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

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## Research Objective

Zeolites can adsorb liquids and gasses, take part in catalytic reactions and serve as cation exchange media. They are commercially available as finely divided powders. Using zeolites to manage radioactive waste is not new, but a process by which zeolites can be made to act both as a host phase and a cementing agent is. It is notable that zeolites occur in nature as well consolidated/cemented deposits. The Romans used blocks of Neapolitan zeolitized tuff as a building material and some of these buildings are still standing. Zeolites are easy to synthesize from a wide range of both natural and man-made precursor materials. The method of making a “hydroceramic” is derived from a process in which metakaolinite (thermally dehydroxylated kaolinite) is slurried with a dilute sodium hydroxide (NaOH) solution and then reacted for hours to days at mildly elevated temperatures (60°-200°C). The zeolites that form in solution are finely divided powders containing micrometer sized crystals.<sup>1</sup> However, if the process is changed and only enough concentrated sodium hydroxide solution (e.g. 12 M) is added to the metakaolinite to give the mixture a putty-like consistency and the mixture is then cured under similar conditions, the mixture becomes a very hard ceramic-like material containing distinct tectosilicate crystallites (zeolites and feldspathoids) imbedded in an X-ray amorphous sodium aluminosilicate hydrate matrix<sup>2,3,4</sup>. Due to the material’s vitreous character, the composite has been called a hydroceramic. Similar to zeolite/feldspathoid powders, a hydroceramic is able to sequester cations and a wide range of salt molecules (e.g., nitrate, nitrite and sulfate) in lattice positions and within structural channels and voids thus rendering them “insoluble” and making them an ideal contingency waste form for solidifying radioactive waste. The obvious similarities between a hydroceramic waste form and a waste form based on solidified Portland-cement grout are 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) have shown that hydroceramics also do a better job of immobilizing the RCRA-toxic and radioactive components of liquid sodium bearing waste (SBW) now in storage at DOE’s Hanford, Savannah River and Idaho sites<sup>5,6,7,8</sup>.

Making a hydroceramic from a liquid SBW is straight forward and less expensive than producing a vitrified waste form from the same waste. Metakaolinite and small amounts of optional powdered vermiculite (improves cesium retention) and sodium sulfide (which acts as a

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<sup>1</sup>Breck, D.W., *Zeolite Molecular Sieves*, 380 pp., Wiley-Interscience (1974).

<sup>2</sup>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)

<sup>3</sup>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,” *Cement Concrete Res.* **29**, 997-1004 (1999)

<sup>4</sup>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. CD published by WM Symposia, Inc., Tucson (1988).*

<sup>5</sup>Krishnamurthy, N., *Zeolitic Hydroceramics for Sodium Bearing Nuclear Wastes*, a M.S. thesis in Environmental Engineering, The Pennsylvania State University, December 2001 (2001)

<sup>6</sup>Siemer, D.D., J. Olanrewaju, B.E. Scheetz, N. Krishnamurthy and M.W. Grutzeck, “Development of Hydroceramic Waste Forms,” in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI*, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., *Ceramic Transactions* **119**, 383-390 (2001)

<sup>7</sup>Bao, Y., S. Kwan, D. D. Siemer and M. W. Grutzeck, *Binders for Granular Hydroceramic Waste Forms*, Submitted to *J. of Materials Science* (March, 2003)

<sup>8</sup>Siemer, D.D., J. Olanrewaju, B.E. Scheetz and M.W. Grutzeck, “Development of Hydroceramic Waste Forms of INEEL Calcined Waste,” in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI*, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., *Ceramic Transactions* **119**, 391-398 (2001)

redox buffer and RCRA metal precipitant) are dry blended with a calcined SBW powder (made from liquid SBW, sucrose and metakaolinite and heated at 525°C) and just enough 4M NaOH solution to produce a thick paste that has a putty-like consistency. The paste is placed in a metal container (canister) and then “soaked” for a few hours at 20°-60°C to allow dissolution and zeolite precursor formation prior to final curing at 80°-90°C in a well-insulated building or at higher temperatures ( $\geq 100^{\circ}$ -200°C) in an autoclave or in sealed canisters designed to withstand pressure while they are heated in a conventional oven<sup>9</sup>. The research objectives of Grant Number DE-FG07-98ER45726 are to work out the details of how the hydroceramic process can be applied to both the caustic-type SBWs stored at the Hanford, Savannah River and Idaho National Engineering & Environmental Laboratory (INEEL) sites and the already calcined acidic SBW in storage at 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/phase chemistry, and developing microstructure on performance.

### Research Progress

During the nearly five years that EMSP Grant DE-FG07-98ER45726 has been in effect, it has been possible to demonstrate that hydroceramic waste forms can be made from simulated SBW similar to that in storage at the Savannah River and Hanford sites. The raw SBW must be mixed with enough metakaolinite (to achieve a minimum 1:1:1 Na:Al:Si molar ratio) and sucrose, dried and then calcined at 525°C overnight. If the calcine is then mixed with additional metakaolinite and 4M NaOH in the same 1:1:1 proportions and the putty like paste is cured at elevated temperatures, the hydroceramic that forms exhibits properties that often exceeded those associated with vitrified waste forms such as EA glass<sup>5,10</sup>. Hydroceramics can be considered a viable contingency waste form. Work in progress has focused upon the steps needed to optimize the performance of hydroceramics as a function of the sodium content of the SBW. Waste pretreatment studies deal with the optimization of SBW calcine compositions on a waste stream-specific basis and the development of a set of rules that are easily applied to any SBW. Calcination studies deal with the optimization of the denitrification process and the applicability of the steam reforming process<sup>11</sup> as a replacement for pretreatment and calcination. Finally, scale-up factors are being studied to insure the technology’s viability in real world applications.

### Summary of Work Completed During Years 1 to 4

During the first four years of the EMSP grant, work has focused on a number of issues relating to implementation of the hydroceramic process. Scoping tests performed with a wide range of potential starting materials ultimately resulted in the selection of a more or less unified approach to producing hydroceramic-type waste forms<sup>12</sup>. SBW simulants representing both the strongly basic supernate salt wastes stored at Savannah River (Tank 44) and Hanford sites

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<sup>9</sup>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.

<sup>10</sup>Krishnamurthy, N., M.W. Grutzeck and S. Kwan, “Hydroceramics for Savannah River Laboratory’s Sodium Bearing Waste,” in Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., Ceramic Transactions 119, 337 (2001)

<sup>11</sup>Jantzen, C., “Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process (U)”, WSRC-TR2002-00317, rev 0 (also listed as SRT-RPP-2002-00163, Rev 0), July 12, 2002.

<sup>12</sup>Siemer, D.D., M.W. Grutzeck, B.E. Scheetz, “Comparison of Materials for Making Hydroceramic Waste Forms,” in Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries V, G.T. Chandler and X. Feng, Eds., Ceramic Transactions 107, 161-167 (2002)

(“average” composition) and INEEL’s already calcined acidic SBW were made from reagent grade chemicals and water. The components of the two basic simulants were sodium hydroxide, sodium nitrate, sodium nitrite, with lesser amounts of sodium aluminate and sodium carbonate. The components of the INEEL simulant were sodium nitrate, aluminum nitrate, and nitric acid.

