Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

X-Ray Diffraction of Slag-based Sodium Salt Waste Forms - 15513

C. A. Langton and D. M. Missimer
Savannah River National Laboratory, Savannah River Nuclear Solutions,
Savannah River Site, Aiken, SC 29808

ABSTRACT

Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. This paper documents sample preparation and x-ray diffraction results for a series of materials made with water or highly alkaline sodium salt simulated waste water and cementitious binders. The objective of this study was to: 1) generate a base line for the evolution of the waste form as a function of time and conditions, 2) design new binders based on mineralogy of the binder, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms for which phase solubility and thermodynamic data are available. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water / leachates.

In summary, mixtures of Type II portland cement, Grade 100 ground granulated blast furnace slag (GGBFS) and carbon burn-out (CBO) Class F Fly ash which were hydrated with water contained hydrated phase assemblages typical of those reported in the literature. The calcium silicate hydrate phase assemblage in samples hydrated with the alkaline 4.4 M sodium salt simulated waste solution was found to be a function of the (CaO + MgO) / (SiO_2 + Al_2O_3) ratio of the samples characterized. No significant differences were detected in samples cured 2 months and 14 months in sealed containers at ambient indoor temperatures.

Slag and a blend of slag and cement hydrated with caustic 4.4 M Na salt solution resulted in the most crystalline matrix. In addition to poorly ordered C-S-H, these samples contained fairly well ordered C-S-H I (a precursor of 14Å tobermorite) and 11 Å Al-substituted tobermorite. These crystalline C-S-H phases did not form or were present in only trace amounts in slag blends containing about 45 to 62 mass percent fly ash. These slag-Class F fly ash blends had a higher silica plus alumina content relative to lime and magnesia than the blends that produced C-S-H I and Al-substituted tobermorite. The calcium silicate binder in the 10:45:45 mixture of cement : slag : fly ash was made up of poorly ordered C-S-H. The sample cured for 14 months may contain a small amount of the more crystalline calcium silicate hydrate phases.

Layered double hydroxides in the hydrotalcite (magnesium-aluminum carbonate hydroxide) and hydrocalumite / AFm phases (calcium aluminum hydroxide) were present in mixtures containing slag. The specific phase(s) were not identified because these phases form solid solutions and have a considerable amount of overlap in their x-ray patterns. Sodium nitrate was the only sodium salt phase identified in x-ray diffraction patterns of the samples hydrated with salt solution. Drying during x-ray diffraction sample preparation may have resulted in precipitation of the sodium nitrate or it may have been present in the samples prior to x-ray sample preparation. Sodium sulfate, aluminate, and carbonate may have been incorporated in the structures of the layered double hydroxide (AFm) type phases. These mixed metal layered double hydroxides make up an important fraction of the matrix in the slag containing blends hydrated with caustic salt solution. They are among the few oxide-based phases that exhibit substantial, permanent anion exchange capacity [Kirkpatrick, et al. 1999, Plamer, et al., 2009, and Zhang and Reardon, 2003]. They also contribute to the structural properties of cementitious matrices [Taylor, 1997].

INTRODUCTION

Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. Matrix phases can stabilize certain contaminants (co-precipitation, substitution, ion exchange, and / or sorption), influence processing properties, and are responsible for physical properties and durability of the cured waste forms. Consequently, characterization of the matrix (binder) mineralogy (chemical compositions and crystalline / non crystalline structures) is important for predicting contaminant leaching and evolution of the materials as a function of time and changing conditions.

This report documents sample preparation and x-ray diffraction results for a series of mixtures of sodium salt waste and cementitious binders.

OBJECTIVE

The objective of this report was to characterize the phase assemblages in the Cementitious Barriers Partnership reference case sodium salt waste form [Langton, 2009]. This information can be used to: 1) generate a base line for the evolution of the waste form as a function of time and conditions, 2) design new binders based on matrix mineralogy, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms and 5) identify appropriate phase solubility and thermodynamic data. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water / leachates.

BACKGROUND

Sodium salt waste forms generated in the DOE complex typically consist of a blend of ground granulated blast furnace slag (GGBFS), portland cement, and Class F fly ash. Blends of these ingredients have been used to treat caustic aqueous sodium salt waste streams generated from separation and recovery of isotopes for defense programs. The objective of the treatment is to provide a diffusion barrier for soluble contaminants, stabilize selected contaminants, and convert a liquid waste into a solid waste form suitable for disposal.

This effort was intended to obtain preliminary phase / mineralogy data for subsequent electron and neutron diffraction and microscopy analyses of the hydrated binder phases. An experimental plan to characterize the matrix phases was developed by SRNL researchers in conjunction E. Pierce, ORNL and documented in Task Technical and Quality Assurance Plan (TT/QAP) [Langton, 2012].

At the present time, the matrices of these cementitous waste forms are not well characterized because a large portion of the matrix is made up of phases that have poorly ordered structures and form solid solutions involving cation and anion substitutions. In addition, the matrix consists of micrometer and sub-micrometer particles inter grown to the extent that individual particles are difficult to characterize using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

EXPERIMENTAL METHOD

ASTM Type I water and a simulated sodium salt waste solution were used as the mixing fluids for the materials analyzed in this study. The simulated waste solution was based on the CBP reference case salt waste form. The simple salt solution composition is provided in Tables 1 and 2. This solution had a density of 1.207 g / ml and contained 25.13weight percent total dissolved solids (TDS).

