Fluidized Bed Steam Reforming (FBSR): A Novel Process for Mineralizing Organic and Halide Containing Wastes

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Carol M. Jantzen

Savannah River National Laboratory
Aiken, SC 29808

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What is Fluidized Bed Steam Reforming (FBSR) ?

- **FBSR is a robust technology**
  - **accommodates wide ranges of feeds**
  - **high sulfate and other anions stabilized in aluminosilicate mineral cage structures**
- **FBSR is a moderate temperature process (625-750°C)**
  - **reactions include organic destruction, denitration, evaporation, dehydration, and hydrothermal reactivity**
  - **operates in the absence of air: organics are pyrolyzed**
  - **temperature low enough not to vaporize radionuclides**
  - **temperature high enough to destroy VOC's and SVOC's**

What is Fluidized Bed Steam Reforming (FBSR) ?

- Produces solid mineral phases from aqueous solutions
  - High NaOH, $NaNO_3$, $NaNO_2$, etc wastes can be made into carbonates, silicates, or Na-Al-Si (NAS) minerals
  - Works for high alkaline earth wastes as well
  - Works for high carbon-containing wastes as well
- Pilot scale demonstrations with highly basic (pH=14) and acidic (pH=1) wastes @ 3-5.2M Na^+ successfully produced NAS mineralized waste products
- FBSR mineral product as durable as borosilicate glass
- FBSR product passes TCLP at the UTS limits when the ferrite spinel phase forms from iron rich catalyst
- Granular product can be monolithed

THOR^{sm} Commercial Operations

- **THOR^{sm} = THermal Organic Reduction**
- **THOR^{sm} currently processes organic resins from nuclear fuel industry in commercial facility**
- **Organics are pyrolyzed in presence of C and absence of air**
  - **superheated steam used as the fluidizing media converts C from all sources including VOC's and SVOC's to CO_2**
  - **Nitrates and nitrites are converted to N_2 by addition of a solid carbon source such as charcoal or sugar**

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Commercial FBSR Organic Destruction

- **FBSR is a proven technology in the destruction of organics**
  - **heavily shielded commercial operations destroy Cs^{137} and Co^{60} organic resins from nuclear power plants at Erwin, TN**
  - **licensed as non-incineration technology by Region IV EPA to handle materials up to 400R/hr**
  - **organic destruction via pyrolysis**

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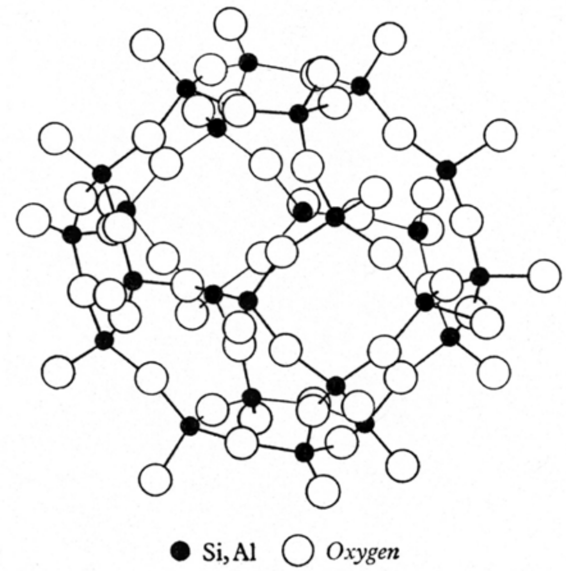
Steam Reformer Na-Al-Si (NAS) Product Mineralogy



- **Feldspathoids**
  - **anhydrous analogs of zeolites**
  - **all have cage structures (nephelines, carnegeites, nosean, sodalite)**
  - **cage structured sodalite and nosean accommodate NaCl, Na_2SO_4, Na_2S, NaF, NaI, Na_2MoO_4, $NaRe^{+7}O_4$**
  - **normal nepheline is hexagonal and has eight 9-membered oxygen rings and six 8-membered oxygen rings**
  - **Na-rich nepheline is cubic; has 12-membered oxygen cages**

Durability of Mineral Phases Previously Studied for Ceramic/Glass-Ceramic Forms

Hanford FBSR (650-750°C)	HLW Ceramic Supercalcines Tailored Ceramics (1300-1500°C)	Glass Bonded Sodalite (HIP@1200°C or sinter @950°C)
Nosean (Sodalite Family)	$(NaAlSiO_4)_6(NaMoO_4)_2$	Sodalite (Cl and I)
2 Nephelines	Nepheline	Nepheline
Corundum from starting bed	Corundum formed from waste	
Hematite + Magnetite from waste and additives	Magnetite from waste	

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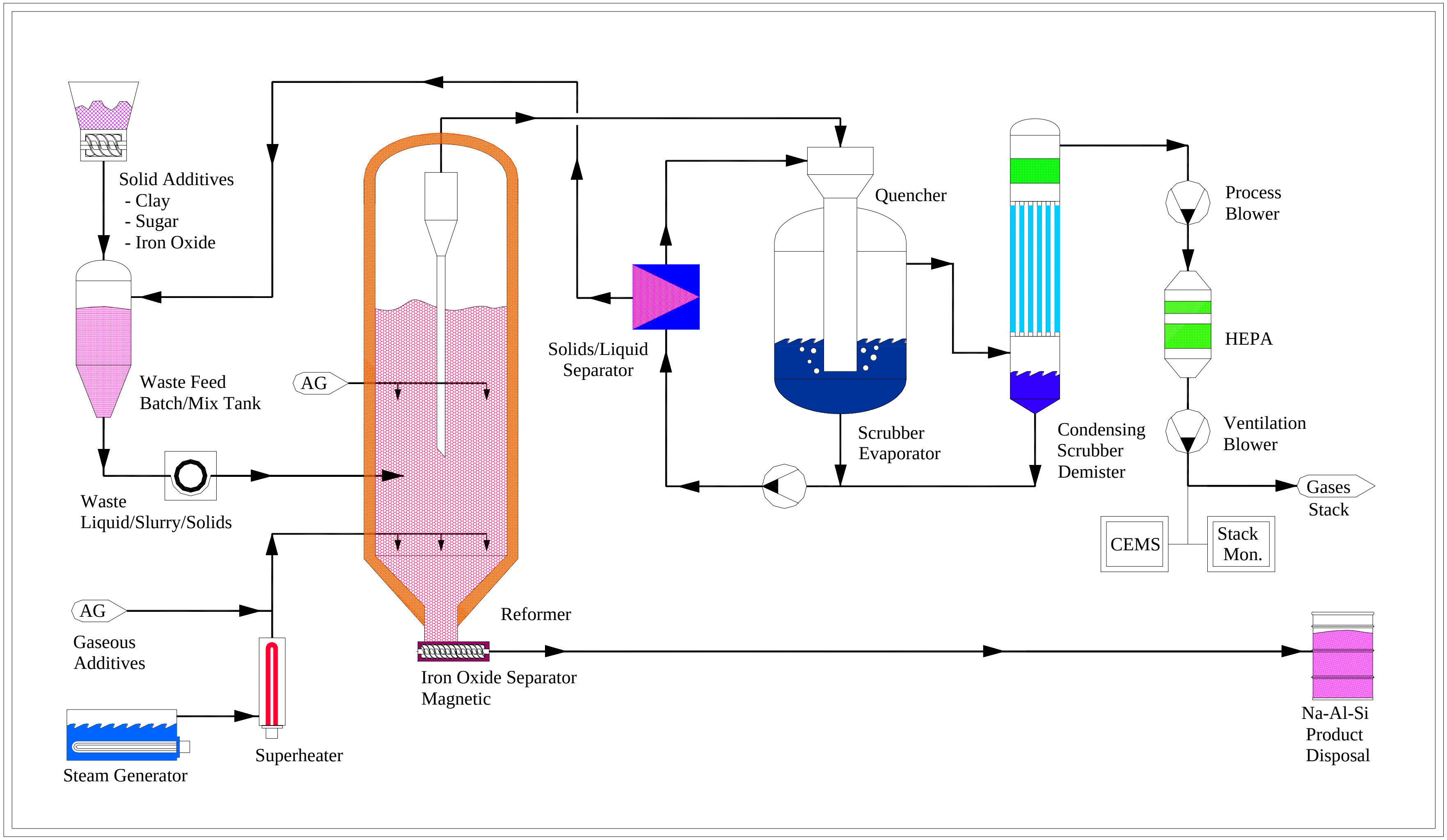
SIMPLIFIED FBSR FLOWSHEET

