Hydroceramic Binders

Yun Bao and Michael W. Grutzeck

Materials Research Institute
Materials Research Laboratory Building
The Pennsylvania State University

in Conjunction with Carol M. Jantzen
Savannah River Laboratory

Supported by DOE DE-FG07-98ER45726

Outline of talk

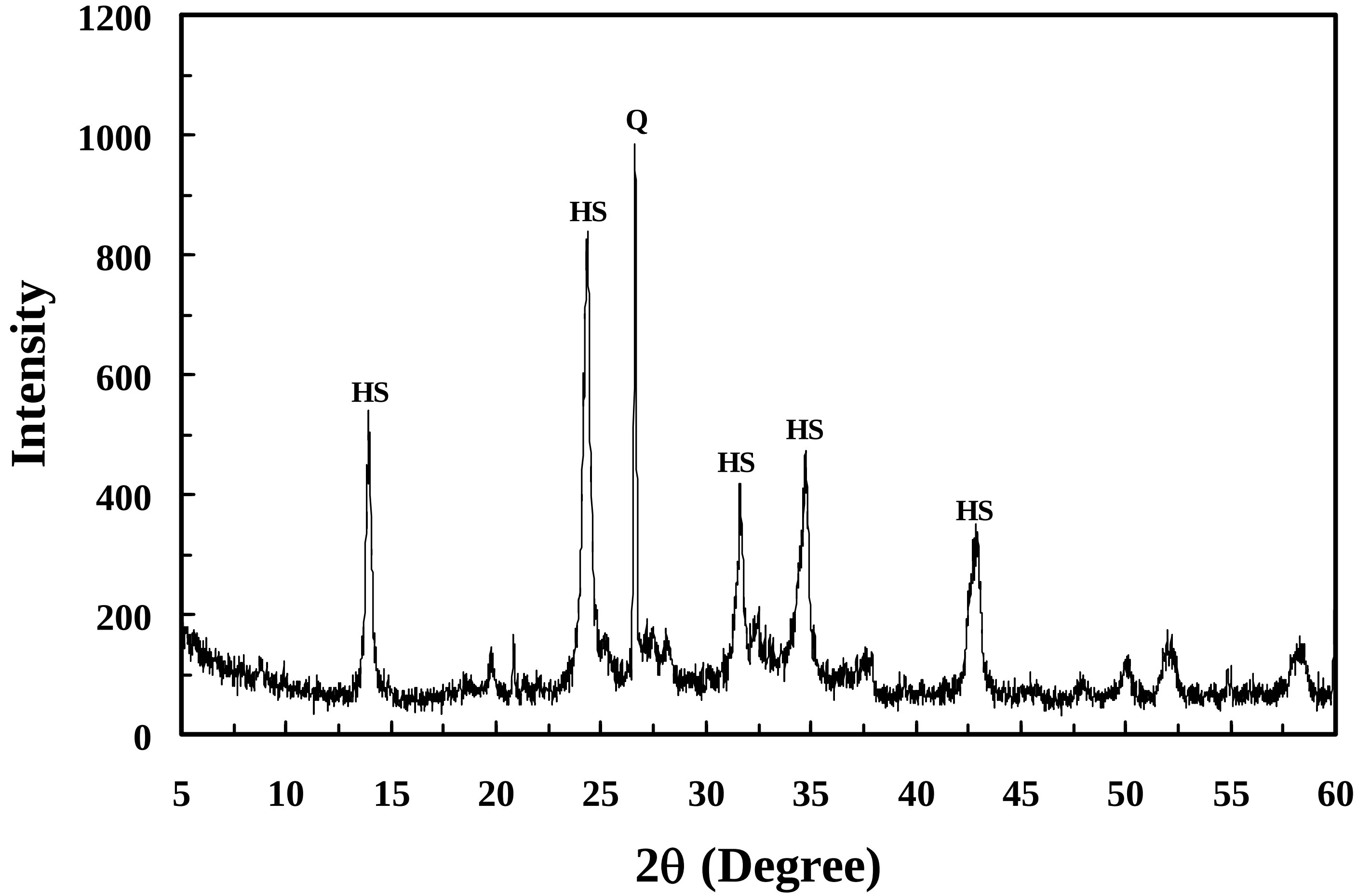
- Definitions
  - Hydroceramic
  - Sodium bearing waste
- Solidification Schemes
  - Direct solidification of SBW
  - Two steps solidification
- Example of Direct Solidification
- Example of Two Step Solidification-Hot Calcination with sucrose
- Example of Two Step Solidification-Cold Calcination with Si & Al powders suitable for in-tank solidification
- Final thoughts

Definitions

A hydroceramic is a monolithic solid made from metakaolin and concentrated NaOH solution. This sample was made with 150 g. metakaolin and 130 g. 15M NaOH. After curing at 90°C overnight, its strength was ~4000 psi.

Hydroceramics are solids in their own right, but they can be also used as a binder for calcines and steam reformed equivalents.

