SRNL™
SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC

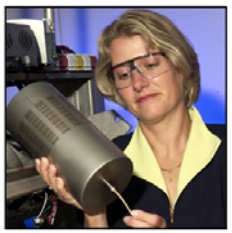
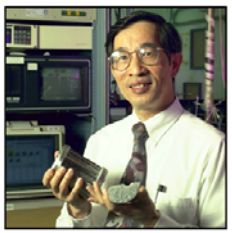
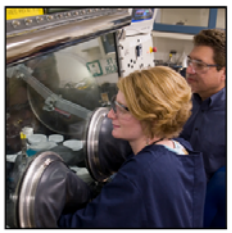
We Put Science To Work

Solidification of Continuous Sludge Leaching Product

J. R. Harbour

Savannah River National Laboratory

November 16, 2010

EM Waste Processing Technical Exchange

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Print

Close

Outline

EM-31 Waste Processing, WP-2.1.4

Solidification of CSL Stream after NaOH Recovery

- **Background**
- **Scope and progress**
- **Candidate waste forms**
- **Discussion of Results**
- **Path forward**

Background – Near Tank Treatment System

- **Continuous sludge leaching**
  - Parsons
  - Aluminum removal from S and SX Tank Farm waste (REDOX)
  - Use NaOH for dissolution of Boehmite and Gibbsite
- **Cs-137 removal as necessary by ion exchange**
- **NaOH recovery**
  - Ceramatec process (NaSICON ceramic membrane)
  - Concentrates and purifies NaOH in cathode for reuse in the process
- **Waste disposition**
  - Solidify the CSL liquid waste stream for transfer to the Integrated Disposal Facility (IDF)
  - The leached HLW sludge is returned to tank farm

Status/Schedule

- 01/29/10 — Task Technical Plan issued
- 04/06/10 — Simulant memo issued
- 04/06/10 to present — Initiated work on solidification options
- 01/30/11 — Interim Report
- 6/01/11 — Milestone – Initial assessment

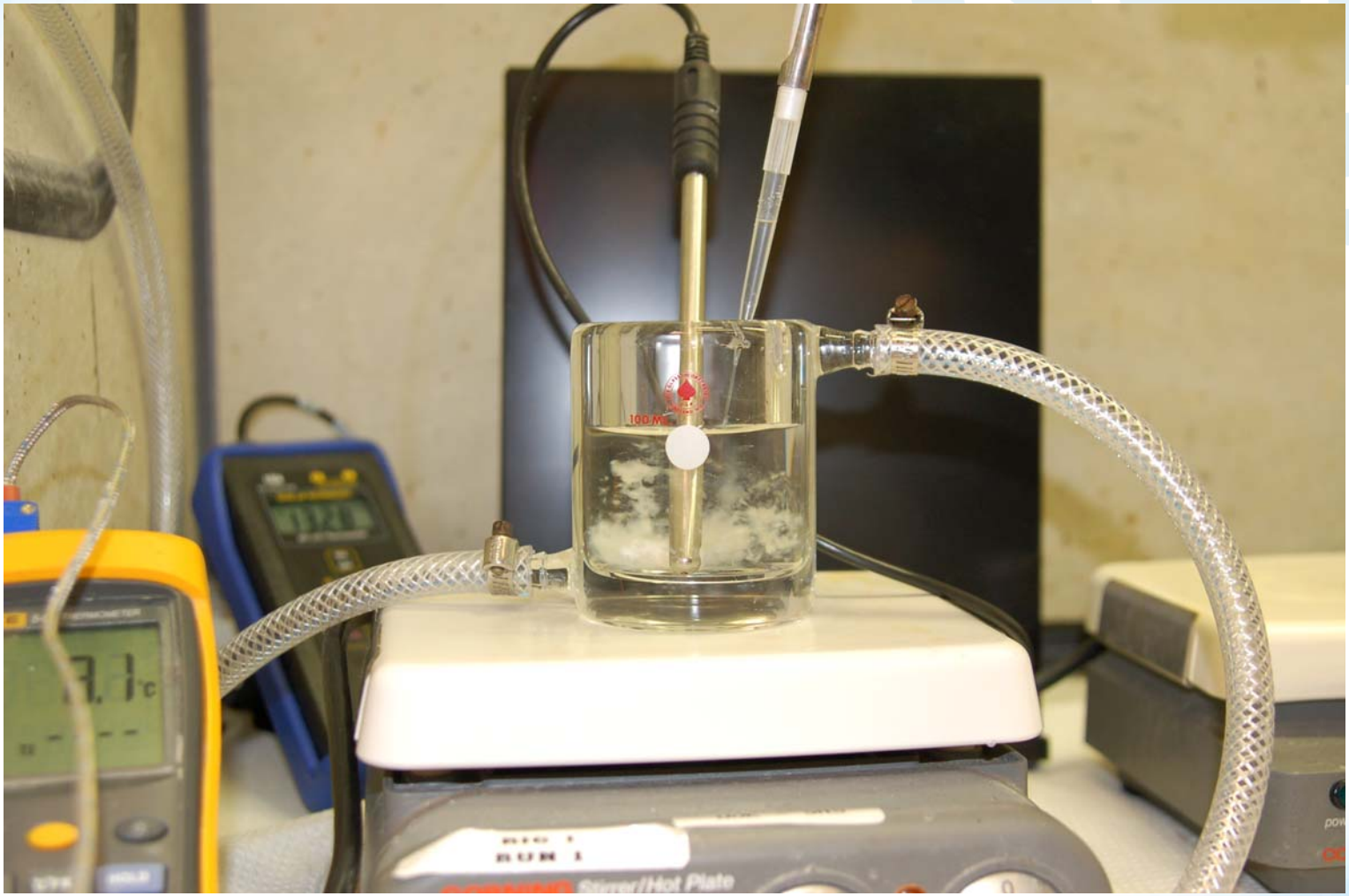
Approach

- Develop simulants for initial testing
- Select set of *waste form* options
- Batch *waste forms*
- Measure selected properties of *waste forms*
- Compare results of options
- Integrate results from other EM-31 concurrent tasks
- Select the most promising option(s)