Table 1. Sodium salt waste solution with a molar composition of a simple simulated sodium salt solution.

Component	M
Na	4.4E+00
Al	1.1E-01
Cr	5.8E-03
Re	1.6E-03
B	1.1E-02
K	5.4E-03
NO_3	2.2E+00
NO_2	3.7E-01
OH	1.8E+00
CO_3	1.4E-01
SO_4	4.6E-02
C_2O_4	9.3E-03
Cl	4.6E-03

Table 2. Ingredients used to prepare the simulated salt solution.

Compound	**g / L**
Water	balance
KNO_3	0.55
$NaNO_3$	154.37
NaOH (50%)	142.4
$Al(NO_3)_3 \cdot 9H_2O$	42.01
$NaNO_2$	25.66
Na_2CO_3	14.73
Na_2SO_4	6.59
Na_2CrO_4	0.94
$Na_3PO_4 \cdot 12H_2O$	1.9
$Na_2C_2O_4$	1.24
H_3BO_3	0.71
NaCl	0.27

The ingredients and proportions in the cementitious materials and mixtures prepared for x-ray diffraction characterization are provided in Table 3. Each mix was prepared as a large batch in a chemical fume hood using a paddle mixer with the blade set about 2 cm above the bottom of a 2000 ml beaker. The cementitious reagents were premixed by shaking them in a sealed plastic bag. The liquid was added to the beaker before the mixer was turned on and the rotational speed was adjusted to about 250 revolutions per minute (rpm). The corner of the bag containing the cementitious reagents was cut, and the contents of the bag were slowly added to the solution. After all of the solid reagents were added, the slurry was mixed for 3 minutes at a paddle speed adjusted to form a vortex but minimize air entrapment. After mixing, each mixture was cast into multiple 70 mL plastic containers. The containers were filled completely and capped. After setting on the bench top for 3 days the samples were over packed in a plastic bag to which a damp cloth was added to provide a moisture curing environment in case the caps were breeched. All samples were cured at ambient laboratory conditions.

Table 3. Material prepared for x-ray-diffraction characterization.

Sample No.	Sample Description (Ingredients and Proportions)					Water to cementitious materials mass ratio
	Portland cement I/II	Ground Granulated Blast Furnace Slag (Grade 100)	Class F fly ash	ASTM Type 1 water	4.4 M Na Salt Waste Simulant	
	(g)					
448-1A, 1B, 1C	Anhydrous cement	--	--	--	--	NA
448-2A, 2B, 2C	--	Anhydrous slag	--	--	--	NA
448-3A, 3B, 3C	--	--	Anhydrous fly ash	--	--	NA
448-4A to 4G	500	--	--	300	--	0.60
448-5A to 5G	--	500	--	300	--	0.60
448-6A to 6G	--	--	500	300	--	0.60
448-7A to 7G	751	--	--	--	602	0.60
448-8A to 8G	--	751	--	--	602	0.60
448-9A to 9G	--	--	751	--	602	0.60
448-10A to 10G	150	601	--	--	602	0.60
448-11A to 11G	150	--	601	--	602	0.60
448-12A to 12G	--	375.5	601	--	602	0.60
448-13A to 13G	75	338	338	--	602	0.60

One sample of each material was sent to E. Pierce, Oak Ridge National Laboratory, Oak Ridge, TN, after curing for 28 days. The intent was to obtain x-ray diffraction powder patterns at the ORNL as a precursor to neutron diffraction analyses at the ORNL Spallation Neutron Source. The neutron diffraction analyses were to be arranged by E. Pierce.

In addition, SRNL Analytical R&D Programs, performed x-ray diffraction analyses on identical samples cured for 14 months to evaluate the effect of curing time on the mineralogy. A Bruker DA Advance x-ray diffractometer with CuKα radiation (1.5405982 Å wave length) was used to generate the diffraction patterns. JADE x-ray analysis software from Materials Data Inc. was used to identify phases along with chemistry of the materials and information from the literature.

APPROACH

X-ray powder diffraction is one of several complimentary techniques for identifying phases in solid materials. In this study, an attempt was made to identify changes in the mineralogy starting with the anhydrous cement, slag, and fly ash and progressing to characterization of these materials hydrated with water and also with sodium salt solution. This information was used to help interpret and characterize the reaction products of selected blends of these cementitious materials as the result of hydration in water and salt solution was also performed.

RESULTS

The results are summarized in this paper. The actual diffraction patterns are provided elsewhere [Langton, 2014].

Anhydrous starting materials: Phases identified in the anhydrous Type II portland cement, Grade 100 GGBFS, and carbon burn-out (CBO) Class F fly[1] ash are listed in Table 8. The mineralogy of these materials is consistent with the phases reported in the literature. The x-ray diffraction techniques used in this study can detect minor amounts (greater than about 3 weight percent) of crystalline phases in the samples. Broad low intensity peaks in the powder x-ray diffraction patterns are indicative of anhydrous and hydrated poorly ordered silicate- based phases.

