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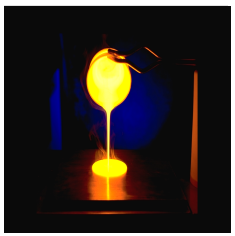
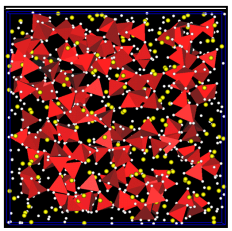
Fluidized Bed Steam Reformer (FBSR) Na-Al-Si (NAS) Waste Form For Hanford LAW and Secondary Waste

C.M. Jantzen and E.M. Pierce

November 17, 2010





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FY10: Participating Organizations

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THOR Treatment Technologies

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Incentive and Objectives

FBSR sodium-aluminosilicate (NAS) waste form has been identified as a promising supplemental treatment technology for Hanford LAW and/or Waste Treatment Plant Secondary Waste (WTP-SW)

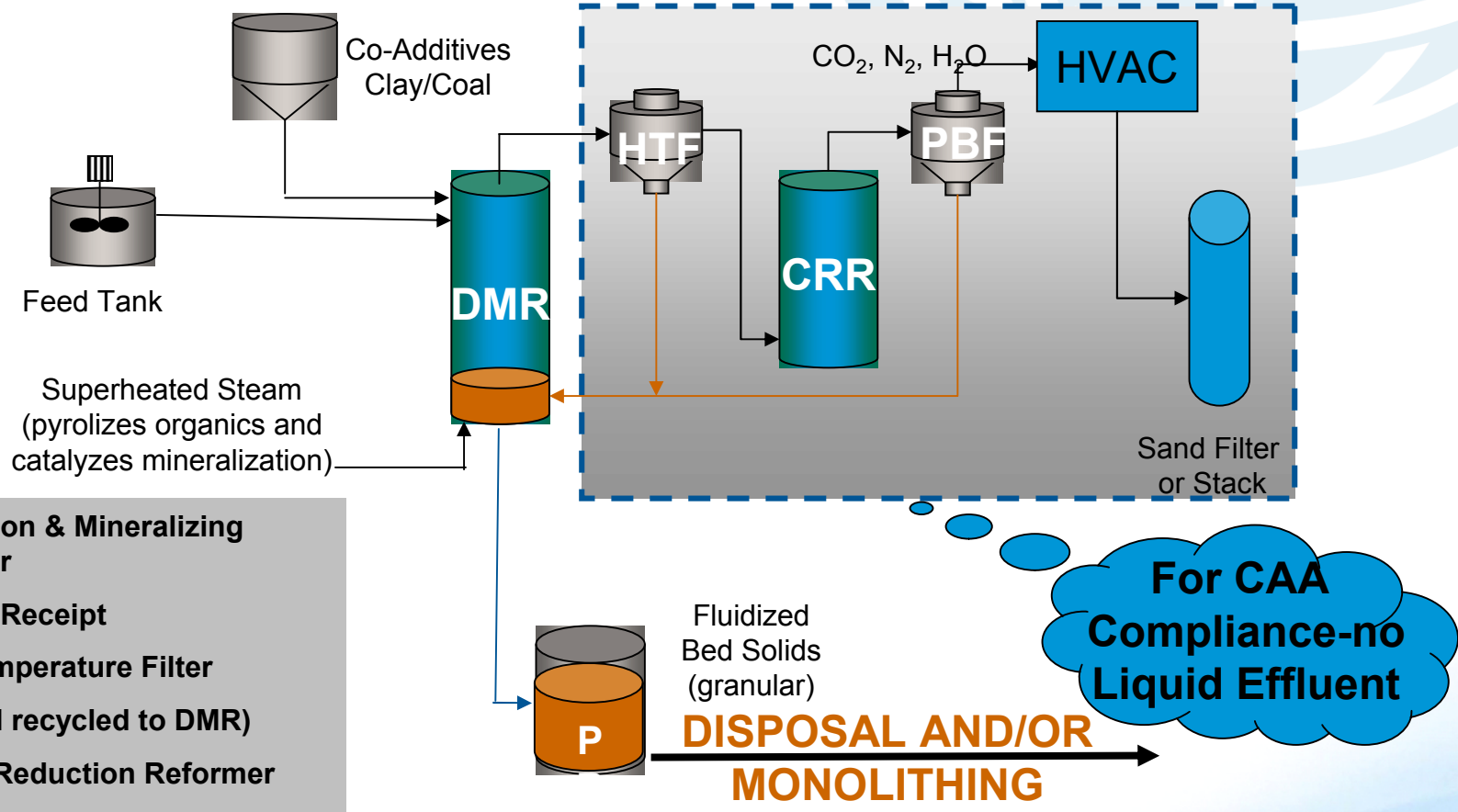
Objectives:

- **Prove the robustness of FBSR as a waste form for either LAW and/or WTP-SW**
  - **Reduce the risk associated with implementing the FBSR NAS waste form as a supplemental treatment technology for Hanford LAW and/or WTP-SW**
    - **Conduct two treatability studies with SRS radioactive wastes that have been shimmed to look like Hanford WTP-SW and LAW**
    - **Conduct three treatability studies with actual Hanford tank wastes**
    - **Fill key data gaps**
    - **Link previous and new results together**

Outline

- FBSR NAS waste form processing
  - Flowsheets
  - Scales
  - Waste types
- FBSR NAS testing program for WTP-SW
- FBSR NAS testing program for LAW
- FBSR NAS testing program
  - Closure of key data gaps

FBSR NAS Waste Form Processing Flowsheets: Dual vs. Single Reformer



DMR =	**Denitration & Mineralizing Reformer**
PR =	**Product Receipt**
HTF =	**High Temperature Filter**
	(material recycled to DMR)
CRR =	**Carbon Reduction Reformer**
	(treats gases only)
PBF =	**Process Bag-house Filter**

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FBSR NAS Waste Form Processing Scales

8-Years of Engineering Scale Test Demonstration (ESTD) with simulated waste

- **Hazen 2001 (auto-catalytically heated 6" single reformer)**
- **SAIC-STAR Test Facility 2003-4 (externally heated 6" single reformer)**
- **Hazen 2006 and 2008 (auto-catalytically heated 15" dual reformer)**

Bench-Scale Steam Reformer (BSR)

