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Durable Materials for GNEP Iodine Waste Streams

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Outline

- **Program Goals**
- **Introduction to Iodine Waste**
  - GNEP needs
- **Experimental History**
  - Program Update
  - Repository Dictates for Iodine Storage
- **Getters and Storage Waste Forms**
  - Aluminosilicates / Zeolite Program Update
    Effects of Pore Sizes, Varying Si/Al ratios, Decomposition Temperature
  - Bismuth Compounds - caustic scrubber
  - CETE (SNL iodine portion) Update
  - Waste Form Baseline
- **In Progress - Low Temperature Binders for Ag-I-Loaded Zeolites**

Overall program Goals

- Waste form by Design - Durable Waste Forms that can be validated
  for GNEP cycle designs
- Flexible for iodine feed stream and sequestration material
  - universal waste form materials
  - able to perform with organic iodides, nitrates, etc.
- Flexible to repository/storage needs, OR properties dictated by repository
- 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 have expanded and amended our program to include approval for receipt of ^{129}I-loaded Ag-Zeolites from CETE* , and to conduct waste form fabrication R&D on these materials

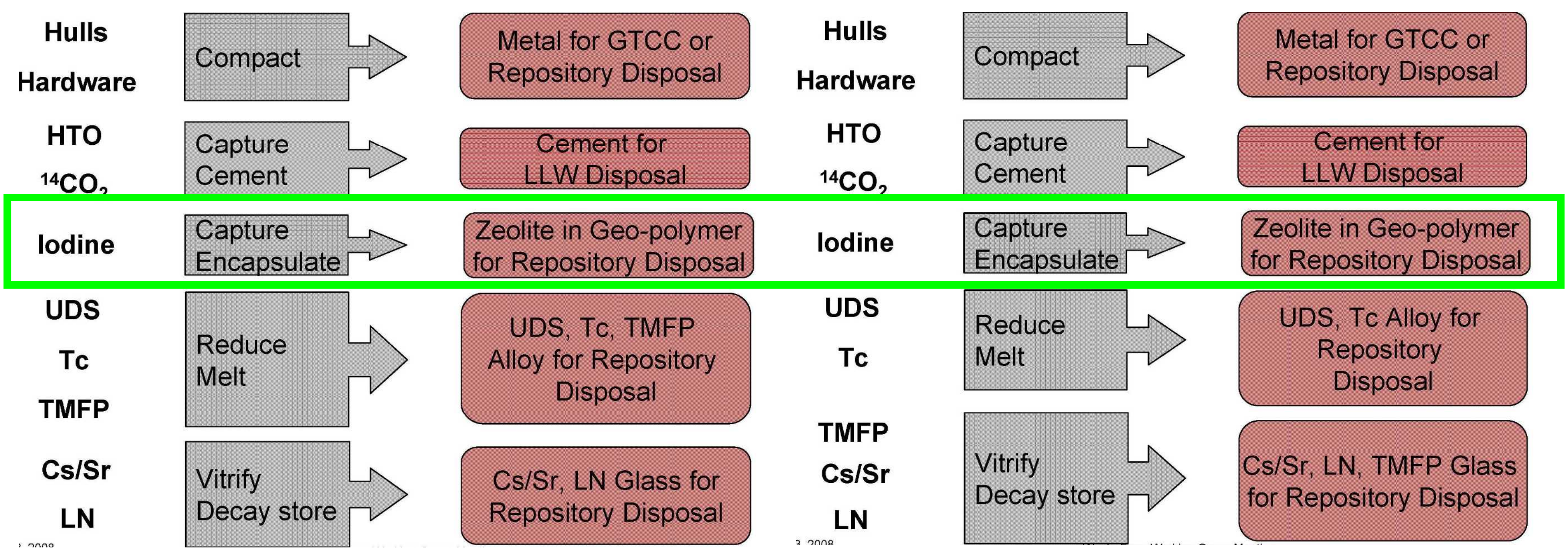
*Coupled End-to-End (CETE) Demonstration - *An ORNL program to tie together GNEP fuel reprocessing steps.*

GNEP Commercial Fuel Reprocessing Strategies

<<<New Slide Replacing Old Flow Charts>>>

- Pu, Am and other actinides recycled to reactors as "TRUOX" fuel
- Reprocessing recovers uranium for separate disposal
- Fission products to various waste streams based on chemistry

Reprocessing Option #1 **Reprocessing Option #2**



SNL Separations Waste Forms Expertise

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

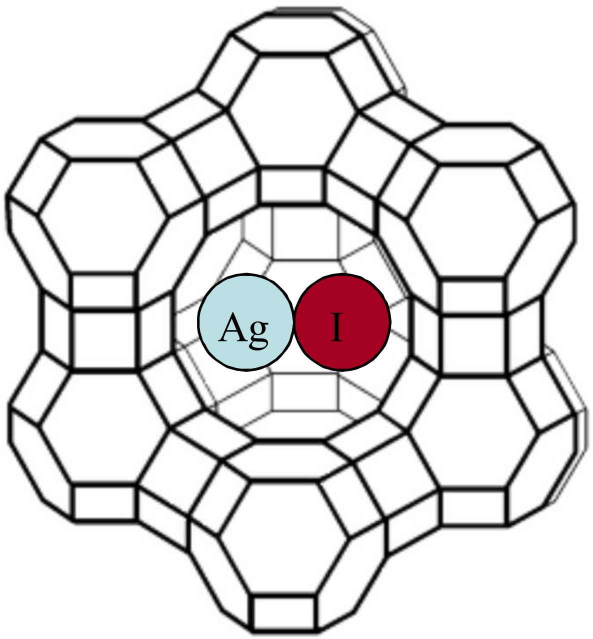
- Ceramic Capture Materials - Ag loaded Mineral Analogs (zeolites)

- Ceramic Waste Forms -Structure/Property relationship studies are key:
  Optimization of I retention by varying of zeolite type and I loading ,
  Binders to encapsulate I-loaded zeolites are actively investigated.