The portland cement, Sample 1A, contained alite (Ca_3SiO_5), larnite (Ca_2SiO_4), a ferrite phase ($Ca_2(Al,Fe)O_5$) and calcite ($CaCO_3$). Neither gypsum nor anhydrite was detected in the x-ray patterns although it is known to be inter-ground with the cement to control the initial hydration reactions. Since this cement contained a low amount of tricalcium aluminate ($Ca_3A_2O_6$) which was below the detection limit for the x-ray diffraction technique used, the amount of calcium sulfate required to control the tricalcium aluminate hydration reaction was probably also low.

The Grade 100 slag, Sample 2A, was predominantly a silicate glass (non-crystalline material) containing a trace amount of akermanite ($Ca_2Mg[Si_2O_7]$), a refractory calcium magnesium silicate phase that formed during the slag production. Calcite was also detected in the x-ray diffraction pattern and was assumed to form as the result of lime in the slag reacting with CO_2 in the air.

The Class F fly ash, Sample 3A, also consists of glassy material (non-crystalline) which contains mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2). The mullite formed as a refractory aluminum silicate phase when clays in the coal were melted and were subsequently crystallized. The quartz is a residual phase from the coal itself.

Hydration of starting materials in water: Phases detected in the cementitious starting materials hydrated in water are also listed in Table 8. These samples were cured in sealed containers at room temperature for 2 and 14 months. The amount of non-crystalline or poorly ordered C-S-H in the cement + water samples, 4A and 4G, may have increased between 2 and 14 months but quantitative x-ray diffraction was not perfomed. Ettringite, an AFt phase, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, calcium aluminum sulfate hydrate, and a trace amount of an AFm phase, probably monosulfoaluminate were detected in the x-ray patterns.

Poorly ordered material, interpreted as unreacted anhydrous glass, was the predominant phase in the GGBFS samples 5A and 5G cured in water for 2 and 14 months, respectively. However, some hydration of the slag in water seems to have occurred in the 14 month old sample as indicated by detection of a

---

[1] Carbon Burn Out consists of combusting residual carbon in fly ash to produce a consistent, low carbon (< 2.5 wt. %) high quality pozzolan. The drivers for CBO are to control the amount of carbon in fly ash to levels acceptable for construction applications and to eliminate ammonia contamination of the ash. Introduction of low NOx burners in recent years at coal fired power plants has resulted in increased levels of residual carbon in the ash. Also ammonia injection is used in some plants to enhance electrostatic precipitator performance and is being applied in selective catalytic reduction and selective non-catalytic flue gas treatment systems to meet the new more stringent NOx off gas standards. (Removal of ammonia is considered for fly ash if it contains more than about 50 -100 ppm if it is to be used in concrete applications.)

Table 4. Phases identified in XRD powder patterns of anhydrous cementitious reagents and individual hydrated materials and the corresponding International Center for Diffraction Data (ICDD) database card numbers.

Material	Sample No. (Cure Time)	Glass NCS	Hyd-rated NCS	CSH 034-0002	11Å Al-Tober-morite 019-0052	Hydro-talcite 041-1428	Hydro-calumite AFm 031-0245	Ettring-ite AFt 041-1451	Port-landite 004-0733	Ca_3SiO_5 049-0442	Ca_2SiO_4 033-0902, 033-0302	Brown-millerite $Ca_2(Al,Fe)O_5$ 042-1469	Gyp-sum 033-0311	Quartz SiO_2 046-1045	Mullite $Al_6Si_2O_{13}$ 015-0776	Aker-manite 035-0592	Calcite $CaCO_3$ 005-0586	Natra-tine $NaNO_3$ 036-1474	Comments
Type II cement	1A	--	--	--	--	--	--	--	--	X	X	X	--	--	--	--	x	--	
Grade 100 slag	2A	X	--	--	--	--	--	--	--	--	--	--	--	--	--	?	?	--	
Class F Fly ash	3A	X	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	--	
Type II Cement + Water	4A (2 mo.)	--	?	?	?	x	--	X	X	--	?	--	--	--	--	--	--	--	Bad pattern
	4G (14 mo.)	--	X	--	?	x	--	X	X	X	--	--	?	--	--	--	--	--	? Calcium iron sulfate hydrate 040-0292
Slag + Water	5A (2 mo.)	X	?	?	?	--	--	--	--	--	--	--	--	--	--	--	--	--	
	5G (14 mo.)	X	?	--	--	x	?	--	--	--	--	--	--	--	--	x	x	--	
Fly ash + Water	6A (2 mo.)	X	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	--	
	6 (14 mo.)	Not evaluated																	

X = Several major peaks identified. x = Peaks identified with low relative intensity. ? = Peaks overlap other peaks, no unique peak identified, Tr = Identified based on small peaks and chemistry. -- = Not identified.

small amount of a hydrotalcite-type phase[2] or a mixture of hydrotalcite and hydrocalumite (AFm). C-S-H may be present in the sample but SEM/EDX or other techniques are required to determine whether it formed. Calcite and possibly akermanite, present in the unreacted slag, were also detected in the GGBFS hydrated in water for 2 and 14 months. Class F fly ash was essentially inert in the presence of water (samples 6A) which was cured for 2 months. The same phases present in the unhydrated the CBO Class F fly ash were detected in this sample, i.e. glass, and the refractory phases mullite and quartz.

