

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

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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 $(\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$ 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 cementitious 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 25.13 weight 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 ₂ O 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 ·9H ₂ O	42.01
NaNO ₂	25.66
Na ₂ CO ₃	14.73
Na ₂ SO ₄	6.59
Na ₂ CrO ₄	0.94
Na ₃ PO ₄ ·12H ₂ O	1.9
Na ₂ C ₂ O ₄	1.24
H ₃ BO 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 breached. 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 CuK α 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 fly¹ 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 ($\text{Ca}_2(\text{Al,Fe})\text{O}_5$) 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 ($\text{Ca}_3\text{A}_2\text{O}_6$) 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 ($\text{Ca}_2\text{Mg}[\text{Si}_2\text{O}_7]$), 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 ($\text{Al}_6\text{Si}_2\text{O}_{13}$) 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 performed. Ettringite, an AFt phase, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, 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	Hydrated NCS	CSH 034-0002	11Å Al-Tobermorite 019-0052	Hydro-talcite 041-1428	Hydro-calumite AFm 031-0245	Ettringite AFt 041-1451	Portlandite 004-0733	Ca ₃ SiO ₅ 049-0442	Ca ₂ SiO 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 ₆ Si ₂ O 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 phase² 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. Additional 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, $\text{Mg}(\text{OH})_2$. The general formula is $\text{Mg}_6\text{Al}_2(\text{OH})_{16}$.

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)	Sili-cate Glass NCS	C-S-H Hydrated NCS	CSH I 034-0002	11Å Al-Tobermorite 019-0052	Hydro-talcite 041-1428	Hydro-calumite 031-0342	Ettringite 041-1451	Hydro-garnet	Port-landite 004-0733	Ca ₃ SiO ₅ 049-0442	Ca ₂ SiO ₄ 033-0902	Ca ₂ (Al,Fe)O ₅ 042-1469	Gyp-sum 033-0311	Quartz 046-1045	Mullite 015-0776	Aker-manite 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	Hydro-talcite 041-1428	Hydro-calumite 031-0245	Ettringite 041-1451	Hydro-garnet	Port-landite 004-0733	Ca ₃ SiO ₅ 049-0442	Ca ₂ SiO ₄ 033-0902, 033-0302	Ca ₂ (Al, Fe)O ₅ 042-1469	Gyp-sum	Quartz 046-1045	Mullite 015-0776	Aker-manite 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 ₂ O ₄ 10•H ₂ O
	10B (14 mo.)	?	X?	X	X	X	?	--	--	--	--	x	--	--	--	--	x	x?	X	061-0217 CaAl ₂ O ₄ 10•H ₂ O
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 ₂ SO 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 NaNO₃. 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 6-7°) 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 NaNO₃.

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, Al₂O₃, Fe₂O₃, and SiO₂, 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) / (SiO₂, Al₂O₃, and Fe₂O₃) 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) / (SiO₂ + Al₂O₃) 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) / (SiO₂ + Al₂O₃)	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) / (SiO₂ + Al₂O₃) 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.

