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## **Iodine Waste Form Summary Report (FY 2007)**

Tina M. Nenoff, James L. Krumhansl, Huizhen Gao, Ashwath Rajan, Kevin McMahon

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## **ABSTRACT**

This new program at Sandia is focused on Iodine waste form development for GNEP cycle needs. Our research has a general theme of “Waste Forms by Design” in which we are focused on silver loaded zeolite waste forms and related metal loaded zeolites that can be validated for chosen GNEP cycle designs. With that theme, we are interested in materials’ flexibility for iodine feed stream and sequestration material (in a sense, the ability to develop a universal material independent on the waste stream composition). We also are designing the flexibility to work in a variety of repository or storage scenarios. This is possible by studying the structure/property relationship of existing waste forms and optimizing them to our current needs. Furthermore, by understanding the properties of the waste and the storage forms we may be able to predict their long-term behavior and stability. Finally, we are working collaboratively with the Waste Form Development Campaign to ensure materials durability and stability testing.

## **ACKNOWLEDGEMENTS**

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## INTRODUCTION

This new program is focused on Iodine waste form development for GNEP cycle needs. Our research has a general theme of “Waste Form by Design” in which we are focused on silver loaded zeolite waste forms and related metal loaded zeolites that can be validated for chosen GNEP cycle designs. With that theme, we are interested in materials’ flexibility for iodine feed stream and sequestration material (in a sense, the ability to develop a universal material independent on the waste stream composition). We also are designing the flexibility to work in a variety of repository or storage scenarios. This is possible by studying the structure/property relationship of existing waste forms and optimizing them to our current needs. Furthermore, by understanding the properties of the waste and the storage forms we may be able to predict their long-term behavior and stability. Finally, we are working collaboratively with the Waste Form Development Campaign to ensure materials durability and stability testing.

In order to have a strong understanding of the structure / property relationship of the materials, we must employ our wide range of analytical capabilities. In house analytical testing for Iodine loaded on inorganic waste forms include: (1) Orion specific ion electrode, (2) PerkinElmer Elan 6100 ICP-MS (3) X-ray fluorescence ARL (Thermo) QUANT’X EDXRF Analyzer, (4) TA Instruments STD 2960 Simultaneous DTA-TGA, (5) BET surface area analysis, (6) Philips CM30 Transmission Electron Microscope (TEM), (7) JEOL JSM-6300V Scanning Electron Microscope (SEM/EDX), and (8) Powder X-ray (XRD) Siemens Kristalloflex D 500 diffractometer. Multiple analytical techniques are desirable as each provides unique insights into some aspect of iodine behavior.

In an effort to have a substantive materials study completed for the June 2008 decision we initially outlined a broad materials study for Iodine waste forms. Our study has primarily focused on two classes of materials for the scavenging of iodine during spent fuel reprocessing and then investigating the conversion of these materials to a limited (e.g., in reduced) number of stable waste forms suitable for geologic disposal: known aluminosilicate zeolites and layered bismuth compounds. Appendix A of this report lists many of the literature references we used in preparing materials for this year’s study.

We are using this year end report to present our data for the year in both aluminosilicate zeolite getter and waste form materials and bismuth-based compounds. We will refocus our effort in FY08 to fully pursue questions associated with zeolite materials for I<sub>2</sub> separations and waste forms associated with GNEP needs. The bismuth research presented here may be of interest in future I<sub>2</sub> research, and we plan to submit our Patent Application in the near future on that work. However, we do not plan to pursue it in FY08.

## ***I. Aluminosilicate Ceramic Waste Forms***

### **Silver Loaded Zeolites (Al/Si) for Iodine Waste Forms:**

Our objects are to understand why Ag-I-Zeolites are stable waste forms and apply to development of other metal-Al/Si lower temperature and high durability waste forms. Experimentally, we will be studying the metal loading versus iodine loading, identifying and studying stability of metal-iodine heat treated phases, and understanding the nature of the captured iodine in various phases.

The basic guidelines we are following to develop and characterize the iodine loading into zeolites and conversion to waste forms are:

- I. Ag-Zeolite Studies:
  - Includes XRD, TEM, SEM /EDX studies on Mordenite
- II. Study variations in Al/Si Framework:
  - change of pores size and acidity of framework
- III. Variations in Amount of Ag in Zeolites:
  - loading level vs. Iodine uptake and retention
- IV. Chemistry of the Ag-I in Zeolite:
  - why does it work? Would anything else work better?
- V. Waste Form Study:
  - materials characterization to locate and understand I<sub>2</sub> loading
- VI. Modeling/Simulation:
  - validation of experimentation and characterization
- VII. Comparison to other transition metals in optimized zeolites:
  - anything cheaper? more environmentally friendly?
- VIII. Work with Waste Form Campaign to study the durability of the waste form

### **Experimental Procedure for loading zeolites and converting the material to a waste form.**

#### **Procedure for loading samples with Iodine:**

Ag ion exchange procedure: 5 grams of the original material **are** mixed with 36 mL of AgNO<sub>3</sub> (0.1N) in a 50-mL centrifuge tube, and capped. The mixture is shaken for 6.5 hrs at 100rpm. The material is then rinsed three times with 50 mL DI water, and dried at 45°C overnight.

**Procedure for reducing Ag:** 5 gram of each material are mixed with 12 mL of AgNO<sub>3</sub> (0.1N) solution in a 50-mL centrifuge tube, respectively, and shaken at 1000 rpm for 3 hours. The material is then filtered without rinsing and dried overnight at 45°C. The material is next calcined at 400°C for 2.5 hr. Finally, to reduce the silver, 2.0g of each calcined sample are mixed with 10.0 mL ascorbic acid solution (0.05M) in a 50-mL centrifuge tube and shake for 20 minutes. Then, they are filtered without rinsing, and dried at 45°C for 8 hr.

**Adsorption of Iodine:** Take 1 gram of the sample in a watch glass. Weigh 0.07-0.08 g of Iodine into a 500-mL Teflon jar, set the watch glass with the sample in the same Teflon jar. Tightly screw down the cap on the jar and set it in the oven at 90°C for about 6 hr.

**Leach testing:** 0.5 g of I-loaded materials in 50 g DI H<sub>2</sub>O. The sealed vials are placed in 90°C oven for 4 days. Use a syringe with 0.2 µm membrane to filter the sample. Collect the supernatant in a 15-mL centrifuge tube. Test supernatant by ICPMS.

Supports studied to date include commercially available zeolites (13X, 5A, and mordenite), silicotitanate zeolites (CSTs), amorphous silica, diatomaceous earth and activated aluminas.

Sample ID of the Iodine Treated Materials:

GG 3-1-I: UOP molecular sieve 13X with Ag ion-exchanged

GG 3-2-I: UOP molecular sieve 5AP with Ag ion-exchanged

GG 3-3-I: Zeolite from Amoco Research Center with Ag ion-exchanged

GG 3-4-I: Permutite (°04) with Ag ion exchanged

GG:3-5-I: Diatomaceous earth with reduced Ag

GG 3-6-I: Aluminum oxide activated with reduced Ag

GG 3-7-I: Silica with reduced Ag

Al<sub>2</sub>O<sub>3</sub>-0-I: aluminum oxide activated original

Al<sub>2</sub>O<sub>3</sub>-1-I: Aluminum oxide activated treated including calcining and reducing except without Ag.