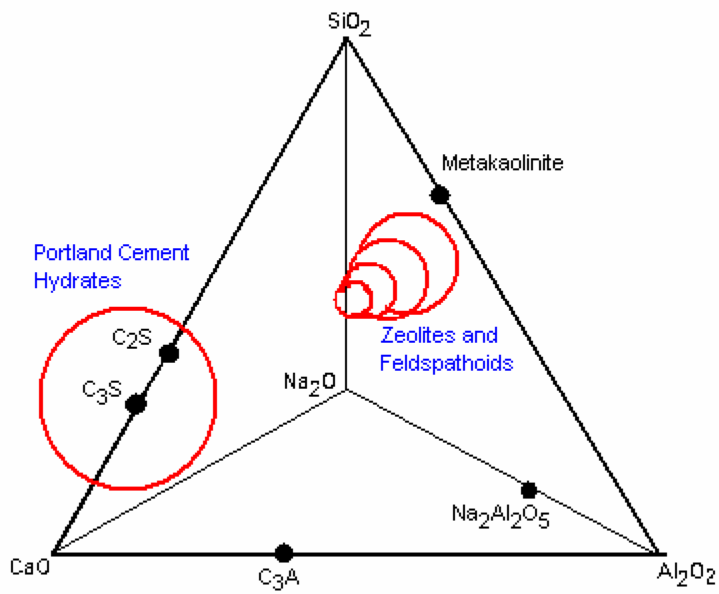
X-ray Diffraction Pattern of Hydroceramic



The hydroceramic matrix consists of a combination of X-ray amorphous and crystalline phases. In this instance hydroxysodalite a zeolite is present. Quartz is an impurity phase found in the metakaolin used to make the monolith.

Portland Cement versus Hydroceramics

Different Phases Having Radically Different Behaviors



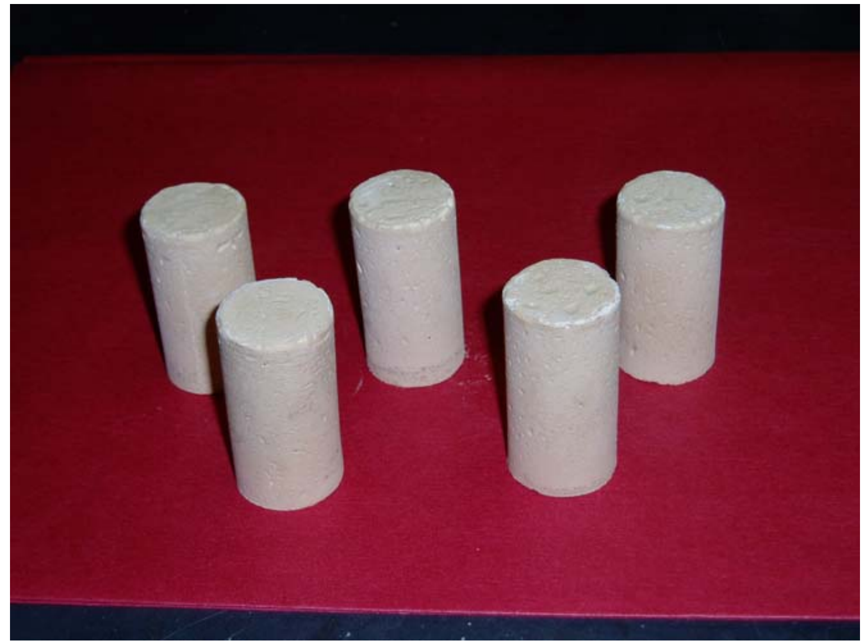
Hydrolysis and condensation to form zeolites in hydroceramics

The root cause for solidification is a hydration reaction. The NaOH solution dissolves the metakaolin ($Al_2O_3.2SiO_2$), the solution becomes supersaturated and nucleation and precipitation occur.

The phases that form are tectosilicates (i.e. network forming silicates) commonly referred to as zeolites and feldspathoids.

Hydroceramic Waste Forms

Hydroceramics made with metakaolin & 4M NaOH (binder) and simulated Hanford calcine cured at 90°C for 24 hours. The monoliths are very strong. They are zeolitic and best of all the reaction itself is very accommodating.



The density of the monolith is ~1.1 g/cm^3. The compressive strength is around 3-4 MPa, which is similar to the strength of Portland cement concrete.

Two ways to use the binder

- As a binder for calcined sodium bearing waste.

- As a fixing agent for low NOx sodium bearing waste-In this case we use the waste itself as the liquid portion of the binder.

Two ways to use the binder

- As a fixing agent for low NOx sodium bearing waste-In this case we use the waste itself as the liquid portion of the binder. Once mixed, the slurry can be containerized or returned to their tanks to harden.
- As a binder for calcined sodium bearing waste.

Reprocessing Wastes

Fuel rods were dissolved in nitric acid to facilitate the removal of fissile elements from them (reprocessing).

The remaining acid waste was either calcined (INEEL) or over neutralized with NaOH and put into steel tanks (Hanford, Savannah River).

After in tank neutralization, insoluble precipitates and salts formed and settled to the bottom of the tanks (sludge, salt cake).

Sodium Bearing Waste

The remaining liquid (supernate) contains soluble salts especially nitrates and nitrites (including Cs and Sr salts). This waste is commonly called sodium bearing waste (SBW).

Sometimes the SBW is also called low activity waste (LAW) because many of the shorter lived elements have decayed and/or Cs and Sr have been removed.

