Project ID: **65366**

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

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FIRST ANNUAL REPORT
September 15, 1998 to September 14, 1999
U.S. Department of Energy

PHYSICAL, CHEMICAL AND STRUCTURAL EVOLUTIION OF ZEOLITE-CONTAINING WASTE FORMS RPODUCED FROM METAKAOLINITE AND CALCINED HLW

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EMSP Project Number 65366
Grant Number DE-FG07-98ER45726

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Prepared June 15, 1999

Objectives

Natural and synthetic zeolites are extremely versatile materials. They can adsorb a variety of liquids and gasses, and also take part in cation exchange reactions. Zeolites are easy to synthesize from a wide variety of natural and man made materials. One combination of starting materials that exhibits a great deal of promise is a mixture of metakaolinite and/or Class F fly ash and concentrated sodium hydroxide solution.[1] Once these ingredients are mixed and cured at elevated temperatures, they react to form a hard, dense, ceramic-like material that contains significant amounts of crystalline tectosilicates (zeolites and feldspathoids).

Zeolites have the ability to sequester ions in lattice positions or within their networks of channels and voids. As such they are nearly perfect waste forms, the zeolites can host alkali, alkaline earth and a variety of higher valance cations. In addition to zeolites, it has been found that the zeolites are accompanied by an alkali aluminosilicate hydrate matrix that is a host, not only to the zeolites, but to residual amounts of insoluble hydroxide phases as well. A previous publication[2] has established the fact that a mixture of a calcined equivalent ICPP waste (sodium aluminate/hydroxide solution containing ~3:1 Na:Al) and fly ash and/or metakaolinite could be cured at various temperatures to produce a monolith containing Zeolite A (80°C) or Na-P1 plus hydroxysodalite (130°C) crystals dispersed in an alkali aluminosilicate hydrate matrix. Dissolution tests have shown these materials (so-called hydroceramics) to have superior retention for alkali, alkaline earth and heavy metal ions.

The zeolitization process is a simple one. Metakaolinte and/or Class F fly ash is mixed with a caustic sodium-bearing calcine and enough water to make a thick paste. The paste is transferred to a metal canister and "soaked" for a few hours at 70-80°C prior to steam autoclaving the sample at ~200°C for 6-8 hours. The waste form produced in this fashion could be a viable alternative for fixation of low activity waste (LAW) calcines. Our objective is to adapt this technology for use in site remediation and clean up of caustic waste solutions now in storage in tanks at Hanford and the Savannah River sites. The proposed work is meant to develop a clearer understanding of the advantages and limitations of producing a zeolite-containing waste form (hydroceramic) from calcined radioactive waste, i.e. the effect of processing variables, reaction kinetics, crystal and phase chemistry, and microstructure on their performance.

Results

Work during the first year of the named grant, has focused on the evaluation of potential starting materials of all kinds in terms of their potential as ingredients for a working waste form formulation. Twenty five parts fly ash (Class C, F, FGD), slag, natural pozzolans (opal, diatomaceous earth,), clays/heat treated clays (kaolinite, montmorillonite, smectite, vermiculite), and zeolites were each mixed with 18 parts of 13 M Na-containing waste simulant (11.5 M NaOH + 1.5 M $NaNO_3$ and 0.069 M CsCl) solutions and cured as above. PCT leaching tests (1 part powder + 10 parts H_2O aged at 90°C for 5-7 hours) narrowed the choice to a limited number of materials. See Table 1 for an example of fly ash screening tests. Conductivity was used to test for the amount of sodium leached. It is an efficient way of screening large numbers of samples.

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[1] Palomo, A., M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez and M.W. Grutzeck, "Chemical Stability of Cementitious Materials Based on Metakaolin," WM'98 Proceedings March 1-5, 1998, Tucson, AZ, WM Symposia, Inc., Tucson (1998); Palomo, A., M.W. Grutzeck and M.T. Blanco, "Alkali Activated Fly-Ashes: A Cement for the Future," Cem. Cocr. Res. (accepted for publication).

