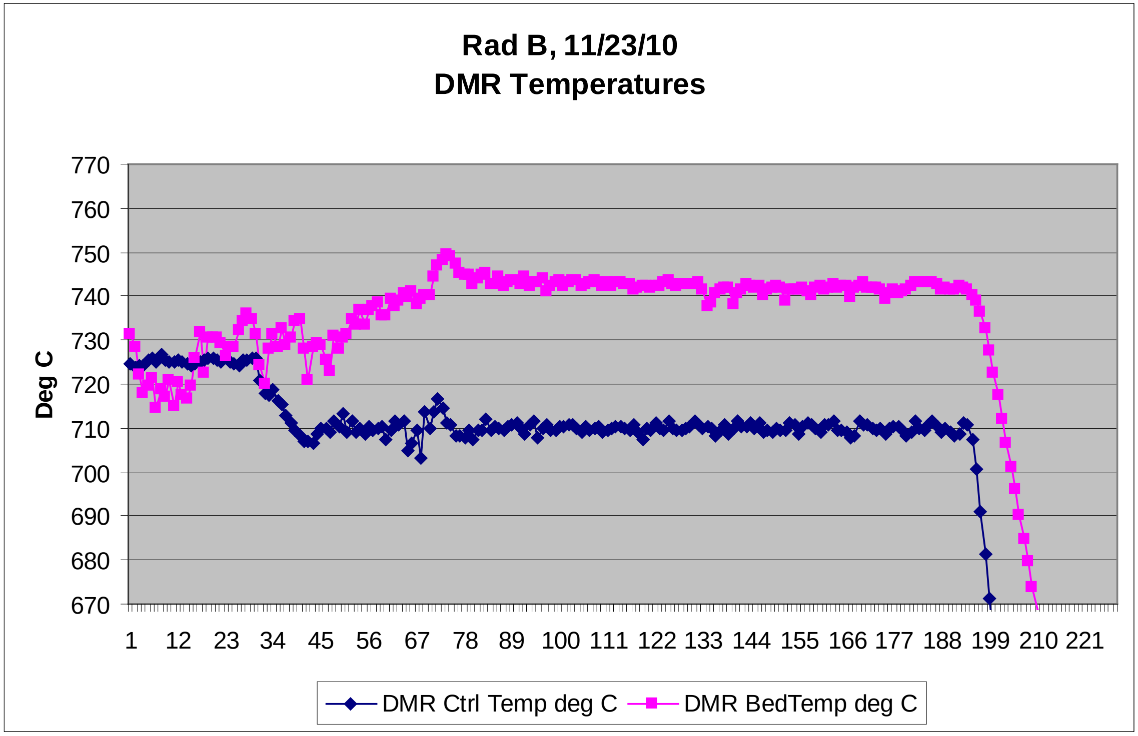

Figure D - 23. Run 11/23/10 Temperatures in DMR

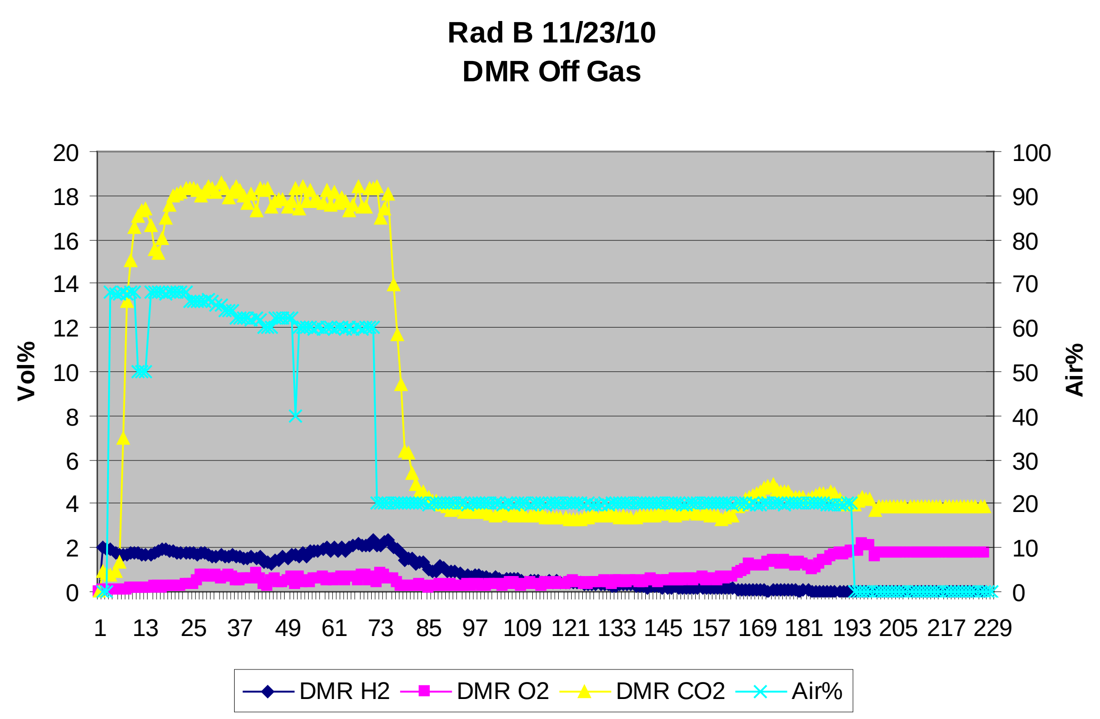

Figure D - 24. Run 11/23/10 Off-Gas Concentrations and Air% Fed

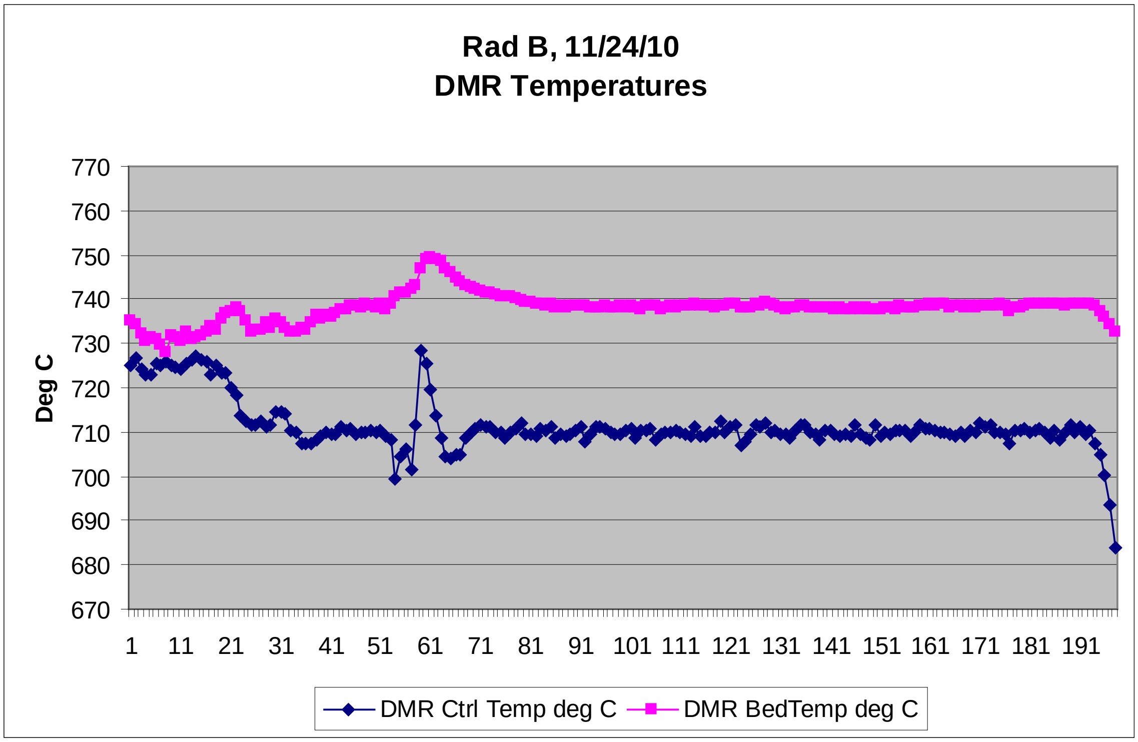

Figure D - 25. Run 11/24/10 Temperatures in DMR

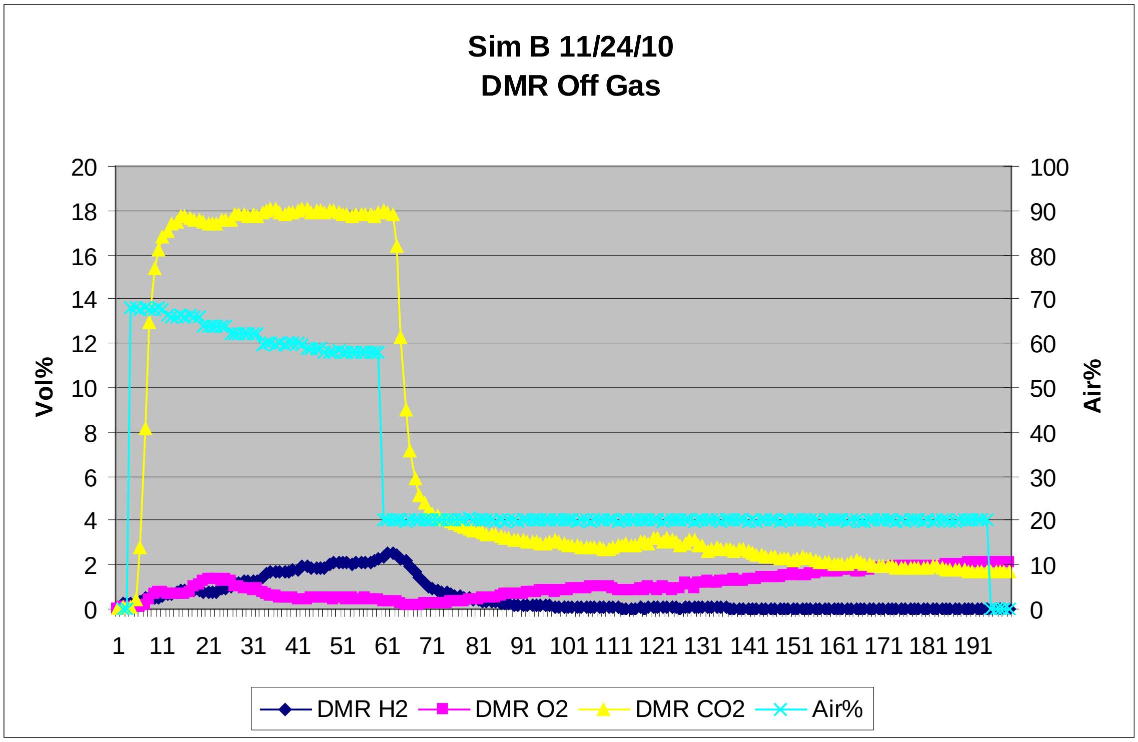

Figure D - 26. Run 11/24/10 Off-Gas Concentrations and Air% Fed

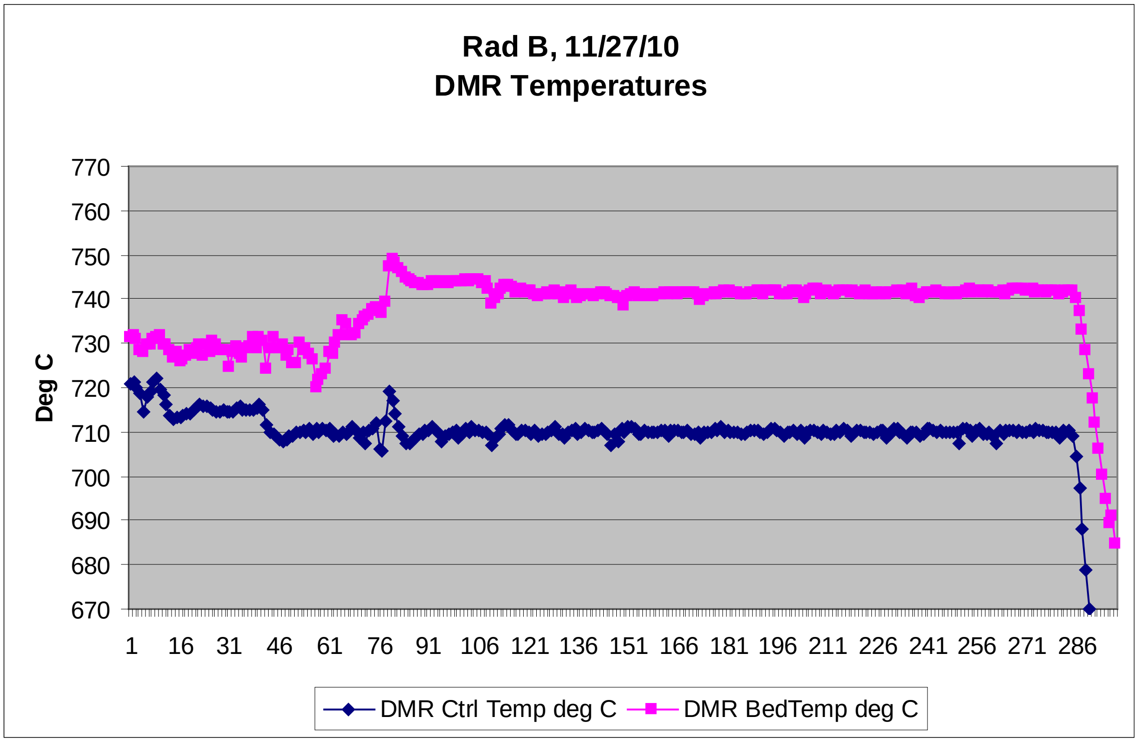

Figure D - 27. Run 11/27/10 Temperatures in DMR

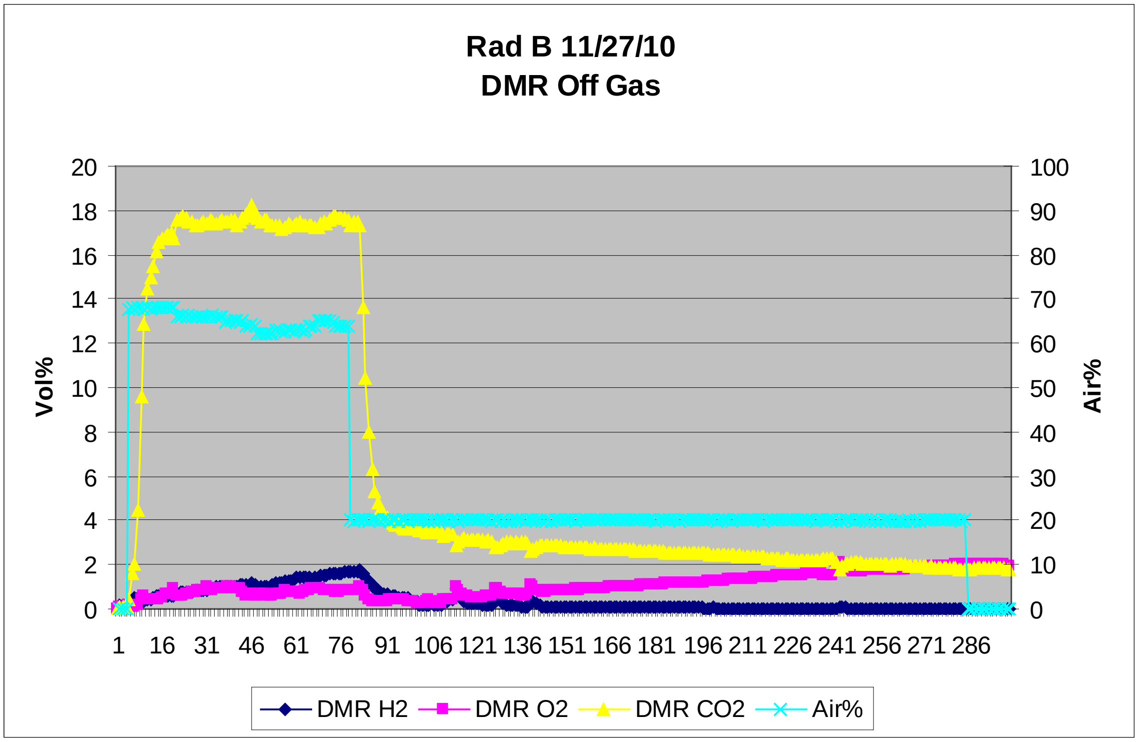

Figure D - 28. Run 11/27/10 Off-Gas Concentrations and Air% Fed

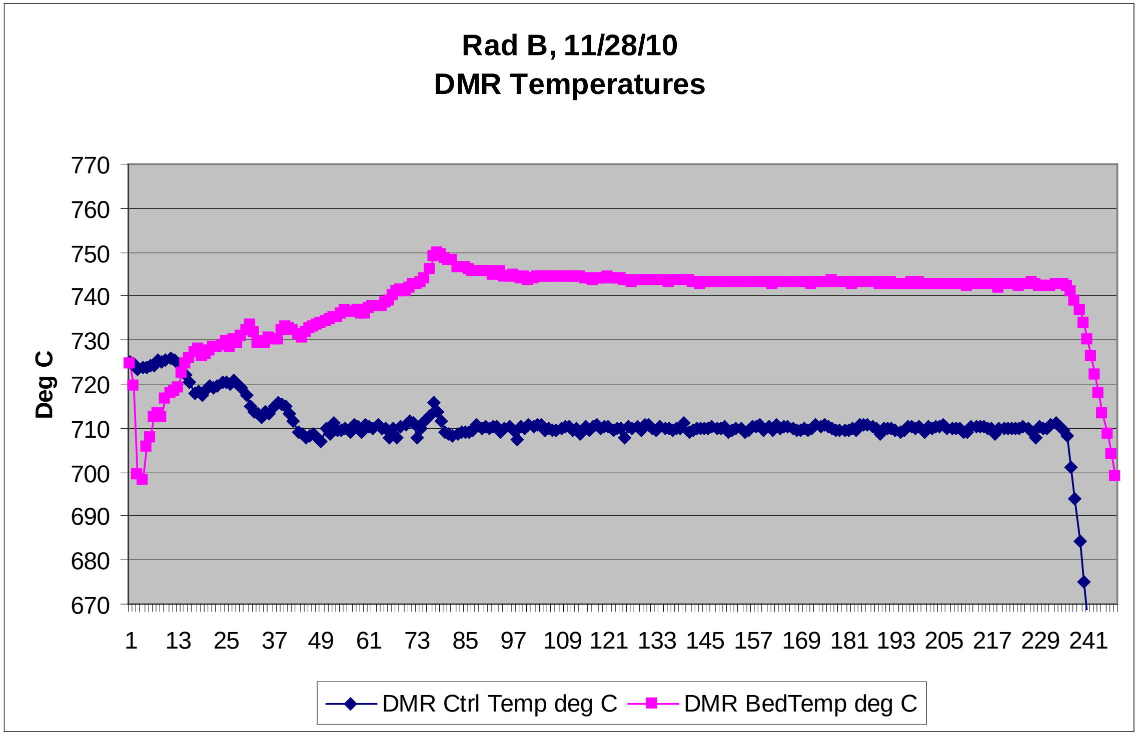

Figure D - 29. Run 11/28/10 Temperatures in DMR

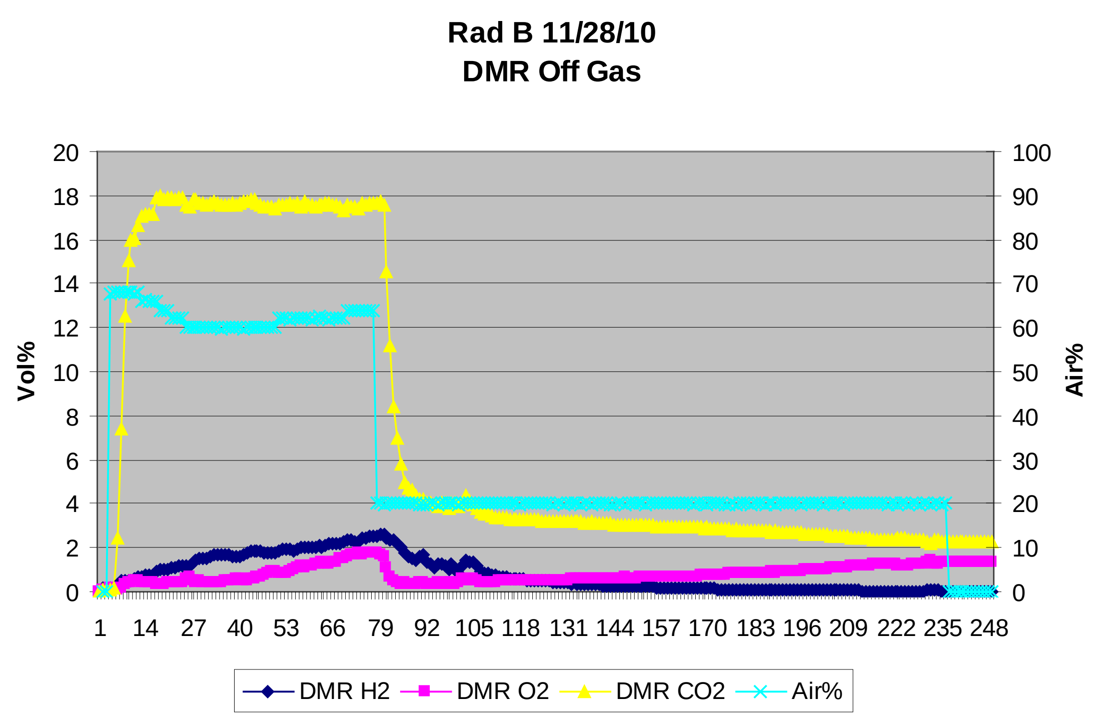

Figure D - 30. Run 11/28/10 Off-Gas Concentrations and Air% Fed

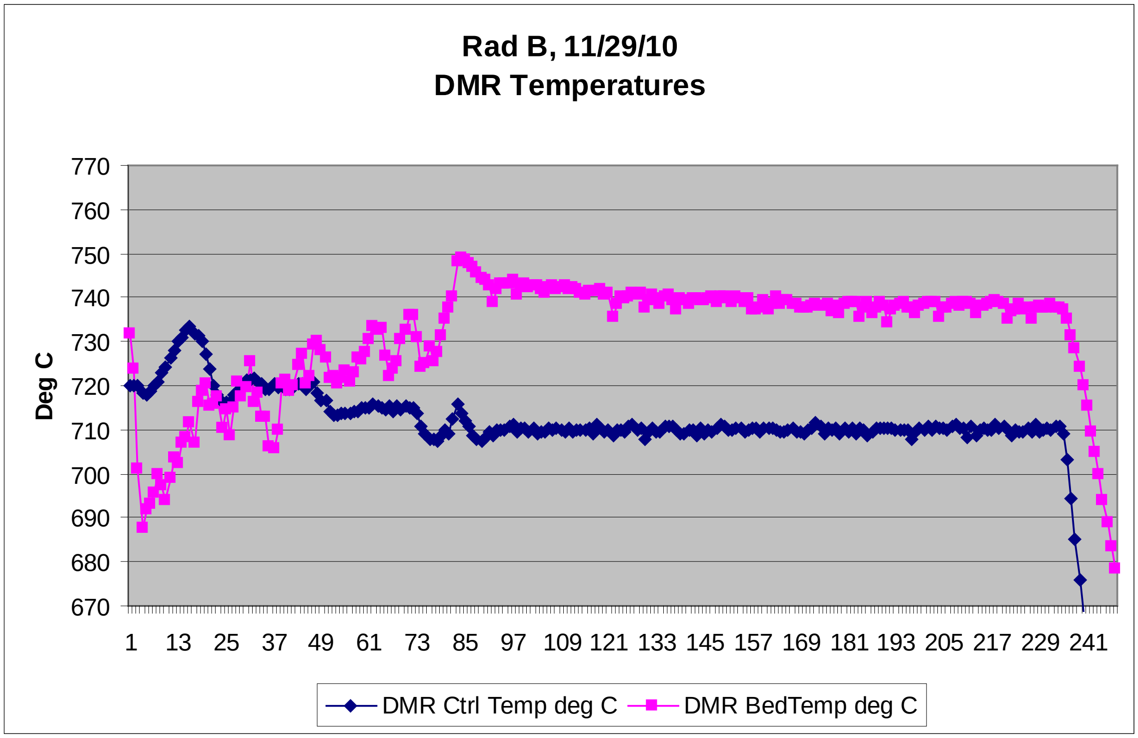

Figure D - 31. Run 11/29/10 Temperatures in DMR

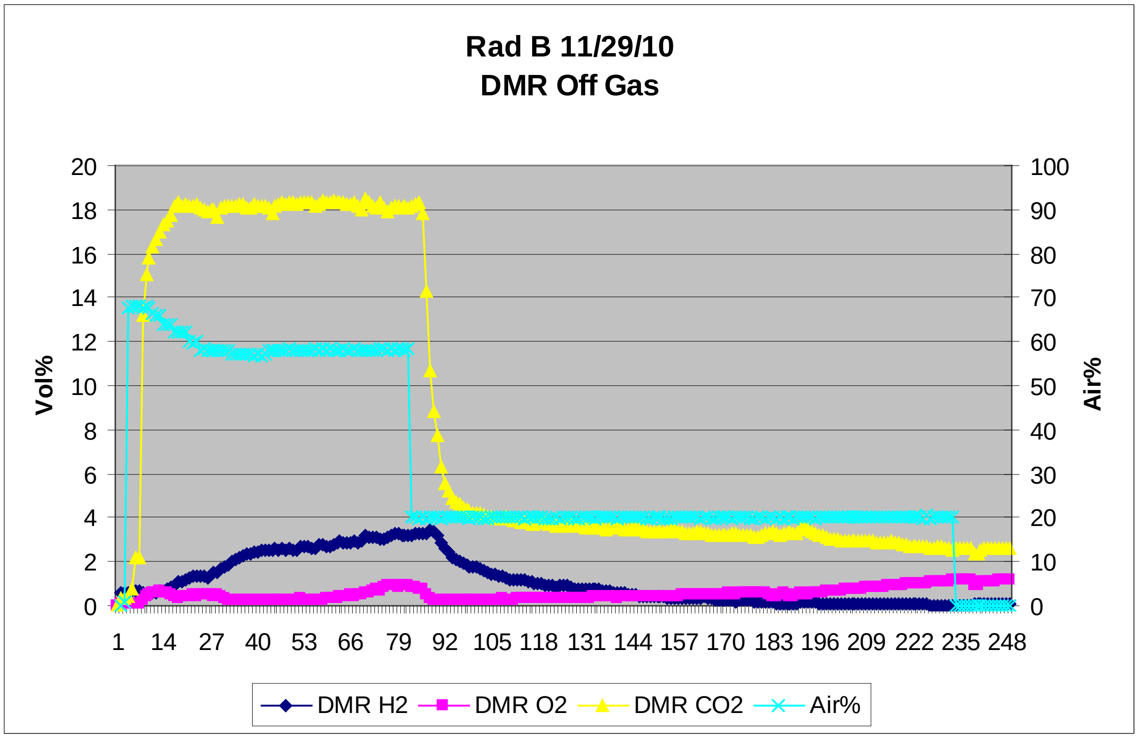

Figure D - 32. Run 11/29/10 Off-Gas Concentrations and Air% Fed

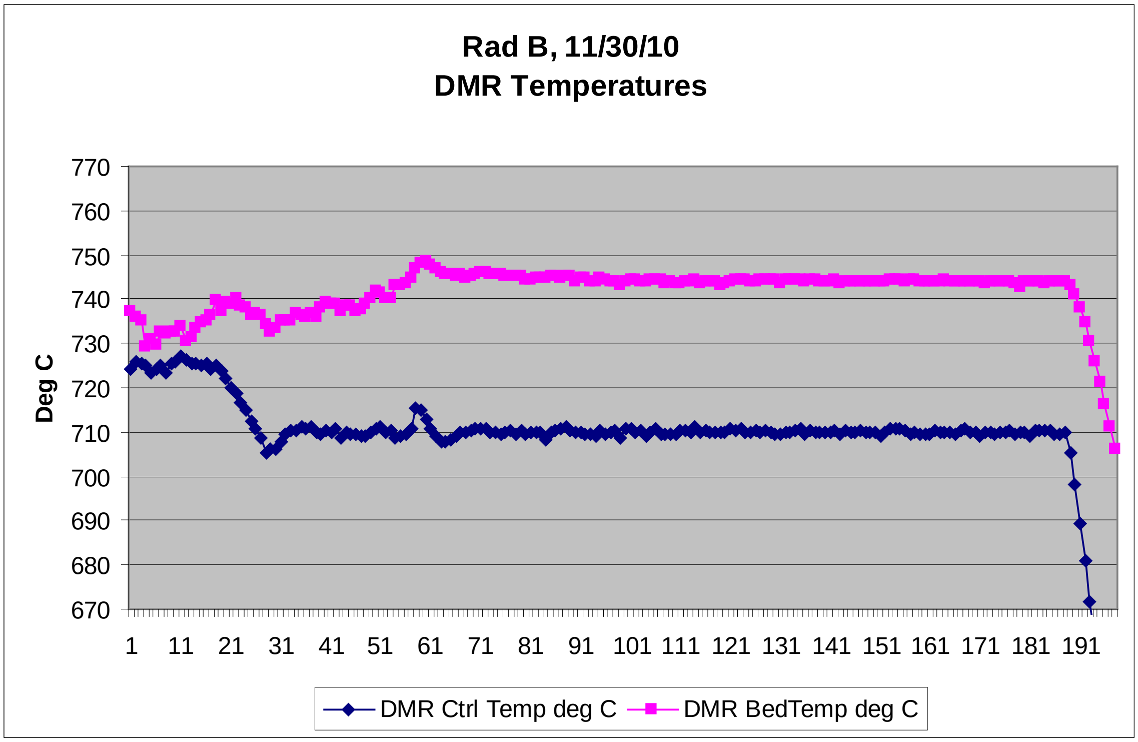

Figure D - 33. Run 11/30/10 Temperatures in DMR

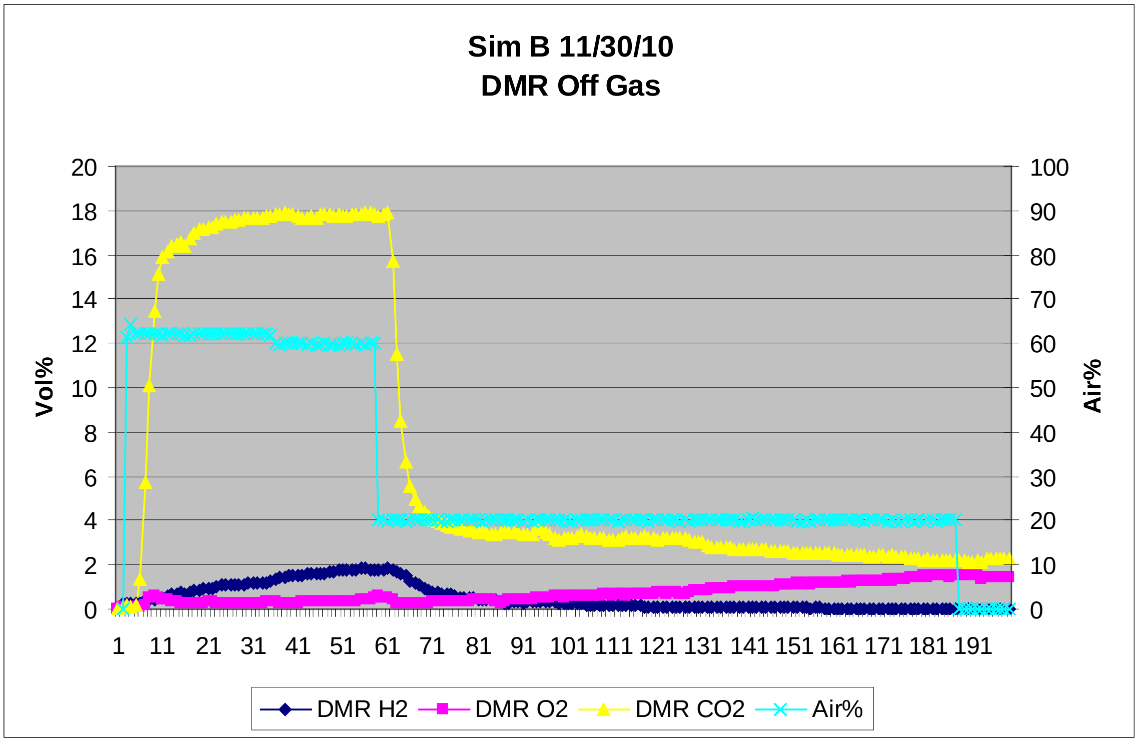

Figure D - 34. Run 11/30/10 Off-Gas Concentrations and Air% Fed

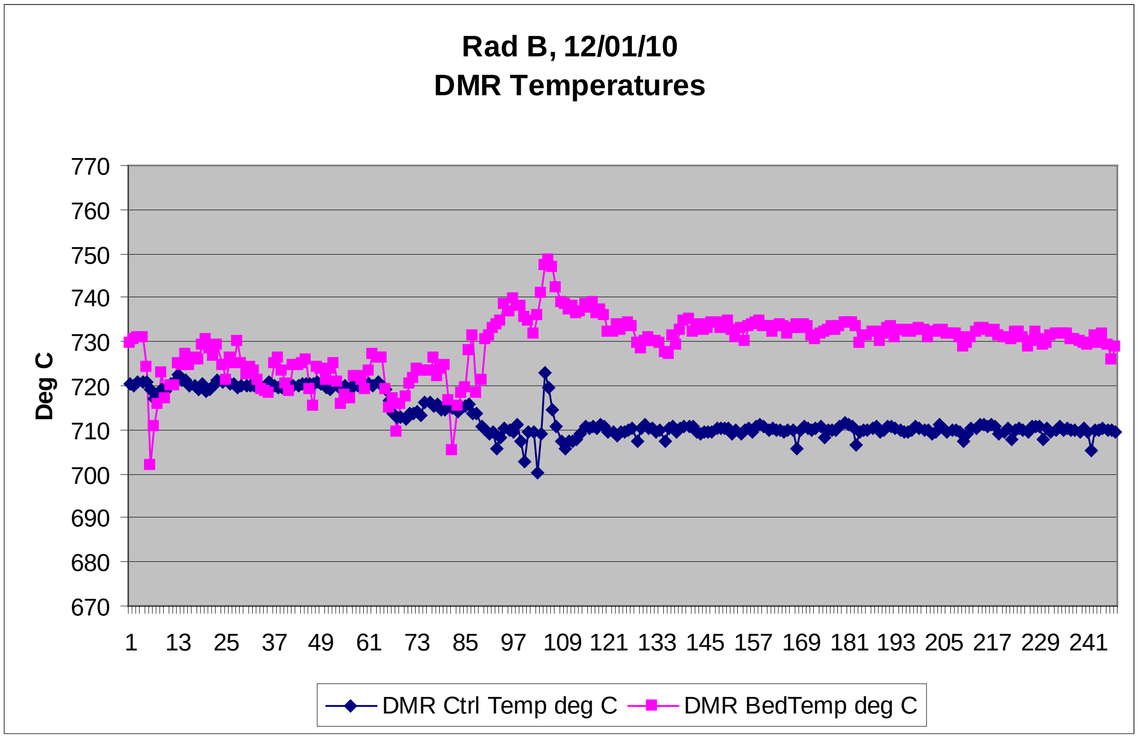

Figure D - 35. Run 12/01/10 Temperatures in DMR

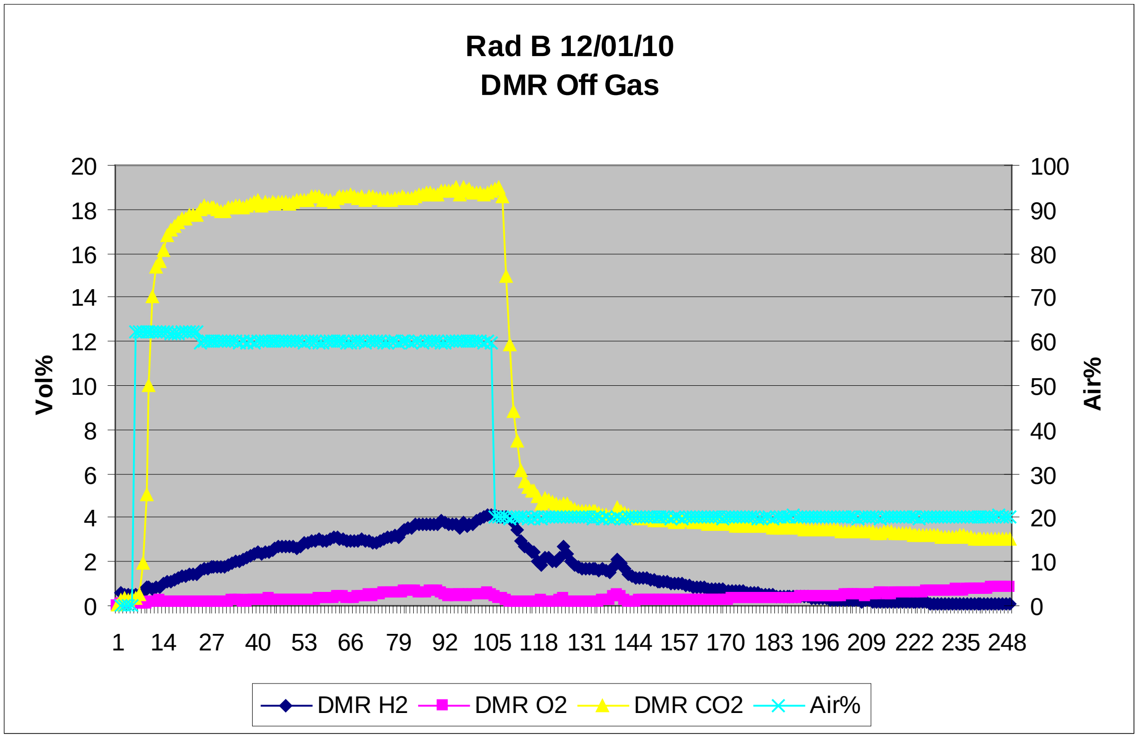

Figure D - 36. Run 12/01/10 Off-Gas Concentrations and Air% Fed

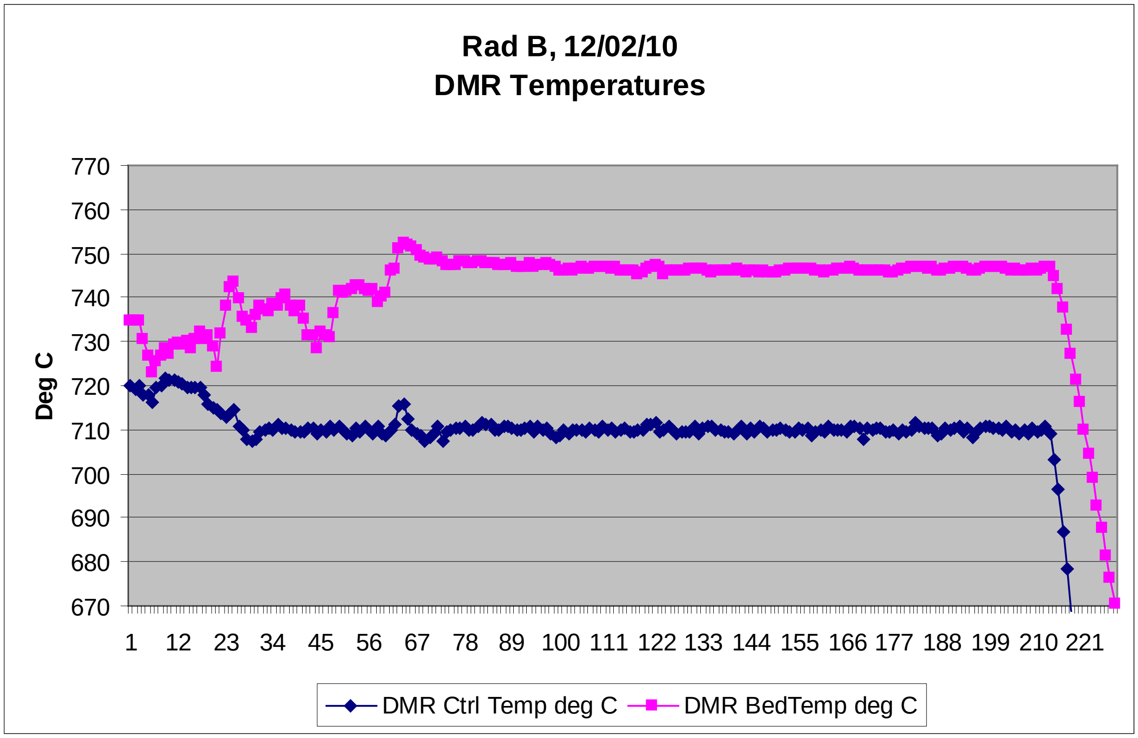

Figure D - 37. Run 12/02/10 Temperatures in DMR

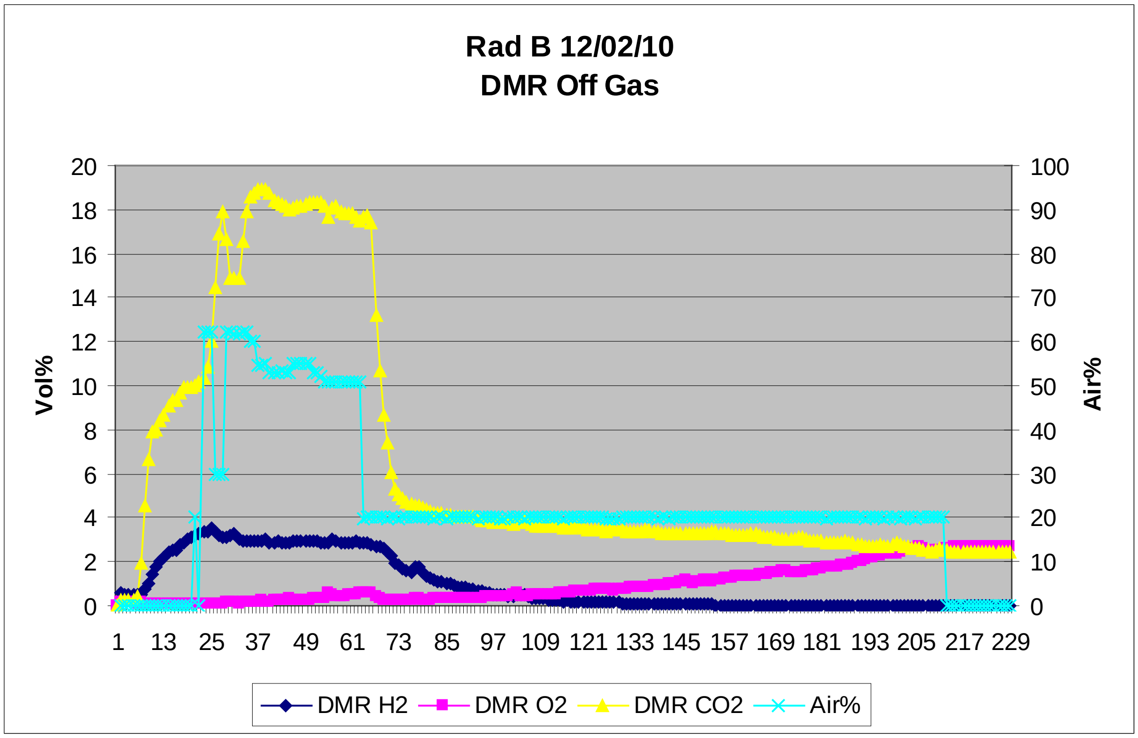

Figure D - 38. Run 12/02/10 Off-Gas Concentrations and Air% Fed

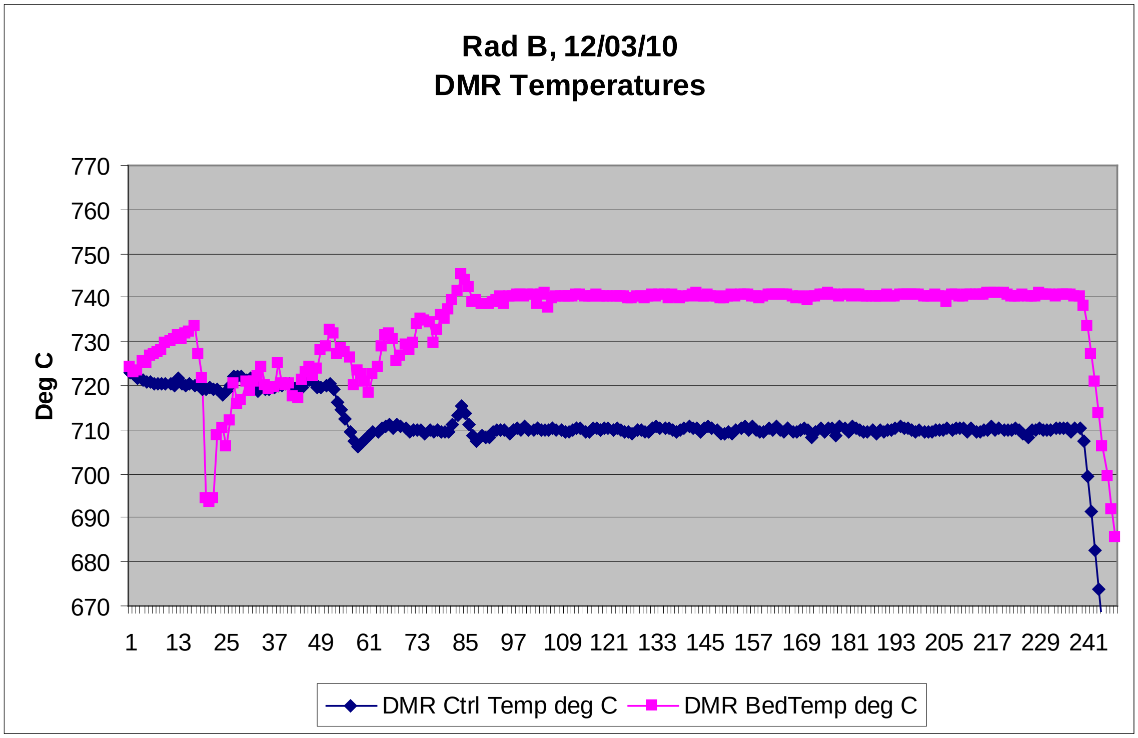

Figure D - 39. Run 12/03/10 Temperatures in DMR

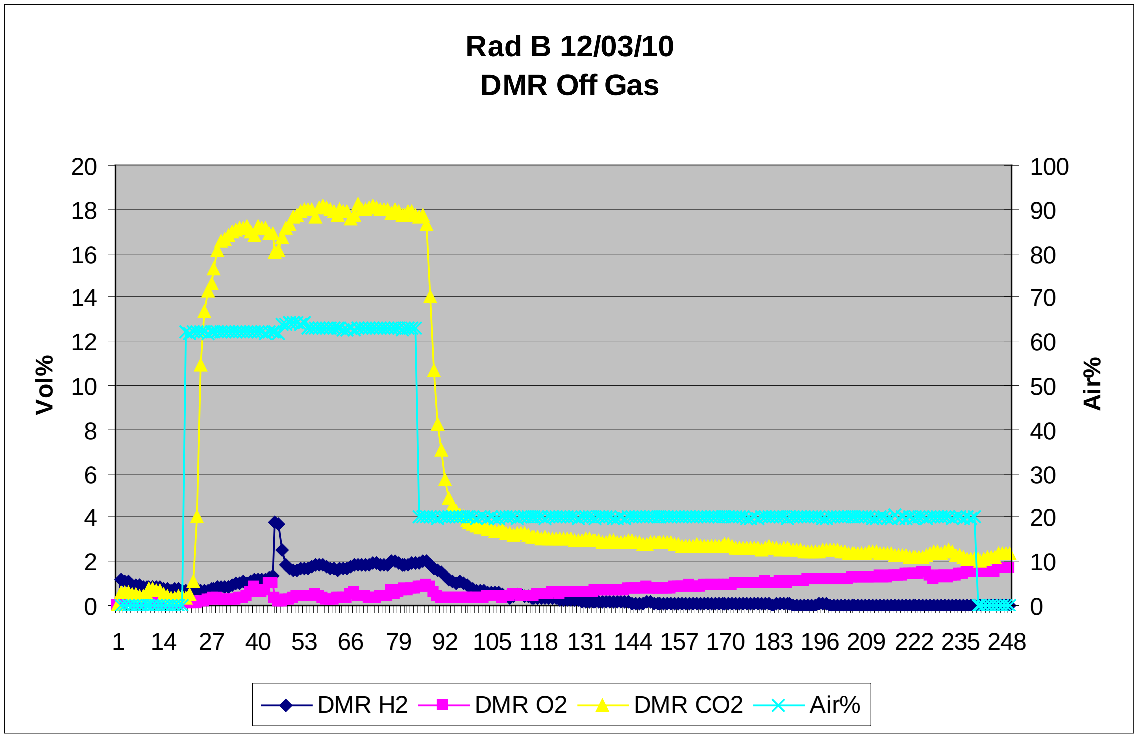

Figure D - 40. Run 12/03/10 Off-Gas Concentrations and Air% Fed

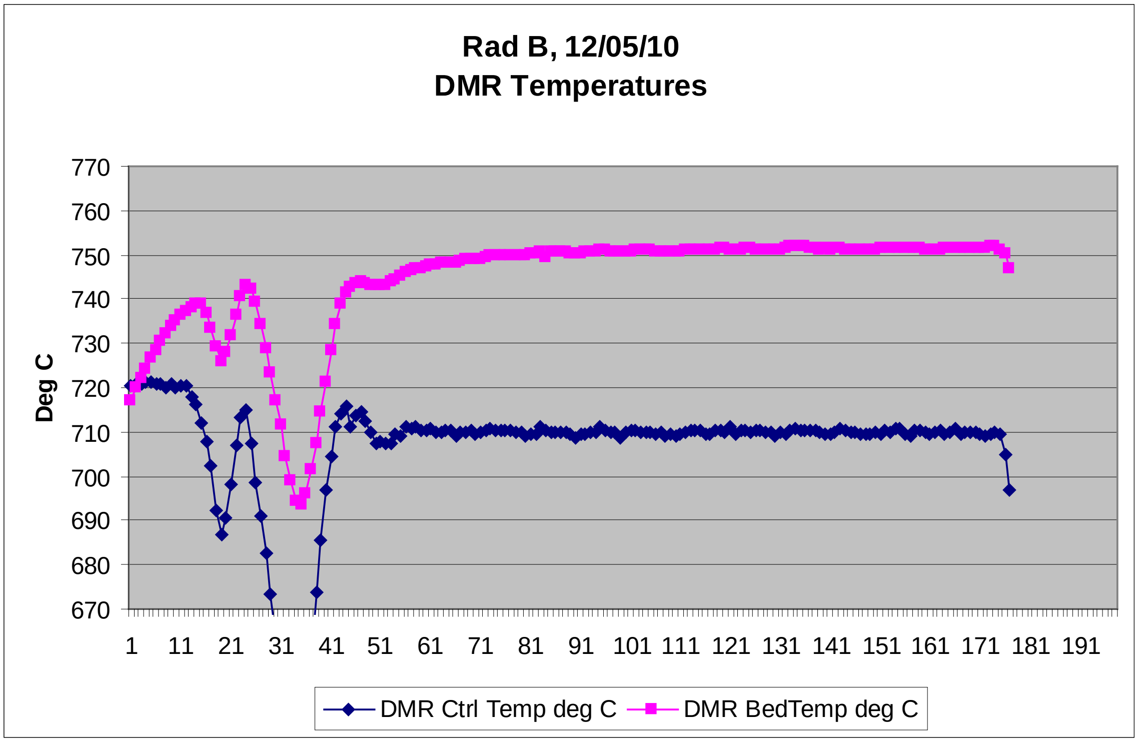

Figure D - 41. Run 12/05/10 Temperatures in DMR

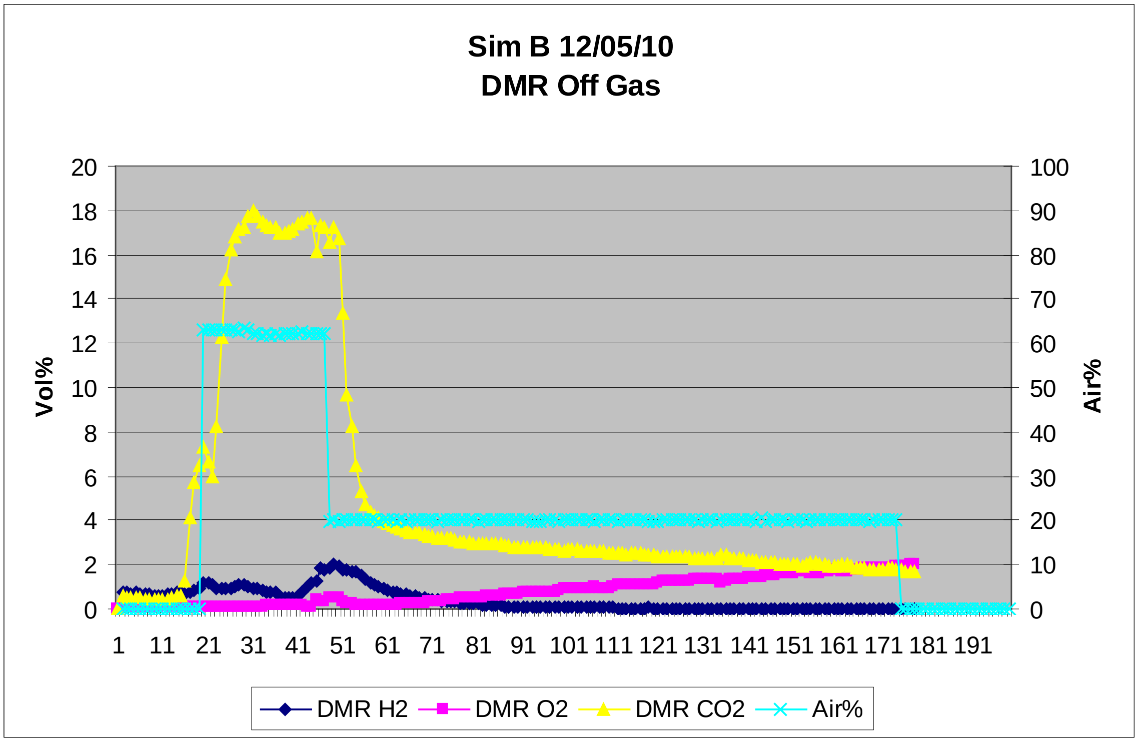

Figure D - 42. Run 12/05/10 Off-Gas Concentrations and Air% Fed

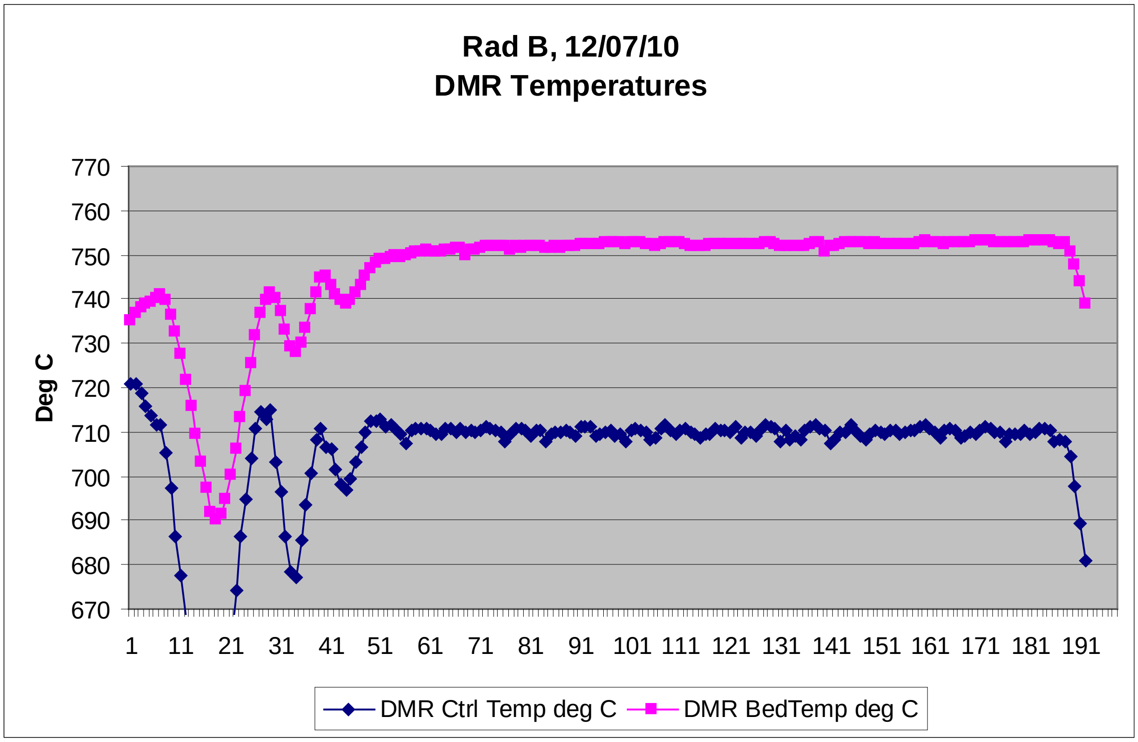

Figure D - 43. Run 12/07/10 Temperatures in DMR

