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Durable Materials for GNEP Iodine Waste Streams

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Albuquerque, NM 87185

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE's NNSA under contract DE-AC04-94AL85000.

Outline

- **Program Goals**
- **Introduction to Iodine Waste**
  - GNEP needs
  - Repository Studies
- **Experimental History**
  - Program Update
  - Budget Status
  - Interfaces
  - Actions
- **Getters and Storage Waste Forms**
  - Aluminosilicates
  - Bismuth Compounds
  - MOFs
- **Future Plans**

Overall program Goals

- Waste form by Design - Ag-I Zeolite Waste Forms and related metal loadings that can be validated for GNEP cycle designs
- Flexible for iodine feed stream and sequestration material - universal materials
- Flexible to repository/storage needs
- Structure/Property Relationship of Waste forms:
  We are pursuing the understanding of the properties of waste and storage forms to predicting their long-term behavior
- We plan to expand our studies to include :
  MD sorption/durability modeling of Waste Forms
  Work collaboratively with Waste Form Development Campaign for materials testing

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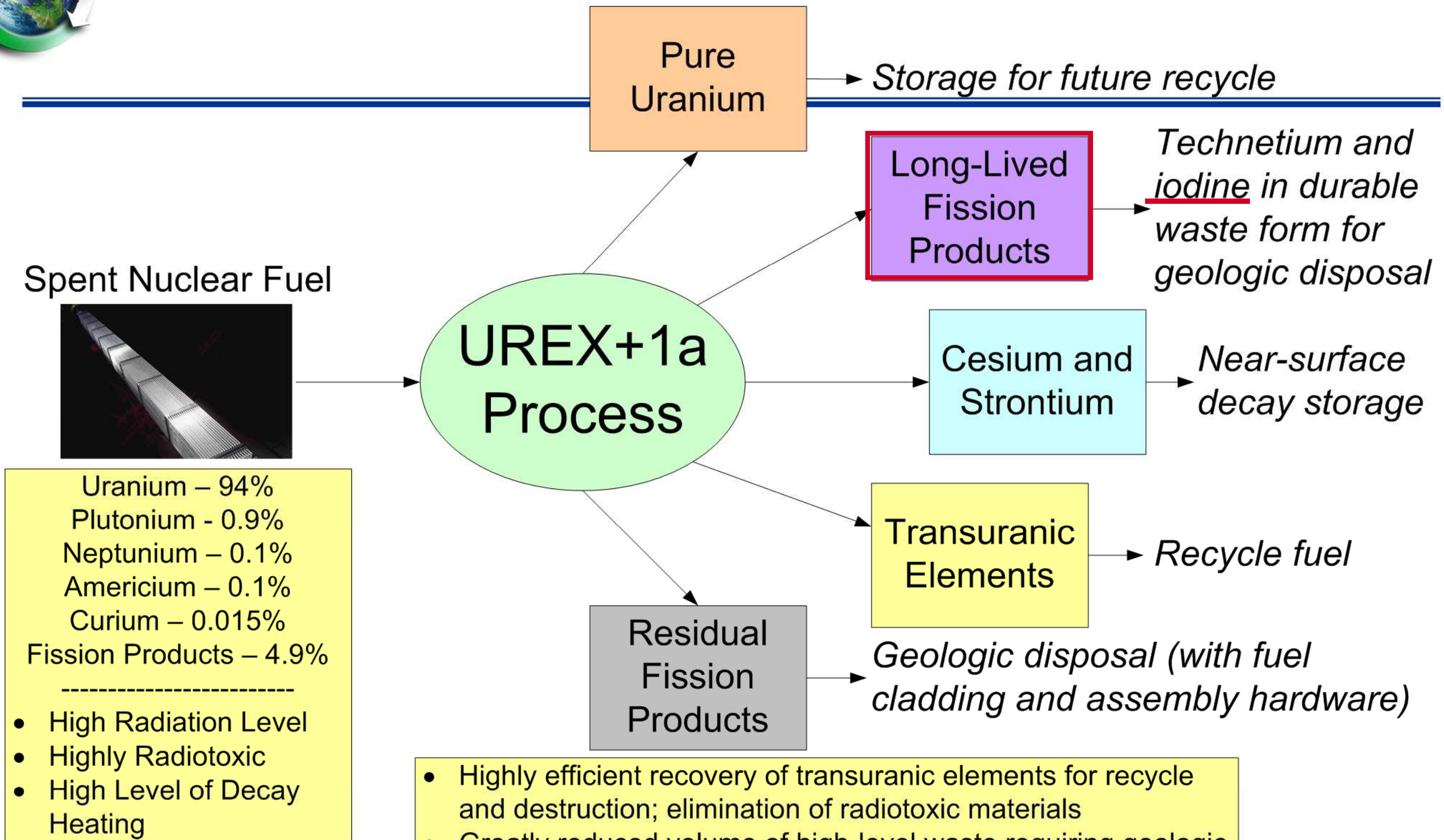
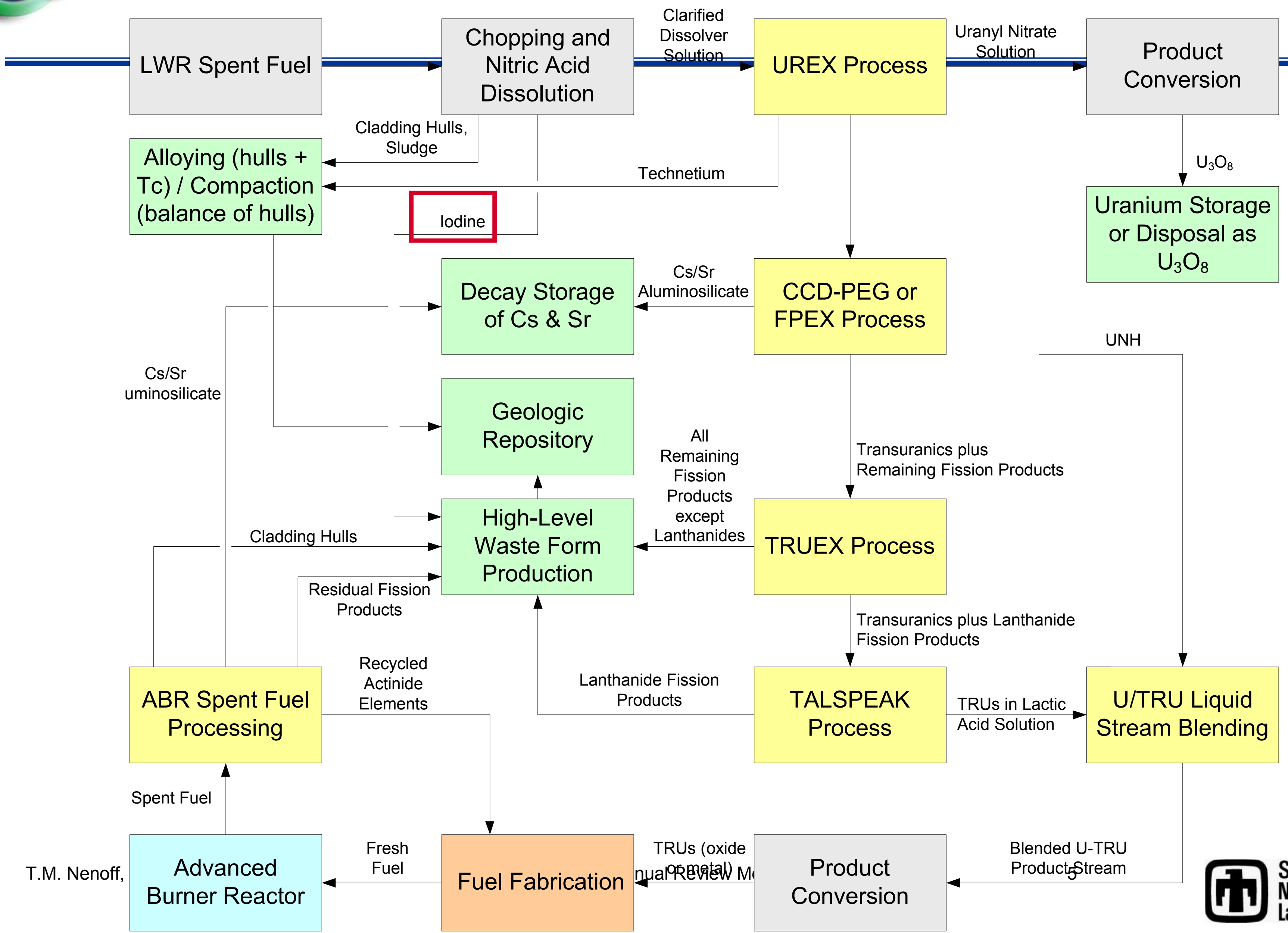
GNEP Commercial Fuel Reprocessing (J. Laidler)