- **Designed and built at SRNL in 2004 (externally heated single reformer)**
- **INL SBW and Hanford Envelope A composite (68 tank) simulant tested**
- **Redesigned for Shielded Cell Facility (SCF) in 2006 (combination unit - externally heated and auto-catalytically heated and dual reformer)**

FBSR NAS Waste Form Processing Scales: From Engineering Scale Pilot to Bench-Scale

NON-RADIOACTIVE

NON-RADIOACTIVE + RADIOACTIVE

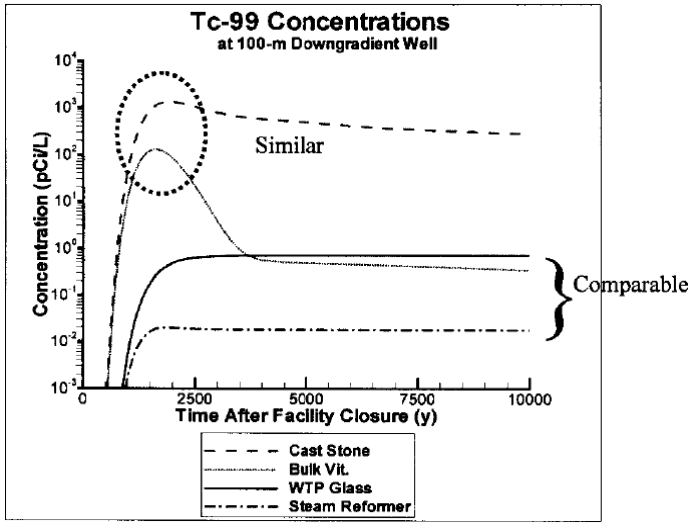
Wastes Processed and Tested at Pilot Scale and BSR

Simulated wastes tested (all doped with Re for Tc)

- Hanford Envelope C Tank Waste (AN-107)
- Hanford Envelope A (68 tank blend) Tank Waste
- Hanford WTP secondary waste
- INL sodium bearing waste

Testing Performed:

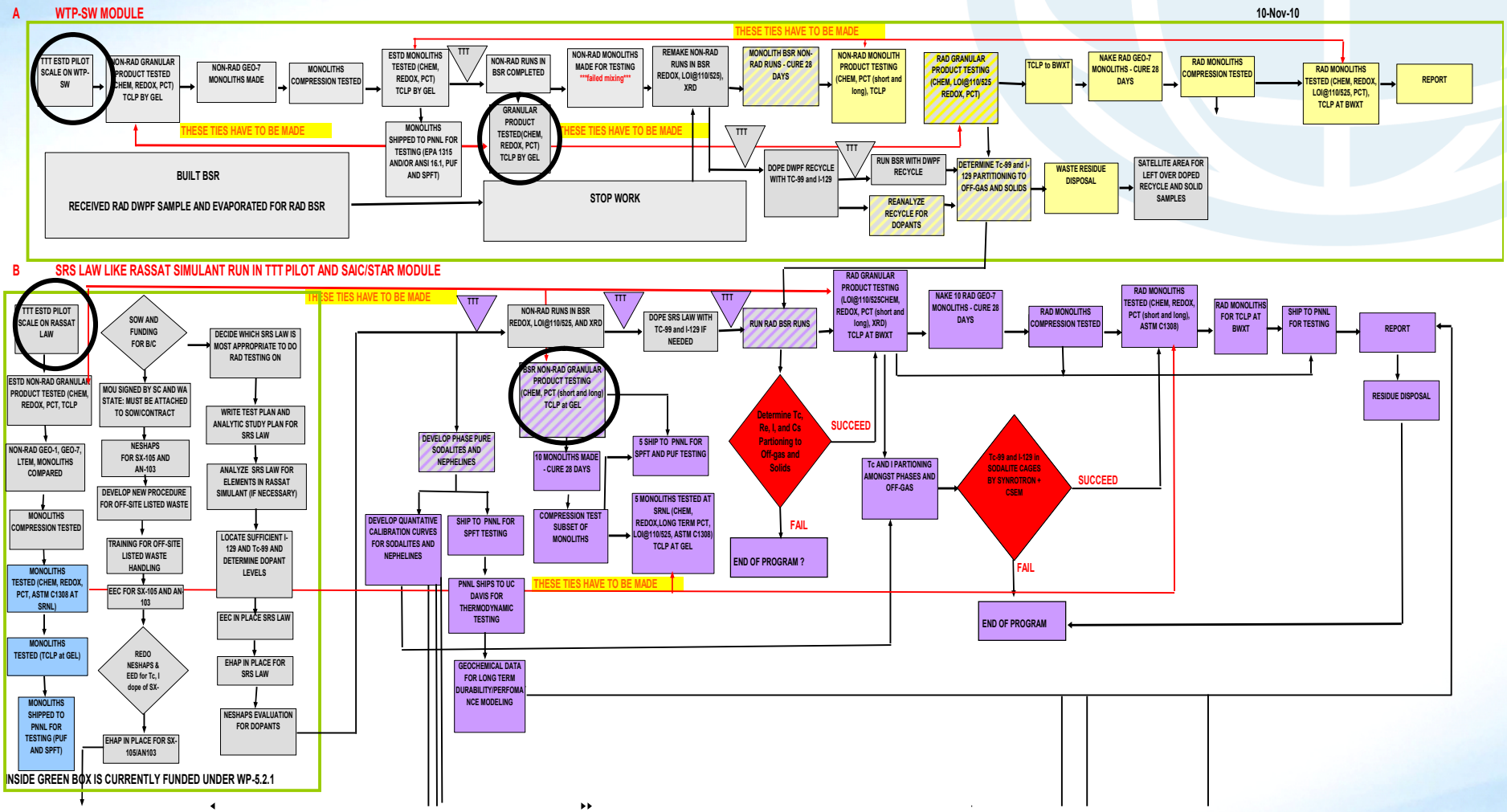
- Product Consistency Test (PCT; ASTM C1285)
  - on bed product (with and without coal removed)
  - on fines (with and without coal removed)
  - Potential Al-buffering mechanism identified
- Single Pass Flow Through (SPFT; ASTM C1662)
  - on bed product (with coal removed)
- Pressure Unsaturated Flow (PUF) test
  - on bed product (with coal removed)
- Preliminary Performance Assessment (PA) performed