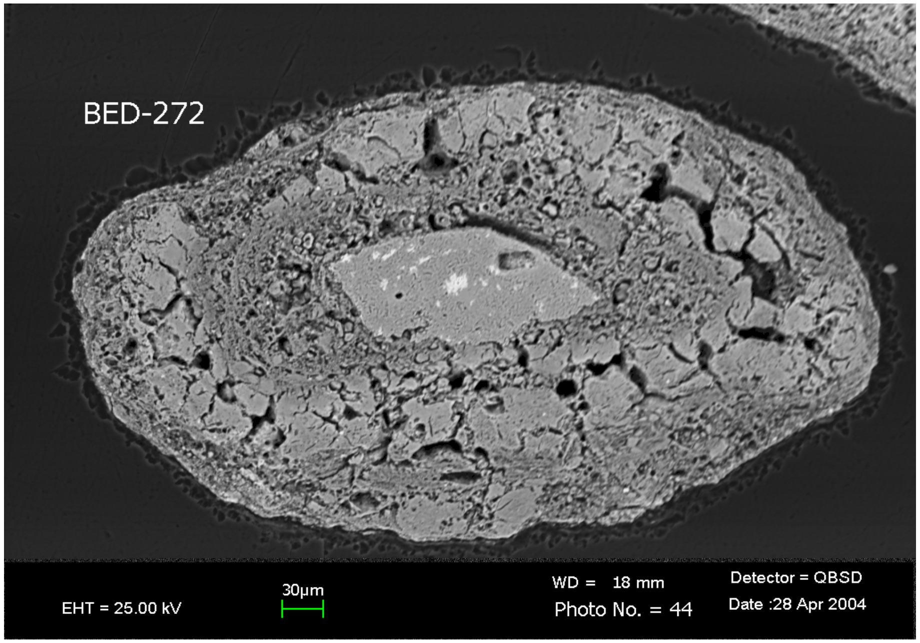


FBSR Hazen Granular Product

mm ruler scale

X-Ray Diffraction and Scanning Electron Microscopy of FBSR NAS Samples (2001-4)

- Nepheline ($NaAlSiO_4$), K-substituted nepheline ($K_{0.25}Na_{0.75}$), high Na nepheline ($Na_{1.53}$), Si-deficient nepheline, nosean, and sodalite are major phases
- Higher NAR produces more carnegeite ($NaAlSiO_4$) than nepheline; carnegeite is enriched in the fines (shorter residence times); carnegeite easily converts to nepheline
- Excess clay is amorphous and forms unreacted cores
- Fe catalyst for NO_x destruction forms ferrite spinels



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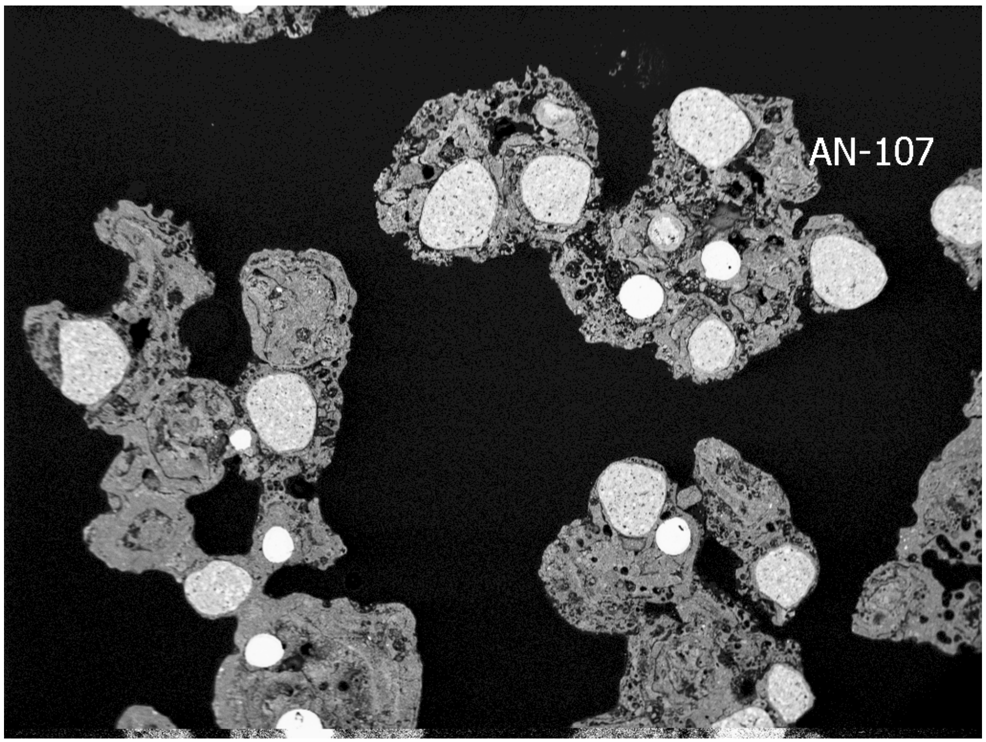
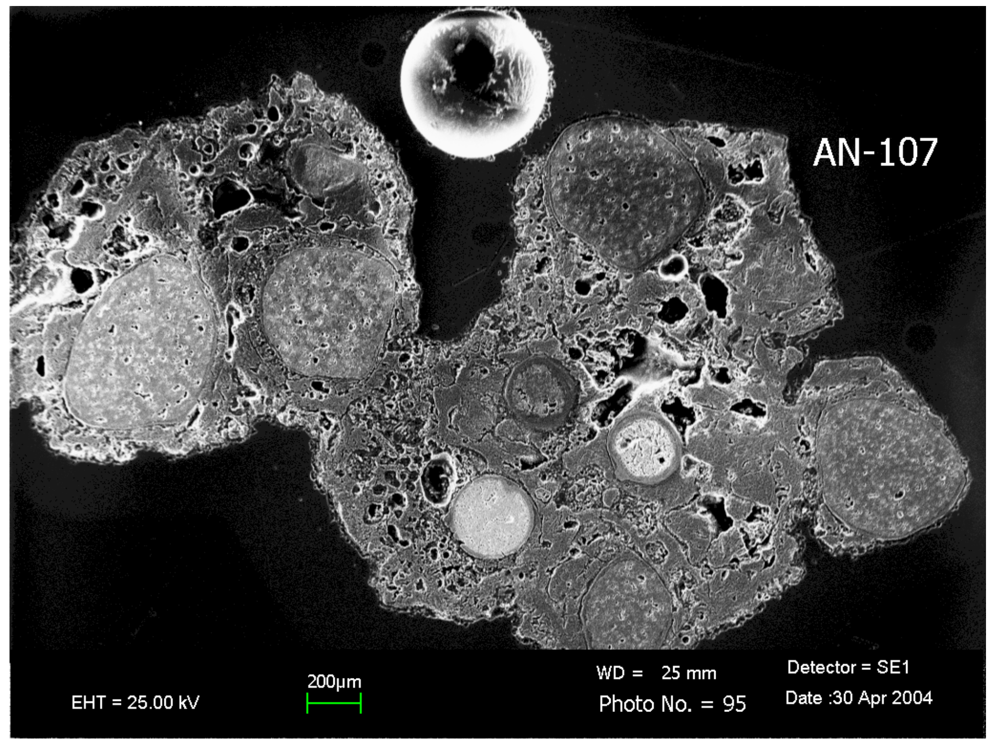
Scanning Electron Microscopy of FBSR Hanford AN-107 Product





Note unreacted clay cores.