Waste Streams – After CSL

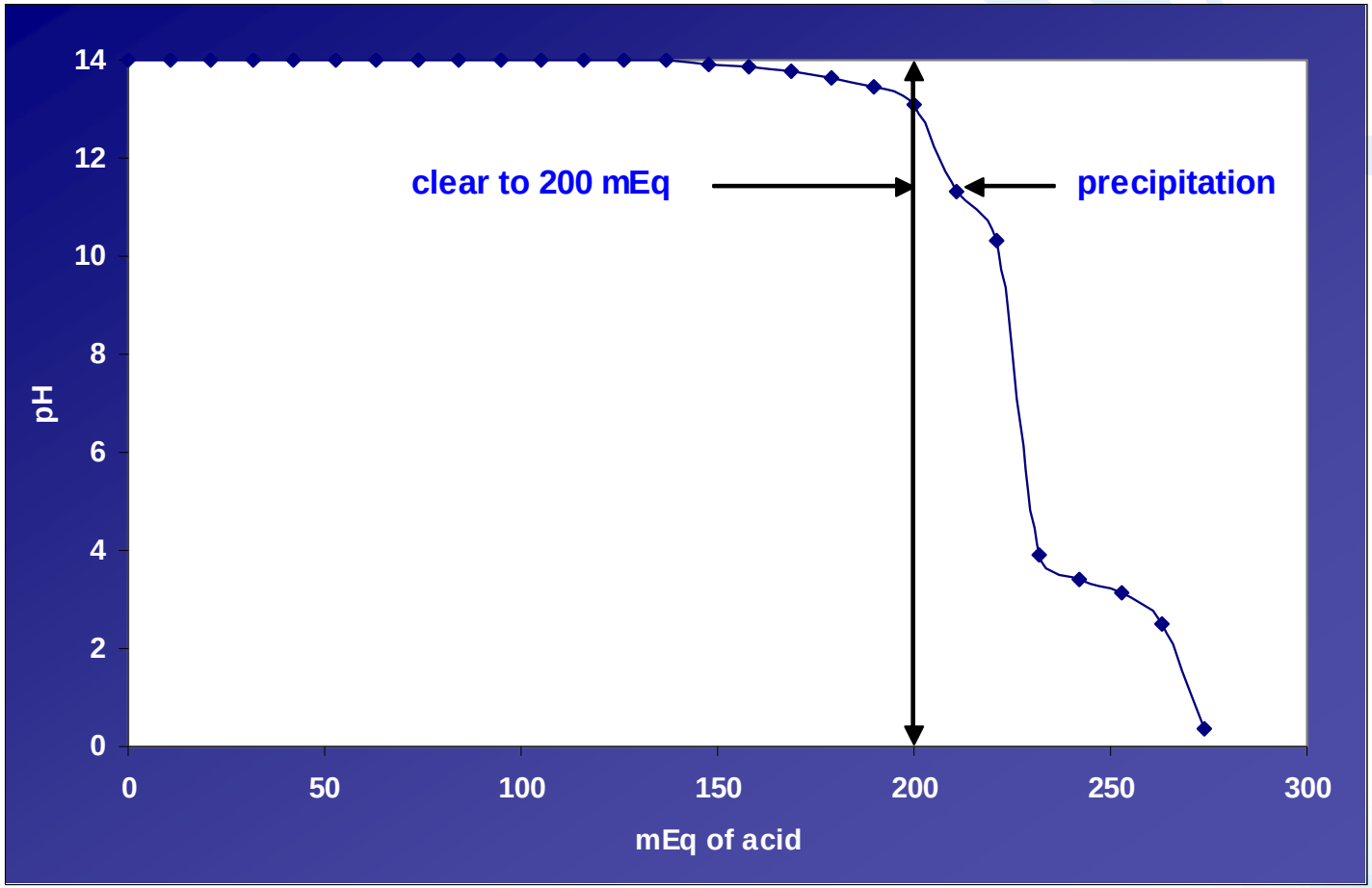
	Low Al (M)	High Al (M)
Chemical	PNNL	PEP Process
NaOH (total)	5.0	7.5
NaOH (free)	4.0	4.5
$NaNO_3$	0.15	0.16
$NaNO_2$	0.06	0.05
Na_2CO_3	0.05	0.05
Na_2SO_4	0.001	0.02
$Al(OH)_4^-$	0.25	0.75
Na_3PO_4	0.002	0.001
Total Na	5.32	7.81