One of the fundamental lessons learned was that the gross composition of both the calcined SBW and hydroceramics made from it should approximate that of sodalite (or cancrinite); i.e., the final calcine and hydroceramic should contain approximately one atom of aluminum for each atom of sodium, at least one atom of silicon for every aluminum atom (i.e. 1:1:1), and not more than twenty-five percent of the total sodium should be present in forms other than oxide, hydroxide, aluminate, or silicate. Since the ratio of “heteroanions” (anions other than oxide, hydroxide, aluminate, or silicate) to sodium in real DOE wastes is typically greater than 25%, most SBWs need to be denitrated before they can be solidified. INEEL utilized two fluidized bed calciners to convert most of their reprocessing waste into a mixture of small granules and powder (calcine). The wastes were sprayed into a ~500°C fluidized bed that served to drive off the volatiles (mostly water and free acid) and decompose thermally labile nitrate salts. Because the temperature was too low to thermally decompose alkali metal (Na & K) nitrate salts, INEEL’s calcination process did not work well with its high-sodium wastes<sup>13</sup>. Consequently, INEEL’s SBW is still stored in large underground steel tanks.

It has been documented that the best way to pretreat virtually any DOE SBW for hydroceramic solidification is to slurry it with thermally treated clay (metakaolinite), add a water-soluble carbohydrate, and then calcine the mixture at a temperature in excess of 500°C. The added carbohydrate (usually sucrose aka table sugar) is a reducing agent that serves to decompose the alkali nitrate salts and converts the bulk of the nitrate to innocuous elemental nitrogen rather than NO<sub>x</sub>. The clay reacts with the nascent sodium oxide to form an amorphous alkali aluminosilicate powder ideally suited for making a hydroceramic. If no clay “calcination aid” is added, “sugar calcination” produces a soluble salt (sodium carbonate), which is no better than sodium nitrate as a starting material for making hydroceramic (or any other sort of) waste form. If a higher-than-usual (e.g 700°C vs ~500°C) calcination<sup>14</sup> (or “reformation”) temperature is employed, the resulting clay/sugar/SBW calcine will exhibit a good deal of leach resistance in its own right. However, because current transport regulations require that Class B or higher radwaste forms be in a monolithic (non dispersible) form, it is currently necessary to consolidate such powders into concrete waste forms.

The kinetics of the hydroceramic curing process is revealing. Figures 1 and 2<sup>15</sup> indicate that long-term curing below 100°C will ultimately achieve leach characteristics similar to that of specimens cured for much shorter times at much higher temperatures<sup>6</sup>. The effect of longer curing times and/or elevated temperature is to increase strength and reduce leachability in water. It is also concluded that impure metakaolinite containing traces of quartz out-performed physical mixtures of colloidal silica and colloidal alumina powders both as a “calcination aid” and as the

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<sup>13</sup>At such temperatures, alkali metal nitrates simply melt to form viscous “glues” that agglomerate the fluidized bed.

<sup>14</sup>This process is called “reformation” when most of the heat input is via the introduction of superheated steam. Jantzen recently described a fluidized bed steam reforming process (FBSR) used to make calcine from Hanford low activity SBW, kaolinite, sucrose and/or charcoal, and a proprietary additive (WSRC-TR-2002-00317). These were sprayed into a fluidized bed calciner having a bed consisting of alumina and/or iron oxide media. The FBSR calcine is essentially the same as our first calcined SBW made with metakaolinite and sucrose.

<sup>15</sup>Siemer, D.D., “Development of Hydroceramic Waste Forms”, Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI, D.R. Spearing, G.L. Smith, R.L. Putnam, Eds., Ceramic Transactions 119, 383-390 (2001)

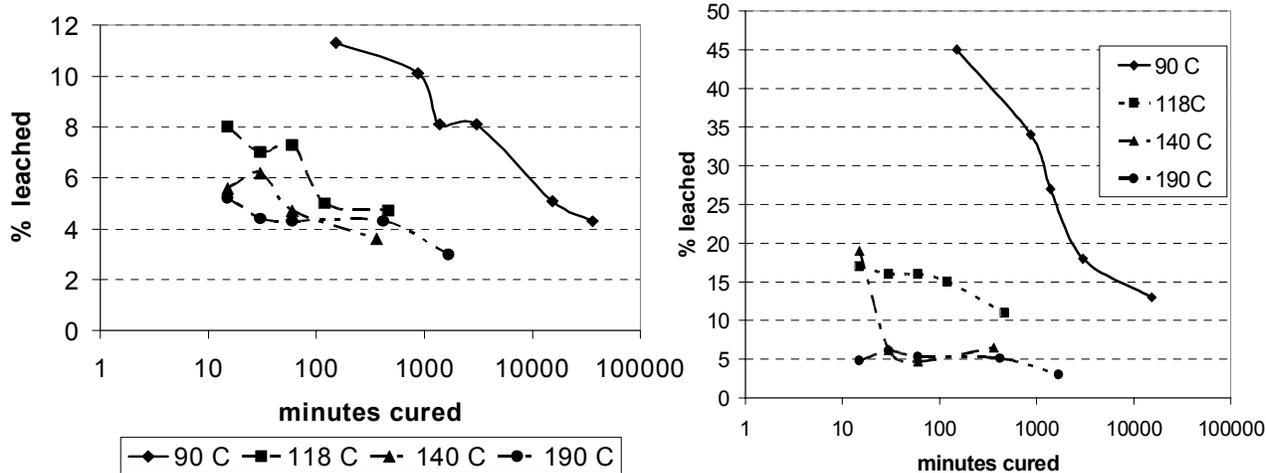


Figure 1. Na leaching vs time and temperature Figure 2. NO<sub>3</sub> leaching vs time and temperature

main ingredient of the subsequent hydroceramic “monolith formation” step. Further, it was observed that hydroceramics made from extremely pure, highly refined metakaolinites (e.g., Engelhard’s MetaMax) exhibited very low water solubilities (their PCT leachabilities were the lowest obtained to date), but the hydroceramics had poor physical characteristics (low strength & low bulk densities). Such metakaolinites also tend to react so quickly that “flash setting” would make it very difficult to implement a large-scale process with them. Relatively “impure” pozzolanic-type clay such as that mined near Hellmar-Bovill ID (Troy clay) was a better starting material mainly due to the small amount of mica and quartz the Troy clay contains. Hydroceramic “grout” formulations made with the Troy clay metakaolinite were easy to mix and cure forming a product having good leach resistance, high bulk density, and reasonable physical strength. It is notable that once MetaMax was mixed with Min-U-Sil or quartz flour, it then became possible to make a suitable monolithic hydroceramic without compromising leach behavior to any great extent<sup>10</sup>.