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Mineral Phases Predicted by Known Phase Relations in the Na_2O-Al_2O_3-SiO_2 System

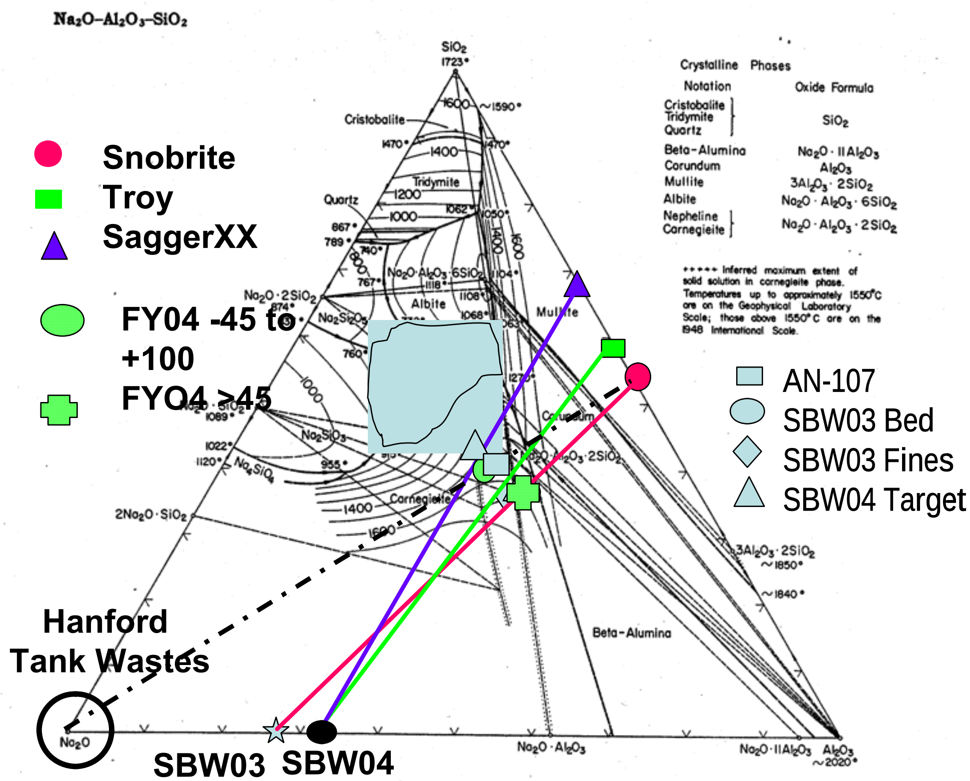

Fig. 501.—System Na_2O–Al_2O_3–SiO_2; composite.

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

Principal References

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

- **Known phase relations used to optimize waste-clay mixtures**
- **Nepheline melts incongruently; if residence times are too rapid you get metastable carnegeite**
- **Known phase relations used to develop MINCALC(#3) process control strategy**

STEAM REFORMING PILOT SCALE DEMONSTRATIONS

1. Hazen Studsvik – April 1997
   - 6” Fluidized Bed, Hanford 5.2M $NaNO_3$ surrogate, carbonate product
   - 15” Fluidized Bed, ion exchange resins, oils, solvents
2. LMITCO INEEL – 2002 (3” Fluidized Bed, SBW surrogate)
3. Hazen Bechtel/Studsvik – Dec. 2001 (6” Fluidized Bed, LAW surrogate, carbonate and NAS products)
4. SAIC STAR – Jan. 2003 (6” Fluidized Bed, SBW surrogate, carbonate)
5. SAIC STAR – Aug. 2003 (6” Fluidized Bed, SRS Tank 48H surrogate, carbonate)
6. SAIC STAR – Nov. 2003 (6” Fluidized Bed, SBW surrogate, carbonate)
7. SAIC STAR – Aug. 2004 (6” Fluidized Bed, LAW surrogate, NAS product)
8. SAIC STAR – July & Sept. 2004 (6” Fluidized Bed, SBW surrogate, NAS)
9. Hazen Engineering Scale – Nov. 2005 through May 2006 (15” Fluidized Bed, SBW surrogate, carbonate product)
10. Hazen Engineering Scale – Sept/Oct 2006 (15” Bed, SRS T48 carbonate product)

Experimental Protocols for NAS Bed and Fines Products

- **Whole element chemistry**
- **REDuction/OXidation (REDOX)**
- **X-ray Diffraction (XRD)**
- **Scanning Electron Microscopy (SEM)**
- **Product Consistency Test (PCT; ASTM C1285-02) @ standard 7 day @ 90°C**
- **Particle Size Determination (BET and Geometric)**
- **EPA Toxic Characteristic Leaching Procedure (TCLP)**

Analyzed Compositions of FBSR NAS Bed and Fines Products (2001-2004)

Volatility is not an issue:

- **Cs** retained in bed; no partitioning to fines
- **Re** retained in bed; Re partitioning to fines inconclusive (spike concentrations were ~10^{-5} M)
- **SO_4, Cl,** and **Cr** retained in bed; no partitioning to fines
- **I** at detection limit of ICP-MS; appears to have been retained (none in Envelope C simulant; Envelope A simulant at ~10^{-5} M)
- Agrees with off-gas scrubber data (<0.10% of total Cs and <0.003% of total Re volatilized with AN-107 in 2001)

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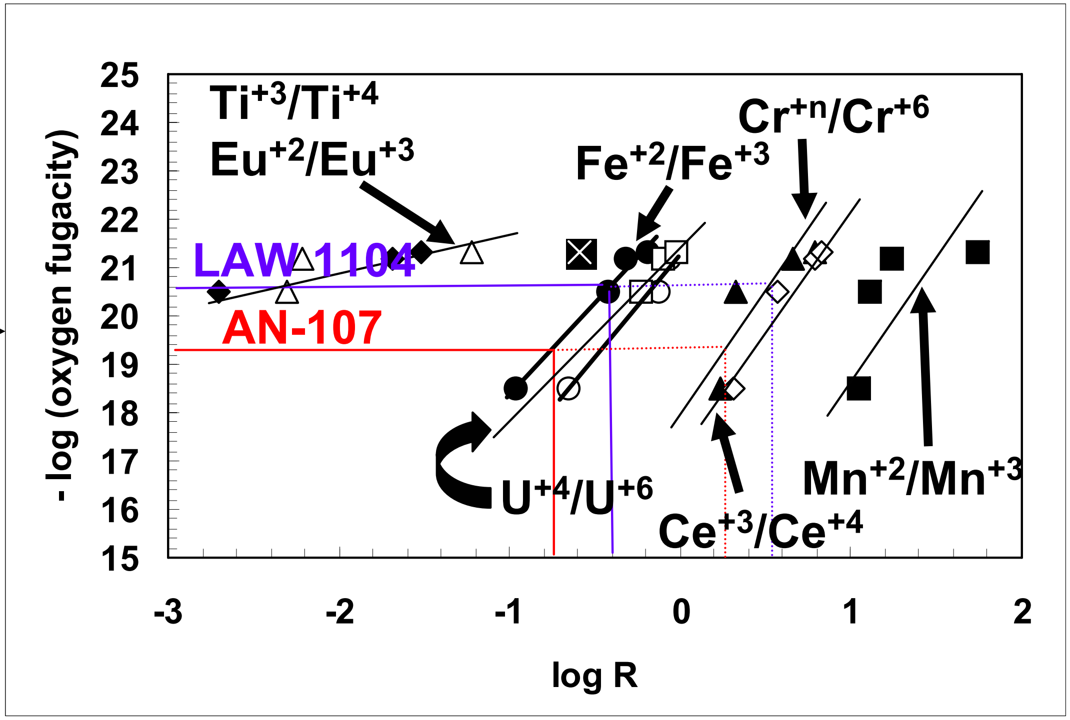
REDOX Speciation of FBSR NAS Bed Products (2001-2004)

Analysis	EA Glass Std	AN107 Avg	LAW Bed 1104
Fe^{+2}	0.088	0.057	0.053
ΣFe	0.458	0.377	0.190
Fe^{+2}/Fe^{+3}	0.237	0.178	0.387

- **FBSR ~ REDOX ratio as HLW glass**
- **EMF series developed to determine oxidation state of other cations like Cr**

