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PHYSICAL, CHEMICAL AND STRUCTURAL EVOLUTIION OF ZEOLITE-CONTAINING WASTE FORMS PRODUCED FROM METAKAOLINITE AND CALCINED SODUIM BEARING WASTE (HLW AND/OR LLW)

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Research Objective

Zeolites are extremely versatile. They can adsorb liquids and gasses and serve as cation exchange media. They occur in nature as well cemented deposits. The Romans used blocks of zeolitized tuff as a building material. Using zeolites for the management of radioactive waste is not new, but a process by which the zeolites can be made to act as a cementing agent is. Zeolitic materials are relatively easy to synthesize from a wide range of both natural and man-made precursors. The process under study is derived from a well known method in which metakaolin (thermally dehydroxylated kaolin a mixture of kaolinite and smaller amounts of quartz and mica that has been heated to ~700°C) is mixed with sodium hydroxide (NaOH) and water and reacted in slurry form (for a day or two) at mildly elevated temperatures. The zeolites form as finely divided powders containing micrometer (µm) sized crystals.[1] However, if the process is changed slightly and just enough concentrated sodium hydroxide solution is added to the metakaolinite to make a thick paste and then the paste is cured under mild hydrothermal conditions (60°-200°C), the mixture forms a concrete-like ceramic material made up of distinct crystalline tectosilicate minerals (zeolites and feldspathoids) imbedded in an X-ray amorphous hydrated sodium aluminosilicate matrix.[2,3,4,5] Due to its vitreous character we have chosen to call this composite a "hydroceramic". Similar to zeolite powders, a hydroceramic is able to sequester cations in both lattice positions and within the channels and voids present in its tectosilicate framework structure. It can also accommodate a wide range of salt molecules (e.g., sodium nitrate) within these same openings thus rendering them insoluble. Due to its fine crystallite size and cementing character, the matrix develops significant physical strength. The obvious similarities between a hydroceramic waste form and a waste form based on solidified Portland cement grout are only superficial because their chemistries are entirely different. In addition to being vastly superior to conventional Portland cement grouts with respect to salt retention, standard radwaste leach protocols (PCT, TCLP, etc.) have shown that hydroceramics also do a better job of immobilizing the RCRA-toxic and radioactive components of "sodium bearing wastes" (SBWs).[5]

Making a hydroceramic waste form is straight forward. Metakaolin, either alone or preblended with small amounts of vermiculite (improves Cs retention) and/or sodium sulfide (which acts as a redox buffer and RCRA metal precipitant) is mixed with properly pretreated (calcined) SBW plus sufficient 4M NaOH solution and shear mixed to produce a modeling clay-like "paste". The paste can be extruded into a metal container and then "soaked" for a few hours at 20°-90°C prior to implementation of the final curing process. If a curing temperature <100°C is chosen, a well-insulated building equipped with space heaters can serve as both an interim storage facility and "curing shed". If a faster cure is desired, curing must be done at higher temperatures in an autoclave ("pressure cooker") or canisters designed to act as pressure vessels[6].

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[1] Breck, D.W., Zeolite Molecular Sieves, 380 pp., Wiley-Interscience (1974).

[2] Grutzeck, M.W. and Siemer, D.D., "Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry," J. Amer. Ceram. Soc. 80, 2449-53 (1997).

[3] 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," WM'98 Proceedings March 1-5, 1998, Tucson, AZ, WM Symposia, Inc., Tucson (1998).

[4] Palomo, A., M.W. Grutzeck and M.T. Blanco, "Alkali Activated Fly-Ashes: A Cement for the Future," Cem. Concr. Res. 29, 1323-1330 (1999).

[5] Siemer, D.D., M.W. Grutzeck, D.M. Roy, B.E. Scheetz, "Zeolite Waste Forms Synthesized from Sodium Bearing Waste and Metakaolinite," WM'98 Proceedings March 1-5, 1998, Tucson, AZ.

[6] Such vessels would not have to be especially massive or expensive; for example, domestic water heaters are designed for pressures up to 150 psig – which corresponds to a curing temperature of 185°C.

A waste treatment system consisting of a relatively simple calciner/reformer close coupled with a hydroceramic grout mixer could prove to be an efficient solution to many of DOE's reprocessing waste treatment problems. The objective of this study is to work out the details of how the process could be applied to both the caustic-type SBWs stored at the Hanford and Savannah River sites and the already calcined acidic SBW in storage at the Idaho National Engineering & Environmental Laboratory (INEEL). The goal is to develop a clearer understanding of the advantages and limitations of hydroceramic waste forms, i.e. the effect of processing variables, reaction kinetics, crystal and phase chemistry, and microstructure on their performance.

Research Progress

During the tenure of our current EMSP grant, it has been possible to provide proof of concept that a monolithic hydroceramic waste form can be produced from nearly all types of SBW. Processing has been optimized for three types of SBW based upon their ratio of nitrate/nitrite to NaOH in the waste. We have also begun to study cold calcination with Al+Si powders, and the potential of using metakaolinite mixed with SBW solutions as hydroceramic tank fill materials. The text below highlights the progress made to date in each of the two past funding periods.

First Three Years

Two waste simulants (SRS 1 and 2) based on Savannah River's Tank 44 waste[7] and a third based upon the average supernate composition of SBW in Hanford tanks[8] were formulated using the recipes given in Table 1. It was realized rather early that their nitrate and nitrite content were detrimental to making hydroceramics by direct mixing processes (Table 2-Raw SBW), they had very high nitrate/nitrite leach rates. Heating the SBW in air with a reducing agent such as sucrose led to the formation of Na_2CO_3 (Table 2-SBW + sucrose) which is soluble and thus

Table 1. Composition of Simulated SBWs used to make SBW Calcines (weights in grams/L)

Component	SRS 1	SRS 2	Hanford
NaOH	456	456	82.682
$Al(NO_3)_3.9H_2O$	32.32	32.32	133.5
$NaNO_2$	95.2	95.2	36.911
$NaNO_3$	95.2	95.2	36.205
Na_2CO_3	21.2	21.2	8.582
$CsNO_3$	-	4.66	-
Na_2HPO_4	-	-	27.787
KCl	-	-	1.833
NaCl	-	-	2.508
$Na_2B_4O_7.10H_2O$	-	-	0.110
Na_2SO_4	-	-	3.894
$Ni(NO_3)_2.6H_2O$	-	-	0.312
$Ca(NO_3)_2.4H_2O$	-	-	0.442
$Mg(NO_3)_2.6H_2O$	-	-	0.034

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[7] Jantzen, C., Personal Communication (2001).

[8] Brough, A.R., A. Katz, T. Bakharev, G-K Sun, R.J. Kirkpatric, L.J. Struble and J.F. Young, pp. 199 in Mater. Res. Soc. Symp. Proc. **370** Mater. Res. Soc., Pittsburgh, 1995

adversely affected leachability as evidenced by the high Na content of the lechate. Thus it was decided to study thermal calcination in the presence of a reducing agent (sucrose) at a variety of temperatures with the addition of various sodium ion "getters" to see if carbonation could be eliminated. It was hypothesized that, were a suitable host available to react with, the nascent Na ions would react with it rather than the CO_2 in the furnace atmosphere. Colloidal aluminum hydroxide, Min-U-Sil, and metakaolinite were added to the SBW + sucrose mixture and fired at a variety of temperatures in order to produce something other than a soluble product. All calcines contained 20 g liquid SBW, 2.5 g sucrose and 11.9 g metakaolinite. The combination containing sucrose and metakaolinite fired in air at 525°C for 24 hours was found to contain the lowest amount of CO_3, and to have acceptably low NO_3 and NO_2 concentrations (Table 2-columns labeled boehmite, quartz and metakaolinite). See Siemer et al.[9] for a more detailed account of the effect of many more additives on carbonation and leachability. Also given in Table 2 (last column) are data for our initial cold calcination experiment. Adding Al metal alone added too much Al to make zeolites. Adding both Al and Si has solved the problem.

Table 2. Chemical analysis of treated SBW calcines based upon SRS Tank 44 Simulant 1.

Wt.% present	Raw SBW	SBW + sucrose	SBW + sucrose + boehmite	SBW + sucrose + 5 μm quartz	SBW + sucrose + metakaolinite	SBW + Al powder
NO_3 (IC)	4.5	<0.1	<0.1	<0.1	<0.1	1.5
NO_2 (IC)	4.8	0.45	0.13	<0.05	0.08	2.3
CO_3	0.83	43	9	15.3	8.0	~0.4
Na (ICPAES)	25.4	41	27.4	22.5	20.0	35.6
Al (ICPAES)	0.8	1.7	30.2	0.64	12.1	14.4

PCT procedures were modified to facilitate rapid testing and evaluation as follows: The sample was ground to a powder in an agate mortar and sieved using piggy-backed 100 mesh and 200 mesh screens (75-149 micron size). One gram of the unwashed but sized sample was placed in Teflon lined Parr bombs with 10 cc deionized water at 90°C for 1 day. The solution was filtered and its electrical conductivity was determined using a conductivity probe and a Quickcheck Model 118 Conductivity-2 meter (Orion). Conductivity rather than a chemical analysis was used to screen the samples. It has been demonstrated that the sodium ion dominates the leachate in these tests. It is so abundant in the SBW and in the zeolites and feldspathoids in the hydroceramic that Na simply overwhelms the solution. Sodium ion concentration had been calculated, until as of late, by using standard conductivity data for NaOH solutions. During the second funding period a more formal approach was taken in which analytical data and conductivity were compared. A plot of the data currently used to screen samples is given in Figure 1. This plot was used to obtain % Na leached during sample screening experiments. For sake of example, a 7 day PCT of EA glass tested out at 6.35 mS/cm which is equivalent to ~11.9 % total Na leached[10]. Seven day PCT test results for calcines made with additives are given in Table 3. Note that the thermal calcination process (525°C for a few hours) has essentially

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[9] Siemer, D.D., M.W. Grutzeck, B.E. Scheetz, "Comparison of Materials for Making Hydroceramic Waste Forms," 161-167 in Ceram. Trans. Amer. Ceramic Society 107, Westerville, OH. (2000).