SBW in Storage can be Divided into Three Types

- Type I-reasonably pure NaOH. More of an asset than liability. Reserve to use as mixing solution for solidifying calcines and steam reformed materials.
- Type II-contains some dissolved sodium nitrate and nitrite salts. Molar fraction of nitrate and nitrite should be < 25% of the total moles Na present.
- Type III-very heavily nitrated and nitrited. Must be calcined or steam reformed in order to solidify.

Guidelines for solidifying SBW

- If NOx is less than 25% can be solidified directly.

- If NOx is greater than 25% the SBW must be denitrated/nitrited to form a calcine.
  - –Heat treatment
  - –Cold calcination

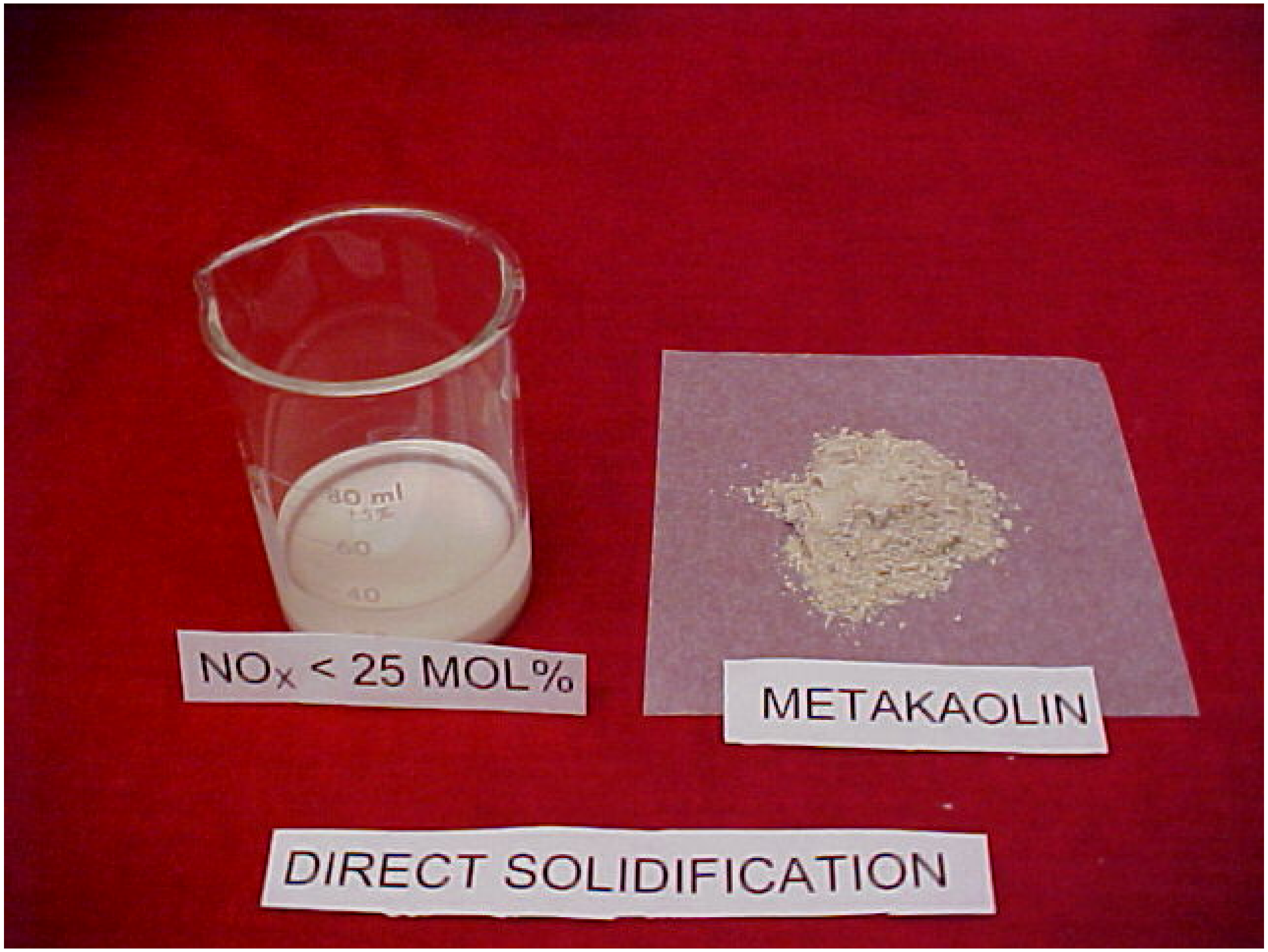
  Then it can be solidified using a hydroceramic binder. This is a two step process.

Type II SBW-SRS

Composition	MW	M	g/L
$CsNO_3$	194.9	0.5	97.45
KNO_2	85.1	0.1	8.51
$NaNO_2$	69.0	0.4	27.60
$NaAlO_2$	82.0	0.2	16.40
NaOH	40.00	4.5	180.00

SRS SBW is loosely based upon Tank 44 waste. Actual waste has had its Cs and Sr removed to facilitate its use in a hood at SRS (Pareizs, personal communication, 2004)

Direct solidification



Shape monolithic hydroceramics

Precured and cured hydroceramics

Properties of Direct Solidification

90°C

Metakaolin mixed with different amounts of SRS SBW, cured at 90°C for 24 hrs.