LAW 1104 Cr^{+n} ~78%
LAW AN-107 Cr^{+n} ~ 62%

***where n can be $Cr^{+3, +4, +5}$**



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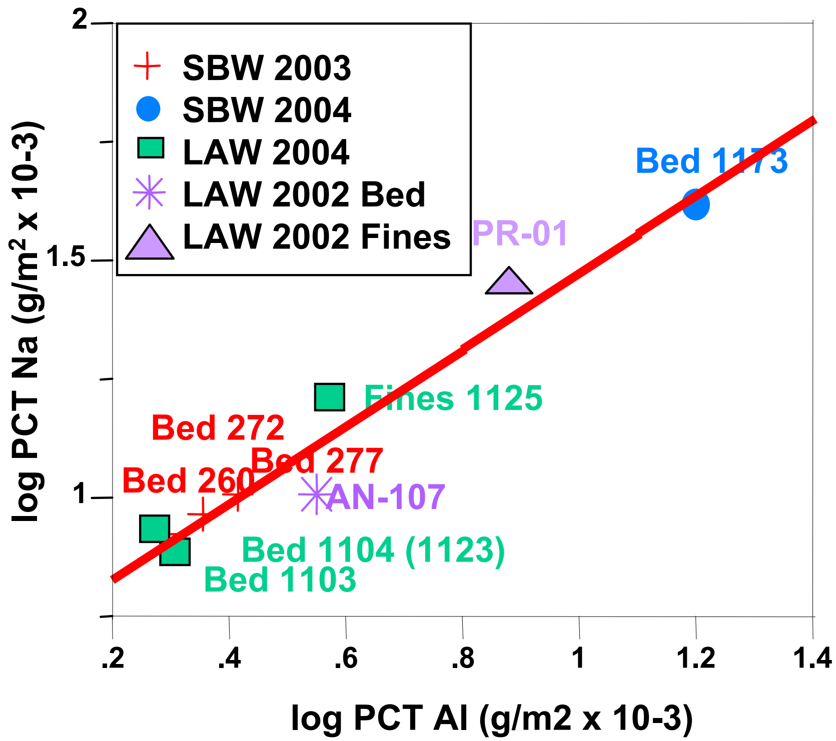
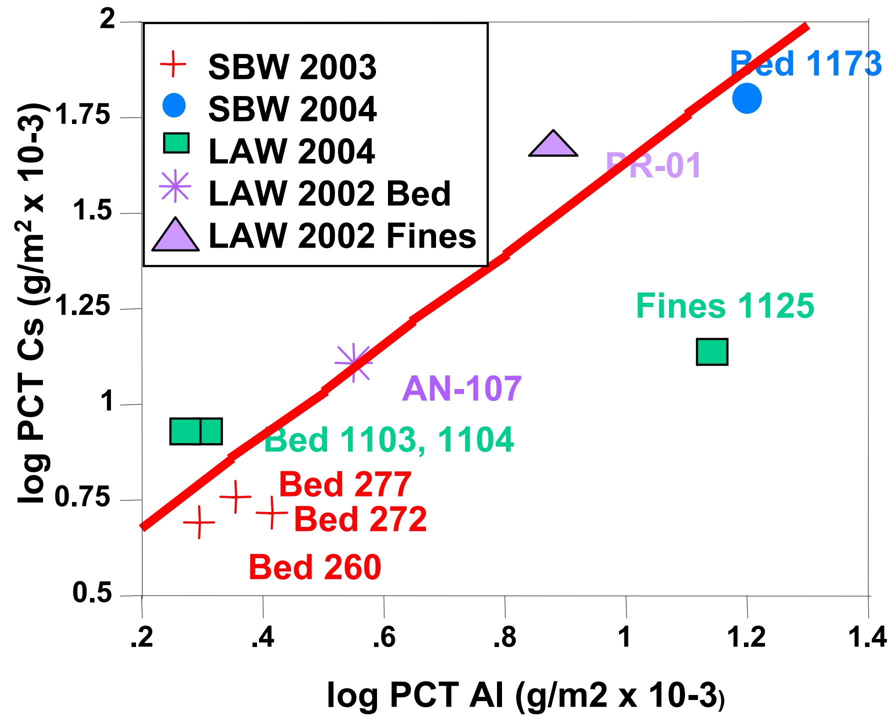
PCT (ASTM C1285-02) Testing of FBSR NAS Mineral Products – Results-Part I





- Alkali release correlates linearly with Al release not with pH
- An Al buffering mechanism from feldspathoid dissolution appears to buffer solution pH

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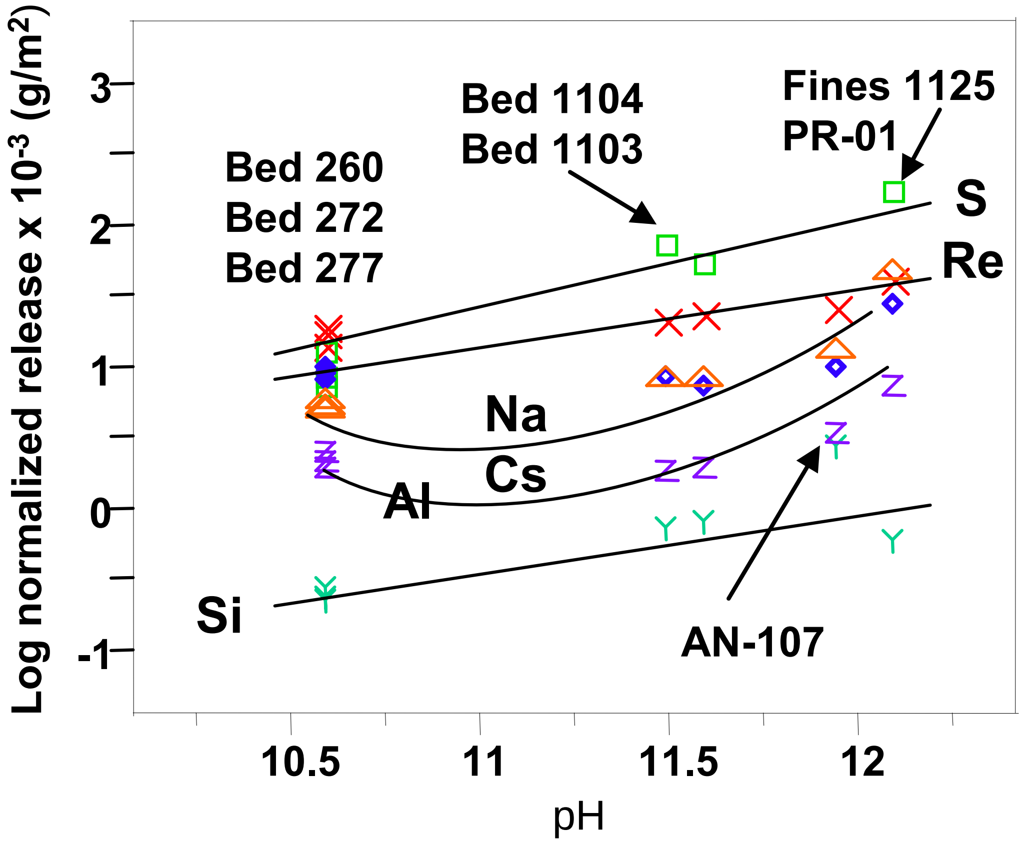
PCT (ASTM C1285-02) Testing of FBSR NAS Mineral Products – Results-Part II



- Re, S, and Si released as a linear function of pH
- Cs, Na, and Al released as a parabolic function of pH
- As durable as glass (no SA normalization)
- More durable than glass (with SA normalization)

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Example of Aluminum Buffering Mechanism

Neutral pH

$$Na_{1.45}Al_{1.45}Si_{0.55}O_4 + 3.45H_2O \xrightarrow{90^\circ C} 1.45Na^+ + 0.55H_2SiO_3 + 1.45Al(OH)_3 + 1.45OH^-$$

pH > 9.25

$$Na_{1.45}Al_{1.45}Si_{0.55}O_4 + 2.9H_2O + 0.55OH^- \xrightarrow{90^\circ C} 1.45Na^+ + 0.55HSiO_3^- + 1.45Al(OH)_4^-$$

pH > 11.7

$$Na_{1.45}Al_{1.45}Si_{0.55}O_4 + 2.9H_2O + 0.55OH^- \xrightarrow{90^\circ C} 1.45Na^+ + 0.55SiO_3^= + 1.45Al(OH)_4^- + 0.55H^+$$

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Monolith vs. Durability

- **Feasibility of monolithing granular Na-Al-Si (NAS) Fluidized Bed Steam Reformer (FBSR) product**
  - **Without compromising durability of the granular NAS waste form**
  - **Keeping the FBSR loading high, e.g. minimizing the amount of binder**
  - **Meeting the compressive strength requirement for shallow land burial**