A ton of Troy clay was purchased from Columbus Clay in Columbus OH<sup>16</sup> and processed into metakaolinite in a 3’ x 30’ rotary kiln by FTE Minerals in Bethlehem, PA (a subsidiary of Fuller Company). The as received raw clay had been ground and sieved to –50 mesh and was packaged in 50 pound bags. A materials residence time of 2 hours and a maximum load temperature ranging from 750°-800°C was used to process the clay. During the calcination process, periodic LOI measurements were taken to ensure the proper material was being made. The resultant product was milled in a micronizing mill to a size characterized as “95% passing 325 mesh”. Samples are available upon request.

A comparison of solidifying agents was undertaken to show whether-or-not Portland cement rather than extra metakaolinite could be used as a binder phase to solidify a simulated metakaolinite-containing Hanford calcine described by Naveen Krishnamurthy in his thesis<sup>5</sup>. Naveen’s Hanford stimulant was prepared by mixing the reagent grade chemicals listed in Table 1 with enough water to make one liter. The solution was then combined with sucrose and metakaolinite at the weight ratio of 20:2.5:11.9. The mud-like mixture was then allowed to dry at 90°C for 24 hours before calcining it at 525°C for 18 hours. The sucrose acted as a reducing agent allowing the nitrate and nitrate to decompose at lower than normal temperatures. The sodium reacted with the reactive metakaolinite rather than the CO<sub>2</sub>, to form an aluminosilicate-based calcine having a tectosilicate structure. Naveen’s calcine was then

<sup>16</sup>This is a dried and powdered version of the Helmar Bovill clay sold to artisans for making conventional ceramics.

Table 1. Ingredients used to make One Liter of “Naveen’s” Hanford Simulant<sup>5</sup> (grams).

Compound	Simulant
NaOH	82.6819
Al(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	133.5
NaNO <sub>2</sub>	36.9106
Na <sub>2</sub> CO <sub>3</sub>	36.2049
NaNO <sub>3</sub>	8.5815
Na <sub>2</sub> HPO <sub>4</sub>	27.7873
KCl	1.8328
NaCl	2.5077
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> •10H <sub>2</sub> O	0.1096
Na <sub>2</sub> SO <sub>4</sub>	3.8945
Ni(NO <sub>3</sub> ) <sub>2</sub> •6H <sub>2</sub> O	0.3115
Ca(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	0.4420
Mg(NO <sub>3</sub> ) <sub>2</sub> •6H <sub>2</sub> O	0.0337

solidified using additional metakaolinite or Type I Portland cement. The hydroceramic and Portland cement solidified samples were made in the usual way using 3 g of Naveen’s Hanford calcine, either 2 g of Troy metakaolinite (MK) or 2 g of Type I Portland cement plus 4.5mL water/caustic mix water (various strength NaOH solutions) to make a thick paste. The total amount of Na in the sample includes the Na in the calcine as well as the added NaOH used during mixing. The amount of alkalis in the Portland cement (~2 wt%) was neglected. Both series of samples were molded in 10 x 10 x 60mm SS molds and then precured at room temperature until hard enough to demold. The samples were then cured at either 90° or 190°C overnight in a steam-saturated atmosphere (Parr bomb). They were then dried at 50°C overnight, ground and sieved using piggy-backed screens [100 mesh (top) and 200 mesh (bottom)]. The resulting 75-149 μm sample was leach tested under PCT conditions (1 gram powder to 10 cc DI

water in a sealed Teflon-lined Parr bomb at 90°C) for 24 hours (rather than 7 days) after which the solution was filtered and its electrical conductivity determined. The conductivity of such solutions is a reasonably accurate indicator of how much salt has leached from the specimen. Since sodium salts are the predominate soluble species, conductivity is directly proportional to sodium leachability (1 mS/cm conductivity corresponds to ~0.005 molar NaOH as given in standard tables for NaOH).

The samples made with Troy metakaolinite and 2-10M NaOH solutions cured at 90° and 190°C tended to have compressive strengths exceeding 300 psi. Samples made with water alone had little strength. All of the NaOH samples contained either zeolite A (low NaOH) or hydroxysodalite (high NaOH) or a mixture of the two (intermediate NaOH). Leachability of the 4M NaOH mixed samples were the lowest, leaching 3.5 and 1.5 % Na at 90° and 190°C respectively. In comparison, those samples made with Type I Portland cement (OPC) and 0-10M NaOH mixing solutions all had “green” high strengths that decreased rather than increased with increasing NaOH concentration and final curing at elevated temperatures. Once again phases consisted of zeolite A and hydroxysodalite, but it was also observed that unhydrated OPC phases remained in the samples. The percentage sodium leached exceeded 10 % for the water sample and increased rapidly as NaOH was added via the mixing solution. The data indicate that Portland cement solidification is inferior to hydroceramic solidification for clay-calcined material such as the Hanford stimulant. The hydroceramic specimens – even those containing a much higher proportion of sodium than the “sodalite” formulation rule-of-thumb recommends - are not only much less water soluble (leachable) than the OPC grouts but also much stronger. The reason for this is that clay-calcined (or possibly “reformed”) SBWs, like most zeolitic materials, are pozzolanic, i.e. they readily react with the “free” lime in Portland cement (OPC is nominally ~65 wt % CaO) to form more calcium silicate hydrate (C-S-H), the matrix phase responsible for most of Portland cement/concrete’s physical and mechanical properties. What happens in this particular case is that the OPC destroys the bond formed between the sodium and the clay during calcination and thus renders virtually 100% of the sodium in the specimen water leachable. Because C-S-H is unable to host sodium in its lattice; pore water in conventional

Portland cement concrete is ~1M NaOH. If SBW calcines are solidified with Portland cement, the concentration of sodium in the pore solution will go even higher.

The conductivity data obtained for hydroceramics suggest that the optimum amount of free hydroxide in the mix water is on the order of 4M NaOH. The leach data for samples mixed with 2-10M NaOH go through a minimum at 4M. The NaOH in the 4M solution provides the 1:1:1 Na:Al:Si ratio needed to form zeolites from the added metakaolinite. The primary XRD-discernable (crystalline) phase in the 4M samples was zeolite A. At higher NaOH concentrations, hydroxysodalite (HS) formed instead. Leach rates were higher due to the fact that there was a stoichiometric excess of free NaOH present (possibly some NaOH was intercalated by the hydroxysodalite) that was easily leached. Like wise, when an insufficient amount of Na was present, the reactivity of the zeolite forming process was reduced, i.e. not all of the free caustic was incorporated by the zeolites and some remained as easily leachable sodium species.