Sample Number	#1	#2	#3	#4	#5	#6
Metakaolin	1 g	1 g	1 g	1 g	1 g	1 g
SBW Simulant	0.5 ml	1.0 ml	1.5 ml	2.0 ml	3.0 ml	3.5 ml
Crystalline Phases	Mk	A	A	HS	HS	HS
Conductivity (mS/cm)	--	7.70	8.90	9.10	--	--
% Na leached	--	10.6	8.9	7.4	--	--

190°C

Metakaolin mixed with different amounts of SRS SBW, cured at 190°C for 24 hrs.

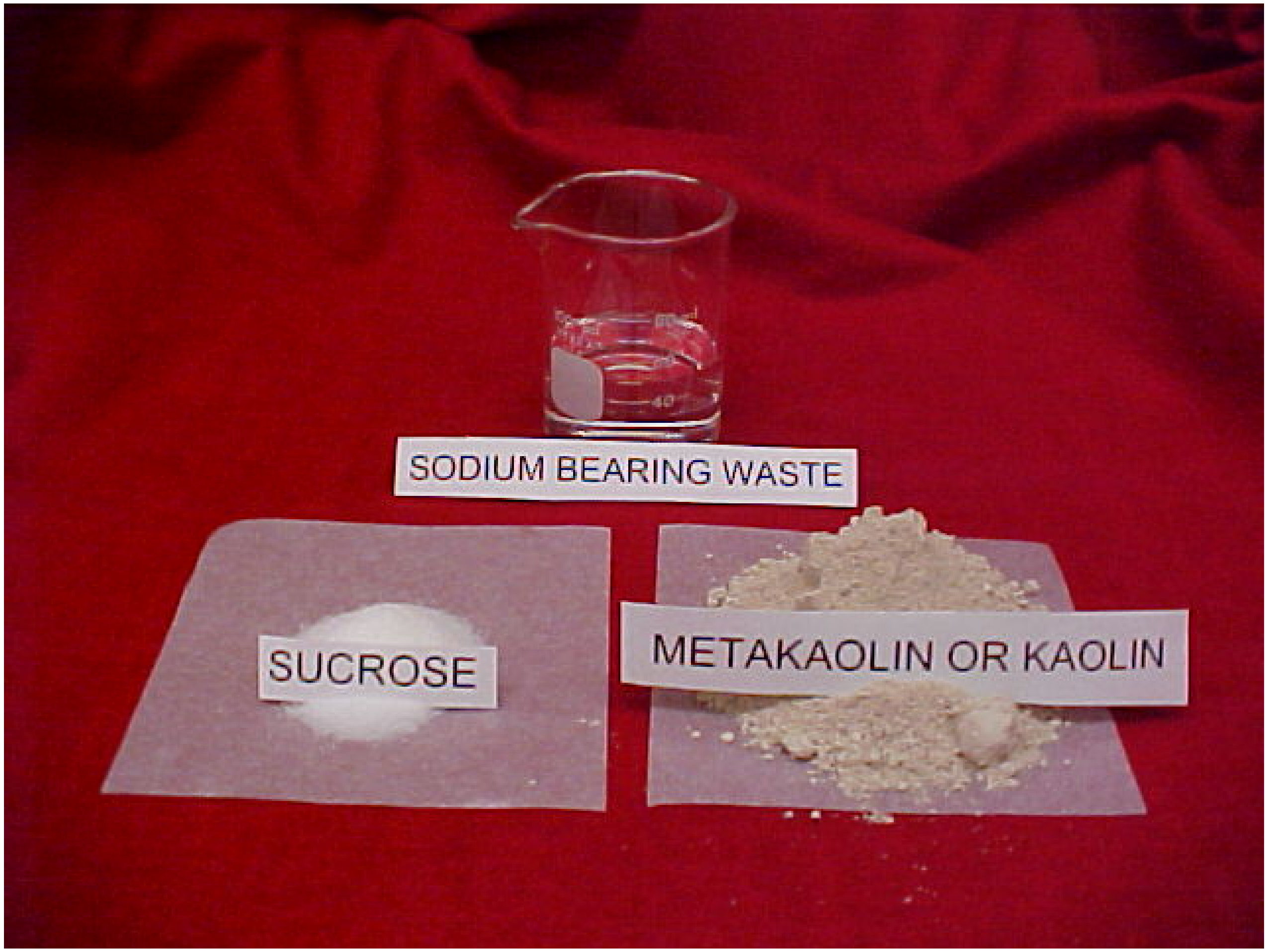
Sample Number	#1	#2	#3	#4	#5
Metakaolin	1 g	1 g	1 g	1 g	1 g
SBW Simulant	0.5 ml	1.0 ml	1.5 ml	2.0 ml	3.0 ml
Crystalline Phases	Mk + Q	Mk + Q + HS	Mk + Q + HS	Q + HS + A	Q + HS + A
Conductivity (mS/cm)	--	4.80	5.30	9.20	--
% Na leached	--	6.6	5.3	7.5	--

