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# Binders for radioactive waste forms made from pretreated calcined sodium bearing waste

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Radioactive waste generated during the reprocessing of fuel rods by the U.S. Department of Energy (DOE) is stored in underground tanks at Hanford, Savannah River and INEEL. The liquid fraction commonly referred to as sodium bearing waste (SBW), is a highly alkaline solution containing large amounts of sodium hydroxide, sodium nitrate and sodium nitrite. It has been shown that SBW can be mixed with a reducing agent and metakaolin and then calcined at 500°–700°C to form a calcine containing sodium aluminosilicate phases such as zeolite A, hydroxysodalite and/or cancrinite. Although calcination of the pretreated SBW produces a reasonable waste form in its own right, existing regulations require that granular calcines must be solidified before they can be shipped off site. It is possible to solidify the calcine in a number of ways. The calcine can be mixed with additional metakaolin and NaOH solution followed by mild curing (90°–200°C). The solid that forms (aka hydroceramic) has both strength and suitably low leachability. The current study examines the feasibility of using a more conventional Portland cement binder to solidify the calcine. Although strength was adequate, the leachabilities of the Portland cement solidified samples were higher than those of companion samples made with metakaolin. 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.

## 1. Introduction

Zeolites are versatile materials. They can adsorb liquids and gasses and serve as cation exchange media. Although natural and synthetic zeolites are normally micrometer-sized, on occasion, zeolites can occur as well-cemented deposits. These deposits are apparently quite durable inasmuch as the Romans used blocks of zeolitized tuff as a building material. Using zeolites for the management of radioactive waste is not a new concept, but a process by which formed in situ zeolites act both as a host phase and a cementitious binder phase for radioactive waste ions is.

## 2. Hydroceramics

Zeolitic materials are relatively easy to synthesize from a wide range of starting materials. The process under study here is derived from a well known method in which metakaolin (thermally dehydroxylated kaolinite, nacrite, dickite, or anauxite) 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 consisting of agglomerated micrometer ($\mu$m) sized crystals [1]. However, if the process is changed slightly and only minimal amounts of concentrated NaOH solution is added to the metakaolin one is able to make a thick paste that can be molded and cured under mild hydrothermal conditions (60°–200°C) to form a ceramic-like material containing crystalline tectosilicates (zeolites and feldspathoids) imbedded in an X-ray amorphous but hydrated sodium aluminosilicate matrix [2–11]. Because of its vitreous character the composite has been called a "hydroceramic". Due to the fact that the hydroceramic contains tectosilicate mineral phases, it is able to sequester cations in both lattice positions and within channels and voids in its structure. These phases

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can also accommodate a wide range of salt molecules (e.g., sodium nitrate, calcium carbonate, calcium sulfate) within these same openings as in cancrinite thus rendering them relatively insoluble. X-ray diffraction data of a typical hydroceramic suggests that it contains both crystalline and non-crystalline material. The amorphous hump present in the X-ray pattern is assumed to be the signature of the sodium aluminosilicate hydrate matrix phase. It is proposed that the development of strength during the curing process is a direct result of varying amounts of matrix and crystalline intergrowth.

## 3. Radioactive waste forms

Hydroceramics are ideally suited to solidify sodium bearing waste (SBW) now in storage at Hanford, Savannah River and Idaho National Engineering & Environmental Laboratory (INEEL). The supernate found in their storage tanks is extremely rich in Na (typically 8–12 M). If the SBW is pretreated with metakaolin and sucrose and then calcined, the SBW can be used to make a hydroceramic waste form. Sodium salts must be denitrated otherwise the process will not work. The obvious similarities between a hydroceramic waste form and a waste form based on hardened 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 [Product Consistency Testing (PCT), Toxic Characteristic Leaching Procedures (TCLP), etc.] have shown that hydroceramics also do a better job of immobilizing the Resource Conservation and Recovery Act (RCRA)-toxic and radioactive components of "sodium bearing wastes" (SBWs) [11].

The process of making a hydroceramic waste form from SBW is straight forward. A mixture of metakaolin blended with lesser amounts of optional powdered vermiculite (improves cesium retention) and sodium sulfide (which acts as a redox buffer and RCRA metal precipitant) is mixed with the suitably pretreated and calcined SBW and sufficient caustic (normally 4 M NaOH) solution to produce a paste having a putty-like consistency. The paste is placed in a metal container (e.g., a stainless steel canister) and then "soaked" for a few hours at 20°–90°C to allow precursor phases to form prior to curing. If a curing temperature below the boiling point of water is to be used, a well-insulated building equipped with supplemental heaters could serve as both the interim storage facility and "curing facility". 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.[1] 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 for many of DOE's reprocessing waste treatment needs.