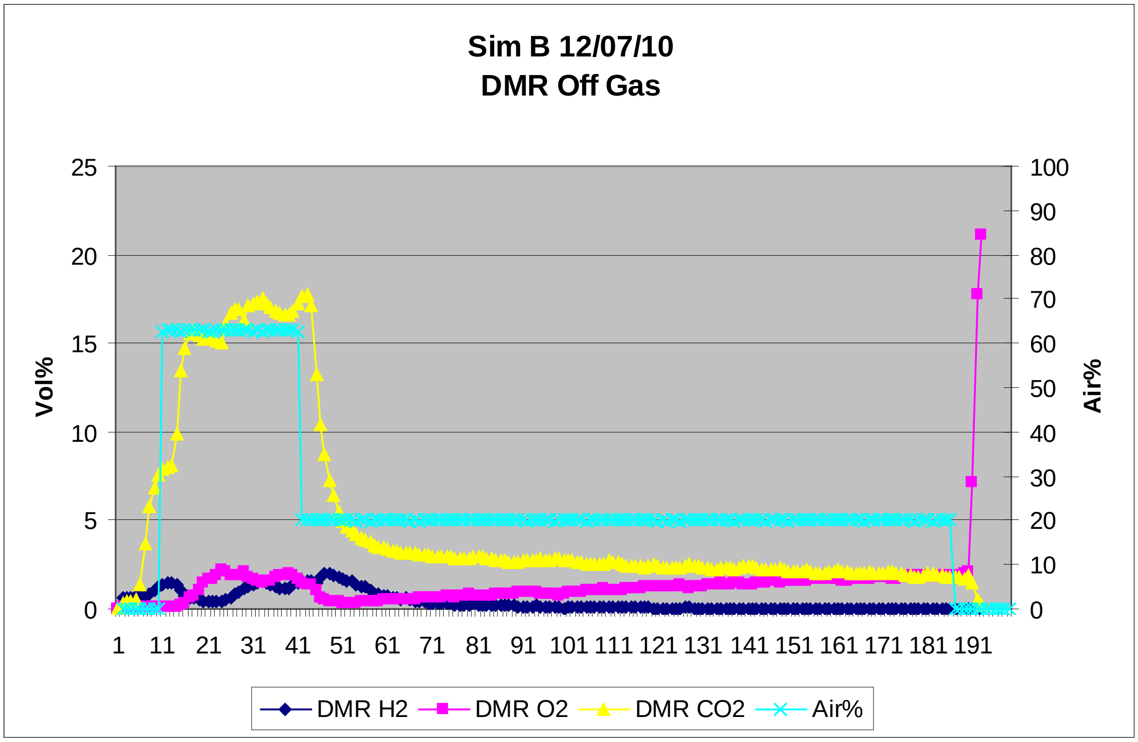

Figure D - 44. Run 12/07/10 Off-Gas Concentrations and Air% Fed

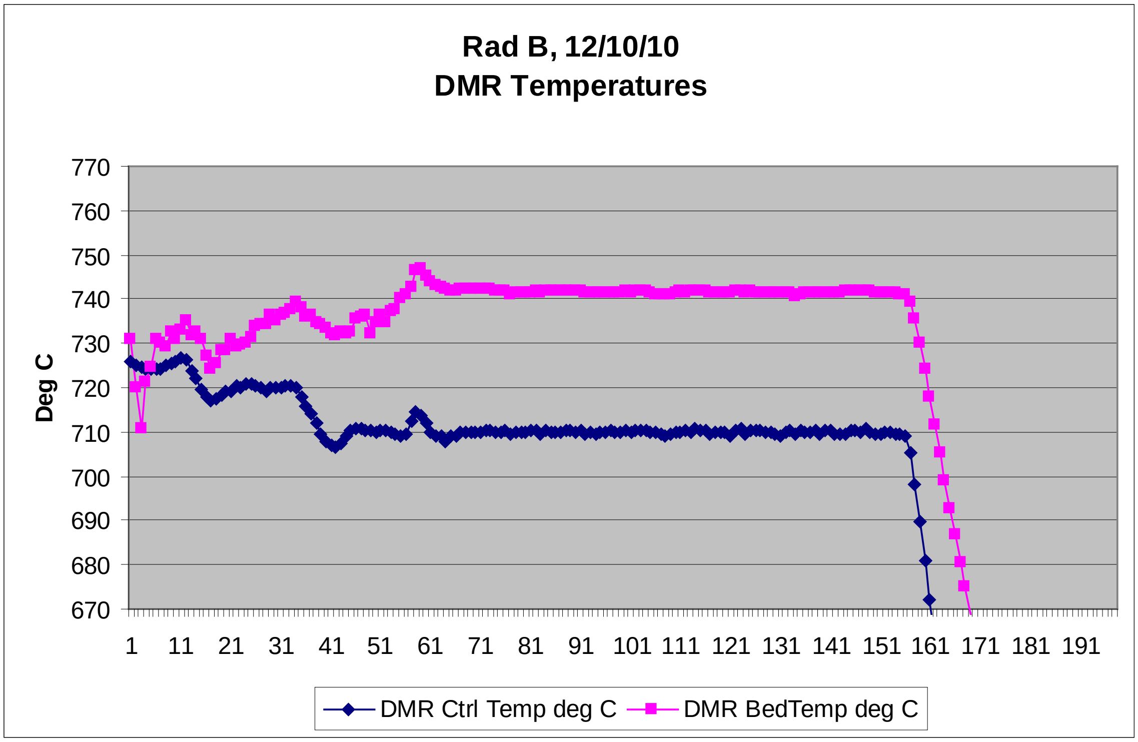

Figure D - 45. **Run 12/10/10 Temperatures in DMR** (Tc-99 spike)

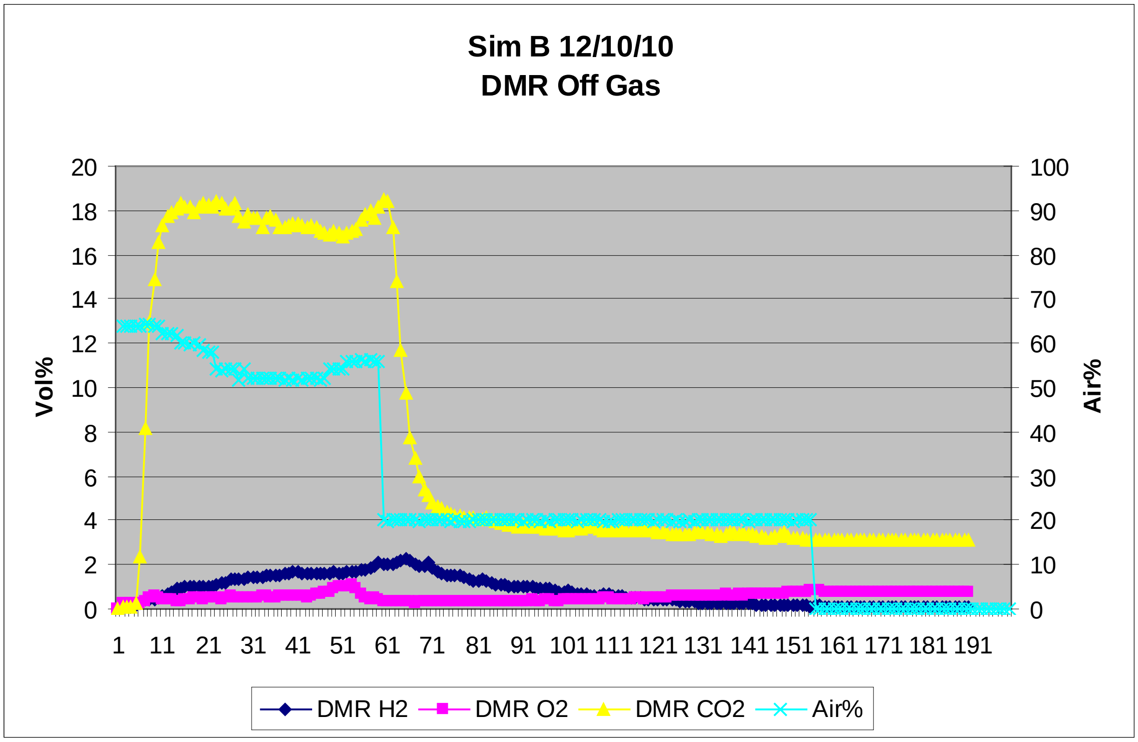

Figure D - 46. **Run 12/10/10 Off-Gas Concentrations and Air% Fed** (Tc-99 spike)

Appendix E. Simulant Module B Mass Balance

Table E - 1 through Table E - 3 give the ICP-ES, IC, and ICP-MS concentrations for the Simulant Mod B granular product samples. The total mass of the composite granular product was 724.37 g and the average concentrations shown were used in the mass balance.

Table E - 1. Simulant Module B Granular Composite Product ICP-ES

Sample	Elemental Concentration (wt%)											
	Ag	**Al**	**As**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.0002	17.30	0.01	0.07	0.13	15.30	<0.002	0.23	0.05	0.35	18.20	< 0.0002
2	< 0.0002	17.40	0.01	0.07	0.14	15.60	<0.002	0.25	0.05	0.37	18.10	< 0.0002
3		18.00				14.50			0.05	0.38		
4		17.90				14.40			0.05	0.34		
Average	< 0.0002	17.65	0.01	0.07	0.13	14.95	<0.002	0.24	0.05	0.36	18.15	< 0.0002
Std. Dev.	na	0.35	0.00	0.00	0.00	0.59	na	0.01	0.00	0.02	0.07	na
%RSD	na	1.99	12.95	3.63	2.11	3.96	na	5.80	1.70	5.13	0.39	na

na=not applicable

Table E - 2. Simulant Module B Granular Composite Product IC

Sample	Species Concentration (wt%)					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	< 0.05	0.21	< 0.10	< 0.10	1.32	0.43
2	< 0.05	0.21	< 0.10	< 0.10	1.30	0.44
Average	< 0.05	0.21	< 0.10	< 0.10	1.31	0.43
Std. Dev.	na	0.01	na	na	0.01	0.00
%RSD	na	2.69	na	na	1.08	0.33

na=not applicable

Table E - 3. Simulant Module B Granular Composite Product ICP-MS Cs-Re

Sample	wt% in product	
	Cs	**Re**
1	0.22	0.038
2	0.22	0.035
3	0.23	
4	0.23	
Average	**0.22**	**0.036**
Std. Dev.	0.00	0.002
%RSD	1.69	4.70

The DMR condensate filtrate composite cation or ICP-ES concentrations for the Simulant module B runs are shown in Table E - 4. The composite DMR condensate filtrate volume was 5.263 L and the average concentrations shown were used in the mass balance.