#### Highlights of Findings for Years 1 to 4

- Hydroceramic waste forms made with representative SBW simulants, metakaolinite, and sodium hydroxide out-performed conventional grouts on standard radwaste leach tests.
- Hydroceramics outperform DOE's HLW benchmark waste form material (EA glass) on the PCT test (this test determines fractional release of sodium during 7-day exposure to 90°C water). This means that a compelling case could be made for sending hydroceramic-solidified reprocessing waste to Yucca Mountain.
- Sugar calcination of SBW without an aluminosilicate "calcination aid" is of questionable value producing only soluble sodium carbonate.
- At least 75% of the sodium in the raw formulation should be present as some combination of oxide, hydroxide, aluminate, or silicate.
- Increasing the curing temperature and pressure invariably improves the leach performance of the final product. However, because the leach resistance of hydroceramics cured at widely different temperatures tend to converge at long curing times, autoclave-type (high T/P) curing may not be necessary.
- Inexpensive pottery-grade metakaolinite proved to be the best starting material. The Troy clay is not kaolinite, *senso stricto* it is halloysite. The chemistry is the same but the latter contains interlayer water molecules. Halloysite platelets roll up and form hollow tubes rather than "books." Morphology and impurities seemingly influence reactions and performance.
- Adding finely divided silica to very pure metakaolinites during the solidification step made the hydroceramics stronger without sacrificing leach performance to any great extent. This makes the process flexible in that a variety of kaolinites can be used to make metakaolinite.
- Properly cured hydroceramics undergo virtually no change when subjected to the "new" vapor hydration test (VHT). Glasses, of course, are not at equilibrium with saturated steam and invariably decompose to form more stable "alteration products". Hydroceramics are more durable than borosilicate glasses because they are formulated/cured under conditions that causes them to be at near equilibrium under the hydrothermal conditions deemed to represent "worst case" repository scenarios.
- As a means of achieving "volume reduction", vitrification is superficially superior to any concrete-making process. However, in actual practice vitrification invariably increases the total amount of radwaste that has to be ultimately disposed of. For example, SRL's high-level melter, DWPF, produces about five gallons of low level waste for each gallon of high-level

slurry processed into glass<sup>17</sup>. Such “incidental” wastes are apt to be left on-site with only cursory treatment. A properly implemented, hydroceramic-based waste solidification process could consolidate virtually everything into a common type of monolithic waste form suitable for transport to more optimally situated geological repository site.

- It now appears that all DOE SBW is amenable to hydroceramic solidification. It also appears that the bulk of this type of waste could/should be pretreated via the implementation of clay-calcination (or steam/clay-reformation). The processing should be carried out under reducing conditions to minimize NO<sub>x</sub> and render species such as Tc, Cr, and Np less water soluble. The high affinity of hydroceramic-type concretes for cesium means that it should not be necessary to remove <sup>137</sup>Cs from SBW streams which are destined to remain on site.
- Portland cement can not be used to stabilize/solidify SBW calcines. Monoliths made with Portland cement have no crystal chemical sites for sodium to occupy. Thus all sodium concentrates in the pore solution and easily “washed out”.

### Work Completed during Year 5

Cylindrical hydroceramic samples (1 by 2 inch long) were made in order to determine the effect of scale up on the properties of hydroceramics. Samples were made from 12 g of Naveen’s Hanford calcine (made from Table 1 SBW and metakaolinite)<sup>5</sup>, 8 g Troy metakaolinite and 20.9 g (18 ml) 4M NaOH solution. Waste loading of Naveen’s Hanford calcine was ~16wt% versus ~26wt % for his SRL 15M Na Tank 44 calcine<sup>10</sup>. This was a result of the decision to hold the calcine recipe constant even though Naveen’s Hanford stimulant contained roughly half as much NaOH as the SRS stimulant (15 versus 8 moles Na). Thus the waste loading and final Na/Si ratio of Naveen’s cylindrical hydroceramic samples is ~9wt% and ≈0.6, respectively.

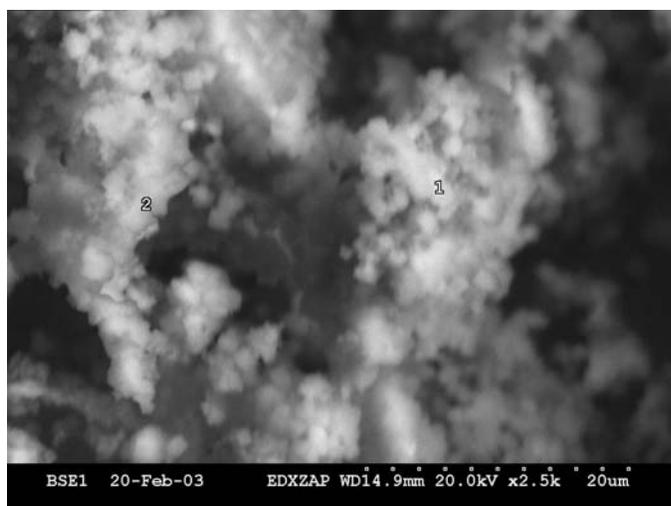
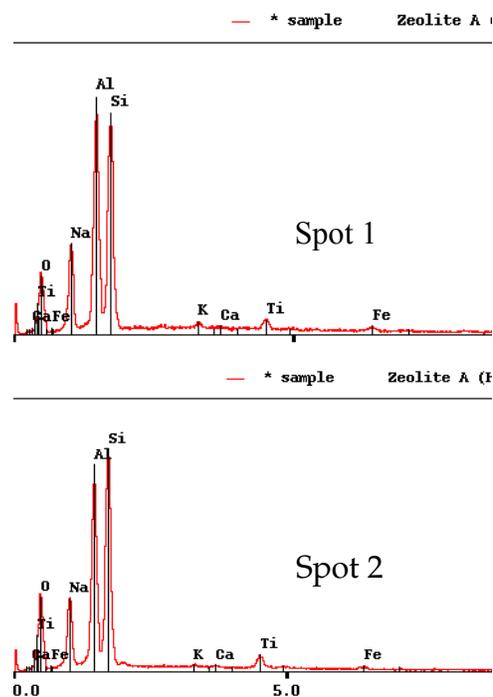


Figure 3. BSE of hydroceramic showing location of analysis points 1 and 2. The spectra reproduced on the right hand side → for each spot (1 and 2) show that both zeolite analyses are the same.



<sup>17</sup>DWPF’s “incidental wastes” are boiled down to reduce their volume. Unfortunately because those streams contain all of the required ingredients (Al, Si and free hydroxide) to make tectosilicates, the evaporators used for that purpose quickly become fouled with the same minerals that make up “hydroceramics” especially NaNO<sub>3</sub>-cancrinite).

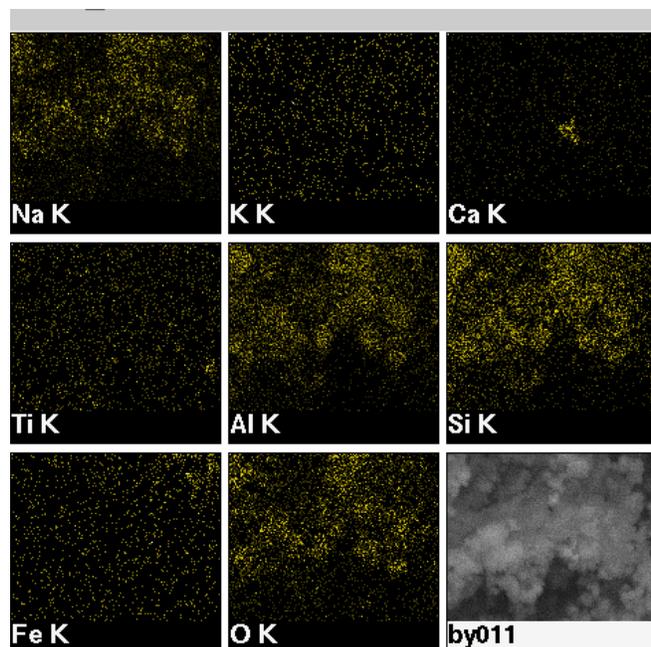


Figure 4. Elemental map of hydroceramic showing its homogeneity, save one Ca-rich area

Samples were prepared at 40°C and 100% humidity overnight, de-molded, and then autoclaved for 24 hrs as a function of temperature at 90, 130, 160 and 190°C. Energy-dispersive X-ray spectrometry (EDX) was used to investigate the homogeneity of the 90°C sample. Powder was dispersed on conductive carbon tape and analyzed without any coating. The results suggest that the chemistries of the subsamples are essentially the same from point to point (Fig. 3) and overall homogeneity is good (Figure 4).