Hydration of Starting Materials in 4.4 M Na Salt Solution: Phases detected in samples of the starting reagents, Type I/II portland cement, GGBFS, and CBO Class F fly ash, hydrated in 4.4 M Na salt solution are listed in Table 9. The phases detected by x-ray diffraction for the cement hydrated in salt solution samples (7A and 7E) included: poorly ordered C-S-H gel phase, portlandite, an AFm phase (calcium aluminate sulfate hydrate), unreacted larnite, and nitratine ($NaNO_3$) a component in the salt solution / pore solution.

Based on the powder pattern phase identifications, hydration of GGBFS in 4.4 M Na solution (Samples 8A and 8G) resulted in formation of fairly well crystallized material C-S-H I and aluminum substituted 11 Å tobermorite, in addition to a hydrotalcite-like phase and / or a mixture of hydrotalcite- and hydrocalumite-like phases. Some material, either unreacted glass or poorly ordered C-(Al)-S-H, may also be present in samples cured for 2 and 14 months. Additional characterization techniques are required to determine if residual slag or poorly ordered C-(Al)-S-H or other amorphous phases are present. Quartz and a calcium iron oxide were identified based on d-spacings but were not detected in the slag and could not have formed during hydration. Addition work is being performed to obtain reasonable phase identification for those d-spacings attributed to those diffraction peaks.

No additional crystalline phases were detected in the Class F fly ash cured in 4.4 M Na salt solution (Samples 9A and 9F). Residual mullite and quartz were detected in the x-ray diffraction patterns along with poorly ordered or amorphous material which is probably a mixture of silicate glass and hydrated glass. Exposure to caustic solutions results in partial to complete dissolution of the fly ash cenospheres.

Hydration of Blends in Salt Solution: Mineralogies of the blended binders are listed in Table 10. Samples 10 A and B were prepared with a 1 : 3 mixture by weight of cement : slag and were hydrated with 4.4 M Na salt solution for 2 and 14 months, respectively. Both samples contained fairly well ordered C-S-H I and aluminum substituted 11 Å tobermorite in addition to more than one AFm-type phase, either hydrotalcite or a mixture of hydrotalcite and hydrocalumite. Poorly ordered C-S-H may be present but could not be differentiated from residual slag glass. Larnite (from the anhydrous cement) and akermanite and calcite (from the anhydrous slag) were also detected in trace amounts. $NaNO_3$ was also present in both x-ray diffraction patterns and in all patterns for materials hydrated with the sodium salt solution. The samples cured for 2 and 14 months had similar phase assemblages.

Samples 11A and 11G were prepared with a 1 : 3 mixture of cement : Class F fly ash. These samples were hydrated for 2 and 14 months with 4.4 M Na salt solution. The reaction product in both of these samples was primarily poorly ordered C-S-H. Residual larnite, mullite, and quartz were also detected in both samples in addition to $NaNO_3$. The 2 and 14 month old samples do indicate changes in the calcium aluminate (sulfate) hydrate phases as a function of curing time. More detailed characterization is required to determine the composition and structure of these layered hydrates.

---

[2] Hydrotalcite-type phases are layered double hydroxides (LDHs) with metal cations in the main layers and anion and water in the interlayers. They are structurally related to brucite, $Mg(OH)_2$. The general formula is $Mg_6Al_2(OH)_{16}$.

Table 5. Phases identified in XRD powder patterns of individual cementitious materials hydrated with 4.4 M Na salt solution and the International Center for Diffraction Data (ICDD) Database Card Numbers.

Material	Sample No. Cure Time (mo)	Silicate Glass NCS	C-S-H Hydrated NCS	CSH I 034-0002	11Å Al-Tobermorite 019-0052	Hydrotalcite 041-1428	Hydrocalu-Mite 031-0342	Ettringite 041-1451	Hydrogarnet	Portlandite 004-0733	Ca_3SiO_5 049-0442	Ca_2SiO_4 033-0902	$Ca_2(Al,Fe)O_5$ 042-1469	Gypsum 033-0311	Quartz 046-1045	Mullite 015-0776	Akermanite 035-0592	Calcite 005-0586	$NaNO_3$ 036-1474	Comments
Cement + Salt Solution	7A (2)	--	X	--	--	--	x 049-0457	--	--	X	--	x	--	--	--	--	--	--	X	
	7E (14)	--	X	--	--	--	x 049-0457	--	--	X	--	x	--	--	--	--	--	--	X	
Slag + Salt Solution	8A (2 mo.)	?	X	X	X	X	?	--	--	--	--	--	--	--	X	--	--	--	X	
	8B (14 mo.)	?	X	X	X	X	?	--	--	--	--	--	--	--	X	--	--	--	X	
Fly ash + Salt Solution	9A (2 mo.)	X	--	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	X	Low Counts
	9F (14 mo.)	X	--	--	--	--	--	--	--	--	--	--	--	--	X	X	--	--	X	X

X = Several major peaks identified. x = Peaks identified with low relative intensity. ? = Peaks overlap other peaks, no unique peak identified, Tr = Identified based on small peaks and chemistry, -- = Not identified.