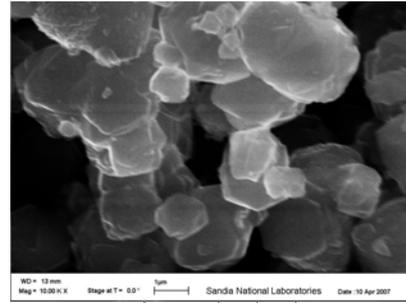
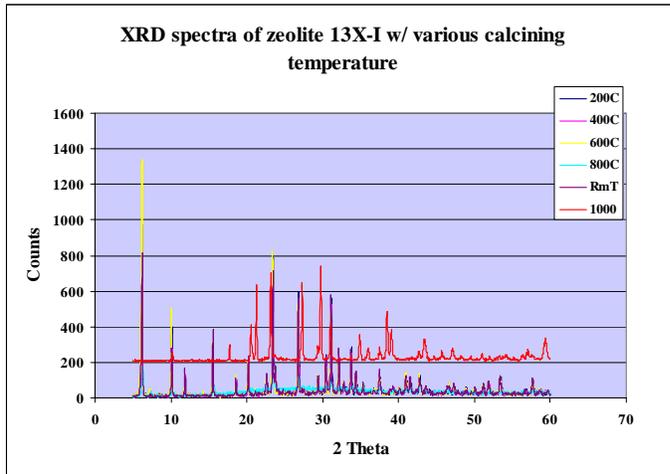
Initial leach testing on possible heat treated waste form ceramics were simple heatings and testings at 200, 400, 600, 800, 1000°C of Zeolite 13X, Amoco A, and Zeolite 5AP. These are commercially available zeolites with varying pore size openings and Si/Al ratios. The 13X is considered a large pored zeolite, and A is a small pored zeolite.

The leaching and XRD studies of samples from the different calcined temperature give matching information. Not surprisingly, the large pored zeolite 13X retains its structure to over 600°C and leaches 20-30% of its occluded Iodine. The Amoco A zeolite leaches up to 85% of the Iodine. This is probably due to simple surface adsorption and desorption processes; no pore occlusion of the iodine occurred. The zeolite 5AP leaches less than 4% iodine over the entire calcination range. Furthermore, the filtration of the samples <800°C is very difficult. This is probably due to colloidal particle formation in solution.

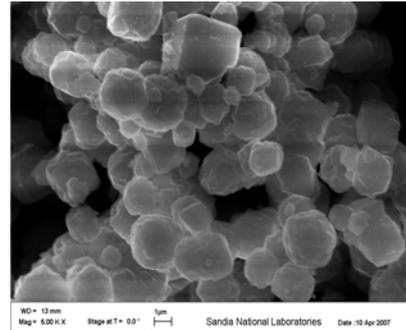
In an effort to fully understand the leach-free materials, fully loaded Ag samples of Zeolite 13X and Zeolite 5AP were made and then heated to 1000°C for 2.5 hours. They were subjected to a longer leach test of 4 days at 90°C in DI H<sub>2</sub>O, centrifuged and then dried at 45°C. The results indicated very little Iodine loss after calcinations. In the Zeolite 13X calcined material, 0.12wt % iodine was leached out; in the Zeolite 5AP, 0.30 wt % iodine was leached out.

SEM and TEM analyses are ongoing as Ag-Zeolite samples and calcined samples (both pre and post leaching) are prepared. SEM data of the as prepared, Ag-I-loaded, calcined and post-leaching Zeolite X are shown in Figure 1. The study shows that even with all the processing of the material, the macroscale particles retain their morphology. This data suggests that the material is durable for this mechanical processing.

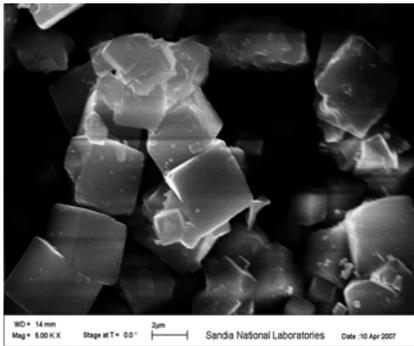
Figure 1: Ag,I – Loaded Zeolite X studies: morphology is maintained through processing



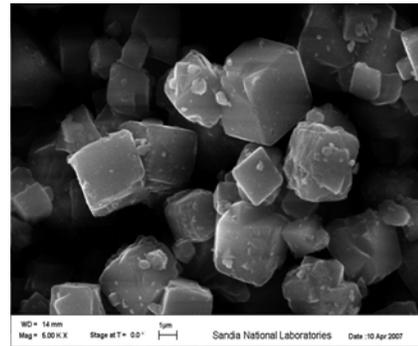
As-synthesized



Ag, I loaded



Post leaching



Calcined 1000°C

High Resolution TEM data of the calcined Ag, I-X Zeolite indicates that the Ag and I remain imbedded in the Na/Ca/Al/Si/O ceramic matrix after heating to 1000°C. This is confirmed by EDX studies on the material. The iodine is unstable in the electron beam, making it difficult to determine the iodine concentration. However, the nanoparticles of Ag/I are stable in comparison to the matrix. Xray diffraction studies are underway on the zeolite and ceramic matrix to better understand the structure.

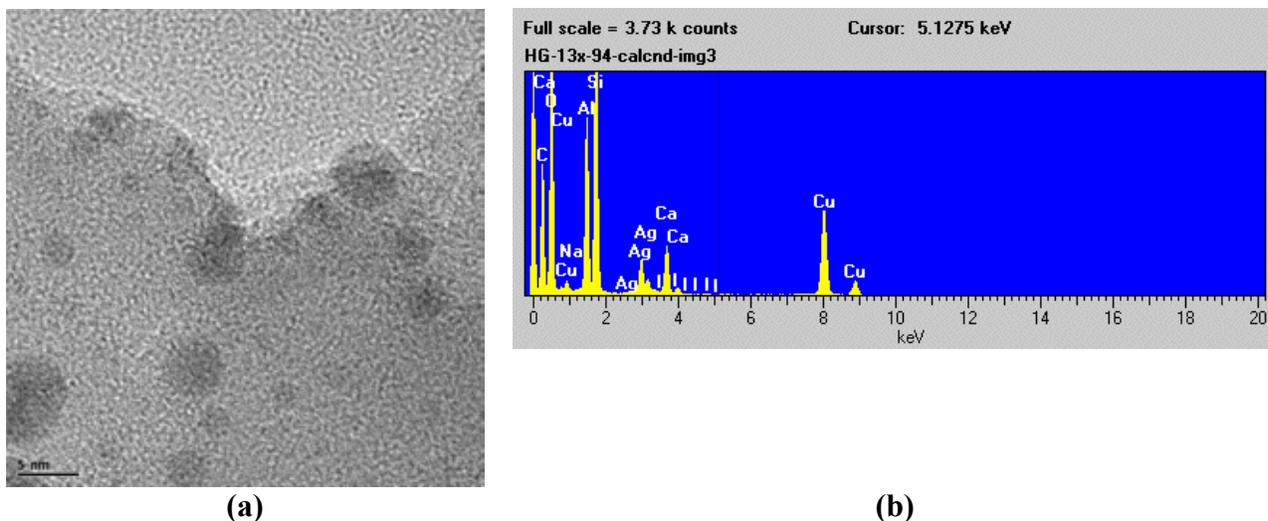


Figure 2: (a) HRTEM of Ag,I-X ceramic. Dark spots are Ag,I nanoparticle clusters; (b) EDX from TEM of matrix and nanoparticles identifying all components

### Copper Loaded Zeolites for I<sub>2</sub> capture and conversion to waste form:

In an effort to start comparing Ag with other transition metals, we loaded copper into the zeolites studied earlier (see above). Zeolite 13X and 5AP were cation exchanged with copper acetate. The copper loaded zeolites were subjected to the same procedures as with the silver (e.g., iodine adsorption, calcination, and leaching test).