Experimentation Has Proceeded from Simple to More Complex

Pilot Scale Facility	Acidic and Basic Wastes	Granular PCT Testing	TCLP Granular Form	Granular SPFT Testing	Preliminary Performance Assessment	Product Tested	Coal	PSD	Monolith	Monolith PCT Testing	Monolith SPFT Testing	Monolith ANSI 16.1/ EPA 1315 Testing	TCLP of Monolithic Form
HRI/ TTT	LAW Env. C	Ref 7	Ref 7	Ref 8,9 also PUF testing	Ref 10	Bed	Removed By Hand	Gaussian	NO	N/A	N/A	N/A	N/A
HRI/ TTT	LAW Env. C	Ref 11,12,13	Ref 11,12,13	None	None	Fines	Removed by 525 °C Roasting	Gaussian	NO	N/A	N/A	N/A	N/A
SAIC/ STAR	SBW	Ref 11,12,13	Ref 11,12,13	None	None	Bed	Removed by 525 °C Roasting	Gaussian	Yes (Samples were combined; 20% LAW, 32 % SBW and 45% Startup Bed	Ref 14,15	NO	NO	NO
SAIC/ STAR	LAW Env. A	Ref 11,12,13	Ref 11,12,13	Ref 16,13,17	This study using data from Ref 16,13,17	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian			NO	NO	NO
SAIC/ STAR	SBW	Ref 11,12,13	Ref 11,12,13	Ref 16,13	None	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian			NO	NO	NO
HRI/ TTT	SBW	Ref 4	Ref 4	None	None	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian	NO	N/A	N/A	N/A	N/A
HRI/ TTT	LAW Env. A	Ref 3	Ref 3	This study	This study	Bed and Fines Together	Not removed	Bi-Modal	YES	This study	This study	This study	This study
HRI/ TTT	WTP-SW (melter recycle)	SRNL 2008 ART's WFO	SRNL 2008 ART's WFO	None	None	Bed and Fines Together	Not removed	Bi-Modal	YES	SRNL 2008 ART's WFO	None	PNNL	SRNL 2008 ART's WFO

Bench-scale Steam Reformer (BSR) - 2009-2010 Program



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FBSR Mineralization Reactions Occur on a Nano-scale

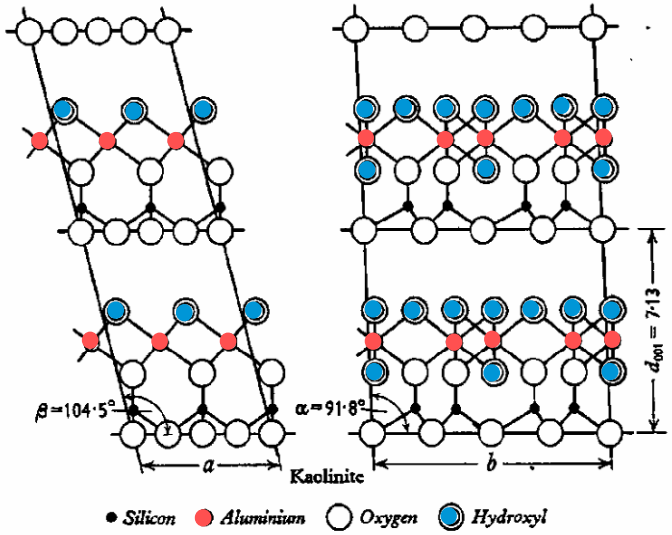
Clays lose hydroxyls at FBSR operating temperature

Loss of hydroxyls destabilizes clay structure at nano-scale level

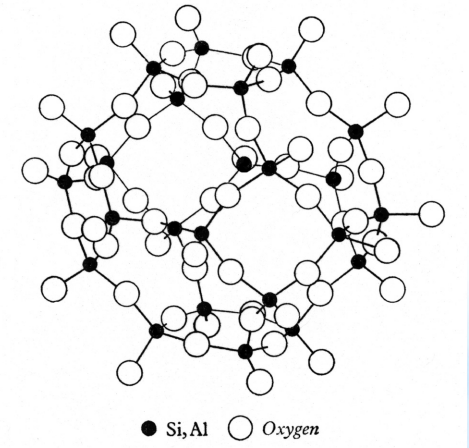
- Al^{+3} atoms form unstable 5-coordinated configuration versus typical 4-coordinated configuration

Alkali from waste "alkali activates" Al^{+3} atoms into a new structures; such as sodalite, nepheline, nosean that contain cage-like structures for halides (Cl, I, F), molybdates, pertechnetates, perrhenates, and sulfates