The overall objective of our hydroceramic research is to work out the details of how the process could be applied to both the caustic-type SBWs stored at the Hanford, Savannah River and 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 and phase chemistry, and microstructure on their performance. The objective of the current work is to explore the feasibility of using conventional Portland cement as an alternate binder phase to solidify pretreated and calcined SBW typifying that found at Hanford.

## 4. Background

At this point in time, it has been shown that a hydroceramic waste form could be used to solidify low activity sodium bearing waste (SBW) now in storage at DOE sites [2–11]. Work now in progress continues to focus on optimization of waste pretreatment (calcinations and/or steam reforming), waste stream-specific optimization of the formulations, and a study of scale-up factors to insure the technology's viability in real world applications. Although glass is still the waste form of choice, it is anticipated that the DOE will adopt hydroceramic waste forms for some of its SBW for the many reasons described below.

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 [2, 3, 6]. SBW simulants representing both the strongly basic supernate salt wastes stored at Savannah River (Tank 44) [7] and Hanford sites (average composition) [8] and INEEL's already calcined acidic SBW [10] 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 (both the calcine and the binder) should approximate that of 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 (i.e., 1:1:1 molar ratio), 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 [2–11].

The Idaho National Engineering & Environmental Laboratory (INEEL) utilized two fluidized bed

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[1] Such vessels would not have to be especially massive or expensive; for example, domestic water heaters are designed for pressures up to 1.034 MPa gauge—which corresponds to an approximate curing temperature of 185°C.

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 and K) nitrate salts, INEEL's calcination process did not work well with its high-sodium wastes.[2] Consequently, those streams were first concentrated to the maximum practicable degree by evaporation and then stored in large underground steel tanks.

To date, it has been documented that the best way to pretreat virtually any DOE SBW for hydroceramic solidification is to slurry it with metakaolin, add a water-soluble carbohydrate, and then calcine the mixture at a temperature in excess of 500°C [7, 8]. The added carbohydrate (usually sucrose, i.e., table sugar) is a reducing agent that serves to decompose the alkali nitrate/nitrite salts and converts the bulk of the nitrate/nitrite to innocuous elemental nitrogen rather than $NO_x$. The metakaolin reacts with the nascent sodium species (oxide/hydroxide) to form a partially crystalline alkali aluminosilicate powder ideally suited for solidification with a binder. If no metakaolin "calcination aid" is added, "sugar calcination" produces a soluble salt (sodium carbonate), which is no better than sodium nitrate/nitrite as a starting material for making hydroceramic (or any other sort of) waste form. If a higher-than-usual (e.g., 700 vs. ∼500°C) calcination[3] (or "reformation") temperature is employed, the resulting clay/sugar/SBW calcine will exhibit a good deal of leach resistance in its own right [12]. However, because current transport regulations require that Class B or higher radioactive waste forms be in a monolithic (non dispersible) form, it is necessary to consolidate such powders into monolithic solids.

The kinetics of the hydroceramic curing process excerpted from [9] and reproduced here as Figs 1 and 2, indicate that long-term curing at temperatures below the boiling point of water will ultimately produce a waste form having leach characteristics similar to that of specimens cured for much shorter periods under autoclave temperatures/pressures (e.g., ∼190°C/∼1.172 MPa gauge). The imposition of more rigorous curing conditions (longer times and greater temperatures/pressures) invariably leads to increased crystallinity and decreased solubility in water.

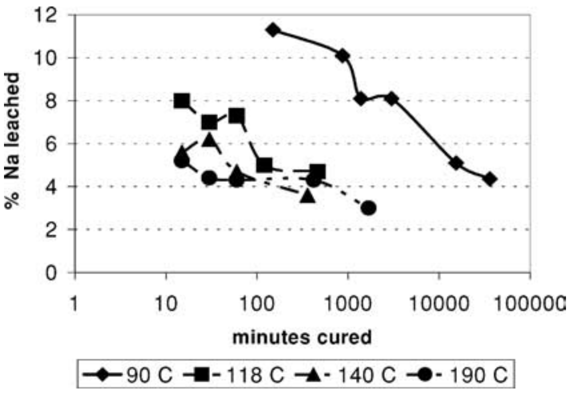

*Figure 1* Sodium leachability vs. time and temperature.