[10] EA Glass contains 16.9 % Na_2O. A conductivity of 6.35 is approximately equivalent to 1.5 g/l Na. Doing the math and converting g Na to moles Na and then to moles Na_2O and then to grams in 10 cc and then dividing that number by 0.169 g Na_2O/g EA Glass one gets ~11.9% leached.

converted all of the nitrate/nitrite in the SBW solution into oxides and carbonates as the sucrose is burnt off. Carbonate is higher than one might want due to the carbonation of the newly formed sodium oxide molecules. This can not be helped, but one does get less carbonate when other substances are added to the raw waste/sucrose mixture during the calcination process. Of the lot, the calcine made with sucrose and metakaolinite had the lowest (% of the total amount available) leachability for Na and Cs as well as very low nitrate/nitrite. For this reason it was decided to focus on waste forms using metakaolin as a calcination aid (sodium getter) and binder phase for the powdered calcines.

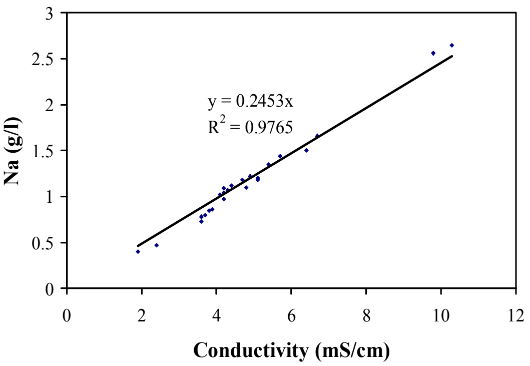

Figure 1. Conductivity versus Na^+ concentration. It is notable that the slope of this curve is approximately the same as that for NaOH .

Table 3. Typical 7-day PCT test results for calcines made with different Na-getters.

Simulant	Raw Waste	Boehmite	Minusil	Metakaolinite	Cold Calcination
Σalk:Al:Si atom ratios	1:1.03:1.58	1:2.12:1.58	1:1.02:2.38	1:1.32:2.06	1:1.35:1.58
% H_2O added	29.3	25.6	27	28.5	28.5
mS/cm @1/100	0.379	0.246	0.236	0.145	0.279
pH	10.7	10.5	10.5	10.3	11.1
Nitrite ppm	555 (26%)	4	<1	<1	4 (0.9%)
Nitrate ppm	302 (14%)	5	<1	4	21 (3.2%)
Na ppm	856 (7.1%)	514 (5.5%)	428 (4.4%)	346 (3.6%)	526 (4.5%)
Al ppm	34	98	35	62	104
Si ppm	43	46	45	42	86
CO_3 ppm	202	38	553	350	462
Cs ppm	0.083 (0.086%)	0.17 (0.22%)	0.053 (0.068%)	0.039 (0.051%)	0.19 (0.21%)

Because the calcines were powders, they were each made into monoliths using a binder consisting of metakaolinite and various solutions mixed to paste-like consistency and then curing them as a function of temperature. It seemed reasonable to proceed in this fashion because zeolites were being formed in the calcines and it was thought that more zeolites would form during the solidification process if metakaolinite and alkali were used as the binder as well. Conductivity measurements described earlier were used to evaluate the PCT leaching performance of the monoliths (Figure 2). It is notable that leach performance improves with time through 14 days and then levels out. Due to the fact that the Tank 44 waste simulate has a great excess of free hydroxide relative to nitrate/nitrite (>4:1 mole wise) it is actually a Type II SBW that one is able solidify directly by mixing it with additional metakaolin. This duality is discussed later the Second Three Years section below.

It was also discovered that very pure metakaolinite (rather than impure metakaolin) such as that sold by Engelhard provided better leach resistance (higher reactivity) when it was used to make a monolith from the calcines, but at the expense of strength because the solids had very little to none at all. However, by adding 5µm quartz (Min-U-Sil) strength was regained without compromising leach resistance.

Lastly, efforts were made to denitrate the waste without the use of heat. One SBW sample was “cold de-nitrated" at room temperature by adding aluminum powder to the caustic rich solution containing nitrate/nitrite salts. The aluminum served as a reducing agent and caused the evolution of ammonia. See Tables 2 and 3 (right-hand most columns). These results have spurred the current thrust on further exploring Al and Si reduction proposed for the coming three years.

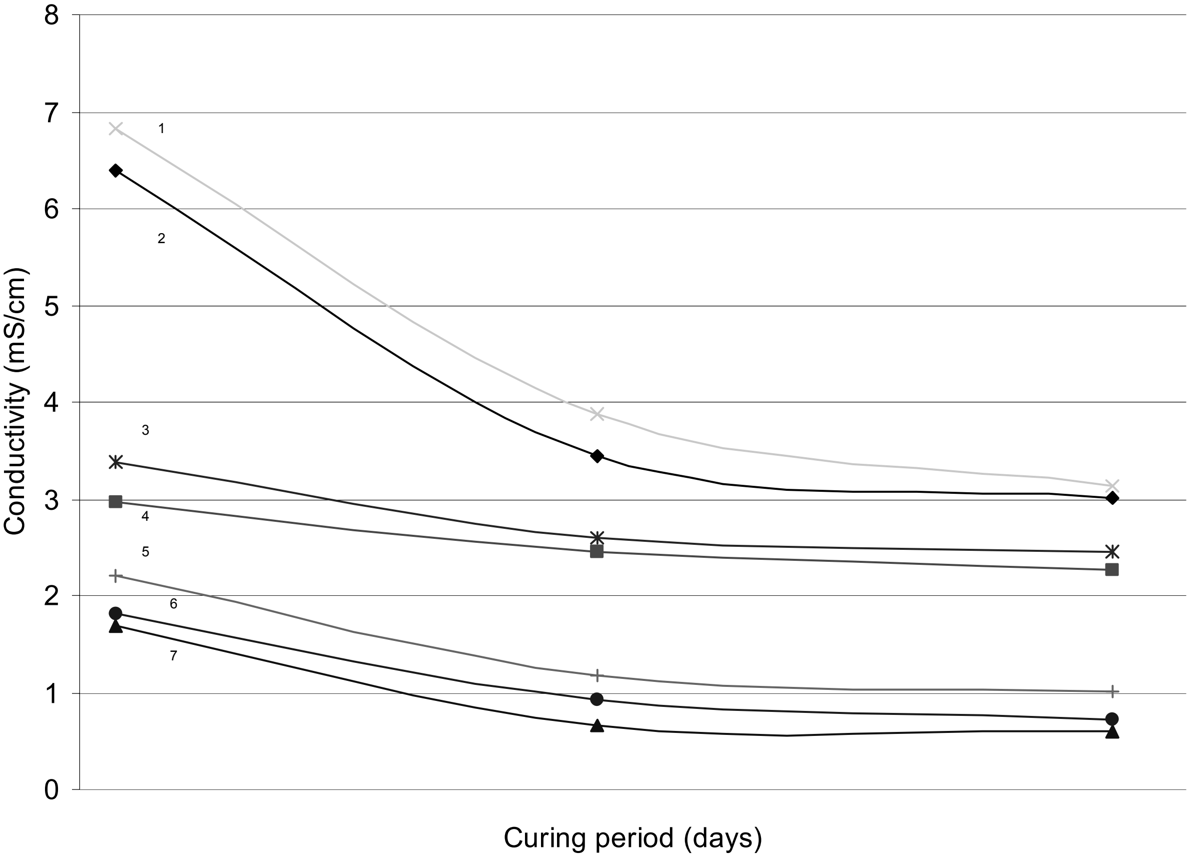

Figure 2. Modified 1-day PCT data for hydroceramics made with 60wt% SRS and Hanford Calcines, 40wt% metakaolinite and solution that were cured at 115°C (Curves 1- 4, 6, 7) or 90°C (Curve 5) as a function of time. Curve 1: SRS Calcine 1 and 2M NaOH; Curve 2: SRS Calcine 1 and water; Curve 3: SRS Calcine 2 and 2M NaOH; Curve 4: SRS Calcine 2 and water; Curve 5: Hanford Calcine and water; Curve 6: Hanford Calcine and 2MNaOH; Curve 7: Hanford Calcine and water.

Conclusions

Calcines as well as hydroceramics made with impure metakaolin from Troy Idaho tended to outperform all other aluminosilicate additives. Hydroceramics have a ceramic structure and contain zeolitic phases such as zeolite A and hydroxysodalite. This makes them accommodate sodium within their matrix with relatively little additional processing. They have low leachability and compare favorably with DOE’s EA glass waste form. Cesium containing calcines were better accommodated by hydroceramics made with additional sodium hydroxide and vermiculite. The overall low cost and low temperature processing enhance the potential utility of hydroceramics in providing an alternate means for the disposal of sodium bearing wastes. By way of summary, Table 3 and Figure 2 almost speak for themselves. The data given there represent the results of PCT tests run on typical calcines and hydroceramic monoliths made from the calcines using a metakaolinite binder. The numbers in parentheses in Table 3 represent the % of the total amount present in the sample that was leached. These are good numbers, comparable to glass waste forms even before being formed into monoliths.