Mk= metakaolin, Q=quartz, HS=hydroxysodalite, A=zeolite A, -- not analyzed

Type III Hanford Simulated SBW

Composition	g/l	Composition	g/l
$Al(NO_3)_3 \bullet 9H_2O$	121.1723	PbO	0.3172
$Ca(NO_3)_2 \bullet 4H_2O$	2.5171	$NaCl$	2.2999
$Na_2Cr_2O_7 \bullet 2H_2O$	0.6532	NaF	5.5596
$CsNO_3$	0.0157	Na_2HPO_4	4.0852
$Fe(NO_3)_3 \bullet 9H_2O$	15.0318	Na_2SO_4	11.7463
KOH	2.0483	$NaNO_2$	69.0892
La_2O_3	0.0307	$NaNO_3$	155.6883
$NaOH$	105.9035	Na_2CO_3	123.0559
NiO	0.4637		

Two Step Process



Denitration to form calcine

SBW Processing

Calcine-a slurry consisting of SBW, metakaolinite and carbonaceous material (sucrose) is fired in air at 525°C for 10-18 hrs.

Studsvik steam reformer-a slurry of SBW and sucrose syrup is injected into a fluidized bed consisting of alumina, kaolin, iron oxide and charcoal that is heated to ~700°C using superheated steam.

Products

- Calcination-Predominantly X-ray amorphous with traces of hydroxysodalite.

- Steam Reforming-Predominantly crystalline consisting of nepheline and cancrinite.

Consistency of Products

Calcine-friable powder with limited mechanical strength. Sand-like consistency when crumbled in your fingers.

Steam Reformer-powder to granules depending upon operating conditions.

Hanford Type III SBW Calcine

Calcine was made from the Hanford SBW simulant by mixing it with sucrose and metakaolin in a weight ratio of 50 SBW : 4.2 sucrose: 63.7 metakaolin, drying the “mud-like” paste at 90°C for overnight and then firing it in air at 525°C for 10 hours.

Calcine is x-ray amorphous, contains little nitrate/nitrite, but some carbonate and sulfate.

Properties of hydroceramics made at different calcination temperatures

Sample	Calcine at 450ºC	Calcine at 525ºC	Calcine at 600ºC
Weight loss on firing (%)	15.0	15.8	16.7
Conductivity (mS/cm)-1 day	6.40	4.20	3.90
Conductivity (mS/cm)-7 day	6.70	5.10	4.80

Solidification of Calcine/Steam Reformed Product

- Seems unlikely that a powdered waste form would be acceptable for any transportation off site. Even if it were inert and harmless one accidental spill of the powder and any dispersal by wind or rain would cause such a public outcry that it would again set nuclear energy back 10-20 years.
- Both calcine and steam reformed product can be made into a monolithic solid using hydroceramic binder. The binder outperforms Portland cement.

