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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 ancient 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 metakaolinite (thermally dehydroxylated kaolin) 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 gel-like 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]

Manufacture of a hydroceramic waste form is straight forward. A mixture of metakaolinite with lesser amounts of powdered vermiculite (improves cesium retention) and sodium sulfide (which acts as a redox buffer and RCRA metal precipitant) is mixed with properly pretreated (calcined) SBW plus sufficient caustic (NaOH) solution to produce a modeling clay-like "paste". This is transferred to a metal container (canister) and then "soaked" for a few hours at 20°-90°C prior to implementation of the curing process. If a curing temperature below the local boiling point of water is to be used, a well-insulated building equipped with space heaters can serve as both the interim storage facility and "curing shed". If a faster cure is desired, curing must be done at higher temperatures. This means either the use of an autoclave ("pressure cooker") or canisters designed to act as pressure vessels while they are heated in a conventional oven[6]. A waste

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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.

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 first three years of our EMSP grant, we provided proof of concept of the proposition that hydroceramics would be a viable contingency waste form. Work in progress focuses upon optimization of waste pretreatment (calcination, steam reforming, etc.), waste stream-specific optimization of the formulations, and a study of scale-up factors to insure the technology's viability in real world applications. An outline of the experiments completed during the first three years of this grant is given below.

Work Completed During Years 1 to 3

During the first three years of our current EMSP grant, work 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. SBW simulants representing both the strongly basic supernate salt wastes stored at Savannah River (Tank 44) and Hanford sites (average composition) and INEEL's already calcined acidic SBW were made from reagent grade chemicals and water The main components of the two basic simulants were sodium hydroxide, sodium nitrate, sodium nitrite, with lesser amounts of sodium aluminate, and sodium carbonate. The primary components of the INEEL simulant were sodium nitrate, aluminum nitrate, and free nitric acid.

One of the fundamental lessons learned was that the gross composition of the raw hydroceramic formulation should approximate sodalite (or cancrinite); i.e., in other words, there should be approximately one atom of aluminum for each atom of sodium, at least one atom of silicon for every aluminum, 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 0.25, most SBWs need some form of pretreatment (aka "denitration") before solidification.

The Idaho National Engineering & Environmental Laboratory (INEL) utilized two fluidized bed calciners to convert most of its reprocessing waste streams to a mixture of small granules and powder (calcine). The wastes were sprayed into a ~500°C bed of rapidly moving particles which served to drive off the volatiles (mostly water and free acid) and decompose thermally labile nitrate salts. Because that temperature is too low to thermally decompose alkali metal (Na & K) nitrate salts, INEEL's calcination process did not work well with its high-sodium wastes[7]. Consequently, those streams were first, concentrated to the maximum practicable degree via evaporation and then stored in large underground steel tanks.

[7] At such temperatures, alkali metal nitrates simply melt to form viscous "glues" that agglomerate the fluidized bed.

It has been documented that the best way to pretreat virtually any DOE SBW for hydroceramic solidification is to slurry it with powdered clay (metakaolinite), add a water-soluble carbohydrate, and then calcine the mixture at a temperature in excess of 500°C.[5] 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 NOx. The clay reacts with the nascent sodium oxide to form an amorphous alkali aluminosilicate powder ideally suited for cementitious solidification. 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[8] (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 necessary to consolidate such powders into concrete waste forms.

The kinetics of the hydroceramic curing process are interesting. Figures 1 and 2, excerpted from one of the papers given at the 2000 Amer. Ceram. Soc. Radwaste Symposium[9] indicate that long-term curing at temperatures below the boiling point of water will ultimately produce a product with leach characteristics similar to that of specimens cured for much shorter periods under typical autoclave temperatures/pressures (e.g., ~190°C/~170 psig). The imposition of more rigorous curing conditions (longer times & greater temperatures/pressures) invariably tends to increase the specimen's degree of crystallinity and decrease its water solubility.