The phases in the sample, density, compressive strength and a modified 1-day PCT leachability<sup>18</sup> of the hydroceramics were determined (Table 2). Figure 5 illustrates the microstructure of the zeolite A that formed in two samples that were autoclaved at 90° (left) and 190°C (right). The 190°C sample prepared at the higher temperature has a lower leachability and its zeolite A cubes are better defined and more highly intergrown.

Compressive strength increases and leachability decreases as the curing temperature is increased. The percent-leached data for the 1 x 2 inch samples (Table 2) are the same as that of the small samples (10 x 10 x 60mm) studied previously (3.5% at 90°C and 1.5% at 190°C).

Table 2. Properties of 1x2 inch Cylinders of Hydroceramic cured as a function of Temperature.

	90°C	130°C	160°C	190°C
Crystalline phase	Zeolite A	Zeolite A	Zeolite A	Zeolite A
Density (g/cm <sup>3</sup> )	0.988	0.990	0.988	1.084
Compressive strength (PSI)	338.7	363.3	512.5	576.0
PCT leach test (mS/cm)	4.80	2.70	2.60	1.80
% Na leached	3.62	2.04	1.96	1.36

An interesting development by Westinghouse (as opposed to Westinghouse Savannah River) has a bearing on current research. Westinghouse commissioned a test of the feasibility of applying Studsvik's fluidized bed-based "steam reformation" (FBSR) process to Hanford-type SBW<sup>11</sup>. Normally, Studsvik's FBSR is run at ~500°C and is used to destroy organic materials. In some cases it has been used to decompose SBW, but without using calcination aids the final product is Na<sub>2</sub>CO<sub>3</sub>. In the work reported by Jantzen<sup>11,14</sup>, Hazen Research Inc. in Golden CO used a 6" FBSR to prepare aluminosilicate containing calcine in a single step. SBW waste, coal and raw kaolin clay slurry was sprayed into an alumina and iron oxide media fluidized bed at 700°C.

<sup>18</sup> 1gram powder to 10 cc water in a hermetically sealed container held at 90°C for 24 hrs rather than 7 days.

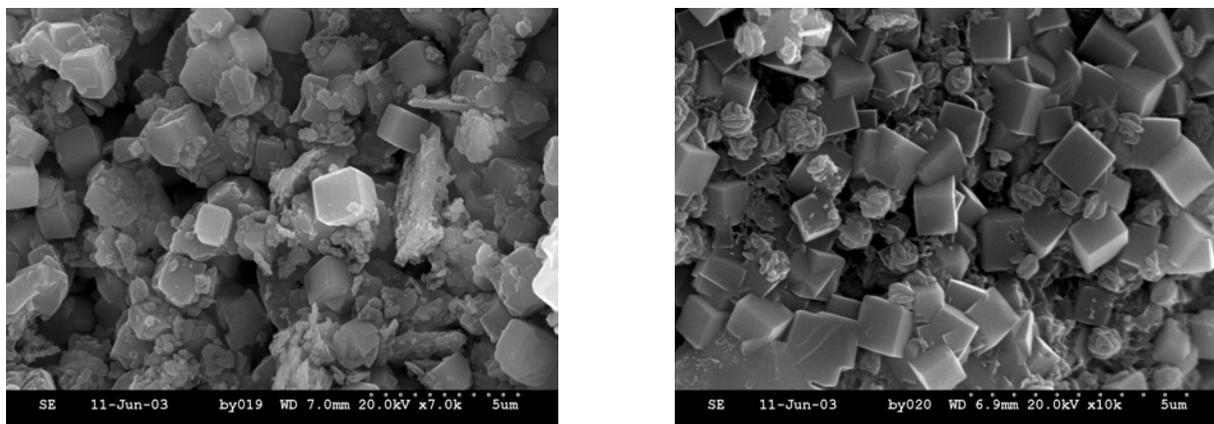


Figure 5. Microstructure of zeolite A formation and intergrowth in hydroceramic samples autoclaved at 90° (left) and 190°C (right). Crystallinity/intergrowth is better developed at 190°C.

Note that the FBSR product is quite similar to what PSU, SRL and INEEL personnel have been doing to pretreat SBW simulants for their hydroceramic work. The major difference is the fact that FBSR calcine is produced using kaolinite and a continuous rather than a batch process. FBSR's two key advantages relative to INEEL's traditional approach to calcination is that FBSR produces far less NO<sub>x</sub> and its product should be more suitable for a second solidification, that is if the large amount of residual elemental carbon in the FBSR calcine does not cause problems. Due to the similarity of the Hanford stimulant described earlier to the clay "reformed" Hanford-type LAW/SBW discussed by Jantzen,<sup>11,14</sup> a hydroceramic process would probably work better than Portland cement for solidifying this waste as well. Samples of "steam reformer" product are being sought from Westinghouse Corporate in order to validate this statement.

After the publication of Jantzen's report, a simulated waste based on the composition of Hanford Tank AN-107 LAW was prepared using the recipe given in the report. As such this calcine is far more complicated than what has been done previously. The ingredients listed below included major and minor elements as well as a number of organic compounds. The synthesis was undertaken in order to compare/contrast results obtained by Westinghouse for their FBSR waste form to those of a monolithic hydroceramic made using a two step process. See Table 3.

Table 3. Chemicals used to make Hanford Tank AN-107 LAW Simulant.