NAS Composite (Bed Products and Fines) Used for Monolithing

Species (wt%)	2003 SBW FBSR	2004 SBW FBSR	2004 LAW Envelope A FBSR	Analyzed Composite	Algorithm Fit
Al_2O_3 (ICP-ES)	39.03	38.36	33.32	63.35	63.350
CaO (ICP-ES)	0.75	3.79	1.96	1.46	1.065
Cs_2O (ICP-MS)	7.12×10^{-2}	3.25×10^{-2}	1.51×10^{-4}	2.26×10^{-2}	1.67×10^{-2}
Fe_20_3 (ICP-ES)	1.74	1.012	0.333	1.389	0.506
K_2O (ICP-ES)	3.31	3.96	0.31	1.283	1.188
Na_2O (ICP-ES)	16.52	16.50	20.87	9.39	. 9.383
P_2O_5 (ICP-ES)	2.12	0.859	0.47	0.344	0.576
ReO_2 (ICP-MS)	2.27×10^{-2}	5.57×10^{-3}	5.34×10^{-3}	3.00×10^{-3}	5.72×10^{-3}
SiO_2 (ICP-ES)	35.63	37.65	38.12	19.056	19.132
TiO_2 (ICP-ES)	1.14	1.19	1.23	0.537	0.612
NaCl (IC)	<0.2	0.152	0.225	BDL	
NaF (IC)	<0.2	<0.2	<0.2	BDL	
NaI (IC)	NM	NM	$<2 \times 10^{-5}$	NM	
SO_3 (ICP-ES)	0.419	0.103	0.766	2.65	0.241
SUM	100.86	104.50	97.85	99.78	96.34

COMPOSITE

~44 Startup Bed
~17% SBW03
~15% SBW04
~20% LAW04

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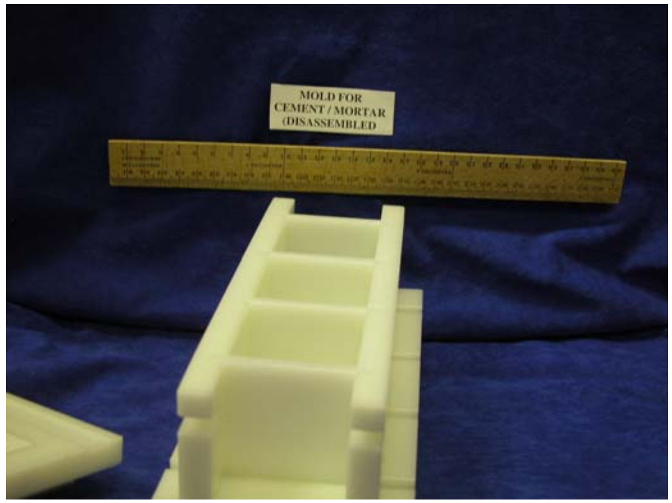
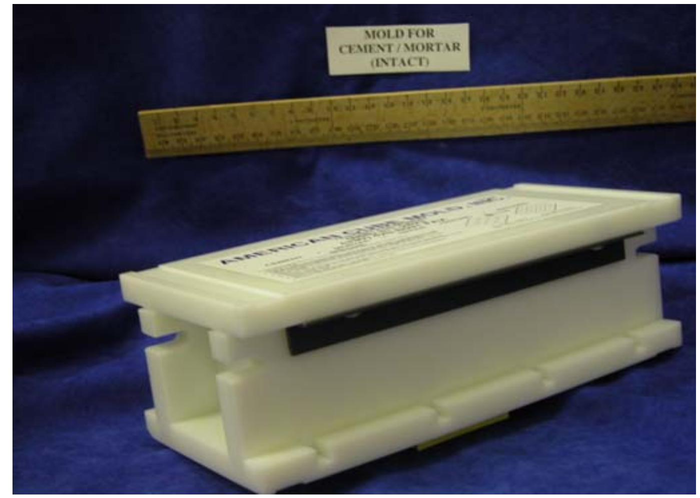
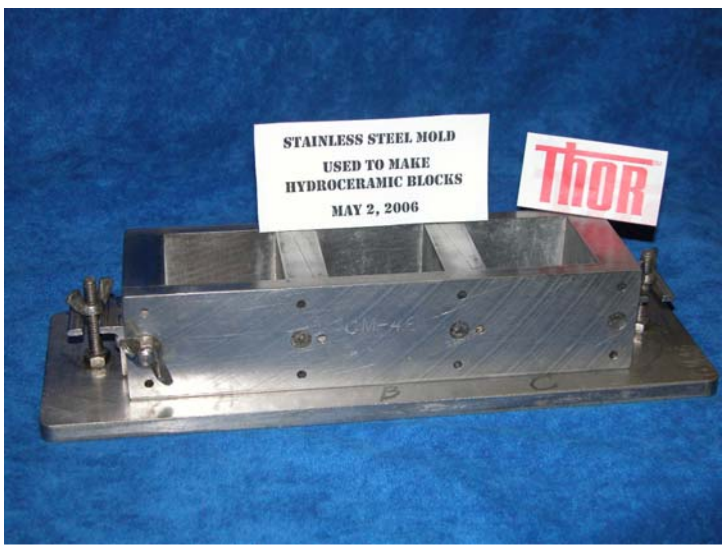
Monolith Binders Tested

- Ordinary Portland Cement (OPC) @ SRNL
  - three without and two with fume SiO_2 (for fly ash)
  - waste loadings 80-87% FBSR product
- Ceramicrete ($MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \bullet 6H_2O$) @ ANL
  - one formulation tested (~1/3 Ceramicrete blend + 1/3 Class C fly ash)
  - waste loading 36% FBSR product
- Hydroceramics (metakaolin + NaOH) @ SRNL
  - three formulations @ three different curing temperatures
  - waste loadings 60-83% FBSR product

Teflon® and/or Steel Molds Make 2" Blocks)