- CETE - Radiological personnel and SNL SSO interactions and approvals

  - Sandia currently approved to receive ^{129}I loaded zeolites from ORNL live fuel dissolution testing.

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



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

Theory: Study and Develop Ag-I-Zeolites as 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

*analysis on a small scale required due to sample heterogeneity

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 & Faujasite
- 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
- Binders for Ag-I loaded zeolite are an active research area.
  Currently we understand temperature limitations on iodine retention and binders must meet these criteria.

Iodine Loading & Heating Conversion to Waste Form

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

1) Prep Zeolite: Note: later studies use commercial grade “as received” Ag-loaded zeolites.
But, in early studies we purchased normal commercially available zeolites,
or made them ourselves, and then loaded them with silver.

2) Loading Ag (Early Studies):
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 (two different procedures)
- Iodine Gas sorption: $I_{2(gas)}$ loaded in Ag-Z at 125°C in sealed chamber (gas) (may be dry, or in the presence of water vapor)
- KI aqueous exchange: 0.1M KI_{aq} w/ Ag-Z, stir at RT for 2hours, filter

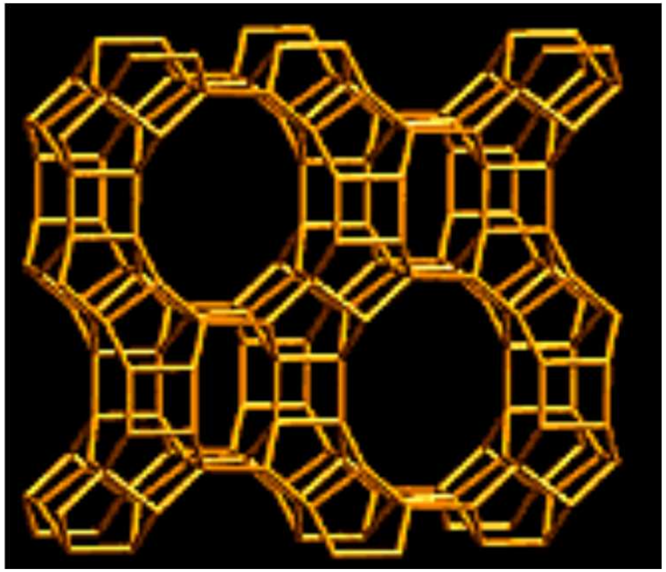
4) Calcination: Heating in a high temp muffle furnace
RT to 500°C, ramp 1-100°C/min, hold at 500°C 2.5 hours, cool to RT

5) Silver Reduction: Models ORNL I_2 capture processes, Uses 3% H2 in inert atmosphere

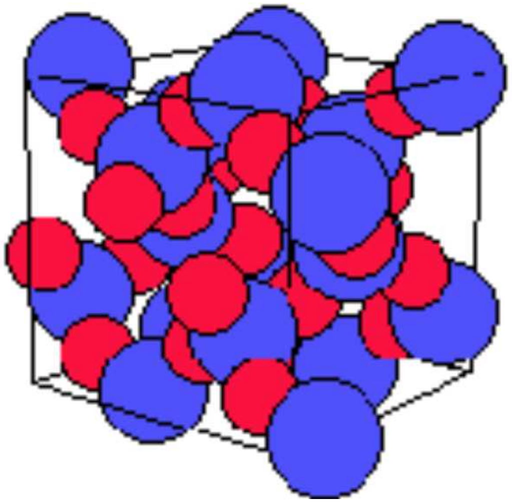
Ag-I-MOR: Crystallographic Phase Transformation

Ideal Mordenite Structure:
Cations & H_2O not shown
In pores

The Ideal β-Cristobalite Structure:
SiO_2 analog



1000° C



Open framework

Condensed framework

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 partially gray colored, indicating Ag-metal on some surfaces.
  May need to develop a "cleaning" process for IONEX

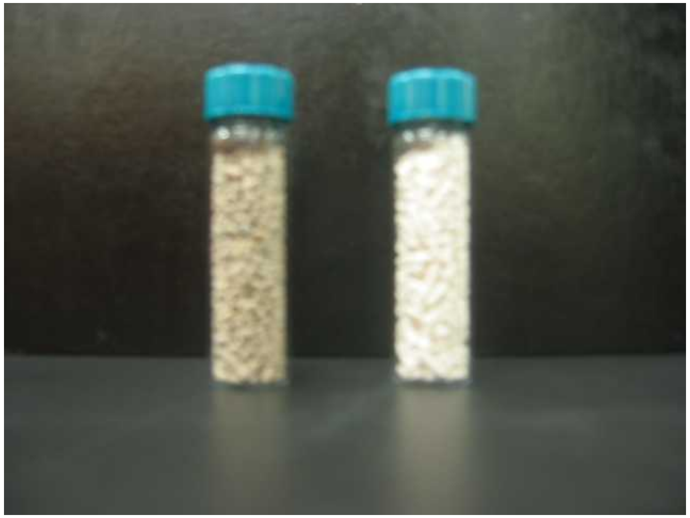
- Crystallographic studies also indicate the material is not zeolite alone,
  but is poorly crystalline.

****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

Ag-I-MOR: As-received IONEX Ag-MORDENITE (Ag-900) Made via ion exchange process. Comes fully mixed.