- Highly efficient recovery of transuranic elements for recycle and destruction; elimination of radiotoxic materials
- Greatly reduced volume of high-level waste requiring geologic disposal; fewer expensive waste containers needed
- Greatly reduced heat generation rate of high-level waste allows increase in repository capacity; one repository will be sufficient to support an expanded nuclear program for at least the rest of the 21st century

UREX+1a Process: Group Extraction of TRUs (J. Laidler)



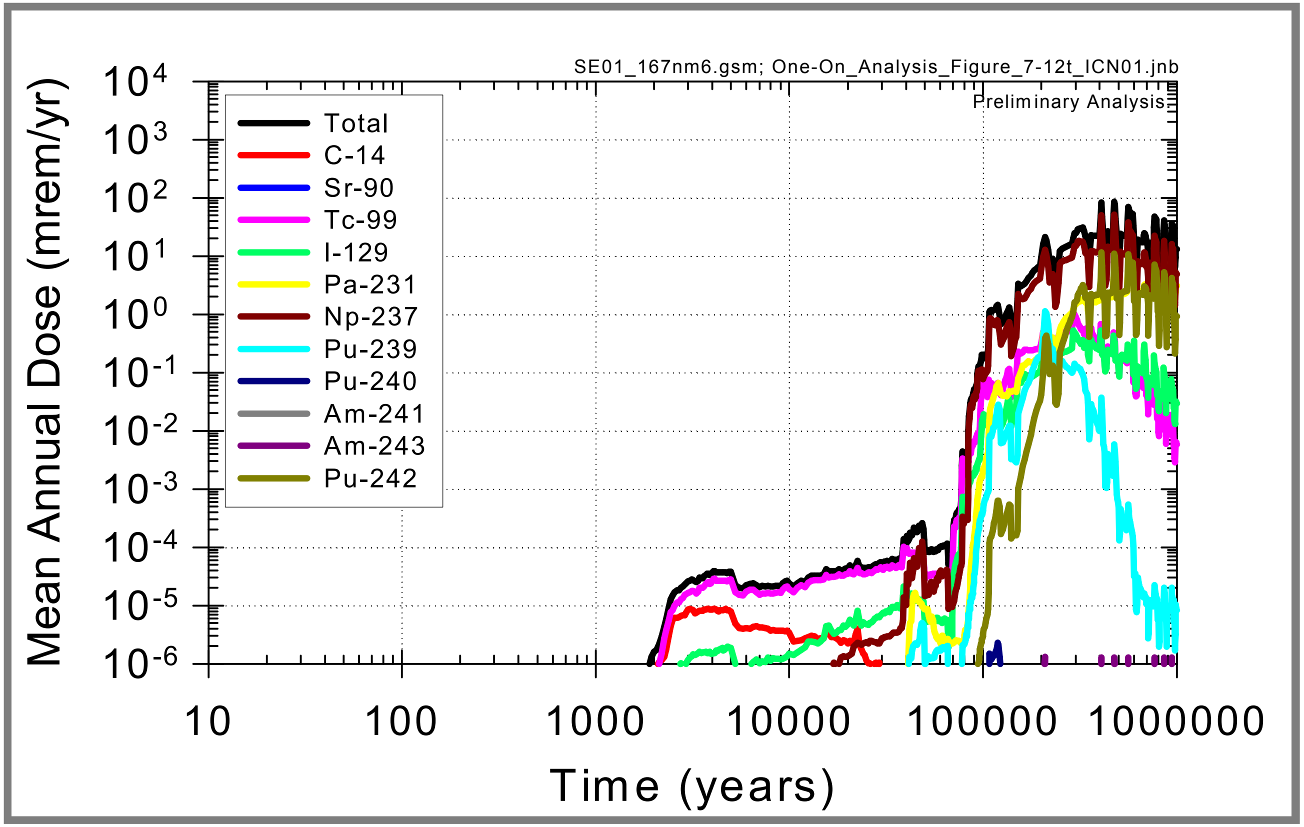
Why Iodine Is Important To Store

I-129 is small in concentration but long-lived
Known participant in Human Metabolic Process

- **2002 SR/FEIS analyses of 1 million year performance indicate that YM will be licensable under proposed EPA peak dose rule assuming current waste forms**
  - Np-237 is the largest contributor to dose, followed by other actinides
  - Tc-99 (half life 213K yr) & I-129 (half-life 15.7M yr) will dominate peak dose if actinides are removed
  - *Iodine-129* tracks with Tc-99, less important than Tc-99 until after 300,000 yr when decay lowers dose from Tc-99.

- **Possible reprocessing impact (2002 SR/FEIS TSPA model)**
  - Total peak dose would have been earlier and almost two orders of magnitude lower in this model if actinides were removed, but peak would still occur far beyond 10K years
  - Separation of 95% of Tc-99 would could reduce dose an additional 20x, peak will still be significantly beyond 10K year
  - Increases in total spent fuel equivalent inventory would increase Tc-99 dose proportionally

Contributors to Nominal Performance Dose 2002 YM TSPA Model (2002 SR/FEIS work)



Results from ANL-WIS-PA-000004 Rev. 00 ICN 00 (“one-on analysis” Case 12).

From Peter Swift, SNL

SNL Separations Waste Forms Expertise

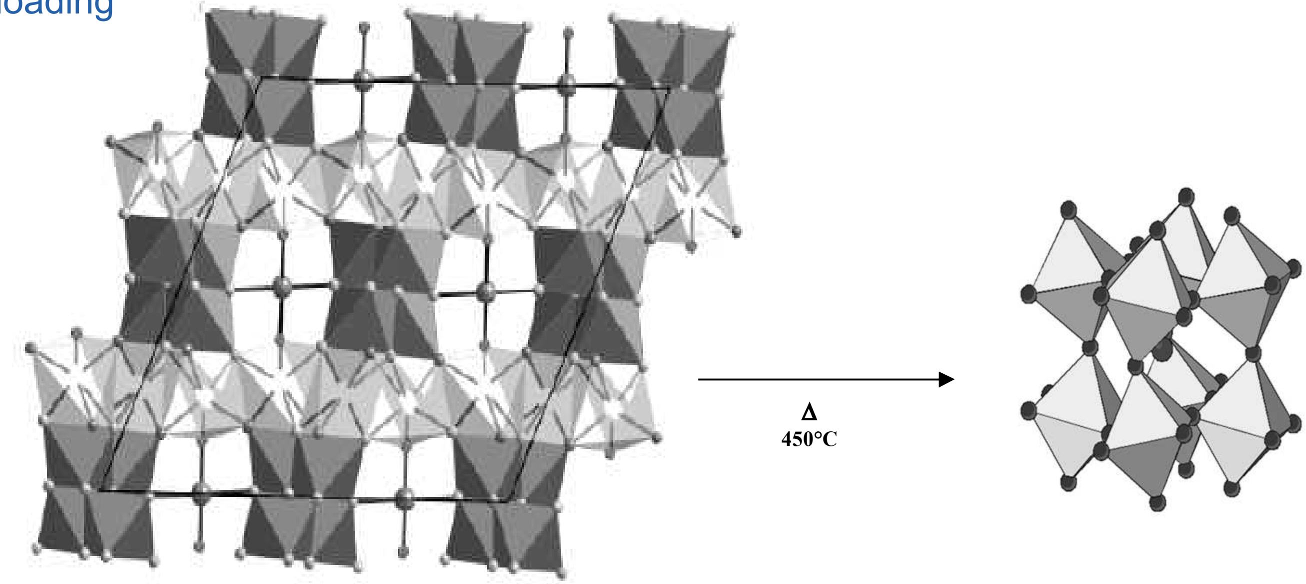
We have a Combination of
Synthetic Chemists, Geochemists, Nuclear & Repository Engineers