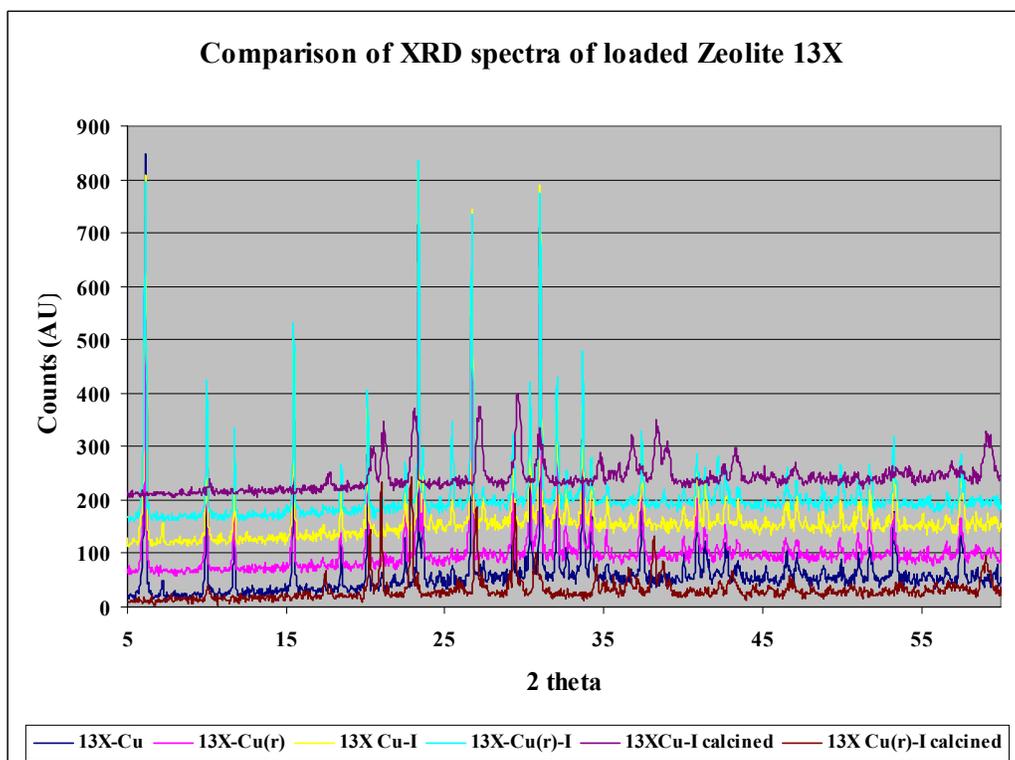


Figure 3: Powder X-ray diffraction patterns of Copper loaded, Iodine loaded Zeolite 13X Calcination was 1000°C. "r" stands for reduced copper.

From the XRD and elemental analysis results in Tables 1 and 2, the data shows:

1. Copper loaded zeolites have less iodine adsorption capacity than silver loaded zeolites.
2. Adsorbed iodine on copper loaded zeolite lose more than that on silver loaded zeolites during calcination.
3. Leaching test shows higher iodine loss for copper-zeolite.

Tables 1 and 2: From ICP/MS and AA analyses.

Sample ID	Average loss, %	
	I	Cu
13X-Cu-I --1	2.99	0.01
13X-Cu-I --2		
13X-Cu(r)-I --1	5.08	0.02
13X-Cu(r)-I --2		
5AP-Cu-I -- 1	8.98	0.02
5AP-Cu-I -- 2		
5AP-Cu(r)-I --1	10.82	0.02
5AP-Cu(r)-I --2		

Cu sample ID	[Cu], ppm	[I], ppm	Ag sample ID	[Ag], ppm	[I], ppm
<b>Zeolite 13X-Cu</b>	95430				
<b>Zeolite 13X-Cu-R*</b>	71760				
<b>Zeolite 13X-Cu-I</b>	93290	1106	<b>Zeolite 13X-Ag-I</b>	7089	7523
<b>Zeolite 13X-Cu-I-R</b>	65160	2923			
<b>Zeolite 13X-Cu-I calcined</b>	99820	1434	<b>Zeolite 13X-Ag-I calcined</b>	7156	8268
<b>Zeolite 13X-Cu-I-R calcined</b>	79070	2563			
<b>Zeolite 5AP Cu</b>	61670				
<b>Zeolite 5AP Cu-R</b>	missed				
<b>Zeolite 5AP Cu-I</b>	56720	6454	<b>Zeolite 5AP-Ag-I</b>	5388	4896
<b>Zeolite 5AP Cu-I-R</b>	59280	5748			
<b>Zeolite 5AP Cu-I calcined</b>	67030	1131	<b>Zeolite 5AP-Ag-I calcined</b>	8776	1348
<b>Zeolite 5AP Cu-I-R calcined</b>	66510	1126			

\* R = copper loaded zeolite has been reduced by ascorbic acid.

**Copper and iodine concentration in zeolite-Cu-I samples after leaching test (EDXRF data)**

sample ID	[Cu], ppm	[I], ppm
Zeolite 13X-Cu-I	101420	1152
Zeolite 13X-Cu(r)-I	77860	1722
Zeolite 5AP-Cu-I	66430	900
Zeolite 5AP-Cu(r)-I	65260	1397

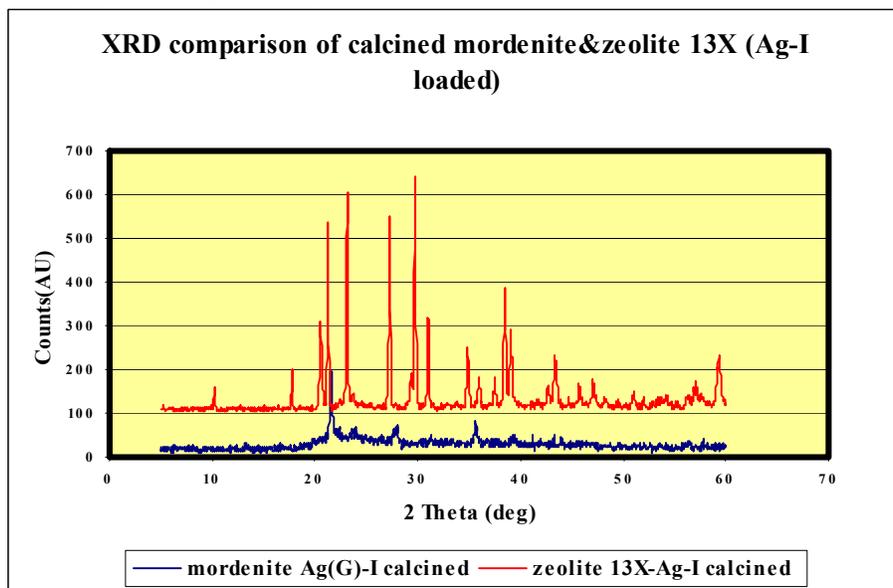
## Commercial IONEX Ag-Mordenite Studies:

IONEX Ag-Mordenite is being used by ORNL as a possible candidate for the CETE end to end study; it is the current commercially available Iodine capture material. For that reason, we chose to study it and compare it to our X and A zeolites. The material arrived already loaded with Ag; it was gray in color. The color indicates a silver coating on the outside of the zeolite; it does not indicate if and how much silver is in the pores. The powder XRD analysis indicates a poorly crystalline sample, see figures 4 and 5. This can be interpreted as either small amounts of mordenite mixed in an amorphous phase, a poorly crystalline mordenite, or mordenite mixed and extruded with a binder. We can also not tell at this time if the surface silver is on mordenite only or on another phase. SEM analysis will be needed to better understand the material. According to the MSDS from the manufacturer, silver content is about 19% of the product.

TGA/DTA (see figure 6) data indicates approximately 12wt% loss with heating (normal range for zeolites) to about 300°C. However, the DTA indicates an endothermic change occurring from 400°C and continuing through 1000°C. this does not correspond to the weight loss events and is not understood at this time. Table 2 lists the elemental analysis of the material at various stages in the process. We are unable to correlate the weight loss data with the mass balance.

From this initial study, we highly recommend (1) developing a washing method for the IONEX prior to Iodine sorption, to remove surface silver, (2) comparing sorption abilities with in house silver loaded mordenite, (3) analyze material for binder, and (4) explore other commercially available samples.

Figure 4: Powder Xray diffraction patterns of calcined IONEX Mordenite and X.