Table E - 4. Simulant Module B DMR Condensate Composite Filtrate ICP-ES

Sample	**Elemental Concentration (mg/L)**											
	Ag	**Al**	**As**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 2.00E-02	3.13E-01	< 1.00E+00	8.10E-02	2.01E-01	6.80E+01	< 2.00E-02	< 1.00E-01	< 2.00E-02	1.28E+01	4.37E+00	< 2.00E-02
2	< 2.00E-02	3.28E-01	< 1.00E+00	9.10E-02	2.11E-01	6.65E+01	< 2.00E-02	< 1.00E-01	< 2.00E-02	1.26E+01	4.44E+00	< 2.00E-02
Average	< 2.00E-02	3.21E-01	< 1.00E+00	8.60E-02	2.06E-01	6.73E+01	< 2.00E-02	< 1.00E-01	< 2.00E-02	1.27E+01	4.41E+00	< 2.00E-02
Std. Dev.	na	1.06E-02	na	7.07E-03	7.07E-03	1.06E+00	na	na	na	1.41E-01	4.95E-02	na
%RSD	na	3.31%	na	8.22%	3.43%	1.58%	na	na	na	1.11%	1.12%	na

na=not applicable

The DMR condensate composite filtrate anion or IC concentrations for the Simulant module B runs are shown in Table E - 5. The composite DMR condensate filtrate volume was 5.263 L and the average concentrations shown were used in the mass balance.

Table E - 5. Simulant Module B DMR Condensate Composite Filtrates IC

Sample	**Species Concentration (mg/L)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	1.82E+01	6.31E+00	5.67E+02	5.04E+01	2.52E+01	< 1.00E+00
2	1.82E+01	6.33E+00	5.77E+02	5.08E+01	2.51E+01	< 1.00E+00
Average	**1.82E+01**	**6.32E+00**	**5.72E+02**	**5.06E+01**	**2.52E+01**	**< 1.00E+00**
Std. Dev.	0.00E+00	1.41E-02	7.07E+00	2.83E-01	7.07E-02	na
%RSD	0.00%	0.22%	1.24%	0.56%	0.28%	na

The trace elemental or ICP-MS concentrations for the DMR condensate composite filtrate are shown in Table E - 6. Since there was only one sample submitted for analyses, these values were used in the mass balance.

Table E - 6. Simulant Module B DMR Condensate Composite Filtrate ICP-MS

Run	**Volume (L)**	**Elemental Concentration (ug/L)**		
		Cs	**Re**	**I**
Composite	0.749	1.07E+03	7.94E+02	5.49E+03

The DMR condensate composite filtered solids concentrations from the Simulant module B are shown in Table E - 7. The DMR condensate composite filtered solids mass was 3.846 g and the average concentrations shown were used in the mass balance.

Table E - 7. Simulant Module B DMR Condensate Composite Filtered Solids ICP-ES

Sample	**Elemental Concentration (wt%)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.002	14.10	0.017	0.05	0.078	9.00	0.0033	0.13	0.07	0.12	0.07	0.004
2	< 0.001	13.50	0.016	0.04	0.076	8.63	0.0030	0.12	0.07	0.11	0.23	0.005
3	< 0.001	14.70	0.017	0.05	0.084	9.46	0.0032	0.13	0.08	0.12	0.10	0.005
Average	**< 0.001**	**14.10**	**0.017**	**0.05**	**0.079**	**9.03**	**0.0032**	**0.13**	**0.07**	**0.11**	**0.13**	**0.005**
Std. Dev.	0.00004	0.60	0.001	0.00	0.005	0.42	0.0001	0.01	0.003	0.01	0.08	0.001
%RSD	2.99	4.26	4.38	3.65	5.83	4.60	4.41	5.23	4.73	7.12	65.22	11.40

Anion or IC analyses were not performed on the Simulant B condensate filtered solid samples, but the SO_4 and PO_4 concentrations can be estimated from the S and P analyses 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 B can be calculated as follows:

$$cs_{SO4} = \frac{0.114\% * 96.0636}{32.0660} = 0.34\%$$

$$cs_{PO4} = \frac{0.127\% * 94.9714}{30.9738} = 0.39\%$$

These composite concentrations are shown in Table E - 8 and were used in the mass balance. The DMR condensate composite filtered solids mass was 3.846 g and the concentrations shown were used in the mass balance.

Table E - 8. Simulant Module B DMR Condensate Composite Filtered Solids Estimated IC

Sample	**Elemental Concentration (wt%)**	
	SO_4	**PO_4**
Composite	0.34	0.39

The Cs, Re, and I wt% concentrations for the DMR Condensate Composite Filtered Solids are shown in Table E - 9. The DMR condensate composite filtered solids mass was 3.846 g and the average concentrations shown in the table were used in the mass balance.

Table E - 9. Simulant Module B DMR Condensate Composite Filtered Solids ICPMS

Sample	**Elemental Concentration (wt%)**		
	Cs	**Re**	**I**
1	0.096	0.016	0.072
2	0.098	0.017	0.066
3	0.104	0.018	0.073
Average	**0.100**	**0.017**	**0.070**
Std. Dev.	0.004	0.001	0.004
%RSD	4.04	5.33	5.03

The crossbar rinse filtrate cation or ICPES concentrations from the runs for Simulant module B are shown in Table E - 10. The crossbar rinse filtrates were separated into a sonicated and non-sonicated batch. For the mass balance, a composite crossbar rinse 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:

$$xf_{Al} = \frac{(2.4689 * 1.68E-01) + (0.4132 * 2.30E-01)}{2.4689 + 0.4132} = \frac{5.10E-01}{2.8821} = 1.77E-01$$

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:

$$xf_{K} = \frac{(0.4132 * 1.485E-01)}{2.4689 + 0.4132} = \frac{6.14E-02}{2.8821} = 2.13E-02$$

The cation or ICPES concentrations based on this method for the crossbar rinse composite filtrate are shown in Table E - 11 and these values were used in the mass balance.

The crossbar rinse filtrate anion or IC concentrations for the Simulant module B are shown in Table E - 12. The crossbar rinse filtrates were separated into a sonicated and non-sonicated batch. For the mass balance, a composite crossbar rinse filtrate was calculated based on each batch average times the volume per batch. For example, the fluoride composite concentration in ug/L was calculated as:

$$xf_{F} = \frac{2.4689 * 1.55E03 + 0.4132 * 1.61E03}{2.4689 + 0.4132} = \frac{4.49E03}{2.8821} = 1.56E03$$

The anion or IC concentrations based on this method for the crossbar rinse composite filtrate are shown in Table E - 13 and these values were used in the mass balance.

Table E - 10. Simulant Module B Crossbar Rinse Filtrates ICP-ES

Batch	Volume (L)	Sample	Elemental Concentration (mg/L)											
			Ag	**Al**	**As**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1 (sonicated)	2.4689	1	<2.00E-02	1.71E-01	<1.00E+00	<2.00E-02	<1.00E-01	8.33E+00	<2.00E-02	<1.00E-01	<2.00E-02	<1.00E+00	1.35E+00	<2.00E-02
		2	<2.00E-02	1.65E-01	<1.00E+00	<2.00E-02	<1.00E-01	6.74E+00	<2.00E-02	<1.00E-01	<2.00E-02	<1.00E+00	1.34E+00	< 2.00E-02
		Average	<2.00E-02	1.68E-01	<1.00E+00	<2.00E-02	<1.00E-01	7.54E+00	<2.00E-02	<1.00E-01	<2.00E-02	<1.00E+00	1.35E+00	<2.00E-02
		Std. Dev.	na	4.24E-03	na	na	na	1.12E+00	na	na	na	na	7.07E-03	na
		%RSD	na	2.53%	na	na	na	14.92%	na	na	na	na	0.53%	na
2	0.4132	1	<2.00E-02	2.28E-01	<1.00E+00	<2.00E-02	1.48E-01	2.87E+01	<2.00E-02	<1.00E-01	<2.00E-02	1.33E+00	6.17E+00	<2.00E-02
		2	<2.00E-02	2.31E-01	<1.00E+00	<2.00E-02	1.49E-01	2.89E+01	<2.00E-02	<1.00E-01	<2.00E-02	1.17E+00	6.22E+00	<2.00E-02
		Average	<2.00E-02	2.30E-01	<1.00E+00	<2.00E-02	1.49E-01	2.88E+01	<2.00E-02	<1.00E-01	<2.00E-02	1.25E+00	6.20E+00	<2.00E-02
		Std. Dev.	na	2.12E-03	na	na	7.07E-04	1.41E-01	na	na	na	1.13E-01	3.54E-02	na
		%RSD	na	0.92%	na	na	0.48%	0.49%	na	na	na	9.05%	0.57%	na

na=not applicable

Table E - 11. Simulant Module B Crossbar Rinse Composite Filtrate ICP-ES

Batch	Volume (L)	Elemental Concentration (mg/L)											
		Ag	**Al**	**As**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	2.8821	< 2.00E-02	1.77E-01	< 1.00E+00	< 2.00E-02	2.13E-02	1.06E+01	< 2.00E-02	< 1.00E-01	< 2.00E-02	1.79E-01	2.04E+00	< 2.00E-02

Table E - 12. Simulant Module B Crossbar Rinse Filtrates

Batch	Volume (L)	Sample	Species Concentration (ug/L)					
			F	Cl	NO_2	NO_3	SO_4	PO_4
1	2.4689	1	1.56E+03	<1.00E+03	<1.00E+03	1.89E+03	<1.00E+03	<1.00E+03
		2	1.54E+03	<1.00E+03	<1.00E+03	1.90E+03	<1.00E+03	<1.00E+03
		Average	**1.55E+03**	**<1.00E+03**	**<1.00E+03**	**1.90E+03**	**<1.00E+03**	**<1.00E+03**
		Std Dev.	1.41E+01	na	na	7.07E+00	na	na
		%RSD	0.91%	na	na	0.37%	na	na
2	0.4132	1	1.61E+03	1.97E+03	<1.00E+03	2.46E+03	2.65E+03	<1.00E+03
		2	1.60E+03	2.11E+03	<1.00E+03	2.50E+03	2.57E+03	<1.00E+03
		Average	**1.61E+03**	**2.04E+03**	**<1.00E+03**	**2.48E+03**	**2.61E+03**	**<1.00E+03**
		Std Dev.	7.07E+00	9.90E+01	na	2.83E+01	5.66E+01	na
		%RSD	0.44%	4.85%	na	1.14%	2.17%	na

na=not applicable

Table E - 13. Simulant Module B Crossbar Rinse Composite Filtrate IC

Batch	Volume (L)	Species Concentration (ug/L)					
		F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	2.8821	1.56E+03	2.92E+02	<1.00E+03	1.98E+03	3.74E+02	<1.00E+03

The crossbar rinse filtrate trace elemental or ICP-MS concentrations for the Simulant module B are shown in Table E - 14. The crossbar rinse filtrates were separated into a sonicated and non-sonicated batch. For the mass balance, a composite crossbar rinse filtrate was calculated based on each batch average times the volume per batch. For example, the cesium composite concentration in ug/L was calculated as:

$$xf_{Cs} = \frac{(2.4689 * 1.36E01) + (0.4132 * 5.69E01)}{2.4689 + 0.4132} = \frac{5.71E + 01}{2.8821} = 1.98E01$$

Table E - 14. Simulant Module B Crossbar Rinse Filtrates ICP-MS

Batch	Volume (L)	Elemental Concentration (ug/L)		
		Cs	Re	I
1	2.4689	1.36E+01	1.32E+01	3.80E+02
2	0.4132	5.69E+01	7.87E+01	1.21E+03

The trace elemental or ICPMS concentrations based on this method for the DMR condensate composite filtrate are shown in Table E - 15 and these values were used in the mass balance.

Table E - 15. Simulant Module B Crossbar Rinse Composite Filtrate ICP-MS

Run	Volume (L)	Elemental Concentration (ug/L)		
		Cs	Re	I
Composite	2.8821	1.98E+01	2.26E+01	4.99E+02

The crossbar rinse filtered solids concentrations for Simulant module B are shown in Table E - 16. The crossbar rinse filtered solids were separated into a sonicated and non-sonicated batch. For the mass balance, a composite crossbar rinse filtered solids was calculated based on each batch average times the mass per batch. For example, the aluminum composite concentration in wt% was calculated as:

$$xs_{Al} = \frac{0.363 * 15.67\% + 0.406 * 17.20\%}{0.363 + 0.406} = \frac{0.1267}{0.769} = 16.48\%$$

The cation or ICP-ES concentrations based on this method for the DMR condensate composite filtered solids are shown in Table E - 17 and these values were used in the mass balance.

Table E - 16. Simulant Module B Crossbar Rinse Filtered Solids ICP-ES

Batch	Mass (g)	Sample	Elemental Concentration (wt%)											
			Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	0.363	1	< 0.0017	15.40	0.02	0.05	0.08	7.40	0.01	0.10	0.08	0.09	0.16	0.01
		2	< 0.0019	15.80	0.02	0.05	0.09	7.60	0.01	0.11	0.09	0.09	0.06	0.01
		3	< 0.0023	15.80	0.02	0.05	0.08	7.65	0.01	0.11	0.09	0.10	0.04	0.01
		Average	**< 0.0020**	**15.67**	**0.02**	**0.05**	**0.08**	**7.55**	**0.01**	**0.11**	**0.09**	**0.09**	**0.09**	**0.01**
		Std Dev.	0.0003	0.23	0.00	0.00	0.01	0.13	0.00	0.01	0.00	0.01	0.06	0.00
		%RSD	15.95	1.47	2.54	3.05	7.15	1.75	9.02	4.95	3.02	8.66	73.22	11.51
2	0.406	1	< 0.0020	16.60	0.03	0.05	0.11	7.93	0.004	0.11	0.090	0.108	0.08	0.02
		2	< 0.0021	17.80	0.03	0.05	0.14	8.52	0.004	0.11	0.094	0.117	0.26	0.02
		3	< 0.0019	17.20	0.03	0.05	0.13	8.25	0.004	0.11	0.093	0.110	0.11	0.02
		Average	**< 0.0020**	**17.20**	**0.03**	**0.05**	**0.13**	**8.23**	**0.00**	**0.11**	**0.09**	**0.11**	**0.15**	**0.02**
		Std Dev.	0.0001	0.60	0.00	0.00	0.01	0.30	0.00	0.00	0.00	0.00	0.10	0.00
		%RSD	6.12	3.49	2.21	2.85	11.19	3.59	4.83	1.86	2.60	4.23	63.76	10.35

Table E - 17. Simulant Module B Crossbar Rinse Composite Filtered Solids ICP-ES

Run	Mass (g)	Elemental Concentration (wt%)											
		Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	0.769	< 0.002	16.48	0.02	0.05	0.11	7.91	0.005	0.11	0.09	0.10	0.12	0.015

Anion or IC analyses were not performed on the SIM B crossbar rinse filtered solids but the SO_4 and PO_4 concentrations were estimated from the S and P analyses using the following logic:

$$xs_{SO4} = \frac{xs_S * MW_{SO4}}{MW_S}$$

$$xs_{PO4} = \frac{xs_S * MW_{PO4}}{MW_P}$$

As an example, the SO_4 and PO_4 concentrations for the crossbar rinse filtered solids for the first batch of Simulant B module runs were calculated as follows:

$$xs_{SO4} = \frac{0.093\% * 96.0636}{32.0660} = 0.28\%$$

$$xs_{PO4} = \frac{0.107\% * 94.9714}{30.9738} = 0.33\%$$

Using this logic, the SO_4 and PO_4 concentrations for the crossbar rinse filtered solids are shown in Table E - 18. Using the same logic shown earlier, the two batches of DMR condensate filtered solids data was represented as one mass of 0.769 g with composite concentrations. These composite concentrations are shown in Table E - 19 and were used in the mass balance.

Table E - 18. Simulant Module B Crossbar Rinse Filtered Solids IC

Batch	Mass (g)	SO_4 (wt%)	PO_4 (wt%)
1	0.363	0.28	0.33
2	0.406	0.33	0.34

Table E - 19. Simulant Module B Crossbar Rinse Composite Filtered Solids IC

Run	Mass (g)	SO_4 (wt%)	PO_4 (wt%)
Composite	0. 769	0.31	0.34

The crossbar rinse filtered solids trace elemental or ICPMS concentrations from the two batches for Simulant module B are shown in Table E - 20. Using the same logic shown earlier, the two batches of DMR condensate filtered solids data was represented as one mass of 0.769 g with the composite concentrations shown in Table E - 21. The composite concentrations were used in the mass balance.

Table E - 20. Simulant Module B Crossbar Rinse Composite Filtered Solids ICP-MS

Batch	Mass (g)	Sample	Species Concentration (wt%)		
			Cs	Re	I
1	0.363	1	0.162	0.011	0.021
		2	0.131	0.009	0.023
		3	0.119	0.008	0.029
		Average	**0.137**	**0.009**	**0.024**
		Std Dev.	0.022	0.002	0.004
		%RSD	16.16	16.47	15.87
2	0.406	1	0.172	0.011	0.040
		2	0.187	0.012	0.042
		3	0.177	0.012	0.040
		Average	**0.179**	**0.012**	**0.041**
		Std Dev.	0.008	0.000	0.001
		%RSD	4.27	3.95	3.34

Table E - 21. Simulant Module B Crossbar Rinse Composite Filtered Solids ICP-MS

Run	Mass (g)	Species Concentration (wt%)		
		Cs	Re	I
Composite	0. 769	0.16	0.011	0.033

Appendix F. Sample Analyses for Radioactive Module B Campaign

Table F - 1 through Table F - 3 give the ICP-ES, IC, and ICP-MS concentrations for the Radioactive B granular product samples. The average concentrations were used in the mass balance.

Table F - 1. Radioactive Module B Granular Composite Product ICP-ES

Sample	**Elemental Concentration (wt%)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.0016	18.50	0.012	0.067	0.13	15.30	< 0.007	0.19	0.14	0.43	18.50	0.0025
2	< 0.0017	18.30	0.013	0.068	0.13	15.20	< 0.007	0.19	0.14	0.43	18.70	0.0023
3	< 0.0015	19.70	0.011	0.069	0.15	16.40	0.0052	0.20	0.15	0.45	18.80	0.0024
4		18.20						0.23	0.12			
5		18.30						0.21	0.13			
6		18.30						0.22	0.12			
Average	**< 0.0016**	**18.55**	**0.012**	**0.068**	**0.14**	**15.63**	**0.0052**	**0.21**	**0.13**	**0.44**	**18.67**	**0.0024**
Std. Dev.	0.0001	0.57	0.001	0.001	0.01	0.67	na	0.02	0.01	0.01	0.15	0.0001
%RSD	5.30	3.08	8.85	1.05	6.14	4.26	na	9.00	7.05	2.32	0.82	3.80

na=not applicable

Table F - 2. Radioactive Module B Granular Composite Product IC

Sample	**Concentration (wt%)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	< 0.100	0.22	< 0.100	< 0.100	1.19	0.45
2	< 0.097	0.17	< 0.097	< 0.097	1.02	0.40
3	< 0.098	0.20	< 0.098	< 0.098	1.30	0.49
Average	**< 0.098**	**0.20**	**< 0.098**	**< 0.098**	**1.17**	**0.45**
Std. Dev.	0.001	0.02	0.001	0.001	0.14	0.05
%RSD	1.34	11.33	1.34	1.34	11.85	10.34

Table F - 3. Radioactive Module B Granular Composite Product ICP-MS

Sample	**Species Concentration (wt%)**		
	Cs*	**Re****	**I**
1	<0.00040	0.038	0.106
2	<0.00036	0.035	0.112
3		0.037	0.108
4		0.035	
5		0.035	
6		0.038	
Average	**<0.00038**	**0.036**	**0.109**
Std. Dev.	0.00003	0.002	0.003
%RSD	6.89	4.20	2.81

*Cs from ICP-MS sweep with mass of 133,
**Re from ICP-MS sweep with mass of 185 at 37.40% and 187 at 62.60%

The radioisotopes of the granular product by gamma analysis for the Radioactive B module are shown in Table F - 4. Note that the ^{125}I concentration values have been corrected for decay from the time the sample was pulled to when it was actually analyzed. The ^{129}I concentration has two averages, the first only considers samples 1 and 2 which are within 1 % RSD of each other and the second average uses all three samples with a slightly higher average but greater %RSD.

Table F - 4. Radioactive Module B Granular Composite Product Gamma Results

Sample	**Concentration (dpm/g)**			
	Cs-137	**I-125**	**I-129**	**Tc-99**
1	1.65E+06	6.74E+03	3420	1.02E+04
2	1.29E+06	5.94E+03	3400	9.87E+03
3	1.14E+06	6.47E+03	*4370*&	1.15E+04
Average	**1.36E+06**	**6.38E+03**	**3.41E+03** **(*3.73E+03*)&**	**1.05E+04**
Std. Dev.	2.62E+05	4.07E+02	1.41E+01 (*5.54E+02*)&	8.62E+02
%RSD	19.27%	6.38%	0.41% (*14.86%*)&	8.19%

&Third sample for I-129 concentration excluded from first set of statistics but included for second set of statistics which are italicized and in parentheses.

The DMR condensate filtrate cation or ICP-ES concentrations for the RAD B module runs are shown in Table F - 5. The DMR condensate filtrates have a volume of 6.4938 L with a density of 0.997 g/ml. The average cation or ICP-ES concentrations were used in the mass balance.

Table F - 5. Radioactive Module B DMR Condensate Composite Filtrate ICP-ES

Sample	Elemental Concentration (mg/L)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 4.30E-02	5.57E-01	3.28E-01	4.02E-02	6.56E+00	8.31E+01	< 4.70E-02	2.92E+00	< 1.46E-01	2.47E+01	6.19E+00	3.43E-02
2	< 4.30E-02	5.69E-01	3.25E-01	4.38E-02	6.73E+00	8.28E+01	< 4.70E-02	2.94E+00	< 1.46E-01	2.40E+01	6.19E+00	2.99E-02
3	< 4.30E-02	5.49E-01	3.22E-01	4.22E-02	6.68E+00	8.28E+01	< 4.70E-02	2.97E+00	< 1.46E-01	2.45E+01	6.26E+00	3.18E-02
Average	**< 4.30E-02**	**5.58E-01**	**3.25E-01**	**4.21E-02**	**6.66E+00**	**8.29E+01**	**< 4.70E-02**	**2.94E+00**	**< 1.46E-01**	**2.44E+01**	**6.21E+00**	**3.20E-02**
Std. Dev.	na	1.01E-02	3.00E-03	1.80E-03	8.74E-02	1.73E-01	na	2.52E-02	na	3.61E-01	4.04E-02	2.21E-03
%RSD	na	1.80%	0.92%	4.29%	1.31%	0.21%	na	0.86%	na	1.48%	0.65%	6.90%

na=not applicable

The DMR condensate composite filtrate anion or IC concentrations from the Radioactive module B runs are shown in Table F - 6. The DMR condensate composite filtrate was 6.494 L and the average condensate composite concentrations were used in the mass balance.

Table F - 6. Radioactive Module B DMR Condensate Composite Filtrate IC

Sample	Species Concentration (mg/L)					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	19	13	400	38	55	< 10
2	19	13	410	38	55	< 10
3	19	13	393	38	54	< 10
Average	**19**	**13**	**401**	**38**	**55**	**< 10**
Std. Dev.	0	0	9	0	0.6	na
%RSD	0.00%	0.00%	2.13%	0.00%	1.06%	na

na=not applicable

The DMR condensate filtrate trace elemental or ICPMS concentrations from the Radioactive module B are shown in Table F - 7. The DMR condensate composite filtrate had a volume of 6.494 L. The average concentrations for the DMR condensate composite filtrate are used in the mass balance.

Table F - 7. Radioactive Module B DMR Condensate Composite Filtrate ICP-MS

Sample	Species Concentration (ug/L)		
	Cs	**Re**	**I**
1	2.04E+00	8.02E+02	5.95E+03
2	1.93E+00	8.18E+02	5.92E+03
3	2.10E+00	8.05E+02	5.94E+03
4		8.18E+02	
5		8.48E+02	
6		8.35E+02	
Average	**2.02E+00**	**8.21E+02**	**5.94E+03**
Std. Dev.	8.62E-02	1.78E+01	1.53E+01
%RSD	4.26%	2.17%	0.26%

The radio isotopes of the DMR Condensate filtrate by gamma analysis for the Radioactive module B are shown in Table F - 8. The average concentrations were used in the mass balance.

Table F - 8. Radioactive Module B DMR Condensate Composite Filtrate Gamma

Sample	**Concentration (dpm/mL)**			
	Cs-137	**I-125**	**I-129**	**Tc-99**
1	1.19E+03	3.25E+01	1.95E+01	1.57E+02
2	1.21E+03	3.03E+01	1.89E+01	1.52E+02
3	1.19E+03	3.60E+01	2.29E+01	1.36E+02
Average	**1.20E+03**	**3.29E+01**	**2.04E+01**	**1.48E+02**
Std. Dev.	1.15E+01	2.85E+00	2.16E+00	1.10E+01
%RSD	0.96%	8.64%	10.56%	7.40%

The DMR condensate filtered solids concentrations from the runs for Radioactive module B are shown in Table F - 9. The DMR condensate filtered solids can be represented as one mass of 3.397 g. The average values were used in the mass balance.

Anion or IC analyses for the Radioactive B DMR Condensate Filtered Solids samples are shown in Table F - 10. There was only one sample.

Table F - 9. Radioactive Module B DMR Condensate Composite Filtered Solids ICP-ES

Sample	**Elemental (wt%)**											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	< 0.00074	12.10	0.01	0.04	0.08	7.81	0.00	0.16	0.09	0.09	0.08	0.01
2	< 0.00075	12.80	0.01	0.04	0.08	8.24	0.00	0.17	0.09	0.09	0.07	0.01
3	< 0.00073	13.00	0.01	0.04	0.08	8.39	0.00	0.18	0.09	0.09	0.07	0.01
4		14.20		0.05				0.20	0.08		13.70	0.010
5		14.40		0.05				0.18	0.10		14.30	0.011
6		14.40		0.05				0.18	0.09		14.60	0.012
Average	**< 0.00074**	**13.48**	**0.01**	**0.05**	**0.08**	**8.15**	**0.0024**	**0.18**	**0.09**	**0.09**	**14.20**	**0.010**
Std. Dev.	0.00001	0.98	0.00	0.01	0.00	0.30	0.0001	0.01	0.00	0.00	0.46	0.002
%RSD	1.11	7.27	2.22	12.94	3.12	3.70	3.63	6.85	5.40	1.14	3.23	16.05

Table F - 10. Radioactive Module B DMR Condensate Composite Filtered Solids IC

Sample	**Species Concentration (wt%)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	< 0.17	< 0.085	< 0.085	< 0.085	0.17	0.41

The DMR condensate filtered solids trace elemental or ICPMS concentrations for the Radioactive module B runs are shown in Table F - 11. The average concentrations were used in the mass balance.

Table F - 11. Radioactive Module B DMR Condensate Composite Filtered Solids ICP-MS

Sample	Concentration (wt%)		
	Cs	Re	I
1	0.00007	0.0037	0.030
2	0.00006	0.0041	
3	0.00006	0.0044	
4		0.0040	
5		0.0041	
6		0.0042	
Average	**0.00007**	**0.0041**	**0.030**
Std. Dev.	0.00001	0.0002	0.00
%RSD	10.56%	5.83	0.00

The radio isotopes of the DMR condensate filtered solids by gamma analysis for the Radioactive module B are shown in Table F - 12. The crossbar rinse filtered solids have a mass of 1.034 g and the average concentrations were used in the mass balance.

Table F - 12. Radioactive Module B DMR Condensate Composite Filtered Solids Gamma

Sample	Concentration (dpm/g)			
	Cs-137	I-125	I-129	Tc-99
1	4.87E+05	1.89E+03	9.49E+02	2.25E-02
2	4.74E+05	1.52E+03	1.05E+03	2.38E-02
3	5.12E+05			2.49E-02
Average	**4.91E+05**	**1.70E+03**	**1.00E+03**	**2.37E-02**
Std. Dev.	1.93E+04	2.64E+02	7.14E+01	1.20E-03
%RSD	3.93%	15.50%	7.15%	5.06%

The crossbar rinse filtrate cation or ICPES concentrations from the runs for Radioactive module B are shown in Table F - 13. The crossbar rinse filtrate total volume was 2.539 L. The average cation or ICP-ES concentrations in Table F - 13 were used in the mass balance.

Table F - 13. Radioactive Module B Crossbar Rinse Composite Filtrate ICP-ES

Sample	Elemental Concentration (mg/L)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
1	<4.30E-02	8.67E-01	1.38E-01	<1.10E-02	<4.00E-01	1.05E+01	<4.70E-02	<1.70E-01	<1.46E-01	<1.50E+00	3.54E+00	8.10E-02
2	<4.30E-02	8.82E-01	1.43E-01	<1.10E-02	<4.00E-01	1.06E+01	<4.70E-02	<1.70E-01	<1.46E-01	<1.50E+00	3.46E+00	7.49E-02
3	<4.30E-02	8.23E-01	1.33E-01	<1.10E-02	<4.00E-01	1.06E+01	<4.70E-02	<1.70E-01	<1.46E-01	<1.50E+00	3.44E+00	7.73E-02
Average	**<4.30E-02**	**8.57E-01**	**1.38E-01**	**<1.10E-02**	**<4.00E-01**	**1.06E+01**	**<4.70E-02**	**<1.70E-01**	**<1.46E-01**	**<1.50E+00**	**3.48E+00**	**7.77E-02**
Std. Dev.	na	3.07E-02	5.00E-03	na	na	5.77E-02	na	na	na	na	5.29E-02	3.07E-03
%RSD	na	3.58%	3.62%	na	na	0.55%	na	na	na	na	1.52%	3.95%

na=not applicable

Anion or IC analyses for the RAD B crossbar rinse filtrate are shown in Table F - 14. The average anion or IC concentrations are used in the mass balance.

Table F - 14. Radioactive Module B Crossbar Rinse Composite Filtrate IC

Sample	**Species Concentration (mg/L)**					
	F	**Cl**	**NO_2**	**NO_3**	**SO_4**	**PO_4**
1	6	< 5	< 5	< 5	< 5	< 5
2	5	< 5	< 5	< 5	< 5	< 5
3	6	< 5	< 5	< 5	< 5	< 5
Average	**5.67**	**< 5**	**< 5**	**< 5**	**< 5**	**< 5**
Std. Dev.	0.58	na	na	na	na	na
%RSD	10.19%	na	na	na	na	na

na=not applicable

The crossbar rinse filtrate trace elemental or ICPMS concentrations for Radioactive module B are shown in Table F - 15. The crossbar rinse filtrate had a volume of 2.5391 L. The average trace elemental or ICPMS concentrations in Table F - 15 were used in the mass balance.

Table F - 15. Radioactive Module B Crossbar Rinse Composite Filtrate ICP-MS

Sample	**Species Concentration (ug/L)**		
	Cs	**Re**	**I**
1	1.29E+00	1.38E+01	3.28E+02
2	1.20E+00	1.36E+01	3.23E+02
3	1.24E+00	1.27E+01	3.23E+02
4		1.35E+01	
5		1.32E+01	
6		1.29E+01	
Average	**1.24E+00**	**1.33E+01**	**3.25E+02**
Std. Dev.	4.51E-02	4.14E-01	2.89E+00
%RSD	3.63%	3.12%	0.89%

The radio isotopes of the crossbar rinse filtrate by gamma analysis for the Radioactive module B are shown in Table F - 16. The composite average concentrations shown in Table F - 16 are used in the mass balance.

Table F - 16. Radioactive Module B Crossbar Rinse Composite Filtrate Gamma

Sample	**Concentration (dpm/mL)**			
	Cs-137	**I-125**	**I-129**	**Tc-99**
1	2.84E+01	1.51E+00	1.03E+00	< 7.06E+00
2	2.21E+01	1.79E+00	1.21E+00	< 7.74E+00
3	2.11E+01	1.70E+00	1.15E+00	< 7.83E+00
Average	**2.39E+01**	**1.66E+00**	**1.13E+00**	**< 7.54E+00**
Std. Dev.	3.96E+00	1.41E-01	9.17E-02	4.21E-01
%RSD	16.58%	8.44%	8.11%	5.58%

The crossbar rinse composite filtered solids ICPES concentrations for the Radioactive module B are shown in Table F - 17. Note that only one sample was analyzed for the composite. The crossbar rinse filtered solids had a mass of 1.034 g. These cation or ICP-ES concentrations for the DMR Condensate Composite filtered solids were used in the mass balance.

Table F - 17. Radioactive Module A Crossbar Rinse Composite Filtered Solids ICP-ES

Run	Elemental Concentration (wt%)											
	Ag	**Al**	**B**	**Cr**	**K**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Zn**
Composite	< 0.02	16.10	< 0.01	0.07	0.80	na	< 0.07	0.11	0.13	< 0.58	16.90	0.02

na=not applicable

Anion or IC analyses for the RAD B Crossbar Rinse Filtered Solids samples are shown in Table F - 18. These values were used in the mass balance.

Table F - 18. Radioactive Module B Crossbar Rinse Composite Filtered Solids IC

Sample	Species Concentration (wt%)					
	F	Cl	NO_2	NO_3	SO_4	PO_4
Composite	< 0.41	< 0.41	< 0.41	< 0.41	0.41	< 0.41

The crossbar rinse composite filtered solids trace elemental or ICP-MS concentrations for Radioactive B module are shown in Table F - 19. The crossbar rinse filtered solids mass was 1.034 g. These composite concentrations were used in the mass balance.

Table F - 19. Radioactive Module B Crossbar Rinse Composite Filtered Solids ICP-MS

Run	I (wt%)
Composite	0.031

The radio isotopes of the crossbar rinse filtered solids by gamma analysis for the Radioactive module B are shown in Table F - 20. The average composite concentrations are shown in Table F - 20and were used in the mass balance.

Table F - 20. Radioactive Module A Crossbar Rinse Filtered Solids Gamma

Run	Concentration (dpm/g)	
	Cs-137	I-125
Composite	6.29E+05	2.39E+03

Appendix G. ASTM 1308 Monolith Data

Physical data from the 1” O.D. by 2” tall monoliths used in the ASTM 1308 monolith leach tests are shown in Table G - 1 for the GEO-7 fly ash monoliths and the latter centroid clay monoliths. All test data shown are averages of duplicate monoliths except for the BSR Simulant Module B centroid clay monolith that was only tested as a single monolith. These data were generated by taking the average outer diameter and height as determined by electronic calipers and the mass of each monolith. Leachate data, time intervals, the ‘C_0’ concentrations, interval and cumulative amounts leached, calculated diffusivity and leach index values are shown in subsequent tables. Leach index vs. time plots are also shown for each monolith.