Second step-Fromation of monolithic hydroceramics

Shape monolithic hydroceramics

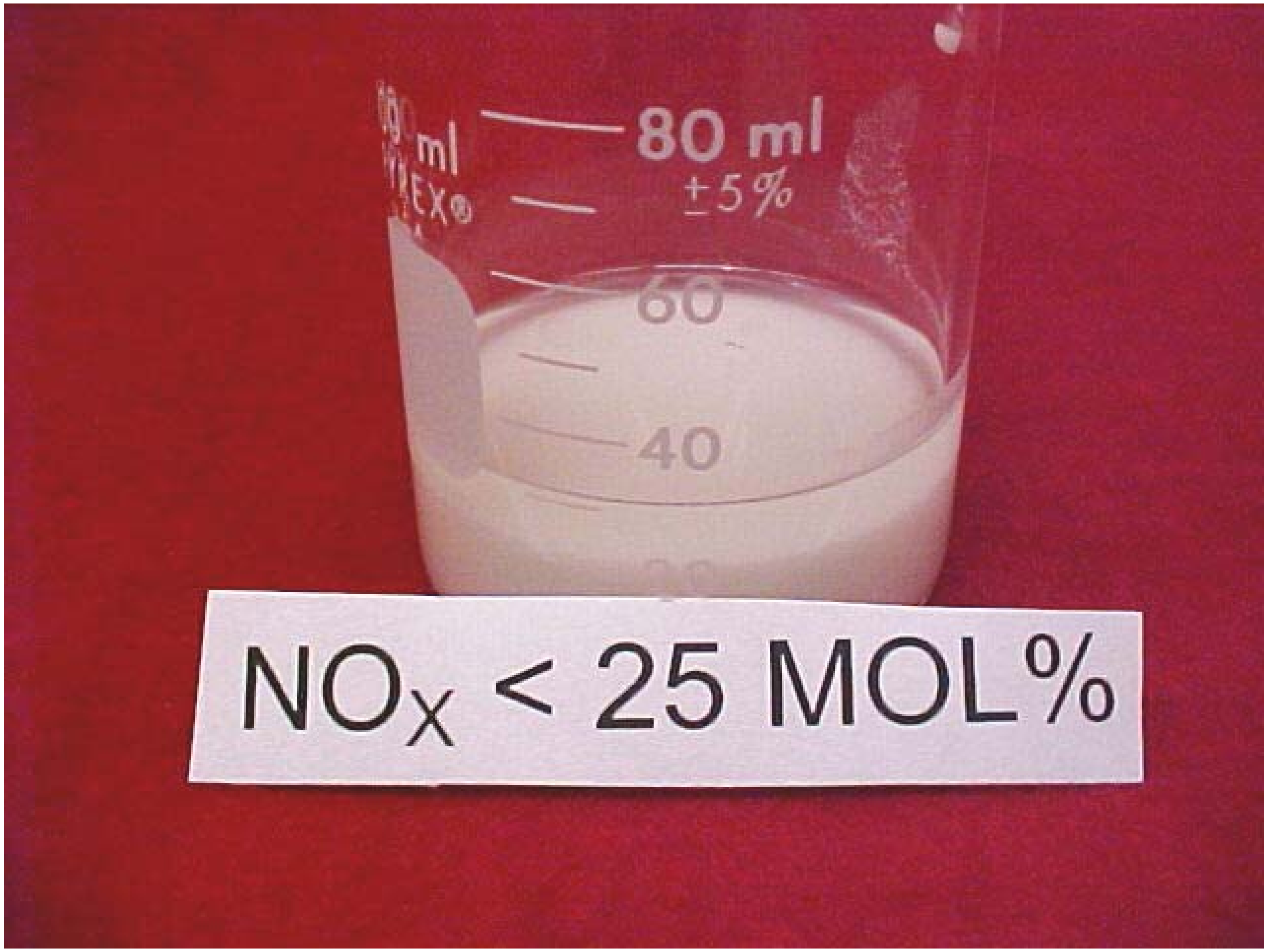
Precured and cured hydroceramics

Properties of Calcines made at different calcination temperatures

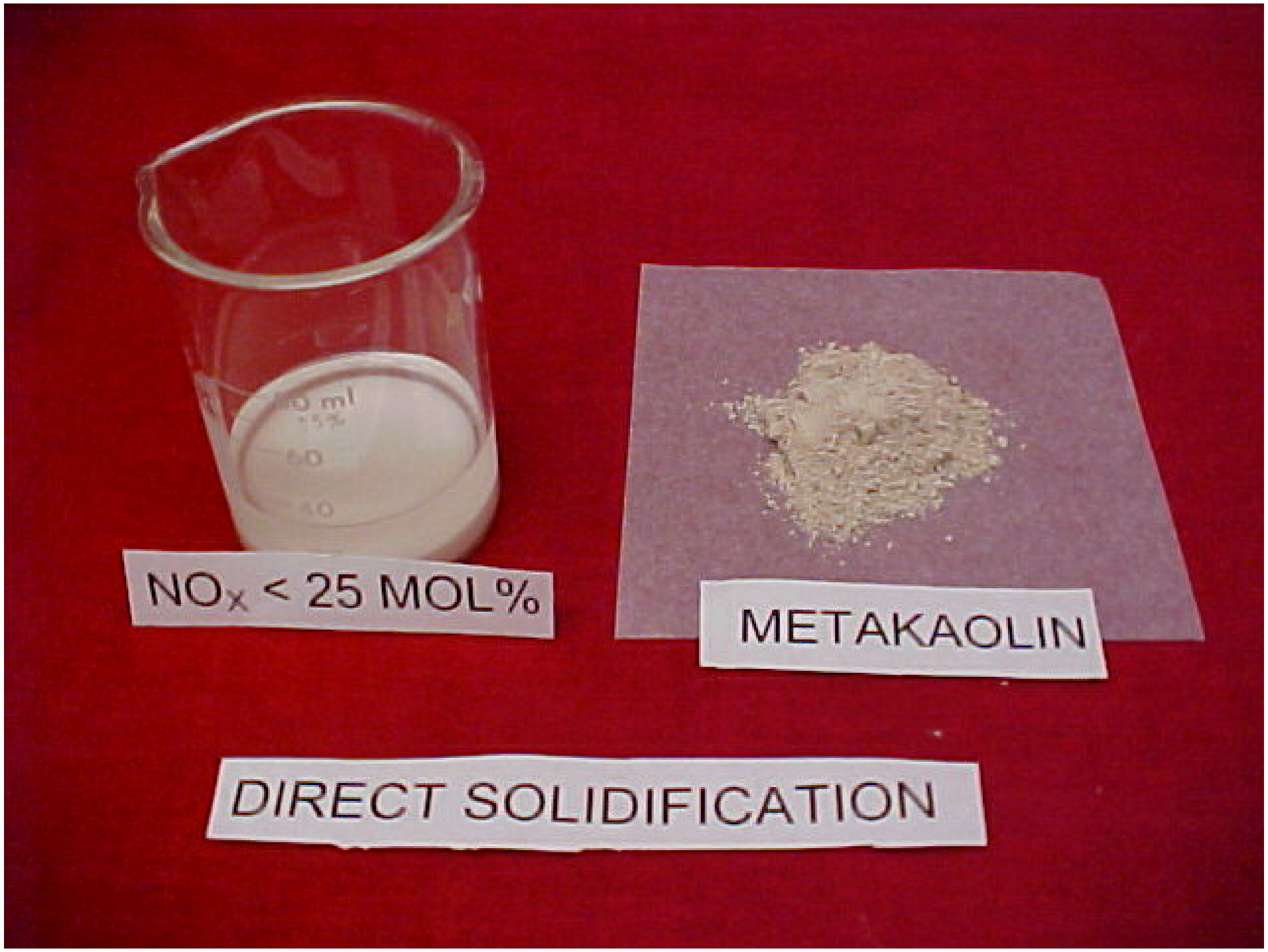
Sample	Calcine at 450^{o}C	Calcine at 525^{o}C	Calcine at 600^{o}C
Density (g/cm^3)	1.08	1.12	1.07
Compressive strength (MPa)	3.52	3.54	3.04
Conductivity (mS/cm)-1 day	4.10	3.60	4.40
Conductivity (mS/cm)-7 day	4.20	3.70	4.70