Table 6. Phases identified in XRD powder patterns of blends of cementitious materials hydrated with 4.4 M Na salt solution and the International Center for Diffraction Data (ICDD) Database Card Numbers.

Material	Sample No. Cure Time (mo)	Glass NCS	Hydrated NCS	CSH I 034-0002	11Å Al-Tobermorite 019-0052	Hydrotalcite 041-1428	Hydrocalumite 031-0245	Ettringite 041-1451	Hydrogarnet	Portlandite 004-0733	Ca_3SiO_5 049-0442	Ca_2SiO_4 033-0902, 033-0302	$Ca_2(Al, Fe)O_5$ 042-1469	Gypsum	Quartz 046-1045	Mullite 015-0776	Akermanite 035-0592	Calcite 005-0586	$NaNO_3$ 036-1474	Comments
Cement + Slag + Salt Solution	10A (2 mo.)	?	X?	X	X	X	?	--	--	--	x	x	--	--	--	--	x	x	X	061-0217 $CaAl_2O_410{\cdot}H_2O$
	10B (14 mo.)	?	X?	X	X	X	?	--	--	--	--	x	--	--	--	--	x	x?	X	061-0217 $CaAl_2O_410{\cdot}H_2O$
Cement + Fly Ash + Salt Solution	11A (2 mo.)	?	X	--	--	--	x	--	--	--	--	x	--	--	X	X	--	--	X	
	11C (14 mo.)	?	X	--	--	--	--	?	--	--	--	x	--	--	X	X	--	--	X	Possibly 2 new phases K_2SO_4, $NaAl(AlSi_3)O_{10}(OH)_2$
Slag + Fly Ash + Salt Solution	12A (2 mo.)	?	X	--	--	--	X	--	--	--	--	--	--	--	X	X	--	--	X	
	12F (14 mo.)	?	X	--	--	--	X	--	--	--	--	--	--	--	X	X	--	--	X	
Cement + Slag + Fly Ash + Salt Solution	13A (2 mo.)	?	X	--	--	X	??	--	--	--	--	--	--	--	x	x	?	?	X	
	13G (14 mo.)	?	X	?	--	X	??	--	--	--	--	--	--	--	X	X	?	x	X	

X = Several major peaks identified. x = Peaks identified with low relative intensity. ? = Peaks overlap other peaks, no unique peak identified, Tr = Identified based on small peaks and chemistry, -- = Not identified.

Samples 12A and 12F were prepared with a 2 : 3 mixture of slag and fly ash and cured for 2 and 14 months, respectively. These samples contained poorly ordered C-S-H and one or more layered double hydroxide phases (hydrotalcite, hydrocalumite, carboaluminate phase or a mixture of these phases) in addition to residual mullite, quartz, and $NaNO_3$. Crystalline C-S-H I and Al substituted tobermorite were not formed in this blend.

Samples 13A and 13G were prepared with a 10 : 45 : 45 mixture of cement : slag : fly ash and were cured for 2 and 14 months, respectively. These samples contained mainly poorly ordered C-S-H and hydrotalcite. Trace amounts of CSH I and / or Na substituted 11 Å tobermorite (2-theta of 6-7º) and one or more layered double hydroxide phases (hydrotalcite, hydrocalumite, or a mixture of these phases), residual mullite, quartz, calcite, and possibly akermanite in addition to $NaNO_3$.

DISCUSSION

The mineralogy of the samples cured for 2 and 14 months is determined by the mineralogy and bulk composition of the hydraulic and pozzolanic components and the chemistry of the mixing water or aqueous salt solution. The compositions of the cement, slag, and fly ash used to prepare the paste samples analyzed in this study are provided in Attachment 2. The values for five oxides, CaO, MgO, Al_2O_3, Fe_2O_3, and SiO_2, which together make up about 90 or more of the mass percent of each binder material were averaged and normalized. See Tables 11 and 12, respectively. The complete oxide compositions for the Portland cement, Grade 100 GGBFS, and Class F fly ash are provided elsewhere [Langton and Missimer, 2014].

The sums of the normalized basic oxides were divided by sums of the acidic oxides, i.e., (CaO and MgO) / (SiO_2, Al_2O_3, and Fe_2O_3) for individual ingredients (cement, slag, and fly ash) and for four blends all of which were hydrated with the 4.4 M Na salt solution. Results are tabulated in Table 12 and plotted in Figure 1. (Aluminum as aluminate in the salt solution was not included in the calculation.)