Table G - 1. Physical Data for Leached Monoliths

GEO-7 Fly Ash Monoliths	**Mass (g)**	**Volume (cm^3)**	**Area (cm^2)**	**Volume Leachant (cm^3)**	**Bulk Density (g/cm^3)**
BSR Simulant Module B	48.97	27.08	52.9	529	1.81
HRI/ESTD	50.40	28.09	53.5	535	1.79
Centroid Clay Monoliths					
BSR Simulant Module B	45.74	27.25	52.9	529	1.68
HRI/ESTD P-1B	45.74	26.82	52.2	522	1.71
HRI/ESTD P-1A	46.85	27.28	53.0	530	1.72

Table G - 2. Leachate Data for BSR Simulant Module B GEO-7 Fly Ash Monoliths

Interval Re (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Re Co (mg/kg)	Re mg Leached	Cumulative Re mg Leached	Cumulative Re Fraction Leached	Re Diffusivity cm^2/sec	Re Leach Index
0.361	0.0833	2	268	0.191	0.191	0.0145	6.1E-09	8.22
0.241	0.208	5		0.127	0.318	0.0242	7.9E-09	8.10
0.497	0.708	17		0.263	0.581	0.0442	6.4E-09	8.19
0.182	1	24		0.096	0.677	0.0516	5.1E-09	8.29
0.388	2	48		0.205	0.882	0.0672	3.4E-09	8.47
0.309	3	72		0.163	1.04	0.0796	3.6E-09	8.44
0.176	4	96		0.0933	1.14	0.0867	1.7E-09	8.78
0.112	5	120		0.0591	1.20	0.0912	8.7E-10	9.06
0.0615	6	144		0.0325	1.23	0.0937	3.2E-10	9.49
0.0271	7	168		0.0143	1.24	0.0948	7.4E-11	10.1
0.0125	8	192		0.0066	1.25	0.0953	1.8E-11	10.7
0.0070	9	216		0.0037	1.25	0.0955	6.4E-12	11.2
0.0058	10	240		0.0030	1.26	0.0958	4.9E-12	11.3
0.0040	11	264		0.0021	1.26	0.0959	2.6E-12	11.6
0.0162	19	456		0.0086	1.27	0.0966	9.3E-13	12.0
0.0233	47	1128		0.0123	1.28	0.0975	3.4E-13	12.5
0.0098	77	1848		0.00519	1.29	0.0979	1.0E-13	13.0
0.0034	90	2160		0.00181	1.29	0.0981	8.9E-14	13.1
Interval Na (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Na Co (mg/kg)**	**Na mg Leached**	**Cumulative Na mg Leached**	**Cumulative Na Fraction Leached**	**Na Diffusivity cm^2/sec**	**Na Leach Index**
627	0.0833	2	181857	331	331	0.0372	4.0E-08	7.40
430	0.208	5		227	558	0.0627	5.5E-08	7.26
914	0.708	17		483	1041	0.117	4.7E-08	7.33
366	1	24		193	1235	0.139	4.5E-08	7.35
716	2	48		378	1613	0.181	2.5E-08	7.60
481	3	72		254	1867	0.210	1.9E-08	7.72
364	4	96		192	2059	0.231	1.5E-08	7.81
260	5	120		137	2197	0.247	1.0E-08	7.99
175	6	144		92.5	2289	0.257	5.6E-09	8.25
118	7	168		62.1	2351	0.264	3.0E-09	8.52
82.3	8	192		43.5	2395	0.269	1.7E-09	8.77
61.4	9	216		32.5	2427	0.273	1.1E-09	8.97
48.1	10	240		25.4	2453	0.275	7.4E-10	9.13
38.9	11	264		20.5	2473	0.278	5.3E-10	9.27
129	19	456		68.2	2541	0.285	1.3E-10	9.89
135	47	1128		71.1	2612	0.293	2.4E-11	10.6
65.2	77	1848		34.5	2647	0.297	9.7E-12	11.0
34.6	90	2160		18.3	2665	0.299	2.0E-11	10.7

Table G - 2. Leachate Data for BSR Simulant Module B GEO-7 Fly Ash Monoliths (Continued)

Interval Cs (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Cs Co (mg/kg)	Cs mg Leached	Cumulative Cs mg Leached	Cumulative Cs Fraction Leached	Cs Diffusivity cm^2/sec	Cs Leach Index
0.522	0.0833	2	1692	0.276	0.276	0.0033	3.2E-10	9.50
0.365	0.208	5		0.193	0.469	0.0057	4.6E-10	9.34
0.641	0.708	17		0.339	0.808	0.0098	2.7E-10	9.57
0.288	1	24		0.152	0.960	0.0116	3.2E-10	9.49
0.572	2	48		0.303	1.26	0.0152	1.9E-10	9.73
0.431	3	72		0.228	1.49	0.0180	1.8E-10	9.75
0.281	4	96		0.148	1.64	0.0198	1.1E-10	9.97
0.197	5	120		0.104	1.74	0.0210	6.7E-11	10.2
0.139	6	144		0.0736	1.82	0.0219	4.1E-11	10.4
0.0956	7	168		0.0505	1.87	0.0225	2.3E-11	10.6
0.0704	8	192		0.0372	1.90	0.0230	1.4E-11	10.8
0.0528	9	216		0.0279	1.93	0.0233	9.2E-12	11.0
0.0421	10	240		0.0222	1.95	0.0236	6.5E-12	11.2
0.0335	11	264		0.0177	1.97	0.0238	4.6E-12	11.3
0.101	19	456		0.0532	2.03	0.0244	9.1E-13	12.0
0.107	47	1128		0.0564	2.08	0.0251	1.8E-13	12.8
0.0575	77	1848		0.0304	2.11	0.0255	8.7E-14	13.1
0.0256	90	2160		0.0135	2.13	0.0256	1.3E-13	12.9
Interval Al (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Al Co (mg/kg)**	**Al mg Leached**	**Cumulative Al mg Leached**	**Cumulative Al Fraction Leached**	**Al Diffusivity cm^2/sec**	**Al Leach Index**
0.668	0.0833	2	140473	0.353	0.353	0.000051	7.5E-14	13.1
0.918	0.208	5		0.485	0.838	0.000122	4.2E-13	12.4
0.874	0.708	17		0.462	1.30	0.000189	7.2E-14	13.1
0.370	1	24		0.196	1.50	0.000217	7.7E-14	13.1
0.677	2	48		0.358	1.85	0.000269	3.8E-14	13.4
0.492	3	72		0.260	2.11	0.000307	3.4E-14	13.5
0.483	4	96		0.255	2.37	0.000344	4.6E-14	13.3
0.417	5	120		0.220	2.59	0.000376	4.4E-14	13.4
0.398	6	144		0.210	2.80	0.000407	4.9E-14	13.3
0.383	7	168		0.202	3.00	0.000436	5.4E-14	13.3
0.462	8	192		0.244	3.25	0.000472	9.0E-14	13.0
0.471	9	216		0.249	3.50	0.000508	1.1E-13	13.0
0.470	10	240		0.248	3.74	0.000544	1.2E-13	12.9
0.497	11	264		0.263	4.01	0.000582	1.5E-13	12.8
1.79	19	456		0.946	4.95	0.000720	4.2E-14	13.4
3.03	47	1128		1.60	6.55	0.00095	2.1E-14	13.7
3.22	77	1848		1.70	8.26	0.00120	4.0E-14	13.4
4.85	90	2160		2.56	10.8	0.00157	6.5E-13	12.2

Table G - 2. Leachate Data for BSR Simulant Module B GEO-7 Fly Ash Monoliths (Continued)

Interval Si (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Si Co (mg/kg)	Si mg Leached	Cumulative Si mg Leached	Cumulative Si Fraction Leached	Si Diffusivity cm^2/sec	Si Leach Index
167	0.0833	2	190600	88.2	88.2	0.00945	2.6E-09	8.59
210	0.208	5		111	199	0.0213	1.2E-08	7.92
401	0.708	17		212	411	0.0440	8.3E-09	8.08
148	1	24		78.2	489	0.0524	6.7E-09	8.18
305	2	48		161	650	0.0697	4.1E-09	8.38
210	3	72		111	761	0.0815	3.3E-09	8.48
167	4	96		88.0	849	0.0909	3.0E-09	8.53
116	5	120		61.3	910	0.0975	1.8E-09	8.73
84.6	6	144		44.7	955	0.102	1.2E-09	8.92
57.9	7	168		30.6	986	0.106	6.6E-10	9.18
43.7	8	192		23.1	1009	0.108	4.4E-10	9.36
32.8	9	216		17.3	1026	0.110	2.8E-10	9.56
24.6	10	240		13.0	1039	0.111	1.8E-10	9.76
20.0	11	264		10.6	1050	0.112	1.3E-10	9.89
78.3	19	456		41.4	1091	0.117	4.3E-11	10.4
87.5	47	1128		46.2	1137	0.122	9.4E-12	11.0
34.6	77	1848		18.3	1155	0.124	2.5E-12	11.6
18.5	90	2160		9.75	1165	0.125	5.1E-12	11.3
Interval P (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**P Co (mg/kg)**	**P mg Leached**	**Cumulative P mg Leached**	**Cumulative P Fraction Leached**	**P Diffusivity cm^2/sec**	**P Leach Index**
9.86	0.0833	2	1661	5.21	5.21	0.0640	1.2E-07	6.93
6.85	0.208	5		3.62	8.83	0.109	1.7E-07	6.78
15.3	0.708	17		8.09	16.9	0.208	1.6E-07	6.80
5.90	1	24		3.12	20.0	0.246	1.4E-07	6.85
12.4	2	48		6.56	26.6	0.327	9.0E-08	7.04
8.56	3	72		4.53	31.1	0.382	7.3E-08	7.14
6.89	4	96		3.64	34.8	0.427	6.6E-08	7.18
5.12	5	120		2.71	37.5	0.460	4.7E-08	7.32
3.66	6	144		1.93	39.4	0.484	3.0E-08	7.53
2.41	7	168		1.27	40.7	0.500	1.5E-08	7.82
1.62	8	192		0.856	41.5	0.510	7.9E-09	8.10
1.11	9	216		0.589	42.1	0.518	4.2E-09	8.37
0.839	10	240		0.444	42.6	0.523	2.7E-09	8.57
0.676	11	264		0.357	42.9	0.527	1.9E-09	8.72
2.20	19	456		1.16	44.1	0.542	4.5E-10	9.35
2.35	47	1128		1.24	45.3	0.557	8.9E-11	10.1
0.978	77	1848		0.517	45.8	0.563	2.6E-11	10.6
0.297	90	2160		0.157	46.0	0.565	1.8E-11	10.8

Table G - 2. Leachate Data for BSR Simulant Module B GEO-7 Fly Ash Monoliths (Continued)

Interval I (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	I Co (mg/kg)	I mg Leached	Cumulative I mg Leached	Cumulative I Fraction Leached	I Diffusivity cm^2/sec	I Leach Index
0.196	0.0833	2	727	0.104	0.104	0.00291	2.4E-10	9.62
0.121	0.208	5		0.0641	0.168	0.00471	2.7E-10	9.56
0.213	0.708	17		0.113	0.281	0.0079	1.6E-10	9.79
0.0733	1	24		0.0387	0.319	0.0090	1.1E-10	9.95
0.174	2	48		0.0920	0.411	0.0116	9.3E-11	10.0
0.121	3	72		0.0640	0.475	0.0134	7.6E-11	10.1
0.0758	4	96		0.0401	0.515	0.0145	4.2E-11	10.4
0.0331	5	120		0.0175	0.533	0.0150	1.0E-11	11.0
0.0159	6	144		0.00839	0.541	0.0152	2.9E-12	11.5
0.0145	7	168		0.00767	0.549	0.0154	2.9E-12	11.5
0.0100	8	192		0.00529	0.554	0.0156	1.6E-12	11.8
0.0100	9	216		0.00529	0.560	0.0157	1.8E-12	11.7
0.00700	10	240		0.00370	0.563	0.0158	9.8E-13	12.0
0.00700	11	264		0.00370	0.567	0.0159	1.1E-12	12.0
0.00990	19	456		0.00523	0.572	0.0161	4.7E-14	13.3
0.0133	47	1128		0.00704	0.579	0.0163	1.5E-14	13.8
0.0099	77	1848		0.00524	0.585	0.0164	1.4E-14	13.9
0.00472	90	2160		0.00249	0.587	0.0165	2.3E-14	13.6

Interval S (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	S Co (mg/kg)	S mg Leached	Cumulative S mg Leached	Cumulative S Fraction Leached	S Diffusivity cm^2/sec	S Leach Index
14.1	0.0833	2	4203	7.43	7.43	0.0361	4.0E-08	7.40
7.44	0.208	5		3.93	11.4	0.0552	3.3E-08	7.48
15.5	0.708	17		8.19	19.6	0.095	2.7E-08	7.56
5.62	1	24		2.97	22.5	0.109	2.1E-08	7.67
11.7	2	48		6.19	28.7	0.140	1.3E-08	7.87
8.37	3	72		4.42	33.1	0.161	1.2E-08	7.93
6.85	4	96		3.62	36.8	0.179	1.1E-08	7.96
4.71	5	120		2.49	39.3	0.191	6.7E-09	8.17
2.89	6	144		1.53	40.8	0.198	3.1E-09	8.51
1.51	7	168		0.798	41.6	0.202	1.0E-09	9.00
0.725	8	192		0.383	42.0	0.204	2.7E-10	9.58
0.417	9	216		0.220	42.2	0.205	9.9E-11	10.0
0.294	10	240		0.155	42.3	0.206	5.5E-11	10.3
0.294	11	264		0.155	42.5	0.206	6.1E-11	10.2
0.668	19	456		0.353	42.8	0.208	6.9E-12	11.2
1.50	47	1128		0.793	43.6	0.212	6.1E-12	11.2
0.294	77	1848		0.155	43.8	0.213	4.0E-13	12.4
0.147	90	2160		0.0777	43.9	0.213	7.2E-13	12.1

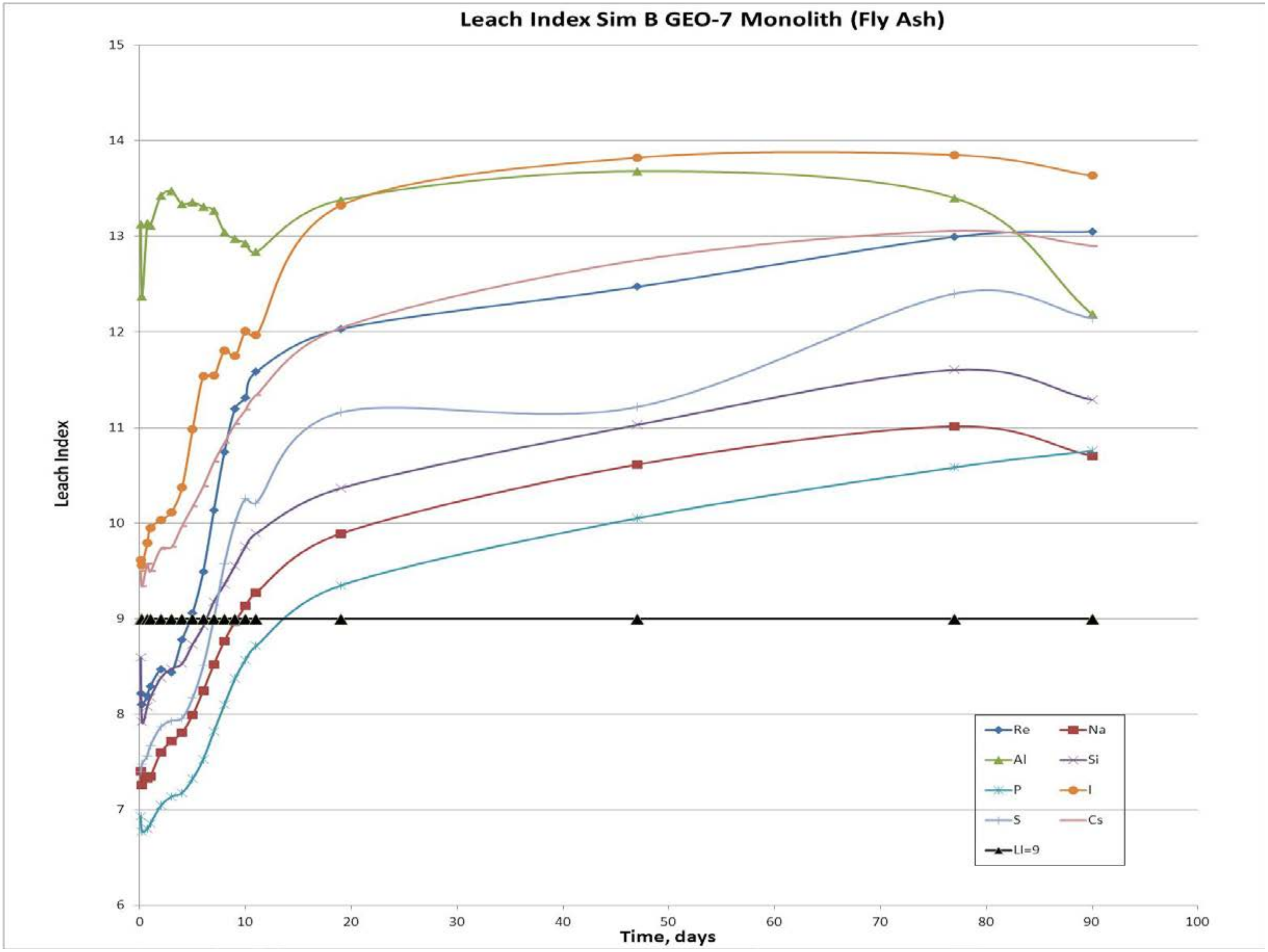

Figure G - 1. Leach Index Values versus Time for BSR Simulant Module B Fly Ash Monolith

Table G - 3. Leachate Data for HRI/ESTD GEO-7 Fly Ash Monolith

Interval Re (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Re Co (mg/kg)	Re mg Leached	Cumulative Re mg Leached	Cumulative Re Fraction Leached	Re Diffusivity cm^2/sec	Re Leach Index
0.279	0.0833	2	248	0.149	0.149	0.0119	4.3E-09	8.37
0.187	0.208	5		0.100	0.249	0.0199	5.7E-09	8.25
0.417	0.708	17		0.223	0.472	0.0378	5.4E-09	8.27
0.176	1	24		0.0938	0.566	0.0453	5.6E-09	8.25
0.472	2	48		0.252	0.818	0.0655	5.9E-09	8.23
0.354	3	72		0.189	1.01	0.0806	5.7E-09	8.24
0.224	4	96		0.120	1.13	0.0902	3.2E-09	8.49
0.200	5	120		0.107	1.23	0.099	3.3E-09	8.48
0.189	6	144		0.101	1.34	0.107	3.6E-09	8.45
0.159	7	168		0.0850	1.42	0.114	3.0E-09	8.52
0.144	8	192		0.0771	1.50	0.120	2.9E-09	8.54
0.122	9	216		0.0654	1.56	0.125	2.3E-09	8.63
0.100	10	240		0.0536	1.62	0.129	1.7E-09	8.76
0.0843	11	264		0.0451	1.66	0.133	1.4E-09	8.86
0.293	19	456		0.156	1.82	0.145	3.6E-10	9.44
0.0753	47	1128		0.0402	1.86	0.149	4.2E-12	11.4
0.0180	77	1848		0.0096	1.87	0.149	4.0E-13	12.4
0.0061	90	2160		0.0033	1.87	0.150	3.4E-13	12.5
Interval Na (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Na Co (mg/kg)**	**Na mg Leached**	**Cumulative Na mg Leached**	**Cumulative Na Fraction Leached**	**Na Diffusivity cm^2/sec**	**Na Leach Index**
346	0.0833	2	153868	185	185	0.0238	1.7E-08	7.77
216	0.208	5		115	300	0.0387	2.0E-08	7.71
438	0.708	17		234	534	0.0688	1.5E-08	7.81
185	1	24		98.7	633	0.0816	1.6E-08	7.79
445	2	48		238	871	0.112	1.4E-08	7.86
328	3	72		175	1046	0.135	1.3E-08	7.90
223	4	96		119	1165	0.150	8.3E-09	8.08
187	5	120		99.7	1265	0.163	7.4E-09	8.13
174	6	144		92.8	1358	0.175	7.9E-09	8.10
149	7	168		79.7	1437	0.185	6.9E-09	8.16
138	8	192		73.8	1511	0.195	6.8E-09	8.17
117	9	216		62.3	1573	0.203	5.5E-09	8.26
100	10	240		53.4	1627	0.210	4.5E-09	8.35
87.8	11	264		46.9	1674	0.216	3.9E-09	8.41
378	19	456		202	1876	0.242	1.6E-09	8.80
416	47	1128		222	2098	0.271	3.3E-10	9.48
176	77	1848		93.8	2192	0.283	1.0E-10	10.0
65.6	90	2160		35.0	2227	0.287	1.0E-10	10.0

Table G - 3. Leachate Data for HRI/ESTD GEO-7 Fly Ash Monolith (Continued)

Interval Cs (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Cs Co (mg/kg)	Cs mg Leached	Cumulative Cs mg Leached	Cumulative Cs Fraction Leached	Cs Diffusivity cm^2/sec	Cs Leach Index
0.816	0.0833	2	1299	0.436	0.436	0.0067	1.3E-09	8.87
0.502	0.208	5		0.269	0.705	0.0108	1.5E-09	8.82
0.863	0.708	17		0.462	1.17	0.0178	8.4E-10	9.08
0.382	1	24		0.204	1.37	0.0209	9.7E-10	9.01
0.836	2	48		0.447	1.82	0.0278	6.8E-10	9.17
0.597	3	72		0.319	2.14	0.0326	5.9E-10	9.23
0.383	4	96		0.205	2.34	0.0358	3.4E-10	9.47
0.315	5	120		0.168	2.51	0.0383	3.0E-10	9.53
0.274	6	144		0.147	2.66	0.0406	2.8E-10	9.56
0.227	7	168		0.121	2.78	0.0424	2.2E-10	9.65
0.203	8	192		0.109	2.89	0.0441	2.1E-10	9.68
0.166	9	216		0.0885	2.97	0.0454	1.6E-10	9.81
0.133	10	240		0.0711	3.05	0.0465	1.1E-10	9.95
0.109	11	264		0.0580	3.10	0.0474	8.3E-11	10.1
0.363	19	456		0.1942	3.30	0.0504	2.0E-11	10.7
0.309	47	1128		0.1654	3.46	0.0529	2.6E-12	11.6
0.138	77	1848		0.0739	3.54	0.0540	8.7E-13	12.1
0.0504	90	2160		0.0270	3.56	0.0544	8.4E-13	12.1

Interval Al (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Al Co (mg/kg)	Al mg Leached	Cumulative Al mg Leached	Cumulative Al Fraction Leached	Al Diffusivity cm^2/sec	Al Leach Index
0.666	0.0833	2	141887	0.356	0.356	0.00005	7.4E-14	13.1
0.307	0.208	5		0.164	0.520	0.00007	4.7E-14	13.3
0.700	0.708	17		0.374	0.894	0.00013	4.6E-14	13.3
0.370	1	24		0.198	1.09	0.00015	7.6E-14	13.1
1.14	2	48		0.610	1.70	0.00024	1.1E-13	13.0
1.34	3	72		0.714	2.42	0.00034	2.5E-13	12.6
0.867	4	96		0.463	2.88	0.00040	1.5E-13	12.8
0.898	5	120		0.480	3.36	0.00047	2.0E-13	12.7
1.02	6	144		0.545	3.90	0.00055	3.2E-13	12.5
0.991	7	168		0.530	4.43	0.00062	3.6E-13	12.4
1.08	8	192		0.575	5.01	0.00070	4.9E-13	12.3
1.00	9	216		0.533	5.54	0.00077	4.7E-13	12.3
0.957	10	240		0.512	6.05	0.00085	4.9E-13	12.3
0.963	11	264		0.515	6.57	0.00092	5.5E-13	12.3
3.78	19	456		2.02	8.59	0.00120	1.8E-13	12.7
5.78	47	1128		3.09	11.7	0.00163	7.5E-14	13.1
7.05	77	1848		3.77	15.4	0.00216	1.9E-13	12.7
6.75	90	2160		3.61	19.1	0.00266	1.3E-12	11.9

Table G - 3. Leachate Data for HRI/ESTD GEO-7 Fly Ash Monolith (Continued)

Interval Si (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Si Co (mg/kg)	Si mg Leached	Cumulative Si mg Leached	Cumulative Si Fraction Leached	Si Diffusivity cm^2/sec	Si Leach Index
81.9	0.0833	2	206839	43.8	43.8	0.0042	5.3E-10	9.28
47.2	0.208	5		25.2	69.0	0.0066	5.2E-10	9.28
86.3	0.708	17		46.1	115	0.0110	3.3E-10	9.48
34.6	1	24		18.5	134	0.0128	3.1E-10	9.50
91.3	2	48		48.8	182	0.0175	3.2E-10	9.49
72.8	3	72		38.9	221	0.0212	3.5E-10	9.46
43.2	4	96		23.1	244	0.0234	1.7E-10	9.77
39.4	5	120		21.1	266	0.0255	1.8E-10	9.74
42.0	6	144		22.5	288	0.0276	2.6E-10	9.59
38.9	7	168		20.8	309	0.0296	2.6E-10	9.59
37.1	8	192		19.8	329	0.0315	2.7E-10	9.57
30.0	9	216		16.0	345	0.0331	2.0E-10	9.70
23.6	10	240		12.6	357	0.0343	1.4E-10	9.86
19.8	11	264		10.6	368	0.0353	1.1E-10	9.96
92.3	19	456		49.3	417	0.0400	5.2E-11	10.3
127	47	1128		67.9	485	0.0465	1.7E-11	10.8
49.7	77	1848		26.6	512	0.0491	4.4E-12	11.4
20.5	90	2160		10.9	523	0.0501	5.4E-12	11.3
Interval P (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**P Co (mg/kg)**	**P mg Leached**	**Cumulative P mg Leached**	**Cumulative P Fraction Leached**	**P Diffusivity cm^2/sec**	**P Leach Index**
5.62	0.0833	2	1410	3.01	3.01	0.0423	5.4E-08	7.27
3.73	0.208	5		1.99	5.00	0.0703	7.0E-08	7.15
7.93	0.708	17		4.24	9.23	0.130	6.0E-08	7.22
3.37	1	24		1.80	11.0	0.155	6.4E-08	7.19
9.39	2	48		5.02	16.1	0.226	7.3E-08	7.14
7.08	3	72		3.79	19.8	0.279	7.0E-08	7.15
4.57	4	96		2.44	22.3	0.314	4.1E-08	7.39
4.27	5	120		2.28	24.6	0.346	4.6E-08	7.33
4.24	6	144		2.26	26.8	0.378	5.6E-08	7.25
3.88	7	168		2.07	28.9	0.407	5.5E-08	7.26
3.81	8	192		2.04	30.9	0.435	6.2E-08	7.21
3.26	9	216		1.74	32.7	0.460	5.1E-08	7.29
2.82	10	240		1.51	34.2	0.481	4.3E-08	7.37
2.47	11	264		1.32	35.5	0.500	3.6E-08	7.44
11.1	19	456		5.91	41.4	0.583	1.6E-08	7.80
8.59	47	1128		4.59	46.0	0.647	1.7E-09	8.78
2.21	77	1848		1.18	47.2	0.664	1.9E-10	9.73
0.696	90	2160		0.372	47.6	0.669	1.4E-10	9.87

Table G - 3. Leachate Data for HRI/ESTD GEO-7 Fly Ash Monolith (Continued)

Interval I (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	I Co (mg/kg)	I mg Leached	Cumulative I mg Leached	Cumulative I Fraction Leached	I Diffusivity cm^2/sec	I Leach Index
0.0425	0.0833	2	693	0.0227	0.0227	0.0007	1.3E-11	10.9
0.0274	0.208	5		0.0147	0.0374	0.0011	1.6E-11	10.8
0.0569	0.708	17		0.0304	0.0678	0.0019	1.3E-11	10.9
0.0178	1	24		0.0095	0.0773	0.0022	7.4E-12	11.1
0.0667	2	48		0.0357	0.113	0.0032	1.5E-11	10.8
0.0454	3	72		0.0243	0.137	0.0039	1.2E-11	10.9
0.0284	4	96		0.0152	0.152	0.0044	6.6E-12	11.2
0.0254	5	120		0.0136	0.166	0.0048	6.8E-12	11.2
0.0226	6	144		0.0121	0.178	0.0051	6.6E-12	11.2
0.0196	7	168		0.0105	0.189	0.0054	5.8E-12	11.2
0.0220	8	192		0.0118	0.200	0.0057	8.5E-12	11.1
0.0186	9	216		0.0100	0.210	0.0060	6.9E-12	11.2
0.0153	10	240		0.00820	0.218	0.0063	5.2E-12	11.3
0.0152	11	264		0.0081	0.227	0.0065	5.7E-12	11.2
0.0670	19	456		0.0358	0.262	0.0075	2.4E-12	11.6
0.179	47	1128		0.0956	0.358	0.0103	3.0E-12	11.5
0.162	77	1848		0.0866	0.445	0.0127	4.2E-12	11.4
0.0830	90	2160		0.0444	0.489	0.0140	8.0E-12	11.1
Interval S (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**S Co (mg/kg)**	**S mg Leached**	**Cumulative S mg Leached**	**Cumulative S Fraction Leached**	**S Diffusivity cm^2/sec**	**S Leach Index**
9.35	0.0833	2	3253	5.00	5.00	0.0305	2.8E-08	7.55
5.98	0.208	5		3.20	8.20	0.0500	3.4E-08	7.47
13.6	0.708	17		7.25	15.4	0.0942	3.3E-08	7.48
5.69	1	24		3.04	18.5	0.113	3.4E-08	7.46
14.9	2	48		7.97	26.4	0.161	3.4E-08	7.46
11.2	3	72		5.96	32.4	0.198	3.3E-08	7.48
6.96	4	96		3.72	36.1	0.220	1.8E-08	7.75
6.23	5	120		3.33	39.5	0.241	1.9E-08	7.73
6.25	6	144		3.34	42.8	0.261	2.3E-08	7.64
5.69	7	168		3.04	45.8	0.280	2.2E-08	7.65
5.47	8	192		2.92	48.8	0.297	2.4E-08	7.62
4.72	9	216		2.52	51.3	0.313	2.0E-08	7.70
3.86	10	240		2.06	53.4	0.325	1.5E-08	7.82
3.38	11	264		1.80	55.2	0.336	1.3E-08	7.89
14.8	19	456		7.91	63.1	0.385	5.4E-09	8.27
8.47	47	1128		4.53	67.6	0.412	3.1E-10	9.51
1.84	77	1848		0.984	68.6	0.418	2.5E-11	10.6
0.556	90	2160		0.297	68.9	0.420	1.6E-11	10.8

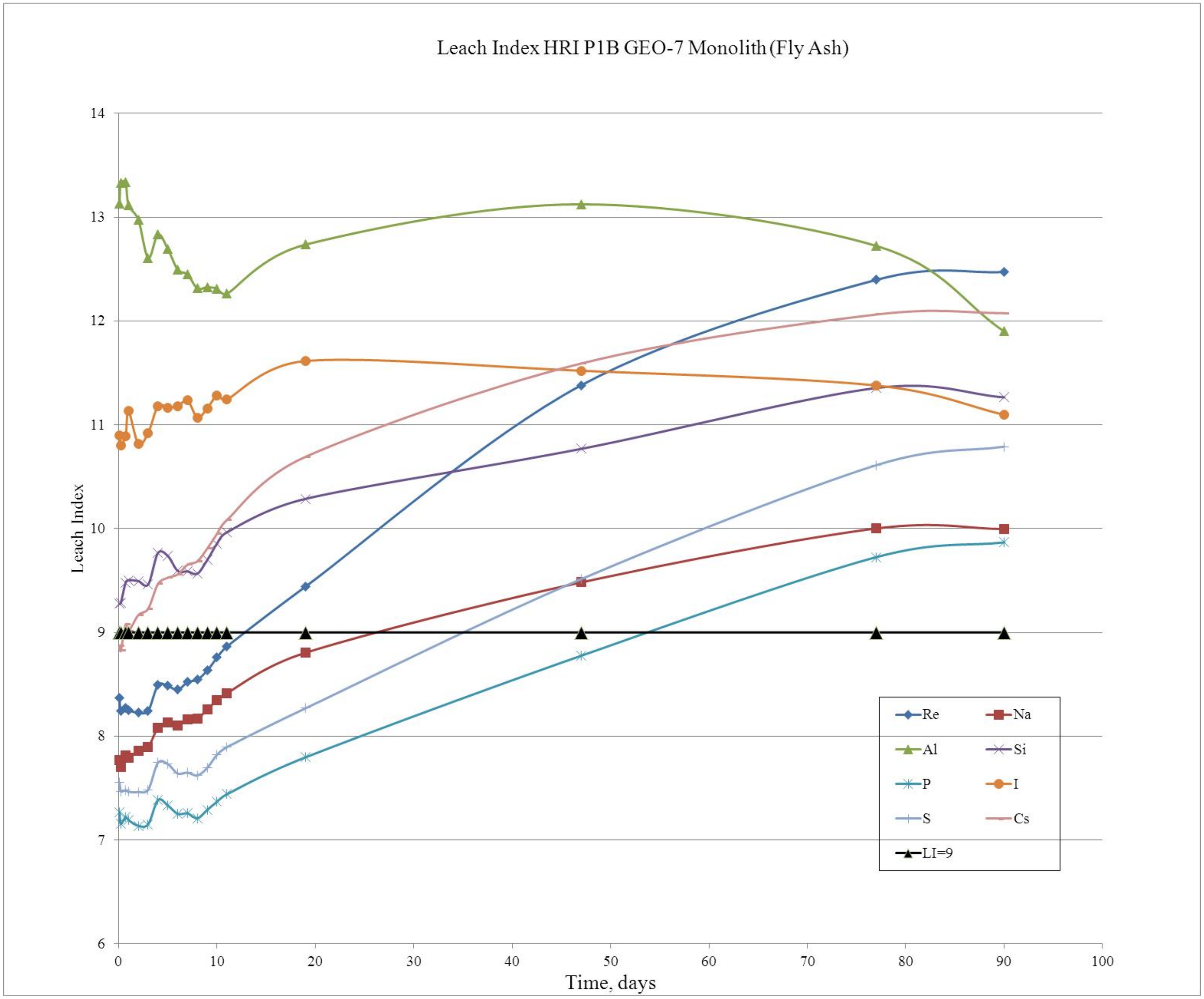

Figure G - 2. Leach Index Values versus Time for HRI/ESTD Fly Ash Monolith

Table G - 4. Leachate Data for BSR Simulant Module B Centroid Clay Monolith

Interval Re (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Re Co (mg/kg)	Re mg Leached	Cumulative Re mg Leached	Cumulative Re Fraction Leached	Re Diffusivity cm^2/sec	Re Leach Index
0.235	0.0833	2	152	0.124	0.124	0.018	9.2E-09	8.04
0.124	0.2083	5		0.066	0.190	0.027	7.6E-09	8.12
0.248	0.7083	17		0.131	0.321	0.046	5.7E-09	8.24
0.083	1	24		0.044	0.365	0.052	3.8E-09	8.42
0.181	2	48		0.095	0.460	0.066	2.6E-09	8.58
0.096	3	72		0.051	0.511	0.073	1.3E-09	8.89
0.050	4	96		0.026	0.537	0.077	4.8E-10	9.32
0.025	5	120		0.013	0.551	0.079	1.5E-10	9.82
0.013	6	144		0.007	0.557	0.080	5.3E-11	10.3
0.007	7	168		0.004	0.561	0.081	1.7E-11	10.8
0.004	8	192		0.002	0.563	0.081	5.1E-12	11.3
0.003	9	216		0.001	0.564	0.081	3.6E-12	11.4
0.003	10	240		0.002	0.566	0.081	4.7E-12	11.3
0.003	11	264		0.002	0.568	0.081	5.2E-12	11.3
0.009	19	456		0.005	0.572	0.082	9.9E-13	12.0
0.011	47	1128		0.006	0.578	0.083	2.8E-13	12.5
0.008	91	2184		0.004	0.583	0.084	1.3E-13	12.9
0.003	107	2568		0.001	0.584	0.084	1.5E-13	12.8
Interval Na (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Na Co (mg/kg)**	**Na mg Leached**	**Cumulative Na mg Leached**	**Cumulative Na Fraction Leached**	**Na Diffusivity cm^2/sec**	**Na Leach Index**
212	0.0833	2	147348	112	112	0.017	8.0E-09	8.10
114	0.2083	5		60.5	173	0.026	6.9E-09	8.16
236	0.7083	17		125	298	0.044	5.6E-09	8.25
95.4	1	24		50.5	348	0.052	5.4E-09	8.27
220	2	48		116	465	0.069	4.2E-09	8.38
158	3	72		83.4	548	0.081	3.6E-09	8.44
115	4	96		61.0	609	0.090	2.7E-09	8.56
89.7	5	120		47.4	656	0.097	2.1E-09	8.67
73.0	6	144		38.6	695	0.103	1.7E-09	8.76
59.0	7	168		31.2	726	0.108	1.3E-09	8.87
49.0	8	192		25.9	752	0.112	1.1E-09	8.97
42.8	9	216		22.6	775	0.115	9.2E-10	9.04
35.5	10	240		18.8	794	0.118	7.1E-10	9.15
33.4	11	264		17.6	811	0.120	6.9E-10	9.16
151	19	456		79.9	891	0.132	3.1E-10	9.51
153	47	1128		80.9	972	0.144	5.6E-11	10.3
87.6	91	2184		0.004	0.583	0.084	1.6E-11	10.8
31.1	107	2568		0.001	0.584	0.084	2.2E-11	10.7