Composition	g/l	Composition	g/l	Composition	g/l
Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	121.1723	PbO	0.3172	Na <sub>2</sub> H <sub>2</sub> EDTA	31.7584
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	0.6532	NaCl	2.2999	CH <sub>3</sub> CO <sub>2</sub> Na·3H <sub>2</sub> O	16.2138
CsNO <sub>3</sub>	0.0157	NaF	5.5596	HCO <sub>2</sub> Na	12.2717
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	15.0138	Na <sub>2</sub> HPO <sub>4</sub>	4.0852	Oxalic Acid Dihydrate	5.817
KOH	2.0483	Na <sub>2</sub> SO <sub>4</sub>	11.7463	Calcium Gluconate	6.0089
La <sub>2</sub> O <sub>3</sub>	0.0307	NaNO <sub>2</sub>	69.0892	70 wt% Glycolic Acid	34.301
NaOH	102.766	NaNO <sub>3</sub>	157.5044	N(CH <sub>2</sub> CO <sub>2</sub> Na)·3H <sub>2</sub> O	10.0361
NiO	0.4636	Na <sub>2</sub> CO <sub>3</sub>	95.3607	Citric Acid	20.3042

One liter of simulant contains 1 M nitrite, 2.93 M nitrate and 8.20 moles of sodium. Its density is 1.364 g/cm<sup>3</sup>. Sucrose was added following the ratio of 38 gram sugar to total mole of nitrite and nitrate established earlier<sup>5,6,7</sup>. However, only 2/3 of the metakaolinite required to

obtain a Na:Si molar ratio of 1:1 was added to the liquid stimulant in order to increase Na waste loading to ~28wt%. After drying at 90°C for 24 hrs, the combined reagent grade chemicals were calcined at 525°C for 10 hrs. The calcine was ground to pass a 325 mesh sieve and then chemically analyzed (Table 4). For sake of comparison, a small aliquot of the Table 3 waste not containing metakaolinite was similarly calcined and analyzed. The chemical composition is also given in Table 4. There are significant differences, most related to whether-or-not Na<sub>2</sub>O forms a carbonate phase during the denitrification step

Table 4. Wet chemical analysis of Simulated Hanford AN-107 Waste

Wt%	Calcine-W/O Metakaolinite	Calcine-with Metakaolinite
Al <sub>2</sub> O <sub>3</sub>	3.830	26.000
B <sub>2</sub> O <sub>3</sub>	<0.005	<0.005
BaO	<0.005	0.040
CaO	0.220	0.930
CoO	<0.005	0.030
Cr <sub>2</sub> O <sub>3</sub>	0.070	0.060
CsO	0.005	<0.005
Fe <sub>2</sub> O <sub>3</sub>	0.780	1.380
K <sub>2</sub> O	0.420	0.920
La <sub>2</sub> O <sub>3</sub>	<0.005	<0.005
MgO	0.010	0.270
MnO	0.005	0.010
MoO <sub>3</sub>	0.005	0.020
Na <sub>2</sub> O	55.000	28.000
NiO	0.110	0.080
PbO	0.040	<0.050
SiO <sub>2</sub>	0.140	35.000
SrO	0.005	<0.005
TiO <sub>2</sub>	0.005	1.270
V <sub>2</sub> O <sub>5</sub>	0.005	0.030
ZnO	0.010	0.030
F	0.400	0.030
Cl	0.340	0.010
NO <sub>2</sub>	0.005	<0.005
NO <sub>3</sub>	0.005	0.040
PO <sub>4</sub>	0.540	0.290
SO <sub>4</sub>	1.280	0.440
CO <sub>2</sub>	36.000	5.310
Total	99.19	100.24

The AN-107 calcine was characterized using SEM (Figure 6a) and X-ray diffraction (Figures 6b and c). The major peaks present in the calcine made with metakaolinite (Figure 6b) are assignable to hydroxysodalite<sup>19</sup>. Most of the sodium in the sample made without metakaolinite has been converted to Na<sub>2</sub>CO<sub>3</sub> (Figure 6c). The chemical analysis suggests that all of the organics were burnt off during the denitrification process. Note that the nitrate and nitrite content of both samples are relatively small. Sodium carbonate is not a reactive phase and further blending of calcines containing sodium carbonate with metakaolinite does not form a very good hydroceramic. The addition of metakaolinite during the process produces an alkali aluminosilicate powder that can be considered the first barrier for retaining nuclear waste.

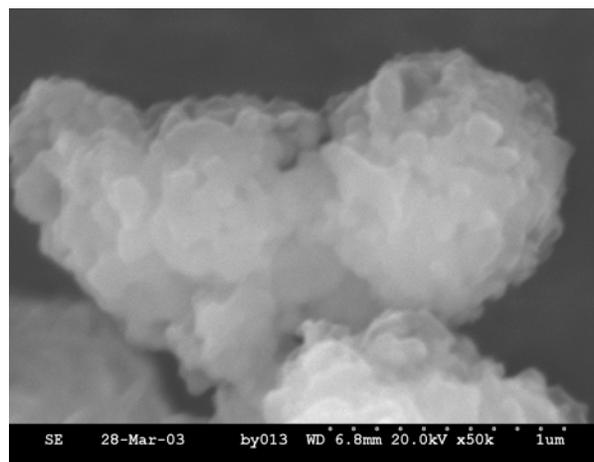


Figure 6a. SEM of Hanford AN-107 calcine. Particle size is submicrometer.

<sup>19</sup>Hydroxysodalite Na<sub>6</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>·8H<sub>2</sub>O has a 1:1:1 Na:Al:Si ratio. In this instance 2/3 the required metakaolinite was added to the SBW because it was assumed that the additional free Na<sub>2</sub>O would be used up during the second step when the additional 1/3 metakaolite was added. This apparently did not occur. What appears to have happened is that the extra 1/3 Na in the SBW became intercalated and formed something like: Na<sub>6</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>·3NaOH·2H<sub>2</sub>O<sup>1</sup>.

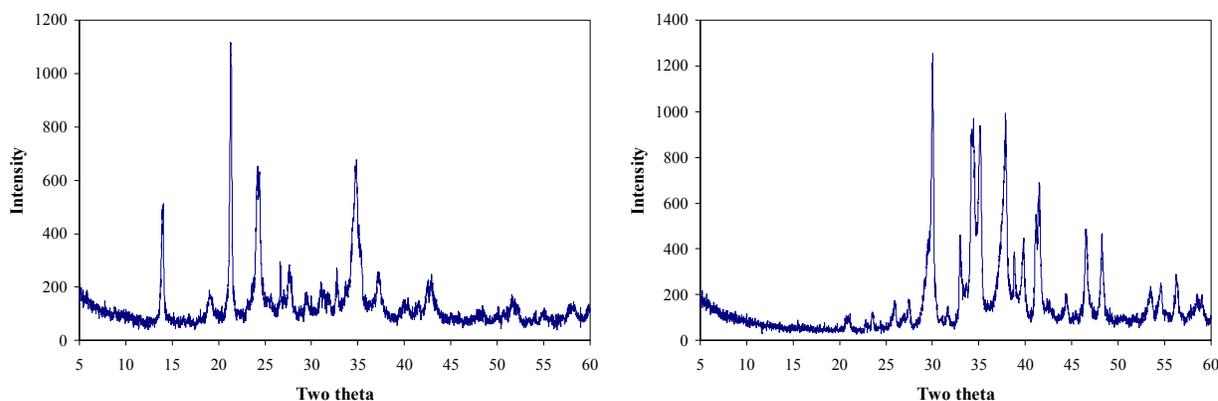


Figure 6b. Calcine made with metakaolinite. Zeolite present is hydroxysodalite.  
Figure 6c. Calcine made without metakaolinite. Phase present is sodium carbonate.