Publications During First Three Years

Grutzeck, M.W., D.D. Siemer, "Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry", J. Amer. Ceram. Soc. 80, 2449-2453 (1997).

Siemer, D.D., M.W. Grutzeck, D.M. Roy, B.E. Scheetz, "Zeolite Waste Forms Synthesized from Sodium Bearing Waste and Metakaolinite", WM98, Tucson AZ, March 1-5, 1998. CD of Proceedings Published September (1998) also published on the World Wide Web.

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," Ed. by Chandler and Feng, Ceram. Trans. Amer. Ceramic Society 107, Westerville, OH. (2000).

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," Ed. by Spearing, Smith and Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001).

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," Ed. by Spearing, Smith and Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001).

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," ed Spearing, Smith, Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001).

Second Three Years

Work has focused on scale-up issues, the development of a classification scheme for low activity SBW, a demonstration of solidification of a Type II SBW (Savannah River Tank 44) in two ways, simulating Hanford's Tank AN-107 waste in response to the publication of a SRL document on steam reformed Hanford's Type III waste treated in a Studsvik reactor[11], using the AN-107 calcine to study Type III waste solidification using a hydroceramic binder, the beginnings of cold calcination studies, and the performance of metakaolin/4M NaOH versus Portland cement/water as a binder phase for preexisting calcines/steam reformed materials.

Scale-Up Testing

Scaling up a reaction provides a challenge not recognized in smaller samples. One issue is certainly the heat of hydration. Although a scale up to a four inch cube made with simulated

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[11] Jantzen, C.M."Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process (U)," WSRC-TR-2002-00317, and SRT-RPP-2002-00163, July 12, 2002 (2003)

AN-107 SBW calcine is not a very large scale up in size, if one considers that previous work was carried out on centimeter sized samples, it is a rather significant step in the right direction. Our intent was to see if scale up would introduce variables in strength, leachability, phase formation and the like depending upon the sampling position in the cube. Testing described below indicated that no such problems were found. The four inch hydroceramic cube was evaluated by taking subsamples from various surfaces, edges and interior and leach testing them as a function of phase composition. The effects of excess heat of reaction were not noticeable.

The simulant used was based upon a recipe published by Jantzen[11] for the SBW in Hanford Tank AN-107. The ingredients used to make the simulant are given later in Table 12. Because this is a Type III SBW it had to be calcined prior to solidification. This was carried out in the usual fashion by adding sugar and metakaolinite to the SBW and calcining it at 525°C. More details are given in the Optimization Section later. To make the cube, 480 g of the AN-107 calcine was blended with 320 g metakaolin and 720 mL 4M NaOH. This formulation is pourable, so it made it easy to transfer the mix to a four-inch cube mold. The sample was precured at 40°C and 50% humidity overnight, then it was demolded and further cured in a sealed can at 90°C for 24 hours. After removing the sample from the can it was dried at 50°C overnight and its volumetric density was determined (1.03 g/cc). Then it was cut into 27 pieces. After sanding, each small cube sample was nominally a 1 x 1 x 1 inch in size. The subsamples consisted of 1 middle piece, 8 corner pieces, 6 side middle pieces and 12 side pieces. The cubes were defined as combinations 123, abc and TML were tracked during leaching and testing. All samples were tested using a 1 day PCT, but several were also tested using a 7 day PCT. The compressive strength of the samples was also tested prior to grinding them for PCT. Both data sets are given in Table 4.

The average compressive stress for the blocks was 3.16 MPa and the average PCT for 1 day was 2.61 (mS/cm). The relationship between compressive strength and conductivity of the leachate is illustrated in Figure 3. The compressive strength and PCT conductivity of the individual blocks have little if any correlation, which indicates that the homogeneity of the four inch sample was quite good. There is just the slightest suggestion that the stronger samples may have lower leachabilities. It is also notable that the 1 and 7 day conductivities are nearly the same, illustrating the suitability of a 1 day test for scoping and other comparative statements.

Table 4. The compressive strength (MPa) and PCT conductivity (mS/cm) of the one inch blocks.

	1aT	2aT	3aT		1aM	2aM	3aM		1aL	2aL	3aL
Strength	3.14	3.41	4.26		3.72	3.25	3.33		2.66	3.28	3.03
PCT-1 d	3.20	3.30	2.80		2.40	2.00	2.20		2.60	2.30	2.40
PCT-7 d	3.40	--	--		--	2.20	2.60		2.60	2.50	--
	1bT	2bT	3bT		1bM	2bM	3bM		1bL	2bL	3bL
Strength	2.52	2.83	3.33		3.28	3.67	3.40		2.56	3.76	2.79
PCT-1 d	3.60	2.70	3.50		2.00	2.50	2.20		2.80	1.90	2.20
PCT-7 d	4.00	--	--		2.30	2.60	--		--	--	--
	1cT	2cT	3cT		1cM	2cM	3cM		1cL	2cL	3cL
Strength	3.57	2.91	3.82		2.73	3.37	3.27		2.00	2.42	3.05
PCT-1 d	3.70	3.80	2.50		2.40	1.90	2.40		2.70	2.10	2.50
PCT-7 d	3.90	--	--		--	2.10	--		--	--	--

The crystalline phases present in the 27 blocks were also investigated using X-ray diffraction. The X-ray diffraction patterns of the samples are similar. Each contains a mix of zeolite A and hydroxysodalite. The ratios of the peak area of zeolite A at d(100) = 1.23 nm and that of hydroxysodalite at d (110) = 0.633 nm was calculated. The ratios are distributed in a small range between 0.8 and 1.7, which also suggests that the sample is homogeneous. The correlation between this ratio and PCT conductivity is given in Figure 4.The data indicate that Na leachability is higher when the sample contains relatively larger amounts of hydroxysodalite. The results suggest that a high compressive strength and a high zeolite A content should provide the best performing hydroceramic waste form.

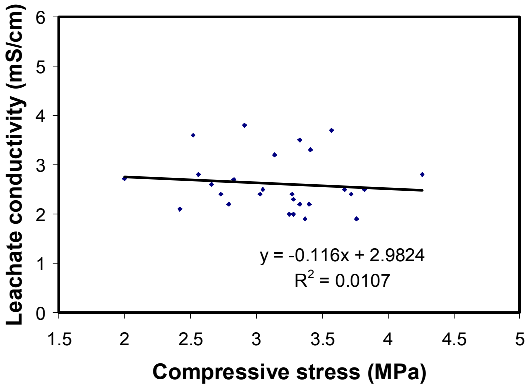

Figure 3. Relationship of Na leachability versus compressive strength.

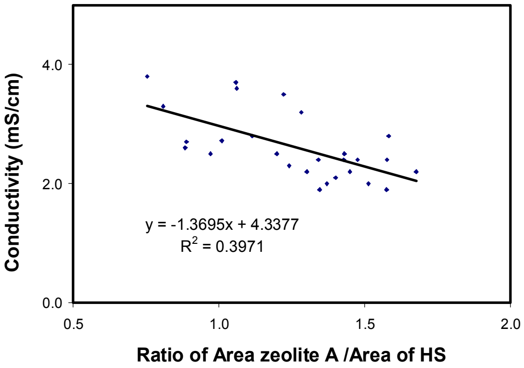

Figure 4. Relationship of Na leachability versus ratio of zeoliteA/hydroxysodalite.

Solidifying a Type II Waste: A Comparison of Options

Savannah River has removed Cs and Sr from a sample of Tank 44 waste to make it possible to work with it in a hood. As a result it is about one half as concentrated in Na as the original (Table 1). The simplified recipe supplied by Savannah River is given in Table 5 and its simulation is given in Table 6. Note however that the nitrate and nitrite concentrations are just about on the cusp between the two Types of SBW defined earlier. The moles of nitrate+nitrite divided by the total moles of sodium in the SBW is ~20%. For this reason two experiments were run and the results compared. In one case the hydroceramic was made using the solution itself without any pretreatement and in the second case the SBW was first calcined with sucrose and metakaolin to make a calcine that was then solidified using additional metakaolin plus 4M NaOH binder.

Table 5. Composition of Tank 44 waste.

Ions present	Concentration (M)
Na^+	5.1
NO_3^-	0.5
NO_2^-	0.5
AlO_2^-	0.2
OH^-	4.5

Table 6. Composition of simulated treated Tank 44.

Composition	MW	M	g/l
$CsNO_3$	194.909	0.5	97.4545
KNO_2	85.107	0.1	8.5107
$NaNO_2$	69.000	0.4	27.6000
$NaAlO_2$	81.979	0.2	16.3958
NaOH	39.998	4.5	179.9910

Metakaolinite was mixed with varying amounts of SBW directly, cured at 90°C and 190°C in a steam saturated atmosphere (Teflon-lined Parr bombs) for 24 hours. Mix proportions, crystalline phases observed in the hydroceramic, Na leachability as calculated using a 1 day unwashed sample PCT test, and a calculated value for the % Na leached versus total Na content of the hydroceramic are given in Tables 7 (90°C cured) and Table 8 (190°C cured). The higher curing temperature provides a slight improvement in leachability, but its implication would come at a very high price. Curing at 90°C can be in can in a warm room, curing at 190°C would have to be carried out in a steam/dry autoclave operating at 12-13 atmospheres pressure.