Based on the (CaO + MgO) / (SiO_2 + Al_2O_3) ratios the mineralogy of the three individual ingredients and four blends hydrated with the alkaline salt solution can be loosely grouped into four categories shown below:

(CaO + MgO) / (SiO_2 + Al_2O_3)	**Binder Phases**
> 2	Poorly ordered C-S-H gel (Ca/Si > 1.5) + $Ca(OH)_2$
~ 1 to 1.3	Ordered CSH I (Ca/Si ~ 1.1 to > 1.5) + 11 Å tobermorite
~ 0.3 to 0.5	Poorly ordered C-S-H gel
~ 0.05	Si dissolution

The (CaO + MgO) / (SiO_2 + Al_2O_3) ratios of the ternary blends currently used and being considered for DOE salt waste forms fall in the 0.3 to 0.5 range and result in poorly ordered C-S-H (possibly with Na and Al substitution) matrix phases. Mineralogy is related to some physical properties, such as, dimensional stability as a function of temperature and moisture conditions, porosity, hydraulic conductivity, and durability. Consequently, mineralogy of waste form matrices is important to performance and evolution as a function of changing conditions and time. Mineralogy is also important for selecting appropriate thermodynamic data for long term equilibrium calculations used in chemical degradation scenarios.

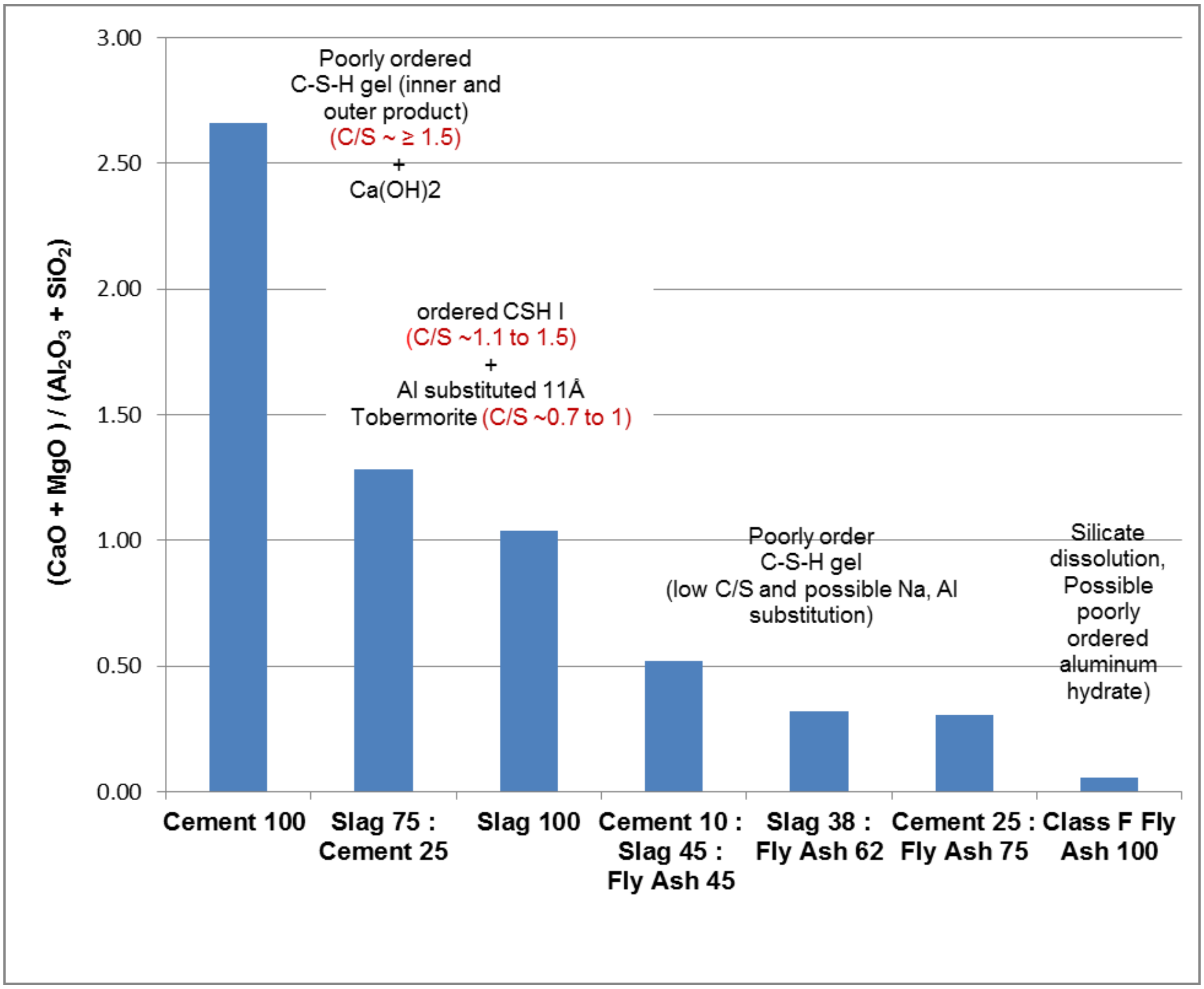

Figure 1. Calcium silicate hydrate phases in binders hydrated with 4.4 M Na salt solution as a function of (CaO + MgO) / (Al_2O_3 + SIO_2) ratio.