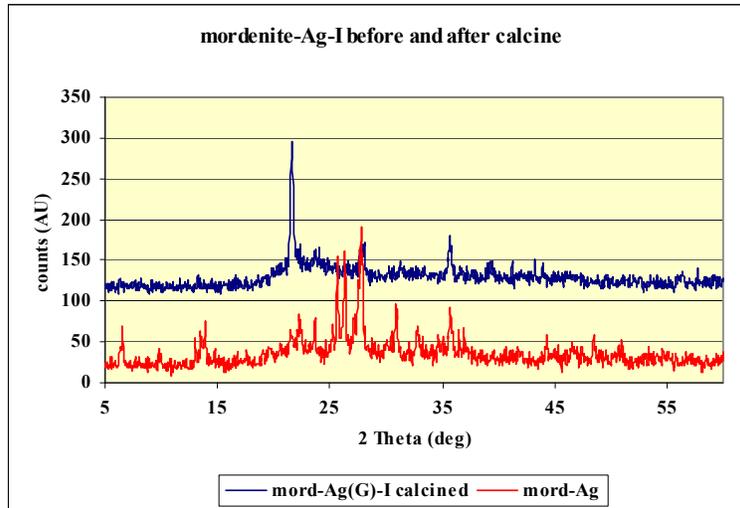


Figure 5: Poor Crystallinity of IONEX Mordenite pre and post calcination

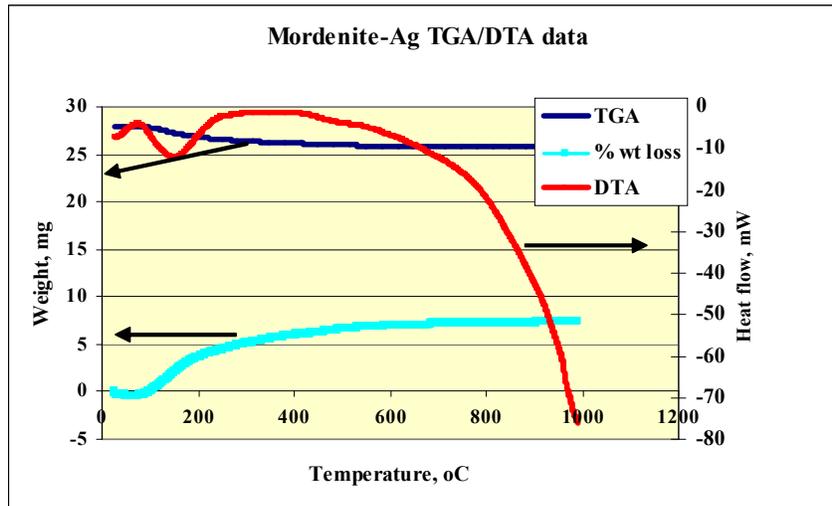


Figure 6: TGA/DTA data of IONEX Mordenite

EDXRF analyses

Sample ID	[Ag], ppm	[I], ppm	Ag/I	Iodine loss, % due to calcine
Mordenite-Ag	57490			
Mordenite-Ag(G)-I*	46170	11930	3.87007544	
Mordenite-Ag(R)-I	44040	12560	3.50636943	
Mordenite-Ag(G)-Icalcined	36000	4585	7.85169029	61.6
Mordenite-Ag(R)-I calcined	44646	5144	8.67923795	59.0
Zeolite 13 X-I	7089	7523	calcined	
Zeolite 13 X-I calcined**	7156	8268	0.86550556	-9.903

Note: \*Sample ID with (G) means that the mordenite-Ag is ground prior to further processes  
(R) means rod, not ground sample.

\*\* This negative result may be a result of dehydration of the zeolite during calcination, because of silver retention in zeolite 13

Table 2: Elemental Analysis of IONEX Mordenite series

## ***II. Bismuth Layered Compounds – Waste Forms***

In FY07, we investigated the synthesis of bismuth oxy-iodide and iodate compounds, in an effort to develop materials for Iodine recovery from caustic waste streams and/or if repository conditions included ambient conditions. A materials and durability study was undertaken to better understand this class of materials.

### **Bismuth oxy-iodide materials synthesis:**

Three sets of samples were prepared by dissolving bismuth nitrate and potassium iodide, mixing them in various ways and then causing a precipitate to form by occasionally adding sodium hydroxide. Specific details of preparation are:

“41 Series” Samples: Appropriate amounts of solid bismuth nitrate and potassium iodide salts were added dry to the bottle. Samples A and B had Bi to I ratios appropriate to preparation of  $\text{Bi}_5\text{O}_7\text{I}$  (Bi:I=5), C and D for  $\text{Bi}_7\text{O}_9\text{I}_3$  (Bi:I=2.33) and E and F for  $\text{Bi}_4\text{O}_5\text{I}_2$  (Bi:I = 2.00). Then, DI water (~ 50 ml), was added and the mixes put on a shaker at room temperature for about an hour. Finally, alternately in every other sample (~ 22 ml) an aliquot of 1 M NaOH (samples B,D,F) or an approximately equal amount of deionized water (samples A,C,E), was added. The mixes were then set back on the shaker overnight. The next afternoon they went into the oven (with the “42 Series” mixes) to age over the weekend at 90°. C. After three days, the samples were cooled to room temperature, the supernate was decanted off (and saved), and the heated solids were rinsed repeatedly with deionized water. At the end of the process the supernates from the B, D and F were still strongly basic (blue pH paper) while A,C and E were quite acid (red pH paper). See Table 3.

“42” Series Samples: Mixes A-F were designed to have the same Bi:I ratios in the “41 Series”, but the order in which the constituents were mixed was different. First the appropriate amounts of bismuth nitrate salts were placed in the bottles and an aliquot (~22 ml) of either 1 M NaOH (samples B,D,F) or deionized water (samples A,C,E) was added. Then, 50 ml of deionized water was added to each bottle and the mixes put on a (room temperature) shaker for 15 minutes. Generally, a white, milky slurry formed as the bismuth nitrate dissolved and hydrolyzed. Finally, the appropriate amounts of KI was added as a solid salt and the bottles returned to the shaker for about two hours. Samples were then placed in the 90° C oven over the weekend. The following Monday the samples were cooled to room temperature, the supernate was decanted off (and saved), and the heated solids were rinsed repeatedly with deionized water. At the end of the process the supernates from the B, D and F were still strongly basic (blue pH paper) while A,C and E were quite acid (red pH paper). See Table 3.

“1-10” series samples were prepared as described below. In this instance rather than trying to mix Bi and I in proportions, which would mimic known bismuth oxy-iodides the Bi to I, ratio was stepped up in 10% increments. These samples were prepared by dissolving bismuth nitrate and potassium iodide in deionized water, and then bringing the pH to near 7 with sodium hydroxide (and occasionally back titrating with a little acetic acid when adding the standard aliquot of NaOH resulted in a pH significantly above 7). Samples were then incubated in the 90° C oven overnight. The bismuth to iodine ratios in the different mixes were increased by 10% increments so that the sample with the greatest content of iodine (Series 10, very light blue, top

pattern) would have a Bi:I molar ratio of 1.4 (conducive to forming the compound  $\text{Bi}_7\text{O}_8\text{I}_5$ ) if all of the iodine had reacted with the bismuth. Parenthetically analysis of the post-synthesis fluids indicated, however, that complete uptake of iodine stopped with the 7<sup>th</sup> sample in the series, so that the synthesis of  $\text{Bi}_7\text{O}_8\text{I}_5$  was not actually achieved.