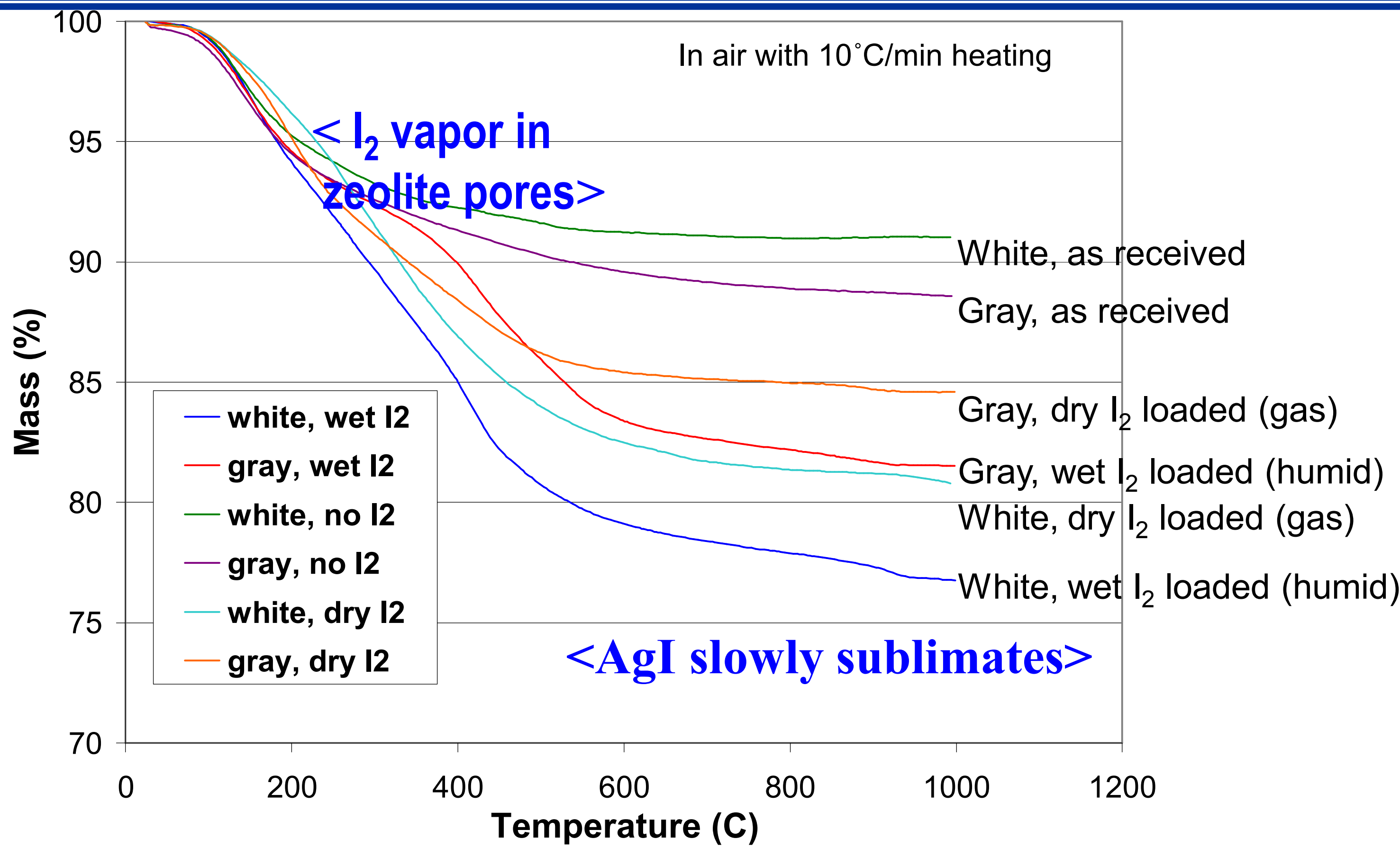
Hand separated two Phases in commercial IONEX Ag-MOR

The Grey Phase of IONEX Ag-900: 0.27g of Iodide (I not I2) per gram of Ag-Zeolite (+/- 0.03g)
The White Phase of IONEX Ag-900: 0.40g of Iodide (I not I2) per gram of Ag-Zeolite (+/- 0.06g)

Gray Phase:
Equal Ratio I:Ag
Most iodine lost at 1000° C, though some by 500° C
Some Ag at 1000° C (≈ 30%)

White Phase:
Excess ratio of Iodine over Ag (≈1.4:1)
Loss of some Iodine at RT
Some iodine lost at 1000° C, though some by 500° C
Retains Ag with heating

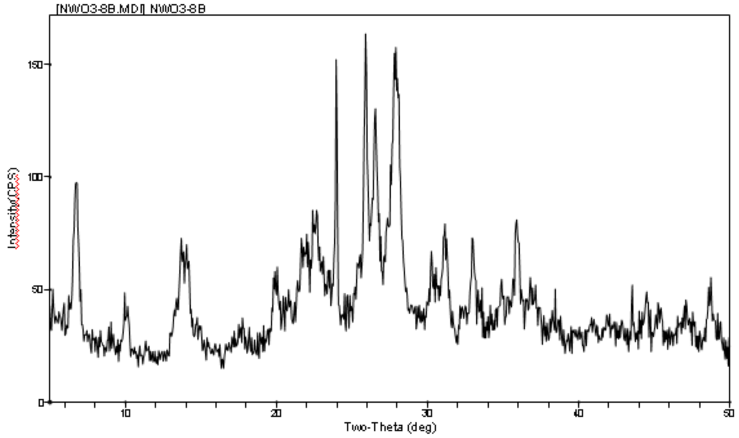
Ag-I-MOR: Thermal Analysis (TGA) - Two forms of iodine on the zeolite are lost at different tempertures.



