DuraLith Geopolymer Low Temperature Waste Forms

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Washington, DC

EM Waste Processing Technical Exchange
Atlanta, Nov. 16 – 18, 2010

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A Geopolymer is ….

…. an inorganic solid formed by poly-condensation:

$$n\{\text{-O-Si-OH} + \text{HO-Al-O-}\} \xrightarrow{\text{NaOH}} \{\text{-O-Si-O-Al-O-}\}_n + nH_2O$$

General formula:

$$(Na,K)_n[(SiO_2)_z\text{-}AlO_2]_n \cdot wH_2O$$

$1 \leq z \leq 3$

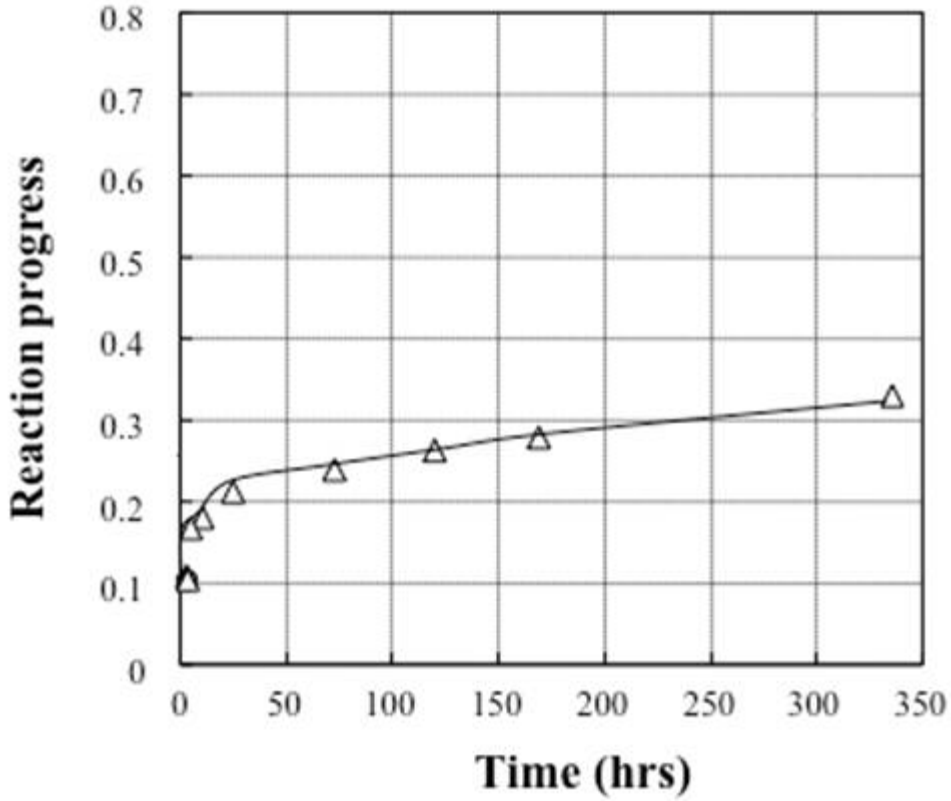
'w' << 1

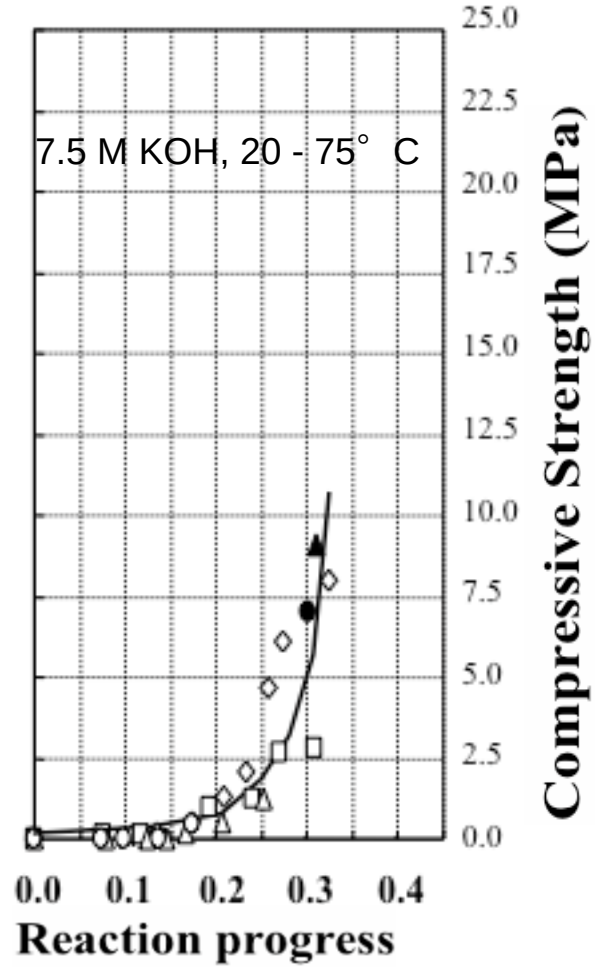
Geopolymers ….

- … can be made at room temperature from any reactive aluminosilicate with alkali hydroxide or alkali polysilicates
- … contain very little water after complete hardening
- … are resistant to acids
- … are stable up to 1200 ºC
- … can incorporate significant amounts of waste elements
- … exhibit high compressive strength
- … can be tailored to increase fixation of radionuclides

Example: Simple Class F Fly Ash Geopolymer
(mix fly ash with KOH solution)

Reaction progress and evolution of strength





Components of 'DuraLith' Geopolymers

- **Solid (binder materials)**:
- **Group 1**. One or two reactive, amorphous, aluminum-silicates, e.g., metakaolin and/or Class F fly ash, and/or ….
- **Group 2**. One or two reactive, amorphous alkali-earth enriched aluminum- silicates, e.g., ground granulated blast furnace slag and/or Class C fly ash
- **Liquid (activator)**:
- The waste solution as-is, or concentrated but amended with alkali hydroxide and silicate