Table 7. Major oxide results for cement, slag and Class F fly ash.

Oxide	Cement A	Cememt B	**Cement Ave**	Slag A	Slag B	**Slag Ave**	Fly Ash A	Fly Ash B	**Fly Ash Ave**
	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %
CaO	64.4	64.4	**64.4**	35.8	36.7	**36.3**	2.4	2.4	**2.4**
MgO	1.19	1.2	**1.2**	13.3	12.9	**13.1**	1.5	1.5	**1.5**
Al_2O_3	5.25	5.1	**5.2**	7.8	8.1	**8.0**	24.9	24.8	**24.9**
Fe_2O_3	3.72	3.9	**3.8**	0.3	0.3	**0.3**	12.8	12.8	**12.8**
SiO_2	19.2	19.7	**19.5**	39.8	39.2	**39.5**	48.4	47.9	**48.2**
TOTAL	93.76	94.3	94.0	97.0	97.2	97.1	90.1	89.4	89.8

Table 8. Normalized selected oxides for starting materials and four blends.

Oxide	**Normalized Blend 10 cement: 45 slag: 45 fly ash**	**Normalized Blend 25 cement: 75 fly ash**	**Normalized Blend 25 cement: 75 slag**	**Normalized Blend 38 slag: 62 fly ash**	**Normalized Cement**	**Normalized Slag**	**Normalized Class F Fly Ash**
	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	
CaO	24.9	19.2	45.1	15.8	68.5	37.3	2.7
MgO	7.0	1.6	10.4	6.2	1.2	13.5	1.7
Al_2O_3	16.7	22.2	7.5	20.3	5.5	8.2	27.7
Fe_2O_3	7.0	11.8	1.3	9.0	4.1	0.3	14.3
SiO_2	44.5	45.4	35.7	48.7	20.7	40.7	53.6
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Oxide Ratios							
$(CaO + MgO) \div (SiO_2 + Al_2O_3)$	0.52	0.31	1.29	0.32	2.66	1.04	0.05
$(CaO + MgO) \div (SiO_2 + Al_2O_3 + Fe_2O_3)$	0.47	0.26	1.25	0.28	2.30	1.03	0.05
$CaO \div (SiO_2 + Al_2O_3)$	0.41	0.28	1.04	0.23	2.61	0.76	0.03

Shaded ratios are plotted in Figure 1.

CONCLUSIONS

The mineralogy of the reaction products for materials and blends of materials hydrated with caustic 4.4 M Na salt solution depended on the mineralogy and proportions of the cementitious ingredients and the bulk oxide compositions of the mixtures. Poorly ordered /amorphous C-S-H was detected in mixtures of cement and slag, cement and fly ash, slag and fly ash and the waste form blend containing cement, slag, and fly ash when hydrated with caustic 4.4 M Na salt solution. Only the neat slag and cement + slag mixture hydrated with caustic 4.4 M Na salt solution contained fairly well crystallized C-S-H I and Al substituted 11 Å tobermorite.

Hydrotalcite and hydrocalumite-like phases and mixtures of these LDH phases were present in the all of the blended samples. However the proportions of these phases and probably their compositions varied. Not surprisingly, the phase assemblage in the 10:45:45 blend of cement : slag : fly ash resembled that of the slag : fly ash blend.

The mineralogy of the hydrated materials evaluated did not change significantly between 2 months and 14 months curing in sealed containers. Characterization of samples cured for much longer times is recommended. Both drying conditions and curing in the presence of excess water are expected to result in changes in the mineralogy.

Cement hydrated for up to 14 months in water and up to 14 months in salt solution contained, poorly ordered C-S-H, portlandite ($Ca(OH)_2$), and an AFm phase. The AFm phase identified in the salt solution hydrated sample was a sodium aluminate sulfate. Ettringite ($Ca_6(Al,Fe)_2(OH)_{12}(SO_4)_3.26H_2O$) was identified in the water hydrated cement sample but not in the salt solution hydrated sample. Unreacted larnite (Ca_2SiO_4) from the cement and $NaNO_3$ from the salt solution were detected in the salt solution hydrated sample.

Class F fly ash showed no significant reaction with water in the samples hydrated for 2 and 14 months. Hydration of the fly ash in salt solution resulted in dissolution of some of the glassy material as indicated by residual mullite “baskets”. The only crystalline phases detected in the x-ray diffraction patterns were the refractory phases, mullite and quartz, present in the anhydrous fly ash.

GGBFS did not hydrate or hydration was very limited after 2 months in water based on x-ray diffraction results. However, after 14 months, a small amount of LDH phase (hydrotalcite and / or hydrocalumite (AFm) or a mixture) was detected in the x-ray pattern. In contrast, activation of the slag in the 4.4 M Na salt solution resulted in formation of fairly well crystallized C-S-H I and Al substituted 11 Å tobermorite ($Ca_5Si_3Al(OH)O_{17}\cdot 5H_2O$). These two ordered calcium silicate hydrates were detected in slag and mixtures of slag and cement hydrated with 4.4 M Na salt solution.