Table 7. Metakaolin mixed with different amounts of supernate and 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	--	--
% total Na leached	--	10.6	8.9	7.4	--	--

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

Table 8. Metakaolin mixed with different amounts of supernate and 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	--
% total Na leached	--	6.6	5.3	7.5	--

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

As stated above, this SBW was also solidified after first calcining it with sucrose and metakaolinite at 525°C overnight. 38 g sugar/L was added to the SBW simulant at the ratio of 38g/mol NO_3+NO_2. In order to reduce the formation of sodium carbonate during calcination 79.3 g and 113.3 g metakaolin were also added to 2 different 100 mL aliquots of the SBW at the mole ratio of metakaolin:Na = 0.7:1 and 1:1. These have been found to be the ratios that most favor the production of tectosilicate phases in the calcine. After slurrying the dry ingredients with the SBW, the slurry was dried at 90°C and then fired at 525°C for 10 hours. The resulting powders are referred to as calcines. Weight lost during firing, crystalline phase formation, conductivity measurements performed using a Modified PCT leaching test and the total % Na leached for the two calcines studied are given in Table 9.

Table 9. Leachability of two simulated Savannah River Tank 44 SBW calcines made with metakaolin and sucrose and heated at 525°C.

Sample Number	Calcine #1 Mk:Na=0.7:1	Calcine #2 Mk:Na=1.0:1
Weight lost during firing	11.6%	9.2%
Crystalline phase	Amorphous + Quartz	Amorphous + Quartz
Conductivity (mS/cm)	7.10	5.10
% total Na leached	9.6	9.0

It is concluded that the Na leachability of the directly solidified SBW and its calcined equivalent are approximately the same. The amount of sodium lost by each sample in terms of the total amount of sodium present in the samples suggests that approximately 5-10% of the total sodium present can be removed by leaching either type of sample at 90°C for 1 day. The calcine made from the SBW mixed with sucrose and metakaolinite and fired at 525°C overnight did not out perform the directly solidified SBW to such an extent to warrant calcining it under pressure at higher temperatures. Note however that the calcine in question is a powder and in order to ship it off site it will have to be solidified. Once so solidified, using additional metakaolin and 4M NaOH as a binder as described below, leachability improved significantly (Tables 10 and 11).

Monolithic hydroceramics were prepared from Calcines 1 and 2 (Table 9) by mixing 12g calcine and 8 g metakaolin with 18 ml 4 M NaOH to form a paste. The pastes were molded in 2 inch by 1 inch diameter of cylinder molds and then precured at 40°C in a 50% humidity chamber overnight. After demolding, the samples were cured at 90° and 190°C in a steam saturated atmosphere (Teflon-lined Parr bombs) for 24 hours. The samples were characterized and tested as before. In addition phase composition, densities and compressive strengths were also determined. See Tables 10 and 11.

The percentages of Na leached from these monolithic solids are the lowest of the tested samples. Strengths are also adequate. The data suggest that a two step process will produce a much better waste form, but the fact remains that the single step process may in fact be sufficient to do the job in its own right. Waste specific testing will have to be carried out in order to show that this is true. If it is not, a two step process could be used instead.

Table 10. Hydroceramic waste forms cured at 90°C for 24 hours

Sample	Monolith #1 Mk:Na=0.7:1	Monolith #2 Mk:Na=1.0:1
Crystalline phase	Zeolite A	Zeolite A
density	1.06	1.07
Compressive strength (mPa)	3.21	3.07
Conductivity (mS/cm)	3.20	3.00
% total Na leached	3.9	4.0

Table 11. Hydroceramic waste forms cured at 190°C for 24 hours

Sample	Monolith #1 Mk:Na=0.7:1	Monolith #2 Mk:Na=1.0:1
Crystalline phase	Analcime + HS	Zeolite A + HS
density	1.05	1.06
Compressive strength (mPa)	3.51	3.42
Conductivity (mS/cm)	2.10	1.10
% total Na leached	2.6	1.5

Optimization

The following set of experiments was meant to determine the optimum calcination temperature for calcining Type III SBW/metakaolinite/sucrose mixtures. It was found that temperature plays a rather significant role up to a point after which further increases in calcination temperature cause only small changes in leachability. The simulated SBW used in the experiments (Table 12) was based upon a recipe originally published by Jantzen[11] that represents the composition of SBW in Hanford's Tank AN-107. The calcines were made by preblending the SBW simulant with metakaolinite and sucrose in the proper proportions needed to reduce nitrate and nitrite ions and form precursor tectosilicate phases. Sodium ion leachability was measured as a function of temperature, which suggested that the optimal (lower volatility and fuel costs, higher reactivity for later solidification with a hydroceramic binder) calcination temperature for this simulated SBW was 525°C overnight in air. The resulting calcines were powders but even so the data show that they have reasonably low leachability in their own right. Nevertheless, in order to store the calcines off site they may have to be solidified if current NRC laws are not changed.

This simulant is clearly a Type III waste, >25 % of the sodium salts present are nitrite/nitrate based (N/Na=0.48) and it contains a significant amount of carbonate as well ($N+CO^-_3/Na=0.62$). At this point in time Type III waste must be de nitrated/denitrited before it can be solidified. Calcining SBW in air or in a steam reformer produces sodium carbonate. Adding a reducing agent such as sucrose and a sodium "getter" able to tie up nascent Na ions as they form allows one to produce sodium aluminosilicates at temperatures ranging from 375 – 675°C (zeolites at low temperatures, feldspathoids at higher temperatures) as described later. Steam reforming also produces the same type of material, but the phases are more nearly feldspathic than zeolitic.

Table 12. Ingredients used to make the AN-107 stimulant. The total moles of nitrate and nitrite anions are 2.93 mol/l. The total Na concentration is 8.2 mol/l. The total ash content using a major oxide basis is 291.7 g/l.

Composition	g/L
$Al(NO_3)_3·9H_2O$	121.1723
$Ca(NO_3)_2·4H_2O$	2.5171
$Na_2Cr_2O_7·2H_2O$	0.6532
$CsNO_3$	0.0157
$Fe(NO_3)_3·9H_2O$	15.0138
KOH	2.0483
La_2O_3	0.0307
NaOH	105.9035
NiO	0.4637
PbO	0.3172
NaCl	2.2999
NaF	5.5596
Na_2HPO_4	4.0852
Na_2SO_4	11.7463
$NaNO_2$	69.0892
$NaNO_3$	155.6883
Na_2CO_3	123.0559

Calcination was carried out in the presence of a reducing agent added at a ratio of 38g sucrose/mol NO_3+NO_2 (111 g sugar/L) and metakaolinite at a Mk:Na ratio of 0.7:1 (1275 g/L) in order to tie up sodium ions as they formed. The aluminosilicates (calcined clay) reacted with the waste to form less soluble aluminosilicates. The slurry that formed after adding the sugar and calcined clay to the AN-107 simulant was dried at 90°C and then 60 g portions of it were calcined at 375 °, 450 °, 525 °, 600 °, and 675 °C for 10 hours. See Table 13.

The calcines were characterized. X-ray Diffraction (XRD) and scanning electron microscopy (SEM) were used to identify the crystalline phase and the morphology of the as-prepared materials. Theoretically, there are 45.1 wt% of Al_2O_3 and 54.1 wt % of SiO_2 in pure metakaolinite. However, due to the presence of quartz impurities in the Troy clay, the composition of SiO_2 is somewhat higher. X-ray diffraction patterns of the calcines show that the calcines are nearly devoid of crystalline components, they are dominated by an "amorphous hump"

Table 13. Weight lost of the calcines and conductivity of the PCT for the calcines with different calcination temperatures.

Cal. Temp	375°C	450°C	525°C	600°C	675°C
Weight lost	13.3%	15.0%	15.8%	16.7%	17.5%
1 day leach (mS/cm)	9.80	6.40	4.20	3.90	3.60
7 days leach (mS/cm)	10.30	6.70	5.10	4.80	3.80

suggesting that they contain a mixture of poorly crystalline short range ordered aluminosilicates. Small amounts of muscovite and quartz which exist in original clay and small amount of hydroxyl sodalite were also detected. Over the range of calcination temperatures used, crystalline nepheline or nosean did not form. This is in contrast with Jantzen's reported findings for a similar waste stream that was steam reformed[11]. The leachabilities and weight losses of the calcines during firing are given in Table 13. PCT tests for 1 and 7 days were also completed using an unwashed sample. The weight loss increased with calcination temperature, suggesting that increasing amounts of volatile fractions (Na_2O) were lost as well as more nearly complete NO_3^- and NO_2^- reduction occurred at the higher temperatures, 525°C seems optimum (Table 14).

It is evident that the leachability of the calcines is dependent on the calcination temperature. The major elements in AN-107 are sodium and aluminum. The concentration of aluminum shows little dependence on the calcination temperature, while the concentration of sodium decreases with the increase of calcination temperature and almost levels off when the calcination temperature is higher than 525 °C. Potassium and cesium exhibit the same trend as sodium, but, since the concentration of cesium in the leachate is close to the detection limit of the ICP instrument, the temperature dependence of cesium is not as clear. The alkaline earth ions exhibit the opposite temperature dependence. Although the alkaline earth compounds are also effectively solidified upon calcination, the concentrations of alkaline earth ions in the leachate increase with increasing calcination temperature. A significant increase in their concentration occurs when the calcination temperature is greater than 525°C. Iron and titanium have the same dependence on calcination temperature as the alkaline earth elements, while the concentration of

Table 14. The elemental composition (mg/l) of the PCT filtrate for the five synthesized Calcines (1 and 7 days).