- **Ceramic Waste forms - metal loaded Mineral Analogs (zeolites & clays)**
- **Structure/Property relationship studies**
  optimization of waste form by variation of zeolite, metal, processing, loading level (metal vs. iodine uptake), stability vs.time
- **Modeling/Simulation - Validation and Optimization**
  Molecular Dynamics of ion permeation and H-bonding

Historical: Direct Thermal Conversion of Sr-loaded Materials to Stable Waste Form

SOMS: Sandia Octahedral Molecular Sieves
Nenoff, etal.
US Patent No. 6,596,254 & 7,122,164
Chem. Mater. **2005**, *17*, 950 (and refs within))
Up to ≈ 35wt% Cs loading

Cs/Sr Baseline Report



Ion Exchanged SOMS
$Na_{12.8}Sr_{3.2}Nb_{12.8}Ti_{3.2}O_{48}8H_2O$

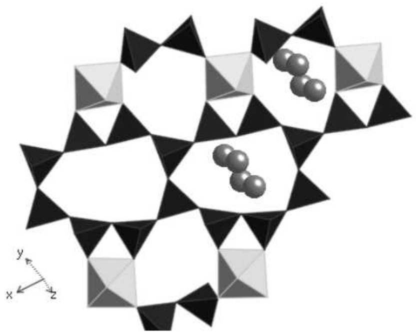
Highly Selective Ion Exchanger
strontium loaded

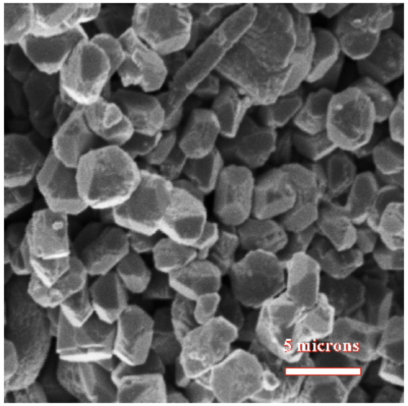
SOMS converted perovskite
3.2 x $Na_4SrNb_4TiO_{15}$

Stable Sr-containing Waste Form
perovskite

Historical: *One-step* Waste forms for Cs

$Cs_2TiSi_6O_{15}$





Silicotitanate Waste Form Phases
In-situ formation around Cs^+ in solution

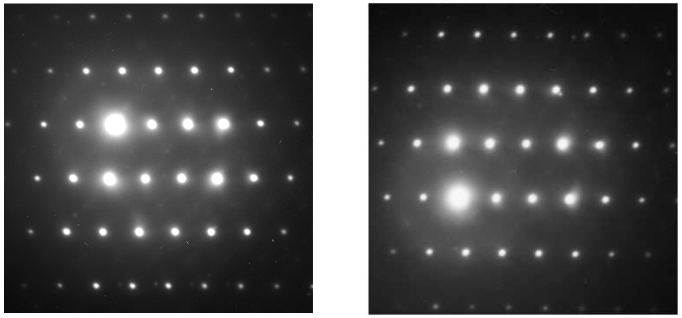
- Low temperature ceramic forms in solution "around" Cs^+ ions

- Very Low Cs leach rate
- Small volume waste form
- Thermally stable to 1000□C

Nenoff, etal., US Patent No. *6,482,380*
Chem. Mater., **2002**, *13*(12), 4603
Chem. Mater., **2000**, *12*, 3449

Cs/Sr Baseline Report

Stable w/increasing Radiation Dose



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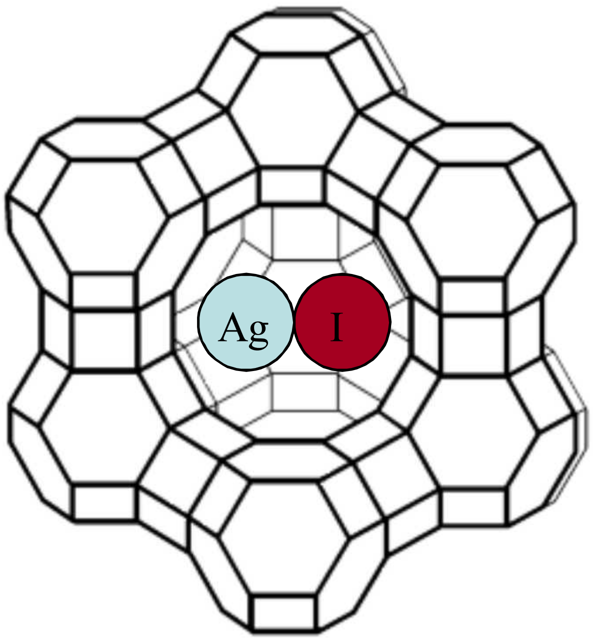
Metal loaded Zeolites (Al/Si) for Iodine Waste Forms



Zeolite-M for ^{129}I capture and Heat treated storage (M = Ag, metals)

Theory: Understand why Ag-I-Zeolites are stable waste forms and apply to development of other metal-Al/Si lower temp, high durability waste forms

Experimental: Study metal loading vs. Iodine loading, identify and study stability of Metal-iodine heat treated phases, understand nature of Iodine capture(many phases tested)

Characterization: XRD, Scanning Electron Microscopy (SEM/EDX), XRF, elemental analysis, surface area analysis

Research Plan for Aluminosilicate / Zeolite Iodine Separations and Waste Forms

Steps to Develop / Characterize Iodine Loading & Conversion to Waste Form

- Ag-Zeolite Studies:
  includes XRD, TEM, SEM /EDX studies on Mordenite
- Study variations in Al/Si Framework:
  change of pores size and acidity of framework
- Variations in Amount of Ag in Zeolites:
  loading level vs. Iodine uptake and retention
- Chemistry of the Ag-I in Zeolite:
  why does it work? Would anything else work better?
- Waste Form Study:
  materials characterization to locate and understand I_2 loading
- Modeling/Simulation:
  validation of experimentation and characterization
- Comparison to other transition metals in optimized zeolites:
  anything cheaper? more environmentally friendly?
- Work with Waste Form Campaign to study the durability of the waste form

Iodine Loading & Heating Conversion to Waste Form

Uniform Preparation of Zeolites, Loading of Iodine, Conversion to Ceramic:

1) **Prep Zeolite**: As received

2) **Loading Ag**:
   Ion exchange process of 5g Zeolite + 36 ml $AgNO_3$
   RT stirring for 6 hours
   Filter in air, rinse with DI H_2O (3x)
   Dry overnight at 45°C; white color

3) **Loading I_2**:
   1g Ag-Zeolite placed into 100 ml Teflon jar
   0.08g Iodine solid into a 20 ml vial
   Place vial into same Teflon jar and sealed
   90°C for 6 hours
   Open Teflon jar to fume hood for 2 days
   for removal and desorption of surface Iodine; brown color