Simulant Development - Titration



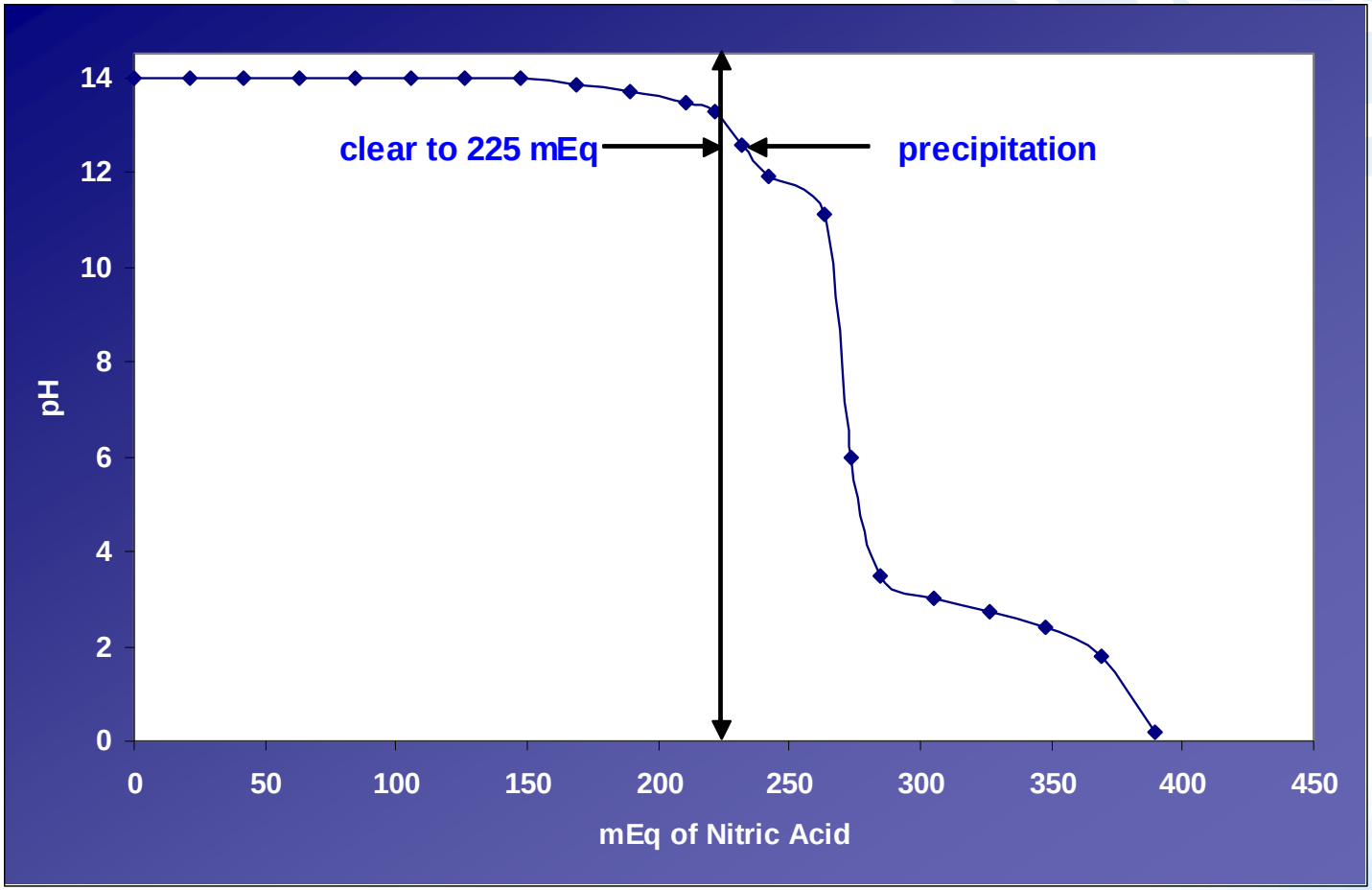
Simulant Development – Low Aluminate

Titration of low Al precursor simulant (200 mEq free OH^-) with nitric acid



Simulant Development – High Aluminate

Titration of the high Al precursor simulant (225 mEq of free OH^-) with nitric acid



Recovery of NaOH – How Much is Too Much?