Composition	375 °C		450°C		525°C		600°C		675°C	
	1 d[a]	7 d[b]	1 d	7 d	1 d	7 d	1 d	7 d	1 d	7 d
Al	460.0	510.0	450.0	470.0	410.0	450.0	410.0	490.0	360.0	400.0
Ca	<0.05	<0.05	<0.05	<0.05	0.1	<0.05	0.3	0.3	0.8	0.5
Cr	8.6	8.6	6.9	6.9	5.0	5.7	4.1	4.4	2.4	2.9
Cs	<0.2	1.5	<0.2	<0.2	0.4	<0.2	2.7	<0.2	<0.2	<0.2
Fe	0.1	0.2	0.5	0.7	1.6	0.9	2.7	2.1	4.2	2.7
K	6.3	8.1	1.7	1.7	0.6	1.7	0.6	1.7	<0.2	<0.2
La	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.3	0.2	0.7	0.4
Na	2560.0	2650.0	1500.0	1660.0	970.0	1200.0	860.0	1100.0	730.0	850.0
Ni	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
P	2.9	1.2	3.5	1.7	4.6	3.5	5.2	5.8	4.6	4.6
Si	27.0	26.0	34.0	26.0	37.0	28.0	34.8	41.0	58.0	27.0
Ti	0.1	0.1	0.1	0.3	0.3	0.3	0.3	0.6	0.6	0.6
F	8.1	10.5	7.5	8.6	10.0	15.8	4.2	15.3	2.8	11.7
Cl	64.0	62.0	48.0	54.0	33.0	45.0	13.2	28.0	0.9	4.7
NO_2	24.2	38.0	6.9	19.7	3.8	6.9	4.1	6.1	0.7	2.8
NO_3	2270.0	2190.0	750.0	940.0	255.0	460.0	46.0	130.0	3.9	14.9
PO_4	1.3	<0.2	3.3	0.3	4.5	2.3	7.2	4.1	4.9	6.1
SO_4	330.0	330.0	270.0	295.0	215.0	225.0	215.0	225.0	140.0	160.0

a. 1 d means that PCT experiment was 1 day long.
b. 7 d means that PCT experiment was 7 days long.

chromium in the leachate decreases with the increasing temperature. The concentration of nickel and lanthanum are below the detection limit. Not surprising since they were not deliberately added. The leachability of Si shows little dependence on calcination temperature. For the anions, the concentrations of all the species decrease except phosphate and fluoride, because they either decompose or are reduced or vaporize at higher temperatures. Phosphate and fluoride are the less volatile species. The rate of nitrate and nitrite reduction becomes slower when calcination is carried out much above 525°C. Based on the observation that PCT based leachates experience minimum values when calcination is carried out at ~525°C[12], it is proposed that 525°C be used to prepare calcines from Type III SBW.

Monolith hydroceramics were prepared from the five calcines in order to determine the benefit of making a monolithic hydroceramic from them. The hydroceramic is acting like a binder in this instance and as such may be useful for solidifying IEENL's existing calcines. The solids were made by mixing 12g calcine and 8 g calcined clay with 18 ml 4 M NaOH to form a paste. The pastes were molded in 2 inch by 1 inch diameter cylinder molds and then precured at 40°C in a 50% humidity chamber overnight. After demolding, the samples were cured at 90°C in a steam saturated atmosphere (Teflon-lined Parr bombs) for 24 hours. See Figure 5. Density, compressive strength and preliminary leach data (conductivity) for the cured solids are given in Table 15.

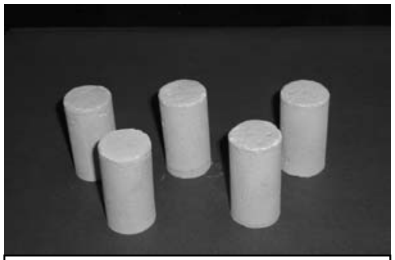

Figure 5. Hydroceramic monoliths produced from the calcines.

The phases in the monoliths were identified by X-ray diffraction. Patterns are given in Figure 6. The main crystalline phases are zeolite A, hydroxysodalite and quartz. Zeolite A, having the general formula of $[Na_{12}[Al_{12}Si_{12}O_{48}]\bullet 27H_2O]$, consists of sodalite cages connected at the four-ring position to create double four ring connections. This causes zeolite A to have two different cages sizes. The first is a smaller sodalite cage accessible through the 6-ring opening that has a diameter of 0.22 nm. The internal cage diameter is 0.66 nm. The second cage is a larger supercage accessible through a 8-ring opening with a diameter of 0.41 nm. The supercage internal diameter is 1.14 nm. The ion in the zeolite is normally Na, but the large cage can accommodate larger cations, such as Cs^+ and NH_4^+. Studies show that zeolite A has cation selectivity for Cs while hydroxysodalite does not[13]. Cs and Sr are HLW fractions of low activity sodium bearing waste and as such should be removed prior to making Saltstone. A hydroceramic binder is better suited for solidifying low activity SBW directly because the Cs and Sr will become part of the zeolite structure. Therefore, using a binder

Table 15. The density, compressive strength and PCT leachability of monolithic HC samples made with listed calcines, additional metakaolinite and 4M NaOH solution and cured at 90°C.

Calcination Temperature	375 °C	450 °C	525 °C	600 °C	675 °C
Density (g/cm^3)	1.09	1.08	1.12	1.07	1.08
Compressive (MPa)	3.58	3.52	3.54	3.04	4.07
1 day leach (mS/cm)	4.20	4.10	3.60	4.40	4.90
7 days leach (mS/cm)	4.30	4.20	3.70	4.70	5.40

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[12] Bao, Y. and M.W. Grutzeck, Solidification of Sodium Bearing Waste using Hydroceramic and Portland Cement Binders, Presented orally Annual Meeting American Ceramic Soc (2004) .In press as part of Proceedings.

[13] Bao, Y., Personal Communication (2004).

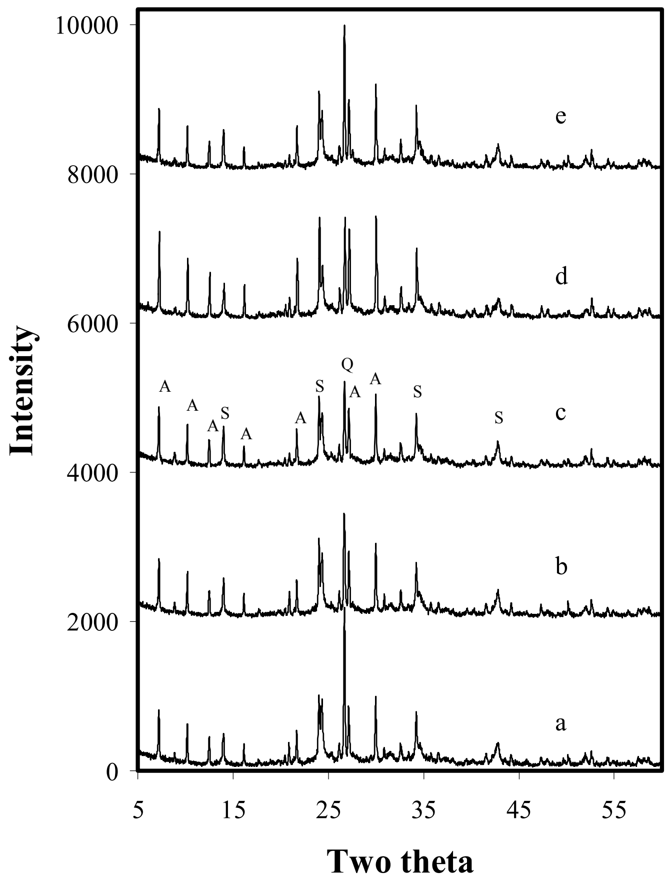

Figure 6. X-ray diffraction patterns of hydroceramics prepared from the Calcines in Table 14 mixed with additional metakaolinite and 4M NaOH and cured at 90°C. Symbols represent the calcination temperature of the calcine in the hydroceramic.: a. 375 °C, b. 450°C, c. 525 °C, d. 600°C, e. 675 °C

that maximizes the formation of zeolite A would serve two purposes. It would encapsulate the calcines and also tie up stray ions emanating from the calcines should they be exposed to water during long term storage. When considering the synthesis conditions that favor zeolite A formation, it seems that, the method of precuring the samples at 40°C in a 50% humidity chamber before demolding and final curing at 90°C introduces low temperature precursor phases that eventually crystallize as zeolite A. Low intensity zeolite A peaks have been found in XRD patterns for the sample after precuring. Though the intensity of the zeolite A peak is low, the precursor zeolite phases can act as the seeds for the further crystallization. This may be one of the reasons that zeolite A forms during the final hydrothermal treatment in our experiments.

The morphology of the resulting hydroceramics was examined by SEM. The images in Figure 7 clearly indicate the existence of ill-defined cubic and spherical phases in the hydroceramic made from the 375°C calcine (view a) versus very crystalline appearing morphologies in the other samples (views b-e). When calcination temperatures reach or exceed 425°C, well crystallized zeolite A and hydroxysodalite crystals form. Higher calcination temperatures cause larger precursor crystals to form that grow during monolith production. Zeolite A forms cubic crystals, and hydroxysodalite takes on a smaller "balls of yarn" appearance. The existence of a range of crystallite sizes may be an advantage, because smaller crystals can occupy the open spaces present in hydroceramics, reducing the rate of transport of ions (radionuclides or other cations and anions) in or out of the structure. Zeolite A also appears to inter-grow with itself and hydroxysodalite (views b-e). The interlocking crystalline structure will also impart high strength to the monolith, which is important if and when the hydroceramic is shipped off site.