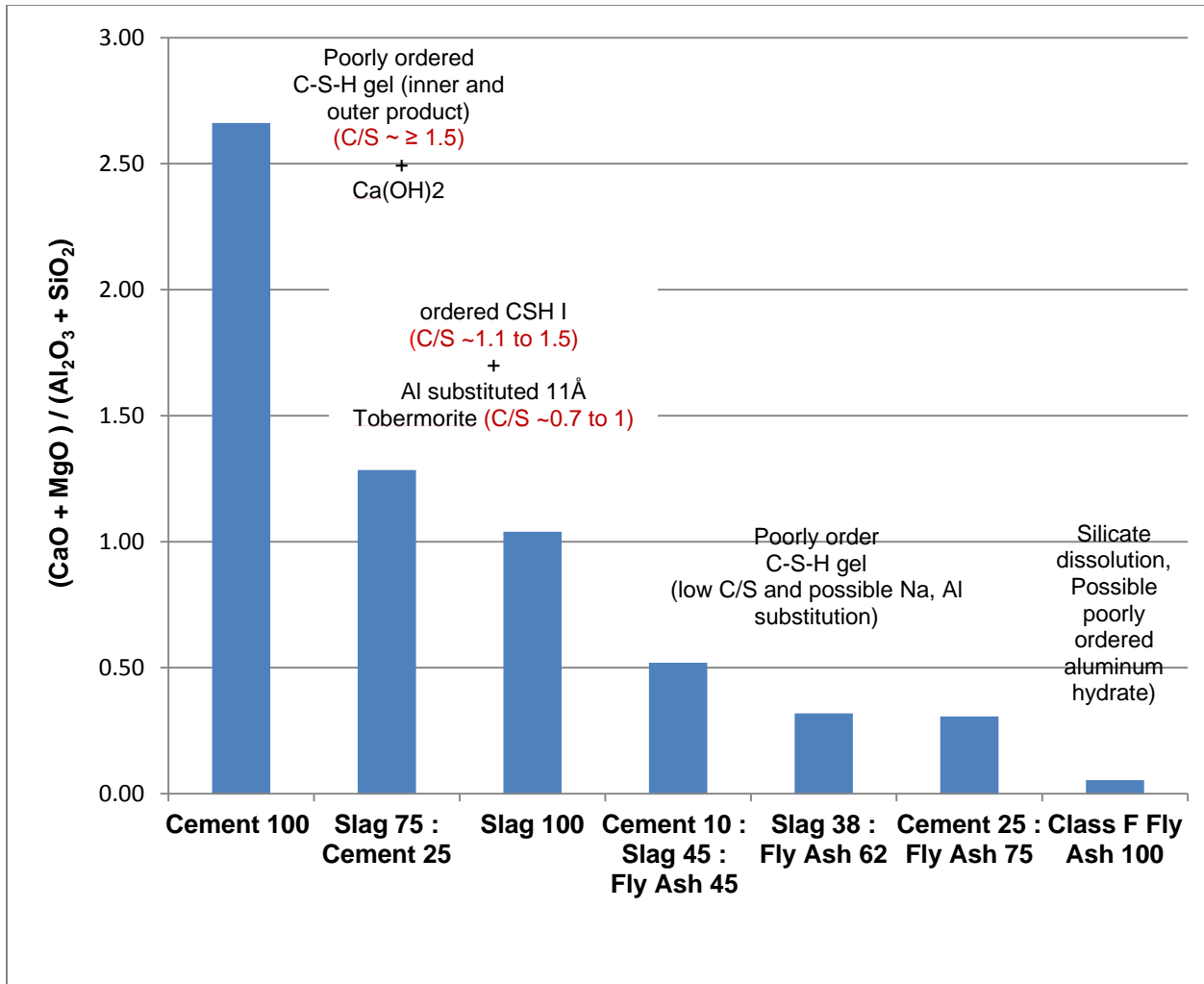


Figure 1. Calcium silicate hydrate phases in binders hydrated with 4.4 M Na salt solution as a function of (CaO + MgO) / (Al₂O₃ + SiO₂) ratio.

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

Oxide	Cement A	Cement 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 ₂ O ₃	5.25	5.1	5.2	7.8	8.1	8.0	24.9	24.8	24.9
Fe ₂ O 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 ₂ O ₃	16.7	22.2	7.5	20.3	5.5	8.2	27.7
Fe ₂ O 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) ÷ (SiO ₂ + Al ₂ O ₃)	0.52	0.31	1.29	0.32	2.66	1.04	0.05
(CaO + MgO) ÷ (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)	0.47	0.26	1.25	0.28	2.30	1.03	0.05
CaO ÷ (SiO ₂ + Al ₂ O 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 ($\text{Ca}(\text{OH})_2$), and an AFm phase. The AFm phase identified in the salt solution hydrated sample was a sodium aluminate sulfate. Ettringite ($\text{Ca}_6(\text{Al,Fe})_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) 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 ($\text{Ca}_5\text{Si}_3\text{Al}(\text{OH})\text{O}_{17} \cdot 5\text{H}_2\text{O}$). 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.