Table G - 4. Leachate Data for BSR Simulant Module B Centroid Clay Monolith (Continued)

Interval Cs (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Cs Co (mg/kg)	Cs mg Leached	Cumulative Cs mg Leached	Cumulative Cs Fraction Leached	Cs Diffusivity cm^2/sec	Cs Leach Index
0.128	0.0833	2	933	0.068	0.068	0.0016	7.2E-11	10.1
0.069	0.2083	5		0.036	0.104	0.0024	6.2E-11	10.2
0.121	0.7083	17		0.064	0.168	0.0039	3.7E-11	10.4
0.051	1	24		0.027	0.195	0.0046	3.9E-11	10.4
0.101	2	48		0.053	0.249	0.0058	2.2E-11	10.7
0.075	3	72		0.040	0.288	0.0068	2.1E-11	10.7
0.055	4	96		0.029	0.317	0.0074	1.5E-11	10.8
0.042	5	120		0.022	0.339	0.0080	1.2E-11	10.9
0.039	6	144		0.021	0.360	0.0084	1.2E-11	10.9
0.033	7	168		0.017	0.377	0.0088	1.0E-11	11.0
0.028	8	192		0.015	0.392	0.0092	8.8E-12	11.1
0.025	9	216		0.013	0.405	0.0095	7.6E-12	11.1
0.022	10	240		0.012	0.417	0.0098	6.8E-12	11.2
0.019	11	264		0.010	0.427	0.0100	5.4E-12	11.3
0.068	19	456		0.036	0.463	0.0108	1.6E-12	11.8
0.062	47	1128		0.033	0.496	0.0116	2.3E-13	12.6
0.036	91	2184		0.019	0.515	0.0121	6.7E-14	13.2
0.020	107	2568		0.011	0.526	0.0123	2.3E-13	12.6
Interval Al (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Al Co (mg/kg)**	**Al mg Leached**	**Cumulative Al mg Leached**	**Cumulative Al Fraction Leached**	**Al Diffusivity cm^2/sec**	**Al Leach Index**
0.369	0.0833	2	162415	0.195	0.195	0.00003	2.0E-14	13.7
0.503	0.2083	5		0.266	0.461	0.00006	1.1E-13	13.0
2.38	0.7083	17		1.26	1.72	0.00023	4.7E-13	12.3
1.34	1	24		0.71	2.43	0.000	8.7E-13	12.1
4.99	2	48		2.64	5.07	0.001	1.8E-12	11.8
5.66	3	72		2.99	8.06	0.001	3.9E-12	11.4
5.63	4	96		2.98	11.0	0.001	5.4E-12	11.3
5.27	5	120		2.79	13.8	0.002	6.1E-12	11.2
5.11	6	144		2.71	16.5	0.002	7.0E-12	11.2
4.51	7	168		2.38	18.9	0.003	6.4E-12	11.2
4.19	8	192		2.22	21.1	0.003	6.4E-12	11.2
4.20	9	216		2.22	23.4	0.003	7.3E-12	11.1
3.96	10	240		2.09	25.5	0.003	7.2E-12	11.1
3.54	11	264		1.87	27.3	0.004	6.4E-12	11.2
17.2	19	456		9.10	36.4	0.005	3.3E-12	11.5
19.3	47	1128		10.2	46.6	0.006	7.3E-13	12.1
18.1	91	2184		9.57	56.2	0.008	5.6E-13	12.3
9.89	107	2568		5.23	61.4	0.008	1.8E-12	11.7

Table G - 4. Leachate Data for BSR Simulant Module B Centroid Clay Monolith (Continued)

Interval Si (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Si Co (mg/kg)	Si mg Leached	Cumulative Si mg Leached	Cumulative Si Fraction Leached	Si Diffusivity cm^2/sec	Si Leach Index
28.2	0.0833	2	216675	14.9	14.9	0.002	6.5E-11	10.2
15.7	0.2083	5		8.32	23.2	0.002	6.0E-11	10.2
37.1	0.7083	17		19.6	42.8	0.004	6.4E-11	10.2
12.8	1	24		6.77	49.6	0.005	4.5E-11	10.3
36.8	2	48		19.5	69.1	0.007	5.4E-11	10.3
28.9	3	72		15.3	84.4	0.009	5.7E-11	10.2
23.8	4	96		12.6	97.0	0.010	5.4E-11	10.3
19.9	5	120		10.5	107	0.011	4.9E-11	10.3
18.1	6	144		9.57	117	0.012	4.9E-11	10.3
14.5	7	168		7.69	125	0.013	3.8E-11	10.4
13.5	8	192		7.17	132	0.013	3.8E-11	10.4
12.4	9	216		6.55	138	0.014	3.6E-11	10.4
11.2	10	240		5.90	144	0.015	3.2E-11	10.5
10.3	11	264		5.47	150	0.015	3.1E-11	10.5
60.2	19	456		31.8	182	0.018	2.3E-11	10.6
62.4	47	1128		33.0	215	0.022	4.3E-12	11.4
34.0	91	2184		18.0	233	0.023	1.1E-12	12.0
12.5	107	2568		6.61	239	0.024	1.7E-12	11.8
Interval P (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**P Co (mg/kg)**	**P mg Leached**	**Cumulative P mg Leached**	**Cumulative P Fraction Leached**	**P Diffusivity cm^2/sec**	**P Leach Index**
4.92	0.0833	2	1021	2.60	2.60	0.0557	9.0E-08	7.0
2.24	0.2083	5		1.19	3.79	0.0811	5.5E-08	7.3
4.96	0.7083	17		2.63	6.42	0.137	5.1E-08	7.3
1.74	1	24		0.921	7.34	0.157	3.7E-08	7.4
4.31	2	48		2.28	9.62	0.206	3.3E-08	7.5
3.03	3	72		1.60	11.2	0.240	2.8E-08	7.6
2.25	4	96		1.19	12.4	0.266	2.2E-08	7.7
1.64	5	120		0.870	13.3	0.284	1.5E-08	7.8
1.26	6	144		0.665	13.9	0.299	1.1E-08	8.0
1.52	7	168		0.806	14.8	0.316	1.9E-08	7.7
0.650	8	192		0.344	15.1	0.323	3.9E-09	8.4
0.476	9	216		0.252	15.3	0.329	2.4E-09	8.6
0.307	10	240		0.162	15.5	0.332	1.1E-09	9.0
0.248	11	264		0.131	15.6	0.335	7.9E-10	9.1
0.680	19	456		0.360	16.0	0.343	1.3E-10	9.9
0.334	47	1128		0.177	16.2	0.346	5.5E-12	11.3
0.322	91	2184		0.170	16.3	0.350	4.4E-12	11.4
0.100	107	2568		0.0529	16.4	0.351	4.8E-12	11.3

Table G - 4. Leachate Data for BSR Simulant Module B Centroid Clay Monolith (Continued)

Interval I (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	I Co (mg/kg)	I mg Leached	Cumulative I mg Leached	Cumulative I Fraction Leached	I Diffusivity cm^2/sec	I Leach Index
0.143	0.0833	2	494	0.0758	0.0758	0.00336	3.3E-10	9.49
0.072	0.2083	5		0.0379	0.114	0.00503	2.4E-10	9.62
0.144	0.7083	17		0.0764	0.190	0.00842	1.9E-10	9.73
0.043	1	24		0.0229	0.213	0.00943	9.8E-11	10.0
0.0977	2	48		0.0517	0.265	0.0117	7.4E-11	10.1
0.0357	3	72		0.0189	0.284	0.0126	1.7E-11	10.8
0.0977	4	96		0.0517	0.335	0.0148	1.8E-10	9.76
0.0371	5	120		0.0196	0.355	0.0157	3.3E-11	10.5
0.0110	6	144		0.00582	0.361	0.0160	3.5E-12	11.5
0.0110	7	168		0.00582	0.366	0.0162	4.1E-12	11.4
0.0110	8	192		0.00582	0.372	0.0165	4.8E-12	11.3
0.0110	9	216		0.00582	0.378	0.0167	5.4E-12	11.3
0.00450	10	240		0.00238	0.381	0.0168	1.0E-12	12.0
0.00450	11	264		0.00238	0.383	0.0170	1.1E-12	11.9
0.00600	19	456		0.00317	0.386	0.0171	4.4E-14	13.4
0.00550	47	1128		0.00291	0.389	0.0172	6.4E-15	14.2
0.00575	91	2184		0.00304	0.392	0.0174	6.1E-15	14.2
0.00400	107	2568		0.00212	0.394	0.0174	3.3E-14	13.5

Interval S (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	S Co (mg/kg)	S mg Leached	Cumulative S mg Leached	Cumulative S Fraction Leached	S Diffusivity cm^2/sec	S Leach Index
3.61	0.0833	2	1511	1.91	1.91	0.0276	2.2E-08	7.66
1.74	0.2083	5		0.922	2.83	0.0410	1.5E-08	7.82
3.94	0.7083	17		2.09	4.92	0.0712	1.5E-08	7.83
1.36	1	24		0.719	5.64	0.0816	1.0E-08	7.98
3.33	2	48		1.76	7.40	0.107	9.1E-09	8.04
2.17	3	72		1.15	8.54	0.124	6.6E-09	8.18
1.44	4	96		0.764	9.31	0.135	4.1E-09	8.39
0.865	5	120		0.458	9.77	0.141	1.9E-09	8.72
0.555	6	144		0.293	10.1	0.146	9.5E-10	9.02
1.47	7	168		0.779	10.8	0.157	7.9E-09	8.10
0.100	8	192		0.0529	10.9	0.158	4.2E-11	10.4
0.100	9	216		0.0529	10.9	0.158	4.8E-11	10.3
0.100	10	240		0.0529	11.0	0.159	5.4E-11	10.3
0.100	11	264		0.0529	11.0	0.160	5.9E-11	10.2
0.100	19	456		0.0529	11.1	0.161	1.3E-12	11.9
0.178	47	1128		0.0942	11.2	0.162	7.2E-13	12.1
0.100	91	2184		0.0529	11.2	0.163	2.0E-13	12.7
0.149	107	2568		0.0788	11.3	0.164	4.8E-12	11.3

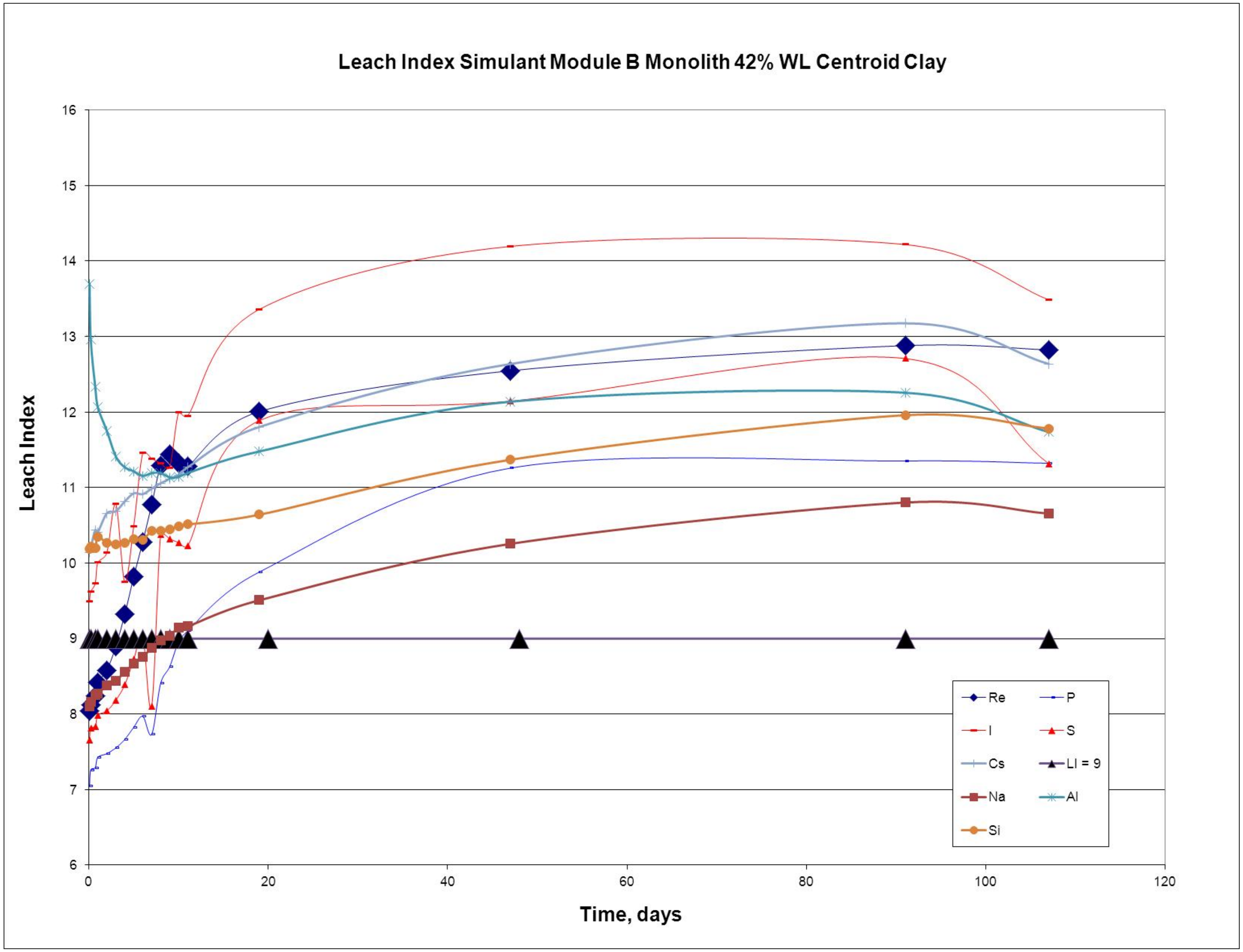

Figure G - 3. Leach Index versus Time for BSR Simulant Module B Centroid Clay Monolith

Table G - 5. Leachate Data for HRI/ESTD P-1B Centroid Clay Monolith

Interval Re (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Re Co (mg/kg)	Re mg Leached	Cumulative Re mg Leached	Cumulative Re Fraction Leached	Re Diffusivity cm^2/sec	Re Leach Index
0.338	0.0833	2	129	0.176	0.176	0.0300	2.5E-08	7.60
0.193	0.2083	5		0.101	0.277	0.0471	2.4E-08	7.62
0.408	0.7083	17		0.213	0.490	0.0833	2.1E-08	7.69
0.136	1	24		0.0711	0.561	0.095	1.4E-08	7.87
0.287	2	48		0.150	0.711	0.121	8.8E-09	8.06
0.141	3	72		0.0736	0.785	0.133	3.6E-09	8.44
0.0729	4	96		0.0381	0.823	0.140	1.4E-09	8.87
0.0364	5	120		0.0190	0.842	0.143	4.3E-10	9.36
0.0204	6	144		0.0107	0.852	0.145	1.7E-10	9.77
0.0113	7	168		0.00591	0.858	0.146	6.1E-11	10.2
0.00766	8	192		0.00400	0.862	0.146	3.2E-11	10.5
0.00545	9	216		0.00285	0.865	0.147	1.8E-11	10.7
0.00467	10	240		0.00244	0.868	0.147	1.5E-11	10.8
0.00442	11	264		0.00231	0.870	0.148	1.5E-11	10.8
0.0277	19	456		0.0145	0.884	0.150	1.3E-11	10.9
0.0368	47	1128		0.0192	0.904	0.154	4.0E-12	11.4
0.0254	91	2184		0.0132	0.917	0.156	1.6E-12	11.8
0.0050	107	2568		0.00263	0.919	0.156	7.2E-13	12.1
Interval Na (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Na Co (mg/kg)**	**Na mg Leached**	**Cumulative Na mg Leached**	**Cumulative Na Fraction Leached**	**Na Diffusivity cm^2/sec**	**Na Leach Index**
194	0.0833	2	150143	101	101	0.0147	6.1E-09	8.22
112	0.2083	5		58.7	160	0.0233	6.0E-09	8.22
237	0.7083	17		124	284	0.0413	5.1E-09	8.29
96.7	1	24		50.5	334	0.0487	5.0E-09	8.30
224	2	48		117	451	0.0657	3.9E-09	8.41
153	3	72		79.9	531	0.0773	3.1E-09	8.51
115	4	96		60.2	591	0.0861	2.5E-09	8.60
90.3	5	120		47.2	638	0.0930	2.0E-09	8.71
70.8	6	144		37.0	675	0.098	1.5E-09	8.83
58.2	7	168		30.4	706	0.103	1.2E-09	8.93
49.0	8	192		25.6	731	0.107	9.7E-10	9.01
41.9	9	216		21.9	753	0.110	8.0E-10	9.10
35.2	10	240		18.4	772	0.112	6.4E-10	9.20
33.2	11	264		17.3	789	0.115	6.2E-10	9.21
169	19	456		88.3	877	0.128	3.5E-10	9.45
172	47	1128		89.9	967	0.141	6.4E-11	10.2
102	91	2184		53.3	1021	0.149	1.9E-11	10.7
30.7	107	2568		16.0	1037	0.151	2.0E-11	10.7

Table G - 6. Leachate Data for HRI/ESTD P-1B Centroid Clay Monolith (Continued)

Interval Cs (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Cs Co (mg/kg)	Cs mg Leached	Cumulative Cs mg Leached	Cumulative Cs Fraction Leached	Cs Diffusivity cm^2/sec	Cs Leach Index
0.0987	0.0833	2	711	0.0515	0.0515	0.00159	7.0E-11	10.2
0.0558	0.2083	5		0.0292	0.0807	0.00248	6.7E-11	10.2
0.106	0.7083	17		0.0556	0.136	0.00419	4.6E-11	10.3
0.0408	1	24		0.0213	0.158	0.00485	4.0E-11	10.4
0.0907	2	48		0.0474	0.205	0.00631	2.9E-11	10.5
0.0607	3	72		0.0317	0.237	0.00728	2.2E-11	10.7
0.0511	4	96		0.0267	0.263	0.00811	2.2E-11	10.7
0.0390	5	120		0.0204	0.284	0.00873	1.6E-11	10.8
0.0393	6	144		0.0205	0.304	0.00936	2.0E-11	10.7
0.0340	7	168		0.0177	0.322	0.00991	1.8E-11	10.7
0.0276	8	192		0.0144	0.336	0.0104	1.4E-11	10.9
0.0244	9	216		0.0127	0.349	0.0107	1.2E-11	10.9
0.0254	10	240		0.0133	0.362	0.0112	1.5E-11	10.8
0.0181	11	264		0.0095	0.372	0.0114	8.3E-12	11.1
0.0692	19	456		0.0362	0.408	0.0126	2.7E-12	11.6
0.0608	47	1128		0.0317	0.440	0.0135	3.6E-13	12.4
0.0352	91	2184		0.0184	0.458	0.0141	1.0E-13	13.0
0.0178	107	2568		0.0093	0.468	0.0144	2.9E-13	12.5

Interval Al (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Al Co (mg/kg)	Al mg Leached	Cumulative Al mg Leached	Cumulative Al Fraction Leached	Al Diffusivity cm^2/sec	Al Leach Index
0.456	0.0833	2	166900	0.238	0.238	0.000031	2.7E-14	13.6
0.479	0.2083	5		0.250	0.488	0.000064	8.9E-14	13.1
2.18	0.7083	17		1.14	1.63	0.000213	3.5E-13	12.5
1.12	1	24		0.584	2.21	0.000290	5.4E-13	12.3
4.78	2	48		2.50	4.71	0.000617	1.5E-12	11.8
5.45	3	72		2.85	7.56	0.00099	3.2E-12	11.5
5.19	4	96		2.71	10.3	0.00135	4.1E-12	11.4
4.89	5	120		2.56	12.8	0.00168	4.7E-12	11.3
4.94	6	144		2.58	15.4	0.00202	5.8E-12	11.2
4.49	7	168		2.35	17.8	0.00233	5.7E-12	11.2
3.89	8	192		2.03	19.8	0.00259	5.0E-12	11.3
4.15	9	216		2.17	22.0	0.00288	6.4E-12	11.2
3.61	10	240		1.89	23.8	0.00312	5.4E-12	11.3
3.25	11	264		1.70	25.5	0.00335	4.8E-12	11.3
18.5	19	456		9.64	35.2	0.00461	3.4E-12	11.5
23.8	47	1128		12.4	47.6	0.00623	9.9E-13	12.0
20.9	91	2184		10.9	58.5	0.00766	6.6E-13	12.2
9.76	107	2568		5.10	63.6	0.008	1.6E-12	11.8

Table G - 7. Leachate Data for HRI/ESTD P-1B Centroid Clay Monolith (Continued)

Interval Si (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Si Co (mg/kg)	Si mg Leached	Cumulative Si mg Leached	Cumulative Si Fraction Leached	Si Diffusivity cm^2/sec	Si Leach Index
16.5	0.0833	2	220562	8.63	8.63	0.00086	2.0E-11	10.7
9.62	0.2083	5		5.03	13.7	0.00135	2.1E-11	10.7
24.6	0.7083	17		12.8	26.5	0.00263	2.5E-11	10.6
8.63	1	24		4.51	31.0	0.00307	1.9E-11	10.7
26.7	2	48		13.9	44.9	0.00446	2.6E-11	10.6
21.6	3	72		11.3	56.2	0.00558	2.9E-11	10.5
17.7	4	96		9.27	65.5	0.00649	2.7E-11	10.6
15.5	5	120		8.10	73.6	0.00730	2.7E-11	10.6
14.7	6	144		7.70	81.3	0.00806	3.0E-11	10.5
14.0	7	168		7.32	88.6	0.00879	3.2E-11	10.5
10.6	8	192		5.53	94.2	0.00933	2.1E-11	10.7
10.3	9	216		5.40	99.6	0.0099	2.3E-11	10.6
8.78	10	240		4.59	104	0.0103	1.8E-11	10.7
8.24	11	264		4.30	108	0.0107	1.8E-11	10.8
52.4	19	456		27.4	136	0.0135	1.6E-11	10.8
61.0	47	1128		31.8	168	0.0166	3.7E-12	11.4
35.1	91	2184		18.3	186	0.0184	1.1E-12	12.0
11.7	107	2568		6.09	192	0.0190	1.3E-12	11.9

Interval P (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	P Co (mg/kg)	P mg Leached	Cumulative P mg Leached	Cumulative P Fraction Leached	P Diffusivity cm^2/sec	P Leach Index
4.86	0.0833	2	1146	2.54	2.54	0.0484	6.5E-08	7.18
2.86	0.2083	5		1.50	4.03	0.0770	6.7E-08	7.17
6.77	0.7083	17		3.54	7.57	0.144	7.1E-08	7.15
2.34	1	24		1.22	8.79	0.168	5.0E-08	7.30
5.88	2	48		3.07	11.9	0.226	4.6E-08	7.33
4.02	3	72		2.10	14.0	0.266	3.7E-08	7.43
2.95	4	96		1.54	15.5	0.296	2.8E-08	7.55
2.23	5	120		1.16	16.7	0.318	2.1E-08	7.69
1.80	6	144		0.940	17.6	0.336	1.6E-08	7.79
1.07	7	168		0.560	18.2	0.346	6.9E-09	8.16
0.912	8	192		0.477	18.6	0.356	5.8E-09	8.24
0.699	9	216		0.365	19.0	0.362	3.8E-09	8.42
0.471	10	240		0.246	19.3	0.367	1.9E-09	8.71
0.397	11	264		0.207	19.5	0.371	1.5E-09	8.82
1.21	19	456		0.632	20.1	0.383	3.1E-10	9.51
0.581	47	1128		0.303	20.4	0.389	1.2E-11	10.9
0.282	91	2184		0.147	20.5	0.392	2.5E-12	11.6
0.100	107	2568		0.0522	20.6	0.393	3.6E-12	11.4

Table G - 8. Leachate Data for HRI/ESTD P-1B Centroid Clay Monolith (Continued)

Interval I (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	I Co (mg/kg)	I mg Leached	Cumulative I mg Leached	Cumulative I Fraction Leached	I Diffusivity cm^2/sec	I Leach Index
1.57	0.0833	2	753	0.819	0.819	0.0238	1.6E-08	7.80
0.917	0.2083	5		0.479	1.30	0.0377	1.6E-08	7.80
1.74	0.7083	17		0.906	2.20	0.0640	1.1E-08	7.96
0.538	1	24		0.281	2.49	0.0721	6.2E-09	8.21
1.03	2	48		0.536	3.02	0.0877	3.3E-09	8.48
0.378	3	72		0.197	3.22	0.0934	7.5E-10	9.12
1.08	4	96		0.566	3.78	0.110	8.7E-09	8.06
0.388	5	120		0.203	3.99	0.116	1.4E-09	8.84
0.0265	6	144		0.0138	4.00	0.116	8.2E-12	11.1
0.0166	7	168		0.00867	4.01	0.116	3.8E-12	11.4
0.0123	8	192		0.00641	4.02	0.117	2.4E-12	11.6
0.0115	9	216		0.00599	4.02	0.117	2.4E-12	11.6
0.0107	10	240		0.00561	4.03	0.117	2.3E-12	11.6
0.0089	11	264		0.00467	4.03	0.117	1.8E-12	11.7
0.0589	19	456		0.0308	4.06	0.118	1.7E-12	11.8
0.0734	47	1128		0.0383	4.10	0.119	4.6E-13	12.3
0.0493	91	2184		0.0258	4.13	0.120	1.8E-13	12.7
0.0104	107	2568		0.0054	4.13	0.120	9.0E-14	13.0

Interval S (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	S Co (mg/kg)	S mg Leached	Cumulative S mg Leached	Cumulative S Fraction Leached	S Diffusivity cm^2/sec	S Leach Index
13.4	0.0833	2	2081	7.03	7.03	0.0738	1.5E-07	6.82
7.84	0.2083	5		4.10	11.1	0.117	1.5E-07	6.82
18.4	0.7083	17		9.62	20.7	0.218	1.6E-07	6.80
6.25	1	24		3.26	24.0	0.252	1.1E-07	6.96
15.2	2	48		7.95	32.0	0.336	9.5E-08	7.02
9.55	3	72		4.99	36.9	0.388	6.3E-08	7.20
6.05	4	96		3.16	40.1	0.421	3.6E-08	7.45
3.81	5	120		1.99	42.1	0.442	1.8E-08	7.74
2.51	6	144		1.31	43.4	0.456	9.7E-09	8.01
0.867	7	168		0.453	43.9	0.461	1.4E-09	8.86
0.718	8	192		0.375	44.2	0.465	1.1E-09	8.96
0.405	9	216		0.212	44.5	0.467	3.9E-10	9.41
0.169	10	240		0.088	44.5	0.468	7.6E-11	10.1
0.100	11	264		0.052	44.6	0.468	2.9E-11	10.5
0.380	19	456		0.198	44.8	0.471	7.6E-12	11.1
0.165	47	1128		0.086	44.9	0.471	3.2E-13	12.5
0.216	91	2184		0.113	45.0	0.473	4.8E-13	12.3
0.100	107	2568		0.0522	45.0	0.473	1.1E-12	12.0

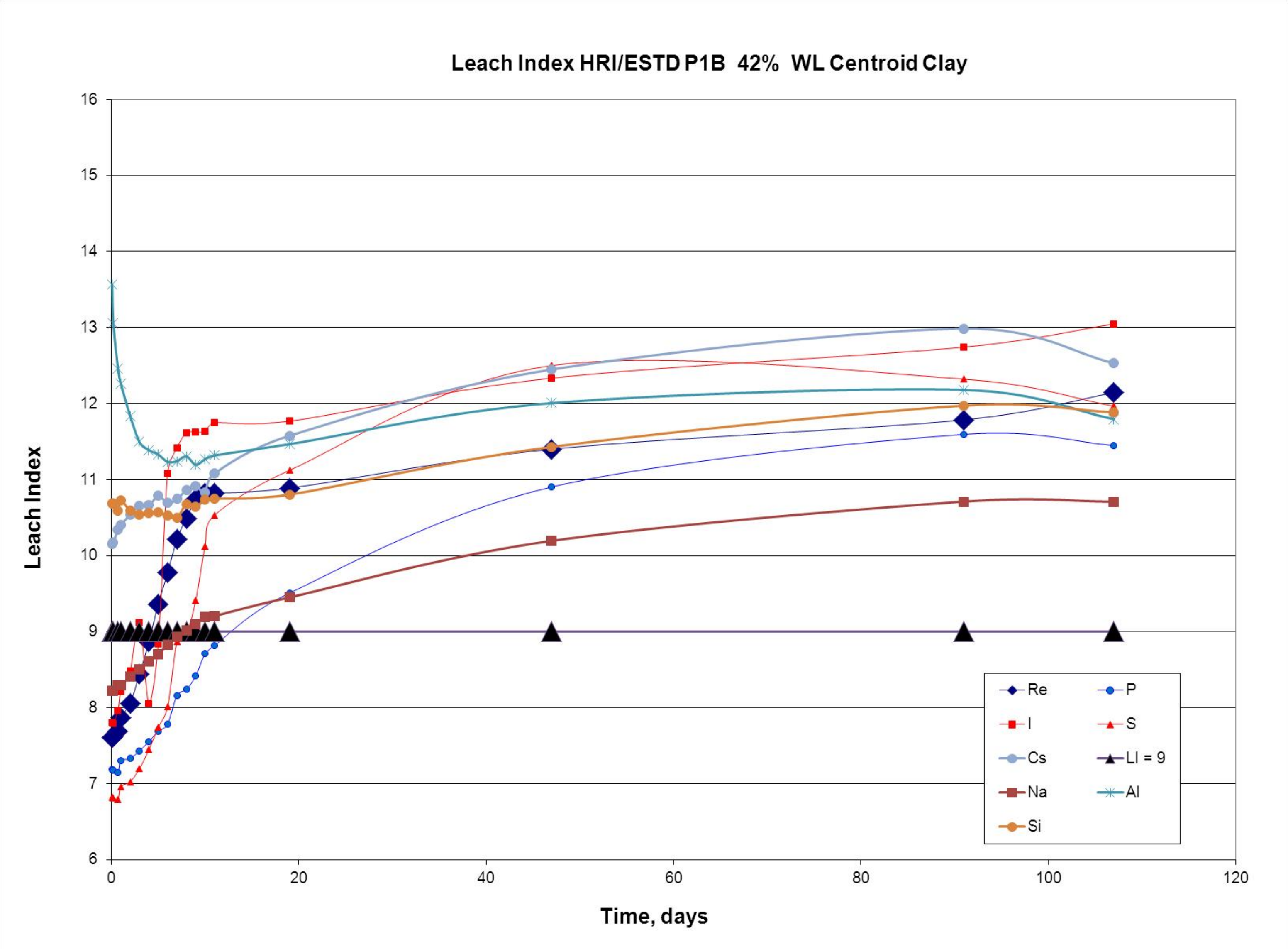

Figure G - 4. Leach Index versus Time for HRI/ESTD P-1B Centroid Clay Monolith

Table G - 9. Leachate Data for HRI/ESTD P-1A Centroid Clay Monolith

Interval Re (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Re Co (mg/kg)	Re mg Leached	Cumulative Re mg Leached	Cumulative Re Fraction Leached	Re Diffusivity cm^2/sec	Re Leach Index
0.258	0.0833	2	225	0.137	0.137	0.0129	4.8E-09	8.32
0.184	0.2083	5		0.097	0.234	0.0222	7.3E-09	8.14
0.406	0.7083	17		0.215	0.449	0.0425	6.7E-09	8.17
0.140	1	24		0.074	0.523	0.0495	4.7E-09	8.33
0.332	2	48		0.176	0.698	0.0662	3.9E-09	8.41
0.212	3	72		0.112	0.810	0.0768	2.7E-09	8.57
0.138	4	96		0.0732	0.884	0.0838	1.6E-09	8.79
0.0985	5	120		0.0521	0.936	0.0887	1.1E-09	8.98
0.0683	6	144		0.0362	0.972	0.0921	6.2E-10	9.21
0.0504	7	168		0.0267	1.00	0.0947	4.0E-10	9.40
0.0391	8	192		0.0207	1.02	0.0966	2.8E-10	9.56
0.0289	9	216		0.0153	1.03	0.0981	1.7E-10	9.77
0.0243	10	240		0.0129	1.05	0.0993	1.4E-10	9.87
0.0198	11	264		0.0105	1.06	0.100	9.9E-11	10.0
0.101	19	456		0.0532	1.11	0.105	5.6E-11	10.2
0.112	47	1128		0.0591	1.17	0.111	1.1E-11	11.0
0.0737	91	2184		0.0390	1.21	0.115	5.1E-12	11.3
0.0166	107	2568		0.0088	1.22	0.115	2.6E-12	11.6
Interval Na (mg/L)	**Cumulative Time (Days)**	**Cumulative Time (Hours)**	**Na Co (mg/kg)**	**Na mg Leached**	**Cumulative Na mg Leached**	**Cumulative Na Fraction Leached**	**Na Diffusivity cm^2/sec**	**Na Leach Index**
194	0.0833	2	149740	103	103	0.0147	6.2E-09	8.21
124	0.2083	5		65.4	168	0.0240	7.4E-09	8.13
246	0.7083	17		131	299	0.0426	5.6E-09	8.25
101	1	24		53.6	353	0.0503	5.6E-09	8.25
233	2	48		123	476	0.0678	4.3E-09	8.36
158	3	72		83.9	560	0.0798	3.4E-09	8.47
119	4	96		63.0	623	0.0888	2.7E-09	8.57
91.9	5	120		48.7	672	0.096	2.1E-09	8.68
73.2	6	144		38.8	710	0.101	1.6E-09	8.79
59.7	7	168		31.6	742	0.106	1.3E-09	8.90
49.3	8	192		26.1	768	0.109	1.0E-09	9.00
42.7	9	216		22.6	791	0.113	8.5E-10	9.07
36.1	10	240		19.1	810	0.115	6.8E-10	9.17
34.0	11	264		18.0	828	0.118	6.7E-10	9.18
171	19	456		90.3	918	0.131	3.7E-10	9.44
172	47	1128		91.1	1009	0.144	6.5E-11	10.2
105	91	2184		55.4	1065	0.152	2.1E-11	10.7
32.4	107	2568		17.2	1082	0.154	2.2E-11	10.7