The leachability of the two Hanford AN-107 calcines was investigated using a modified PCT test<sup>18</sup>. The conductivity of the leachate of the metakaolinite calcine is 45 mS/cm. Assuming 1 mS/cm equals  $\sim 0.005$  molar NaOH, the total sodium leached is 23%, much higher than Naveen's hydroceramic. Note that the calcine made without metakaolinite consists mainly of sodium carbonate that is soluble. Equivalent leachability would approach 100% were this sample to be tested.

Hydroceramic samples were made using 3 g calcine, 2 g of Troy metakaolinite and 4.5 mL water or different concentrations of NaOH solutions to make a thick paste that was molded into 10 x10 x 60mm bars and then cured for 1 day at 90°C as described earlier. The crystalline phase formation, compressive strength and PCT data for the hydroceramic samples are given in Table 5. The data indicate that again, the monolithic hydroceramic prepared with 4M NaOH has the lowest leachability and the highest strength, but the % Na leached values for the AN-107 hydroceramic are approximately 3 times larger than the equivalent data for Naveen's hydroceramic discussed earlier<sup>7</sup>, probably due to the lesser amount of metakaolinite used to make the calcine. Phase chemistry is now dominated by hydroxysodalite, but strengths developed during curing are about the same. In addition the formation of a zeolitic matrix around the calcine provides a secondary barrier for the nuclear waste.

Table 5. Crystalline Phase Present, Compressive Strength and PCT of AN-107 Hydroceramics.

4.5 mL H <sub>2</sub> O/NaOH	H <sub>2</sub> O	2 M	4 M	6 M	8 M	10 M
Crystalline phase	HS	HS	HS	HS	HS	HS
Compressive strength (PSI), green	Weak	135.2	277.6	278.8	232.6	185.5
Compressive strength (psi) autoclaved	Weak	296.2	995.5	1157.6	998.1	157.0
Weight of monolith (10x10x60mm), g	5.33	5.73	6.12	6.19	6.27	6.35
Leachability (mS/cm)	15	17	18	34	49	77
pH	11.69	11.72	11.76	12.03	12.29	12.75
Moles Na in leachate	0.0008	0.0008	0.0009	0.0017	0.0024	0.0038
Total moles Na in solid	0.0055	0.0067	0.0079	0.0091	0.0104	0.0117
% Na leached	13.6	12.7	11.4	18.7	23.6	32.9

The effect of curing temperature on properties of larger cylindrical samples made with the AN-107 calcine was also investigated. Instead of 10x10x60mm bars, 1" OD by 2" long cylinders were prepared using 12 g AN-107 calcine, 8 g Troy metakaolinite and 20.9 g (18 ml) 4M NaOH solution. The samples were precured at 40°C and 100% humidity overnight, demolded, and then autoclaved for 24 hrs at 90°, 130°, 160° and 190°C. The crystalline phases, density, compressive stress and modified PCT data for the monolithic cylinders were determined (Table 6). Figure 7ab shows the microstructure of cylinders autoclaved at 90°C and 190°C, respectively. The results show that hydroceramics prepared at higher autoclave temperatures generally have lower leachabilities and higher strengths. The intersecting platy shape of the hydrosodalite agglomerates at 90°C become less well defined at 190°C. The agglomerates now appear almost "fused" together and much less porous overall. These changes could account for the improved properties of the samples cured at higher temperatures.

Table 6. The Effect of Curing Temperature on AN-107 Hydroceramics

	90°C	130°C	160°C	190°C
Crystalline phase	HS	HS	HS	HS+analcime
Density (g/cm <sup>3</sup> )	0.982	0.988	0.993	1.011
Compressive stress (PSI)	395.7	400.6	543.6	740.3
PCT leach test (mS/cm)	17.00	12.80	12.20	10.20
Moles Na leachate	0.0009	0.00064	0.00061	0.00051
Moles Na solid	0.007893	0.007893	.007893	0.007893
% leached	10.8	8.11	7.73	6.46

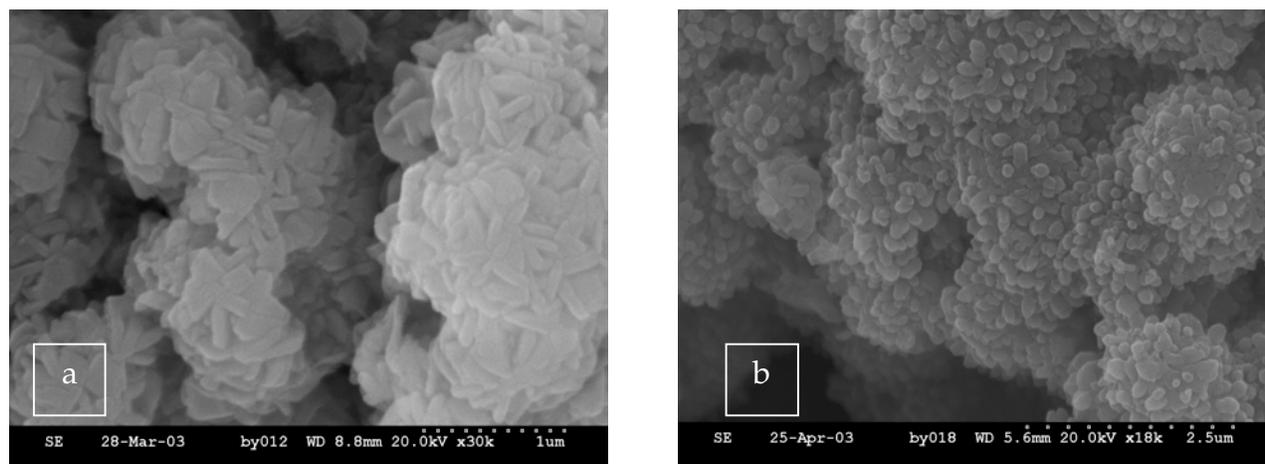


Figure 7ab. Micrographs of 90°C (a) and 190°C (b) AN-107 (4M NaOH) hydroceramics.

Although the data are not strictly comparable, it is somewhat informative to comment on the relative PCT performance of the AN-107 FBSR calcine, Naveen's Hanford hydroceramic and the AN-107 hydroceramic. First and foremost, the two-step hydroceramic described here produces a solid rather than a granular product. This may be important if the sample is to be shipped, unless DOE's rules change. Second, the leachability of both hydroceramic waste forms

vis à vis AN-107 FBSR calcine are within a reasonable range of each other. In as much as Jantzen did not give the recipe used to make the FBSR calcine, it is assumed that she followed a 1:1:1 rule of thumb. The values given by Jantzen are in  $\text{g/m}^2$  for a 7 day test. Her AN-107 Na PCT value is  $1.74 \text{ g/m}^2$  which is a good number. The PCT for Naveen's  $90^\circ\text{C}$  hydroceramic tested after 1 day<sup>20</sup> is  $\sim 1.81 \text{ g/m}^2$  and the PCT for the  $190^\circ\text{C}$  AN-107 hydroceramic also tested after 1 day is  $\sim 3.23 \text{ g/m}^2$ . The latter is higher than expected because only 2/3 of the stoichiometric amount of metakaolinite was used during calcination. When stoichiometric or excess amounts of metakaolinite are used to make a given SBW calcine, PCT performance values improve markedly. It now seems as if a hydroceramic waste form could be used as an alternate to vitrification. Although comparable PCT values are achievable using a fluidized bed stream reformer rather than calcination, it may be more cost effective for the DOE to use/modify existing evaporators/calciners and or build a new calciner at SRL and Hanford to calcine their SBW using long established and proven non-proprietary processes, equipment and ingredients. Calciners can run at  $525\text{-}575^\circ\text{C}$  (reducing off gas losses) rather than at  $725^\circ\text{C}$  under reducing conditions. The calcine can then be solidified using metakaolinite and NaOH at  $90^\circ\text{C}$ . Hydroceramics are attractive from both a safety and cost point of view.

