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Physical, Chemical and Structural Evolution of Zeolite - Containing Waste Forms Produced from Metakaolinite and Calcined HLW

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RESULTS TO DATE: During the seventh year of the current grant (DE-FG02-05ER63966) we completed an exhaustive study of cold calcination and began work on the development of tank fill materials to fill empty tanks and control residuals. Cold calcination of low and high NOx low activity waste (LAW) SRS Tank 44 and Hanford AN-107 simulants, respectively with metallic Al + Si powders was evaluated. It was found that a combination of Al and Si powders could be used as reducing agents to reduce the nitrate and nitrite content of both low and high NOx LAW to low enough levels to allow the LAW to be solidified directly by mixing it with metakaolin and allowing it to cure at 90oC. During room temperature reactions, NOx was reduced and nitrogen was emitted as N2 or NH3. This was an important finding because now one can pretreat LAW at ambient temperatures which provides a low-temperature alternative to thermal calcination. The significant advantage of using Al and Si metals for denitration/denitrition of the LAW is the fact that the supernate could potentially be treated in situ in the waste tanks themselves. Tank fill materials based upon a hydroceramic binder have been formulated from mixtures of metakaolinite, Class F fly ash and Class C flue gas desulphurization (FGD) ash mixed with various concentrations of NaOH solution. These harden over a period of hours or days depending on composition. A systematic study of properties of the tank fill materials (leachability) and ability to adsorb and hold residuals is under way.

Cold Calcination

Three experiments were carried out. In the first, additions of various combinations of Al+Si metal powders were used to monitor the NOx levels in a Cs doped SRS low NOx LAW (SRS Simulated Tank 44). In the second, the effect of aging on the remaining SRS LAW solution and the precipitates was studied. In the third, a high NOx Hanford LAW (Simulated Tank AN-107) was similarly denitrated/denitrated and the products of reaction studied as a function of the amount of Al/Si added. In all cases the concentrations of ions left in the supernate after the addition of Al and Si were analyzed as a function of time. It was shown that the addition of a combination of Al and Si had two effects on the liquid waste. One was denitration/denitrition and the other was the formation of cesium/sodium aluminosilicates (zeolites) which selectively removed Cs ions from the solution. Finally, the products resulting from the reduction reaction (liquid plus zeolite precipitate) were successfully mixed with metakaolin to form hydroceramic waste forms that had extremely low leachabilities. The production of precipitate is the result of the oxidation-reduction and acid-base reactions. All potentials are larger than zero meaning that all reactions in a thermodynamic sense can occur spontaneously.

Reduction of NOx with Al and Si powders (SRS Low NOx LAW) A LAW solution simulant (SRS LAW) was prepared using the chemical composition of a simplified Tank 44 supernate supplied by SRS as a guide (Table 1). Note that the simulant actually contains 1/2 mole of CsNO3. The higher concentration of Cs made it easier to observe the effect of the addition of Al and Si on the behavior of Cs during the reduction process and during subsequent solidification.

Table 1. Composition of Simulated Tank 44. Composition MW M g/L CsNO3 194.909 0.5 97.4545 KNO2 85.107 0.1 8.5107 NaNO2 69.000 0.4 27.6000 NaAlO2 81.979 0.2 16.3958 NaOH 39.998 4.5 179.9910

Experimental procedure

Different amounts and combinations of Al and Si powder were added to the SRS low NOx LAW; five 25 ml liquid simulant samples were prepared and either Al, Si or a combination of Al and Si were slowly added to the stirred solutions (see Table 2).

Table 2. The Addition of Series of Metals to the Liquid Waste*

	#1	#2	#3	#4	#5
Amount of Al (g)	0.54	-	0.20	0.20	0.54
Amount of Si (g)	-	0.70	0.35	0.35	0.70
Mole of Al/Si	-	-	1	1	1
Mole of Al/NO3	2	-	1	1	2
Mole of Si/NO3	-	2	1	1	2
Mole of metal(s)/NO3	2	2	2	2	4
Mole of metal(s)/NOx	1	1	1	1	2

*Moles of Al includes the amount of AlO2- in the waste solution. The concentrations of NO3- and NO2- are equal in SRS LAW. Al was first added followed by Si in Reactions #3 and #5. Si was first added followed by Al in the Reaction #4. Both metals were added at the same time in Reaction #5.