4) **Calcination**: Heating in a high temp muffle furnace
   RT to 1000°C, ramp 20°C/min, hold at 1000°C 2.5 hours, cool to RT

Ag,I - Loaded Zeolite X (FAU) Studies

Leach results: *Initial* studies as determined by XRD and ICP/MS; % leached iodine

Calcine T, °C	200	400	600	800	1000
Zeolite 13 X	22	21	34	2	1
Amoco A	39	46	86	6	6
Zeolite 5AP	4	2	3	2	2

Using larger samples (to decrease possible experimental error), samples of X and AP were Fully loaded and heat treated to 1000°C for 2.5 hours

Final wt loss due to leaching (%):

Zeolite 13 X = 0.12
Zeolite 5AP = 0.30

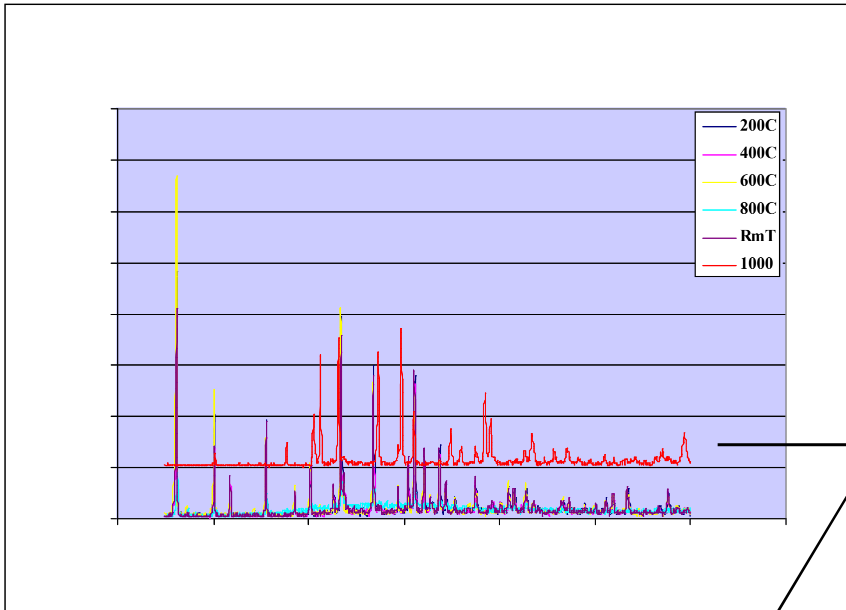
Next steps: Study the structure of the "Ag-I-Zeolite" as-synthesized and heat treated phases

Using developed metal & Iodine loading methods, study a variety of metals for more economical waste forms

Complete structure determination of ceramic waste form

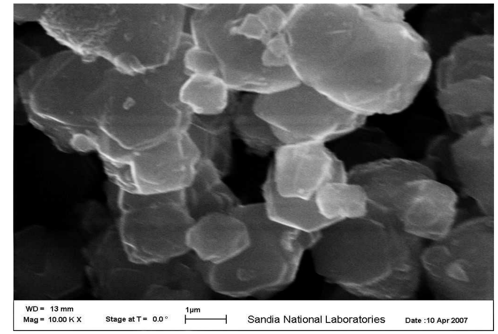
Ag,I - Loaded Zeolite X Studies:
Morphology is maintained through processing

XRD:

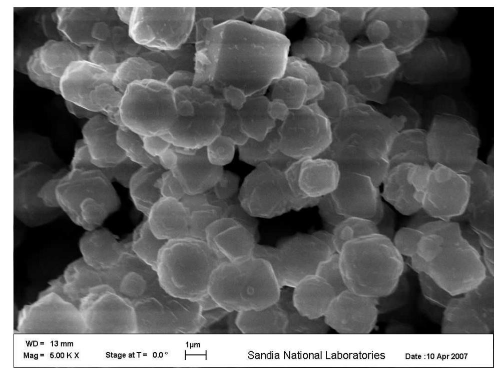


SEM:

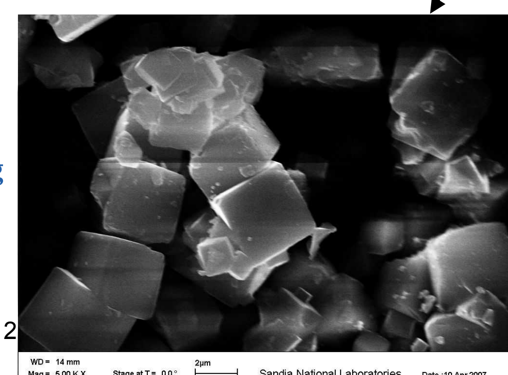
As-synthesized



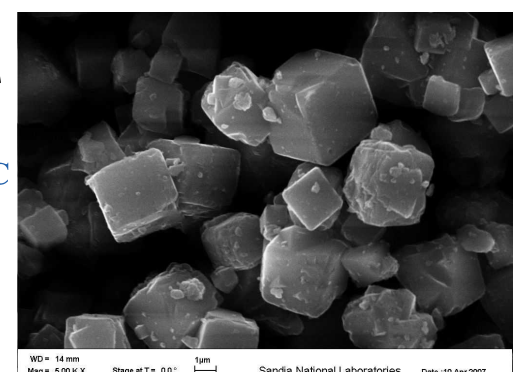
Ag, I loaded



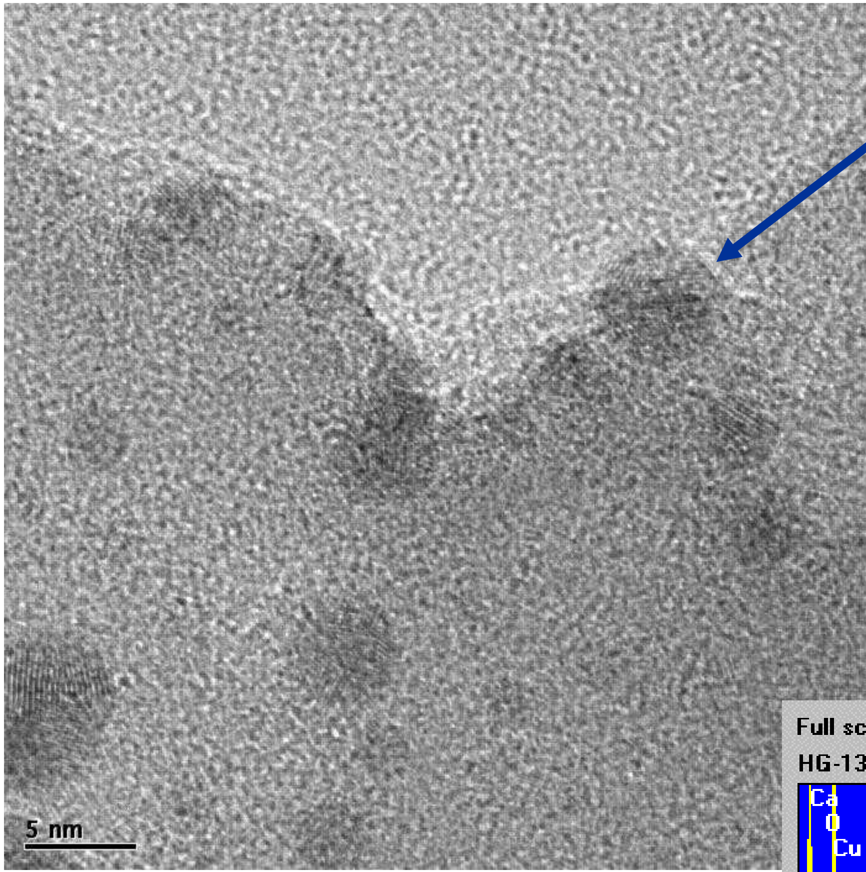
Post leaching



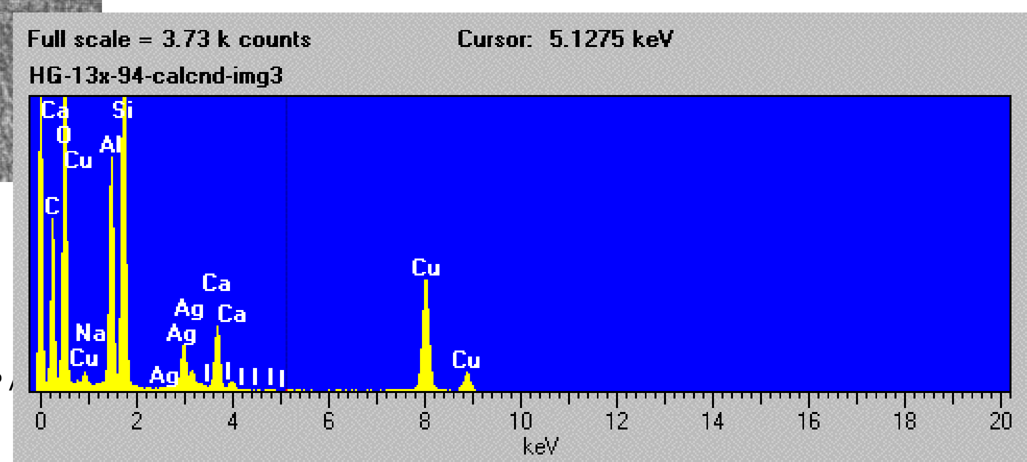
Calcined 1000°C



HRTEM studies of Ag-I-ZeoX Ceramic Waste Form

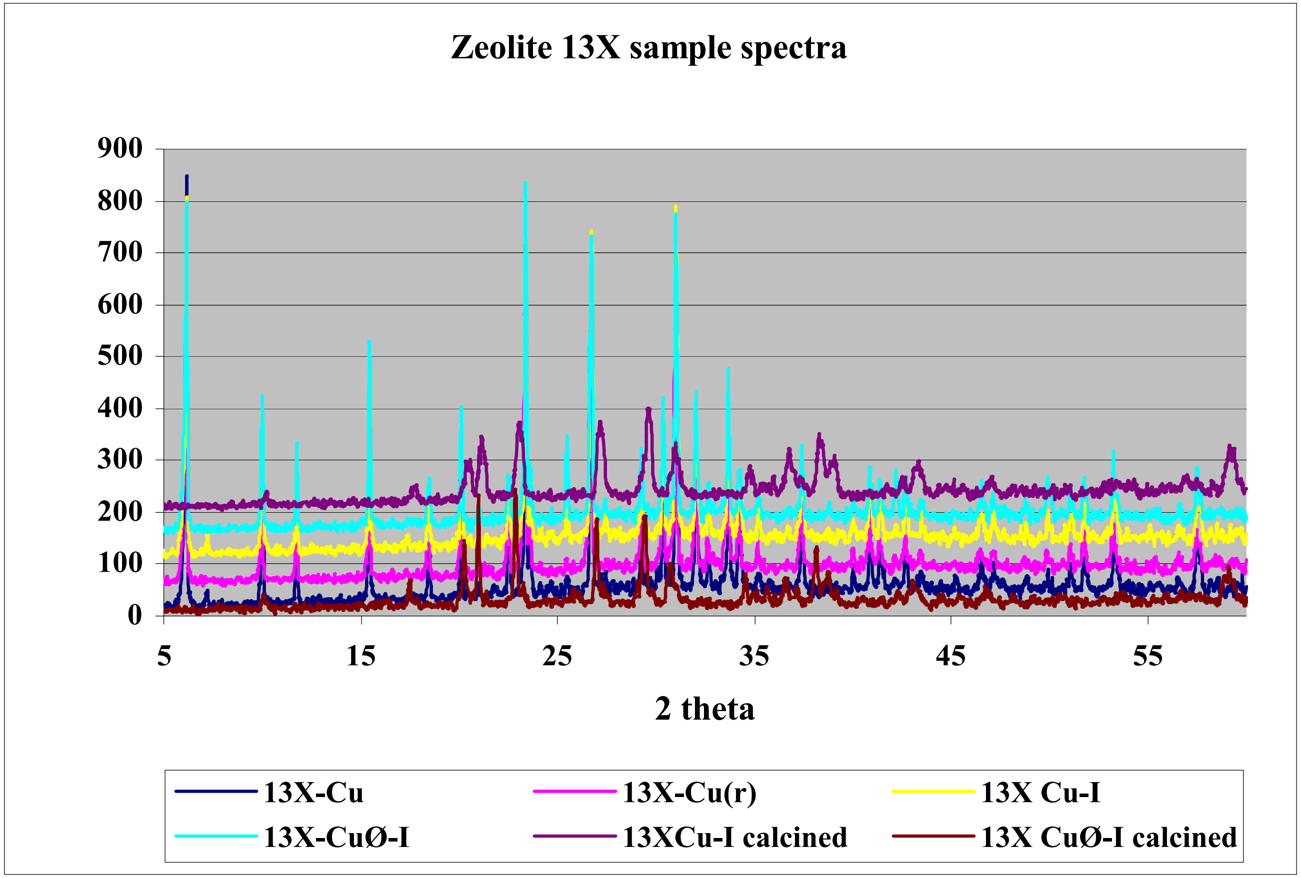


- Ag-I nanoparticles embedded in ceramic matrix (Na/Ca/Al/Si) - 1000°C
- Iodine is unstable in e^- beam, difficult to determine concentration
- Nanoparticles are stable in comparison to matrix
- Need to study thermodynamics to maximize stability to environment
- Crystal structure studies underway



X-ray diffraction studies to elucidate the structure are underway at SNL

Cu,I - Loaded Zeolite X (FAU) Studies



We were able to synthesize a Cu-based zeolite waste form but…
Cu loading is lower than Ag waste form versions; Awaiting Leach test, TEM and SEM
How do other transition metals compare??

T.M. Nenoff

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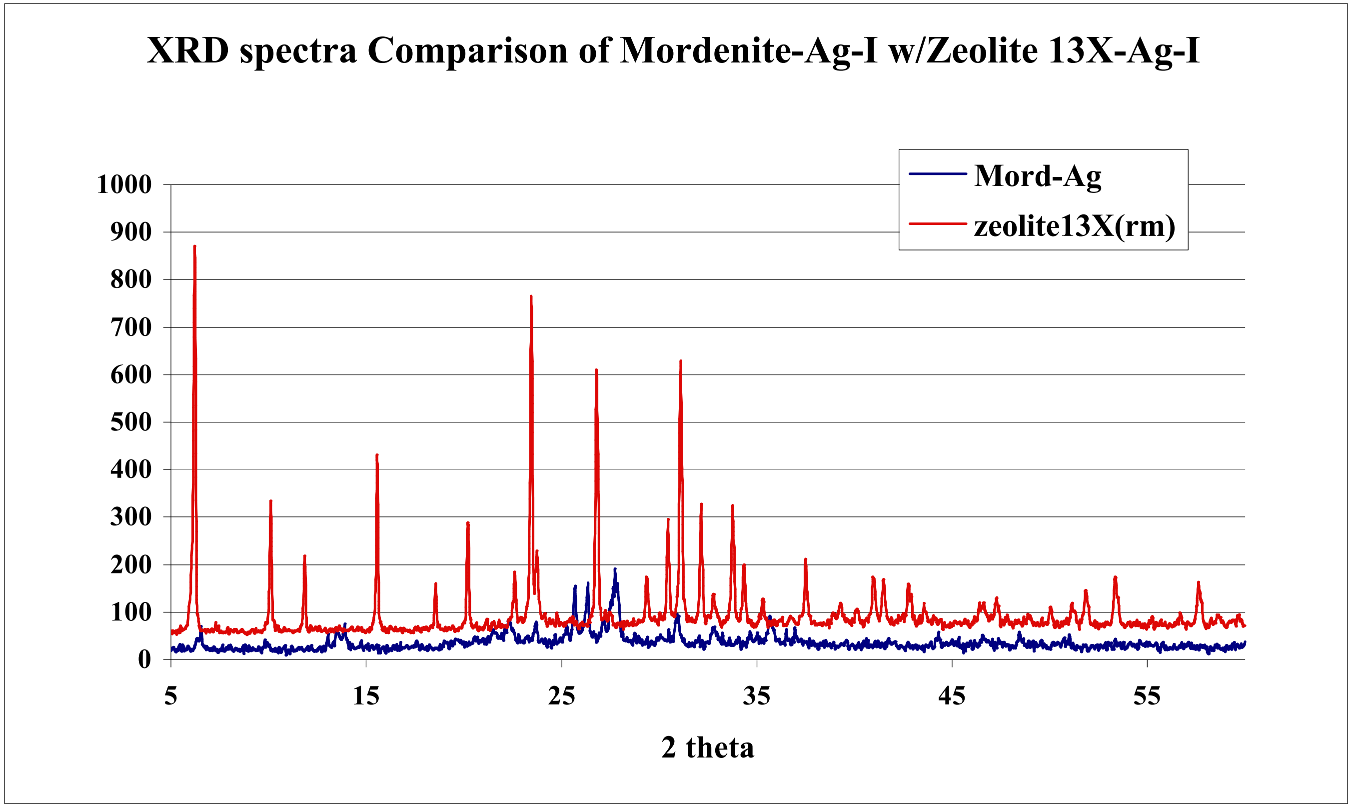
Engineered Pelletized Waste Form: Commercial Form testing of Mordenite (IONEX)