Kaolin



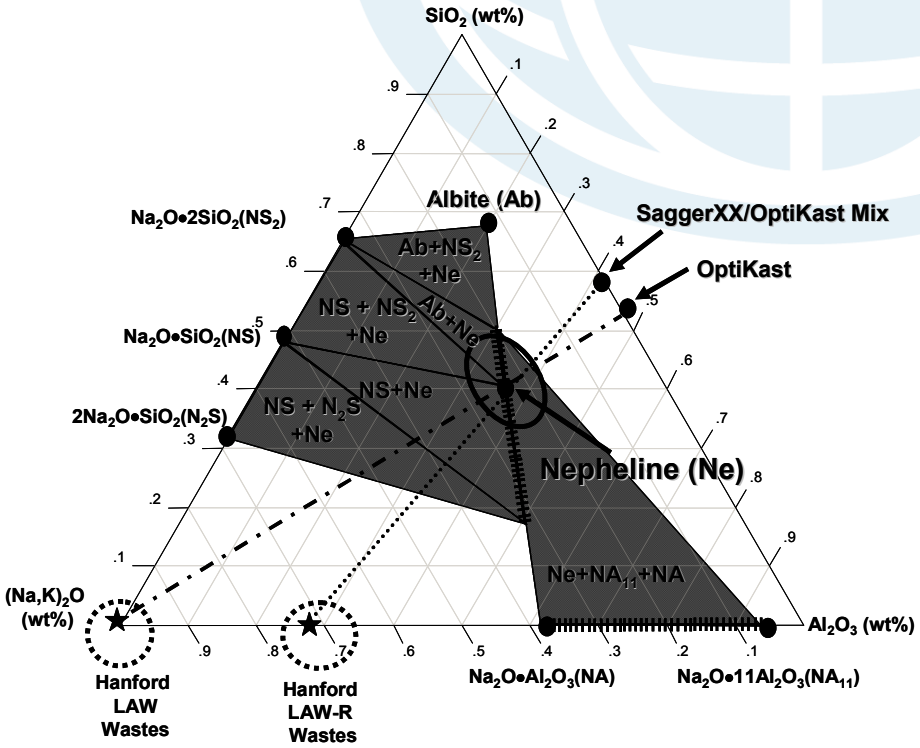
Sodalite



Target Waste Loadings and Clay Type with SRNL Process Control MINCALC™

Oxides and Anions	Oxide/Anion Content (wt%)	Nitrate Content (wt%)
HANFORD TANK WASTES (Composition Envelope "A" Rassat HRI Pilot 2008)		
$(Na,K)_2O$	86.53	50.28
Al_2O_3	1.81	
SO_4	7.11	
Cl	1.42	
F	0.74	
Cr_2O_3	0.44	
HANFORD PROJECTED MELTER OFF-GAS RECYCLE WASTES WTP SW (HRI Pilot 2008)		
$(Na,K)_2O$	60.18	90.91
Al_2O_3	20.21	
SO_4	0.56	
Cl	4.48	
F	6.65	
Cr_2O_3	0.33	

* RCRA metals (Sb, As, Ag, Cd, Ba, and Tl) and radionuclide surrogates (Re, I, Cs) were doped in at 10-1000X



WL=32wt% WL=26wt%

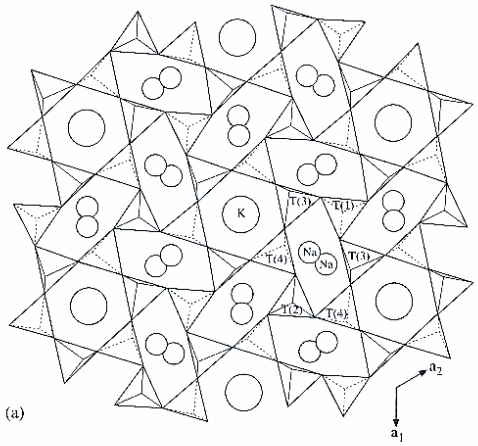
Mineral Phases Formed

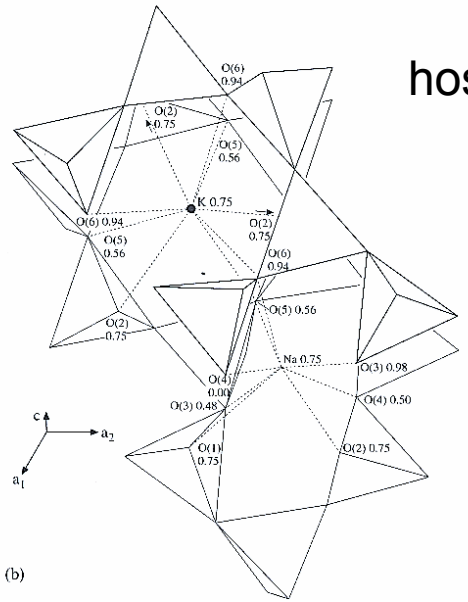
	Low-Carnegieite Nominally $NaAlSiO_4$	Nepheline Nominally $NaAlSiO_4$ or $K_{0.25}Na_{0.75}AlSiO_4$	Nosean $Na_6[Al_6Si_6O_{24}](Na_2SO_4)$ and/or Sodalite $Na_6[Al_6Si_6O_{24}](2NaX$ where X=Cl,F,I)	Other Minor Components
HANFORD ENVELOPE "C" LAW WASTES (2002) $Fe^{+2}/\Sigma Fe$ of Bed = 0.15				
SCT02-098-FM		X	Y	Al_2O_3, Fe_2O_3, Fe_3O_4
Fines PR-01	X	X	Y	Al_2O_3, Fe_2O_3, Fe_3O_4
HANFORD ENVELOPE "A" LAW WASTES (2004) $Fe^{+2}/\Sigma Fe$ of Bed = 0.28-0.81				
Bed 1103	X	X	Y	TiO_2
Bed 1104	X	X	Y	TiO_2
Fines 1125	X	Y		TiO_2
INL SBW WASTES (2003-4) $Fe^{+2}/\Sigma Fe$ of Bed = 0.51-0.61				
Bed 260	Y	X	TR	Al_2O_3 and TiO_2
Bed 272	Y	X	TR	TiO_2
Bed 277	Y	X	TR	TiO_2
Bed 1173		X	TR	Al_2O_3, SiO_2, $NaAl_{11}O_{17}$ and $(Ca,Na)SiO_3$
HANFORD ENVELOPE "A" LAW WASTES (2008) $Fe^{+2}/\Sigma Fe$ of Bed = 0.41-0.90				
PR Bed Product 5274 (P1A)	Y	Y		Al_2O_3,
PR Bed Product 5316 (P1A)	Y	Y		Pyrophyllite*
HTF Fines 5280 (P1A)	Y	Y		$NaAl_{11}O_{17}$,TiO_2
HTF Fines 5297 (P1A)	Y	Y	Y	SiO_2
PR Bed Product 5359 (P1B)	Y	Y		Pyrophyllite*
PR Bed Product 5372 (P1B)	Y	Y		Pyrophyllite*
HTF Fines 5351 (P1B)	Y	Y		SiO_2
HTF Fines 5357 (P1B)	Y	Y		TiO_2
Composite (P1A)	Y	Y		SiO_2 and TiO_2
Composite (P1B)	Y	Y		SiO_2 and TiO_2
HANFORD MELTER OFF-GAS RECYCLE (WTP SW) WASTES (2008) $Fe^{+2}/\Sigma Fe$ =0.41-0.90				
PR 5475 (P2A)	Y	Y	Y	Pyrophyllite*
HTF Fines 5471 (P2A)	Y	Y		SiO_2
PR 5522 (P2B)	Y	Y	Y	Pyrophyllite*, TiO_2
HTF Fines 5520 (P2B)	Y	Y		SiO_2 and TiO_2
Composite (P2B)	Y	Y	Y	SiO_2

Why important: impacts contaminant release

- Multi-phase waste form – Nepheline, Sodalite, & Nosean
- Nepheline – dominant mineral
  - Dissolution may affect other minerals
- Sodalite & Nosean - minor phases dependent on anion content of waste
  - Both are 6 unit cells of nepheline in a configuration that creates a cage
- Sodalite expected to contain COC's
- Anion content may compete with Tc for "cage" sites