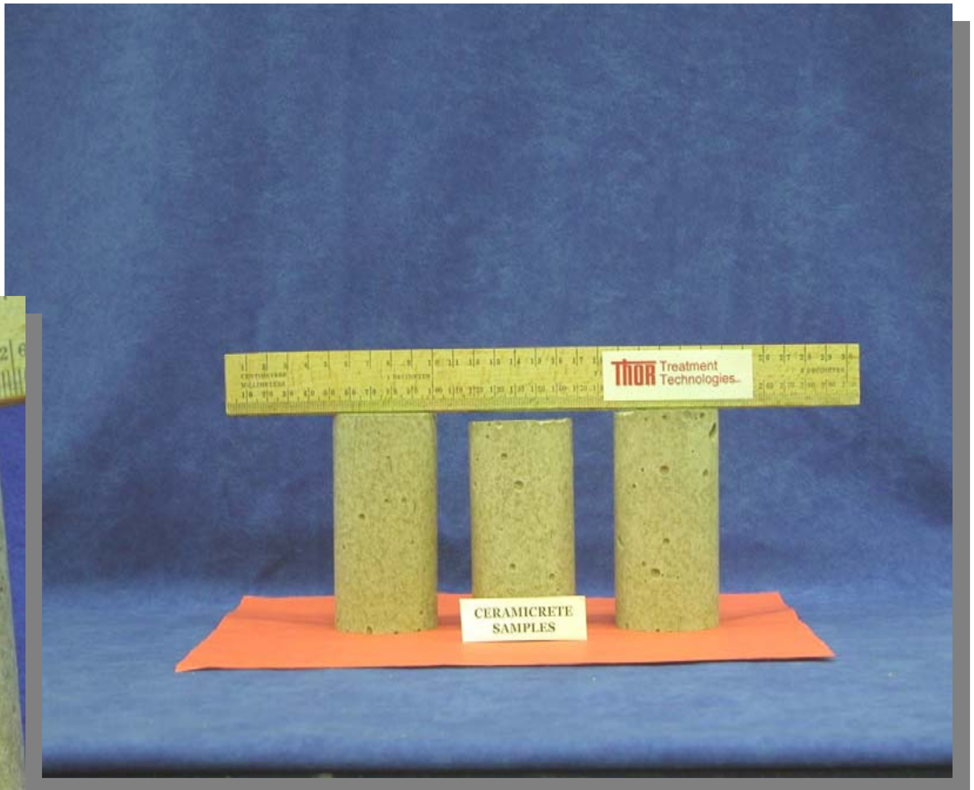


Cement Monoliths

- Cement blocks set for 7 days at ambient temperature

Ceramicrete Monoliths

- Set at ANL for 14 days at ambient conditions



Hydroceramic Monoliths

- Set 3-7 days; 40-90°C in steam

Compressive Strength Tests

ASTM C39-04

ASTM C109-02

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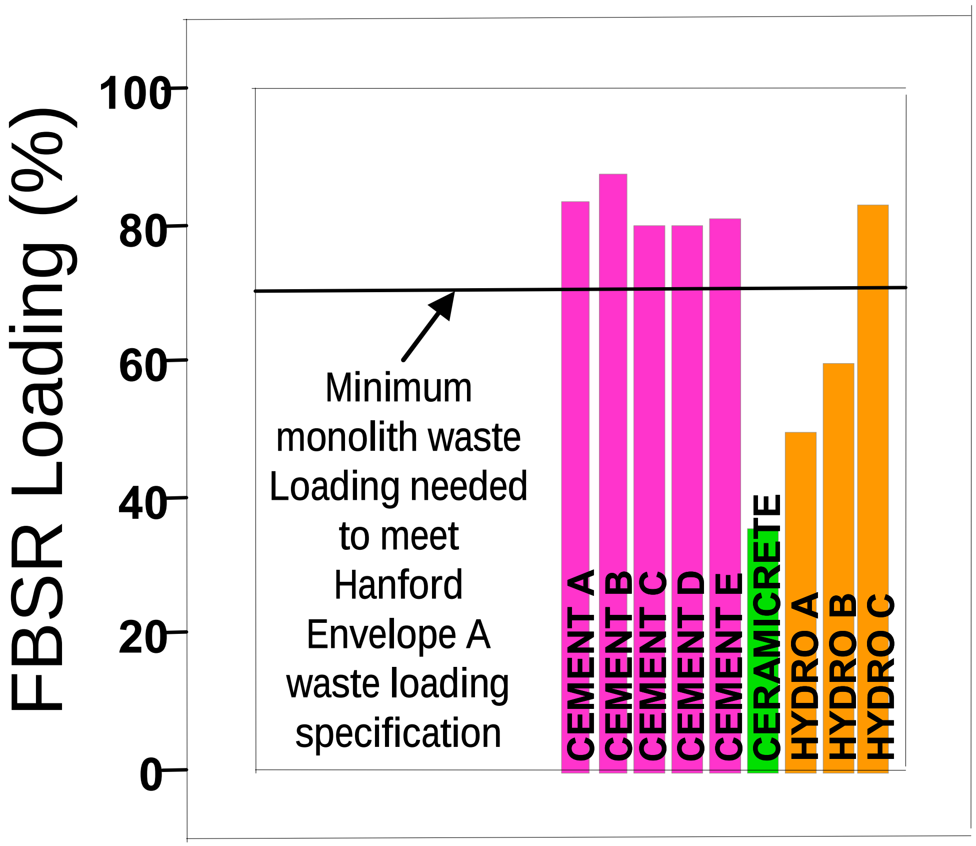
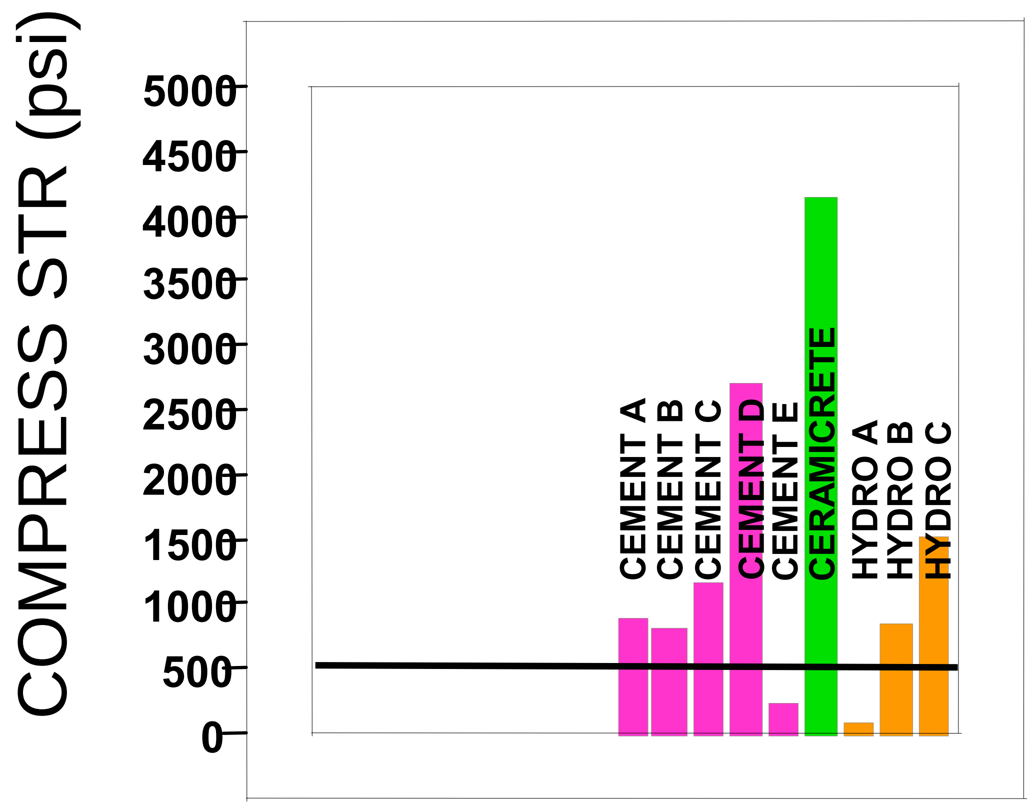
Density & Compressive Strength Test Results





Even without optimization, 5 Monoliths met the Hanford Envelope A waste loading and 500 psi strength requirements

Are the NAS Phases Retained in the Matrix?

PHASES	FBSR COMPOSITE	CEMENT	CERAMICRETE	HYDROCERAMIC
Al_2O_3 (startup bed)	MAJOR	---	MAJOR	---
Nepheline $Na_{6.8}Al_{6.3}Si_{9.7}O_{32}$ or $NaAlSiO_4$	MAJOR	MAJOR	MAJOR	MAJOR
Sodalite $Na_8Al_6Si_6O_{24}Cl_2$	MINOR	---	---	Anhydrous Zeolite A
Nosean $Na_8Al_6Si_6O_{24}SO_4$	MINOR	---	---	Anhydrous Zeolite A
SiO_2	MINOR	MINOR	---	MINOR
Calcite $CaCO_3$	---	MINOR	---	---
$AlPO_4$	---	MINOR	---	---
$KMgPO_4 \bullet H_2O$	---	---	MAJOR	---

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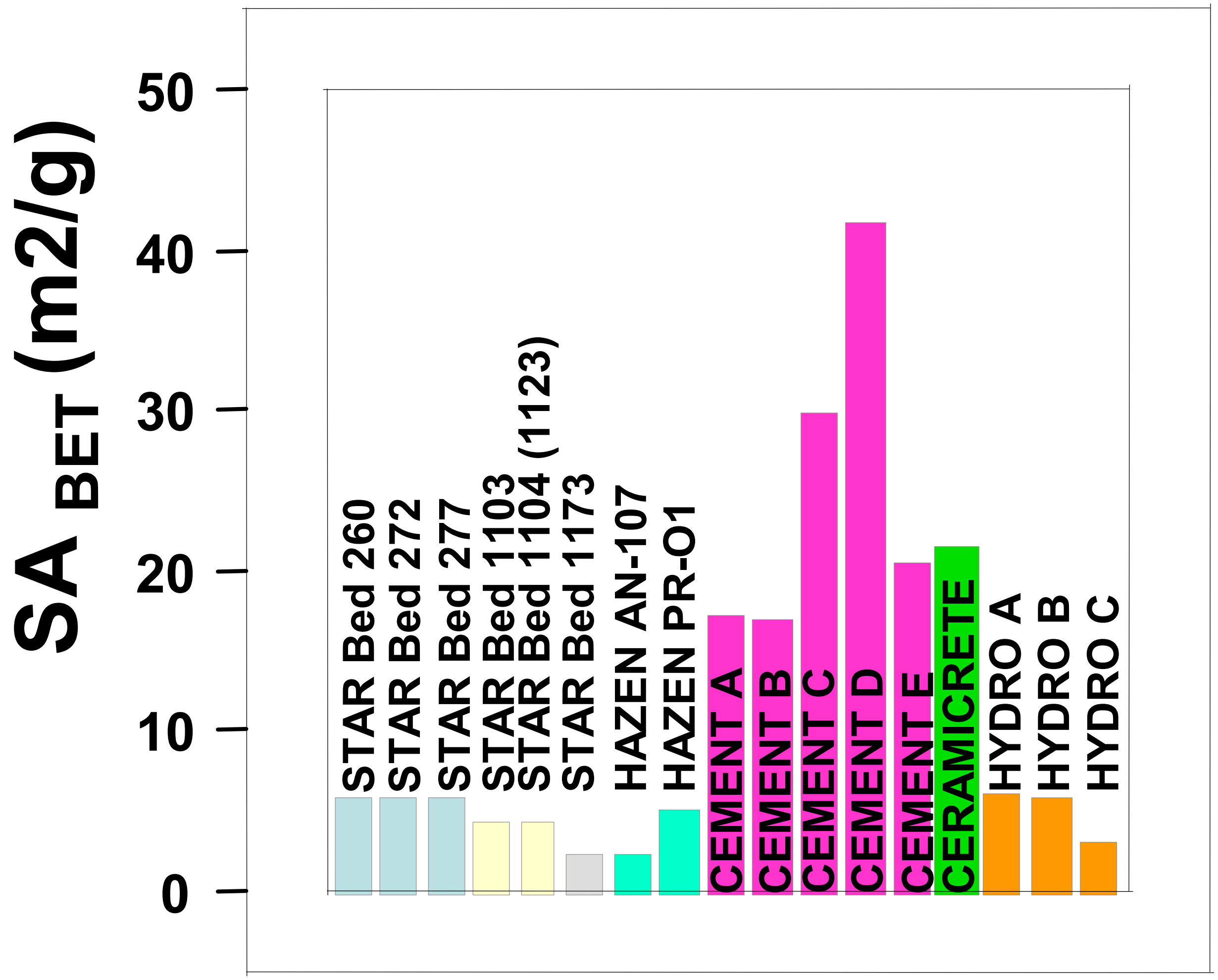
What is the SA of the Monolith Product vs the Granular Product?