Results

The reaction of metallic Al powder with the LAW simulant was vigorous and exothermal. The reaction of Si with the liquid waste also produced heat and gas, but the reaction was generally less vigorous. Generally, after several minutes the solution cleared indicating that the reaction products were soluble. However, during the combined addition of Al and Si, large amounts of black precipitate were produced. The black precipitate became white after the sample was allowed to age at room temperature for two days and the Si reacted. The solid was then centrifuged and separated from the solution. The concentrations of NO2-, NO3-, Na+, Cs+, NH4+ in the solution are listed in Table 3.

Table 3. Concentrations of the Ions Remaining in the Liquid Waste (ppm)

Sample	NO2-	NO3-	NH4+	Na+	Cs+
Original LAW	22400	29100	0	116000	68000
#1, 2Al/NO3	10500	22900	5418	115900	65000
#2, 2Si/NO3	21300	26700	607.9	115800	65000
#3, (Al+Si)/NO3	18000	27300	1356	115800	55000
#4, (Si+Al)/NO3	19700	26300	1348	115800	54000
#5, 2(Al+Si)/NO3	15900	26100	2210	115600	22000

The results show that Al is the best and Si the least effective reducing agent. The order that Al and Si are added to the LAW does not influence the reduction reaction. The concentrations of Na left in solution are almost the same for the five different reactions, only a minor amount of Na was removed for all five reactions. The concentration of Cs left is high in the solution with only addition of Al or Si, but decreases with the combined addition of Al and Si. When more Al and Si are added, the concentration of Cs remaining in solution further decreases due to the formation of a Cs zeolite. The major crystalline phase present is cesium aluminum silicate hydrate (Zeolite D). The EDS for the autoclaved sample shows that the precipitate contains a relatively large amount of Cs suggesting that its formation removed Cs from solution. More CsAlSiO4 precipitate formed when more Al and Si were added, explaining the decrease of the concentration of Cs remaining in solution as additions of Al and Si were increased.

Kinetics: Effect of Time on Change of Ion Concentration of Supernate (SRS Low NOx LAW)

The ion concentrations remaining in the liquid simulant after the addition of both Al and Si powder were investigated as a function of time. In this experiment, 0.49 g Al was first slowly added followed by 0.84 g Si to 60 mL of stirred SRS LAW; a large volume of liquid LAW simulant was used in order to keep the volume approximately the same when aliquots were taken from the liquid sample. The final mole ratios of Al/Si, Al/NO3 and (Al+Si)/NOx in the liquid were 1, a ratio similar to Experiment #3 in Table 3. Prior to sampling, the sample was shaken and then about 1 mL of suspension was collected in a syringe after 1, 2, 3, 5, 7, and 14 days. After the solution was separated from the solid with a centrifuge, the concentrations of ions remaining in the solution were analyzed using wet chemical techniques. The separated solids were cured at 90oC in Parr bombs for 24 hrs.

Results

The concentrations of ions remaining in solution were analyzed using wet chemical techniques (Table 4). The amount of Cs and Na removed from the solution by the precipitate was calculated by subtracting the remaining amount of Cs and Na in the solution from the starting concentration. The weight ratio and mole ratio of the removed Cs and Na were calculated and the data also listed in Table 4. The concentrations of NO2-, NO3- clearly decrease after the addition of Al + Si, but then they level off with extended time, indicating that most of the reduction reaction happens right after the addition of the metals. The concentration of Na remaining in the liquid simulant stays relatively constant at longer times. However, the concentration of Cs remaining in the simulant decreases as a function of time, which is the result of more Cs being incorporated into the solids with longer soaking time. The weight and mole ratio of Cs/Na are larger than one, which indicates that the combined addition of Al and Si selectively remove Cs over Na from the simulant.

Table 4. The Concentrations of NO2-, NO3-, Na+ and Cs+ Remaining in Solution as a Function of Time.

Time	NO2	NO3	Na	Cs	Removed Cs/Na(wt)*	Removed Cs/Na(mole)*
0	22400	29100	116000	68000	-	-
1 day	19300	28000	115850	62000	40	6.92
2 days	19000	27900	115800	55000	65	11.2
3 days	18800	27300	115800	45000	115	19.8
5 days	18300	27000	115750	37000	124	21.4
7 days	18300	26800	115800	36000	160	27.6
14 days	17700	26000	115800	32000	180	31.1

*Wt means weight ratio of removed Cs/Na. Mole means mole ratio of removed Cs/Na.