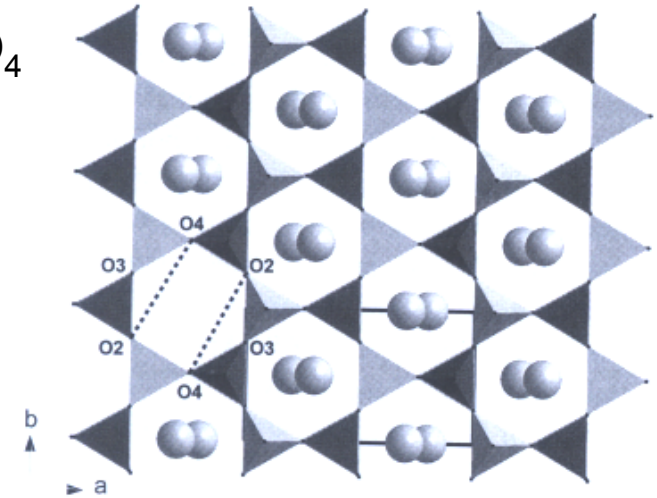
Nepheline Structures - 9 and 12 Member Ring Structures



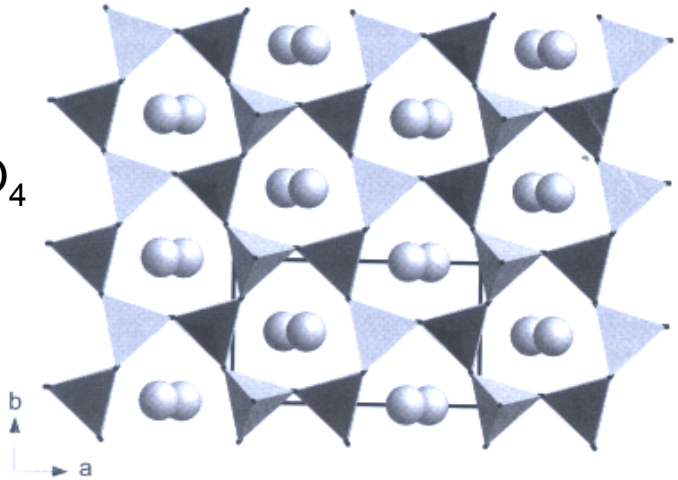


host for K, Na,Ca,
Fe, Ti and Mg

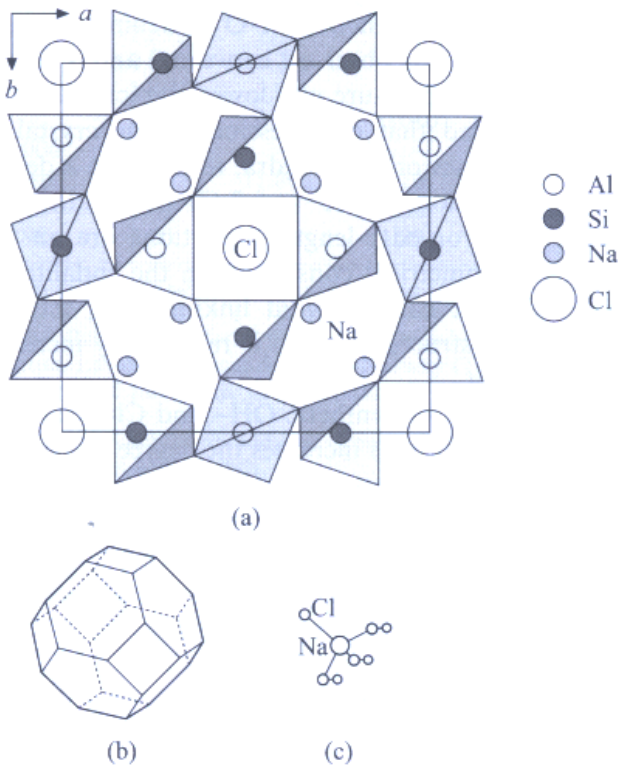
$CsAlSiO_4$

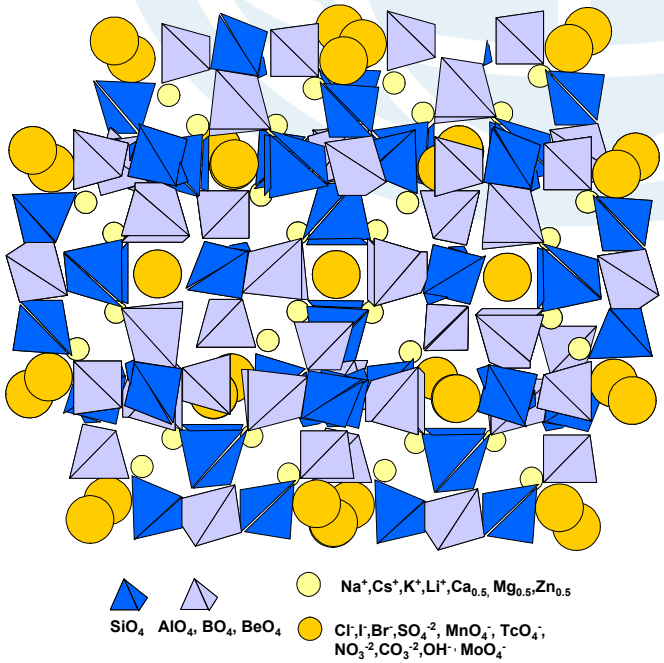


$RbAlSiO_4$



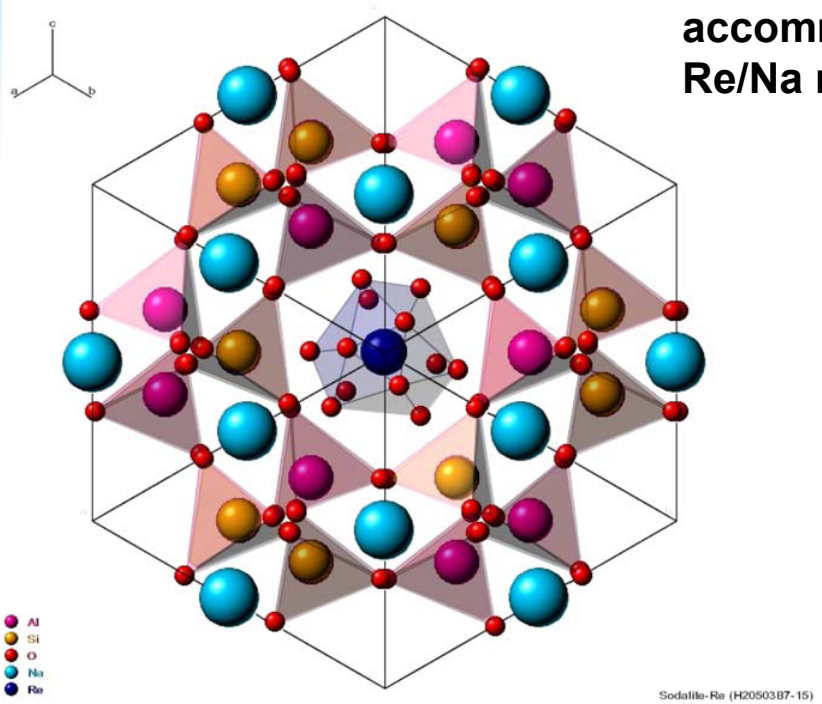
Sodalite/Nosean Structures





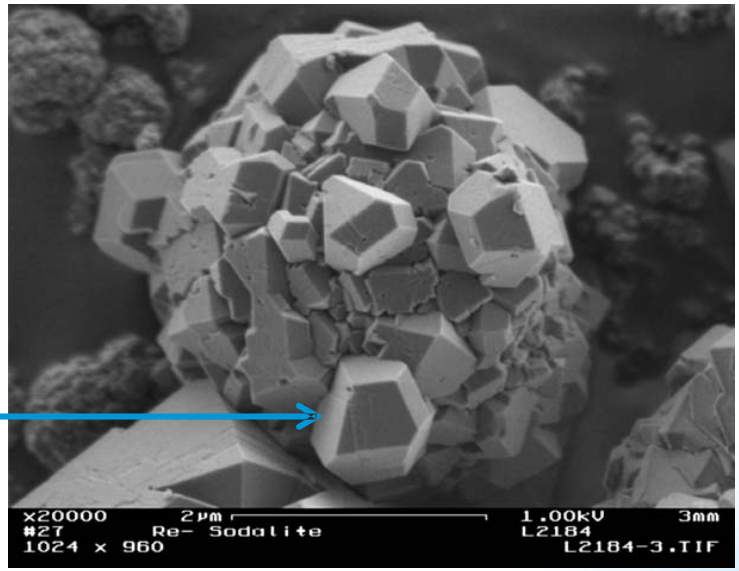
accommodates 7.9 wt% Cl - (Cl/Na ratio = 0.25)
accomodates 28.3 wt% I - (I/Na ratio = 0.25)