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ABSTRACT

The Waste Treatment and Immobilization Plant (WTP) in Hanford, Washington, is the nation's largest environmental remediation construction project. In 2012, at the WTP's High-Level Waste (HLW) Facility, the U.S. Department of Energy (DOE), Office of River Protection (ORP) restricted construction work at the Hazard Category 2 nuclear facility because of unresolved technical issues associated with the facility and of misalignment of the design and nuclear safety basis. By 2013, as additional issues were discovered, ORP limited HLW design and procurement activities.

Addressing the technical issues and the misalignment of the design basis with the Preliminary Documented Safety Analysis (PDSA) is a priority for ORP. A proposal was developed to use the concept of a safety design strategy (SDS), as documented in DOE-STD-1189-2008, *Integration of Safety into the Design Process*, as a planning mechanism to support facility design and PDSA alignment. The standard provides the processes to develop an SDS that will ensure safety is integrated into design early in the project, by the start of preliminary design. Ultimately, as design progresses, an SDS is intended to support development of the project's PDSA. However, in this unique case, the HLW Facility design and construction phase has progressed beyond Critical Decision 3 and DOE-STD-1189-2008 was issued in 2008, 6 years after ORP approved the first WTP PDSA.

In July 2013, ORP and the contractor recognized that the unresolved technical issues and design - safety basis misalignment should be addressed through a renewed look at nuclear safety requirements, and agreed that developing an SDS tailored to the criteria in DOE-STD-1189-2008 provided the best path forward to better integrate design and safety. Development of the SDS for the HLW Facility was one of many goals ORP established in a plan that describes how ORP will determine whether, and under what conditions, the contractor should be authorized to proceed with production engineering, procurement, and construction activities for the HLW Facility.

Over the next several months, the contractor developed the draft SDS, identifying design basis accidents and control strategies for those accidents. ORP monitored progress and, when appropriate, provided recommendations.

In April 2014, the contractor provided a draft SDS to ORP for initial review by an independent DOE Review Team. The Review Team was comprised of representatives from nuclear safety, criticality safety,

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engineering, fire protection, the Office of Environmental Management, the Assistant Manager WTP, and the DOE Chief of Nuclear Safety. A unique draft document review and interactive review process, facilitated through work sessions and continuous communication with the contractor, culminated in the development of 147 technical comments on topics varying from SDS implementation to hydrogen deflagration in vessels.

Comment resolution sought to improve project clarity, delineation of control strategies, and, holistically, facilitate integration of safety into design in the SDS, as it will guide the restart of the HLW Facility production engineering and limited procurement and construction activities. All comments were resolved in support of a contractor submission of the final SDS to ORP at the end of June 2014. Successful resolution of these comments was achieved by continuing the real-time response and incorporation interaction with the contractor to ensure that mutual objectives were satisfied. The response times were facilitated through telephone, email, and a shared file server accessible to contractor and DOE reviewers across the DOE complex. As a measure of success of this process, the Safety Basis Approval Authority (ORP Manager) and the WTP Federal Project Director approved the SDS on August 1, 2014, with no conditions of approval.

DOE and the contractor recognized that it would be difficult to implement the SDS without changes to the existing contractor's engineering and nuclear safety processes. Accordingly, the contractor developed or revised a significant number of engineering and nuclear safety plans and procedures to implement the SDS into the design process. Over the coming year, the contractor will conduct a gap analysis between the SDS and the presently approved PDSA to incorporate the design basis accidents and preferred control strategies developed from the SDS into the PDSA. In addition, ORP will conduct an assessment of the contractor's implementation of the SDS into the design process at the appropriate stage of implementation, within 6 to 12 months of approval. Although the SDS was developed late in the HLW project timeline, the document will facilitate alignment of design and the safety basis, and is a key step in the return to full production engineering for the HLW Facility.