### Composition of bismuth oxy-iodide materials:

Table 3: Composition and other characteristics of the Series “41” and “42” samples

	Chemical Analysis			intensity	color	Prep - NaOH Added?	~8.6 A Peak	25-35 deg. 2-Theta Peaks
	by XRF I/Bi-molar	by XRF Bi/I-molar	by Design Bi:I					
41A	0.006	<sup>159</sup>	<sup>5</sup>	light	brown	no	major	5, 1 major
41B	0.214	<b>4.68</b>	<b>5</b>	medium	orange	yes	trace	6, 3 major
41C	0.011	<sup>91</sup>	<sup>2.33</sup>	dark	orange	no	major	4, 1 major
41D	0.433	<b>2.31</b>	<b>2.33</b>	dark	orange	yes	trace,shifted	3 major
41E	0.007	<sup>140</sup>	<sup>2</sup>	light	brown	no	small	4, 3 major
41F	0.520	<b>1.92</b>	<b>2</b>	dark	orange	yes	trace,shifted	6, 5 major
42A	0.009	<sup>114</sup>	<sup>5</sup>	medium	brown	no	major	5, 3 major
42B	0.213	<b>4.69</b>	<b>5</b>	light	yellow	yes	none	5, 3 major
42C	0.015	<sup>68</sup>	<sup>2.33</sup>	dark	brown	no	major	5, 3 major
42D	0.405	<b>2.47</b>	<b>2.33</b>	light	orange	yes	none	5, 1 major
42E	0.024	<sup>42</sup>	<sup>2</sup>	dark	brown	no	major	5, 1 major
42F	0.521	<b>1.92</b>	<b>2</b>	light	orange	yes	none	2 major

The rationale for carrying out the “1-10 Series” synthesis experiments was to approach the matter of synthesis in a more controlled manner. Toward this end more system variables were assessed as well as having the Bi:I proportions in the starting mixes incremented in smaller steps. After synthesis two parameters were measured on the remaining supernate, the pH and the residual iodine left in the solution from which the solids had precipitated (Table 4). Although the pH of the synthesis fluid was nearly neutral in all samples prior to the final incubation at 90° C, the heating process resulted in further reactions in samples 1-3, which lowered the pH. At present it is unclear what result would have been obtained had the synthesis been carried out in such a way that the final post-heating pH of samples 1-3 been near to 7, but experiments are underway to address this uncertainty. For the moment it is sufficient to note that for these samples a post-test iodide analysis of the supernate revealed that effectively all of the iodine added in the initial mix was, in fact, taken up by the low pH samples.

In contrast, for samples 8-10 an analysis of the post-heating supernate suggests that not all of the iodine provided in the synthesis ended up on the solids. This picture was confirmed by the XRF analysis of the solids (Fig. 7), which showed that after sample 7 the iodine content of the solids no longer increased in spite of the fact that additional iodine was provided by the synthesis recipe. The actual weight percent of iodine in the samples, of course, depends on all of the components in the compound. In this case the amount of oxygen assumed to be present was computed based on what would be needed to maintain charge balance in a compound containing only oxygen, iodine (as iodide) and bismuth. Earlier FTIR studies on similar compounds had

confirmed that neither hydroxide nor carbonate (as a contaminant in the NaOH used in the preparation) were present in significant amounts so this is a reasonable assumption.

Table 4: Composition and other characteristics of the "1-10" Series samples

	wt % Bi	wt % I	molar I:Bi	molar Bi:I	moles O	wt % I	% I in the Supernate	pH after heating
1	79.4	4.62	0.114	8.792	1.44	4.98	0.41%	2.1
2	72.22	6.445	0.174	5.732	1.41	7.45	0.31%	2.3
3	77.99	14.206	0.356	2.808	1.32	14.19	0.32%	2.3
4	74.8	17.99	0.470	2.127	1.26	17.98	0.30%	4.7
5	69.9	21.8	0.610	1.640	1.20	22.22	0.27%	5.2
6	57.37	17.7	0.603	1.658	1.20	22.03	0.29%	6.5
7	67.72	28.1	0.811	1.233	1.09	27.69	0.27%	6.8
8	61.33	24.33	0.775	1.289	1.11	26.77	12.86%	6.9
9	63.77	27.38	0.839	1.191	1.08	28.40	15.55%	6.8
10	66.16	25.87	0.764	1.308	1.12	26.48	26.50%	6.7

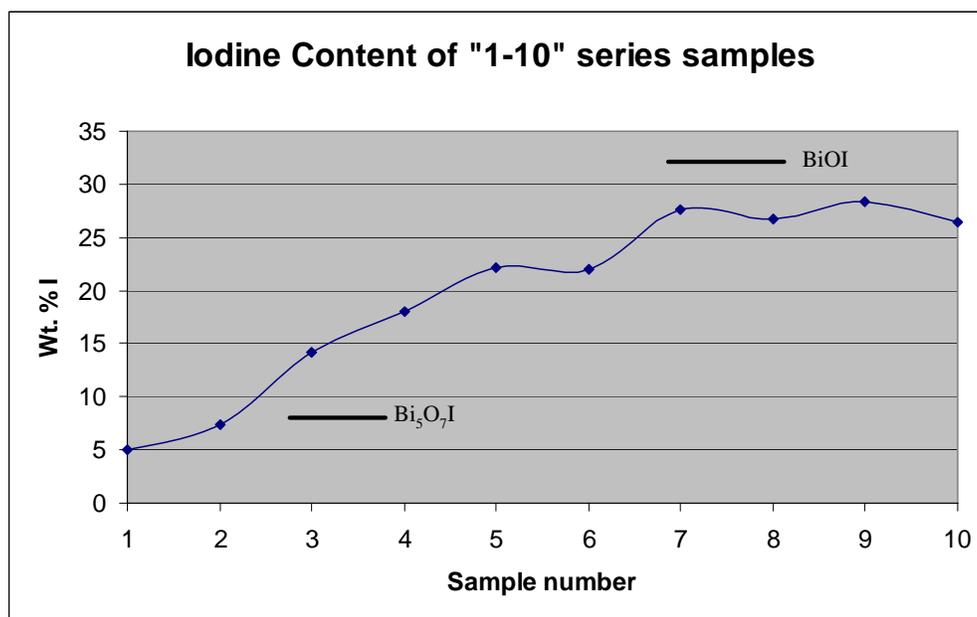


Figure 7: Iodine content of "1-10" series samples. Solid horizontal bars show theoretical iodine contents of two reference materials tentatively identified by X-ray diffraction.

### X-ray diffraction studies on bismuth oxy-iodide materials:

Powder X-ray diffraction patterns have been obtained for all of the materials described above. In general, many of the patterns exhibit similar features though in detail there are significant differences which have entailed some effort to resolve. Figures 8 and 9 provide diffraction data on the three "41" and "42" samples (respectively) which exhibited significant uptake of iodine (e.g., B, D, and F). Figure 10 provides a full display of all ten traces from the "1-10" series materials. These traces ultimately provided the basis for identifying the materials which are the most stable and contained the highest proportions of iodine (and hence make the most attractive targets for potential waste form development).

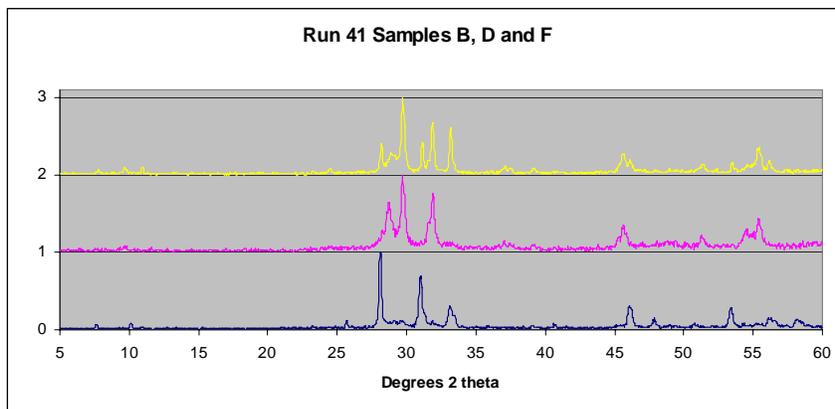


Figure 8: X-ray diffraction patterns for series 42 samples: B (bottom), D (middle), F (top).