- **Enhancers (optional)**:
- Additives to improve fixation of water-soluble radionuclides (^{129}I, ^{99}Tc, ^{137}Cs)

Role of DuraLith Binder Materials

- **Group 1**: Metakaolin and/or Class F fly ash produce alumino-silicate gel (AAS gel) when activated by alkali
- **Group 2**: Ground granulated blast furnace slag and/or Class C fly ash produce calcium-silicate-hydrate gel (CSH gel) when activated by alkali
- The gel is the matrix phase of the solid geopolymer, providing mechanical and chemical durability
- Blending 1 and 2 may increase chemical and mechanical durability of a waste form

Examples of Enhancers for Radionuclide Fixation in DuraLith

For iodide	For rhenium (technetium)	For cesium
Ag-zeolite (reduced)	SnF_2	Vermiculite
Ag-zeolite (ion-exchanged)	Copper slag	Zeolites (molecular sieves), e.g. zeolite 13X
$AgNO_3$	Na_2S	clinoptilolite
Ag-activated carbon	FeS	
	$FeSO_4$	

Materials Properties During Mixing and Curing of DuraLith Pastes

Mixing

- Homogeneous incorporation of waste constituents such as nitrate, sulfate, borate, oxalate, etc., at room temperature
- Free-flowing viscous, pump-able paste
- Duration of workability can be adjusted as needed, typically 90 min

Curing

- Typically 28 days at room temperature
- Practically no shrinkage or swelling
- No bleeding, no deposits on the surface
- No free water

DuraLith Waste Forms Have Been Developed for:

- **INL sodium bearing waste**
- **Hanford LAW off-gas recycle stream**
- **SRS Tank 48H Waste**