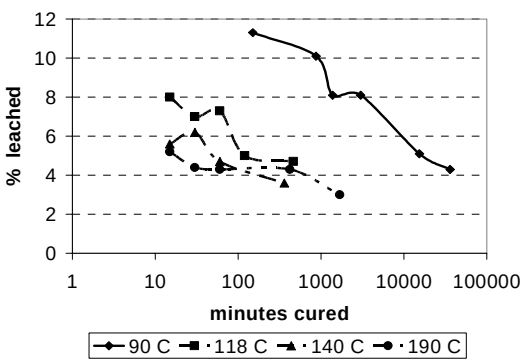

Figure 1. Leaching vrs time and temperature.

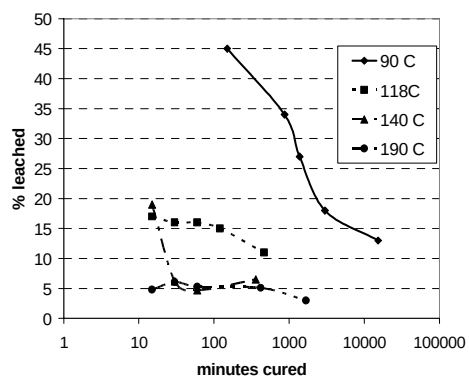

Figure 2. Leaching vrs time and temperature

It is also concluded that crude metakaolinite out-performed physical mixtures of colloidal silica and colloidal alumina powders both as a "calcination aid" and as the main ingredient of the subsequent hydroceramic "monolithification" step. Because the Savannah river Tank 44 waste simulant studied contained an excess of free hydroxide relative to other anions (OH>4:1

[8] 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 propritory 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.

[9] Grutzeck, M.W., B.E. Scheetz, J. Olandreju, N. Krishnamurthy and D.D. Siemer, "Development of Hydroceramic Waste Forms", Ceramic Transactions 119, pp. 383-390 (2001).

nitrate/nitrite mole wise), it was possible to make a competent (low leachability) hydroceramic out of it with or without a pretreatment step. However this is an atypical situation.

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 very poor physical characteristics (low strength & low bulk densities). Such clays also tend to react so quickly that "flash setting" would make it very difficult to implement a large-scale process with them. We discovered that 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 with good leach resistance, high bulk density, and reasonable physical strength.

Highlights of Findings for Years 1 to 3

- 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 hydroceramic concretes cured at widely different temperatures tends to converge at long 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 strictro it is halloysite. The chemistry is the same but the latter contains interlayer water molecules. Halloysite platelets rool up and form hollow tubes rather than "books." This morphology as well as impurities may influence reactions and performance.
- Properly cured hydroceramics undergoe 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[10]. Such "incidental" wastes are apt to be left on-site with only

[10] 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 $NaNO_3$-cancrinite).

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.

Summary of Progress during Years 1 to 3

It 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 as described below). The processing should be carried out under reducing conditions to minimize NOx 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 ^{137}Cs from SBW streams which are destined to remain on site.

Work Completed during Year 4

The focus of our current work is an investigation of scale-up factors. A ton of Troy clay was purchased from Columbus Clay in Columbus OH[11]. The as received raw clay had been preground to –50 mesh and was packaged in 50 pound bags. We purchased 40 such bags and sent them to FTE Minerals in Bethlehem, PA to be processed into metakaolinite in a 3' x 30' rotary kiln utilizing a materials residence time of 2 hours and a maximum load temperature of 750-800°C. 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". We now possess four 55 gallon drums of Troy metakaolinite. Samples are available upon request. While waiting for the "new" metakaolinite to be processed, our new graduate assistant completed a study of the effect of solidifying a previously sugar/clay calcined Hanford stimulant (see Table 1) with Portland cement versus metakaolinite. Details are given below.