INTRODUCTION

The U.S. Department of Energy (DOE) is contracting with Bechtel National, Inc. (Bechtel) to design, construct, and commission the Waste Treatment and Immobilization Plant (WTP) to pretreat and vitrify high-level waste (HLW) and low-activity waste as a means of remediating the Hanford tank farm inventory. The WTP mission is to process and stabilize approximately 212 thousand cubic meters (56 million gallons) of mixed radioactive and chemical waste currently stored at the Hanford Site. The waste will be removed from 177 aging underground storage tanks, enabling follow-on remediation of these tanks. Approximately one third of the tanks have leaked, contaminating the subsurface and threatening the nearby Columbia River. Given the magnitude of potential consequences to the nearby population and the acreage affected by the Columbia River, cleanup of these tanks is a national priority and DOE instituted a design-build paradigm for the WTP Project. The design-build approach called for construction of the facilities to begin prior to completion of the design. Construction of the WTP began in October 2001.

High-Level Waste Facility

WTP is a complex project with a construction site spanning 26 hectares (65 acres) and a facility design life of 40 years. The overall WTP scope includes designing, constructing, and operating four nuclear facilities to receive waste from the Hanford tank farms and to process and vitrify that waste. One of the facilities, the HLW Facility, will be a 46.5 thousand square meter (half million square feet) facility composed of a five-story, concrete and steel structure with melter cave areas that house the vitrification systems for production of immobilized HLW. The HLW Facility design production capacity is 7.5 metric tons of glass per day. Two identical melters immobilize concentrated HLW feed. Electrodes are used in the melters to attain nominal glass melt pool temperatures between 1,100°C and 1,200°C. Molten glass will be poured into immobilized HLW canisters as permanent packaging for disposal. The *Preliminary Documented Safety Analysis to Support Construction Authorization; HLW Facility Specific Information* to support construction authorization was initially approved by DOE in August 2002. Subsequently, there have been 38 updates and revisions to the document through July 2013.

Problem Statement

From August 2012 to March 2013, technical, design, and safety basis issues were identified with the HLW Facility heretofore under construction with design completion proceeding in parallel in accordance with the original design-build approach. At the time, the HLW Facility was approximately 89 percent design complete and 43 percent construction complete. Due to the technical, design, and safety basis issues, DOE Office of River Protection (ORP) issued direction to Bechtel that restricted HLW construction, procurement, and engineering activities. In order to resolve this situation, an approach was needed to address a partially constructed facility with a historically approved Preliminary Documented Safety Analysis (PDSA) that affects many technical issues that had arisen subsequent to that approval. The challenge is to resolve those issues in a manner that utilizes existing components and structures to the extent practical while ensuring timely completion of a facility that can be safely operated in compliance with the applicable regulatory requirements.

In July 2013, Bechtel proposed to DOE that resolution of the technical issues related to the design and construction of the HLW Facility be addressed through an update to the nuclear safety basis to ensure integration of safety into design. The path forward envisioned the development of a safety design strategy (SDS) for the HLW to facilitate this process by adapting the guidance provided by DOE-STD-1189-2008, *Integration of Safety into the Design Process*, as applicable for this unique project given its advanced stage of construction and incomplete final design.

High-Level Waste Safety Design Strategy Development

In October 2013, DOE developed a process to allow resumption of HLW Facility engineering, procurement, and the ramp up of construction. Among the requirements in the plan to support this process

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was a Bechtel developed and DOE approved HLW SDS document. Bechtel initiated development of the document in September 2013 and provided a draft in April 2014 for DOE review.