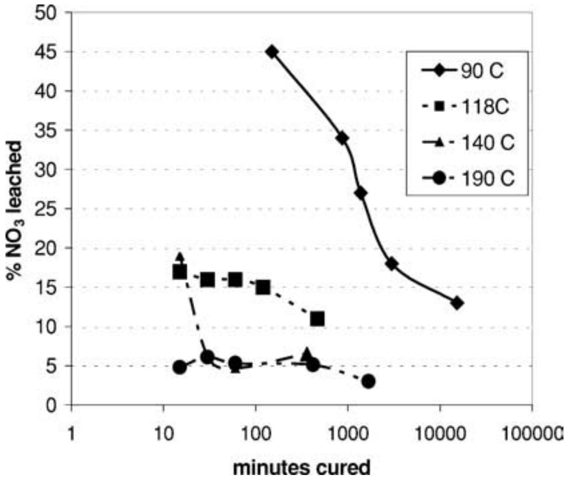

*Figure 2* Nitrate leachability vs. time and temperature.

It has been found that metakaolin containing impurity phases such as quartz and mica outperformed equivalent calcine/hydroceramic samples prepared from SBW mixed with colloidal silica and colloidal alumina, or phase pure metakaolinite [6]. Hydroceramics made from extremely pure, highly refined metakaolin (e.g., Engelhard's MetaMax is pure metakaolinite) exhibited very low water solubilities (their PCT leachabilities were the lowest obtained to date), but they tended to have low strengths and low bulk densities. Metakaolinites tend to "flash set" making it difficult to prepare samples and implement large-scale processing. Rather, it was found that impure clays such as those mined near Troy Idaho (aka Troy clay, a clay mined in Helmer Idaho that is a member of the Helmar-Bovil formation in Latah County), made a better starting material. Augmenting MetaMax with micrometer quartz provided the same effect. Strength is related to the small amount of mica and quartz that Troy clay contains. Hydroceramic "grout" formulations made with the Troy metakaolin were easy to mix and cure, forming a product with good leach resistance, high bulk density, and reasonable physical strength [8].

An interesting development attributed to Westinghouse Corporate (distinct from Westinghouse Savannah River) has a direct bearing on this 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 as an alternative to calcination.[3] 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 [12], Hazen Research Inc. in Golden CO used a 6" FBSR to prepare a hydroceramic

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

[3] This process is called "reformation" rather than calcination when most of the heat input is via the introduction of superheated steam.

like material. The simulated waste used for the test was based upon the composition of supernate in Hanford's Tank 107. The SBW was mixed with elemental carbon, sucrose, raw kaolin (not metakaolin) and a proprietary additive and sprayed into a fluidized bed consisting of alumina and iron oxide media held at ~700°C. Note that the FBSR product is quite similar to what PSU, SRL and INEEL personnel[4] have been doing to pretreat simulants for ongoing hydroceramic work, except for the fact that the reforming process is a continuous rather than a batch process. Steam reforming's two key advantages relative to INEEL's traditional approach to calcination is that it produces far less $NO_x$ and its product should be much better suited for a second solidification: "Should" because residual elemental carbon in the FBSR calcine might cause problems—only additional hands-on experimentation will tell.

## 5. Properties of hydroceramic waste forms

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 by Jantzen). The processing should be carried out under reducing conditions to minimize $NO_x$ and render species such as Tc, Cr, and Np less water soluble. The high affinity of hydroceramic-type waste forms for cesium and strontium means that it should not be necessary to remove $^{137}$Cs or $^{90}$Sr from SBW streams which are destined to remain on site.