- With ORNL's guidance, we purchased commercial IONEX Ag-loaded Mordenite
  For comparison to other zeolites and also for End-to-End process I_2 studies.
- The sample was gray colored, indicating the presence of Ag on the zeolite surface.
  May need to develop a "cleaning" process for IONEX
- Crystallographic studies also indicate the material is not zeolite alone,
  but is poorly crystalline.

****Probably due to a binder material used to form extrudate forms of the zeolite**

- Difficult to compare it to high surface area, pure zeolites
- Not optimized development Form
  - need work on binder choice, amount & extrudate

IONEX : Commercial Mordenite / Pelletized



As purchased, IONEX is a very poorly crystalline material. Much of the crystallinity was lost in the pelletization process as compared to SNL synthesized FAU (X) zeolite

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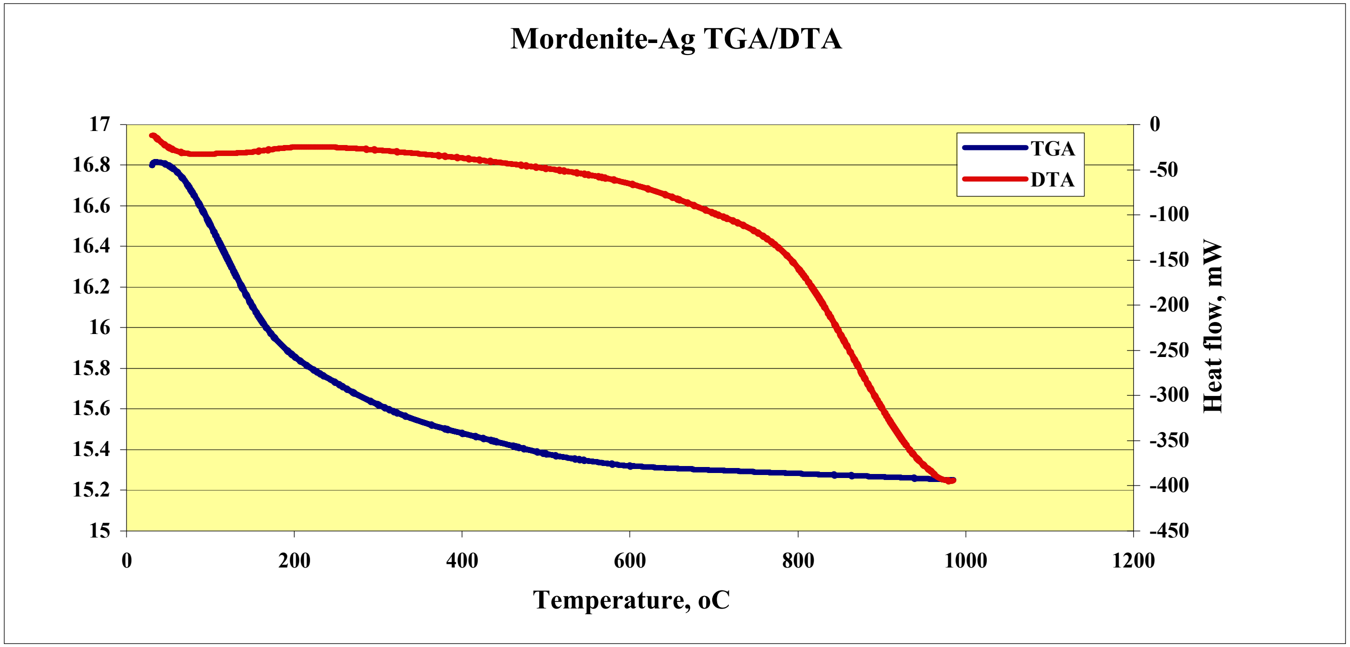
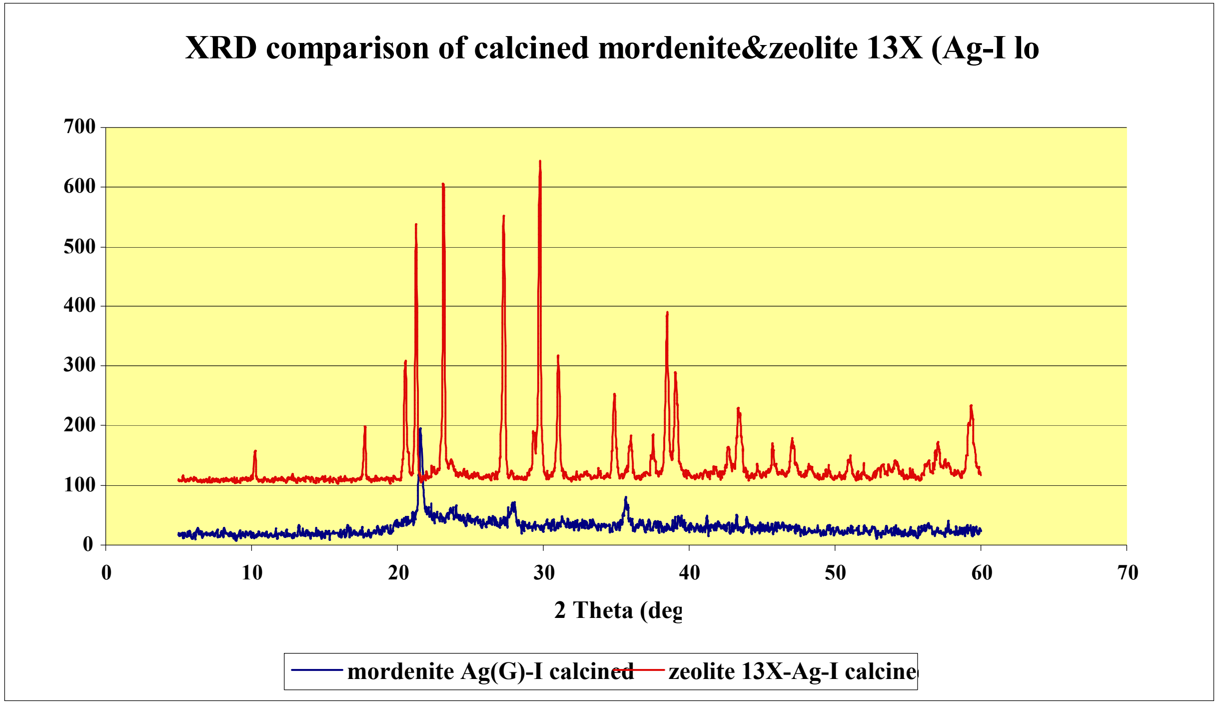
IONEX : Commercial Mordenite / Pelletized



Thermal analysis of the commercial mordenite shows ≈12wt% loss with heating (occluded water or surface iodine?)