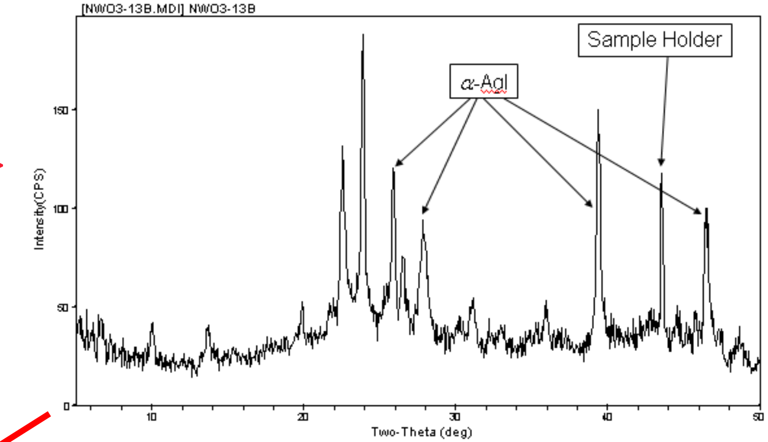
Thermal Analysis (TGA): On heating Iodine is lost from both gray and white types. Below 600° C loss Is primarily from I_2 initially captured in the zeolite pores. At higher temperatures AgI slowly sublimates.

Note, Iodine vapor evolves off white samples in lab at RT in a few days!

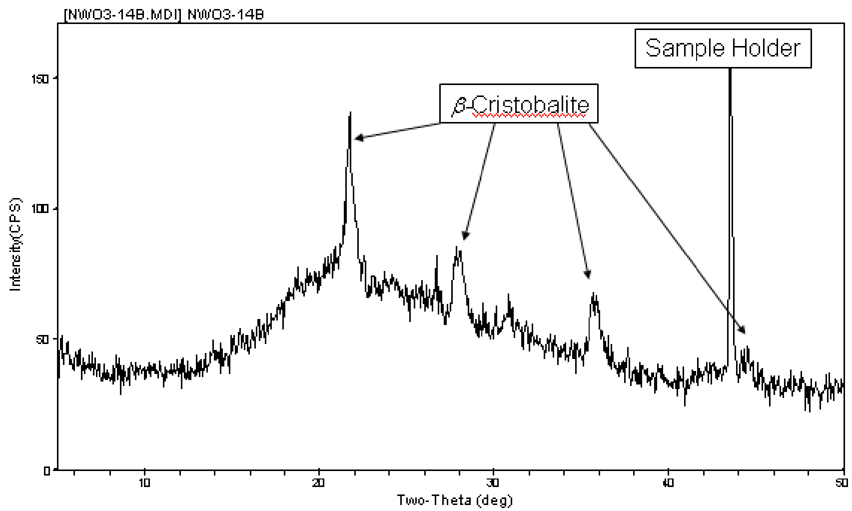
Ag-I-MOR: Heat Treatment Results of Gray Phase