[2] Grutzeck, M.W. and Siemer, D.D., "Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry," J. Amer. Ceram. Soc. 80, 2449-53 (1997).

Table 1. Screening Tests of Fly Ashes

Fly Ash	electrical conductivity	% Cs leached
NSP (F FGD)	167	
Midwest Power (C)	134	
Tucson Electric (C)	129	
Hatfield (F)	81	0.35
Holtwood (F)	81	0.35
Montour (F)	52	
PP&L (F)	48	

Three types of ash were tested: Class C, F and F containing flue gas desulfurization products (FGD). The best of the lot were the Class F fly ashes. Electrical conductivities are low as are Cs concentrations in the leachates. Typical results of a second type of screening test are given in Table 2. In this instance Rhone Poulenc flash calcined alumina (RP) and condensed silica fume (SF) were added to some of the best starting materials that were determined using Table 1 testing.

The blends used are indicated in Table 2 as follows: for example 21 parts Montour Class F fly ash were blended with 4 parts RP alumina which in turn were blended with 18 parts of the 13M simulant described above. The samples were then cured and tested using PCT protocol as above but in this case samples were soaked for a total of 35 hours. It can be seen that the RP alumina aids in improving the properties of the waste form.

Table 2. Screening of Waste Form Formulations

Pozzolan + RP Alumina ± Silica (SF)	% Na leached	$\%NO_3$ leached	% Cs leached
21 Montour + 4RP	3.6	2.2	0.11
18 Montour + 4RP + 3SF	3.8	5.7	0.1
21 Troy Clay + 4RP	3.6	4.9	0.1
25 Metakaolinite	3.9	18.	0.07
15 Silica Flour + 10RP	2.8	1.4	0.28

All of the samples listed show promise as potential host formulations for continued testing. The lechates have compositions well within the desirable range for waste forms in general; sodium levels are well below DOE glasses. Efforts are underway to produce more realistic simulated calcines. Two simulants representative of solutions in storage at the Hanford and Savannah River sites are being prepared. Because nitrate is detrimental to the process, it is proposed to calcine some of the LAW at various temperatures (w/wo sugar) to maximize the reactivity of the resultant mix of oxide phases while minimizing the loss of volatiles.

Plans for the Coming Year

Various calcines containing oxides and traces of nitrate will be mixed with varying amounts and types of the Table 2 formulations, small amounts of other chemicals (alkali hydroxides and/or carbonates, zeolite seeds, templating agents) and enough water to make a paste. The paste can then be cured (in-can) at a variety of temperatures (80°-100°C). Once reaction rates for the process are established, MAS NMR and TEM will be used to study the atomic-level structure of the solids. X-ray diffraction will be used to examine the degree of crystallinity of the waste forms. On occasion an electron microprobe will be used to analyze the phases in the waste form. Attempts will be made to relate changes in phase chemistry and microstructure to distribution coefficients and dissolution data.

Compressive and bending strength tests will be used to determine mechanical behavior and standard leach tests will be used to determine the potential consequences of cation exchange reactions. Knowing that simulated waste is not an adequate predictor, a major portion of the proposed work will be carried out by Dr. Carol Jantzen at the Savannah River Technology Center; she will run parallel studies using actual LAW samples obtained from the Savannah River site. The value of running parallel studies of this type is self-evident. Given these data, it is expected that it will be possible to piece together a coherent picture of how the crystal and phase evolution of an actual di-phasic zeolite-containing waste form made from LAW governs its performance and its durability once placed into service.

Publications

Siemer, D.D., M.W. Grutzeck and B.E. Scheetz, “Comparison of Materials for Making Hydroceramic Waste Forms,” Accepted for Publication, Proc. Amer. Ceram. Soc. Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries, Indianapolis IN April 25-28, 1999, Amer. Ceramic Society, Westerville, OH.