Hanford Secondary Waste (HSW), mol/L

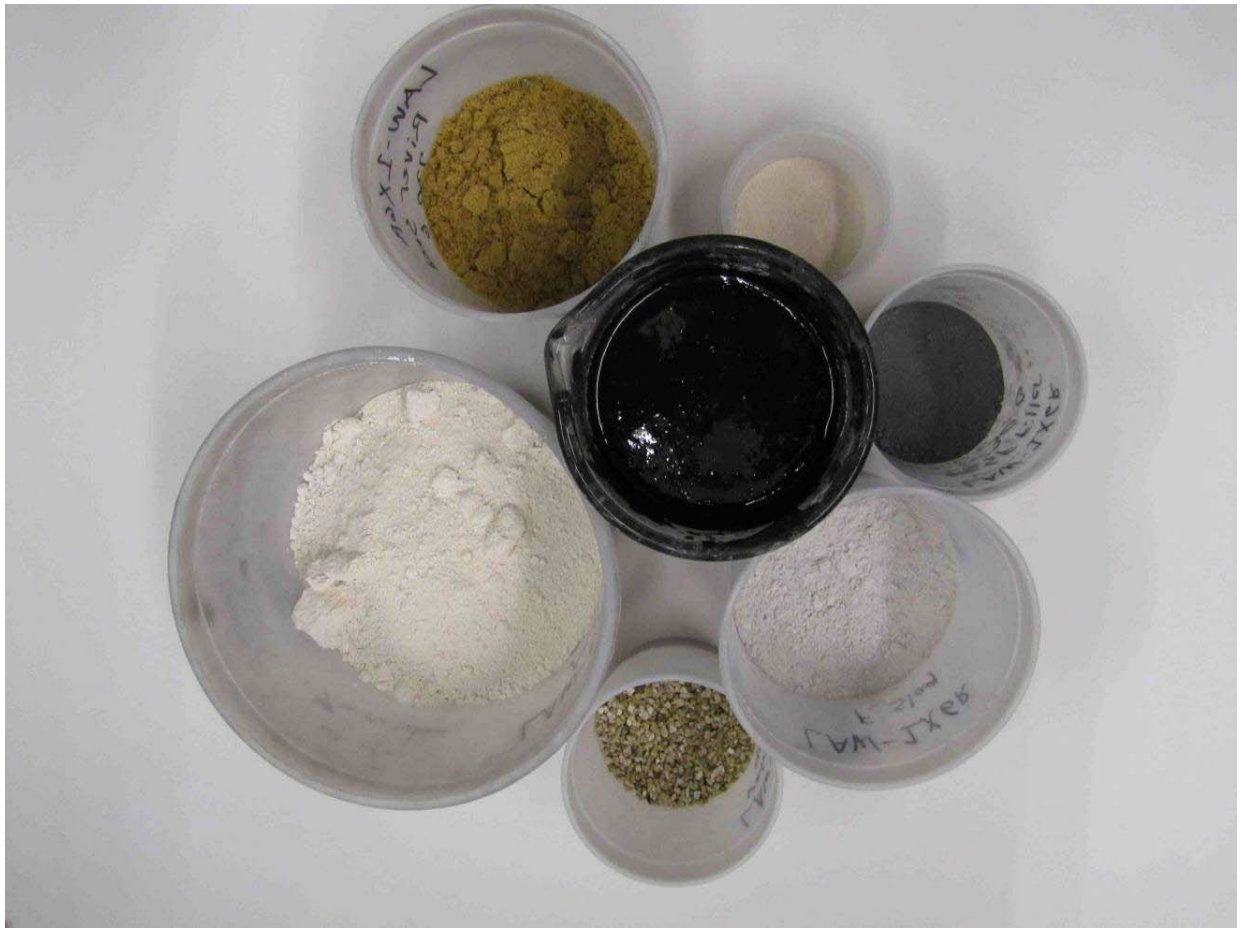
Na	OH	NO_3	Al	TOC	Si	K	CO_3	Cl	NO_2	PO_4	SO_4
2.0	0.798	0.656	0.188	0.188	0.004	0.001	0.046	0.045	0.024	0.0137	0.009