Cold Calcination

Precipitation formed during the reduction reaction



Direct solidification of the reduced liquid waste



Shape monolithic hydroceramics

Precured and cured hydroceramics

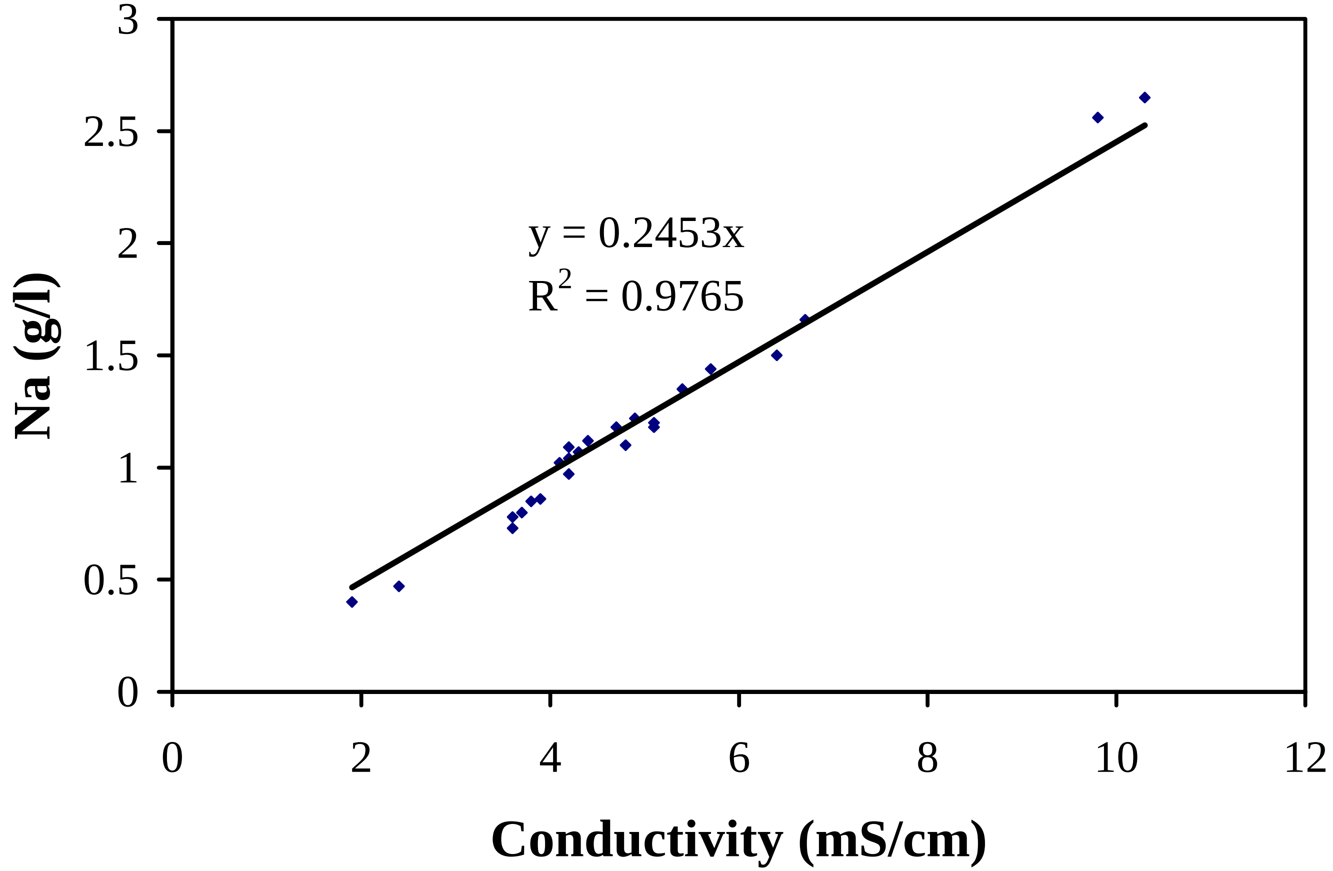
Leachability of Cold Calcined Hydroceramic

Sample ID	#1	#2	#3	#4	#5
Mole ratio of metallic Al/NO_3 in waste	1.5	1.5	1.5	1.5	1.5
Mole ratio of metallic Si/NO_3 in waste	1.5	1.5	1.5	1.5	1.5
Total mole Na/Al after additional metakaolin	1:0.5	1:0.8	1:1.0	1:1.2	1:1.5
Leachate conductivity (mS/cm)	11.70	8.10	4.50	5.40	6.00
Leachate pH	10.39	10.20	9.60	9.89	10.00

Final Thoughts

- Hydroceramics are well suited for the task of solidifying all types of SBW and calcines derived from them.
- Could possibly be used for in tank solidification.
- % Na lost compares favorably with EA Glass which lost 11.9% of its Na in a 7 day PCT test.
- Zeolite and feldspathoid phases compatible with Yucca Mountain strata. No alteration expected.