As-received



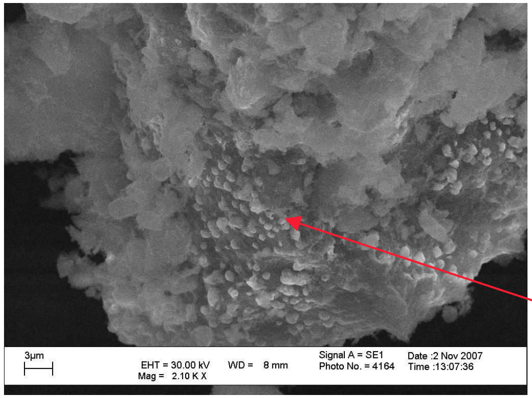
Iodine loaded, α-AgI present

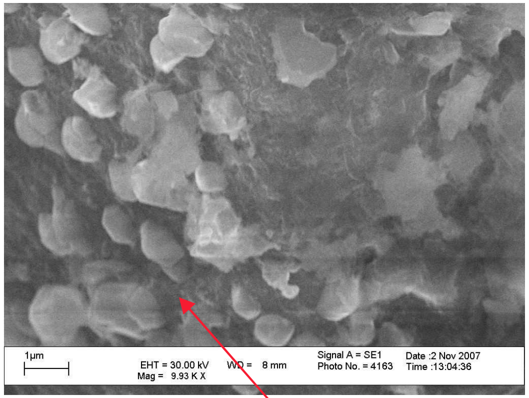


Ceramic formation at 1000º C – Beta-cristobalite phase

No AgI present in X-ray

Ag-I-MOR: Location of Ag-I in/on MOR

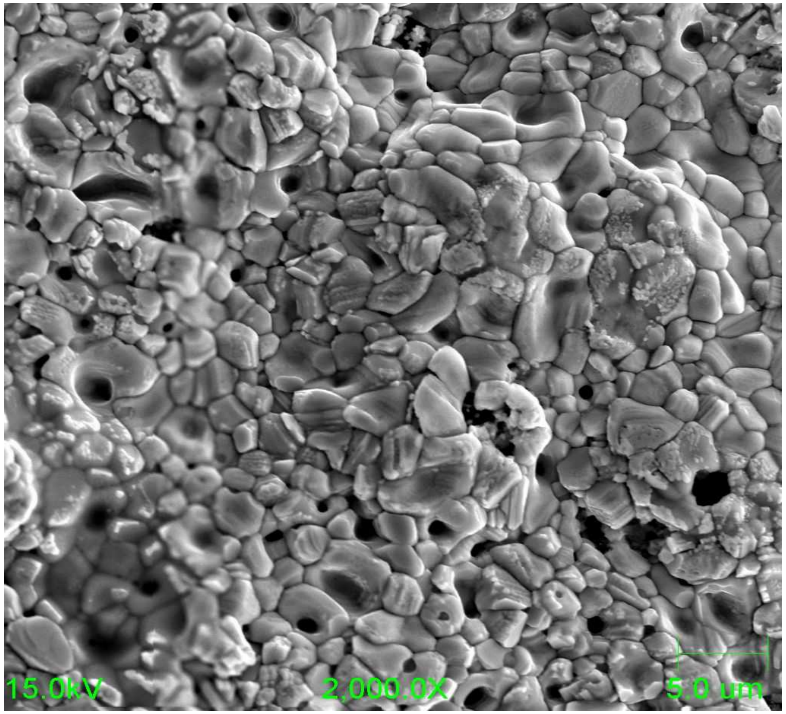




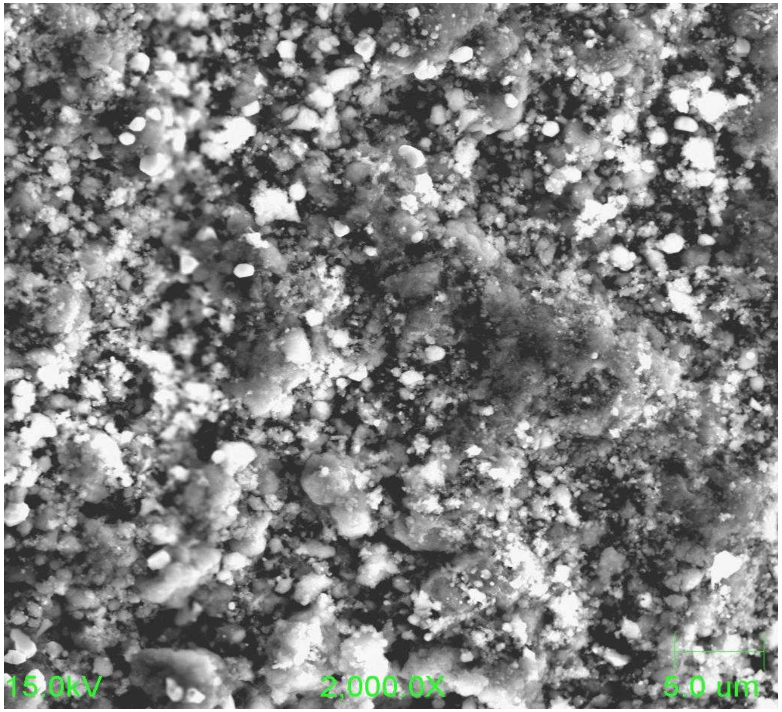
Scanning Electron Microscopy (SEM): *hex* Ag-I crystals on the surface of the gray phase at room temp.

Combined with Xray data, TGA/DTA, SEM: Exposure of Ag-Mor to I_2 gas at RT results in AgI formation (all on surface?)

Ag-I-MOR: Environmental Impacts on Loading



Wet-loaded Mordenite coated with AgI crystals



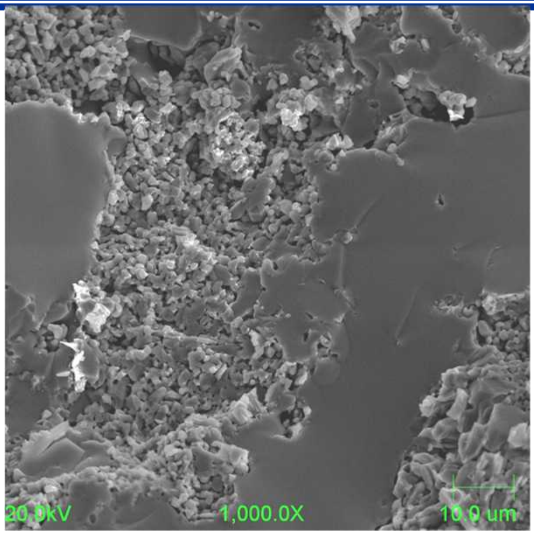
Dry-loaded Mordenite with isolated AgI crystals

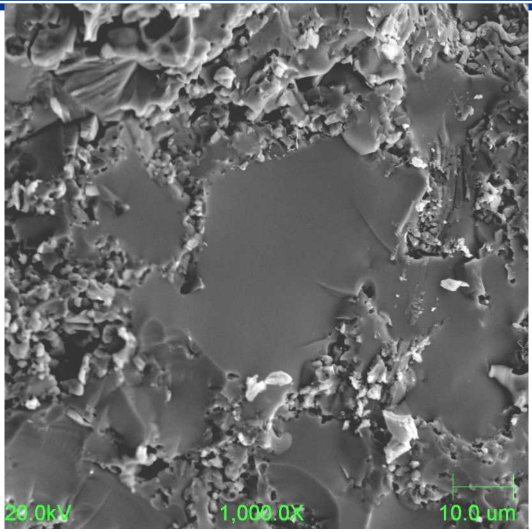
Scanning Electron Microscopy (SEM): Dry loading forms isolated Ag I crystals on zeolite grains while adding water vapor during loading causes a continuous layer of AgI crystals to form. Neither process left the AgI in the zeolite channels where thermal collapse treatments could capture it. **Because of this binders have become an priority R&D topic!**

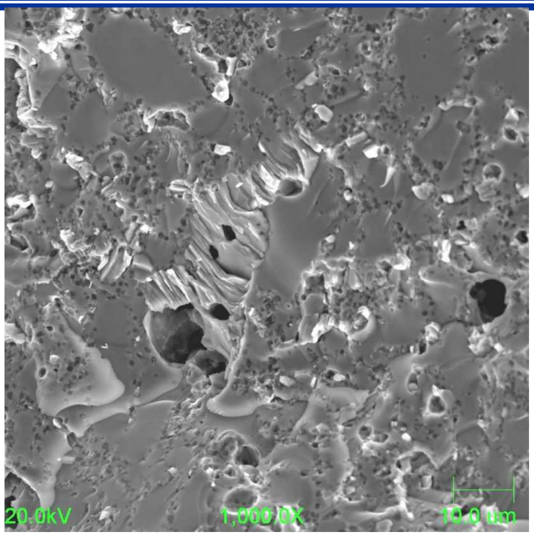
Initial Glass Binder Studies Underway:

- Low melting temperature glass binders were selected to minimize I_2(gas) losses on heating.
  - Pretreatment with sodium formate permits zeolites to retain iodine to 500° C
- Various compositions of crystallizing and amorphous glasses were identified and ordered.
- Initial studies on 3 crystallizing glasses underway. Glass formation confirmed for various sized Ag-I-Zeolite particles <550°C.
- Preliminary PCT-like leach tests started on crystallizing glasses (90° C, two weeks, deionized water). Some surface reactions on all three glasses.
- Ongoing research: evaluate different compositions and amorphous glasses, as well as other materials.
- Decay of ^{129}I to stable ^{129}Xe is also a factor in binder selection.

Different Behaviors of Low Melting Point "ferro-glass" binders with AgI (fused at 400^{o} C)







Pb-B-Si Glass **Pb-B-Zn Glass** **Bi-B-Zn Glass**

Discrete Glass and AgI Domains Remain After Fusion

AgI Dissolved in Molten Glass

<u>Ongoing Research</u>: Further testing needed with Ag-I-Zeolites to determine which option is actually preferable.

CETE: SNL Iodine Testing

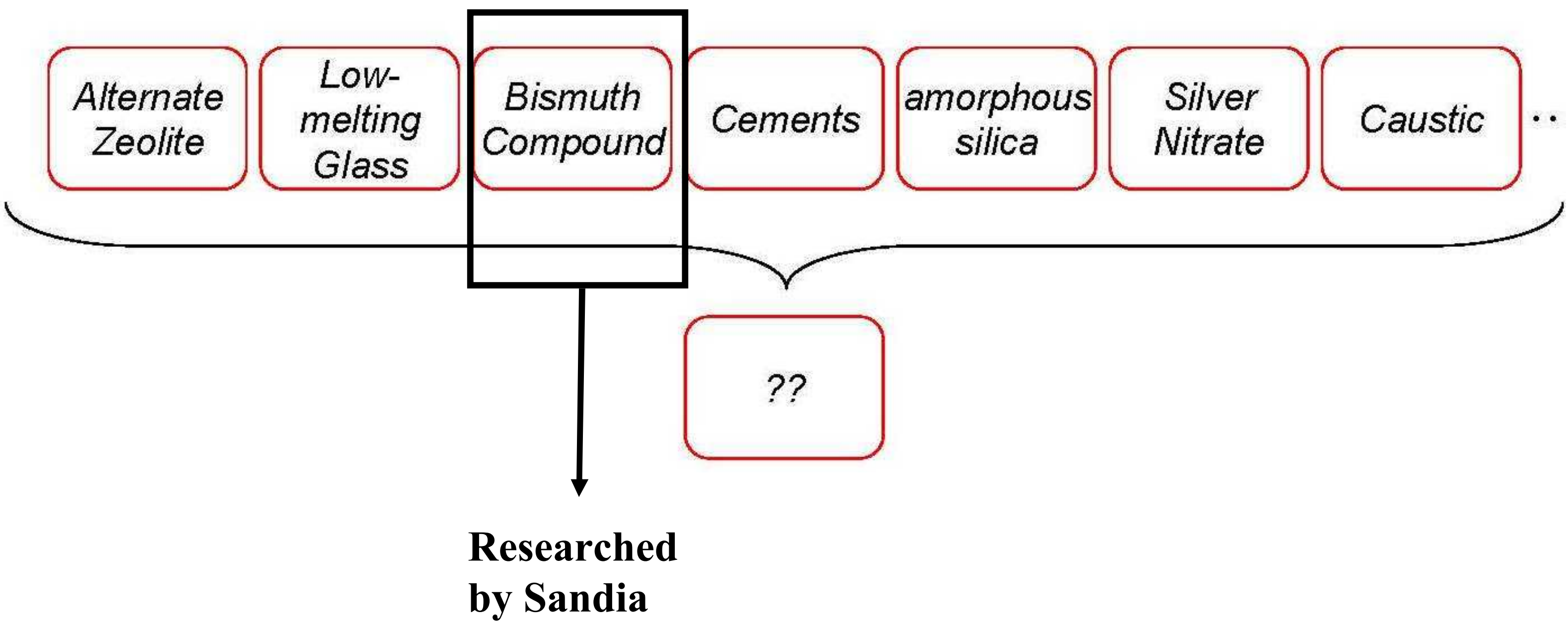
- Baseline Iodine Waste Form determination ongoing
- Radiological Experiments at Sandia:
  All necessary documentation completed to allow Sandia to receive ^{129}I loaded Ag-zeolites from ORNL

Iodine Waste Forms:

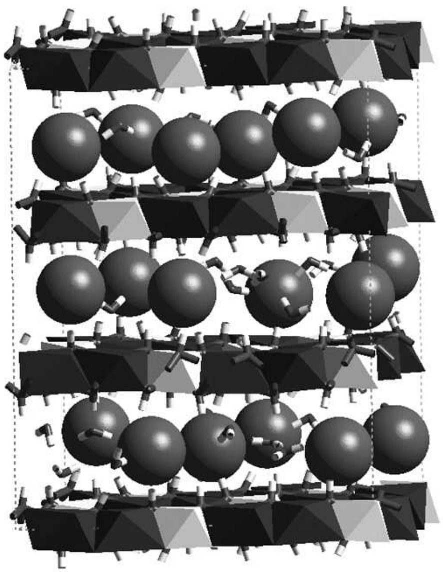
- Specific Iodine Waste Forms Testing Protocols to be determined
- For now, ANSI 16.1 durability testing (PCT)
- Selectivity in mixed waste streams (organic iodides, nitrates, etc.)