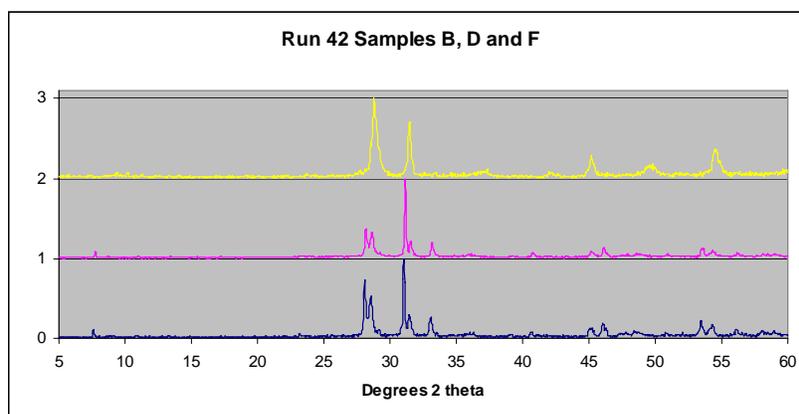


Figure 9: X-ray diffraction patterns for series 41 samples: B (bottom), D (middle), F (top).

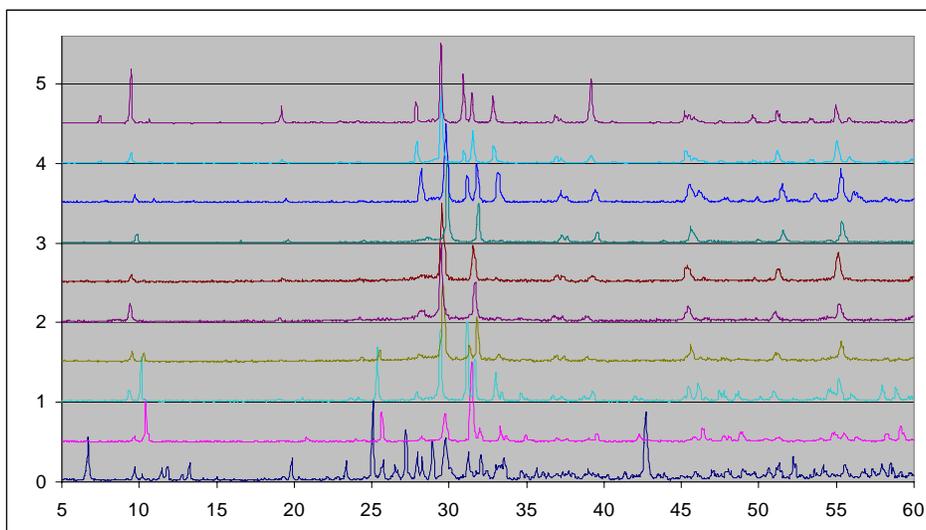


Figure 10: Series "1-10" X-ray diffraction patterns" series arranged in ascending sample number order: the compound with the most iodide initially present in the synthesis (#10, top) is at the top of the stack and the mix with the smallest initial iodide content is at the bottom (#1, bottom)

**Solubility studies on bismuth oxy-iodide materials:**

The solubility of bismuth oxy-iodide compounds can be approached from two directions; solubility in pure deionized water with the PCT test protocol, and the solubility in normal groundwaters (e.g., with Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). Fortunately, basic thermodynamic data is available for both BiOI and Bi<sub>5</sub>O<sub>7</sub>I. Calculations involving these data, and experiments still in progress to date, indicate that both HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> will quantitatively displace iodide from the waste even if only present at concentrations of just a few tens of parts per million. Thermodynamic data for the sulfate solubility is not available. Thus, to model the performance of a repository one can simply equate the outward iodide flux to the incoming flux of chloride plus bicarbonate (and maybe sulfate), provided that the basic solubility of the waste form is significantly less than the indigenous concentrations of the common groundwater anions.

Table 5, and Figures 11 and 12 summarize the results of deionized water solubility measurements for both the “1-10” and “41-42” series materials from room temperature to 90° C.

*Table 5a: Solubility, as ppm iodine, of bismuth oxy-iodide materials in deionized water.*

Temp - °C	ASH3-#2	ASH3-#4	ASH3-#6	ASH3-#8	ASH3-#10
25	0.03	0.01	0.04	0.52	0.91
47	0.07	0.01	0.01	1.03	1.30
75	0.76	0.07	0.01	2.61	2.67
90	2.62	0.21	0.04	3.69	3.62

Temp - °C	JLK-41B	JLK-41D	JLK-41F	JLK-42B	JLK-42D	JLK-42F
25	0.08	0.06	0.10	0.05	0.14	0.68
47	0.24	0.12	0.41	0.04	0.49	0.43
75	0.22	0.31	1.81	0.02	0.30	1.39
90	0.27	0.55	2.19	0.06	0.42	1.99

*Table 5b: Post-test quench pH values of solubility experiment fluids after sitting for 2-3 weeks at RT.*

Temp - °C	ASH3-#2	ASH3-#4	ASH3-#6	ASH3-#8	ASH3-#10
25	3.10	3.46	3.7	4.54	4.45
47	2.98	3.52	3.60	4.54	4.55
75	3.70	3.35	3.61	4.20	4.17
90	3.08	3.15	3.56	4.04	4.05

Temp - °C	JLK-41B	JLK-41D	JLK-41F	JLK-42B	JLK-42D	JLK-42F
25	4.19	3.81	4.29	3.92	3.72	3.98
47	3.92	3.76	4.18	3.88	3.66	3.82
75	3.73	3.65	3.91	3.68	3.36	3.69
90	3.66	3.64	no spl. left	3.71	3.44	3.67

The level of iodine leached from the various materials is a few parts per million. Figure 8 clearly demonstrates that there is a significant difference in the overall stability of the different materials, with the materials giving relatively well defined patterns for BiOI holding a distinct advantage (e.g. lower solubility and hence greater stability) over materials at either end of the compositional spectrum. In a general sense this picture is also supported by the series “41-42”

samples (Fig. 9), though, since these experiments did not explore the low-iodine end of the spectrum curves analogous to ASH3-#2 in Fig.8 do not appear in Fig. 9

Figure 11: Solubility of select “1-10” series materials in deionized water

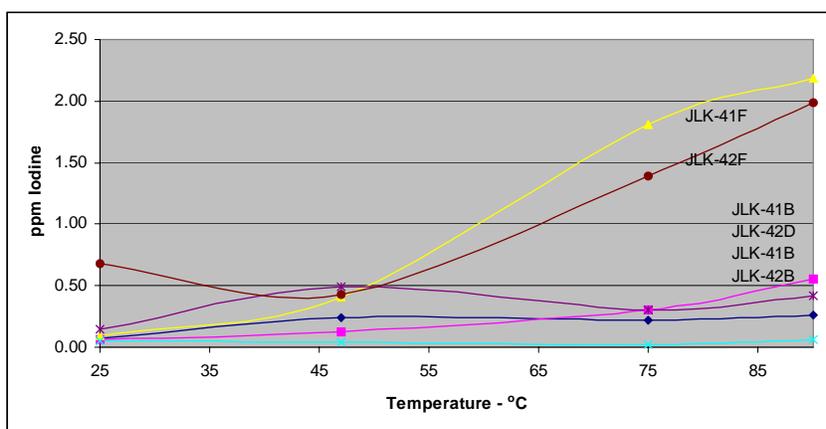
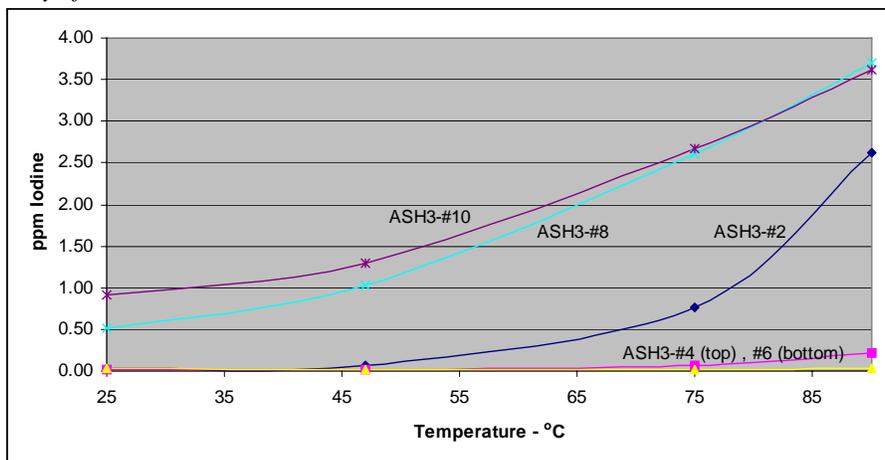