Analyses based on Conductivity



PUBLICATIONS WORTH READING FOR FURTHER INFORMATION ON HYDROCERAMICS

- Bao, Y. and S. Kwan, D.D. Siemer and M.W. Grutzeck, "Binders for Radioactive Waste Forms made from pretreated Calcined Sodium Bearing Waste," J. Materls. Sci. **39**, p. 481-488 (2004).
- Bao, Y. and M.W. Grutzeck, "Solidification of Sodium Bearing Waste using Hydroceramic and Portland Cement Binders," given orally and accepted for publication as part of the Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries Symposium Proceedings at the 2004 annual meeting of the Amer. Ceram. Soc in Indianapolis 2004 (in press).
- Bao, Y. and M.W. Grutzeck, "The Effect of Calcination Temperature on the Leachability of Hydroceramic Waste Forms," written and will be submitted to J. Materials Research shortly (to be submitted).
- Grutzeck, M.W. and D.D. Siemer, "Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry," J. Amer. Ceram. Soc. 80, 2449-53 (1997).
- Krishnamurthy, N., <u>Zeolitic Hydroceramics for Sodium Bearing Nuclear Wastes</u>, a M.S. Thesis in Environmental Engineering, The Pennsylvania State University, December 2001 (2001).
- Krishnamurthy, N., M.W. Grutzeck, S. Kwan and D.D. Siemer, "Hydroceramics for Savannah River Laboratory's Sodium Bearing Waste," 337-344 in "Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI," edited by D.R. Spearing, G.L. Smith and R.L. Putnam, Ceram. Trans. Amer. Ceramic Society <u>119</u>, Westerville, OH. (2001).
- LaRosa, J.L., S. Kwan, M.W. Grutzeck, "Zeolite Formation in Class F Fly Ash Blended Cement Pastes," J. American Ceramic Society<u>75</u>:1574-1580 (1992a).
- LaRosa, J.L., S. Kwan, M.W. Grutzeck, "Self-Generating Zeolite-Cement Composites." pp. 211-216 in <u>Advanced Cementitious Systems: Mechanisms and Properties</u>. Eds. F.P. Glasser, G.J. McCarthy, J.F. Young, T.O. Mason. Symp. Proc. <u>245</u>, Materials Research Society, Pittsburgh, PA (1992b).
- Palomo, A. and F.P. Glasser, "Chemically-Bonded Cementitious Material Based on Metakaolin," Br. Ceram. Trans. J91, 107-112 (1992).
- Palomo, A., M.T. Blanco-Varela, M.L Granizo, F. Puertas, T. Vazquez and M.W. Grutzeck, "Chemical Stability of Cementitious Materials Based on Metakaolin," Cem. Concrete Res. <u>29</u>, 997-1004 (1999a).
- Palomo, A., M.W. Grutzeck and M.T. Blanco, "Alkali-Activated Fly Ashes a Cement for the Future," Cem. Concr. Res. <u>29</u>, 1323-1329 (1999b).
- Siemer, D.D., M.W. Grutzeck, D.M. Roy and B.E. Scheetz, "Zeolite Waste Forms Synthesized from Sodium Bearing Waste and Metakaolinite," WM'98, March 1-5, 1998, Tucson, AZ. Proceedings Published on the WWW at http://www.wmsym.org (1998)
- Siemer, D.D., M.W. Grutzeck, B.E. Scheetz, "Comparison of Materials for Making Hydroceramic Waste Forms," 161-167 in "Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries V," edited by G.T. Chandler and X. Feng, Ceram. Trans. Amer. Ceramic Society <u>107</u>, Westerville, OH. (2000).
- Siemer, D.D., J. Olanrewaju, B.E. Scheetz, N. Krishnamurthy and M.W. Grutzeck, "Development of Hydroceramic Waste Forms," 383-390 in "Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI," edited by D.R. Spearing, G.L. Smith and R.L. Putnam, Ceram. Trans. Amer. Ceramic Society <u>119</u>, Westerville, OH. (2001a).
- Siemer, D.D., J. Olanrewaju, B.E. Scheetz, and M.W. Grutzeck, "Development of Hydroceramic Waste Forms for INEEL Calcined Waste," 391-398 in "Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI," edited by D.R. Spearing, G.L. Smith and R.L. Putnam, Ceram. Trans. Amer. Ceramic Society <u>119</u>, Westerville, OH. (2001b).
- Siemer, D.D., Performance of Hydroceramic Concretes on Radwaste Leach Tests," 369-397 in "Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VII," edited by D.R. Spearing, G.L. Smith and S.K. Sundaram, Ceram. Trans. Amer. Ceramic Society <u>132</u>, Westerville, OH. (2001b).