Application of an SDS to a project beyond Critical Decision 3 is unique and was achieved by focusing on consistency in the SDS with the following principles underlying DOE-STD-1189-2008:

- Guiding philosophies and assumptions to be used in continuing development of the project
- Safety-in-design and safety goal considerations for the project
- Approach to developing the overall safety design basis for the project
- Significant discipline interfaces impacting safety.

Bechtel initiated the HLW SDS development by selecting task teams from across operations, nuclear safety, and engineering disciplines to work on discrete sections of the document and provided training on DOE-STD-1189-2008 requirements to those personnel selected. Major tasks included compilation of design basis accidents descriptions, discussion of technical issue resolution in support of the safety basis, evaluation of historical safety basis issues, and Bechtel commitments related to the HLW Facility.

As the task teams' deliverables began to mature, a smaller core of operations, nuclear safety, and engineering personnel began to pull together the discreet sections into an integrated document. As the HLW SDS development proceeded, two safety-in-design-integration teams reviewed the products. The Safety Design Integration Team (SDIT) and the Senior Management SDIT were composed of Bechtel management level personnel with accountabilities in production engineering (design agency), plant engineering, and technical issue resolution teams (design authority). Project nuclear safety managers chaired the teams. The SDIT was made up of HLW Facility mid-level management personnel and the Senior Management SDIT was comprised of project level senior management personnel. As the document being developed neared completion, Bechtel conducted a self-assessment of the draft product against the stated objectives of the HLW SDS and its review plan.

REVIEW PROCESS

DOE developed a review plan for the HLW SDS, drawing on criteria documented in the Chief of Nuclear Safety (CNS) *Standard Review Plan, Safety Design Strategy* (DOE 2014) (written for new project SDS documents that must comply with DOE-STD-1189-2008), and established a Review Team to review draft and final HLW SDS documents. The Review Team process consisted of reviews and comments on several drafts with direct feedback to Bechtel, comment resolution and incorporation into the draft HLW SDS by Bechtel, and, ultimately, DOE review of the final HLW SDS document submitted by Bechtel to verify that agreed-upon dispositions were appropriately incorporated. The final HLW SDS, Rev. 0 was transmitted to DOE in June 2014.

The Review Team for the review and approval of the HLW SDS included representatives from the ORP Nuclear Safety Division, ORP Chief Engineer, DOE CNS, and DOE Office of Environmental Management (EM-40). Additional subject matter experts provided technical and administrative support to the Review Team, but were not assigned as primary Review Team members. Significant contributions were provided by ORP Fire Protection Engineering and the WTP Engineering Division.

The Review Team reviewed the draft HLW SDS transmitted on April 9, 2014, and associated supporting documentation including control strategy documents and Bechtel HLW SDS Support Team reports. On April 23 the Review Team met with Bechtel engineering, nuclear safety, and SDIT personnel to provide initial feedback to Bechtel relative to questions, issues, and concerns developed during the review period. At that meeting, the Review Team provided an informal draft summary of 45 questions, concerns, and issues, and discussed several of the items in detail with Bechtel. Additional informal meetings with Bechtel were conducted to discuss and resolve questions, issues, and concerns over the next 2 weeks.

On May 8, 2014, a final outbrief of the draft HLW SDS document review was conducted with Bechtel. Following the outbrief, the Review Team lead provided Bechtel formal review comment record

documents, reviewed and signed by the Review Team lead and the WTP Federal Project Director, containing 152 comments on the HLW SDS for Bechtel's disposition. Additional meetings were held with Bechtel to discuss resolutions over the next few weeks. Bechtel provided their initial feedback in writing on many of the issues on May 16. On May 28, Bechtel provided their formal review comment record disposition document to DOE for acceptance. Throughout the process, the Review Team lead provided weekly status reports to Review Team members, support members, and senior ORP and WTP personnel.