The precipitate obtained after 14 days was identified as Zeolite D. Once hydrothermally cured the Zeolite D converted into hydroxycancrinite. The EDS patterns of the autoclaved samples show the ratio of Cs/Na for the sample after 14 days reaction is higher than that for the sample after 2 days reaction, which indicates that the Cs incorporation in the solid is higher for a longer reaction time. The EDS result showing more Cs incorporation in the solids is consistent with the elemental analysis result that less Cs remains in the solution with longer reaction times (Table 4).

Denitration/Denitrition by Successive Addition of Al and Si to a High NOx LAW (Hanford)

In order to control the reaction rate and also satisfy the goal of 25%, an experiment was carried out in which≤reducing the mole ratio of NOx/Na small amounts of Al and Si were added to a simulated Hanford LAW in four consecutive steps. We first added 1.976 g Al and 2.057 g Si [mole ratio of Al/NO3=0.5, Si/NO3=0.5, (Al+Si)/NOx=0.75] to 50 mL of simplified Hanford LAW waste simulant (Table 5). A suspension consisting of a black precipitate formed. After gases were no longer observed, the sample was sealed and kept in an oven at 50oC in order to accelerate the reaction. The precipitate in the solution became white after one day, after which a 1 mL aliquot was taken. The solution was separated from the solids by centrifuging the aliquot. The concentrations of NO3- and NO2- in the solution were measured and the crystalline phases present in the solid was examined by XRD. In the second and third steps, we added a total of   0.988 g Al and 1.029 g Si resulting in a total mole ratio of Al/NO3=1, Si/NO3=1, (Al+Si)/NOx =1.49. In the forth step, we added 1.976 g Al and 2.057 g Si. In toto, the total mole ratio of Al/NO3=1.5, Si/NO3=1.5 and (Al+Si)/NOx=2.24. The same separation and characterization procedures were performed after each incremental addition.

Table 5. The Composition of a Simplified Hanford LAW Simulant

Compounds	Concentration (mol/l)	Molecular Weight	Concentration (g/l)
NaNO3	2.93	84.999	249.05
NaNO2	1.00	69.000	69.00
NaOH	4.27	39.998	170.79

Total Na: 8.2 mol/l, NO3-: 2.93 mol/l, NO2-:1.00 mol/l, molar ratio of NOx-/Na=48% requiring pretreatment

The crystalline phases present in all four precipitates are a “sodium hydroxycancrinite” (Na6Al6Si6O24.2NaNO3.4H2O) and hydroxysodalite (Na4Al3Si3O12OH), which are different phases from those obtained from the SRS LAW studied earlier. The results in Table 6 show that the concentration of NO3- and NO2- in the liquid decreased continuously with successive additions of Al and Si. When Al and Si with mole ratios of Al/NO3-=0.75 and Si/NO3-=0.75, the mole ratio of the total NOx to Na reached less than 25%, which is the maximum amount of NOx that can be incorporated in cancrinite.

Table 6. Concentration of NO3- and NO2- in the Liquid Simulant and the Mole Ratio of the Remaining NOx/Na after Successive Addition of Al and Si Metals Mole Al or Si /NO3- NO2- (ppm) NO3- (ppm) NO2- (M) NO3- (M) Total NO2- +NO3- Total NOx/Na 0 51000 155000 1.109 2.500 3.608 0.440 0.5 26900 100000 0.585 1.613 2.198 0.268 0.75 19700 88000 0.428 1.419 1.847 0.225 1 12700 74000 0.276 1.193 1.470 0.179 1.5 5400 57000 0.117 0.919 1.037 0.126

The NOx versus Na molar ratio of the Hanford LAW was reduced to below 25%, so it was then mixed with different amounts of metakaolin and just enough water to make thick pastes. The five resulting monoliths had total Na/Al/Si mole ratios of: 1:0.5:0.5, 1:0.8:0.8, 1:1:1, 1:1.2:1.2 and 1:1.5:1.5. The monoliths were autoclaved at 90oC in Parr bombs for 24 hrs to form a hydroceramic waste form. The XRD patterns for these 5 samples contain mainly hydroxycancrinite and hydroxysodalite. PCT 7 day leaching experiments were performed on the five hydroceramics (Table 7). The data show that the hydroceramics have low leachability and could make acceptable waste forms. The Na/Al/Si=1:1:1 hydroceramic has the lowest leachability. Comparing cold denitration/denitrition with thermal calcination the room temperature process uses much less metakaolin resulting in higher waste loading.