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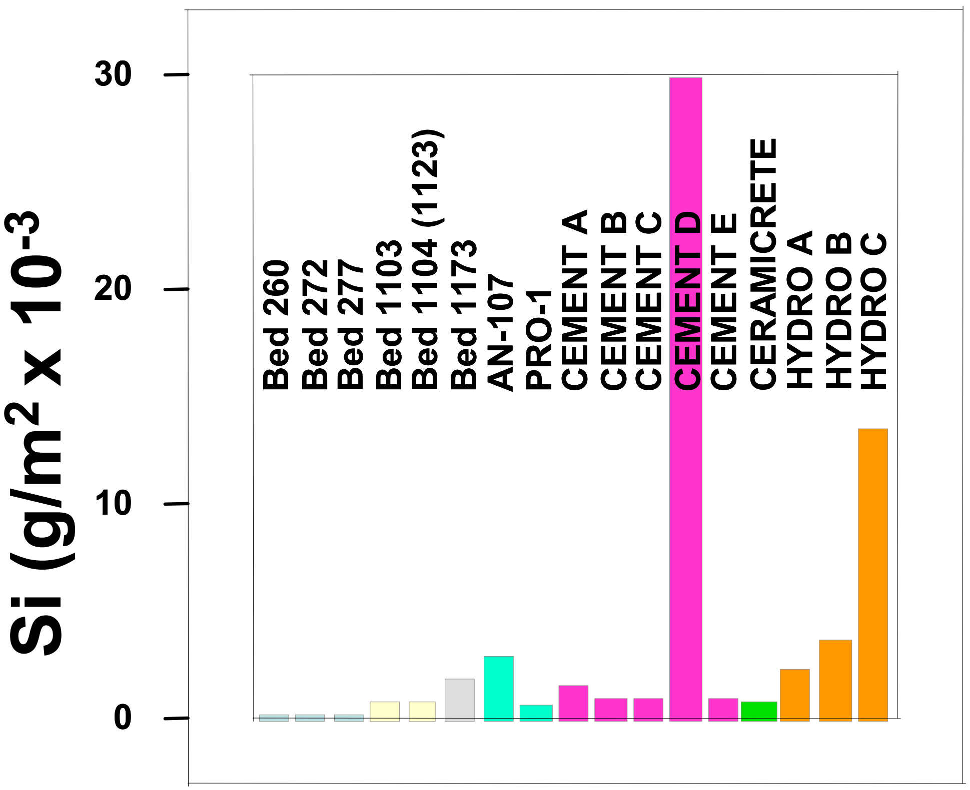
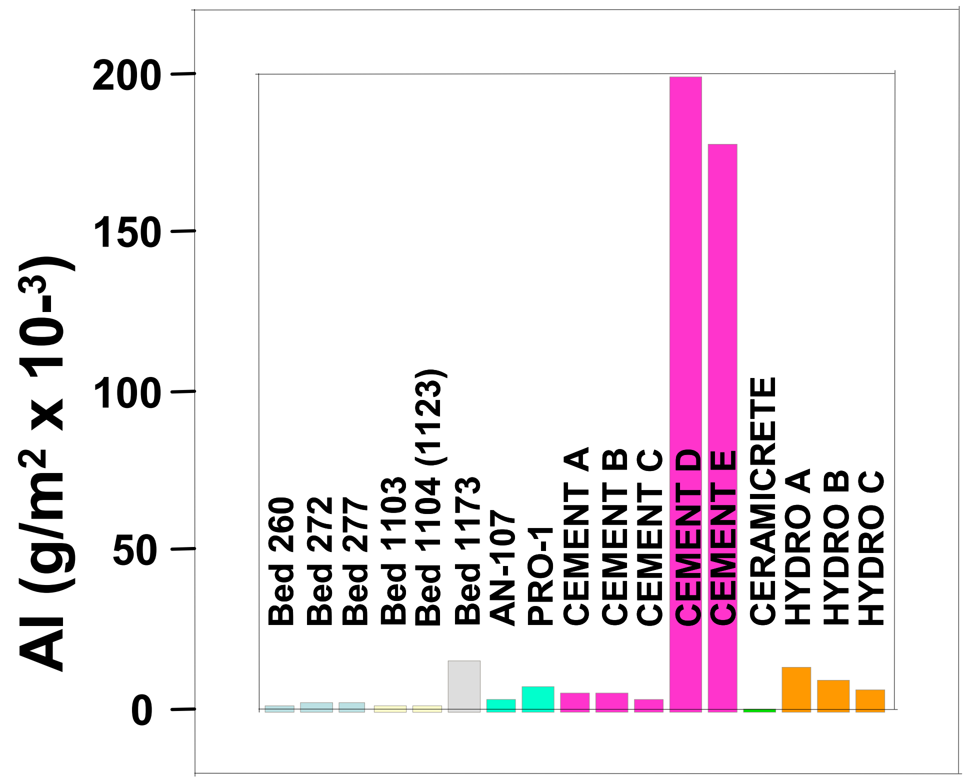
PCT Durability of Monolith vs. Granular Forms - I