Figure 12: Solubility of “41-42” series materials in deionized water

We discovered an intermediate composition of Bi-O-I materials (#4-6, Table I-1, containing 17-22 weight percent iodine, and having an X-ray diffraction patterns similar to BiOI, see figure 13) that leaches out significantly less iodine than materials synthesized with either more or less iodine (relative to the amounts of Bi in the mix). In terms of sample identification, the #10 pattern could be matched by a mix of 2 “parts” Bi<sub>5</sub>O<sub>7</sub>I and 5 “parts” BiOI (Fig.14 ). Relative iodine releases are illustrated below (Fig. 15). We have also assessed the stability of two of the materials (#6 and #8) with regard to the presence of common groundwater anions thought to have a propensity for interacting with these potential waste forms (Fig. 16). Carbonate is apparently the anion of greatest concern.

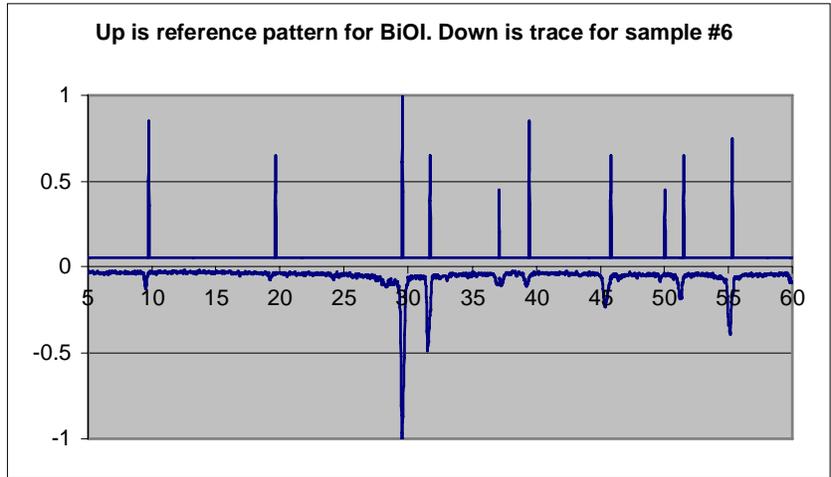


Figure 13: XRD match between the reference pattern for BiOI and pattern #6

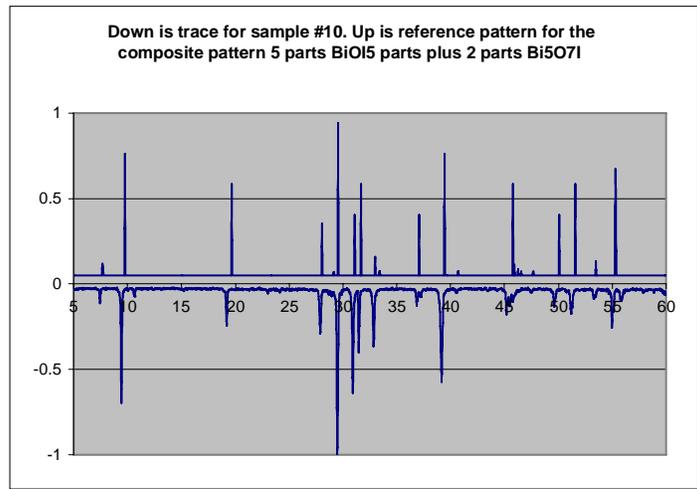


Figure 14: Match between Sample #10 trace and a composite reference pattern of five parts BiOI plus two parts Bi<sub>5</sub>O<sub>7</sub>I. Reference pattern points up, actual trace for #10 points down.

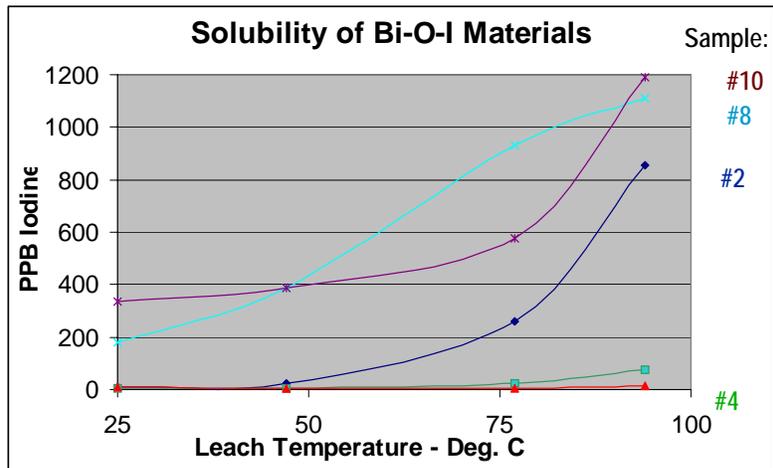


Figure 15; Iodine-deionized water (“PCT”) leach test results for “1-10” series samples (~50 mg of solid in ~50 ml of fluid). Note superior performance of samples #4 and #6

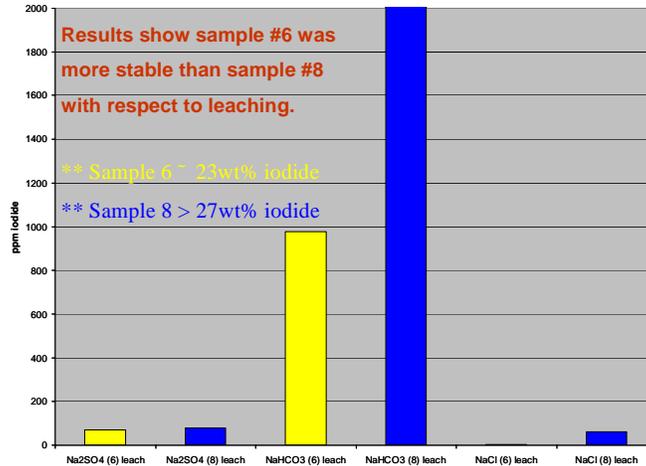


Figure 16: Contrasting iodine releases in 0.005 molar sodium sulfate, bicarbonate and chloride solutions (0.1 – 0.2 g of solid in 20 ml of leach fluid).

### III. Cancrinite-Zeolite In-situ Waste Form Preliminary Study:

The trapping of iodine in a NaOH wash is an alternate method of scrubbing radioiodine from reprocessing offgases before they are vented from the plant. One unique method of sequestration might be in-situ growth of a zeolite “around” iodine trapped in a caustic solution.

The mineral cancrinite can be readily synthesized by simply adding kaolinite clay to a strong NaOH solution and heating the mix at 90° C for a few days. To test this method, concentrated NaOH solutions were doped with varying amounts of iodide (Series 9 materials) and iodate (Series 14 materials). Details of the mixes used are provided below (Tables 6 and 7)

After being mixed in the proportions shown, the slurries were aged over the weekend at 90° C and then rinsed repeatedly with deionized water to wash away excess iodine. The material is then analyzed by XRF for elemental composition. Our preliminary data shows that both forms of iodine (as either iodide or iodate) can be incorporated into a cancrinite structure. This duality is an important since when elemental iodine is scavenged using NaOH solutions it disproportionates to form both iodide and iodate. Thus, any waste form intended for use in conjunction with a NaOH based capture technology should be able to sequester both forms of iodine. Also, in some cases the amounts of iodine sequestered in ‘cancrinite’ compete favorably with what can be scavenged by silver-loaded zeolites.