Hanford Low-Activity Waste (LAW), mol/L

Na	OH	NO_3	Al	TOC	Si	K	CO_3	Cl	NO_2	PO_4	SO_4
5.0	0.74	2.51	0.06	0.29	-	0.01	0.48	0.44	0.42	0.05	0.09

Minor constituents: ^{129}I, ^{99}Tc (HSW), ^{99}Tc, ^{137}Cs (LAW) heavy and other metals

Typical DuraLith Components
Activator Solution (black)* + Binder Materials



*fumed silica contains carbon

Pouring Activator Solution into Binder Materials

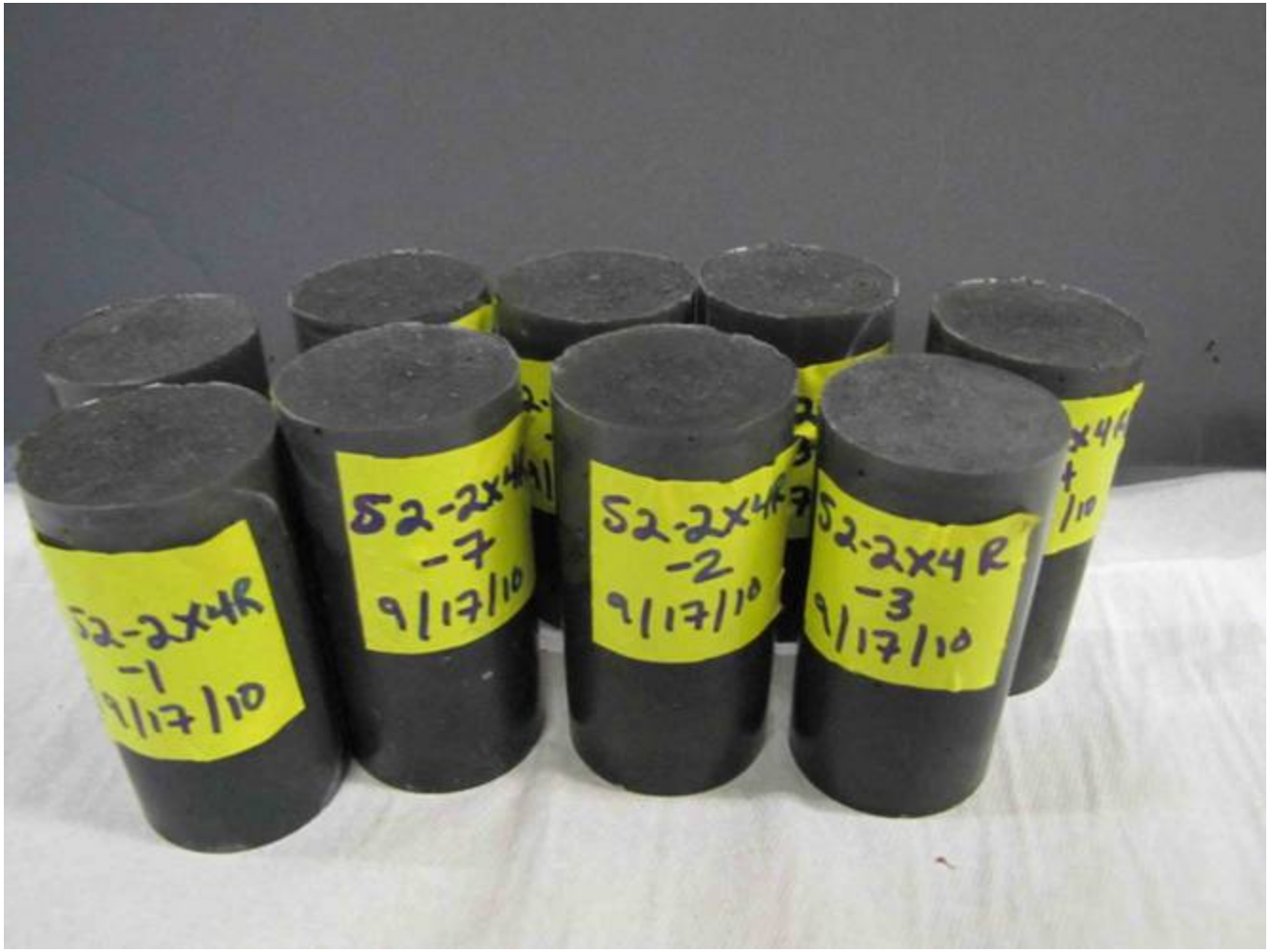
Mixing Binders and Activator

Paste Beginning to Form

Two Minutes Later: Paste is Ready to Pour

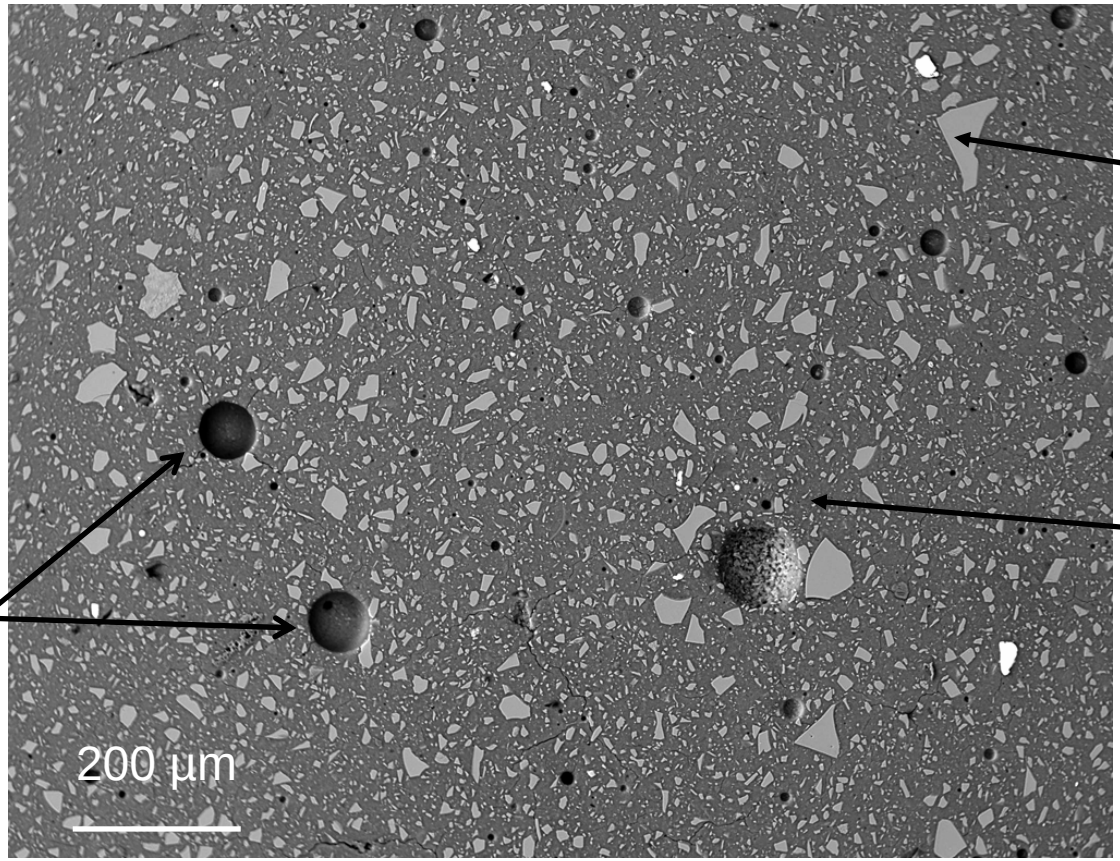
Ten Minutes Later: 2”x4” Molds Filled with Paste on Vibrating Table to Release Bubbles