The optimum firing temperature for the calcines used to make the monoliths in Figure 5 was further evaluated by leaching the hydroceramic monoliths using a 1 and 7 day PCT test. In the past it has been observed that 525°C calcines are reactive and have acceptably low leachabilites. The conductivities of the leachates for the monoliths are given in Table 16. Conductivities for the hydroceramic monoliths are much lower than those for the equivalent calcines illustrating the fact that a hydroceramic is a better waste form than the calcines.

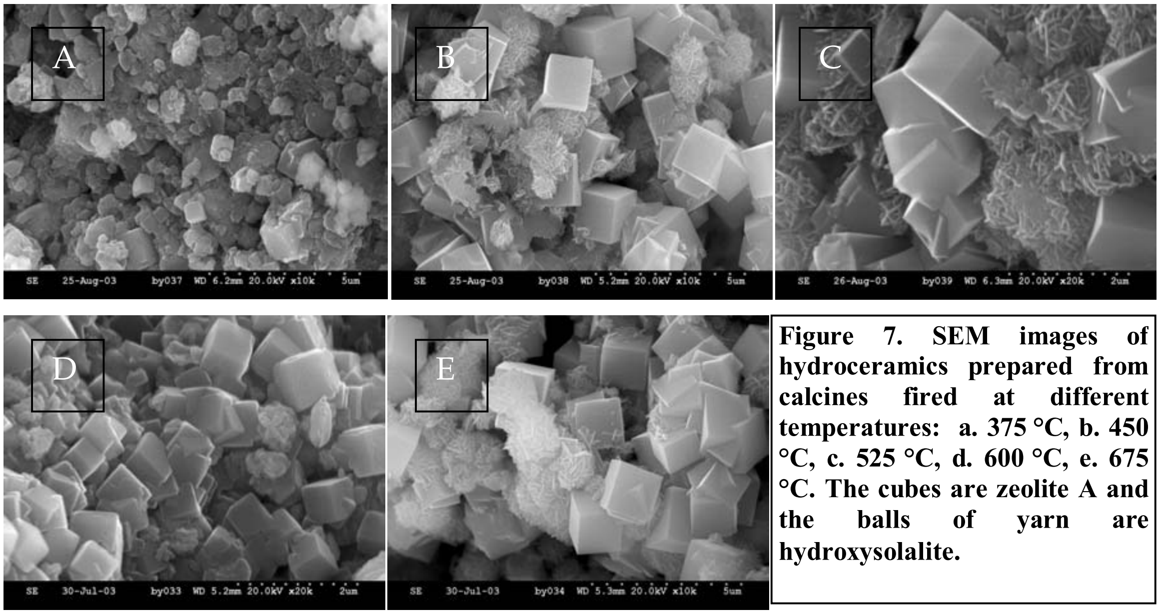

Figure 7. SEM images of hydroceramics prepared from calcines fired at different temperatures: a. 375 °C, b. 450 °C, c. 525 °C, d. 600 °C, e. 675 °C. The cubes are zeolite A and the balls of yarn are hydroxysolalite.

However, unlike the calcines that continue to perform better (lower Na leachability) as the calcination temperature rises, the conductivity of the leachates for the calcines solidified with NaOH metakaolinite and 4M NaOH only worsen with higher calcination temperatures. The data also suggest that a minimum occurs when the SBW is calcined at 525°C. This is consistent with SEM observations that the 525°C hydroceramic has the largest amount of intergrowth and the least amount of porosity.

The elemental analyses of the PCT leachates for these same samples are given in Table 16. The concentration of the main components in the leachate (Na^+, Al^{3+}, NO_3^- and SO_4^{2-}) are much lower for the monoliths than they are for the calcines they contain indicating that a hydroceramic binder will either further encapsulate or chemically bind ions to a greater degree than the raw calcines. The concentration of other minor components (Cl, NO_2^-, Cr, etc.) is also further reduced by the formation of hydroceramics. The concentration of sodium is at a minimum in the 525°C calcine containing hydroceramic, which is in keeping with the aforementioned lowest value experienced by this same sample. Other species e.g. K, P, Si, and SO_4^{2-} also appear to have the lowest concentration in the leachate for the 525°C. However, the concentration of F^-, PO_4^{3-}, Fe, and Si in the leachate from this hydroceramic is higher than those of the other calcines. At this time, the reason for the behavior of these particular ions is unknown.

There are several possible ways that the various nuclides can be immobilized in a hydroceramic waste form: surface adsorption, trapped in structural voids, occupying a lattice site, and cation exchange. There are several possible routes for the leaching of the nuclides: desorption, dissolution, diffusion, and cation exchange. Hydroceramics have a zeolitic structure. They are relatively insoluble, much more than Portland cement. Zeolites are also good adsorbents. When making a hydroceramic by direct mixing with Type I and II low activity SBW, the zeolites that form will preferentially encapsulate larger ions or ions with a higher charge than sodium. Nuclides can be incorporated in the zeolite cages. Once so encapsulated ion mobility could be hindered by the sizes of the openings in the zeolite structures that form. Cation exchange is also a well-known phenomena for zeolites. Literature results show that zeolites have selective cation exchange properties for Cs and Sr which are present in small amounts in SBW. A potential use for this property would be the use of a Type I or II directly solidified SBW as a tank fill material. In this case secondary sources of these ions such as in empty tanks could be attracted and held by the zeolite in the hydroceramic. Many zeolites are also very stable, which is important for the long-term storage and isolation of these long lived radionuclides. Metamict damage of hydroceramics is also expected to be minor. The alteration of radionuclides to daughter products may not have as great an effect in a zeolite because there is latitude in space in the cages and channels which can accommodate changes in size without dramatic effects as in glass or crystalline waste forms. Furthermore, the thermal study of the stability of zeolite A shows that it can be fired at temperature around 1000°C to produce a ceramic if necessary.

A hydroceramic produced either by direct solidification of Type I and II SBW with metakaolinite or as a hydroceramic binder for existing calcines is a promising way to solidify all SBW. The leachability of zeolitic hydroceramics is significantly lower than that of the calcines. XRD, SEM, and leachability experiments demonstrated that the optimized calcination temperature for the preparation of calcines and zeolitic hydroceramics is 525°C. Under these conditions, the calcine and hydroceramic have lowest leachability. The formation of zeolitic phases and their intergrowth are important for the overall performance of the hydroceramic waste form.

Table 16. Elemental analyses of the PCT solution for hydroceramics made with the listed calcines (mg/L)

Composition	375 °C		450°C		525°C		600°C		675°C	
	1 d[a]	7 d[b]	1 d	7 d	1 d	7 d	1 d	7 d	1 d	7 d
Al	100.0	175.0	37.0	48.0	110.0	125.0	29.0	31.0	20.0	22.0
Ca	0.2	<0.05	0.2	0.2	0.3	<0.05	<0.05	<0.05	<0.05	<0.05
Cr	0.2	0.3	0.4	0.5	0.3	0.4	0.2	0.6	0.2	1.0
Cs	<0.2	0.3	0.4	<0.2	0.5	0.5	<0.2	<0.2	<0.2	<0.2
Fe	3.6	0.5	4.3	1.4	5.2	0.7	1.3	0.6	1.3	0.3
K	6.3	6.9	6.3	7.5	5.8	5.2	9.2	8.6	9.2	10.4
La	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mg	0.6	<0.05	0.6	0.2	0.8	<0.05	0.2	<0.05	0.3	<0.05
Na	1090.0	1070.0	1020.0	1040.0	780.0	800.0	1120.0	1180.0	1220.0	1350.0
Ni	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
P	6.9	5.2	8.1	7.5	5.8	4.6	8.6	5.8	6.9	6.9
Si	56.0	47.0	90.0	69.0	80.0	58.0	100.0	69.0	130.0	105.0
Ti	1.0	0.3	1.1	0.6	1.2	0.3	0.6	0.4	0.8	0.3
--	--	--	--	--	--	--	--	--	--	--
F	41.0	40.0	53.0	59.0	66.0	49.0	48.0	59.0	47.0	45.0
Cl	34.0	33.0	25.1	25.0	17.6	19.1	13.5	15.2	8.0	9.7
NO2	17.3	20.7	8.6	6.9	2.8	2.1	3.1	2.4	3.8	3.8
NO3	370.0	470.0	175.0	195.0	85.0	95.0	40.0	90.0	20.6	30.0
PO4	11.7	7.8	14.8	13.0	7.0	7.1	14.2	10.2	12.9	12.0
SO4	13.7	15.1	8.8	11.5	4.6	5.9	6.2	8.3	7.4	9.9

a. 1 d means that PCT experiment was performed in 1 day
b. 7 d means that PCT experiment was performed in 7 days

Binder Experiments

In this set of experiments an optimized Hanford calcine was solidified using both a hydroceramic binder and a conventional Portland cement grout. The calcine was prepared from the Table 12 simulant by mixing it with sucrose and metakaolinite at the weight ratio 20:2.5:11.9 which produced a slurry with the consistency of mud. After drying at 90°C for 24 hours, the dried material was calcined at 525°C for 18 hours. The calcine was granular and the X-ray diffraction pattern suggested that it was mainly X-ray amorphous with an amorphous hump centered at a location suggesting that it contains network structured phases. A chemical analysis of this type of calcine suggests that its nitrate and nitrite content are quite low (< 1 wt%) but carbonate still weighs in at ~8 wt%[14]. As an aside, it is of interest to mention at this point that the calcine in question contains almost the identical raw materials used by Westinghouse in its SBW reforming trials run at 725°C in a Studsvik steam reformer[11]. Other differences related to temperature are improved crystallinity and lower leachability but in principle the end product is the same as the calcined SBW we have been studying for 6 years. It now seems that the DOE has recognized the merits of making hydroceramic waste forms from SBW and is pushing forward with experiments (current DOE grant to Penn State) and on site demonstrations of steam reforming both off and on site.