Table 1. Ingredients of Hanford Simulant used to make One Liter (weights in grams)

Compound	Simulant
$NaOH$	82.6819
$Al(NO_3)_3 \cdot 9H_2O$	133.5
$NaNO_2$	36.9106
Na_2CO_3	36.2049
$NaNO_3$	8.5815
Na_2HPO_4	27.7873
KCl	1.8328
$NaCl$	2.5077
$Na_2B_4O_7 \cdot 10H_2O$	0.1096
Na_2SO_4	3.8945
$Ni(NO_3)_2 \cdot 6H_2O$	0.3115
$Ca(NO_3)_2 \cdot 4H_2O$	0.4420
$Mg(NO_3)_2 \cdot 6H_2O$	0.0337

The Hanford stimulant was prepared by mixing the various amounts of reagent grade chemicals listed in Table 1 with sufficient water to make one liter of simulant. The solution was then combined with sucrose and metakaolinite at the weight ratio 20:2.5:11.9 which produced a slurry with the consistency of mud. After being allowed to dry at 90°C for 24 hours, the dried material was calcined 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_2, to form a aluminosilicate-based calcine having a tectosilicate structure.

[11] This is a dried and powdered version of the Helmar Bovill clay sold to artisans for making conventional ceramics.

The hydroceramic samples discussed in Tables 2-4 were made using 3 g of this calcine, 2 g of Troy metakaolinite (MK) 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 Hanford calcine as well as the added NaOH used during mixing The pastes were molded in a 60mm X 10mm X 10 mm SS mold 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 ground and the powder was placed onto piggy-backed 100 mesh (top) and 200 mesh (bottom) screens. The resulting 75-149 micron size cut was leach tested under PCT conditions (1 gram powder to 10 cc water in a hermetically sealed container held at 90°C) for 24 hours 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 will be the predominate soluble species, conductivity is directly proportional to sodium leachability (1 mS/cm corresponds to ~0.01 molar Na as given in Tables 3 and 5).

Table 2. Crystalline Phases Present and Compressive Strength of Hydroceramics made from Calcined Hanford Simulant, Troy MK and Solution and then Cured at 90°C or 190°C for 24 hrs.

5g Solids Mixed with 4.5 mL of Solution below	Total Mol Si/Na	Total Mol Al/Na	90°C Cured			190°C Cured		
			Crystalline Phases Present	Green Strength (psi)	Cured Strength (psi)	Crystalline Phases Present	Green Strength (psi)	Cured Strength (psi)
H_2O	2.689	2.103	MK	~5-30	~5-30	MK	~5-30	30
2M NaOH	1.689	1.321	A	~5-40	344	A	104	609
4M NaOH	1.231	0.963	A	309	515	A	336	580
6M NaOH	0.969	0.758	A+HS	764	919	A+HS	697	662
8M NaOH	0.799	0.624	HS	369	889	HS	790	650
10MNaOH	0.679	0.531	HS	210	575	HS	662	610

Table 3. Leachability of above Hydroceramics Containing Calcined Hanford Simulant

Total Mol of Na in 1g PCT Samples	90°C Cured				190°C Cured			
	Leach-ability (mS/cm)	Mol of Na Leached	% Na Leached	pH of Leachate	Leach-ability (mS/cm)	Mol of Na Leached	% Na Leached	pH of Leachate
0.00304	3.40	0.00034	11	10.6	3.60	0.00036	12	10.8
0.00484	4.80	0.00048	10	10.2	3.20	0.00032	7	10.4
0.00664	4.80	0.00048	7	10.7	2.00	0.00020	3	10.7
0.00844	7.00	0.00070	8	10.6	4.90	0.00049	6	10.8
0.01024	11.40	0.00114	11	10.7	15.30	0.00153	15	12.6
0.01204	>100	-	-	13.0	>100	-	-	13.0