The Review Team evaluated the Bechtel review comment record disposition document and, after multiple iterations with Bechtel up through June 25, 2014, accepted all proposed dispositions for the draft document. All of the dispositions were satisfactorily incorporated into Rev. 0 of the HLW SDS, received by ORP on June 25, 2014, with one exception to be incorporated upon the initial revision to the HLW SDS.

Review of the HLW SDS draft and final documents focused on the suitability of the document to fulfill its purpose as defined in the HLW SDS, which is to "guide future hazard analyses, design activities, and technical issue resolutions, culminating in a revised preliminary documented safety analysis (PDSA) to be submitted for approval." This includes the plans and procedures to guide the restart of design and construction by addressing philosophies and assumptions to be used in resolution of outstanding technical issues and complete the design for HLW, the requirements and criteria that will govern preparation and approval of the final project documented safety analysis, and the strategy for involving ORP in the design completion process. The HLW SDS is intended to ensure an efficient process that yields an integration of design and safety bases, approvable PDSA updates, an approvable PDSA revision, and, ultimately, an approvable HLW documented safety analysis.

The HLW SDS is not a safety basis document and approval action does not require a DOE safety evaluation report. Subsequent PDSA updates and a revision will be subject to the safety basis approval process. Hence, the purpose of the review process was to document the DOE basis for approving the HLW SDS and, if appropriate, to recommend approval.

As previously discussed, reviews of the draft HLW SDS document and, subsequently, of the final document were conducted following the guidance provided by the CNS Standard Review Plan (DOE 2014) as implemented by the Review Plan for the HLW SDS document. In accordance with the CNS Standard Review Plan, the HLW SDS must be approved by the Safety Basis Approval Authority (ORP Manager) and the WTP Federal Project Director, following concurrence of EM-40 and the CNS. The CNS Standard Review Plan also specifies that the approval basis may be in the form of a letter formally transmitted to the contractor, which is the process followed by the Review Team. In accordance with the CNS Standard Review Plan, the DOE lead reviewer shall ensure that the formal correspondence package addresses whether the following elements have been met:

- HLW SDS is prepared by the design contractor's SDIT
- HLW SDS format and content are consistent with DOE-STD-1189-2008, Appendix E, "Safety Design Strategy"
- HLW SDS is submitted to DOE prior to official submission of a facility's conceptual design documents
- EM-40 and the CNS have concurred.

Each of the four elements were met with the exception of the third bullet above concerning HLW SDS submission to DOE prior to official submission of a facility's conceptual design documents. Given the present status of the HLW design and construction, this requirement cannot be met for those portions of the HLW design that have progressed beyond conceptual design or are constructed provided they are aligned with the HLW SDS (those that are inconsistent are, in effect, returned to the conceptual design

stage). However, this requirement was met for conceptual, preliminary, and final design of new safety strategies (i.e., those not in the current design) that are to be implemented as recommended in the HLW SDS.

APPROVAL BASES

This section addresses the basis for approving the HLW SDS. It relied on meeting the HLW SDS content guidance from DOE-STD-1189-2008, the performance objectives and criteria (PO&C) from the CNS Standard Review Plan (DOE 2014) and, as previously discussed, satisfactory resolution of Review Team comments.

DOE-STD-1189-2008, *Safety Design Strategy Content Expectations*

The HLW SDS follows the suggested format of major section headings from DOE-STD-1189-2008, Appendix E, and includes more detailed information than might be expected of an initial HLW SDS document in subsections on hazard and accident analyses due to the advanced developmental status of the HLW Facility design relative to the conceptual design as addressed in Appendix E. The HLW SDS addresses the content topics that are important to the HLW Facility safety strategy given its present design status. For example, anticipated safety functions of safety class and safety-significant structures, systems, and components are summarized to clearly define those safety functions to prevent or mitigate accidents, and expected functional requirements as well as, to a lesser degree, performance criteria, have been defined.