Figure from S. F. Agnew, J. G. Reynolds and C. T. Johnson, WM2009, Phoenix

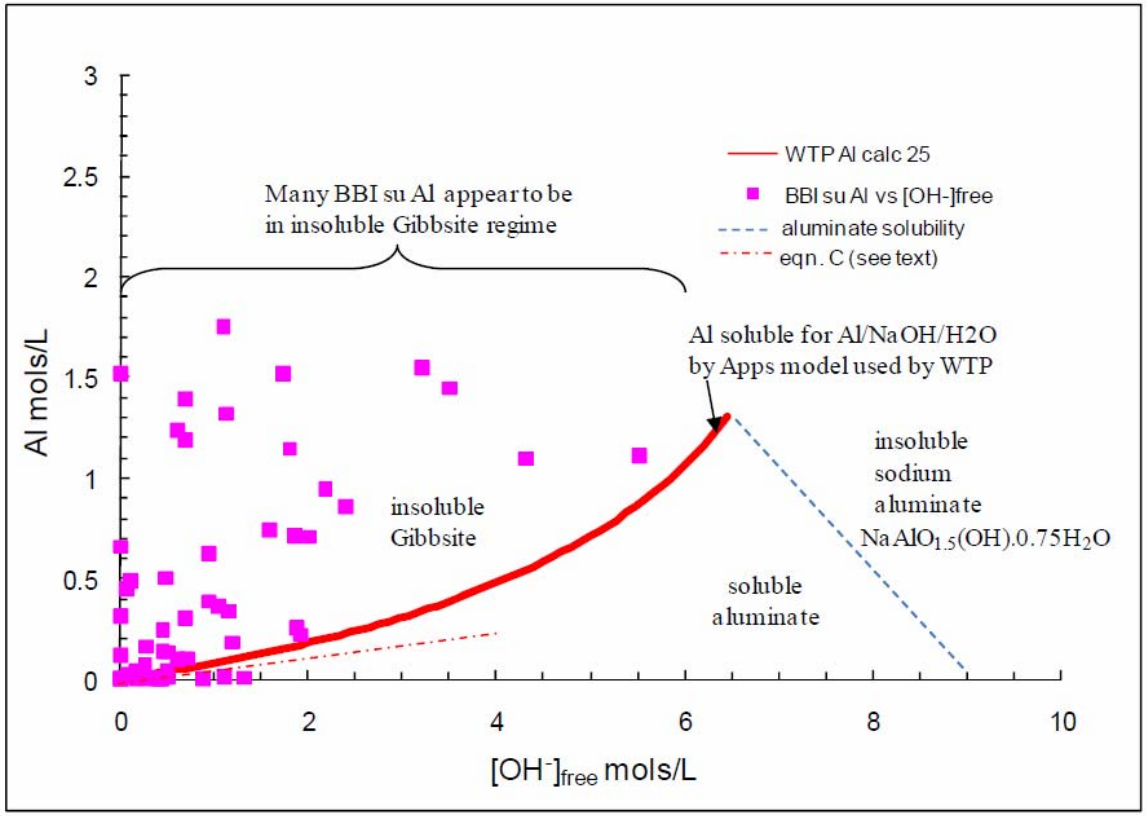


Fig. 1. Plot showing Apps [2] solubility at 25 C (solid red line) versus free hydroxide. Also shown are BBI supernatant Al concentrations (purple boxes), equilibrium Al solubility from eqn. C (dot-dash red line), and boundary for insoluble aluminate (dashed blue line).

Simulant Compositions

Simulants based on 1 M free hydroxide

	Simulants	
Chemical	Low Al (M)	High Al (M)
NaOH (total)	2.0	4.0
NaOH (free)	1.0	1.0
$NaNO_3$	0.15	0.16
$NaNO_2$	0.06	0.05
Na_2CO_3	0.05	0.05
Na_2SO_4	0.001	0.02
$Al(OH)_4^-$	0.25	0.75
Na_3PO_4	0.002	0.001
Total Na	2.3	4.4

Five Options Selected

Part 1 Iron Phosphate Glass

Part 2 Borosilicate Glass

Part 3 Steam Reformed product

Part 4 Geopolymers

Part 5 Saltstone/Cast stone

Iron Phosphate Glasses

Cheol-Woon Kim and Delbert Day, MO-SCI Corporation

Fabienne Johnson, SRNL

Experimental Methods

- **MO-SCI**
  - Developed iron phosphate glass formulations for both the high and low aluminate waste streams and sent samples to SRNL
- **SRNL**
  - Heat treatment according to the LAW centerline canister cooling (ccc) profile
  - Chemical composition measurements
  - X-ray Diffraction (XRD) analysis
  - Vapor Hydration Testing (VHT) → ongoing
  - Durability testing via the Product Consistency Test (PCT)
    - Quenched and ccc glasses

Candidate Selection

- **Candidate glasses were selected by SRNL for both the high aluminate and low aluminate waste streams based on the PCT response**
  - PCT responses are below the 4 g/L limit (equivalent to 2 g/m^2)

Sample ID	Normalized Leachate (g/L)		
	Na	Si	Al
MS-HAL-5	1.73	0.76	0.61
MS-HAL-5ccc	1.83	1.13	1.12
MS-LAL-7	1.64	0.69	0.58
MS-LAL-7ccc	1.71	1.25	1.13

Candidate Glass Formulations

MS-HAL-5 (26% WL)	
Oxide	Target Composition (wt%)
Al_2O_3	13.60
Na_2O	20.30
P_2O_5	40.04
SO_3	0.21
Bi_2O_3	2.00
CaO	1.50
Fe_2O_3	10.99
La_2O_3	1.00
SiO_2	5.00
ZnO	4.36
ZrO	1.00

MS-LAL-7 (24% WL)	
Oxide	Target Composition (wt%)
Al_2O_3	13.60
Na_2O	20.34
P_2O_5	40.04
SO_3	0.02
Bi_2O_3	2.00
CaO	1.5
Fe_2O_3	11.14
La_2O_3	1.00
SiO_2	5.00
ZnO	4.36
ZrO	1.00

Actual compositions are consistent with targets.

XRD Results

- **MS-HAL-5**
  - Quenched glass → amorphous
  - Heat treated glass → crystallized
    - Sodium iron phosphate, hematite and possibly a sodium lanthanum phosphate
- **MS-LAL-7**
  - Quenched glass → amorphous
  - Heat treated glass → crystallized
    - Sodium iron phosphate, sodium lanthanum phosphate and possible hematite

Iron Phosphate Glasses - Waste Loading

By Volume		
Volume of Waste (liters)	Volume of Glass (liters)	Volume Factor
1.0	0.12	0.12

By Mass			
Mass of I L of Waste (grams)	Mass of Glass (grams)	Mass Factor	% Na_2O (mass basis)
1086 - 1147	354	0.33	20.3

Borosilicate Glasses

Fabienne Johnson, SRNL

Experimental Methods

- **Glass formulations developed by SRNL**
- **Samples were fabricated and characterized at SRNL**
  - Heat treatment according to the LAW centerline canister cooling (ccc) profile
  - Chemical composition measurements
  - X-ray Diffraction (XRD) analysis
  - Vapor Hydration Testing (VHT) → ongoing
  - Durability testing via the Product Consistency Test (PCT)
    - Quenched and ccc glasses

Candidate Selection

- **Candidate glasses were selected for both the high aluminate and low aluminate waste streams based on the PCT response**
  - PCT responses are well below the 4 g/L limit (equivalent to 2 g/m^2)