Alternate Process/Form Development

- Evaluate potential backup technologies for iodine capture and immobilization
- Perform process and form testing on selected alternate(s)



In-situ Bi-compounds for Iodine storage : Derived from caustic I_2 capture processing



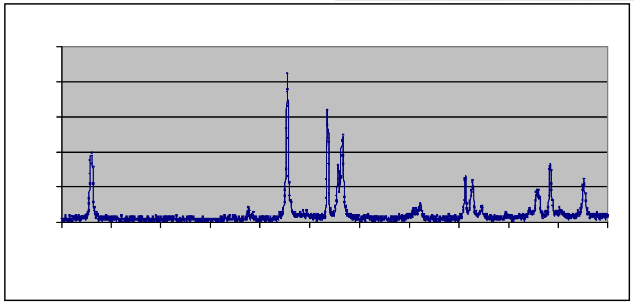
In-situ waste form:
Oxides (HTCs)
Bi-Cmpds

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

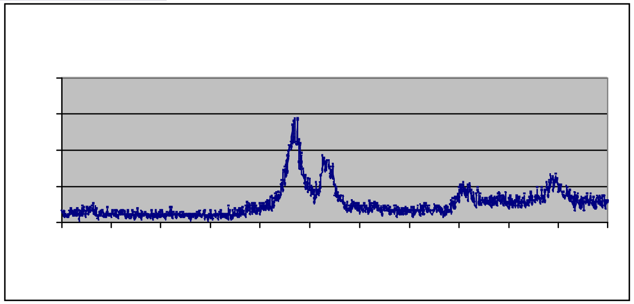
Experimental: Low temperature aqueous crystallization synthesis; Bi/M/I/O compounds. Variation of synthetic procedure: reactants, reactant ratios, order of mixing, time