accomodates 4.2 wt% F - (F/Na ratio = 0.25)
accomodates 10.76 wt% SO_4- (SO_4/Na ration = 0.125)

Sodalite/Nosean Structure



accommodate 40.7 wt% Re (equivalent to 21.7 wt% Tc)
Re/Na ratio = 0.25, Tc/Na ratio = 0.25

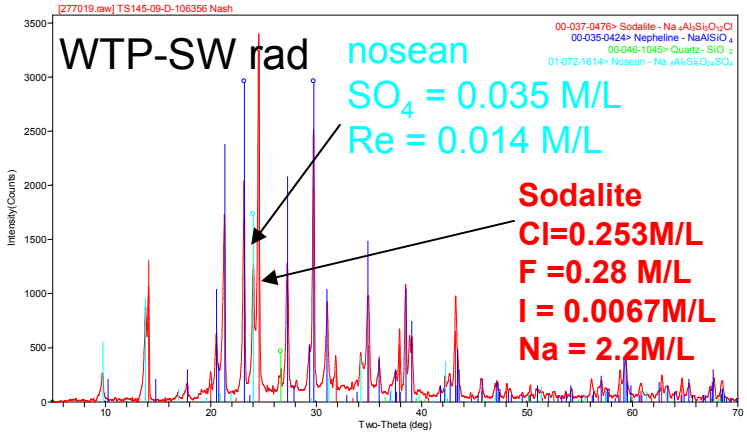
Re-sodalite crystal

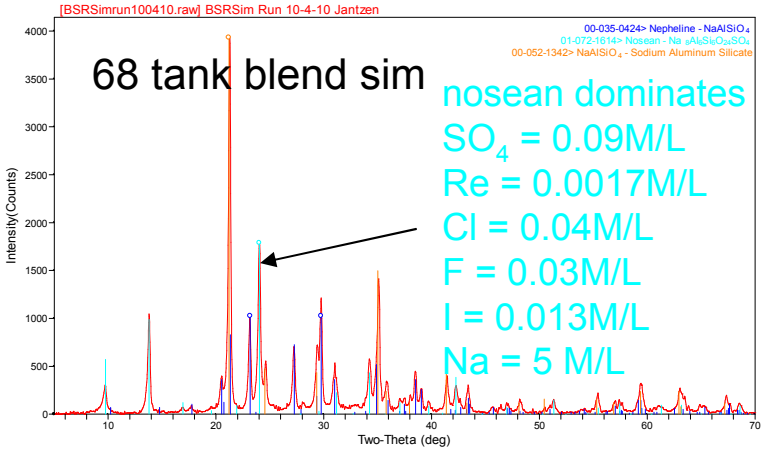


Minerals Found In WTP-SW and LAW Relate to Anions in Waste

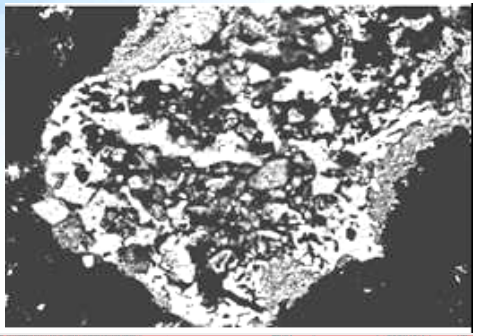
SRNL developed process control strategy (MINCALC™) to estimate mole % or wt% of each phase in the FBSR product