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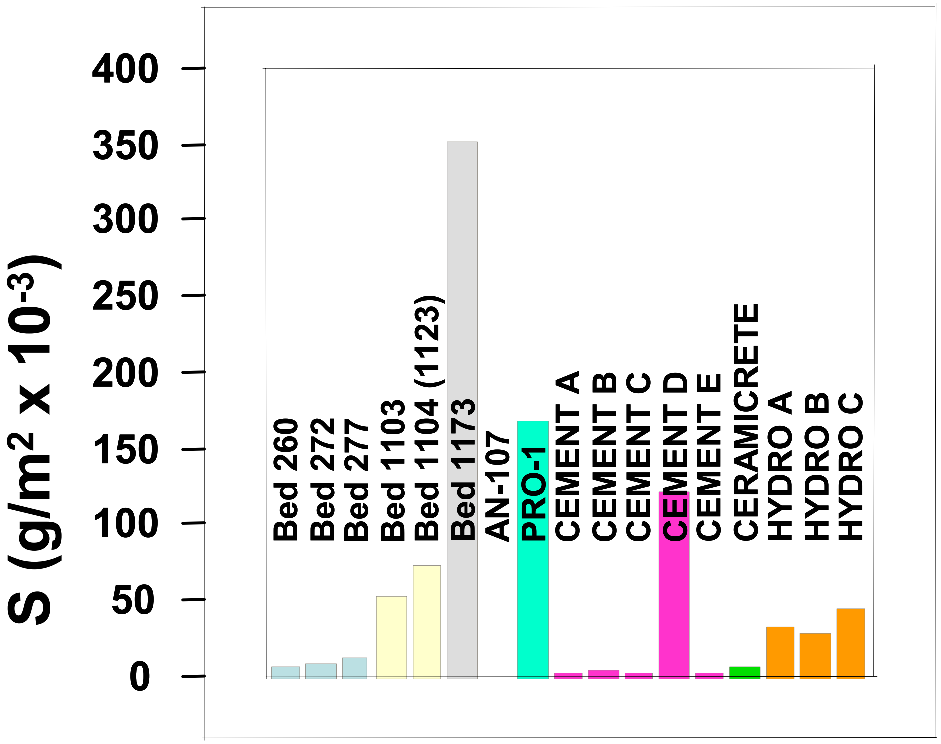
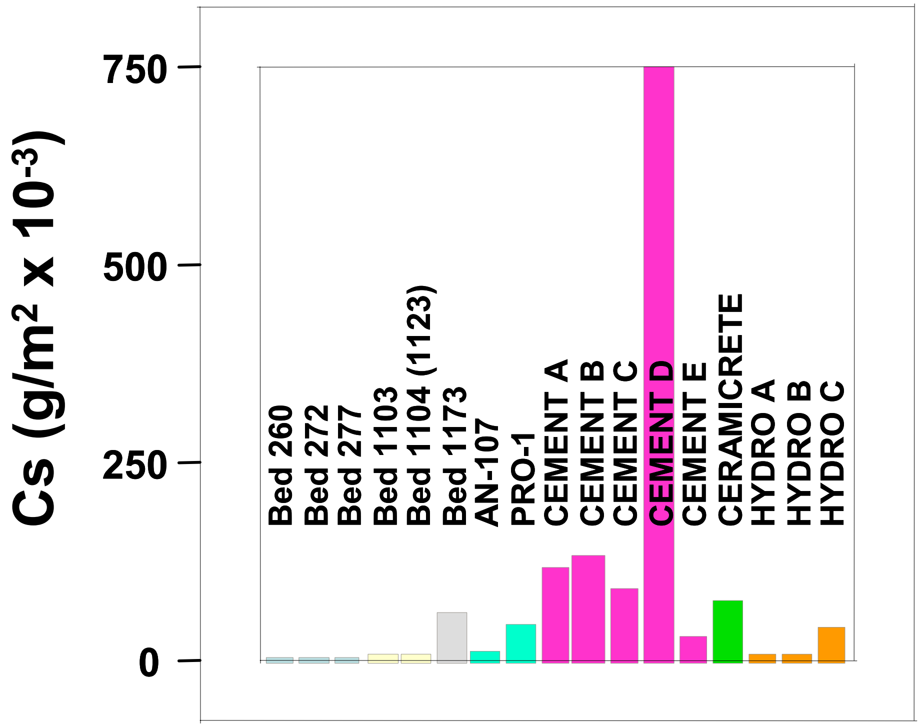
PCT Durability of Monolith vs. Granular Forms - II





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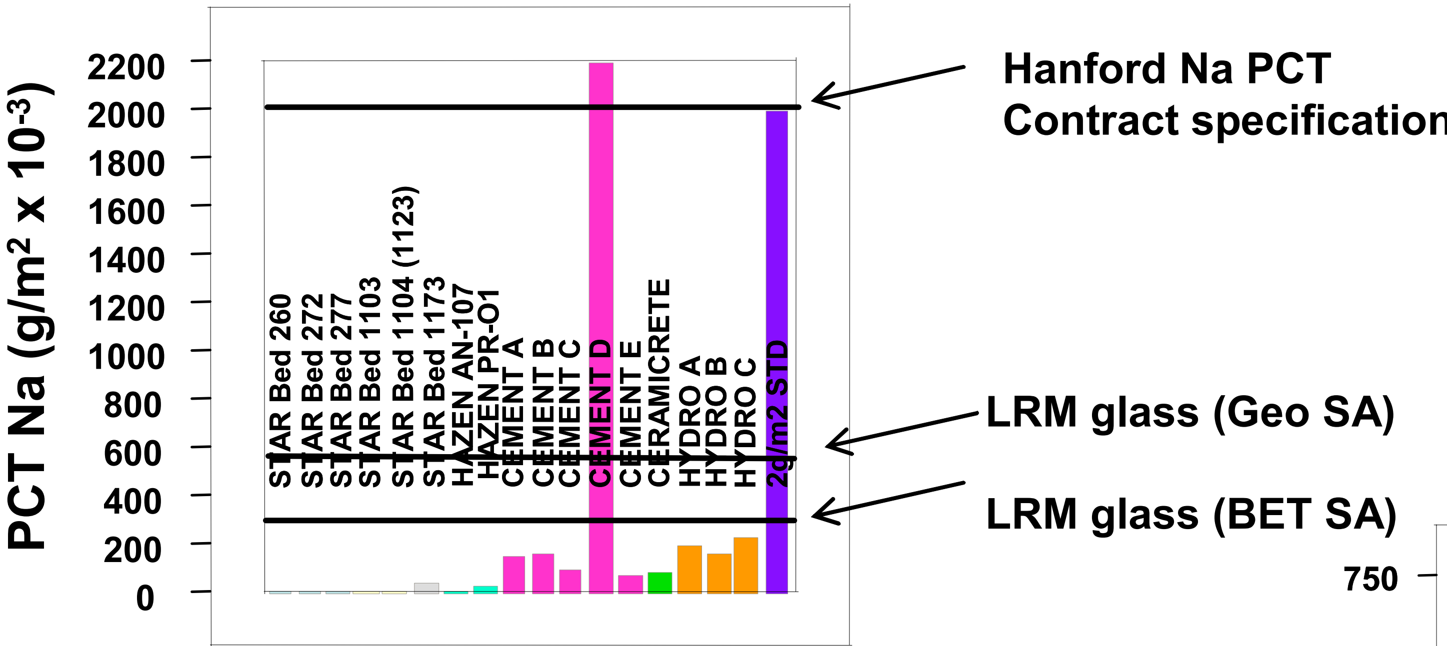
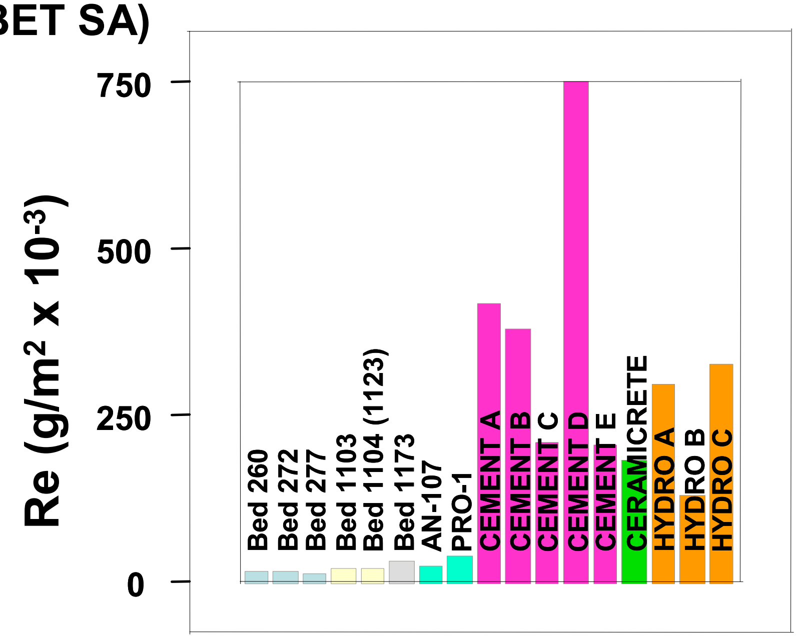
PCT Durability of Monolith vs. Granular Forms - III





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Conclusions

Monolith	Waste Loading Criteria for Hanford LAW Envelope A	≥ 500 psi Compressive Strength	PCT Durability $<2 g/m^2$
Cement A	YES	YES	YES
Cement B	YES	YES	YES
Cement C	YES	YES	YES
Cement D	YES	YES	NO
Cement E	YES	NO	YES
Ceramicrete	NO**	YES	YES
Hydroceramic-A	NO	NO	YES
Hydroceramic-B	NO	YES	YES
Hydroceramic-C	YES	YES	YES

Many of the monoliths tested met the criteria even though optimization was not a study goal

** not an optimized waste form

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Conclusions

- **FBSR is a robust technology that mineralizes high sodium wastes with the addition of kaolin clay and an iron catalyst**
- **FBSR product is ~2 orders of magnitude more durable than glass in g/m^2 or comparable to glass in g/L**
  - **an aluminum buffering mechanism appears to control dissolution**
  - **the aluminum buffering mechanism is known in nature**
- **FBSR product passes TCLP at the UTS limits when the ferrite spinel phase is provided by use of catalyst**
- **Granular product can be monolithed**

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Future Work

- **Evaluate additional binders (PCT and Compressive Strength)**
  - **high Al_2O_3 containing cements**
  - **geopolymers (kaolin clay and water glass)**
    - **demonstrated at the pilot scale for mining waste remediation**
  - **hydroceramics with different clays**

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