Although the format and content guidance contained in DOE-STD-1189-2008, Appendix E, were used by Bechtel in the development of the HLW SDS, the standard is not directly applicable to HLW, as the WTP Contract between DOE and Bechtel does not include DOE-STD-1189-2008 as a requirement, nor is it adopted relative to providing implementation guidance in support of other regulatory (e.g., 10 CFR 830, “Nuclear Safety Management,” Subpart B, “Safety Basis Requirements”) or contractual requirements (e.g., DOE O 420.1C, *Facility Safety* or DOE O 413.3B, *Program and Project Management for the Acquisition of Capital Assets*). The HLW SDS summarized the previous DOE determination in Section 3.1 of the document, “Safety Guidance and Requirements,” as follows:

DOE determined that WTP does not need to meet the requirements of DOE STD 1189-2008 because the project was well into construction at the time the standard was issued in 2008. However, DOE O 413.3B still requires integration of safety into the design. As such, the DOE-STD-1189-2008 was used for the SDS format and content, as well as guidance where it made reasonable sense to apply.

High-Level Waste Safety Design Strategy Review Performance Objectives and Criteria

The Review Plan requires that the Review Team ensure that established PO&C, developed from Appendix A of the CNS Standard Review Plan (DOE 2014), are addressed and have been met in the HLW SDS. Bechtel personnel and the Review Team assessed the HLW SDS against the PO&C review criteria concurrently but independently, and the Bechtel self-assessment incorporated opportunities for improvement in the HLW SDS development process.

The information contained in or referenced by the draft HLW SDS was evaluated against each of the review criteria, and the results were verified upon receipt of the final HLW SDS document. For each individual review criterion, a summary is provided in that section of the report to document how that criterion has been met. Review of the HLW SDS indicated that all applicable PO&Cs were met, although, in a few cases, compliance is achieved in a manner consistent with the unique project status and contractual requirements.

The PO&Cs were developed to evaluate the content of project HLW SDS documents complex wide against the implementation guidance found in DOE-STD-1189-2008. Although the format and content guidance contained in DOE-STD-1189-2008, Appendix E, was used by Bechtel in the development of the

HLW SDS, the standard is not directly applicable to HLW, as discussed earlier. The results of the Review Team assessment were documented in the Review Report.

LESSONS LEARNED

Due to the interactive nature of the review and approval process developed between DOE and Bechtel, the process resulted in opportunities to identify areas of improvement. The application of the wealth of knowledge and experience gained will benefit the development of an SDS for the Pretreatment Facility at WTP, and the review and approval process described in this paper may benefit the development of future SDS documents throughout the DOE complex.

High-Level Waste Safety Design Strategy Development

During HLW SDS development, use of multi-disciplined teams to work on the SDS collaboratively was a positive approach. However, that approach, to use multiple personnel on discreet task teams, was labor intensive and, from a scheduling perspective, was not efficient. On the future SDS effort for the Pretreatment Facility, Bechtel will use a small core team drawing on subject matter experts as needed and involving the management safety in design integration teams earlier in the process, as previously discussed in this paper.

The modular nature of the HLW SDS development and tiered management review yielded process benefits, efficiencies, and inefficiencies. The teaming approach fostered collaborative problem solving and broke down traditional stove-pipe functional roles. However, the SDITs did not involve themselves early enough in the process to share common expectations across the task teams. This led to disjointed deliverables from the task teams and rework to craft a final product that met Bechtel management and DOE expectations.

Although development of the HLW SDS took longer than originally anticipated, the benefit the document is providing to the project in linking the design and safety bases to support continuation of construction of the HLW Facility is of significant value in meeting the ultimate mission of reducing the risk posed by the Hanford waste tanks.