Table 4. Crystalline Phases Present and Compressive Strength of Hydroceramics made from Calcined Hanford Simulant, Portland Cement and Solution and then Cured at 90°C or 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 (psi)	Cured Strength (psi)	Crystalline phases Present	Green Strength (psi)	Cured Strength (psi)
H_2O	1.877	1.291	C_3S^*	42	5	$Ca_3(SiO_4)O$	50	-
2M NaOH	1.180	0.812	A+C_3S	554	593	HS+ C3A	572	374
4M NaOH	0.861	0.592	HS+C_3S	443	510	HS+C3A	432	233
6M NaOH	0.677	0.466	HS+ C_3S	234	145	HS+ C3A	353	200
8M NaOH	0.558	0.384	HS+C_3S	311	181	HS+C3A	298	145
10MNaOH	0.475	0.327	HS+C_3S	213	129			

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

Table 5. Leachability of above Hydroceramics Containing Calcined Hanford Simulant

Total mol of Na in 1g PCT samples	90°C cured				190°C cured			
	Leach-ability (mS/cm)	Mol of Na Leached	% Na leached	pH of Lechate	Leach-ability (mS/cm)	leached mol of Na	% Na leached	Leached pH
0.00305	8.40	0.00084	28	12.3	6.6	0.00066	22	12.2
0.00485	15.50	0.00155	32	12.8	11.0	0.00110	23	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			

Table 2-4 indicate that Portland cement solidification is inferior to hydroceramic solidification for clay-calcined material such as the Hanford stimulant discussed above. Due to the similarity of the Hanford stimulant to the clay "reformed" Hanford-type LAW/SBW discussed by Jantzen[12] (see below), the hydroceramic process would probably work better than Portland cement for this waste as well. The hydroceramic specimens – even those containing a much higher proportion of sodium than what our "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 "reformed") SBWs, like most zeolitic materials, is pozzolanic, i.e. it readily reacts 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 (Table 5). C-S-H is unable to host sodium in its lattice. Pore water in conventional concrete is ~1M NaOH. If SBW calcines are solidified with Portland cement, the concentration of sodium in the pore solution could go even higher.

The conductivity data also suggest that the optimum amount of free hydroxide in the mix water is on the order of 4 M. The leach data experience a minimum at this point. The extra amount of Na added provides the 1:1 Na:Al ratio needed to form zeolites. The primary XRD-discernable (crystalline) phase in those samples was zeolite A. At higher NaOH concentrations, hydroxysodalite (HS) predominated. The leach rates were higher primarily due to the fact that there was a stoichiometric excess of free caustic present in the formulations (more than what could fit into sodalite "cages"). The photomicrographs (Figure 3) compare the microstructures of 190°C-cured samples made with 4 and 8M NaOH. The HS-sample on the right is more porous looking than its zeolite A counterpart on the left.