Sample ID	Normalized Leachate (g/L)		
	B	Na	Si
FCJHAL-1	0.94	0.95	0.39
FCJHAL-1ccc	0.79	0.88	0.38
FCJLAL-3	1.07	1.19	0.48
FCJLAL-3ccc	0.95	1.08	0.46

Candidate Glass Formulations

FCJHAL-1 (30% WL)	
Oxide	Target Composition (wt%)
Al_2O_3	6.53
Na_2O	23.16
P_2O_5	0.08
SO_3	0.24
B_2O_3	9.00
CaO	2.00
Fe_2O_3	6.00
MgO	1.60
SiO_2	45.00
TiO_2	1.01
ZnO	2.00
ZrO	3.38

FCJLAL-3 (30% WL)	
Oxide	Target Composition (wt%)
Al_2O_3	6.60
Na_2O	25.33
P_2O_5	0.05
SO_3	0.02
B_2O_3	8.00
CaO	2.00
Fe_2O_3	5.50
MgO	1.60
SiO_2	44.50
TiO_2	1.01
ZnO	2.00
ZrO_2	3.39

Actual compositions are consistent with targets.

XRD Results

- **FCJHAL-1 and FCJLAL-3**
  - Quenched glass → amorphous
  - Heat treated glass (ccc) → amorphous

Doping Study

- **Both the high and low aluminate glasses were doped with 0.2 wt% Re_2O_7 and 0.57 wt% I (in glass)**
  - Concentrations of waste components remained constant
  - Remaining components were re-normalized to include the dopants
- **Glasses were fabricated and characterized**
  - Heat treatment according to the LAW centerline canister cooling (ccc) profile
  - Chemical composition measurements
  - Vapor Hydration Testing (VHT) → ongoing
  - Durability testing via the Product Consistency Test (PCT)
    - Quenched and ccc glasses

Doping Study – Results

- PCT leachate was measured by ICP-MS
- Concentrations of Iodine and Rhenium in the ppb range

Sample ID	Leachate Concentration (mg/L)	
	I	Re
FCJHAL-1	0.004	0.007
FCJHAL-1ccc	0.001	0.004
FCJLAL-3	0.010	0.006
FCJLAL-3ccc	0.005	0.005

Borosilicate Glasses - Waste Loading

By Volume		
Volume of Waste (liters)	Volume of Glass (liters)	Volume Factor
1.0	0.10	0.10

By Mass			
Mass of I L of LA Waste (grams)	Mass of Glass (grams)	Mass Factor	% Na_2O (mass basis)
1086 - 1147	282	0.26	25.4

Steam Reformed Product

Charles Crawford and Carol Jantzen, SRNL

Steam Reforming - Status

- **Formulations developed**
  - Low aluminate waste stream
  - High aluminate waste stream
- **Used Optikast and Sagger mixed Clays**
  - ~ 310 grams of wet clay per liter of low aluminate simulant
  - ~ 460 grams of wet clay per liter of high aluminate simulant
- **Coal added to control redox**
  - ~ 65 to 93 grams per liter of coal added

Steam Reforming - Status

- **Bench Scale production of steam reformed product (BSR)**
  - Sufficient material produced to characterize BSR product and to monolith the BSR products to produce the final waste forms
  - XRD data were obtained for both products
  - Simulant waste streams were doped with I and Re
- **PCT leaching of BSR product**
  - Measurements will include I and Re by ICP-MS
  - Measurements of compositions of the BSR products in progress
- **Monolithing of the BSR product**
  - Geopolymer binder will be used
  - Monolith will be crushed and tested by PCT leaching

Steam Reforming – Projected Waste Loadings

By Volume in Monolith Product		
Volume of Waste (liters)	Volume of Monolith (liters)	Volume Factor
1.0	0.49 to 0.56	0.49 to 0.56

By Mass in the Monolith Product		
Mass of I L of Waste (grams)	Mass of Monolith (grams)	Mass Factor
1086 - 1147	917 - 1049	0.84 to 0.92

Geopolymers

Katy Gustashaw, University of Texas

Geopolymers

- **Approach considers two options**
  - Option 1. Geopolymer solidification after CSL and NaOH recovery
  - Option 2. Geopolymer solidification for solutions produced after CSL
- **Status**
  - Geopolymers batched and characterized with low aluminate simulant (Option 2)
  - Geopolymers in development for high aluminate simulant (Option 2)
- **Path Forward**
  - Complete development of geopolymers for Option 2
  - Develop geopolymers for Option 1 including Duralith
  - Measure performance properties of geopolymer waste forms

Geopolymers

- **Geopolymer blends were batched for Option 2**
  - Used low aluminate simulant prior to NaOH recovery
  - Batched at 0.60 water-to-cementitious materials ratio
  - Introduced slag as a reductant for pertechnetate

Sample ID	Blends	
	Fly Ash (85 %)	Slag (15 %)
Mix-1	Class F (Big Brown Raw)	Holcim
Mix-2	Class F (Belews)	Holcim
Mix-3	Class C (Boral)	Holcim

Geopolymers

- **Results**
  - Compressive strength (500 psi requirement)
  - Bleed volume and gel time
  - Waste Loading is similar to Saltstone/Cast Stone results

Sample ID	Compressive Strength (psi) 28 days	Bleed (volume %)	Gel time (minutes)
Mix-1	4602	None	10
Mix-2	1094	1.16	30
Mix-3	2658	None	10

Saltstone and Cast Stone

John Harbour, SRNL

Saltstone / Cast Stone

- Mixes batched at 0.60 water-to-premix ratio
- Included both the low and high aluminate simulants
- Premix composition provided in the following table