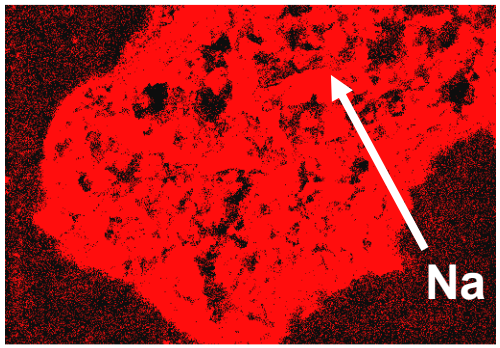
- **sodalite family of minerals have cage structures that accommodate Cl, F, I, SO_4 or S, B, Mo, Re, Tc, Be, Zn, Mn, P**
  - **sodalites known to sequester these species in other HLW waste forms (glass bonded sodalites and supercalcine ceramics)**
  - **Re sodalite made phase pure by Mattigod at PNNL and structure determined**
  - **known from XRD patterns of simulants containing high Cl and F (WTP-SW) produce sodalite; high SO_4 simulants produce nosean (sodalite analog with sulfate)**

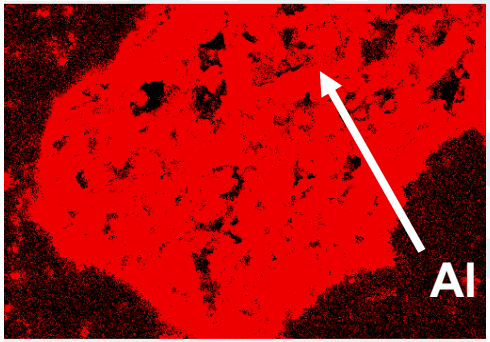


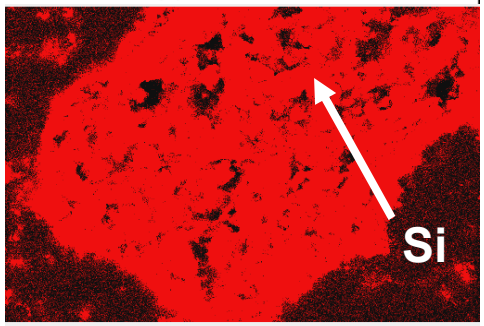


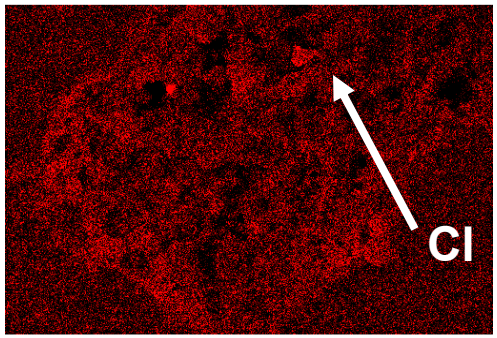
SEM Data on BSR Non-Radioactive LAW



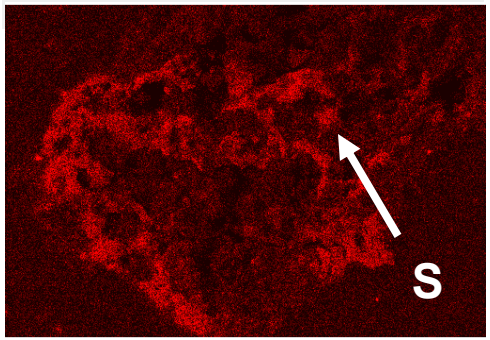




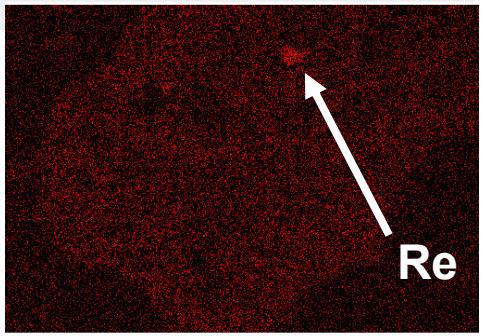




Cl Ka1



S Ka1

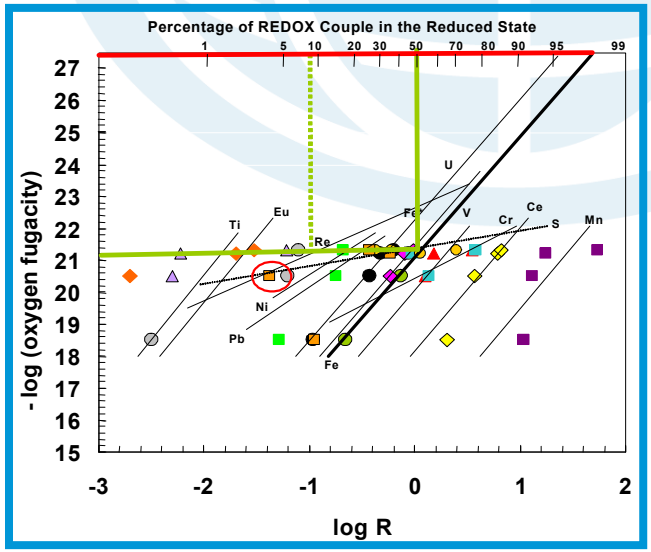


Re La1

Relation of DMR REDOX and Oxygen Fugacity to Mineral Structure

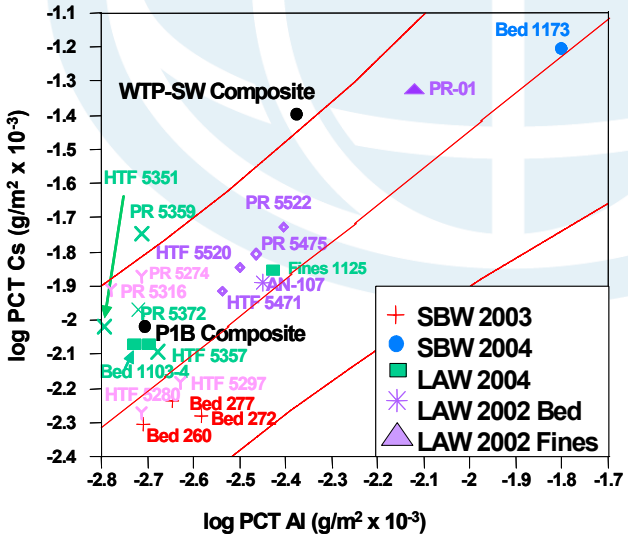
Sample	Vessel	Waste	$Fe^{+2}/\Sigma Fe$	Re^{+7}	S^{+4}
5274	PR	LAW	0.410	94%	86%
5316	PR	LAW	0.581		
5359	PR	LAW	0.508		
5372	PR	LAW	0.500		
5475	PR	WTP SW	0.410	95%	89%
5522	PR	WTP SW	0.463		