Table 7. Hydroceramics Prepared with Different Amounts of Metakaolin* Sample ID #1 #2 #3 #4 #5 Mole metallicAl/NO3 1.5 1.5 1.5 1.5 1.5 Mole metallic Si/NO3 1.5 1.5 1.5 1.5 1.5 Total mole Na/Al 1:0.5 1:0.8 1:1 1:1.2 1:1.5 PCT-7 (mS/Cm) 11.70 8.10 4.50 5.40 6.00 pH 10.39 10.20 9.60 9.89 10.00 *Total mole ratio of Na/Al/Si is calculated after the addition of metakaolin. The metakaolinite (Al2O3.2SiO2, MW=222.14) was used in calculation.

Tank Fill Materials

Based on completed and ongoing work, it has been possible to begin our study of tank fill materials for the empty HLW storage tanks at SRS and Hanford. Once the tanks are emptied they will be cleaned as thoroughly as possible, but it is being discovered that beneath the salt cake and sludge the tanks contain a very tenacious layer of tightly adhering ?crud.? Aside from hammering and chipping and possibly puncturing the tank this residual waste can not be removed. Recently Hanford has been granted permission to leave this residual material in place and can now go ahead with its plans to fill the tanks with a cementitious material (currently Portland cement concrete) and abandon them. Because of earlier stated concerns regarding Portland cement based concrete tank fill materials, a study of possible hydroceramic tank fill materials has been started. The objective of the study is to develop a set of candidate materials based upon NaOH mixed with metakaolinite, Class F fly ash and a dry flue gas desulfurization (FGD) Class C ash that are fluid enough to be pumped into the tanks and at the same time ?set up? and harden within a day or two. We are in effect proposing to make a hydroceramic with aggregate that will perform better (in a regulatory sense) than Portland cement concrete. Preliminary work has been encouraging.

DELIVERABLES:

Publications During Year Seven Bao, Y. and M.W. Grutzeck, “Preparation and Properties of Hydroceramic Waste Forms Made with Simulated Hanford Low Activity Waste,” Journal of the American Ceramic Society, 2005, Accepted as a featured article. Bao, Y. and M.W. Grutzeck, “Hydroceramic Waste Forms: Procedures and Properties,” International Workshop on Geopolymers and Geopolymer Concrete in Civil Engineering 28-29 September 2005, Perth, Australia, Accepted. Bao, Y. and M.W. Grutzeck, “General Recipe and Properties of a Four Inch Hydroceramic Waste Form,” Proceedings of 107th Annual Meeting of The American Ceramic Society, S21 Ceramic/Glass Science and Technology for Nuclear and Environmental Industries, April 11-13, 2005 in Baltimore, MD (In Press). Bao, Y. and M.W. Grutzeck, “In-tank Denitration of Sodium Bearing Waste Using Al and Si Powders Followed by Solidification with Metakaolin to Produce a Hydroceramic Waste Form/Tank Fill Material,” presented in 107th Annual Meeting of The American Ceramic Society, S21-Ceramic/Glass Science and Technology for Nuclear and

Environmental Industries, April 11-13, 2005 in Baltimore, MD. Bao, Y. and M.W. Grutzeck, “Preparation and Characterization of Hydroceramic Nuclear Waste Forms Having a Zeolitic Structure,” presented in107th Annual Meeting of The American Ceramic Society, S21-Ceramic/Glass Science and Technology for Nuclear and Environmental Industries, April 11-13, 2005 in Baltimore, MD. Bao, Y. and M.W. Grutzeck, “Nature’s Waste Form,” presented in 8th Annual Environmental Chemistry Student Symposium, April 1-2, 2005 in State College, Pennsylvania. Bao, Y., “Design and Characterization of Microporous Zeolitic Hydroceramic Waste Forms for the Solidification and Stabilization of Sodium Bearing Wastes,” Ph.D. Thesis, The Pennsylvania State University, 2005 Bao, Y. and M.W. Grutzeck, “Metallic Denitration/Denitrition: A Mild Path to Make Hydroceramics,” In preparation.