The mineralogy of the cured cementitious material influences the physical properties (strength, stiffness, etc.) of the cured material due to the degree of polymerization (chain length) and tetrahedron arrangement. Information about the mineralogy of hydrated cementitious materials and blends of these ingredients is needed to design waste form matrices, select ingredients and make adjustments in material proportions. Information presented in this report is an initial step in developing phase diagrams for the hydrated systems in which caustic sodium salt solutions are used as the hydration fluid for waste forms.

REFERENCES

ASTM C150-12. "Standard Specification for Portland Cement," 2012, ASTM International, West Conshohochen, PA, 19428.

ASTM C989-14. "Standard Specification for Slag Cement for Use in Concrete and Mortars," 2014, ASTM International, West Conshohochen, PA, 19428.

ASTM D1193-11. "Standard Specification for Reagent Water," 2011, ASTM International, West Conshohochen, PA, 19428.

Bumrongjaroen, W., I. S. Muller, and I. L. Pegg, 2007. "Characterization of Glassy Phase in Fly Ash from Iowa State University", VSL-07R520X-1, Vitreous State laboratory, Washington DC, 2007.

Chen, W, H. J. H. Brouwers, 2007. "The hydration of slag, Part 1: Reaction models for alkali-activated slag," J. Mater. Sci. 42:428-443.

Chen, W, H. J. H. Brouwers, and Z. H. Shui, 2007. "Three-dimensional computer modeling of slag cement hydration," J. Mater. Sci., 42:9595-9610.

Katsioti, M, P.E. Tsakiridis, P. Giannatos, Z.Tsibouki, and J. Marinos, 2009. "Characterization of various cement grinding aids and their impact on grindability and cement performance," Construction and Building Mat., 23(5):1954-1959.

Keppeler, J.G. and W.T.Frady, 2009. "Carbon Burn-Out, commercialization and experience update," http:/www.pmiash.com/cbo/acaa01paper.html.

Kirkpatrick, R. J., P. Yu, X Hou, and Y. Kim, 1999. "Interlayer structure, anion dynamics, and phase transitions in mixed-metal layered hydroxides: Variable temperature 35Cl NMR spectroscopy of hydrotalcite and Ca-Aluminate hydrate (hydrocalumite)," Am. Min. 4:1186-1190.

Langton, C.A. and D. M. Missimer, 2014. "X-ray Diffraction of Slag-Based Sodium salt Waste forms," Cementitious Barriers Partnership, CBP-TR-2014-0005, Savannah River National Laboratory, Savannah River Site, Aiken, South Carolina 29808.

Langton, C.A. and H.H. Burns, 2012. "Characterization of phases in Savannah River Site saltstone using neutron diffraction at the ORNL Spallation Neutron Source, Task Technical and Quality Assurance Plan (TT/QAP)", SRNL-RP-2012-00448, Savannah River National Laboratory, Aiken, SC 29801.

Langton, C.A., D.S. Kosson, A.C. Garrabrants, and K.G. Brown, 2009. "Reference cases for us in the Cementitious Barriers Partnership Project," SRNL-STI-2009-00005, WM Symp, 2009.

Li, Chao, H. Sun, and L.Li, 2011. "Glass phase structure of blast furnace slag," *Advanced Materials Research*, 168-170:3-7.

Matschei, T., B. Lothenbach, F.P. Glasser, 2007. The AFm phase in portland cement," Cem. And Concrete Res. 37:118-130

McCarthyG. J., 1988. "X-ray powder diffraction for studying the mineralogy of fly ash." Fly ash and coal conversion by-products: characterization, utilization and disposal," Mat. Res. Soc. Proc., 113:75-86.

Myers, R. J., S. A. Bernal, R.S.Nicolas, and J. L. Provis, 2013. "Generalized structural description of calcium-sodium aluminosilicate hydrate gels: The cross-linked substituted tobermorite model," Langmuir, 29:5294-45406.

Palmer, S.J., T. Nguyen, and R. L. Frost, 2009. "Hydrotalcites and their role in coordination of anioins in Bayer liquors: Anion binding in layered double hydroxides," Coordination Chemistry Reviews 253(1-2):250-267.

Richardson, I.G. and G. W. Groves, 1992. "Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag," J. Mater. Sci. 27:6204-6212.

Stutzman, P., 2014. Personal communication.

Taylor, H. F. W, 1997. Cement Chemistry, 2nd ed., Thomas Telford, NY, NY.

Zhang, M and E. J. Reardon, 2003. "Removal of B, Cr, Mo, and Se from wastewater by incorporation into hydrocalumite and ettringite," Environ. Sci. Technol., 37(13):2947-295.

ACKNOWLEDGEMENTS

The authors acknowledge E. Pierce, Oak Ridge National Laboratory for performing the x-ray diffraction analyses on samples cured for 2 months.

This paper was prepared in conjunction with work accomplished at the Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, in support of the Savannah River Nuclear Solutions Cooperative research Agreement (CRADA) CR-08-001 (Cementitious Barriers Partnership) under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

DISCLAIMER