Material	Category	Vendor	Premix wt %
Portland Cement	Type II	Holcim	10
Blast Furnace Slag	Class 1	Holcim	45
Fly Ash	Class F	SEFA	45

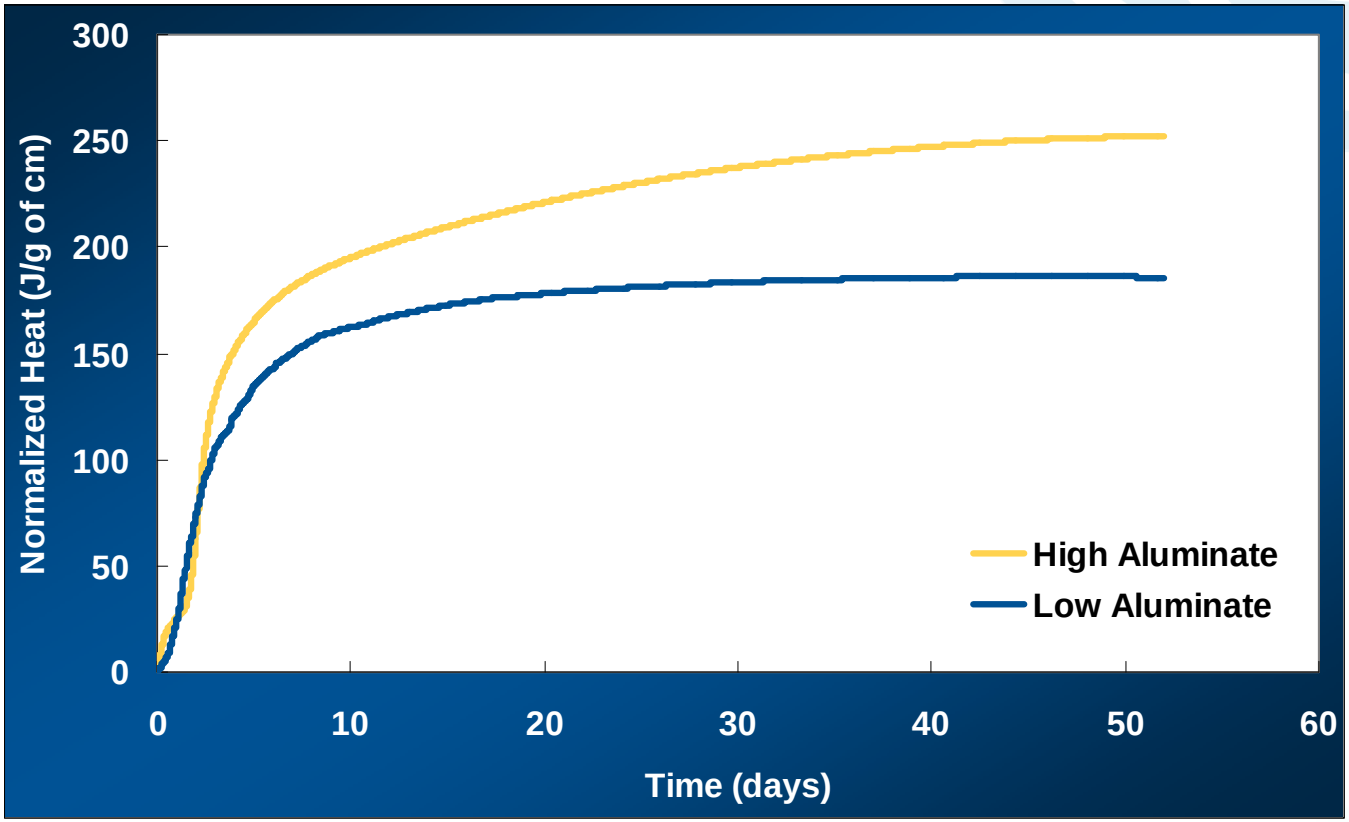
Saltstone / Cast Stone

Processing Properties

Properties	Low Aluminate	High Aluminate
Gel Time	10 minutes	20 minutes
Set Time	1 day	3 days
Bleed Volume	None	None
Density	1.67 g/mL	1.71 g/mL
Yield Stress	7.1 Pa	2.0 Pa
Consistency	0.08 Pa·s (80 cP)	0.02 Pa·s (20 cP)