#### Future Directions

Work continues on the optimization of the calcination and hydroceramic making processes. The rule of thumb that is evolving seems to suggest that both the calcining process and the second hydroceramic making process should, at a minimum, strive to achieve a 1:1:1 molar Na:Al:Si ratio for optimum results. It also seems prudent to reduce waste loading of the calcine by adding slightly more than the required stoichiometric amount of metakaolinite to the SBW prior to calcinations as illustrated by the PCT testing of the two calcines studied this year. The hydroceramic making step can remain the same, i.e. 1:1:1. The zeolites that form bind the existing zeolites together. There seems to be a limited amount of interaction between the calcine and the developing matrix. The existing zeolites act almost like a filler rather than a reactive filler. Seven day PCT tests will be carried out replete with chemical analyses in order to validate these rules. Scale up work will continue eventually making some  $\text{dm}^3$ -sized samples. These will be cured as a function of temperature ( $90^\circ$  to  $200^\circ\text{C}$ ), and then characterized as a function of "distance to center line"; i.e., test coupons will be removed from various points within the specimens. It is also planned to examine at the potential viability of a "two-grout" approach to dealing with INEEL's SBW. This scenario would simplify the calcination of that site's waste because it could be implemented with its existing calciner without having to first modify it to handle slurry-type feeds<sup>21</sup>. The idea is to sugar-calcine the waste without adding clay. This would produce a calcine consisting primarily of sodium carbonate. If that calcine were to be slurried with water and lime, virtually all of the carbonate plus the majority of the metals (RCRA, TRU, most cladding materials, plus most of the fission products – cesium would be the main exception) would immediately precipitate out as a mixture of carbonates, hydroxides,

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<sup>20</sup>It has been found that a 1 day PCT test for a hydroceramic sample will contain more than 90% of the available sodium in the hydroceramic making it nearly equivalent to a 7 day PCT test of a glass or in this case the FBSR calcine.

<sup>21</sup>The "straight" sugar-calcination of INEEL SBW was successfully demonstrated almost forty years ago: for example, see, J. C. Petrie, "Report on Run 12, Twelve-Inch Diameter Calciner", letter Petr-13-65A to E. J. Bailey, dated December 30, 1965. (a "production" run). Basically the same thing was demonstrated with a Hanford-type SBW seven years ago: see, "Fluid Bed Calciner Test Report-Final" VECTRA GSI Report # WHC-VIT-03, WHC-SD-WM-VI-031 Aug. 1995. The actual work was subcontracted to and performed by PROCEDYNE.

and/or hydroxycarbonates in a matrix dominated by calcium carbonate. This “low solubility” fraction could be readily separated & then solidified with the same Portland cement-based “grouting” process that Great Britain (BNFL) applied to its “historic” reprocessing waste. The readily soluble elements (Na, K, Cs, etc.) in the slurry would remain in solution accompanied by sufficient free hydroxide<sup>22</sup> to make that liquor an excellent “mix water” for the manufacture of hydroceramic waste forms – which (of course) would do a much better job of retaining both sodium and <sup>137</sup>Cs than would the OPC-based grout.

#### Publications during First Five Years

- Grutzeck, M.W., D.D. Siemer, “Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry”, *J. Amer. Ceram. Soc.* **80**, pp. 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 by WM Symposia, Inc., Tucson (1998).
- Krishnamurthy, N., M.W. Grutzeck and S. Kwan, “Hydroceramics for Savannah River Laboratory's Sodium Bearing Waste,” in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI*, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., p. 337, *Ceramic Trans.* **119**, Amer. Ceram. Soc., Westerville, OH (2001)
- Siemer, D.D., J. Olanrewaju, B.E. Scheetz, N. Krishnamurthy and M.W. Grutzeck, “Development of Hydroceramic Waste Forms,” in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI*, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., p. 383, *Ceramic Trans.* **119**, Amer. Ceram. Soc., Westerville, OH (2001).
- Siemer, D.D., J. Olanrewaju, B.E. Scheetz, and M.W. Grutzeck, “Development of Hydroceramic Waste Forms for INEEL Calcined Waste,” in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VI*, D.R. Spearing, G.L. Smith and R.L. Putnam, Eds., p. 391, *Ceramic Trans.* **119**, Amer. Ceram. Soc., Westerville, OH (2001).
- Krishnamurthy, N., Zeolitic Hydroceramics for Sodium Bearing Nuclear Wastes, a M.S. thesis in Environmental Engineering, The Pennsylvania State University, December (2001).
- Roy, D.M., J. Olanrewaju, M.W. Grutzeck, B.E. Scheetz and D.D. Siemer, "Hydroceramics as a New Cementitious Approach to Nuclear Waste Immobilization," Abstract of a Talk, ACI Session on Concrete for Radioactive Waste Management," co-sponsored by Committees 227 and 349, Thursday November 1, 2001, Dallas, TX.
- Scheetz, B.E., M.W. Grutzeck, J. Olanrewaju, D.M. Roy and D.D. Siemer, “Stability of Hydroceramic Waste Form during VHT Test,” abstract of a talk given at MRS in Boston, MA (2001).
- Bao, Y., S. Kwan, D.D. Siemer and M.W. Grutzeck, “Binders for Granular Hydroceramic Waste Forms,” Submitted to *J. of Materials Science* (March 2003).
- Krishnamurthy, N., S. Kwan, Y. Bao, M. W. Grutzeck and D. D. Siemer, “Effect of Sodium Concentration and Temperature on Phase Development and Leachability of Hydroceramic Waste Forms made with Simulated Hanford Sodium Bearing Waste,” To be submitted to *Cement and Concrete Research* (2003).
- Grutzeck, M.W., Kwan, S., Scheetz, B.E. and D.D. Siemer, "Vapor Hydration Testing of EA Glass and Hydroceramic Waste Forms," In preparation.

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<sup>22</sup> This is the same approach employed by Kraft paper mills to recycle caustic.

Krishnamurthy, N., S. Kwan, Y. Bao and M.W. Grutzeck, and D.D. Siemer, "Effect of Composition, Metakaolinite Source and Curing Temperature on Properties of Hydroceramic Waste Forms", to be submitted to the J. Amer. Ceram. Soc. (2003)

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