- Hydroceramic waste forms made with representative SBW simulants, metakaolin, and sodium hydroxide out-performed conventional grouts on standard radioactive waste 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). In addition, hydroceramics contain tectosilicate phases similar to those present in Yucca Mountain. This means that a strong case could be made for sending hydroceramic-solidified reprocessing waste to the Yucca Mountain site.
- Calcination or FBSR of SBW augmented with sucrose but without an aluminosilicate "calcination aid" is of questionable value producing only soluble sodium carbonate. Recent tests by two vendors at INEEL have shown this to be true.
- At least 75% of the sodium in a SBW or calcine derived from it should be present as some combination of oxide, hydroxide, aluminate, or silicate. A SBW having these characteristics can be solidified with metakaolin and water without calcination. If the SBW contains less than 75% of these species, it must first be pretreated (mixed with metakaolin, sucrose and calcined).
- Increasing the curing temperature and pressure improves the leach performance of the hydroceramic. However, because the leach resistance of hydroceramic solids cured at widely different temperatures tends to converge at long times, autoclave-type (high T/P) curing may not be necessary.
- Properly cured hydroceramics undergo virtually no change when subjected to the "new" vapor hydration test (VHT) [13]. 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 cause them to be at or 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 grout-making process. However, in actual practice vitrification invariably increases the total amount of radioactive waste 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. Such "incidental" wastes are apt to be left on-site with only cursory treatment (evaporation).[5] 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.

## 6. Experimental methods

The objective of the reported work is to evaluate the effectiveness of using ordinary Portland cement (OPC) as an alternate binding material for finely divided calcines and granular FBSR waste forms that have been prepared with an organic reducing agent and aluminosilicate, i.e., they already contain sodium aluminosilicates. Inasmuch as radioactive waste forms are often required to be monolithic, experiments were carried out in order to compare the feasibility of using a conventional OPC grout as a substitute for the conventional metakaolin/NaOH binder used to make a hydroceramic. Starting materials included a ton of calcined Helmar-Bovil clay (aka Troy clay) purchased from Columbus Clay in Columbus OH. The as received clay mined in Helmer Idaho by Wentz Pottery had been preground to −50 mesh and was packaged in 50 pound bags.[6] FTE Minerals in Bethlehem, PA processed the clay into

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[4] Jantzen (SRL) and Grutzeck (PSU) are co-investigators on a DOE EMSP funded grant to study the feasibility of using hydroceramics to encapsulate simulated and actual low activity SBW, respectively. Siemer is employed by INEEL and provides input to both programs on an as needed basis. INEEL provides no funding for his work.

[5] 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).

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

TABLE I Ingredients used to make one liter of Hanford simulant (weights in grams)

| Compound | Simulant (g)[a] |
|---|---|
| NaOH | 82.6819 |
| $Al(NO_3)_3 \cdot 9H_2O$ | 133.500 |
| $NaNO_2$ | 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 |

[a] The actual amounts used are not critical, because the waste is an "average" representing the composition of supernate in many tanks. The four significant figures represent what was added to the current stimulant and then used to calculate the amount of sodium, aluminum and silicon in the calcine and final waste forms.

metakaolin in a 0.9 m OD × 9 m long rotary kiln utilizing a materials residence time of 2 h and a maximum temperature of 750–800°C. During the 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." X-ray diffraction and SEM examination of the Troy raw clay suggest that it is predominantly kaolinite containing traces of muscovite, quartz and perhaps halloysite.

The pretreated and calcined simulated Hanford SBW used in the study is the same as that described by Krishnamurthy [8]. The simulation is based on an "average" Hanford low activity SBW recipe originally published by Brough *et al.* [14]. The simulated calcine was prepared by mixing the reagent grade chemicals listed in Table I with sufficient water to make one liter, and then mixing the solution with sucrose and Troy metakaolin at a weight ratio of 20:2.5:11.9. The final slurry had the consistency of thick mud. After drying at 90°C for 24 h, the simulant was calcined at 525°C for 18 h. The sucrose acted as a reducing agent making it possible to decompose the nitrate and nitrite at lower than normal temperatures. The X-ray diffraction pattern for the calcine is nearly devoid of crystalline components, but the location of an "amorphous hump" suggests that it contains a mixture of poorly crystalline feldspathoids. Chemical analyses of calcines of this type have shown that the nitrate/nitrite content of the sample has been reduced to very low levels. Although a few percent of the newly formed Na species combine with $CO_2$ in the air, most of the sodium combines with the metakaolin to form aluminosilicate precursors.