Table G - 10. Leachate Data for HRI/ESTD P-1A Centroid Clay Monolith (Continued)

Interval Cs (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Cs Co (mg/kg)	Cs mg Leached	Cumulative Cs mg Leached	Cumulative Cs Fraction Leached	Cs Diffusivity cm^2/sec	Cs Leach Index
0.133	0.0833	2	1105	0.0706	0.0706	0.0014	5.4E-11	10.3
0.0826	0.2083	5		0.0438	0.114	0.0022	6.1E-11	10.2
0.149	0.7083	17		0.0792	0.194	0.0037	3.8E-11	10.4
0.103	1	24		0.0545	0.248	0.0048	1.1E-10	10.0
0.123	2	48		0.0654	0.313	0.0061	2.2E-11	10.7
0.0841	3	72		0.0445	0.358	0.0069	1.8E-11	10.8
0.0671	4	96		0.0356	0.393	0.0076	1.6E-11	10.8
0.0526	5	120		0.0279	0.421	0.0081	1.2E-11	10.9
0.0461	6	144		0.0244	0.446	0.0086	1.2E-11	10.9
0.0382	7	168		0.0202	0.466	0.0090	9.5E-12	11.0
0.0320	8	192		0.0169	0.483	0.0093	7.7E-12	11.1
0.0276	9	216		0.0146	0.498	0.0096	6.5E-12	11.2
0.0240	10	240		0.0127	0.510	0.0099	5.5E-12	11.3
0.0214	11	264		0.0113	0.522	0.0101	4.8E-12	11.3
0.0836	19	456		0.0443	0.566	0.0109	1.6E-12	11.8
0.0770	47	1128		0.0408	0.607	0.0117	2.4E-13	12.6
0.0463	91	2184		0.0245	0.631	0.0122	7.5E-14	13.1
0.0170	107	2568		0.0090	0.640	0.0124	1.1E-13	12.9

Interval Al (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Al Co (mg/kg)	Al mg Leached	Cumulative Al mg Leached	Cumulative Al Fraction Leached	Al Diffusivity cm^2/sec	Al Leach Index
0.441	0.0833	2	164995	0.233	0.233	0.00003	2.6E-14	13.6
0.495	0.2083	5		0.262	0.496	0.00006	9.8E-14	13.0
2.24	0.7083	17		1.19	1.68	0.00022	3.8E-13	12.4
1.16	1	24		0.612	2.30	0.00030	6.0E-13	12.2
4.98	2	48		2.64	4.93	0.00064	1.6E-12	11.8
5.63	3	72		2.98	7.92	0.00102	3.5E-12	11.5
5.10	4	96		2.70	10.6	0.00137	4.1E-12	11.4
4.78	5	120		2.53	13.1	0.00170	4.6E-12	11.3
4.55	6	144		2.41	15.6	0.00201	5.1E-12	11.3
4.22	7	168		2.24	17.8	0.00230	5.2E-12	11.3
3.69	8	192		1.95	19.7	0.00255	4.6E-12	11.3
3.59	9	216		1.90	21.6	0.00280	4.9E-12	11.3
3.34	10	240		1.77	23.4	0.00303	4.8E-12	11.3
3.09	11	264		1.64	25.1	0.00324	4.5E-12	11.3
17.6	19	456		9.32	34.4	0.00445	3.2E-12	11.5
23.3	47	1128		12.3	46.7	0.00604	9.8E-13	12.0
21.5	91	2184		11.4	58.1	0.00751	7.2E-13	12.1
10.2	107	2568		5.38	63.5	0.00821	1.8E-12	11.7

Table G - 11. Leachate Data for HRI/ESTD P-1A Centroid Clay Monolith (Continued)

Interval Si (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	Si Co (mg/kg)	Si mg Leached	Cumulative Si mg Leached	Cumulative Si Fraction Leached	Si Diffusivity cm^2/sec	Si Leach Index
17.6	0.0833	2	220209	9.30	9.30	0.00090	2.3E-11	10.6
11.2	0.2083	5		5.94	15.2	0.00148	2.8E-11	10.5
27.2	0.7083	17		14.4	29.7	0.00287	3.2E-11	10.5
9.5	1	24		5.02	34.7	0.00336	2.3E-11	10.6
29.7	2	48		15.7	50.4	0.00488	3.2E-11	10.5
23.6	3	72		12.5	62.9	0.00610	3.5E-11	10.5
18.7	4	96		9.92	72.8	0.00706	3.1E-11	10.5
16.2	5	120		8.60	81.4	0.00789	3.0E-11	10.5
14.1	6	144		7.48	88.9	0.00862	2.8E-11	10.6
12.6	7	168		6.65	95.6	0.00926	2.6E-11	10.6
10.8	8	192		5.72	101	0.00982	2.2E-11	10.7
10.1	9	216		5.33	107	0.0103	2.2E-11	10.7
8.82	10	240		4.67	111	0.0108	1.9E-11	10.7
8.37	11	264		4.43	116	0.0112	1.9E-11	10.7
54.1	19	456		28.6	144	0.0140	1.7E-11	10.8
64.7	47	1128		34.2	179	0.0173	4.2E-12	11.4
40.6	91	2184		21.5	200	0.0194	1.4E-12	11.8
12.9	107	2568		6.83	207	0.0201	1.6E-12	11.8

Interval P (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	P Co (mg/kg)	P mg Leached	Cumulative P mg Leached	Cumulative P Fraction Leached	P Diffusivity cm^2/sec	P Leach Index
4.04	0.0833	2	1078	2.14	2.14	0.0424	5.2E-08	7.29
2.82	0.2083	5		1.49	3.63	0.0719	7.4E-08	7.13
6.29	0.7083	17		3.33	6.97	0.138	7.1E-08	7.15
2.18	1	24		1.15	8.12	0.161	5.0E-08	7.30
5.54	2	48		2.93	11.1	0.219	4.7E-08	7.33
3.82	3	72		2.02	13.1	0.259	3.8E-08	7.42
2.71	4	96		1.44	14.5	0.287	2.7E-08	7.57
2.04	5	120		1.08	15.6	0.309	2.0E-08	7.70
1.61	6	144		0.850	16.4	0.326	1.5E-08	7.83
1.17	7	168		0.622	17.1	0.338	9.5E-09	8.02
0.810	8	192		0.429	17.5	0.346	5.2E-09	8.28
0.621	9	216		0.329	17.8	0.353	3.5E-09	8.46
0.423	10	240		0.224	18.0	0.357	1.8E-09	8.74
0.355	11	264		0.188	18.2	0.361	1.4E-09	8.85
1.06	19	456		0.561	18.8	0.372	2.7E-10	9.56
0.427	47	1128		0.226	19.0	0.377	7.7E-12	11.1
0.268	91	2184		0.142	19.2	0.379	2.6E-12	11.6
0.100	107	2568		0.053	19.2	0.381	4.1E-12	11.4

Table G - 12. Leachate Data for HRI/ESTD P-1A Centroid Clay Monolith (Continued)

Interval I (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	I Co (mg/kg)	I mg Leached	Cumulative I mg Leached	Cumulative I Fraction Leached	I Diffusivity cm^2/sec	I Leach Index
2.41	0.0833	2	753	1.28	1.28	0.0362	3.8E-08	7.42
1.41	0.2083	5		0.748	2.02	0.0574	3.8E-08	7.42
2.84	0.7083	17		1.51	3.53	0.100	2.9E-08	7.53
0.658	1	24		0.348	3.88	0.110	9.3E-09	8.03
1.59	2	48		0.842	4.72	0.134	8.0E-09	8.10
0.583	3	72		0.309	5.03	0.143	1.8E-09	8.74
1.64	4	96		0.870	5.90	0.167	2.0E-08	7.69
0.615	5	120		0.326	6.23	0.176	3.7E-09	8.44
0.0529	6	144		0.0280	6.25	0.177	3.3E-11	10.5
0.0462	7	168		0.0245	6.28	0.178	3.0E-11	10.5
0.0292	8	192		0.0155	6.29	0.178	1.4E-11	10.9
0.0271	9	216		0.0144	6.31	0.179	1.4E-11	10.9
0.0235	10	240		0.0125	6.32	0.179	1.1E-11	10.9
0.0247	11	264		0.0131	6.33	0.179	1.4E-11	10.9
0.137	19	456		0.0726	6.41	0.182	9.4E-12	11.0
0.174	47	1128		0.0919	6.50	0.184	2.6E-12	11.6
0.120	91	2184		0.0636	6.56	0.186	1.1E-12	12.0
0.0285	107	2568		0.0151	6.58	0.186	6.8E-13	12.2

Interval S (mg/L)	Cumulative Time (Days)	Cumulative Time (Hours)	S Co (mg/kg)	S mg Leached	Cumulative S mg Leached	Cumulative S Fraction Leached	S Diffusivity cm^2/sec	S Leach Index
8.27	0.0833	2	1397	4.38	4.38	0.0669	1.3E-07	6.89
5.56	0.2083	5		2.95	7.33	0.112	1.7E-07	6.76
12.4	0.7083	17		6.56	13.9	0.212	1.6E-07	6.79
4.19	1	24		2.22	16.1	0.246	1.1E-07	6.96
10.3	2	48		5.48	21.6	0.330	9.8E-08	7.01
6.43	3	72		3.41	25.0	0.382	6.5E-08	7.19
3.95	4	96		2.09	27.1	0.414	3.4E-08	7.47
2.48	5	120		1.31	28.4	0.434	1.7E-08	7.76
1.95	6	144		1.03	29.4	0.450	1.3E-08	7.88
1.18	7	168		0.625	30.1	0.459	5.7E-09	8.25
0.402	8	192		0.213	30.3	0.462	7.6E-10	9.12
0.206	9	216		0.109	30.4	0.464	2.3E-10	9.64
0.100	10	240		0.0530	30.4	0.465	6.0E-11	10.2
0.100	11	264		0.0530	30.5	0.466	6.6E-11	10.2
0.239	19	456		0.127	30.6	0.468	8.3E-12	11.1
0.324	47	1128		0.172	30.8	0.470	2.7E-12	11.6
0.207	91	2184		0.110	30.9	0.472	9.4E-13	12.0
0.100	107	2568		0.0530	30.9	0.473	2.4E-12	11.6

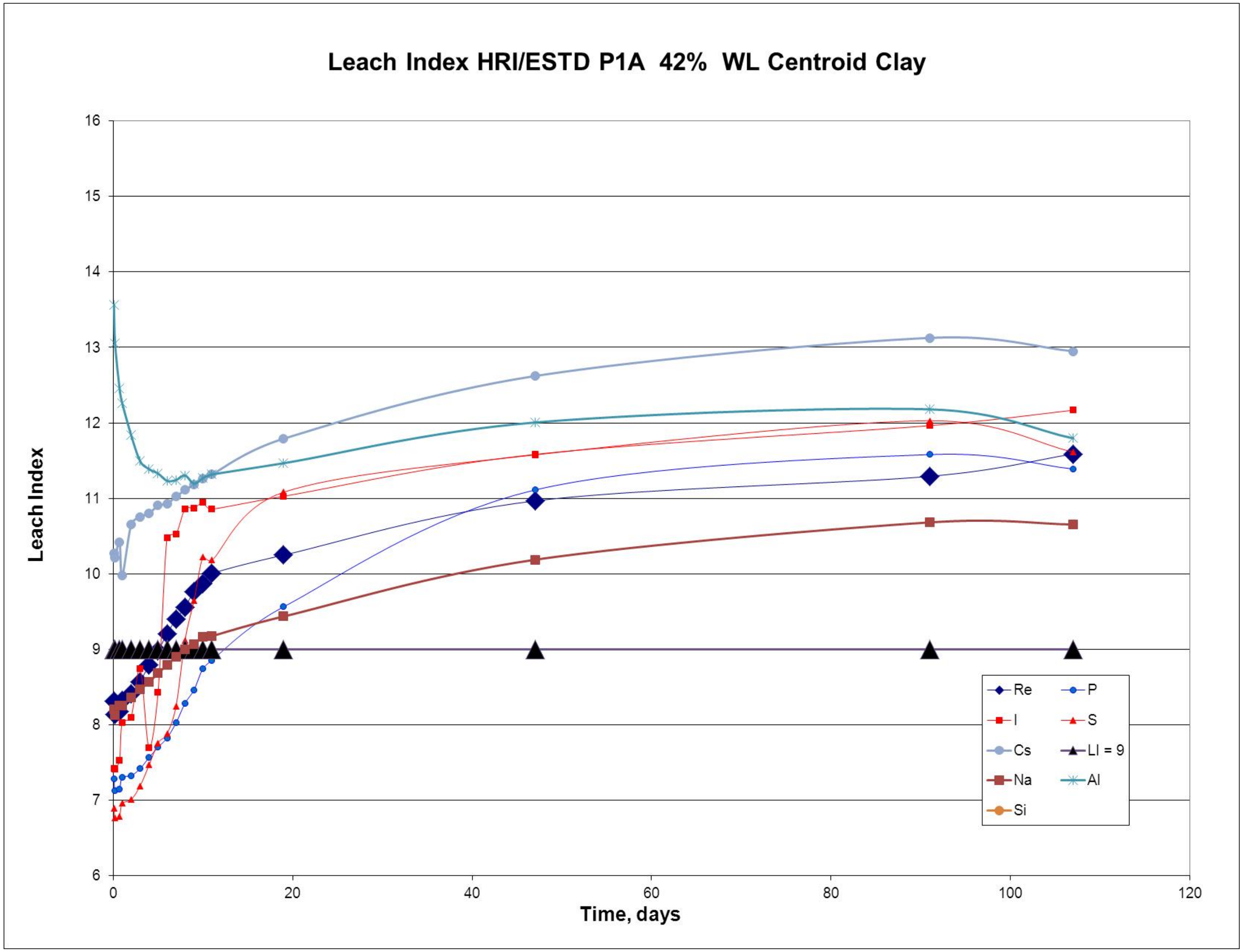

Figure G - 5. Leach Index Versus Time for HRI/ESTD P1A Centroid Clay Monolith

Appendix H. PCT Data

PCT Data for Short Term Tests

All short term PCT data includes ARM and LRM data for comparison to referenced leachate concentrations. Table H – 1 shows as measured leachate concentrations (mg/L) for HRI ESTD granular and fly ash GEO-7 monolith 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 Table H - 2. Similar as measured leachate and corrected leachate data are shown in Table H - 3

and Table H - 4 for the BSR Module B granular short term tests. No ARM glass was included in this short term data set. Similar as measured leachate and corrected leachate data are shown in Table H - 5 and

Table H - 6 for the BSR Module B fly ash GEO-7 monolith short term tests.

As measured leachate and corrected leachate data are shown in Table H - 7 and
Table H - 8 for the BSR Radioactive Module B granular short term tests. Similar as measured leachate and corrected leachate data are shown in Table H - 9 and Table H - 10 for the BSR Radioactive Module B centroid clay monolith short term tests.

These short term PCT data show that all the measured ARM 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 (see green shaded cells in tables below).[1] These data also show that all the measured LRM 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 BSR 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 H - 1. Leachate Data for HRI ESTD Granular and Monolith Short Term PCT

Sample	**Al**	**Cr**	**Fe**	**K**	**Na**	**P**	**Pb**	**S**	**Si**	**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**	**ug/L**	**ug/L**	**ug/L**
Blk-1	<1.00	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	6.36	<1.00	<0.100	<10.0	<10.0			
Blk-2	<1.00	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	4.13	<1.00	<0.100	<10.0	<10.0			
Blk-3	<1.00	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	0.323	<1.00	<0.100	<10.0	<10.0			
Blk-4	<1.00	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	0.237	<1.00	<0.100	<10.0	<10.0			
LRM-1	8.26	<0.100	1.34	<10.0	103	<10.0	<1.00	5.86	55.6	0.760					
LRM-2	8.67	<0.100	1.41	<10.0	99.2	<10.0	<1.00	6.14	57.7	0.827					
LRM-3	8.76	<0.100	1.43	<10.0	99.7	<10.0	<1.00	6.55	58.0	0.879					
ARM-1	3.65	<0.100	<0.100	<10.0	22.3	<10.0	<1.00	5.68	38.9	<0.100					
ARM-2	3.71	<0.100	<0.100	<10.0	22.2	<10.0	<1.00	4.56	39.0	<0.100					
ARM-3	3.64	<0.100	<0.100	<10.0	22.8	<10.0	<1.00	3.40	38.0	<0.100					
P1B-1	95.7	0.160	0.1	10	618	70.8	1	158	35.9	0.1	<10.0	<10.0	1.78E+04	6.04E+03	1.83E+03
P1B-2	95.6	0.218	0.1	10	603	69.1	1	160	34.8	0.1	<10.0	<10.0	1.88E+04	6.14E+03	1.90E+03
P1B-3	95.8	0.184	0.1	10	603	70.4	1	155	37.1	0.1	<10.0	<10.0	1.83E+04	6.14E+03	1.83E+03
P1B GEO-7 Monolith-1	5.8	0.193	<0.100	47.8	2824	70.2	<1.00	94.4	670	<0.100	12.1	<10.4	5.46E+03	2.39E+03	8.99E+02
P1B GEO-7 Monolith-2	4.09	0.19	<0.100	49.1	3113	72.0	<1.00	102	458	<0.100	12.6	<10.5	5.68E+03	2.32E+03	9.05E+02
P1B GEO-7 Monolith-2	7.95	0.264	<0.100	56.6	3399	82.9	<1.00	117	471	<0.100	13.3	<10.6	6.01E+03	2.67E+03	1.04E+03

Table H - 2. Corrected Leachate Data, pH and BET SA for HRI ESTD Granular and Monolith Short Term PCT

Sample ID	**BLK**				**ARM**			**LRM**			**Geo7 4-2**			**P1B**		
Replicate ID	**BLK-1**	**BLK-2**	**BLK-3**	**BLK-4**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**Geo7 4-2-1**	**Geo7 4-2-2**	**Geo7 4-2-3**	**P1B-1**	**P1B-2**	**P1B-3**
Vessel ID	X5	X7	T149	T152	X28	X31	X33	X40	X42	T45	T46	T164	T171	T238	T245	T142
pH	6.71	6.77	6.55	6.45	10.01	10	9.97	10.66	10.68	10.66	12.34	12.38	12.44	11.64	11.62	11.62
Empty Mass (g)	111.159	110.751	114.893	113.087	111.54	111.261	111.267	111.266	111.135	111.004	112.059	115.191	114.42	113.515	113.391	114.407
Mass w/Sample (g)					113.044	112.764	112.772	112.766	112.63	112.496	113.055	116.194	115.414	114.618	114.493	115.506
Mass w/Water and Sample (g)	126.159	125.751	129.893	128.085	127.986	127.736	127.703	127.722	127.591	127.464	122.95	126.123	125.453	125.652	125.521	126.554
Mass w/Lug, Start (g)	126.159	125.751	129.893	128.085	127.986	127.736	127.703	127.722	127.591	127.464	122.95	126.123	125.453	125.652	125.521	126.554
Mass w/Lug, Finish (g)	126.068	125.244	129.802	128.012	127.707	127.633	127.512	127.07	127.403	126.814	122.869	125.913	125.347	125.505	125.465	126.365
Use PCT A Surface Area / Volume?					Yes			Yes								
Measured Surface Area (m^2/g)											15.12			4.1		
Leachate Dilution Factor	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667
Sample Mass (g)	NA	NA	NA	NA	1.504	1.503	1.505	1.5	1.495	1.492	0.996	1.003	0.994	1.103	1.102	1.099
Water Mass (g)	15.00	15.00	15.00	15.00	14.942	14.972	14.931	14.956	14.961	14.968	9.895	9.929	10.039	11.034	11.028	11.048
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	6.1E-03	6.2E-03	6.1E-03	1.4E-02	1.4E-02	1.5E-02	9.7E-03	6.8E-03	1.3E-02	1.6E-01	1.6E-01	1.6E-01
Cr	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	3.2E-04	3.2E-04	4.4E-04	2.7E-04	3.6E-04	3.1E-04
Fe	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.2E-03	2.3E-03	2.4E-03	1.7E-04	1.7E-04	1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04
K	<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	<1.7E-02	<8.0E-02	<8.2E-02	<9.4E-02	1.7E-02	1.7E-02	1.7E-02
Na	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	3.7E-02	3.7E-02	3.8E-02	1.7E-01	1.7E-01	1.7E-01	4.7E+00	5.2E+00	5.7E+00	1.0E+00	1.0E+00	1.0E+00
P	<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	<1.7E-02	1.2E-01	1.2E-01	1.4E-01	1.2E-01	1.2E-01	1.2E-01
Pb	<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	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03
S	1.1E-02	6.9E-03	5.4E-04	3.9E-04	9.5E-03	7.6E-03	5.7E-03	9.8E-03	1.0E-02	1.1E-02	1.6E-01	1.7E-01	2.0E-01	2.6E-01	2.7E-01	2.6E-01
Si	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	6.5E-02	6.5E-02	6.3E-02	9.3E-02	9.6E-02	9.7E-02	1.1E+00	7.6E-01	7.9E-01	6.0E-02	5.8E-02	6.2E-02
Zr	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.3E-03	<1.4E-03	<1.5E-03	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04
Cl	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02							<1.2E-02	<1.3E-02	<1.3E-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	<1.1E-02	<1.1E-02	<1.0E-02	<1.0E-02	<1.0E-02
I											5.5E-03	5.7E-03	6.0E-03	1.8E-02	1.9E-02	1.8E-02
Cs											4.0E-03	3.9E-03	4.5E-03	1.0E-02	1.0E-02	1.0E-02
Re											1.5E-03	1.5E-03	1.7E-03	3.1E-03	3.2E-03	3.1E-03

Table H - 3. Leachate Data for BSR Module B Granular Short Term PCT

Sample	**Al**	**Fe**	**K**	**Na**	**P**	**Pb**	**S**	**Si**	**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**	**ug/L**	**ug/L**	**ug/L**
BLK-1	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	<0.100	<0.100	<0.100	<10.0	<10.0			
BLK-2	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	<0.100	<0.100	<0.100	<10.0	<10.0			
LRM-1	7.73	<0.100	<0.100	87.3	<1.00	<1.00	<0.100	40.2	0.112					
LRM-2	8.03	<0.100	<0.100	86.4	<1.00	<1.00	<0.100	40.5	0.118					
LRM-3	8.17	<0.100	<0.100	89.2	<1.00	<1.00	<0.100	41.1	0.118					
MOD-B-1	88.2	2.03	<0.100	348	63.8	<1.00	31.0	38.0	0.324	13.9	23.7	1.15E+03	4.96E+03	6.46E+02
MOD-B-2	86.8	1.54	<0.100	377	62.9	<1.00	33.7	38.2	0.407	13.3	24.3	2.80E+02	5.07E+03	6.52E+02
MOD-B-3	87.1	9.75	<0.100	358	63.3	<1.00	33.3	38.5	0.548	14.3	25.7	2.90E+02	5.22E+03	7.01E+02
MOD-B-4	82.3	1.02	<0.100	344	61.9	<1.00	32.6	34.7	0.223	18.4	26.6	2.79E+02	5.03E+03	6.83E+02

Table H - 4. Corrected Leachate Data, pH and BET SA for BSR Module B Granular Short Term PCT

Sample ID	**BLK**		**LRM**			**MODULE-B**			
Replicate ID	**BLK-1**	**BLK-2**	**LRM-1**	**LRM-2**	**LRM-3**	**MOD-B-1**	**MOD-B-2**	**MOD-B-3**	**MOD-B-4**
Vessel ID	177	178	179	180	183	184	187	192	193
pH	6.53	6.58	10.76	10.76	10.76	11.4	11.41	11.4	11.39
Empty Mass (g)	124.998	127.342	125.826	125.705	126.095	125.911	126.863	125.043	126.555
Mass w/Sample (g)			127.328	127.204	127.599	127.413	128.368	126.546	128.055
Mass w/Water and Sample (g)	139.999	142.344	142.329	142.206	142.6	142.409	143.368	141.545	143.055
Mass w/Lug, Start (g)	339.433	340.694	342.803	341.556	344.229	343.032	344.477	341.307	343.106
Mass w/Lug, Finish (g)	339.393	340.68	342.737	341.55	344.056	343.031	344.464	341.304	343.053
Use PCT A Surface Area / Volume?			Yes						
Measured Surface Area (m^2/g)						3.33			
Leachate Dilution Factor	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667
Sample Mass (g)	NA	NA	1.502	1.499	1.504	1.502	1.505	1.503	1.5
Water Mass (g)	15.001	15.002	15.001	15.002	15.001	14.996	15	14.999	15
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	<1.7E-04	<1.7E-04	1.3E-02	1.3E-02	1.4E-02	1.5E-01	1.4E-01	1.5E-01	1.4E-01
Cr	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.1E-03	2.1E-03	2.2E-03	2.1E-03
Fe	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	3.4E-03	2.6E-03	1.6E-02	1.7E-03
K	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04
Na	<1.7E-04	<1.7E-04	1.5E-01	1.4E-01	1.5E-01	5.8E-01	6.3E-01	6.0E-01	5.7E-01
P	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	<1.7E-03	1.1E-01	1.0E-01	1.1E-01	1.0E-01
Pb	<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
S	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	5.2E-02	5.6E-02	5.6E-02	5.4E-02
Si	<1.7E-04	<1.7E-04	6.7E-02	6.8E-02	6.9E-02	6.3E-02	6.4E-02	6.4E-02	5.8E-02
Zr	<1.7E-04	<1.7E-04	1.9E-04	2.0E-04	2.0E-04	5.4E-04	6.8E-04	9.1E-04	3.7E-04
Cl						1.4E-02	1.3E-02	1.4E-02	1.8E-02
F						2.4E-02	2.4E-02	2.6E-02	2.7E-02
I						1.2E-03	2.8E-04	2.9E-04	2.8E-04
Cs						8.3E-03	8.5E-03	8.7E-03	8.4E-03
Re						1.1E-03	1.1E-03	1.2E-03	1.1E-03

Table H - 5. Leachate Data for BSR Module B Monolith Short Term PCT

Sample	Al	Ca	Cr	Fe	K	Na	P	Pb	S	Si	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	<1.00	<1.00	<0.100	<0.100	<10.0	<0.100	<10.0	<0.100	<0.100	<1.00	<0.100	<10.0	<10.0			
BLK-2	<1.00	<1.00	<0.100	<0.100	<10.0	<0.100	<10.0	<0.100	<0.100	<1.00	<0.100	<10.0	<10.0			
ARM-1	4.94	<1.00	<0.100	<0.100	<10.0	20.4	<10.0	<0.100	<0.100	35.5	<0.100					
ARM-2	4.67	<1.00	<0.100	<0.100	<10.0	19.7	<10.0	<0.100	<0.100	34.3	<0.100					
ARM-3	4.65	<1.00	<0.100	<0.100	<10.0	19.9	<10.0	<0.100	<0.100	34.5	<0.100					
LRM-1	8.67	<1.00	0.118	1.23	<10.0	93.2	<10.0	<0.100	<0.100	49	0.701					
LRM-2	8.71	<1.00	0.128	1.26	<10.0	95.6	<10.0	<0.100	<0.100	49.1	0.779					
LRM-3	8.73	<1.00	0.115	1.22	<10.0	96.9	<10.0	<0.100	<0.100	49.6	0.801					
Mod B Sim Mono-1	17.9	1	0.653	0.405	34.4	3270	24.7	1	120	281	0.1	<10.0	<10.0	1180	1960	1330
Mod B Sim Mono-2	16	1	0.554	0.286	32.6	3670	23.1	1	107	371	0.1	<10.0	<10.0	1130	2060	1460
Mod B Sim Mono-3	14.1	1	0.458	0.246	31.8	3180	22.6	1	100	375	0.1	<10.0	<10.0	1030	1910	1270

Table H - 6. Corrected Leachate Data, pH and BET SA for BSR Module B Monolith Short Term PCT

Sample ID	**BLK**		**ARM**			**LRM**			**MODULE B SIMULANT**		
Replicate ID	**BLK-1**	**BLK-2**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**MOD B SIM-1**	**MOD B SIM-2**	**MOD B SIM-3**
Vessel ID	P144	P146	P152	P159	P183	P185	P186	P187	P188	P189	P190
pH	6.61	6.58	10.26	10.26	10.31	10.95	10.98	10.98	12.55	12.61	12.52
Empty Mass (g)	121.235	121.198	120.105	120.644	121.144	119.928	122.963	121.394	122.425	120.115	121.177
Mass w/Sample (g)			121.605	122.145	122.645	121.427	124.463	122.894	123.925	121.613	122.677
Mass w/Water and Sample (g)	136.237	136.198	135.105	137.106	137.644	136.426	139.465	137.895	138.927	136.614	137.675
Mass w/Lug, Start (g)	336.668	335.979	335.892	336.621	337.698	336.511	340.224	339.216	338.733	336.254	337.224
Mass w/Lug, Finish (g)	336.438	335.874	335.842	336.614	337.692	336.504	340.217	339.21	338.69	335.843	337.218
Use PCT A Surface Area / Volume?			Yes			Yes					
Measured Surface Area (m^2/g)									4.23		
Leachate Dilution Factor	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667
Sample Mass (g)	15.002	15	1.5	1.501	1.501	1.499	1.5	1.5	1.5	1.498	1.5
Water Mass (g)	136.237	136.198	13.5	14.961	14.999	14.999	15.002	15.001	15.002	15.001	14.998
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	<1.7E-03	<1.7E-03	8.2E-03	7.8E-03	7.8E-03	1.4E-02	1.5E-02	1.5E-02	3.0E-02	2.7E-02	2.4E-02
Ca	<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	<1.7E-03	<1.7E-03
Cr	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.0E-04	2.1E-04	1.9E-04	1.1E-03	9.2E-04	7.6E-04
Fe	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.1E-03	2.1E-03	2.0E-03	6.8E-04	4.8E-04	4.1E-04
K	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	5.7E-02	5.4E-02	5.3E-02
Na	<1.7E-04	<1.7E-04	3.4E-02	3.3E-02	3.3E-02	1.6E-01	1.6E-01	1.6E-01	5.5E+00	6.1E+00	5.3E+00
P	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	<1.7E-02	4.1E-02	3.9E-02	3.8E-02
Pb	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-03	<1.7E-03	<1.7E-03
S	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	2.0E-01	1.8E-01	1.7E-01
Si	<1.7E-03	<1.7E-03	5.9E-02	5.7E-02	5.8E-02	8.2E-02	8.2E-02	8.3E-02	4.7E-01	6.2E-01	6.3E-01
Ti	<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	<1.7E-03	<1.7E-03
Zr	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	<1.7E-04	1.2E-03	1.3E-03	1.3E-03	<1.7E-04	<1.7E-04	<1.7E-04
Cl	<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
I									1.2E-03	1.1E-03	1.0E-03
Cs									3.3E-03	3.4E-03	3.2E-03
Re									2.2E-03	2.4E-03	2.1E-03