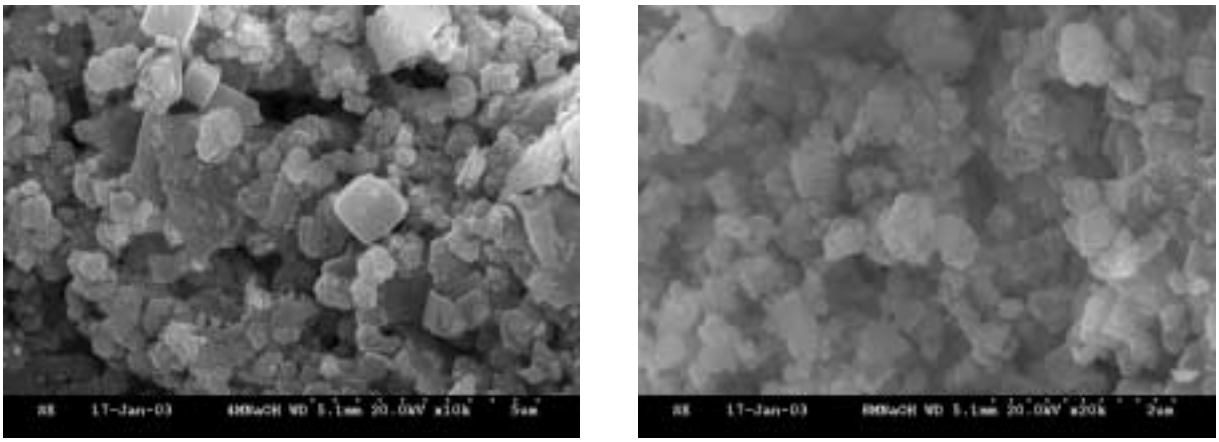

Figure 3. Comparison of microstructures of hydroceramic samples made with 4 and 8M NaOH. The figure on the left contains zeolite A (cubes) while the figure on the right contains hydroxysodalite (bead shaped crystallites).

An interesting development coming out of Westinghouse Corporate (as opposed to Westinghouse Savannah River) has a direct bearing on our work. Westinghouse Corporate recently commissioned a test of the feasibility of applying Studsvik's fluidized bed-based "steam reformation" (FBSR) process to Hanford-type SBW[12]. Normally, Studsvik's FBSR is run at ~500°C and is used to destroy organic materials. It has been used in some instances to decompose SBW as well but without using calcinations aids the final product is soluble Na_2CO_3. In the current work reported by Jantzen, Hazen Research Inc. in Golden CO used a 6" FBSR to prepare a hydroceramic like material in a single step. The waste containing elemental carbon and raw kaolin (clay) was sprayed into a fluidized bed consisting of alumina and/or iron oxide media. Note that the FBSR product is quite similar to what PSU, SRL and INEEL personnel have been doing to pretreat simulants for our hydroceramic work, except for the fact that it is a continous rather than batch process. Steam reforming's two key advantages relative to INEEL's traditional approach to calcination is that it produces far less NOx and its product should be much better

[12] 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.

suited for a second solidification. “Should” because there’s apt to be a good deal of residual elemental carbon in the FBSR calcine which might cause problems – only additional hands-on experimentation will tell. Samples of “steam reformer” product are being sought from Westinghouse Corporate. Also larger batches of Hanford calcine are being prepared using recipes in our previous work plus that published by Jantzen in her report.

Future Directions

At this point, we are planning to make some 5 gallon-sized samples, cure them at temperatures ranging from 90° to 200°C, and then characterize them as a function of “distance to center line”; i.e., test coupons will be removed from various points within the specimens. We also plan 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[13]. 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, and/or hydroxycarbonates in a matrix dominated by of 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[14] 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 ^{137}Cs than would the OPC-based grout.

Publications during First Four 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.

Krishnamurthy, N., M.W. Grutzeck and S. Kwan, “Hydroceramics for Savannah River Laboratory's Sodium Bearing Waste,” Accepted for Publication, Proc. Amer. Ceram. Soc. Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries, St. Louis, MO, April 29-May 3, 2000, Amer. Ceramic Society, Westerville, OH.

Siemer, D.D., J. Olanrewaju, B.E. Scheetz, N. Krishnamurthy and M.W. Grutzeck, “Development of Hydroceramic Waste Forms,” Accepted for Publication, Proc. Amer. Ceram. Soc. Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries, St. Louis, MO, April 29-May 3, 2000, Amer. Ceramic Society, Westerville, OH.

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[13] 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.

[14] This is the same approach employed by Kraft paper mills to recycle caustic.

Siemer, D.D., J. Olanrewaju, B.E. Scheetz, and M.W. Grutzeck, “Development of Hydroceramic Waste Forms for INEEL Calcined Waste,” Accepted for Publication, Proc. Amer. Ceram. Soc. Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries, St. Louis, MO, April 29-May 3, 2000, Amer. Ceramic Society, Westerville, OH.

Krishnamurthy, Naveen, 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 Imobilization," Abstract of a Talk, ACI Session on Concrete for Radioactive Waste Management," co-sponsored by Committees 227 and 349, Thursday Novemeber 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).

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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