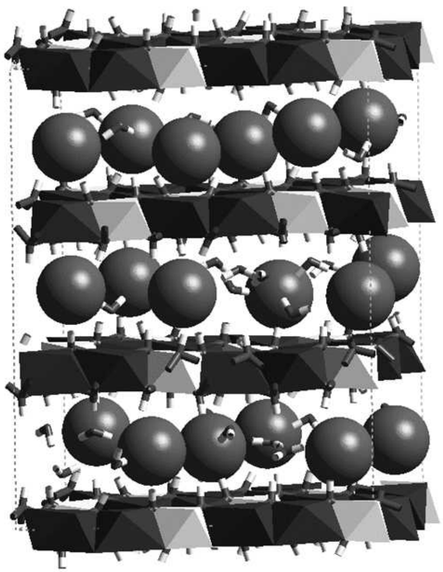
Condensation (endothermic) phase evident in waste form formation, not completed?

IONEX : Commercial Mordenite / Pelletized



EDXRF result (before leaching)	[Ag], ppm	[I], ppm	leaching sample wt, g	mass in the leaching sample Ag,µg	I,µg	percentage of Ag and I leached Ag, %	I, %
Mordenite-Ag(G)-Icalcined	36000	4585	0.5204	18734	2386	26.7	0.0545
			0.5176	18634	2373	30.5	0.1296
Mordenite-Ag(R)-I calcined	44646	5144	0.5068	22627	2607	23.9	0.0106
			0.5131	22908	2639	18.8	0.0082

In-situ Bi-compounds for Iodine storage



In-situ waste form:
Oxides (HTCs)
Bi-Cmpds

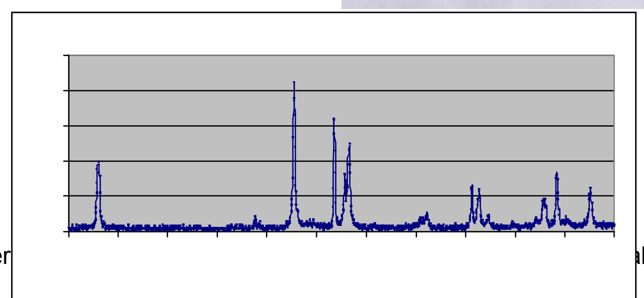
Theory: Using caustic Iodine feed streams (Areva scenario), we are pursuing an *in-situ* waste form. Stable to temperatures and aqueous solutions mimicking possible repository conditions

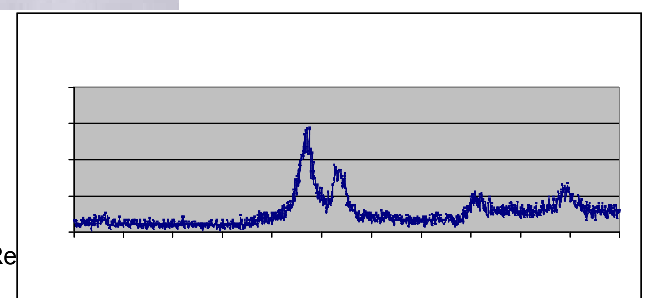
Experimental: Low temperature aqueous crystallization synthesis; Bi/M/I/O compounds. Variation of synthetic procedure: reactants, reactant ratios, order of mixing, time

Characterization: X-ray diffraction (XRD), elemental analysis, leach testing and thermal studies (TGA/DTA); Stability testing in aqueous solutions, carbonate and chloride solutions, with temperature