Table H - 7. Leachate Data for BSR Radioactive Module B Granular Short Term PCT

	Al	Cr	Fe	K	Na	P	Pb	S	Si	Zr	Cl	F	I-129	Cs-137	Tc-99	Re	I-125	I-127
	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	dpm/mL	ug/L
Blk-1	<0.19				<0.17				<0.19									
Blk-2	<0.19				<0.17				<0.19									
ARM-1					6.69				11.8									
ARM-2					6.98				12									
ARM-3					7.05				12.2									
LRM-1					31.9				14.2									
LRM-2					33.5				14.9									
LRM-3					31				14.1									
RAD-MODB-G-1	57.9	0.247	0.317	<0.698	154	18.8	<1.21	26.6	8.54	<0.009	<10	<10	<0.75	241	25.5	2.97E+02	<0.384	1.47E+02
RAD-MODB-G-2	54.8	0.233	0.387	<0.698	144	17.5	<1.21	24.6	8.98	<0.009	<10	<10	<1.67	211	18.7	3.30E+02	<0.862	1.37E+02
RAD-MODB-G-3	54	0.226	0.347	<0.698	142	17.7	<1.21	24.9	8.54	<0.009	<10	<10	<0.639	255	14.9	2.99E+02	<0.348	1.31E+02

Table H - 8. Corrected Leachate Data, pH and BET SA for BSR Radioactive Module B Granular Short Term PCT

Sample ID	**Blk**		**ARM**			**LRM**			**RADIOACTIVE MOD B GRANULAR**		
Replicate ID	**Blk-1**	**Blk-2**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**RAD-MOD B-G-1**	**RAD-MOD B-G-2**	**RAD-MOD B-G-3**
Vessel ID	T143	T154	T155	T166	T167	T181	T185	T199	T207	T214	T215
pH	6.76	6.61	10.03	10.06	10.07	10.59	10.61	10.6	11.22	11.26	11.26
Empty Mass (g)	110.957	113.16	113.318	115.292	108.685	114.662	110.809	113.293	114.951	115.416	114.604
Mass w/Sample (g)	NA	NA	114.433	116.395	109.781	115.765	111.895	113.393	116.22	116.58	115.817
Mass w/Water and Sample (g)	121.962	124.189	125.433	127.429	120.802	126.77	122.946	125.411	127.178	127.711	126.856
Mass w/Lug, Start (g)	121.962	124.189	125.433	127.429	120.802	126.77	122.946	125.411	127.178	127.711	126.856
Mass w/Lug, Finish (g)	121.888	124.057	125.348	127.273	120.598	126.691	122.88	125.288	127.077	127.604	126.728
Use PCT A Surface Area / Volume?			Yes			Yes					
Measured Surface Area (m^2/g)									3.5		
Leachate Dilution Factor	5	5	5	5	5	5	5	5	5	5	5
Sample Mass (g)	NA	NA	1.115	1.103	1.096	1.103	1.086	0.1	1.269	1.164	1.213
Water Mass (g)	121.962	124.189	11	11.034	11.021	11.005	11.051	12.018	10.958	11.131	11.039
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	<9.40E-04	<9.40E-04							2.90E-01	2.74E-01	2.70E-01
Cr									1.24E-03	1.17E-03	1.13E-03
Fe									1.59E-03	1.94E-03	1.74E-03
K									<3.49E-03	<3.49E-03	<3.49E-03
Na	<8.65E-04	<8.65E-04	3.35E-02	3.49E-02	3.53E-02	1.60E-01	1.68E-01	1.55E-01	7.70E-01	7.20E-01	7.10E-01
P									9.40E-02	8.75E-02	8.85E-02
Pb									<6.05E-03	<6.05E-03	<6.05E-03
S									1.33E-01	1.23E-01	1.25E-01
Si	<9.55E-04	<9.55E-04	5.90E-02	6.00E-02	6.10E-02	7.10E-02	7.45E-02	7.05E-02	4.27E-02	4.49E-02	4.27E-02
Zr									<4.50E-05	<4.50E-05	<4.50E-05
Cl									<5.00E-02	<5.00E-02	<5.00E-02
F									<5.00E-02	<5.00E-02	<5.00E-02
I-129									<9.57E-06	<2.13E-05	<8.15E-06
Cs-137									6.24E-09	5.46E-09	6.60E-09
Tc-99									3.39E-06	2.48E-06	1.98E-06
Re									1.49E-03	1.65E-03	1.50E-03
I-127									7.35E-04	6.85E-04	6.55E-04
I-125									<4.98E-14	<1.12E-13	<4.51E-14

Table H - 9. Leachate Data for BSR Radioactive Module B Centroid Clay Monolith Short Term PCT

	Al	B	Ca	Cr	Fe	K	Na	P	Pb	S	Si	Ti	Zr	I-129	Cs-137	Tc-99	Re	I-127
	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	dpm/mL	dpm/mL	dpm/mL	ug/L	ug/L
Blk-1	0.172	0.299	0.0632	<0.0892	<0.0492	<0.952	1.38	<0.486	<1.84	<24	0.769	<0.0232	<0.0196					
Blk-2	<0.16	0.199	0.0672	<0.0892	<0.0492	<0.952	1.35	<0.486	<1.84	<24	0.769	<0.0232	<0.0196					
ARM-1	4.82	10.4	0.294	<0.0892	<0.0492	<0.952	23.9	0.599	<1.84	<24	38.4	<0.0232	<0.0196					
ARM-2	4.93	11.3	0.154	<0.0892	<0.0492	<0.952	26	0.657	<1.84	<24	41	<0.0232	<0.0196					
ARM-3	4.61	11.3	0.169	<0.0892	<0.0492	<0.952	25.6	0.64	<1.84	<24	42.5	<0.0232	<0.0196					
LRM-1	11.4	19.7	0.152	0.233	1.84	1.93	125	0.558	<1.84	<24	59.9	0.1	1.12					
LRM-2	11.4	21	0.157	0.246	1.94	1.57	130	0.706	<1.84	<24	62.1	0.098	1.18					
LRM-3	11.3	19.5	0.163	0.238	1.75	1.77	123	0.602	<1.84	<24	60.2	0.0892	1.11					
RAD Mod B Mono-65-1	14.3	1.68	0.125	0.228	0.0858	<0.952	805	8.86	<1.84	25.4	14.9	<0.0232	<0.0196	<1.66	<12.0	<18	270.87	57.00
RAD Mod B Mono-65-2	14.6	0.889	0.105	0.269	0.0654	<0.952	948	10.7	<1.84	31.8	15.2	<0.0232	<0.0196	<1.19	19.1	<19.1	321.24	58.70
RAD Mod B Mono-65-3	14.1	0.779	0.102	0.236	0.0706	<0.952	835	9.57	<1.84	28.1	15.3	<0.0232	<0.0196	<2.12	<15.6	<16.5	285.41	66.80

Table H - 10. Corrected Leachate Data, pH and BET SA for BSR Radioactive Module B Centroid Clay Monolith Short Term PCT

Sample ID	**Blk**		**ARM**			**LRM**			**RAD Mod B Mono-65**		
Replicate ID	**Blk-1**	**Blk-2**	**ARM-1**	**ARM-2**	**ARM-3**	**LRM-1**	**LRM-2**	**LRM-3**	**RAD Mod B Mono-65-1**	**RAD Mod B Mono-65-2**	**RAD Mod B Mono-65-3**
Vessel ID	X4	X5	X7	X8	X9	X12	X16	X37	X31	X33	X37
pH	6.81	6.9	9.37	9.36	9.38	10.15	10.14	10.14	10.33	10.32	10.34
Empty Mass (g)	111.324	111.16	110.754	111.485	111.171	111.245	111.406	111.229	111.263	111.267	111.576
Mass w/Sample (g)	NA	NA	112.253	112.982	112.665	112.745	112.912	112.734	112.21	112.297	112.578
Mass w/Water and Sample (g)	126.325	126.164	127.248	127.986	127.667	127.741	127.91	127.725	122.998	122.392	122.631
Mass w/Lug, Start (g)	126.325	126.164	127.248	127.986	127.667	127.741	127.91	127.725	122.998	122.392	122.631
Mass w/Lug, Finish (g)	126.219	125.93	126.948	127.123	127.364	127.506	127.382	127.295	122.227	122.323	122.51
Use PCT A Surface Area / Volume?			Yes			Yes					
Measured Surface Area (m^2/g)									6.82		
Leachate Dilution Factor	1	1	1.340	1.356	1.314	1.328	1.335	1.347	2.223*	1.969*	2.120*
Sample Mass (g)	NA	NA	1.499	1.497	1.494	1.5	1.506	1.505	0.947	1.03	1.002
Water Mass (g)	15.001	15.004	14.995	15.004	15.002	14.996	14.998	14.991	10.788	10.095	10.053
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	1.7E-04	<1.6E-04	6.5E-03	6.7E-03	6.1E-03	1.5E-02	1.5E-02	1.5E-02	3.2E-02	2.9E-02	3.0E-02
B	3.0E-04	2.0E-04	1.4E-02	1.5E-02	1.5E-02	2.6E-02	2.8E-02	2.6E-02	3.7E-03	1.8E-03	1.7E-03
Ca	6.3E-05	6.7E-05	3.9E-04	2.1E-04	2.2E-04	2.0E-04	2.1E-04	2.2E-04	2.8E-04	2.1E-04	2.2E-04
Cr	<8.9E-05	<8.9E-05	<1.2E-04	<1.2E-04	<1.2E-04	3.1E-04	3.3E-04	3.2E-04	5.1E-04	5.3E-04	5.0E-04
Fe	<4.9E-05	<4.9E-05	<6.6E-05	<6.7E-05	<6.5E-05	2.4E-03	2.6E-03	2.4E-03	1.9E-04	1.3E-04	1.5E-04
K	<9.5E-04	<9.5E-04	<1.3E-03	<1.3E-03	<1.3E-03	2.6E-03	2.1E-03	2.4E-03	<2.1E-03	<1.9E-03	<2.0E-03
Na	1.4E-03	1.4E-03	3.2E-02	3.5E-02	3.4E-02	1.7E-01	1.7E-01	1.7E-01	1.8E+00	1.9E+00	1.8E+00
P	<4.9E-04	<4.9E-04	8.0E-04	8.9E-04	8.4E-04	7.4E-04	9.4E-04	8.1E-04	2.0E-02	2.1E-02	2.0E-02
Pb	<1.8E-03	<1.8E-03	<2.5E-03	<2.5E-03	<2.4E-03	<2.4E-03	<2.5E-03	<2.5E-03	<4.1E-03	<3.6E-03	<3.9E-03
S	<2.4E-02	<2.4E-02	<3.2E-02	<3.3E-02	<3.2E-02	<3.2E-02	<3.2E-02	<3.2E-02	5.6E-02	6.3E-02	6.0E-02
Si	7.7E-04	7.7E-04	5.1E-02	5.6E-02	5.6E-02	8.0E-02	8.3E-02	8.1E-02	3.3E-02	3.0E-02	3.2E-02
Ti	<2.3E-05	<2.3E-05	<3.1E-05	<3.1E-05	<3.0E-05	1.3E-04	1.3E-04	1.2E-04	<5.2E-05	<4.6E-05	<4.9E-05
Zr	<2.0E-08	<2.0E-08	<2.6E-08	<2.7E-08	<2.6E-08	1.5E-06	1.6E-06	1.5E-06	<4.4E-08	<3.9E-08	<4.2E-08
I-127									1.3E-04	1.2E-04	1.5E-04
I-129									<9.9E-06	<7.7E-06	<1.3E-05
Cs-137									<2.2E-10	1.9E-10	<2.1E-10
Tc-99									<1.1E-06	<1.0E-06	<9.3E-07
Re									6.0E-04	6.3E-04	6.1E-04

* Leachate dilution factor for I-129 and I-127 are 2.345, 2.542 and 2.340

PCT Data for Long Term Tests

The as measured and corrected leachate data for long term PCTs for the HRI ESTD granular and fly ash GEO-7 monoliths are shown in Table H - 11 and Table H - 12. Similar as measured and corrected leachate data for long term PCTs for the BSR Module B granular and fly ash GEO-7 monoliths are shown in Table H - 13 and Table H - 14. These long term tests conducted for up to twelve months did not include any ARM or LRM samples.

Table H - 11. Leachate Data for HRI ESTD Granular and Fly Ash GEO-7 Monolith Long Term

Sample	Al	Ca	Cr	Fe	K	Na	P	Pb	S	Si	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
1mo BLK-1	<1.00	<10.0	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	<1.00	<1.00	<0.100	<10.0	<10.0			
1mo-a BLK-1a	<1.00	<1.00	<0.100	<0.100	<10.0	<10.0	<10.0	<1.00	<1.00	<1.00	<0.100	<10.0	<10.0	4.00	3.91	1.00
3mo-a BLK-4a	<1.00	<1.00	<0.100	<0.100	<10.0	<10.0	<1.00	<1.00	<1.00	<1.00	<0.100	<10.0	<10.0			
3mo BLK-5	<1.00	<1.00	<0.100	0.349	<10.0	8.24	<1.00	<1.00	<1.00	<1.00	<1.00	<10.0	<10.0			
6mo BLK-2	<1.00	<1.00	<0.100	<0.100	<10.0	<10.0	<1.00	<1.00	<1.00	<1.00	<0.100	<10.0	<10.0			
6mo-a BLK-3a	<1.00	<1.00	<0.100	<0.100	<10.0	<10.0	<1.00	<1.00	<1.00	<1.00	<1.00	<10.0	<10.0			
12mo BLK-4	<1.00	<1.00	<0.100	<0.100	<0.100	<10.00	<10.00	<1.00	<1.00	<1.00	<1.00	<10.0	<10.0		7.69	
12mo BLK-2a	<1.00	<1.00	<0.100	<0.100	<10.0	<10.0	<1.00	<1.00	<1.00	<1.00	<1.00	<10.0	<10.0		11.9	
1mo HRI Geo7 4-2-2	73.4	<10.0	2.57	<0.100	54.6	3930	60.8	1.75	150	133	<0.100	51.2	<10.0	3.59E+03	1360	513
1mo HRI Geo7 4-2-8	7.11	<10.0	0.169	<0.100	22.8	1708	35.5	1.07	49.9	335	<0.100	11.1	<10.0	8.48E+04	3520	8950
3mo HRI Geo7 4-2-1	42.5	<1.00	3.75	0.388	50.9	2650	43.7	<1.00	161	32.5	<1.00	106	<10.0	6.43E+04	2470	6490
3mo HRI Geo7 4-2-3	60.6	<1.00	3.56	0.386	49.1	3500	40.9	<1.00	150	25.9	<1.00	98.3	<10.0	2.57E+04	2640	2980
6mo HRI Geo7 4-2-4	13.8	<1.00	4.41	<0.100	64.4	2760	50.9	<1.00	198	26.2	<0.100	124	<10.0	8.18E+04	3600	8880
6mo HRI Geo7 4-2-5	13.9	<1.00	4.35	<0.100	65.0	2680	50.8	<1.00	193	77.6	<0.100	123	<10.0	6.83E+04	2650	7350
12mo HRI Geo7 4-2-8a	86.1	<1.00	0.746	<0.100	<10.0	863	61.5	<1.00	158	6.7	<1.00	178	<10.0	1.29E+05	3030	1.68E +04
1mo P1-B gran-1a	107	<1.00	0.644	<0.100	<10.0	736	66.3	<1.00	176	25.2	<0.100	107	<10.0	3.34E+04	9320	2990
1mo P1-B gran-8a	105	<1.00	0.608	<0.100	<10.0	716	64.6	<1.00	175	26.5	<0.100	107	<10.0	3.13E+04	8610	2810
3mo P1-B gran-4a	106	<1.00	<0.100	<0.100	<10.0	782	64.2	<1.00	151	16.6	<0.100	<10.0	<10.0	3.37E+04	7470	2960
3mo P1-B gran-6a	108	<1.00	<0.100	<0.100	<10.0	684	54.3	<1.00	115	19.8	<0.100	<10.0	<10.0	2.89E+04	5850	2380
6mo P1-B gran-3a	110	<1.00	0.774	<0.100	<10.0	861	71.5	<1.00	168	12.6	<1.00	12.2	<10.0	3.73E+04	9390	3380
6mo P1-B gran-7a	109	<1.00	0.732	<0.100	<10.0	836	69.1	<1.00	175	13.2	<1.00	11.5	<10.0	3.31E+04	7890	3050
12mo P1-B-gran-2a	53.3	<1.00	3.08	<0.100	12.2	2470	50	<1.00	216	3.43	<1.00	<10.0	<10.0	2.99E+04	4550	2730
12mo P1-B-gran-5a	112	<1.00	2.55	<0.100	<10.0	443	7.16	<1.00	102	4.88	<1.00	<10.0	<10.0	3.71E+04	1070	3090

Table H - 12. Corrected Leachate Data, pH and BET SA for HRI ESTD Granular and Monolith Long Term PCT

Sample ID	**1mo HRI Geo7 4-2**		**3mo HRI Geo7 4-2**		**6mo HRI Geo7 4-2**		**12mo HRI Geo7 4-2**
Replicate ID	**1mo HRI Geo7 4-2-2**	**1mo HRI Geo7 4-2-8**	**3mo HRI Geo7 4-2-1**	**3mo HRI Geo7 4-2-3**	**6mo HRI Geo7 4-2-4**	**6mo HRI Geo7 4-2-5**	**12mo HRI Geo7 4-2-8a**
Vessel ID	X45	T86	X38	T49	T52	T54	X15
pH	12.58	12.32	12.49	12.49	12.77	12.81	11.94
Empty Mass (g)	111.336	113.323	111.21	115.346	114.704	113.038	111.351
Mass w/Sample (g)	112.337	114.31	112.207	116.34	115.704	114.028	112.356
Mass w/Water and Sample (g)	122.308	134.38	122.223	126.504	125.686	124.018	122.3
Mass w/Lug, Start (g)	122.308	134.38	122.223	126.504	125.686	124.018	122.3
Mass w/Lug, Finish (g)	122.076	134.015	121.137	125.559	124.033	122.369	120.781
Use PCT A Surface Area / Volume?							
Measured Surface Area (m^2/g)	15.12		15.12		15.12		15.12
Leachate Dilution Factor	2	2	2	2	2	2	2
Sample Mass (g)	1.001	0.987	0.997	0.994	1	0.99	1.005
Water Mass (g)	9.971	20.07	10.016	10.164	9.982	9.99	9.944
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	1.5E-01	1.4E-02	8.5E-02	1.2E-01	2.8E-02	2.8E-02	1.7E-01
Ca	<2.0E-02	<2.0E-02	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
Cr	5.1E-03	3.4E-04	7.5E-03	7.1E-03	8.8E-03	8.7E-03	1.5E-03
Fe	<2.0E-04	<2.0E-04	7.8E-04	7.7E-04	<2.0E-04	<2.0E-04	<2.0E-04
K	1.1E-01	4.6E-02	1.0E-01	9.8E-02	1.3E-01	1.3E-01	<2.0E-02
Na	7.9E+00	3.4E+00	5.3E+00	7.0E+00	5.5E+00	5.4E+00	1.7E+00
P	1.2E-01	7.1E-02	8.7E-02	8.2E-02	1.0E-01	1.0E-01	1.2E-01
Pb	3.5E-03	2.1E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
S	3.0E-01	1.0E-01	3.2E-01	3.0E-01	4.0E-01	3.9E-01	3.2E-01
Si	2.7E-01	6.7E-01	6.5E-02	5.2E-02	5.2E-02	1.6E-01	1.3E-02
Ti	<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-03	<2.0E-03	<2.0E-04	<2.0E-04	<2.0E-03
Cl	5.1E-02	1.1E-02	1.1E-01	9.8E-02	1.2E-01	1.2E-01	1.8E-01
F	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
I	2.6E-02	3.6E-03	6.8E-02	6.4E-02	8.5E-02	8.2E-02	1.3E-01
Cs	5.3E-03	2.7E-03	5.3E-03	4.9E-03	7.0E-03	7.2E-03	6.1E-03
Re	6.0E-03	1.0E-03	1.5E-02	1.3E-02	1.8E-02	1.8E-02	3.4E-02

Table H - 12. Corrected Leachate Data, pH and BET SA for HRI ESTD Granular and Monolith Long Term PCT (Continued)

Sample ID	**1mo P1-B gran**		**3mo P1-B gran**		**6mo P1-B gran**		**12mo P1-B-gran**	
Replicate ID	**1mo P1-B gran-1a**	**1mo P1-B gran-8a**	**3mo P1-B gran-4a**	**3mo P1-B gran-6a**	**6mo P1-B gran-3a**	**6mo P1-B gran-7a**	**12mo P1-B-gran-2a**	**12mo P1-B-gran-5a**
Vessel ID	X16	X43	X21	X27	20	X30	X19	X22
pH	11.53	11.59	11.29	11.49	10.59	10.64	10.26	10.32
Empty Mass (g)	111.4	111.284	111.018	111.456	111.698	111.205	111.296	112.436
Mass w/Sample (g)	112.395	112.282	112.012	112.456	112.704	112.207	112.292	113.438
Mass w/Water and Sample (g)	122.358	122.268	122.015	122.221	122.69	122.202	122.283	123.443
Mass w/Lug, Start (g)	122.358	122.268	122.015	122.221	122.69	122.202	122.283	123.443
Mass w/Lug, Finish (g)	120.59	120.583	121.234	121.356	121.19	120.768	121.574	121.064
Use PCT A Surface Area / Volume?								
Measured Surface Area (m^2/g)	4.1		4.1		4.1		4.1	
Leachate Dilution Factor	2	2	2	2	2	2	2	2
Sample Mass (g)	0.995	0.998	0.994	1	1.006	1.002	0.996	1.002
Water Mass (g)	9.963	9.986	10.003	9.765	9.986	9.995	9.991	10.005
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	2.1E-01	2.1E-01	2.1E-01	2.2E-01	2.2E-01	2.2E-01	1.1E-01	2.2E-01
Ca	2.0E-03	2.0E-03	2.0E-03	2.0E-03	2.0E-03	2.0E-03	2.0E-03	2.0E-03
Cr	1.3E-03	1.2E-03	2.0E-04	2.0E-04	1.5E-03	1.5E-03	6.2E-03	5.1E-03
Fe	2.0E-04	2.0E-04	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	2.4E-02	<2.0E-02
Na	1.5E+00	1.4E+00	1.6E+00	1.4E+00	1.7E+00	1.7E+00	4.9E+00	8.9E-01
P	1.3E-01	1.3E-01	1.3E-01	1.1E-01	1.4E-01	1.4E-01	1.0E-01	1.4E-02
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	3.5E-01	3.5E-01	3.0E-01	2.3E-01	3.4E-01	3.5E-01	4.3E-01	2.0E-01
Si	5.0E-02	5.3E-02	3.3E-02	4.0E-02	2.5E-02	2.6E-02	6.9E-03	9.8E-03
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	1.1E-01	1.1E-01	<1.0E-02	<1.0E-02	1.2E-02	1.2E-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	3.3E-02	3.1E-02	3.4E-02	2.9E-02	3.7E-02	3.3E-02	3.0E-02	3.7E-02
Cs	1.9E-02	1.7E-02	1.5E-02	1.2E-02	1.9E-02	1.6E-02	9.1E-03	2.1E-03
Re	6.0E-03	5.6E-03	5.9E-03	4.8E-03	6.8E-03	6.1E-03	5.5E-03	6.2E-03

Table H - 13. Leachate Data for BSR Module B Granular and Fly Ash GEO-7 Monolith Long Term PCT

Sample	Al	Ca	Cr	Fe	K	Na	P	Pb	S	Si	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 B Mono-1-5	44.5	1.31	4.5	<0.100	21.6	3620	<10.0	<1.00	227	124	<0.100	46.2	<10.0	2.14E+04	NM	6.62E+03
1M Sim MOD B Mono-1-6	42.3	1.29	3.57	<0.100	17.6	3310	<10.0	<1.00	179	98.4	<0.100	36.4	<10.0	1.79E+04	NM	5.09E+03
1M Sim MOD B Gran-1-4	78.8	1.18	0.698	1.78	<10.0	330	<10.0	<1.00	28	33.3	<0.100	<10.0	<10.0	7.78E+02	NM	5.69E+02
1M Sim MOD B Gran-1-6	85.1	1.09	0.84	1.3	<10.0	403	<10.0	<1.00	41.8	55.7	<0.100	<10.0	<10.0	9.42E+02	NM	6.96E+02
3M Sim MOD B Mono-7	47.6	<1.00	4.36	<0.100	19.2	2950	<10.0	<1.00	164	38.4	<0.100	100	<10.0	4.54E+04	2.73E+03	8.96E+03
3M Sim MOD B Mono-8	55.6	<1.00	4.41	<0.100	19.1	2930	<10.0	<1.00	165	38.8	<0.100	100	<10.0	4.52E+04	2.71E+03	9.09E+03
3M Sim MOD B Gran-7	67.1	<1.00	0.667	0.774	<10.0	381	54	<1.00	31.3	17.2	<0.100	<10.0	<10.0	8.89E+02	3.92E+03	5.88E+02
3M Sim MOD B Gran-8	67	<1.00	0.652	0.643	<10.0	371	53.5	<1.00	31.7	17.5	<0.100	<10.0	<10.0	8.96E+02	3.69E+03	5.76E+02
6M Sim MOD B Mono-1	60	<1.00	6.16	<0.100	19.4	3050	<1.00	<1.00	214	23.7	<0.100	113	<10.0	6.58E+04	2.21E+03	1.24E+04
6M Sim MOD B Mono-2	58.7	<1.00	6.18	<0.100	20.2	3090	<1.00	<1.00	215	23.7	<0.100	140	<10.0	6.50E+04	2.06E+03	1.22E+04
6M Sim MOD B Gran-1	72.3	<1.00	0.645	<0.100	<10.0	427	58.2	<1.00	32.7	11.2	<0.100	<10.0	<10.0	9.39E+02	3.08E+03	6.49E+02
6M Sim MOD B Gran-5	69.2	<1.00	0.673	<0.100	<10.0	439	60.2	<1.00	34.9	9.89	<0.100	<10.0	<10.0	9.88E+02	3.19E+03	6.04E+02
12M Sim MOD B Mono-3	1.8	<1.00	8.25	<0.100	26.6	3480	<1.00	<1.00	277	12.8	<0.100	139	<10.0	7.09E+04	4.18E+03	1.60E+04
12M Sim MOD B Mono-4	5.33	<1.00	8.19	<0.100	22.5	3360	<1.00	<1.00	277	12.9	<0.100	138	<10.0	6.63E+04	3.94E+03	1.63E+04
12M Sim MOD B Gran-2	65.4	<1.00	0.725	<0.100	<10.0	516	65.4	<1.00	38.8	8.09	<0.100	<10.0	<10.0	8.51E+02	4.30E+03	6.63E+02
12M Sim MOD B Gran-3	67.6	<1.00	0.81	<0.100	<10.0	530	70.1	<1.00	40.4	7.63	<0.100	<10.0	<10.0	9.28E+02	4.80E+03	7.52E+02

Table H - 14. Corrected Leachate Data, pH and BET SA for BSR Module B Granular and Fly Ash GEO-7 Monolith Long Term PCT

Sample ID	**1M Sim MOD B Mono-1**		**1M Sim MOD B Mono-2**		**1M Sim MOD B Gran-1**		**1M Sim MOD B Gran-2**	
Replicate ID	**1M Sim MOD B Mono-1-5**	**1M Sim MOD B Mono-1-6**	**1M Sim MOD B Mono-2-5**	**1M Sim MOD B Mono-2-6**	**1M Sim MOD B Gran-1-4**	**1M Sim MOD B Gran-1-6**	**1M Sim MOD B Gran-2-4**	**1M Sim MOD B Gran-2-6**
Vessel ID	t132	t134	t132	t134	T43	T64	T43	T64
pH	12.62	12.65	12.62	12.65	11.1	11.09	11.1	11.09
Empty Mass (g)	112.981	113.013	112.981	113.013	111.22	112.397	111.22	112.397
Mass w/Sample (g)	113.985	114.013	113.985	114.013	112.22	113.412	112.22	113.412
Mass w/Water and Sample (g)	123.98	124.015	123.98	124.015	123.22	123.414	123.22	123.414
Mass w/Lug, Start (g)	123.98	124.015	123.98	124.015	123.22	123.414	123.22	123.414
Mass w/Lug, Finish (g)	122.225	123.482	122.225	123.482	122.876	122.213	122.876	122.213
Use PCT A Surface Area / Volume?								
Measured Surface Area (m^2/g)	4.23		4.23		3.33		3.33	
Leachate Dilution Factor	1.667	1.667	2	2	1.667	1.667	2	2
Sample Mass (g)	1.004	1	1.004	1	1	1.015	1	1.015
Water Mass (g)	9.995	10.002	9.995	10.002	11	10.002	11	10.002
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	7.4E-02	7.1E-02			1.3E-01	1.4E-01		
Ca	2.2E-03	2.2E-03			2.0E-03	1.8E-03		
Cr	7.5E-03	6.0E-03			1.2E-03	1.4E-03		
Fe	<1.7E-04	<1.7E-04			3.0E-03	2.2E-03		
K	3.6E-02	2.9E-02			<1.7E-02	<1.7E-02		
Na	6.0E+00	5.5E+00			5.5E-01	6.7E-01		
P	<1.7E-02	<1.7E-02			<1.7E-02	<1.7E-02		
Pb	<1.7E-03	<1.7E-03			<1.7E-03	<1.7E-03		
S	3.8E-01	3.0E-01			4.7E-02	7.0E-02		
Si	2.1E-01	1.6E-01			5.6E-02	4.5E-02		
Ti	<1.7E-03	<1.7E-03			<1.7E-03	<1.7E-03		
Zr	<1.7E-04	<1.7E-04			<1.7E-04	<1.7E-04		
Cl			4.6E-02	3.6E-02			<1.0E-02	<1.0E-02
F			1.0E-02	1.0E-02			1.0E-02	1.0E-02
I			2.1E-02	1.8E-02			7.8E-04	9.4E-04
Cs	NM	NM	NM	NM	NM	NM	NM	NM
Re	1.1E-02	8.5E-03			9.5E-04	1.2E-03		

Table H - 14. Corrected Leachate Data, pH and BET SA for BSR Module B Granular and Fly Ash GEO-7 Monolith Long Term PCT (Continued)

Sample ID	**3M Sim MOD B Mono**		**3M Sim MOD B Gran**		**6M Sim MOD B Mono**		**6M Sim MOD B Gran**	
Replicate ID	**3M Sim MOD B Mono-7**	**3M Sim MOD B Mono-8**	**3M Sim MOD B Gran-7**	**3M Sim MOD B Gran-8**	**6M Sim MOD B Mono-1**	**6M Sim MOD B Mono-2**	**6M Sim MOD B Gran-1**	**6M Sim MOD B Gran-5**
Vessel ID	T137	T139	T108	T111	T114	T128	X36	T50
pH	12.54	12.58	10.47	10.49	12.44	12.51	10.01	10
Empty Mass (g)	115.344	113.457	110.673	111.423	111.169	113.471	111.188	113.312
Mass w/Sample (g)	116.335	114.453	111.671	112.423	112.175	114.475	112.198	114.318
Mass w/Water and Sample (g)	126.327	124.444	121.671	122.417	122.178	124.466	122.221	124.32
Mass w/Lug, Start (g)	126.327	124.444	121.671	122.417	122.178	124.466	122.221	124.32
Mass w/Lug, Finish (g)	125.595	123.727	120.925	121.735	120.754	123.101	120.807	122.931
Use PCT A Surface Area / Volume?								
Measured Surface Area (m2/g)	4.23		3.33		4.23		3.33	
Leachate Dilution Factor	2	2	2	2	2	2	2	2
Sample Mass (g)	0.991	0.996	0.998	1	1.006	1.004	1.01	1.006
Water Mass (g)	9.992	9.991	10	9.994	10.003	9.991	10.023	10.002
Element	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**	**g/L**
Al	9.5E-02	1.1E-01	1.3E-01	1.3E-01	1.2E-01	1.2E-01	1.4E-01	1.4E-01
Ca	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
Cr	8.7E-03	8.8E-03	1.3E-03	1.3E-03	1.2E-02	1.2E-02	1.3E-03	1.3E-03
Fe	<2.0E-04	<2.0E-04	1.5E-03	1.3E-03	<2.0E-04	<2.0E-04	<2.0E-04	<2.0E-04
K	3.8E-02	3.8E-02	<2.0E-02	<2.0E-02	3.9E-02	4.0E-02	<2.0E-02	<2.0E-02
Na	5.9E+00	5.9E+00	7.6E-01	7.4E-01	6.1E+00	6.2E+00	8.5E-01	8.8E-01
P	<2.0E-02	<2.0E-02	1.1E-01	1.1E-01	<2.0E-03	<2.0E-03	1.2E-01	1.2E-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	3.3E-01	3.3E-01	6.3E-02	6.3E-02	4.3E-01	4.3E-01	6.5E-02	7.0E-02
Si	7.7E-02	7.8E-02	3.4E-02	3.5E-02	4.7E-02	4.7E-02	2.2E-02	2.0E-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-04	<2.0E-04	<2.0E-04	<2.0E-04
Cl	1.0E-01	1.0E-01	<1.0E-02	<1.0E-02	1.1E-01	1.4E-01	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	4.5E-02	4.5E-02	8.9E-04	9.0E-04	6.6E-02	6.5E-02	9.4E-04	9.9E-04
Cs	5.5E-03	5.4E-03	7.8E-03	7.4E-03	4.4E-03	4.1E-03	6.2E-03	6.4E-03
Re	1.8E-02	1.8E-02	1.2E-03	1.2E-03	2.5E-02	2.4E-02	1.3E-03	1.2E-03

Table H - 14. Corrected Leachate Data, pH and BET SA for BSR Module B Granular and Fly Ash GEO-7 Monolith Long Term PCT (Continued)

Sample ID	**12M Sim MOD B Mono**		**12M Sim MOD B Gran**	
Replicate ID	**12M Sim MOD B Mono-3**	**12M Sim MOD B Mono-4**	**12M Sim MOD B Gran-2**	**12M Sim MOD B Gran-3**
Vessel ID	t130	t131	x39	x41
pH	13.08	13.05	10.57	10.02
Empty Mass (g)	114.363	114.707	111.668	112.39
Mass w/Sample (g)	115.367	115.709	112.668	113.391
Mass w/Water and Sample (g)	125.372	125.703	122.665	122.386
Mass w/Lug, Start (g)	125.372	125.703	122.665	122.386
Mass w/Lug, Finish (g)	125.014	125.359	122.284	122.026
Use PCT A Surface Area / Volume?				
Measured Surface Area (m^2/g)	4.23		3.33	
Leachate Dilution Factor	2	2	2	2
Sample Mass (g)	1.004	1.002	1	1.001
Water Mass (g)	10.005	9.994	9.997	8.995
Element	**g/L**	**g/L**	**g/L**	**g/L**
Al	3.6E-03	1.1E-02	1.3E-01	1.4E-01
Ca	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
Cr	1.7E-02	1.6E-02	1.5E-03	1.6E-03
Fe	<2.0E-04	<2.0E-04	<2.0E-04	<2.0E-04
K	5.3E-02	4.5E-02	<2.0E-02	<2.0E-02
Na	7.0E+00	6.7E+00	1.0E+00	1.1E+00
P	<2.0E-03	<2.0E-03	1.3E-01	1.4E-01
Pb	<2.0E-03	<2.0E-03	<2.0E-03	<2.0E-03
S	5.5E-01	5.5E-01	7.8E-02	8.1E-02
Si	2.6E-02	2.6E-02	1.6E-02	1.5E-02
Ti	<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
Cl	1.4E-01	1.4E-01	1.0E-02	1.0E-02
F	1.0E-02	1.0E-02	1.0E-02	1.0E-02
I	7.1E-02	6.6E-02	8.5E-04	9.3E-04
Cs	8.4E-03	7.9E-03	8.6E-03	9.6E-03
Re	3.2E-02	3.3E-02	1.3E-03	1.5E-03