Cured HSW DuraLith Samples (2”x 4”)



Scanning Electron Micrograph of Polished Sample

(DuraLith Waste Form with Gel Matrix Phase)



Angular grains of furnace slag

AAS/CSH-gel matrix

Air bubbles

DuraLith for Hanford Secondary Waste (HSW)

Major task objectives

- Incorporate waste at 2 molar Na (2X) concentration and higher
- Fixate Tc (Re) and I^-
- Fixate hazardous elements
- Measure retention of Tc (Re) and I^- under TCLP conditions
- Measure retention of hazardous elements under TCLP conditions
- Measure retention of Tc (Re) and I^- by ANS-16.1 leach procedure
- Characterize robustness of products vis-à-vis process variations
- Measure evolution of heat (temperature rise)
  a) in 5-gal freshly mixed paste and b) during curing

DuraLith Composition Optimization

- About 80 batches (8 to 9 samples/batch) have been prepared to optimize mixing, duration of workability, and other properties for HSW and LAW
- Test data used for subsequent composition refinement
- For HSW, it is expected that waste concentration by 6X or higher will be used, depending on TCLP results and mechanical performance (in progress).
- Optimum treatment for LAW appears to be solidification as-is (no further concentration of the waste)
- ANS 16.1 leach tests in progress, results not yet available
- Many TCLP tests still in progress

Two Typical Compositions of HSW DuraLith
(10 kg batch)

Ingredients, grams	Furnace slag-based	Metakaolin-based	Order of addition
liquid waste	2033	2090	Activator 1
solid SnF_2	47	47	2
solid KOH	927	1585	3
solid NaOH	380	189	4
fumed silica	1041	1416	5
metakaolin	**1482**	**2646**	Binder solids 6
furnace slag	**3671**	**1738**	7
fine river sand	2293	2327	8
Ag-zeolite*	121	122	9
fumed silica	241	245	10

*Enhancer for iodine fixation

Incorporation of HSW at Baseline and Higher Concentrations

DuraLith waste loading
(2 molar '2X' is baseline)

Concentration	Waste loading (wt%)	Compressive strength
2X	2.5	> 10,000 psi (> 70 MPa)
4X	5.0	> 10,000 psi (> 70 MPa)
6X	7.5	> 10,000 psi (> 70 MPa)
8X	10.5	> 10,000 psi (> 70 MPa)
12X	14.5	Not yet measured

All pastes can be poured for at least 90 min.
There is no free water and no bleeding.

TCLP Results for Re (Tc), I, Cs, and Hazardous Elements

Element	Leachate (mg/L)	Retention (%)	TCLP limit (mg/L)
Re		> 80	
I		85 - 98	
Cs		> 95	
As	< 0.25		5.0
Ag	< 0.07		5.0
Cd	< 0.03		1.0
Cr	≤0.0.2		5.0
Cu	< 0.02		
Pb	< 0.3		5.0
Sn	< 0.25		

Robustness of Product with Respect to Process Variations

- The following deviations from baseline (2X) conditions were tested:

  -10% MK, BFS, SF, KOH, respectively
  +10% MK, BFS, SF, KOH, respectively

- Workability is good (paste remains pourable for at least 90 min)
- All products expected to have CS > 10,000 psi (> 70 MPa)
- No free water, no bleeding
- No cracking

Summary

- DuraLith geopolymer low temperature waste forms have been developed for a variety of waste streams
- The present work focused on HSW and LAW streams at Hanford
- Recommended HSW composition will be most likely furnace slag-based because of slightly better overall performance than metakaolin-based DuraLith waste forms
- Workability of paste of about 90 min
- HSW waste loading most likely $\geq$7.5 wt% ($\geq$ 6X concentration), depending on final leach data
- No bleeding and no free water
- Compressive strength $\geq$10 kpsi ($\geq$70 MPa)
- Optimization and sample characterization work ongoing

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