The pretreated calcine was mixed with either ordinary Portland cement (Type I OPC) or additional Troy metakaolin and various liquids and then cured as a function of temperature. Experimental variables included the composition of the mixing solution (0–10 M NaOH) and curing temperature (90° and 200°C). Hydroceramic samples were made using 3 g of Hanford calcine, 2 g Troy metakaolin (MK) plus 4.5 mL of solution to make a putty-like paste. The total amount of Na in the sample (reported below) includes the Na in the calcine as well as the added NaOH used during mixing. The pastes were molded in 60 mm × 10 mm × 10 mm stainless steel molds and then precured at room temperature until hard. After demolding, the samples were cured at 90° or 190°C overnight in a steam-saturated atmosphere (Teflon-lined Parr bombs). They were then ground to a powder in an agate mortar and sieved using piggy-backed [100 mesh (top) and 200 mesh (bottom)] screens. The resulting 75–149 micron size cut was leach tested under modified PCT conditions (1 gram powder immersed in 10 cc water in sealed containers held at 90°C for 1 day rather than 7 days). The solution was tested after 1 day because it was found that ~80–90% of the leachable sodium was removed after 1 day, enough to allow one to rank relative performance. The solution was filtered and its electrical conductivity determined using a Quikchek Model 118 conductivity-2 meter manufactured by Orion. Since predominate soluble species are sodium salts, conductivity is directly proportional to sodium leachability (1 mS/cm corresponds to ~0.005 molar NaOH). This value was used to calculate the molar sodium concentrations and the molar percentage sodium lost reported in Tables III and V.

## 7. Results

Leach data, compressive strength and phase composition data are given in Tables II–V. Tables II and III represent the physical and mechanical properties of the monolithic waste forms made with Troy metakaolin. The data in Tables IV and V represent the properties for identically cured samples made with Type I OPC. Because the samples were small and the strength values were based on one or two samples (typically 1$\sigma$ for 2 samples equals ±0.2 MPa) the values should be regarded as only approximate. It is notable however that most are high enough to pass the required strength needed to ship waste off site.

Tables III and V can be used to compare the percent of the total sodium leached from each sample. The hydroceramic waste forms made with metakaolin binder had consistently lower % Na losses than comparable samples solidified using OPC. At best, the water mixed Portland cement samples lost twice as much sodium as the equivalent water mixed hydroceramic samples, suggesting that solidification with metakaolin is a superior binder for pretreated denitrated SBW such as the Hanford stimulant. Furthermore, the series of hydroceramic samples exhibit a minimum in leachability that occurs when 4 M NaOH was used as mixing solution; adding more NaOH improved leachability! In the case of the Portland cement solidified samples, leachability deteriorated badly as NaOH solutions were used to mix the samples. Due to the similarity of the Hanford stimulant to the clay "reformed" Hanford-type SBW discussed by Jantzen [12], the use of a metakaolin/NaOH binder rather than OPC/water would probably produce a better waste form as well. The hydroceramic waste forms—even those containing a

TABLE II Crystalline phases present and compressive strengths of hydroceramics made from calcined Hanford simulant, Troy MK and solution and then cured at 90° or 190°C for 24 h

| 5 g 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 (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 |
| 2 M NaOH | 1.689 | 1.321 | A | 0.27 | 2.37 | A | 0.72 | 4.20 |
| 4 M NaOH | 1.231 | 0.963 | A | 2.13 | 3.55 | A | 2.32 | 4.00 |
| 6 M NaOH | 0.969 | 0.758 | A + HS | 5.27 | 6.34 | A + HS | 4.80 | 4.56 |
| 8 M NaOH | 0.799 | 0.624 | HS | 2.54 | 6.13 | HS | 5.45 | 4.48 |
| 10 MNaOH | 0.679 | 0.531 | HS | 1.45 | 3.96 | HS | 4.56 | 4.20 |

MK = Troy metakaolin, A = zeolite A, HS = hydroxysodalite.

TABLE III Leachability of Table II 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 |

TABLE IV Crystalline phases present and compressive strength of waste forms made from calcined Hanford simulant, Portland cement and solution and then cured at 90° or 190°C for 24 h

| 5 g 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 | $C_3S$[a] | 0.29 | 0.03 | $C_3S$ | 0.34 | – |
| 2 M NaOH | 1.180 | 0.812 | A + $C_3S$ | 3.82 | 4.09 | HS + $C_3S$ | 3.94 | 2.58 |
| 4 M NaOH | 0.861 | 0.592 | HS + $C_3S$ | 3.05 | 3.52 | HS + $C_3S$ | 2.98 | 1.61 |
| 6 M NaOH | 0.677 | 0.466 | HS + $C_3S$ | 1.61 | 1.00 | HS + $C_3S$ | 2.43 | 1.38 |
| 8 M NaOH | 0.558 | 0.384 | HS + $C_3S$ | 2.14 | 1.25 | HS + $C_3S$ | 2.05 | 1.00 |
| 10 MNaOH | 0.475 | 0.327 | HS + $C_3S$ | 1.47 | 0.89 |  |  |  |

[a] $C_3S$ is an abbreviation for the anhydrous calcium silicate phase that comprises ~60 wt% of Portland cement ($Ca_3SiO_5$). Other symbols described at bottom of Table II.