Should either technology be adopted, the end product will eventually have to be solidified and transported to a repository of some sort-be it Yucca Mountain or some other site. In order to make the waste “road ready” it will have to be solidified. Here we report the results of an experiment in which the Hanford calcine described above was solidified using metakaolinite and a variety of solutions ranging from water to 10M NaOH solutions.

Table 17 gives the mechanical and phase properties of a set of hydroceramics made from the Hanford calcine. Different amounts of various molar NaOH solutions were used to make the pastes that were then cured at 90° and 190°C. It is notable that strength development is adequate for all of the NaOH containing samples and phases that developed include zeolite A and hydroxysodalite. Table 18 provides 1 and 7 day PCT leach performance data on the stability of these same samples. The sample made with 4M NaOH had the lowest Na loss as percentage Na in the sample.

Table 17. Crystalline phases present and compressive strengths of hydroceramics made from Hanford calcine, metakaolin and various solutions that were cured at 90° and 190°C for 24 hrs.

5g Solids Mixed with 4.5 mL of Solution below	Total Mol Si/Na	TotalMol Al/Na	90°C Cured			190°C Cured		
			Crystalline Phases Present	Green Strength (MPa)	Cured Strength (MPa)	Crystalline Phases Present	Green Strength (MPa)	Cured Strength (MPa)
H_2O	2.689	2.103	Mk	0.21	0.21	Mk	0.21	0.21
2M NaOH	1.689	1.321	A	0.27	2.37	A	0.72	4.20
4M NaOH	1.231	0.963	A	2.13	3.55	A	2.32	4.00
6M NaOH	0.969	0.758	A+HS	5.27	6.34	A+HS	4.80	4.56
8M NaOH	0.799	0.624	HS	2.54	6.13	HS	5.45	4.48
10MNaOH	0.679	0.531	HS	1.45	3.96	HS	4.56	4.20

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[14] 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,” Ed. by Spearing, Smith and Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001).

Tables 19 and 20 contain data for the same Hanford calcine but this time it was solidified with a Portland cement binder. Strengths are similar but phase formation and leachability are dramatically different. The percentage Na leached is at best roughly 10 times as high as the hydroceramic.

Table 18. Leachability of Table 17 Hydroceramics made with metakaolin binder.

Total mol of Na in PCT samples	90°C Cured				190°C Cured			
	Leach-ability (mS/cm)	Na Leached (mol•10^4)	% Na Leached	pH of Leachate	Leach-ability (mS/cm)	Na Leached (mol•10^4)	% Na Leached	pH of Leachate
0.00304	3.40	1.70	5.5	10.6	3.60	1.80	6.0	10.8
0.00484	4.80	2.40	5.0	10.2	3.20	1.60	3.5	10.4
0.00664	4.80	2.40	3.5	10.7	2.00	1.00	1.5	10.7
0.00844	7.00	3.50	4.0	10.6	4.90	2.45	3.0	10.8
0.01024	11.40	5.70	5.5	10.7	15.30	7.65	7.5	12.6
0.01204	>100	--	--	13.0	>100	--	--	13.0

-- = not determined

Table 19. Crystalline phases present and compressive strength of waste forms made from Hanford calcine, Portland cement and various solutions that were cured at 90° and 190°C for 24 hrs.

5g Solids Mixed with 4.5 mL of Solution below	Mol Si/Na	Mol Al/Na	90°C cured			190°C cured		
			Crystalline Phases Present	Green Strength (MPa)	Cured Strength (MPa)	Crystalline phases present	Green Strength (MPa)	Cured Strength (MPa)
H_2O	1.877	1.291	C_3S*	0.29	0.03	C_3S	0.34	--
2M NaOH	1.180	0.812	A+C_3S	3.82	4.09	HS+ C_3S	3.94	2.58
4M NaOH	0.861	0.592	HS+C_3S	3.05	3.52	HS+C_3S	2.98	1.61
6M NaOH	0.677	0.466	HS+ C_3S	1.61	1.00	HS+ C_3S	2.43	1.38
8M NaOH	0.558	0.384	HS+C_3S	2.14	1.25	HS+C_3S	2.05	1.00
10MNaOH	0.475	0.327	HS+C_3S	1.47	0.89	--	--	--

***C_3S is an abbreviation for the anhydrous calcium silicate phase that comprises ~60 wt% of Portland cement (Ca_3SiO_5), A=zeolite A, HS=hydroxysodalite.**

We believe that the poor performance of the Portland cement binder in solidifying a sodium aluminosilicate (zeolitic) calcine was due to the reaction of the $Ca(OH)_2$ produced during Portland cement hydration with the zeolite, a known pozzolanic reaction. The zeolitic phases in the calcine acted like pozzolans and reacted with the $Ca(OH)_2$ in the Portland cement binder forming additional calcium silicate hydrate (C-S-H). Typically C-S-H is unable to host large amounts of sodium ions in its structure, thus a majority of the sodium present in the zeolites became concentrated in the pore solution present in the Portland cement binder and readily entered the leachant during PCT testing. In this instance metakaolin mixed with NaOH proved to be a superior binder for solidification purposes.

The "sodalite" rule of thumb has been touted as a guide to formulating a hydroceramic waste form[13],[15] (Siemer et al., 2000, 2001ab). The minimum in conductivity exhibited by the hydroceramic sample made with 4M NaOH mixing solution (Tables 19 and 20) had an overall 1:1:0.8 Na:Al:Si molar ratio and thus came closest to sodalite's 1:1:1 molar ratio. The minimum in the data seemingly confirms the validity of this rule.

Table 20. Leachability of Table 11 waste forms made with Portland cement binder.

Total mol of Na in PCT samples	90°C cured				190°C cured			
	Leach-ability (mS/cm)	Na Leached (mol•10^4)	% Na leached	pH of Leachate	Leach-ability (mS/cm)	Na Leached (mol•10^4)	% Na Leached	pH of Leachate
0.00305	8.40	4.20	14.0	12.3	6.6	3.30	11.0	12.2
0.00485	15.50	7.75	16.0	12.8	11.0	5.50	11.5	12.8
0.00665	>100	--	--	12.9	>100	--	--	12.8
0.00845	>100	--	--	13.2	>100	--	--	13.1
0.01025	>100	--	--	13.2	>100	--	--	13.2
0.01205	>100	--	--	13.2	>100	--	--	--

-- = not determined

Finally, Portland cement is commonly used to solidify low level wastes of all kinds. Savannah River uses OPC blended with blast furnace slag and fly ash to solidify its Cs- and Sr-free nitrate/nitrite bearing SBW to produce a product they call Saltstone. British Nuclear Fuel Limited (BNFL) has used OPC based grouts to solidify Great Britain's "historic" reprocessing waste. Because OPC is widely used for solidification, conceivably OPC might be considered at some future time as a binder for pretreated and calcined/reformed Hanford SBW. Given this possibility, the current study was undertaken in order to determine how a sample of OPC solidified Hanford calcine would perform relative to an equivalent hydroceramic sample. The results show that OPC can be used, but its leachability could be many times higher than a similarly solidified metakaolin/NaOH sample.

Conclusions

Based on performance, hydroceramics made using metakaolin additions to SBW prior to calcination and later as a binder phase are worth considering should the DOE need a contingency waste form to replace vitrification of low activity SBW in storage at DOE's Hanford, Savannah River and INEEL sites. All of the values for % Na lost by the samples fell below the 11.9 % value for E Glass making all of them at least in principle adequate waste forms. Based on selectivity of zeolite A for Cs and Sr, it seems possible that the hydroceramic waste form can be

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[15] 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," Ed. by Spearing, Smith and Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001a), and
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," Ed. by Spearing, Smith and Putnam, Ceram. Trans. Amer. Ceramic Society 119, Westerville, OH. (2001b).

prepared from SBW without removing Cs and Sr. If this proves to be true, significant cost savings could be realized vis à vis glass melting.

Publications during the Second Three Years

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).

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,” Ed. by Spearing, Smith and Sundaram, Ceram. Trans. Amer. Ceramic Society 132, Westerville, OH. (2001b).

Siemer, D.D., B.E. Scheetz and M.W. Grutzeck, “Cementitious Solidification of Steam Reformed DOE Salt Waste,” DOE’s Alaska DOE Meeting 2003. To be published in the Proceedings of the meeting.

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 American Ceramic Society in Indianapolis IN 2004 (in press).

Bao, Y. and M.W. Grutzeck, “The Effect of Calcination Temperature on the Leachability of Hydroceramic Waste Forms,” the paper is written and forms a good part of the above Progress section. It will be submitted shortly.

Grutzeck, Bao, Y., M.W. Grutzeck, Kwan, S., Scheetz, B.E. and D.D. Siemer, "Vapor Hydration Testing of EA Glass and Hydroceramic Waste Forms," In preparation.