Table 6: Synthesis details of iodide-bearing cancrinites

Page 9 of Ashwath's notebook

	g Kaolinite	g KI	g NaOH	di H <sub>2</sub> O	wt % I
Clay 1	4.052	0.322	0.327	20 ml	0.113
Clay 2	4.093	2.513	0.327	20 ml	1.538
Clay 3	4.032	1	1.063	20 ml	7.73
Clay 4	4.052	0.309	2.514	20 ml	5.426
Clay 5	4.035	2.506	2.506	20 ml	31.55

Table 7: Synthesis details of iodate-bearing cancrinites

Page 14 of Ashwath's notebook

	g Kaolinite*	g KIO3	g NaOH	wt % I
14-1	2.052	0.207	0.178	0.178
14-2	2.001	1.648	0.171	0.416
14-3	2.009	0.67	0.545	4.381
14-4	2.035	0.191	1.201	31.09
14-5	2.061	1.624	1.312	66.97

\* Note: clay cut in half from page 9 recipes because we were running low on it .

These materials have also been characterized by X-ray diffraction (Fig. 17). Although some runs did produce cancrinite, there are instances where part of the kaolinite failed to react. Also, in some experiments something zeolitic, but not cancrinite was formed.

We completed preliminary leach data in deionized water at 90° C (Table 8) on the iodine-loaded zeolites. In general, these materials do not retain iodine as well as the bismuth-based waste forms, with ppm level releases being the rule. These materials were all are very difficult to wash.

Although we were successful at demonstrating the uptake of iodine in a both bismuth and cancrinite structures, and they both offer unique research for the future, we will pursue other avenues of zeolite based research for Iodine uptake.

Figure 17: X-ray diffraction patterns of zeolites synthesized as per Tables 6 and 7.

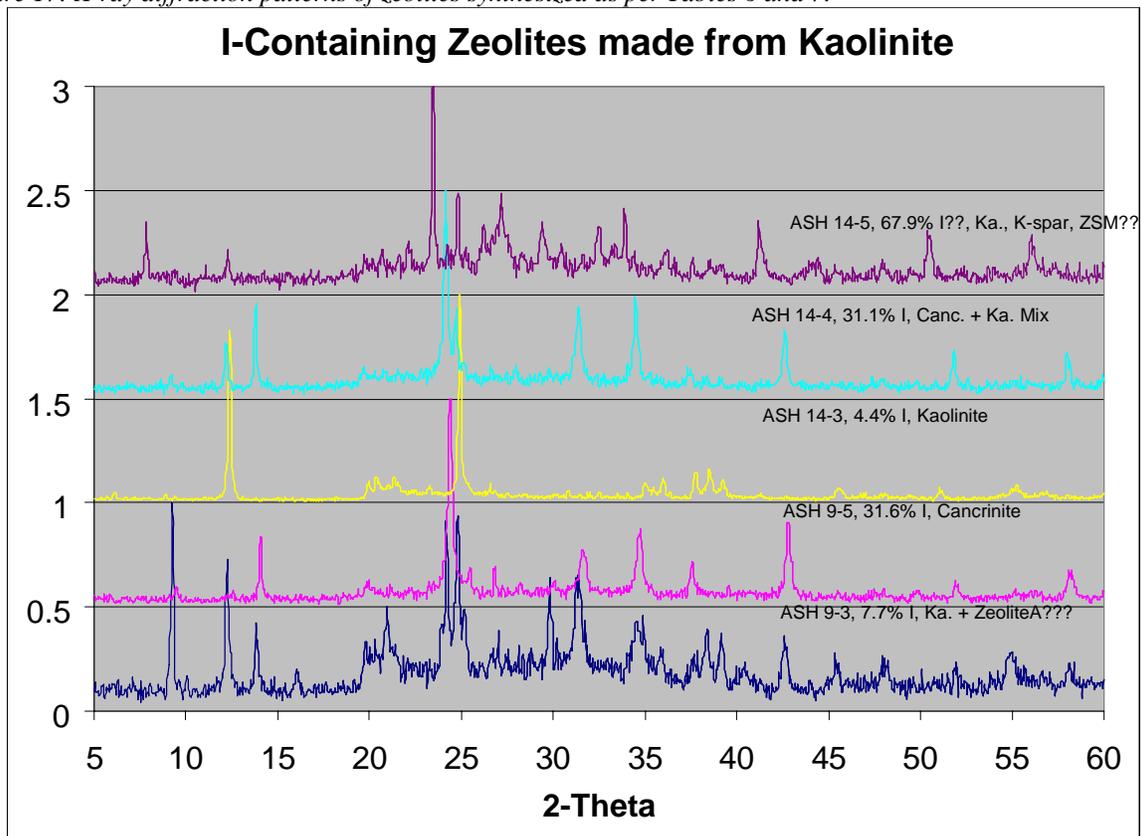


Table 8: Leach test results in deionized water at each 90° C.

Sample #	ppm I in leach fluid
14-3	4.2
9-3	0.48
9-4	19.0
9-5	13.5

### Conclusion:

During this first year of the project, we have focused on a few different classes of materials for iodine removal from the GNEP cycles. In general, there were two groups of materials: (1) metal-loaded aluminosilicate zeolites and (2) in-situ crystallization of layered materials including bismuth and cancrinite (Al/Si).

To date, our preliminary results show that the silver loaded X (FAU) zeolite has the highest loading of iodine, the least leaching after calcinations at 1000°C and is mechanically durable through calcination and leaching. We have also started comparing this material to commercially produced silver loaded (IONEX) mordenite. Our initial data indicates that this mordenite might not have the crystallinity or the entrapped silver content needed for an optimized iodine storage material.

Our work with the in-situ crystallization of waste forms around I<sub>2</sub> from caustic solutions, as those possibly found in the Areva processes, netted some interesting materials. The series of phases in the Bi-I-O phase space produced a mixture of related phases. These phases, their crystallinity, iodine loading and solubility is all closely related to the structures and mixtures of structures. For example, we were able to attain over 20wt% Iodine loading into a phase that has low solubility; we have identified it as having BiOI plus two parts Bi<sub>5</sub>O<sub>7</sub>I. Further research into the phase identification would possibly yield detailed information on the structure/property relationships of the phases and their iodine uptake and retention. However, our plans for FY08 only include completion of a technical advance for a patent submission.

Our proof of concept was successful in the case of in-situ crystallization of cancrinite zeolite around iodine from a base solution of NaOH. Optimization of the process is needed if phase pure cancrinite were to be made and all iodine captured. However, much like with the bismuth compounds, we are completing our current experiments and do not have plans to continue this line of research in FY08.

In FY08, we will continue research on the zeolite-Al/Si waste form development. In particular, we will focus on the structure/property relationship between the type of zeolite and the performance, the metal type versus iodine uptake, the amount of metal versus iodine uptake, and heat treatment methods versus iodine retention. Furthermore, we plan to focus on the optimization of the waste form but studying the surface areas, binder compositions, pellet size, etc. This will eventually allow us to work on scale up studies of the optimized waste form.

In collaboration with the GNEP Waste Form Campaign, we will perform testing and durability of the materials synthesized in this program.

## Appendix A: Examples of Literature Search Results

### *Iodine*

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L. L. Burger; R. D. Scheele; C. L. Matsuzaki, "Methyl Iodine Sorption by Reduced Silver Mordenite" June 1983. PNL-4498/UC-70

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## Distribution List

- 5 MS1415 Tina M. Nenoff, 1114
- 1 MS0754 James Krumhansl, 6316
- 1 MS0779 Huizhen Gao, 6772
- 1 MS0779 Kevin McMahon, 6772
- 1 MS0166 Sandhya Rajan, 121261
- 1 MS1415 Carlos Gutierrez, 1114
- 1 MS0754 Mark Rigali, 6316
- 1 MS0736 Veena Tikare, 6771
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