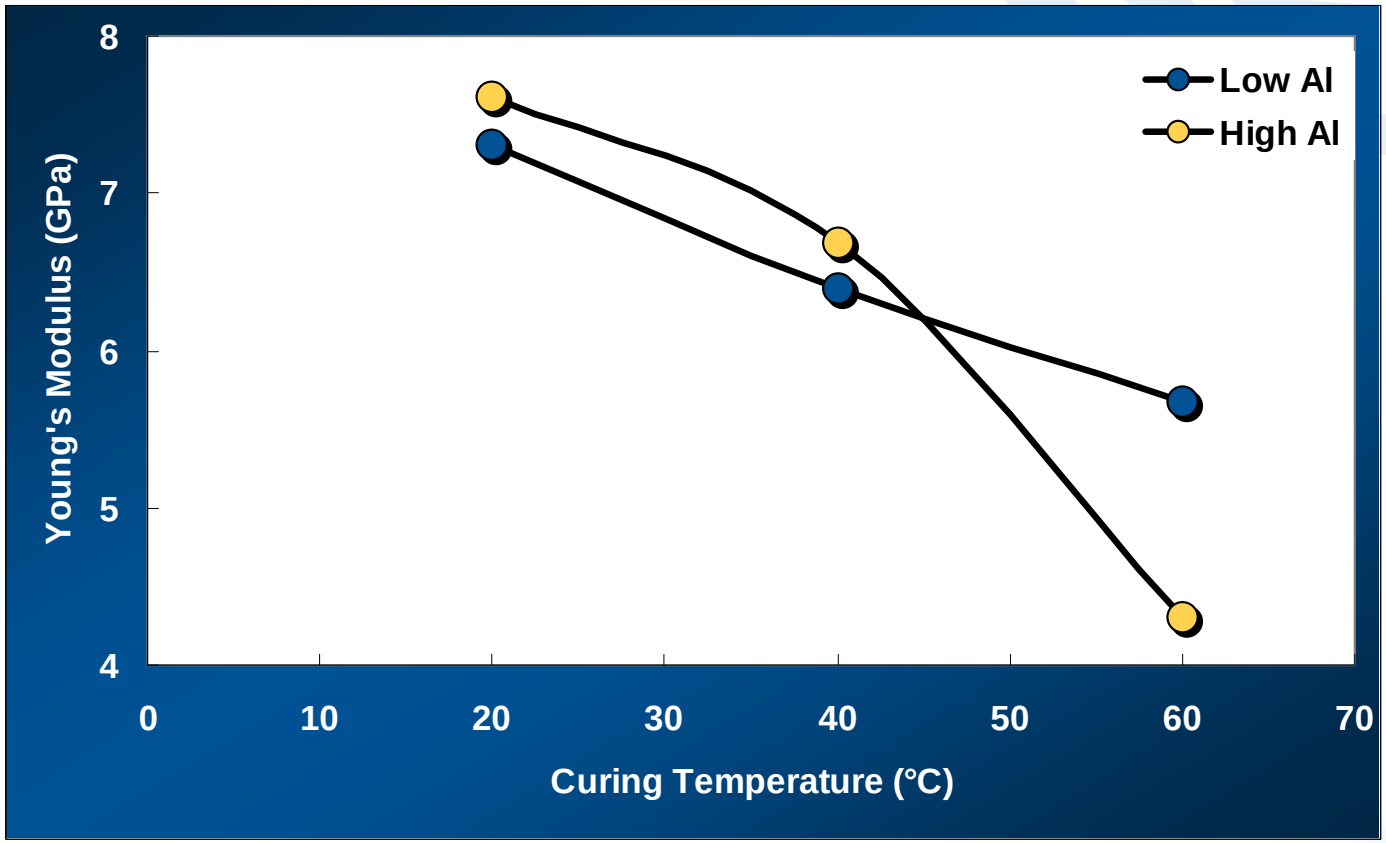
Saltstone / Cast Stone

Heat of hydration by isothermal calorimetry at 25 °C

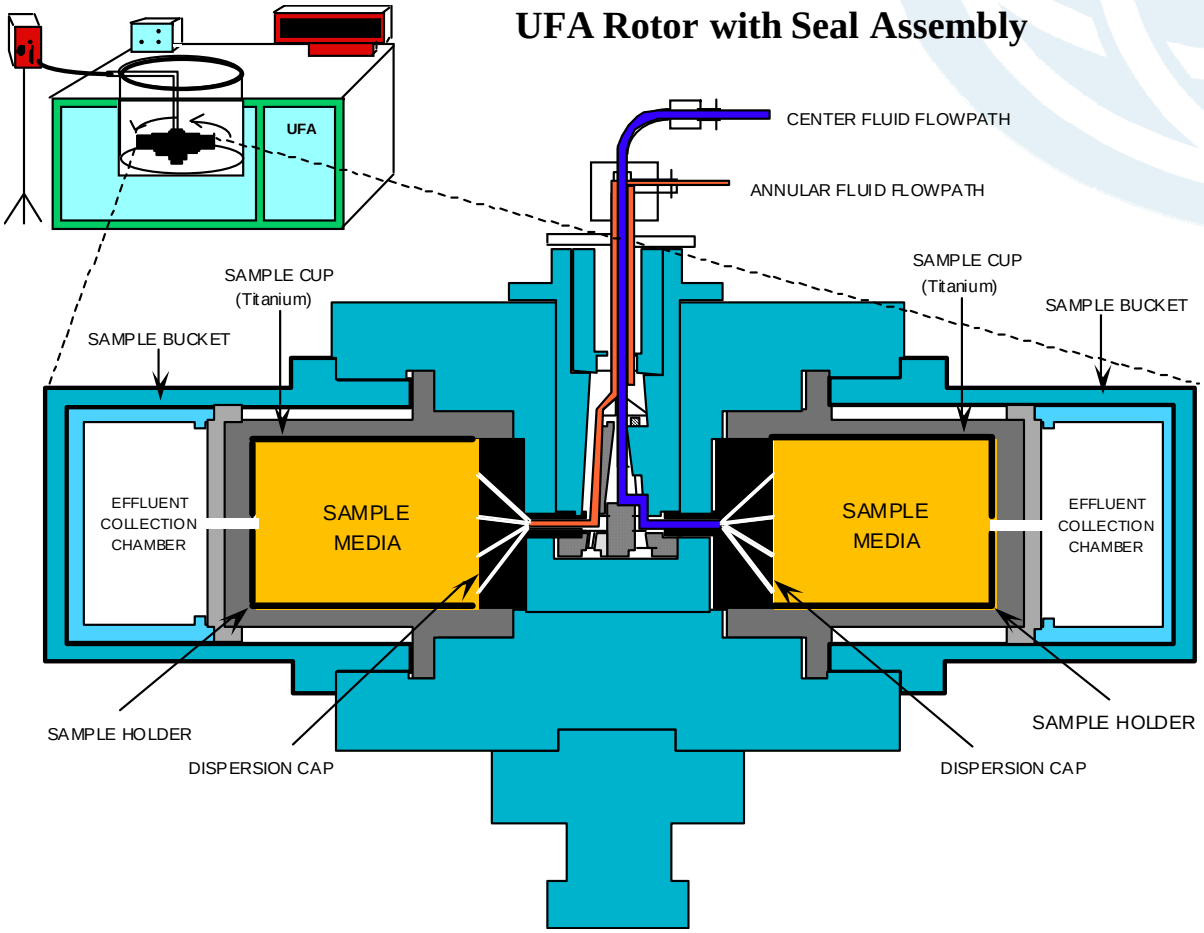


Saltstone / Cast Stone

Dynamic Young's Modulus (E) after 29 days

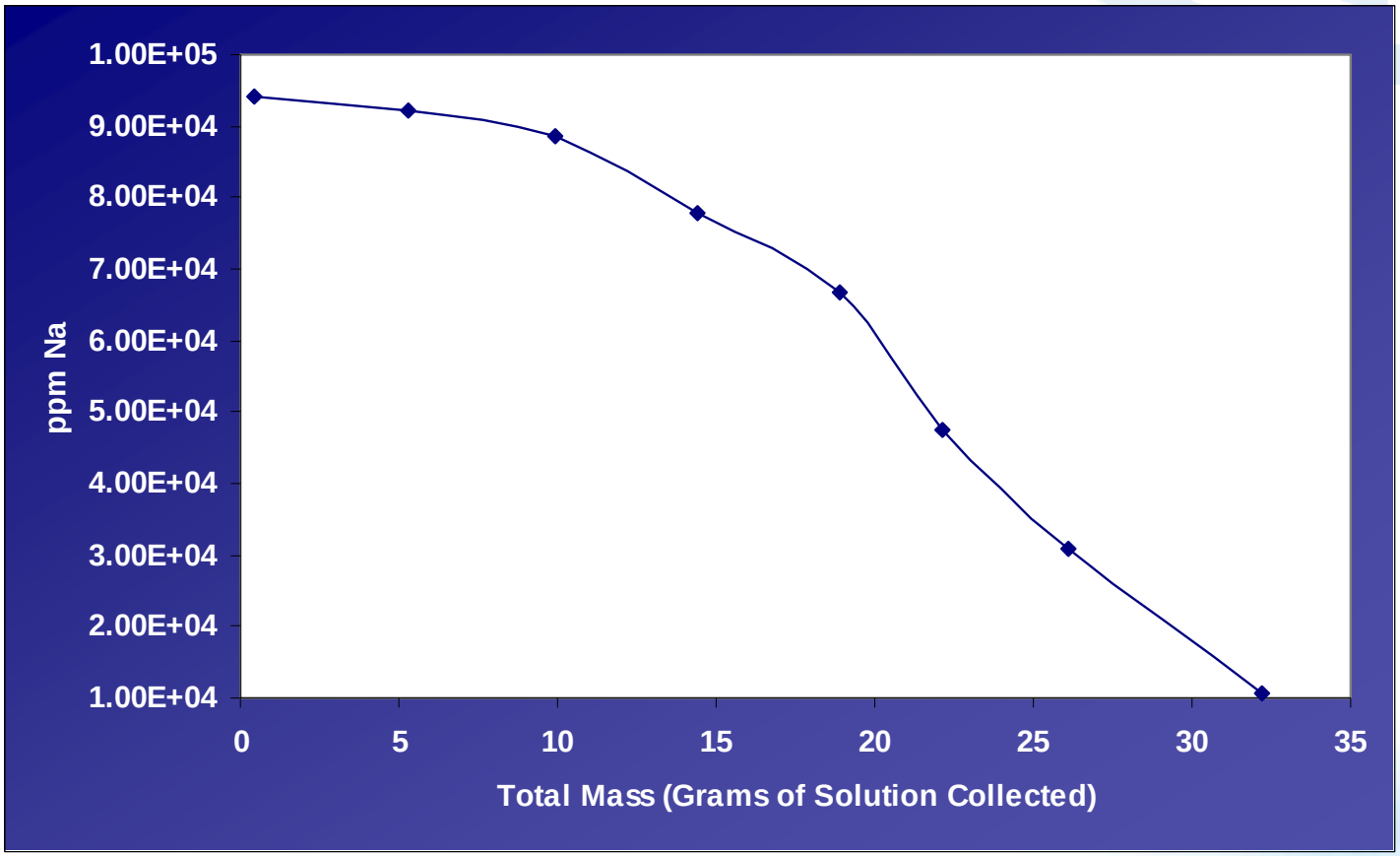


Saltstone / Cast Stone – Pore Solution Composition by UFA Technique



Pore Solution – Permeability Mode with UFA

- Saltstone low aluminate mix at 0.60 water/premix ratio ~ 4M Na^+
- Cured for 5 days – Each sample contains ~ 22 g pore solution



Saltstone/Cast Stone - Waste Loading

By Volume			
Volume of Waste (liters)	% Loading (in grout)	Volume of Grout (liters)	Volume Factor
1.0	40.1	1.58 to1.61	1.58 to 1.61

By Mass		
Mass of I L of Waste (grams)	Mass of Grout (grams)	Mass Factor
1086 - 1147	2680 to 2705	2.34 to 2.49

Path Forward

- Continue batching and characterization of waste forms
- Evaluate and compare results for compliance to specifications
- Evaluate and compare waste loading for each waste form
- Estimate the total volume of waste form produced for each case
- Estimate the daily production rates required for each option
- Provide recommendation in June of 2011