Appendix I. X-Ray Diffraction Spectra

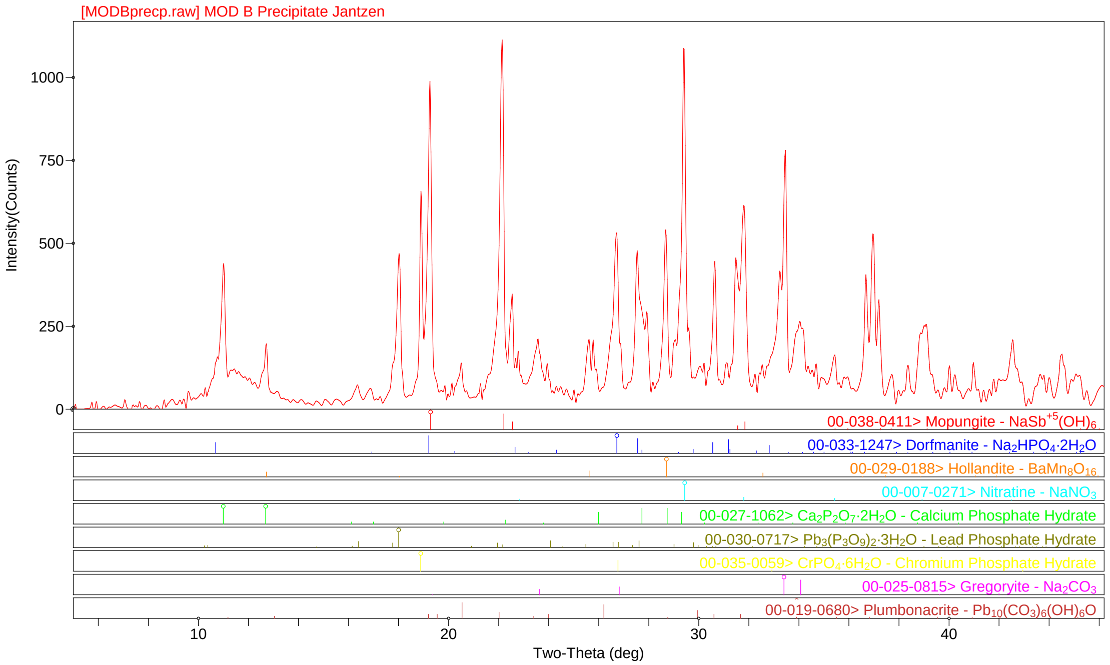

Figure I - 1. XRD for Figure 4-1

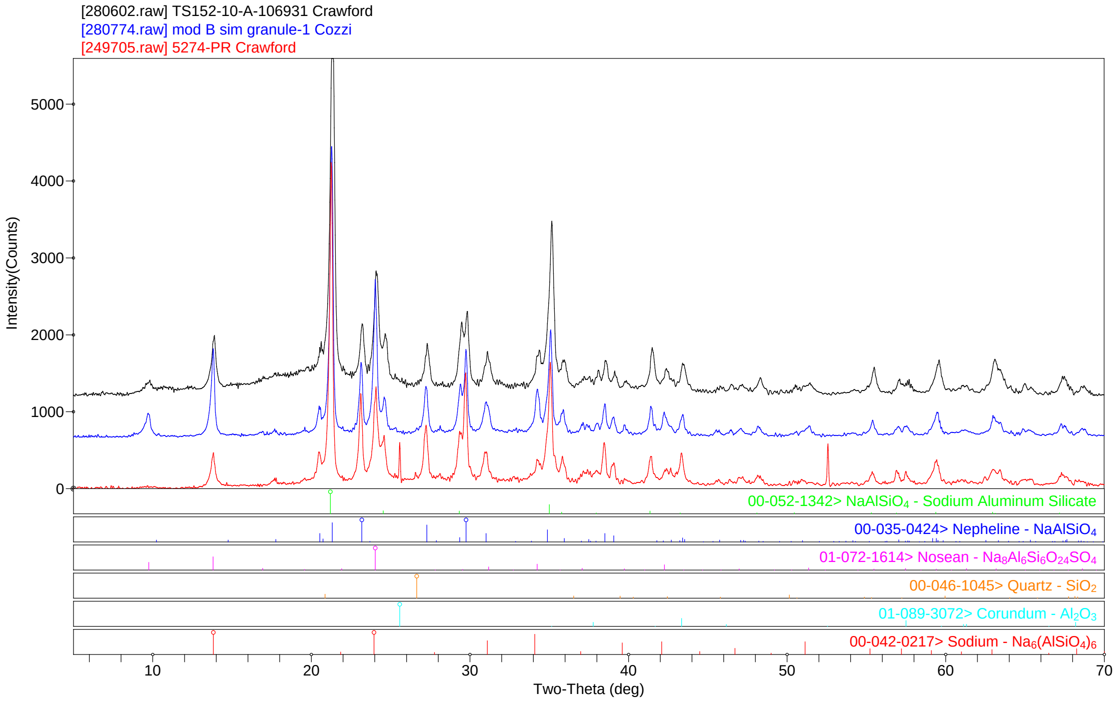

Figure I - 2. XRD's for Figure 5-8 Overlays

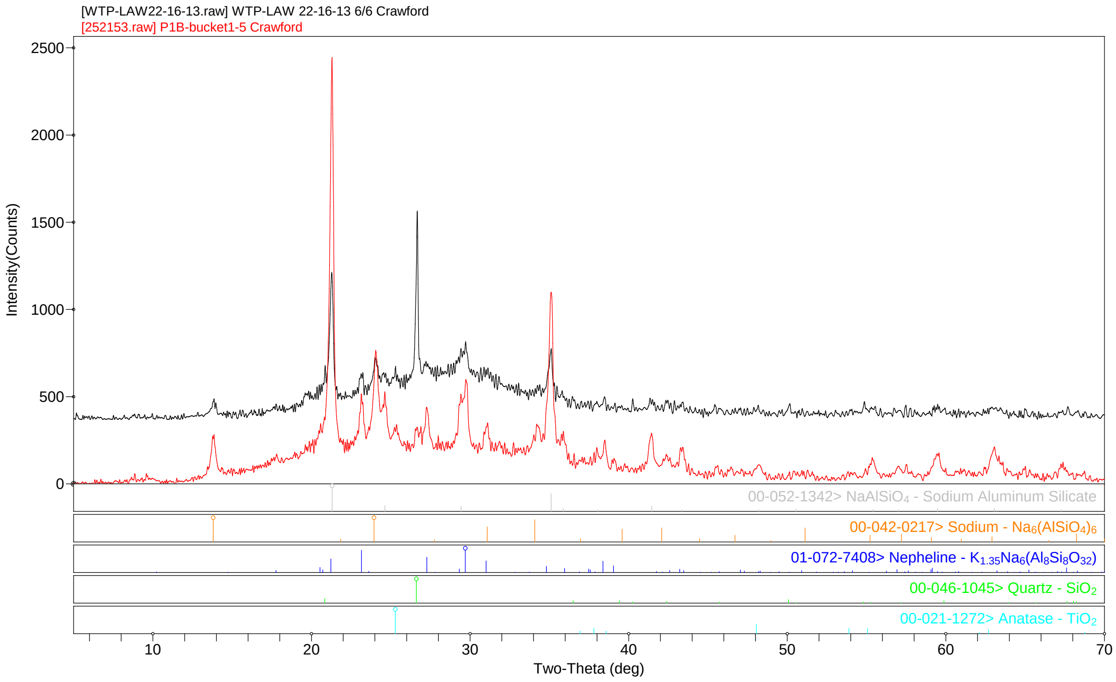

Figure I - 3. XRD's for Figure 5-9 Overlays

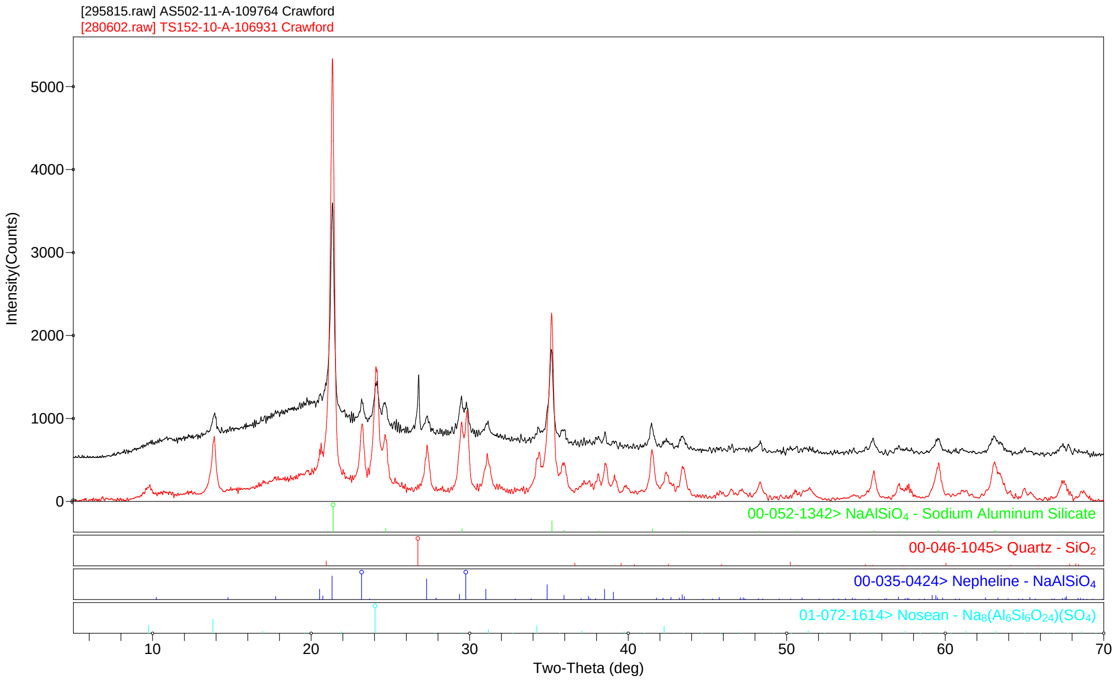

Figure I - 4. XRD for Figure 5-10 Top Overlay

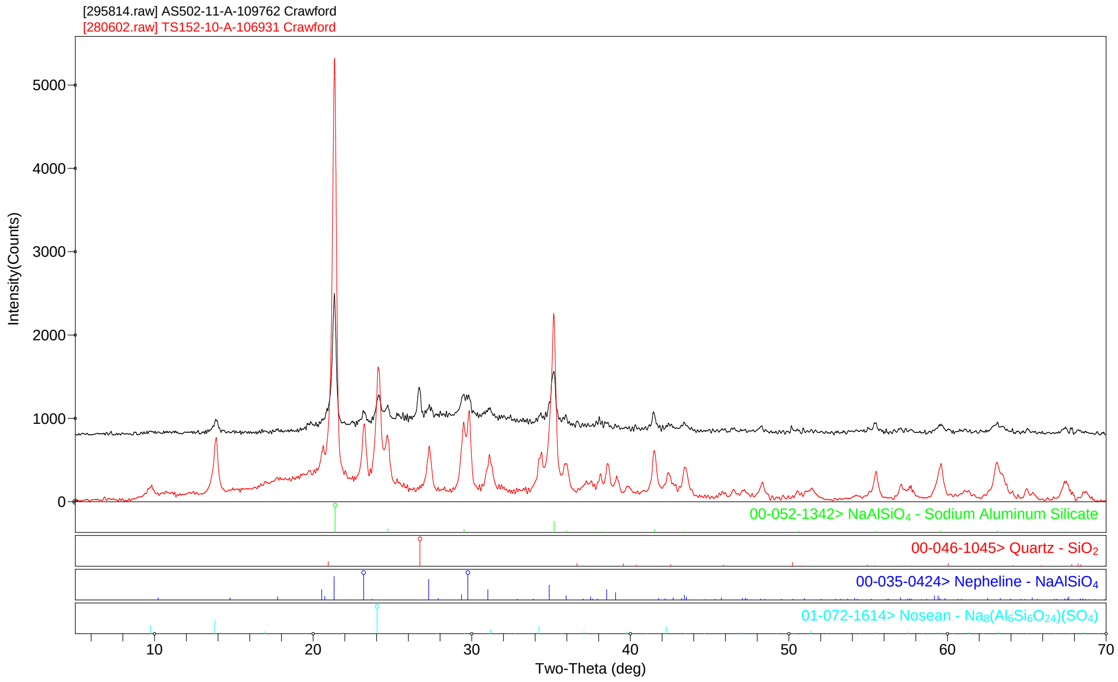

Figure I - 5. XRD for Figure 5-10 Bottom Overlay

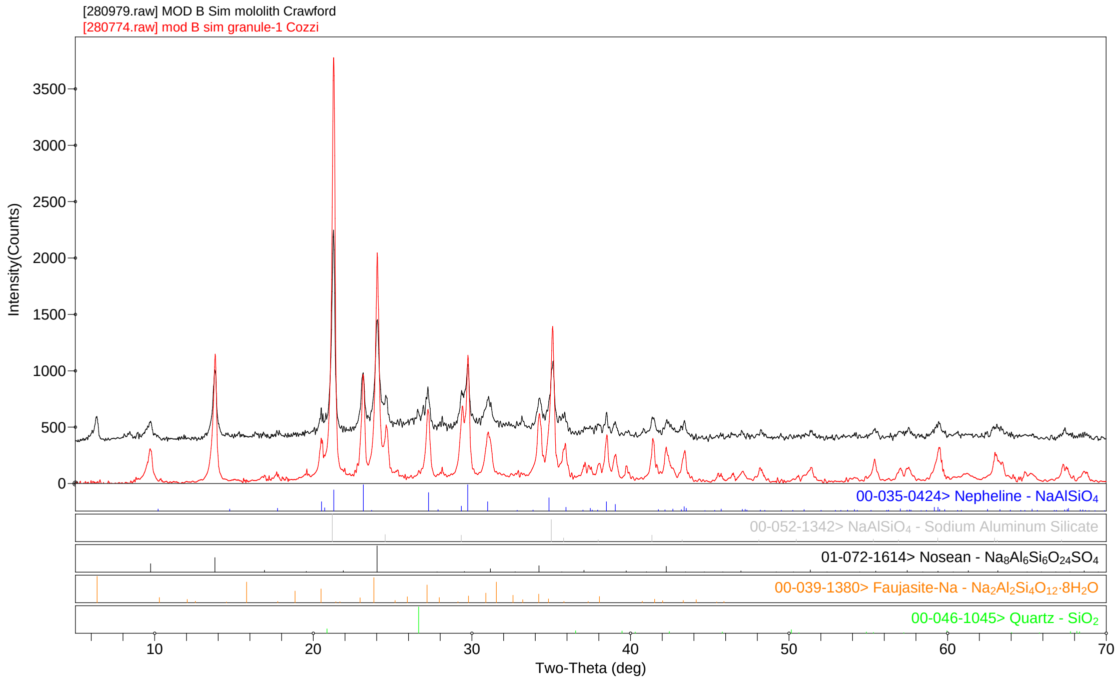

Figure I - 6. XRD for Figure 5-11 Overlay

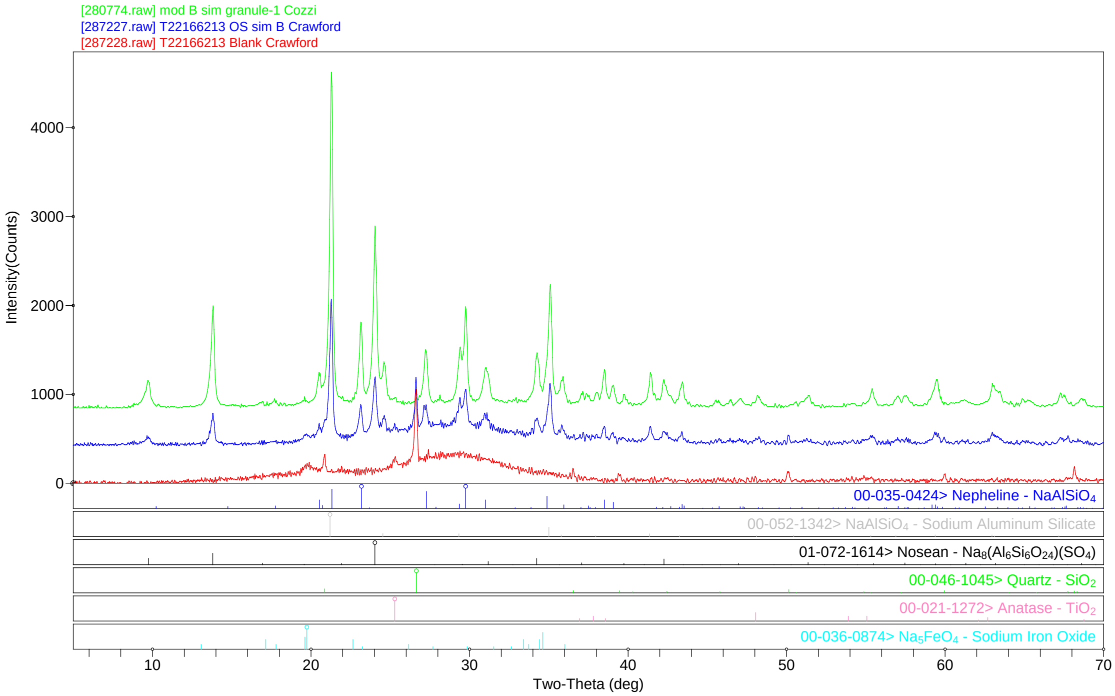

Figure I - 7. XRD for Figure 5-12 Overlay

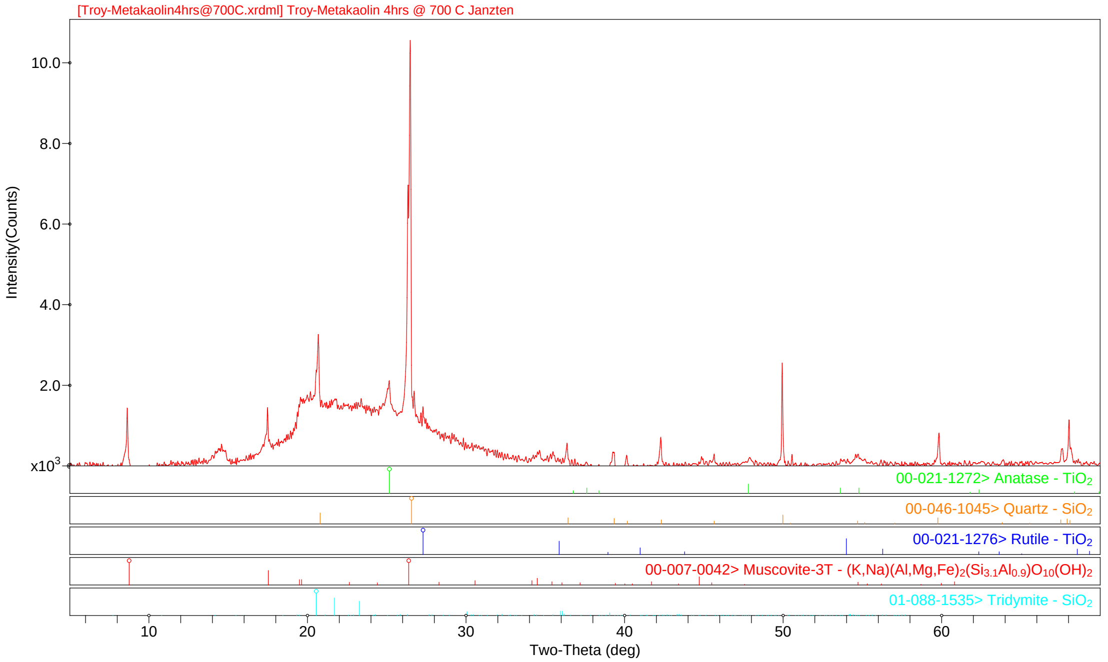

Figure I - 8. XRD for Figure 5-13

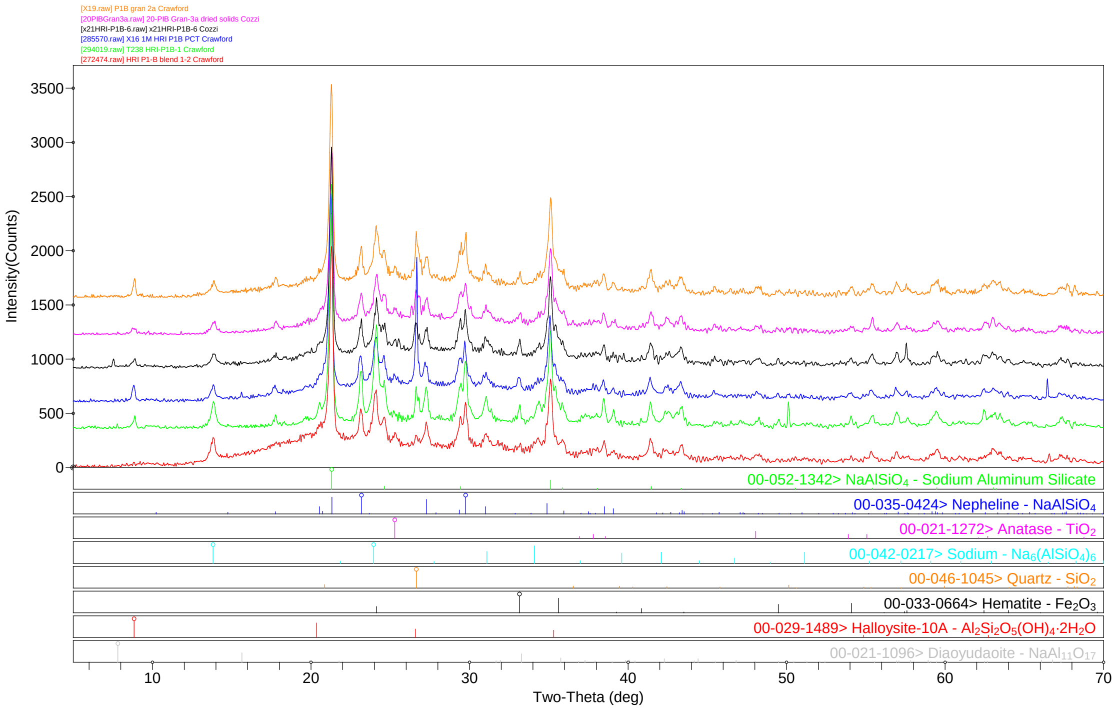

Figure I - 9. XRD for Figure 5-26 Overlay

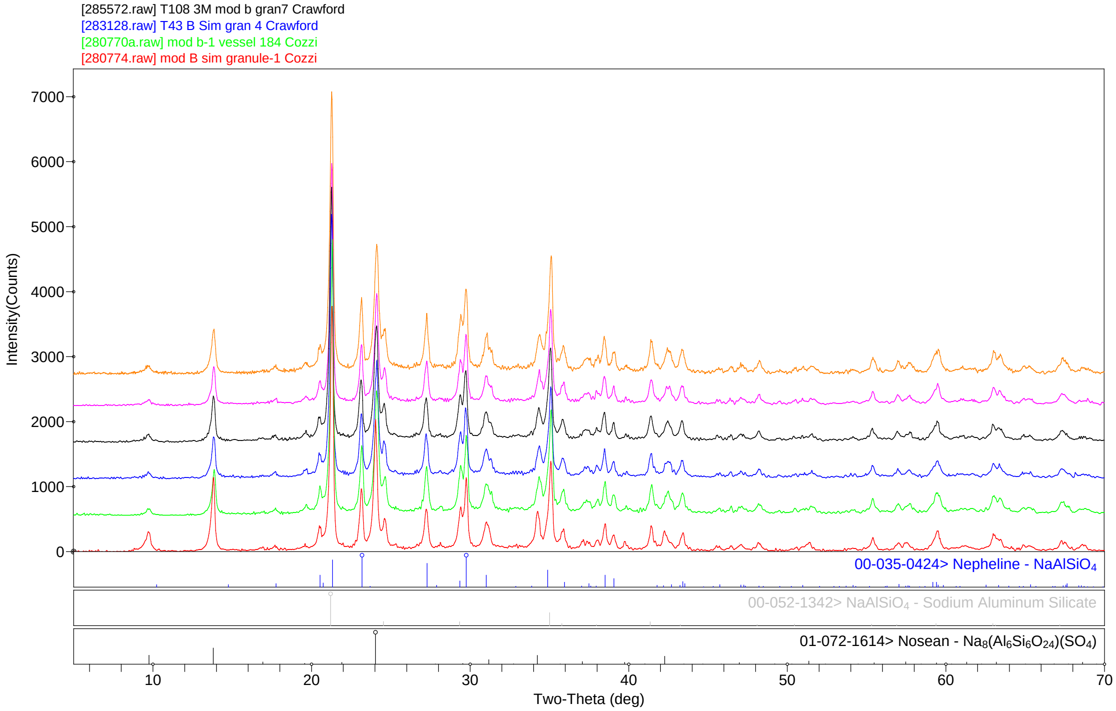

Figure I - 10. XRD for Figure 5-28 Overlay

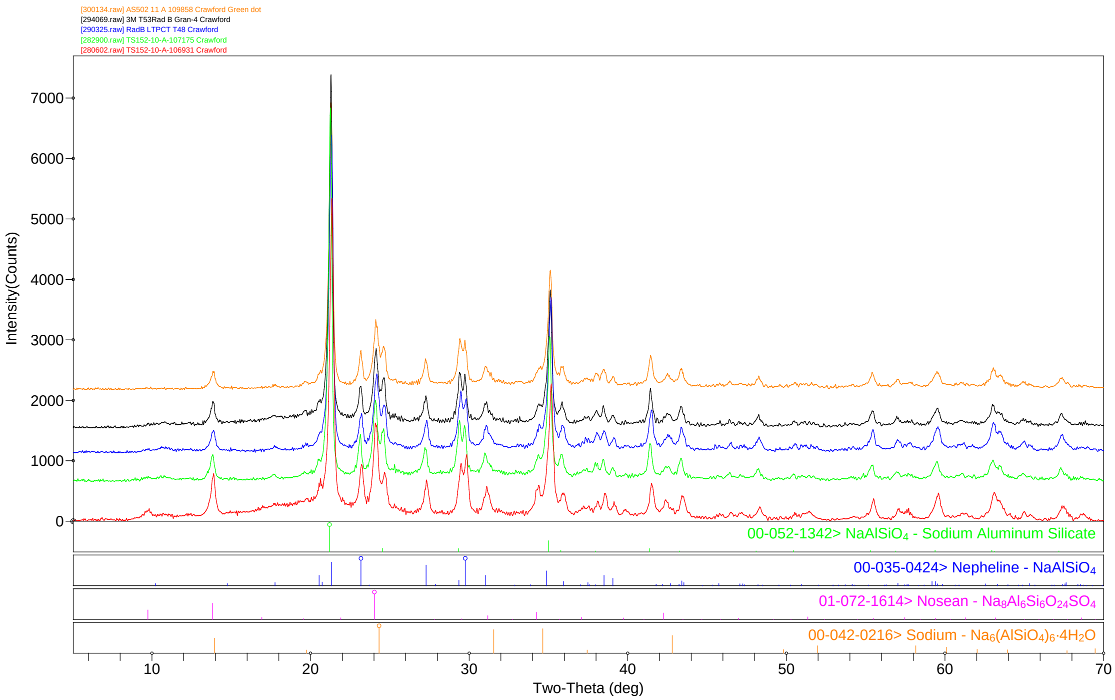

Figure I - 11. XRD's for Figure 5-30 Overlays

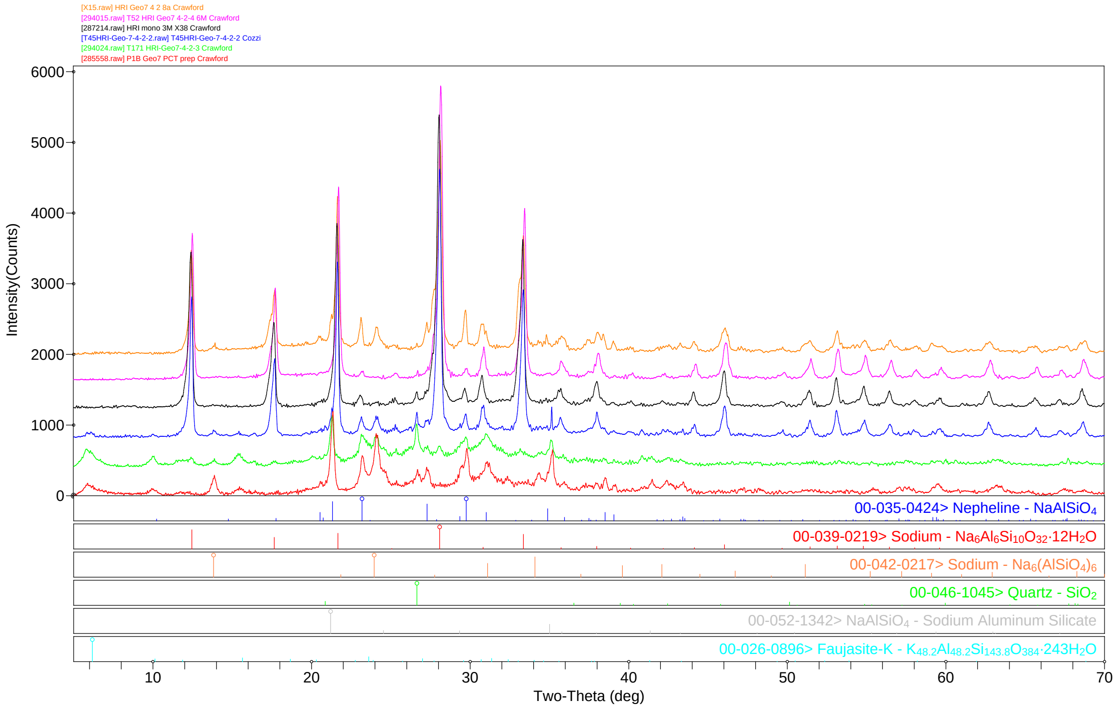

Figure I - 12. XRD's for Figure 5-32 Overlays

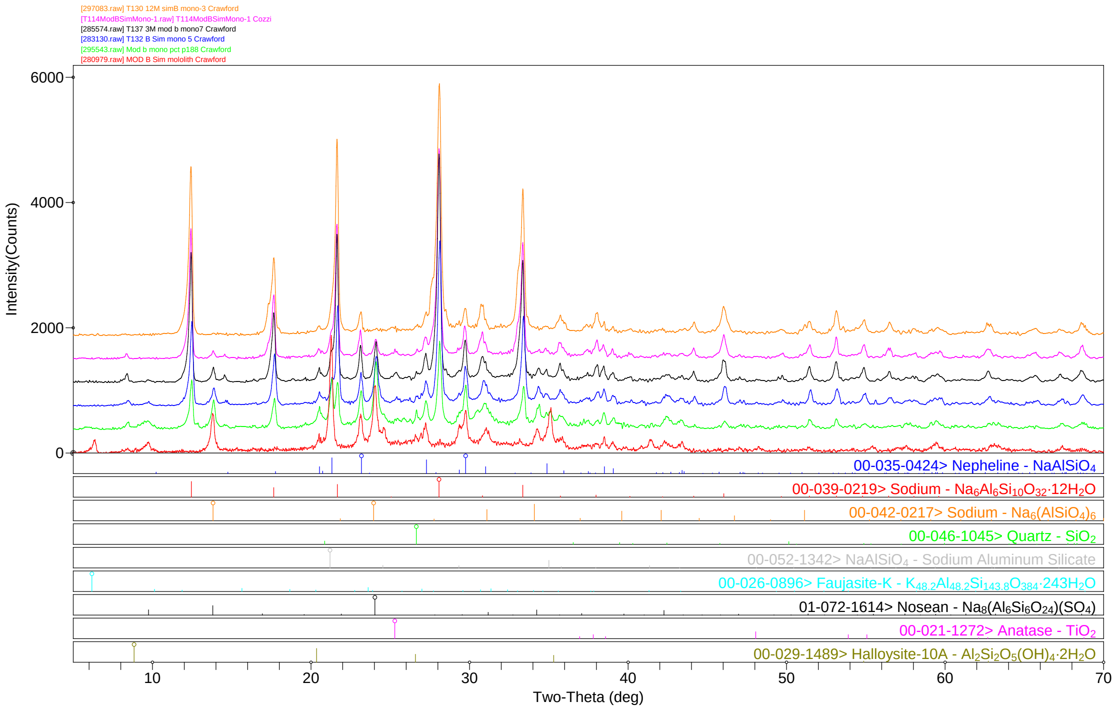

Figure I - 13. XRD's for Figure 5-34 Overlays

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, 730-4B
C. L. Crawford, 773-42A
W. E. Daniel, 999-W
D. H. Miller, 999-W
D. M. Missimer, 773-A
M. F. Williams, 999-W

P. R. Jackson, 703-46A

T. W. Fletcher, DOE-ORP
S. H, Pfaff, DOE-ORP

D. J. Swanberg, WRPS
R. A. Robbins, WRPS
L. E. Thompson, WRPS
W. G. Ramsey, WRPS
P. A. Cavanah, WRPS

C. Brown, PNNL
N. Quafoku, PNNL
R. A. Peterson, PNNL
G. Smith, PNNL

E. M. Pierce, ORNL