Proposed work for the next three years

Based on the work completed above and the work that is still ongoing, it is proposed to carryout the following additional work during the next three years. Three areas of interest to both Hanford and Savannah River are described below. It is anticipated that the work in progress as well as the proposed work will be completed at the end of three years and thus this will be the last funding requested. It is expected that all joint work will also be completed and joint reports will also be written during this final period of funding.

Optimized Type II and III hydroceramic waste forms

Optimized Type II and III hydroceramic waste forms will be produced, characterized, leached (PCT, ANS/ANSI 16.1, MCC-I) and documented. It is proposed to run parallel tests at Savannah River using actual Tank 44 SBW and AN-107. A joint report with SRS will be issued that will serve as a manual for making hydroceramics. The report will also include a discussion of the underlying causes for the observed behavior of the hydroceramic waste forms as a function of time and temperature. Microstructure and phase development will be linked to dissolution data. If it is possible to obtain simulated calcines from actual production runs using a Studsvik reformer or from INEEL these will be incorporated into the program at Penn State

Cold calcination with Al + Si

Cold calcination of Type III SBW (AN-107) with Al + Si will be fully explored. Nitrate/nitrite and ionic content will be tracked as a function of NaOH concentration. Precipitates will be analyzed for Cs and Sr. Cr and Tc (Re as simulant) valences will be tracked as well. It is proposed to carry out these experiments in parallel with Savannah River using actual AN-107 waste in storage at Savannah River. It has been found that a combination of equal molar amounts of micrometer sized Al and Si powders added to an 8M NaOH solution containing molar quantities of NO_3^- and NO_2^- will act as reducing agents and convert both nitrate and nitrite to ammonia gas. The beauty of the finding is that the half cell reactions as described below (Table 21) occur slowly over a matter of days providing a controlled reaction that minimizes potentially dangerous off gassing of the ammonia. All off gases can be collected in a bubbler containing HCl. The metals enter the solution phase where they then form insoluble sodium aluminosilicate hydrate precipitates. The residue is normally X-ray amorphous but upon heating in a Parr bomb at 90°-180°C, the precipitate crystallizes to cancrinite. The denitrated/denitrated SBW (hopefully we can go from Type III to Type II or lower), now little more than NaOH solution can be concentrates/diluted and mixed with metakaolinite and molded and cured at 90°C to form a robust and highly stable waste form that contains tectosilicate phases similar to those found in Yucca mountain. An issue under study will be the fate of Cr^{6+} and Tc (Re simulant) ions in the SBW as well as Cs and Sr. If we are correct, Cs and Sr will also be tied up in the zeolites that form and the Cr^{6+} and Tc ions might be reduced to lower valence states and form insoluble precipitates that will be encapsulated or accommodated on lattice sites as a replacement for Na in the zeolites that form.

Table 21. Half cell reactions for nitrate and nitrite ions reacting with Al and Si powders in a concentrated NaOH solution.

$NO^{3-} + 8e^-$------NH_3OH^-	-0.12 V
$NO^{2-} + 6e^-$------NH_3	-0.44 V
2Al--------------$2Al^{3+} + 6e^-$	+2.31 V
2Si--------------$2Si^{4+} + 8e^-$	+1.69 V
$NO_3^- + Al^0 +$ --------$NH_4OH^- + Al^{3+}$	+2.19 V (spontaneous)
$NO_3^- + Si^0 +$ --------$NH_4OH^- + Si^{4+}$	+1.57 V (spontaneous)
$NO_2^- + Al^0 +$ --------$NH_4OH^- + Al^{3+}$	+1.86 V (spontaneous)
$NO_2^- + Si^0 +$ --------$NH_4OH^- + Si^{4+}$	+1.25 V (spontaneous)

The 1:1 molar ratio is important for two reasons: first Si by itself does not work, but in the presence of Al it does, second a 1:1 ratio causes an insoluble zeolite to precipitate. It settles to the bottom of the reaction flask and should it contain all the Cs in the waste (which it might because Cs tends to be selectively incorporated), the process could be used to separate Cs as well as other ions from the remaining, now nitrate and nitrite reduced NaOH. The liquid can then be used to make a hydroceramic by mixing it with metakaolinite and low temperature curing it for a few weeks or months. Or, alternately, the cancrinite could be retained and commingled with the developing zeolites in the hydroceramic. It is proposed to study the fate of TcO_4^- (Re^{7+} as a stand-in) and CrO_4^{2-} because they too like nitrate and nitrite could be reduced to lower valence state ions that are less mobile and more easily retained by the zeolite matrix.

Hydroceramic fill materials

Hydroceramic fill materials will be formulated using Type I and II SBW. These are proposed as an alternate to Portland cement used to fill and close empty waste tanks. The leach performance of hydroceramics is expected to be superior to Portland cement both in terms of incorporating sodium and other ions of concern as well as provide secondary protection for stray radionuclides remaining in the tanks. In order to make tank fill materials the hydroceramic grouts must be pourable. Some of the samples reported on above were pourable, so this is not an insurmountable factor. Heat of hydration and strength and leachability could be somewhat compromised by the scale up but work to date suggests this may not be a factor either. Nevertheless these properties will be measured again for hydroceramic grouts made with Types I and II SBW. It is an attractive idea to be able to fill tanks with a monolith zeolite fill material that has all the properties of a loose zeolite in its ability to tie-up stray radionuclides as well as encapsulate and hold existing SBW ions in its lattice sites. Overall leachability would be much lower than Saltstone in as much as the tank fill material is a waste form rather than Portland cement. Finally, because the tanks are used to house the hydroceramic grouts, limited or no additional storage facilities would have to be constructed—essentially nothing like Saltstone disposal sites would be needed.

Future Directions

As we move forward with a possible third three year renewal, this final portion of the work will be the most exciting and also the most fruitful. Testing and documentation of optimized hydroceramic monolith production for all three types of SBW will be carried out and joint reports will be written. Calcination and steam reforming are expensive to implement and replete with yet unknown pitfalls and as such are not necessarily viable alternates to vitrification in glass plants. Since Types I and II SBW can be solidified directly, this is a cost effective alternate. In order to make Type III waste solidification equally attractive one must consider a different scenario—something like cold calcination which does not require calcination or steam reforming. A SBW can be treated in tank by slowly dispersing enough Al and Si powder into the tank to reduce its NO_3 and NO_2 concentration to some low level (~<25 wt% of the sodium salt content of the SBW) such that the SBW can then be used to make a hydroceramic waste form without any calcination or steam reforming. In the laboratory, the reduction process is slow and controlled. There is no eruptive gas production. The off gas is ammonia perhaps mixed with some N_2. Work is underway to optimize the process. A joint report will be issued at the end of the funding period. Finally, it seems as if hydroceramics could be used as tank fill material. They have more than adequate strength and are far superior to Portland cement in encapsulating and isolating radioactive waste ions. Stray radionuclides in the tank should be adsorbed via cation exchange.

Knowing that simulated waste is not an adequate predictor, a major portion of the proposed work on actual Tank 44 and An-107 low activity SBW will be carried out by Dr. Carol Jantzen at Savannah River who currently is running parallel testing using Tank 44 waste. She will take our best simulation recipes and best calcination schemes and recreate the same waste forms that we are using at Penn State. In the next funding period she will be making hydroceramic samples from Tank 44 waste by direct solidification, and she will be studying the cold calcination of AN-107 SBW followed by direct solidification. She will leach the samples and begin to explore how best to control these species in actual SBW and whether-or-not cold calcination is a viable technique. The value of running parallel studies of this type is self-evident. Given these data, it is expected that it will be possible to piece together a coherent picture of how the crystal and phase evolution of an actual di-phasic zeolite-containing waste form made from low activity SBW governs its performance and its durability once placed into service. Joint reports as well as individual investigator reports will be generated by the end of the project.

At this point in time it has been demonstrated that hydroceramic waste forms and/or a hydroceramic binder could be less costly and also a safer alternatives to vitrification of SBW present in tanks at Savannah River and Hanford. DOE has been presented with a rare opportunity to optimize a new technology that may well outperform current options at a lower cost both in terms of monetary investment and safety because processing can potentially be carried out at 90° C. By endorsing the technology, DOE has the chance to pretreat existing waste streams to make them more amenable to the zeolitization process. Unlike INEEL we have the opportunity to add calcination aids to the waste stream prior to calcination. We have choices of oxidizing/reducing environments and the addition of calcination aids such as clays and reducing agents prior to calcination. Furthermore, we have the choice of separation or no separation of Cs and Sr. Hydroceramics can be used to solidify SBW defined as HLW. It seems to us that it would be less expensive and certainly safer to workers if performance based definitions were adopted and state and federal regulations were changed to accommodate the new regulations. Hydroceramics will ultimately be good enough to allow one to use them as tank fill which is on site burial but used a much less leachable product than Saltstone.

Hydroceramics could play an important role in our nation's waste management scheme. The estimated 100 million gallons of SBW defined as HLW could be solidified as hydroceramic at lower cost using a mixing and curing process that is inherently safer than vitrification. Processing would be carried out at 90°C rather than 1100°C. By casting the hydroceramic in the same stainless steel canister as SRL's glass, without melting, costs could be reduced significantly. Rather than $1,000,000 per canister, it is conceivable that it could cost little more than the cost of the canister and the labor to fill it, but this is yet to be seen as the project evolves. These are rough estimates, but we are convinced that hydroceramic waste forms could turn the SBW issue around. Many of the current problems concerning separation of Cs and Sr, volatile content, Tc and TRU, and volume increases due to vitrification might simply go away if hydroceramics are proven to work as well as we think they can.