High-Level Waste Safety Design Strategy Review and Approval Process

As a measure of the success of the process outlined in this paper, the Safety Basis Approval Authority (ORP Manager) and the WTP Federal Project Director approved the HLW SDS on August 1, 2014, with no conditions of approval. This success hinged on strong communication and integrative tools presented below:

1. Integration of ORP nuclear safety, engineering, and fire protection in addition to the approval authorities, CNS and EM-40, from conception of the Review Plan, throughout the review process and into final approval fostered a common understanding and objective. This led to expedited knowledge of challenges identified and their resolution.
2. A unique draft document review and interactive review process, facilitated through work sessions and continuous communication with the contractor, culminated in the development and resolution of 147 technical comments on topics varying from SDS implementation to hydrogen deflagration in vessels in less than 2 months. The interactive review process was facilitated by real-time response with comment incorporation and interaction with the contractor to ensure that mutual objectives were satisfied. The real-time response times were facilitated through telephone, email, and a shared file server accessible to contractor and DOE reviewers across the DOE complex.
3. Comment resolution sought to improve project clarity, delineation of control strategies, and, holistically, facilitate integration of safety into design in the HLW SDS through mutual respect and responsiveness. As a result, all comments were resolved in support of a contractor submission of the final HLW SDS that expedited the ORP approval process.

4. Important issues requiring a consensus for resolution between the HLW SDS development and the DOE review teams were, when appropriate, elevated to the proper level of DOE and Bechtel management in a timely manner for real-time discussion, with feedback to the team. Bechtel and DOE personnel at the working level were not burdened with solving all issues at their level, and escalating the discussion to management was not seen as a negative by Bechtel or DOE.
5. Review of the HLW SDS draft and final documents success was achieved by clearly defined criteria focusing on the suitability of the document to fulfill its purpose as defined in the HLW SDS, which is to “guide future hazard analyses, design activities, and technical issue resolutions, culminating in a revised preliminary documented safety analysis (PDSA) to be submitted for approval.”
6. The determination as to what will constitute the approval process and how the HLW SDS would be utilized in this application was restricted to the HLW SDS not being a safety basis document and approval not requiring a DOE safety evaluation report. Subsequent PDSA updates and a revision to the PDSA will be subject to the safety basis approval process. This understanding facilitated the resolution for implementation issues identified early in the review process.
7. With some Review Team personnel not experienced in the SDS approval process, especially in this unique application to align the design and safety bases, the CNS Standard Review Plan (DOE 2014) provided the guidance necessary to develop and implement the HLW SDS Review Plan.

CONCLUSION

The ORP Review Team determined that the HLW SDS, in conjunction with Bechtel implementation plans and procedures, is adequate and suitable to guide the restart of limited engineering, procurement, and design of the HLW Facility. The HLW SDS will support:

- Alignment of the design and safety bases
- Resumption of limited engineering, procurement, and construction
- Updates and ultimately a revision of the HLW PDSA.

Development of the HLW SDS has successfully achieved the significant benefit for Bechtel of gaining coordination and agreement among engineering, operations, and nuclear safety personnel with respect to a documented HLW SDS, which will support the design process and identifies a preferred control set of safety class and safety-significant structures, systems, and components. The iterative comment resolution process between the Review Team and the Bechtel SDITs, as well as between senior ORP and Bechtel management, for resolutions of issues helped to achieve general agreement and understanding among all parties. Successful utilization of the HLW SDS to complete the HLW design will require strict adherence to supporting plans and procedures as well as care and planning by Bechtel to coordinate the resolution of the remaining conceptual design issues with other parallel efforts, including procurement and construction of released systems, to finalize the design.

To ensure that Bechtel effectively executes the HLW SDS process to align design and safety bases in strict adherence to approved implementation plans and procedures, the Review Team recommended that the WTP Federal Project Director initiate an independent assessment to review the HLW SDS implementation process at an appropriate stage of implementation.

The Review Team recommended that the *Safety Design Strategy for the High-Level Waste Facility* be approved with no conditions of approval cited.

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