TABLE V Leachability of Table IV 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 | Leached pH |
| 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 |  |  |  |

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 stronger. The reason for this is that clay-calcined (or "reformed") SBW, 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 V). C—S—H does not have a large capacity for alkali ions. Over time, the pore solutions extracted from OPC

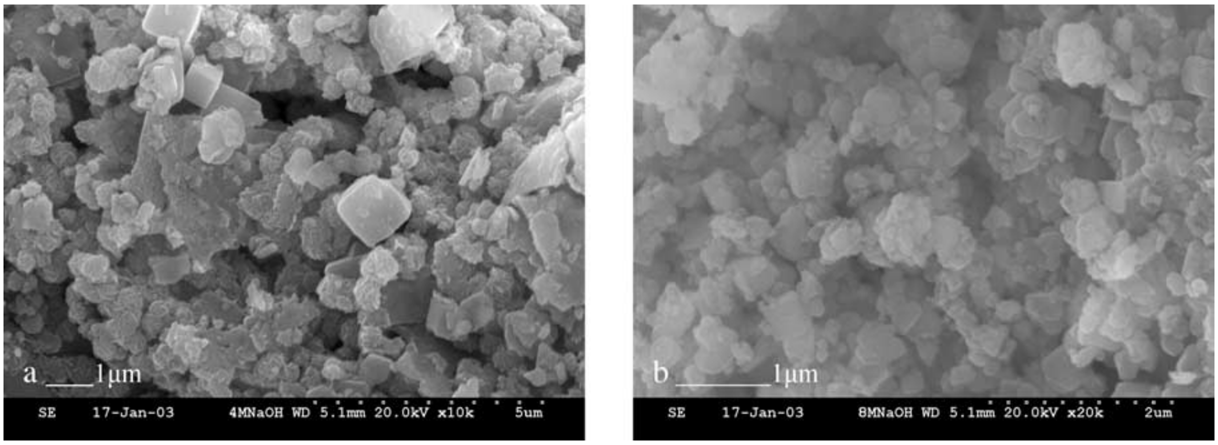

*Figure 3* Comparison of microstructures of hydroceramic samples made with 4 and 8 M NaOH. View (a) depicts zeolite A (cubic crystals) imbedded in a massive matrix. Some "balls of yarn" representing zeolite Na-P1 is also evident growing on the surface of the matrix. View (b) depicts intergrown hydroxysodalite (bead shaped) crystallites. There is decidedly less matrix phase present in the hydroxysodalite sample.

pastes (W/C ratio of 0.4) typically will have concentrations equivalent to ~0.25 M $Na^+$ and 0.41 M $K^+$. This represents a loss of 60 and 80% of OPC's Na and K, respectively [15]. 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 for the "best" binder occurs at 4 M NaOH. The extra amount of Na added provides the 1:1:1 Na:Al:Si ratio needed to form zeolites such as sodalite. The primary XRD-discernable (crystalline) phase in the 4 M samples was zeolite A. At higher NaOH concentrations, hydroxysodalite (HS) became the predominant phase. The HS samples had higher leach rates due to the fact that there was a stoichiometric excess of free caustic present in the formulations that could not be accommodated by sodalite-like "cages". Hydroxysodalite is able to incorporate 1 NaOH molecule in its structure as a replacement for $2H_2O$ molecules. This sodium is presumed to be more mobile and thus easily leachable. The photomicrographs given in Fig. 3a and b can be used to compare the microstructures of two 190°C samples made with 4 and 8 M NaOH, respectively. The HS-sample (view b) appears more crystalline and also more porous than its zeolite A counterpart (view a). The zeolite A crystallites in view (a) are bound together by massive matrix material, whereas the HS crystallites present in view (b) are more or less intergrown.

## 8. Conclusions

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 two times higher than a similarly solidified metakaolin/NaOH sample. The "sodalite" rule of thumb has been touted as a guide to formulating a hydroceramic waste form. The minimum in conductivity exhibited by the hydroceramic sample made with 4 M NaOH mixing solution 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. 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. Based on selectivity of zeolite A for Cs and Sr, it seems possible that the hydroceramic waste form can be 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.

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