Crystalline Phase

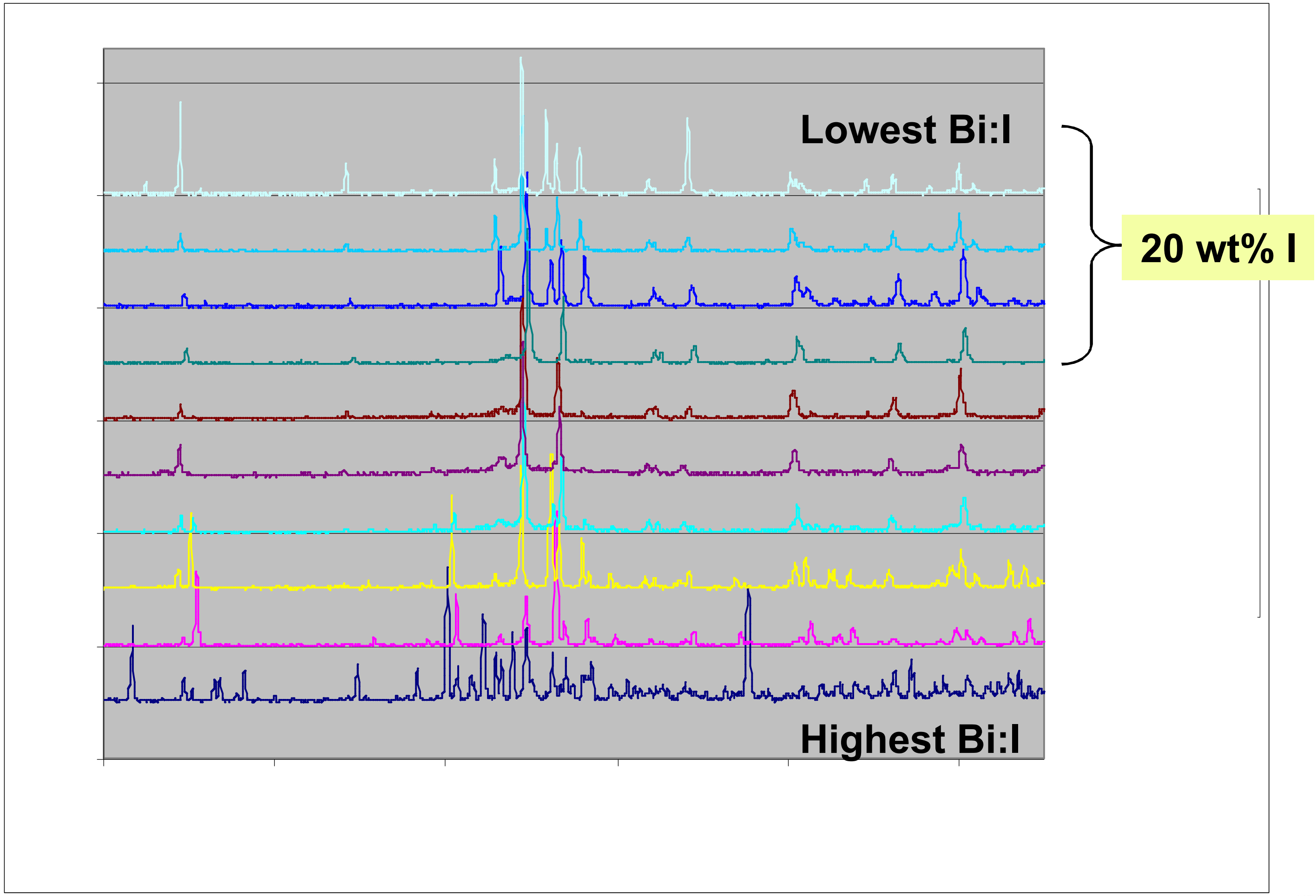
“Amorphous” Layered Phase





Bi-O-I Compounds Identified

Generally 4 distinct phases with variations due to Bi:I ratio



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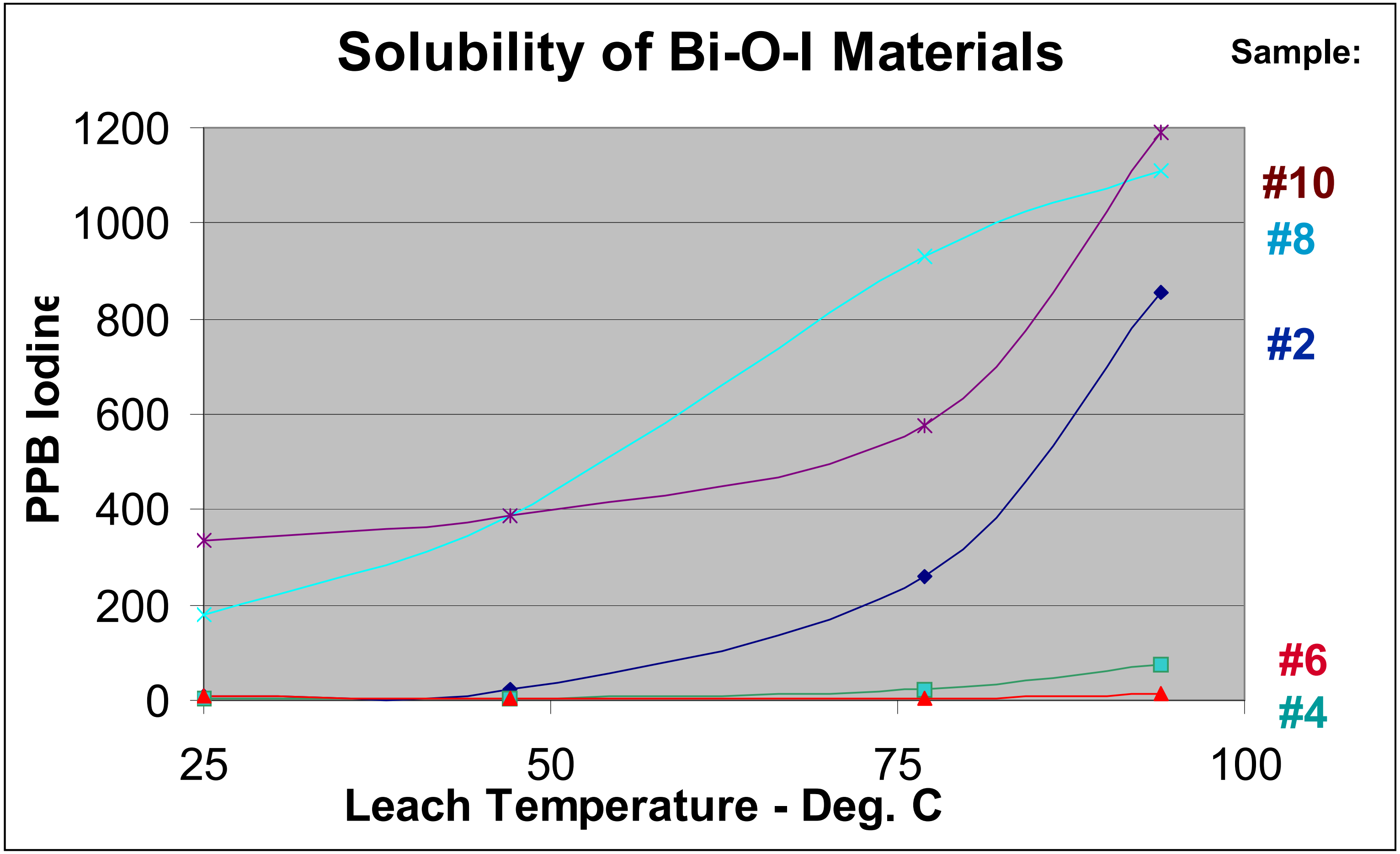
Relative PCT Solubility Results:
Note Superior Performance of Intermediate Materials



Completion Steps: Final reports, patents and publications

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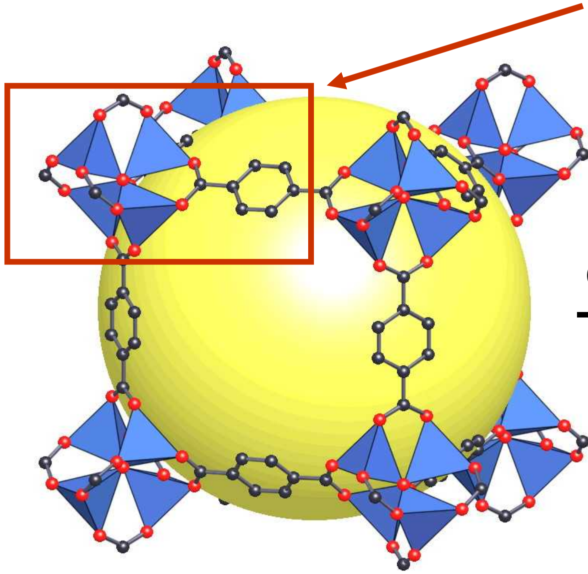
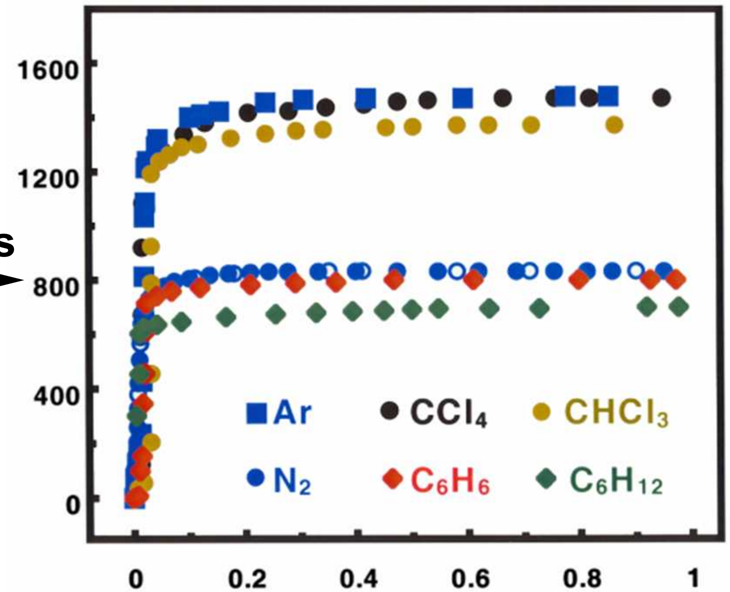
Future Materials Research for I_2 Uptake include high pore volume Metal-Organic-Frameworks (MOFs)

Extreme Tunability to gas uptake: gas sorption tuned by MOF building units



Sorption of Gaseous Species



$Zn_4O(BDC)_3$	**I_2 (gaseous)** →	$Zn_4O(I_2BDC)_3 \bullet (I_2)_x$
IRMOF-1		(Iodinated IRMOF-1)

N. W. Ockwig, SNL

Future Plans

- In FY08, we will continue on the zeolite-Al/Si waste form development.
  - Structure/Property relationship between type of zeolite and performance
  - metal type (Ag vs. Transition metals) vs Iodine uptake
  - amount of metal vs. Iodine uptake
  - heat treatment methods vs. iodine retention in waste form
  - powder vs. pelletized getter
- Focus on Optimized Waste Form (combination of binders and zeolites to form final waste form), such as surface area, binder composition, pellet size, etc.
- We will incorporate tuned porous MOFs for high I_2 loading and pursue the structure/property relationships between waste form and durability
- Scale Up Studies with Optimized Waste Forms
- We will perform testing and durability of materials in collaborative Waste Form Campaign