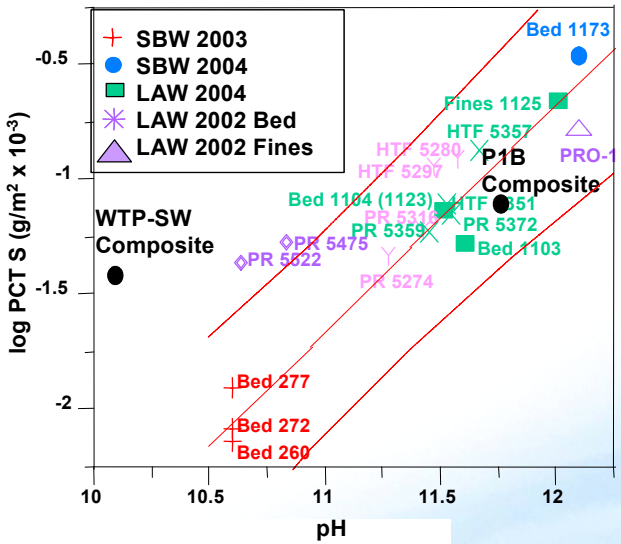
*PR = product receipt vessel



Potential Release Mechanism

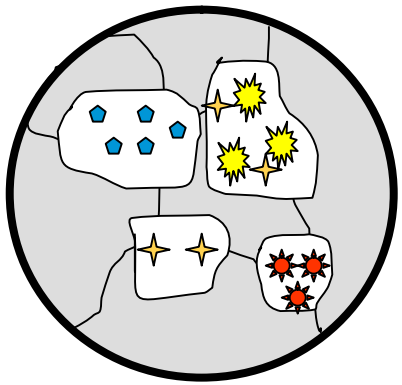
- Alkali release correlates linearly with Al release not with pH
- An Al buffering mechanism buffers solution pH
- New data follows same general trends when fines and bed samples are tested separately
- Composites follow trend but problematic in estimation of surface area for bimodal size distribution





Geopolymers Chosen as Monolith Media by Downselect

FBSR product is granular
Chemical composition of geopolymer binder (Na-Al-Si) similar to FBSR product
Heats of curing and compression optimized



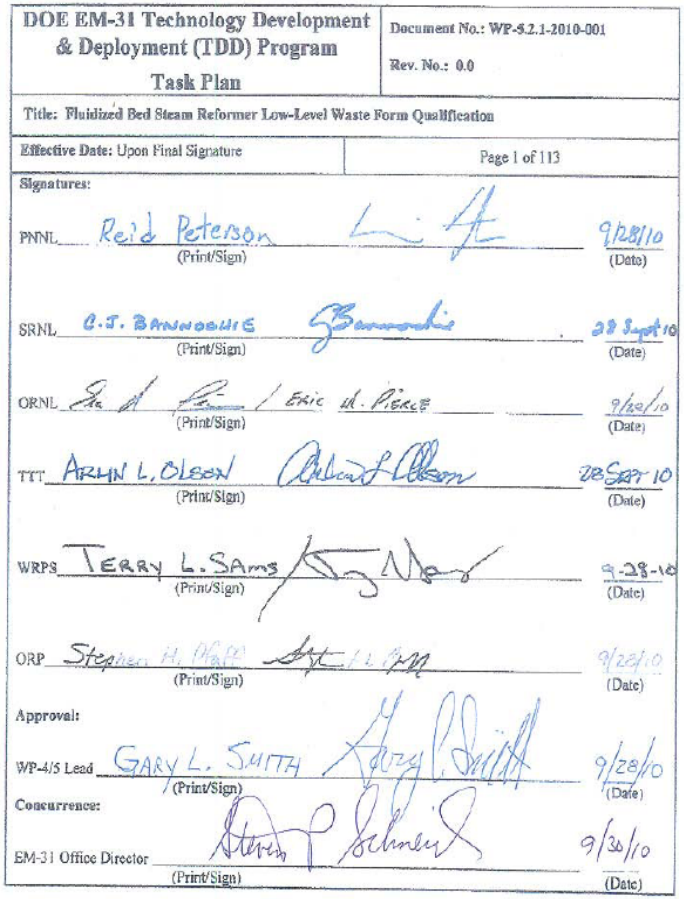
Composite Ceramic/Mineral Waste Forms Are Atomically Bonded & Encapsulated

(3”× 6” and 6”×12”)

(6”×12”)

Path Forward: FY10 Program Overview

- Provide support to EIS team to improve assumptions on FBSR performance
- Develop EM-30 Integrated FBSR WFQ Task Plan
- Perform WTP Secondary Waste BSR run
  - Supports Hanford baseline activities on immobilization of WTP secondary waste
- Identify/select samples of actual Hanford LAW for BSR product production
- Treat/ship Hanford LAW samples to SRNL
- Initiate BSR run with 68 Tank Blend sample
  - SRS shim simulant and actual SRS LAW



DOE EM-31 Technology Development & Deployment (TDD) Program Task Plan

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Rev. No.: 0.0

Title: Fluidized Bed Steam Reformer Low-Level Waste Form Qualification

Effective Date: Upon Final Signature

Page 1 of 113

Signatures:

PNNL Reid Peterson (Print/Sign) 9/28/10 (Date)

SRNL C.J. BANNOCHIE (Print/Sign) 28 Sept 10 (Date)

ORNL / ERIC M. PIERCE (Print/Sign) 9/28/10 (Date)

TTT ARLIN L. OLSON (Print/Sign) 28 SEPT 10 (Date)

WRPS TERRY L. SAMS (Print/Sign) 9-28-10 (Date)

ORP Stephen H. Pfaff (Print/Sign) 9/28/10 (Date)

Approval:

WP-4/5 Lead GARY L. SMITH (Print/Sign) 9/28/10 (Date)

Concurrence:

EM-31 Office Director (Print/Sign) 9/30/10 (Date)

Path Forward: FY10 Program Overview

- Evaluate the impact, if any, of the monolithing (binder) process on material performance
- Determine the effect of chemical affinity on contaminant release for multi-phase material
- Develop rate law parameter and thermochemical data for the major mineral phases contained in FBSR NAS waste form
- Determine transport properties of monolith waste form –diffusion release
- Develop a modified waste form release/radionuclide source term model for the FBSR NAS waste form