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

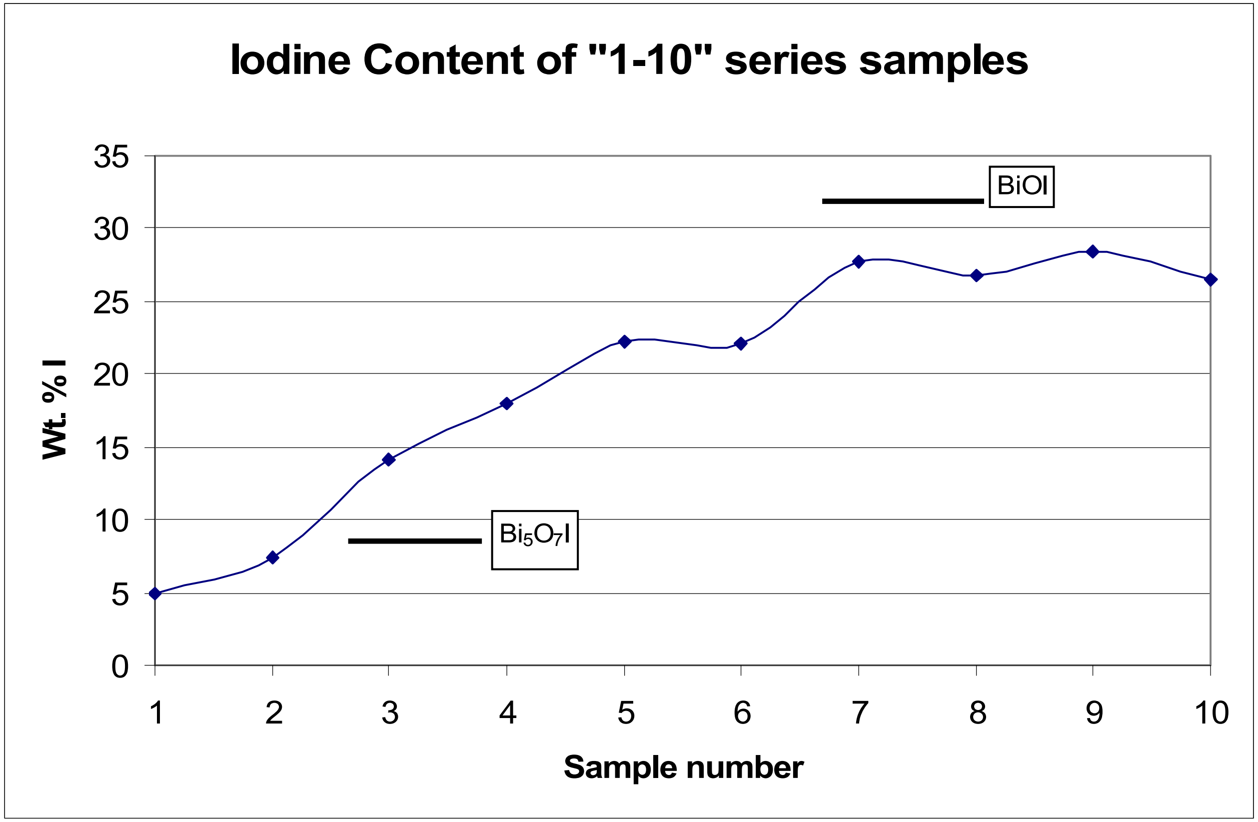


“Amorphous” Layered Phase



Mixture of Phases for Optimized Iodine Uptake

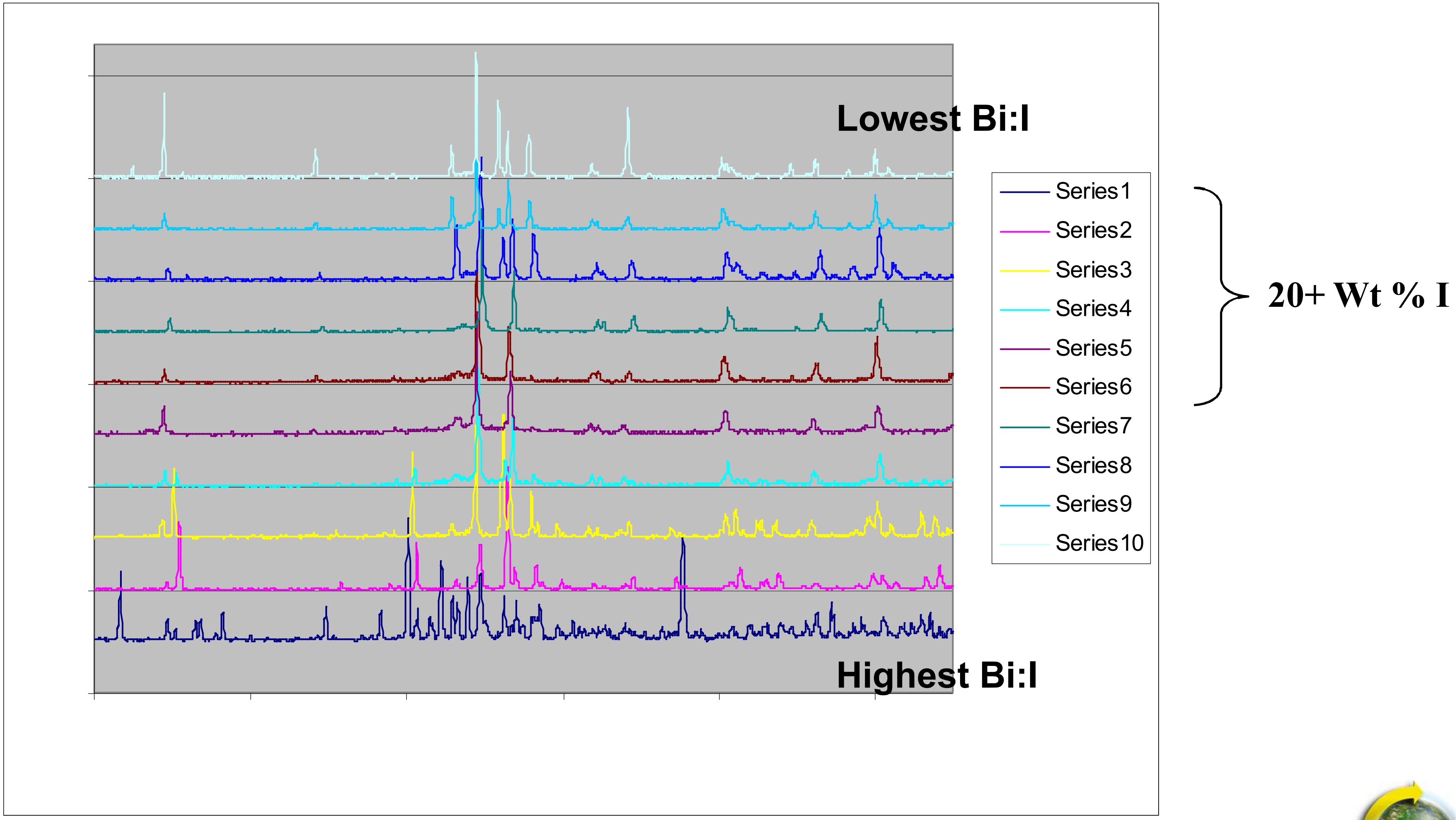
Nenoff, Krumhansl, US Patent Technical Advance
SD-10928, 2007



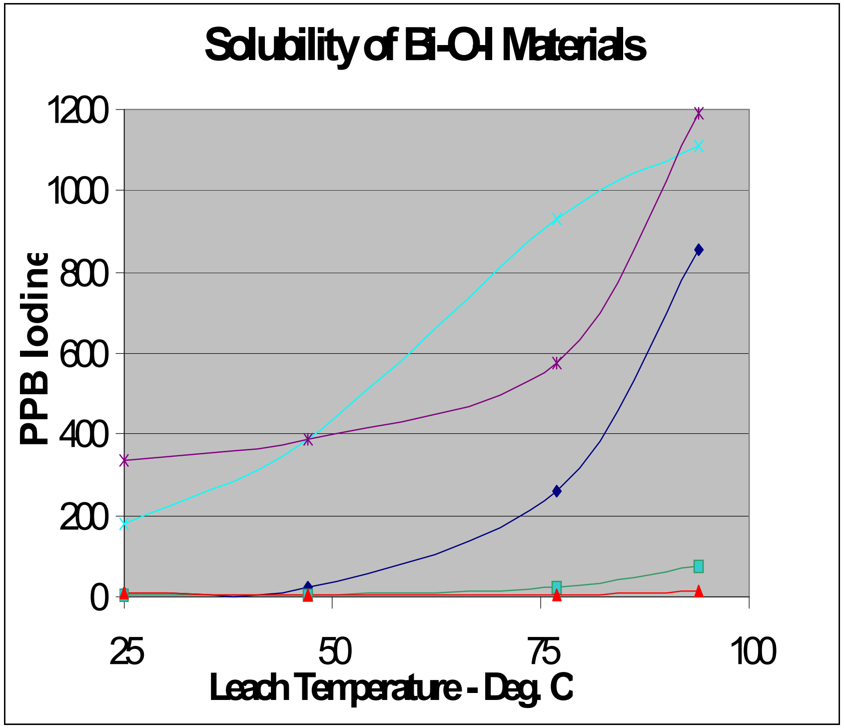
A combination of Bi_5O_7I and BiOI phases are necessary to optimized iodine uptake (on a weight % basis).

Bi-O-I Compounds Identified

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

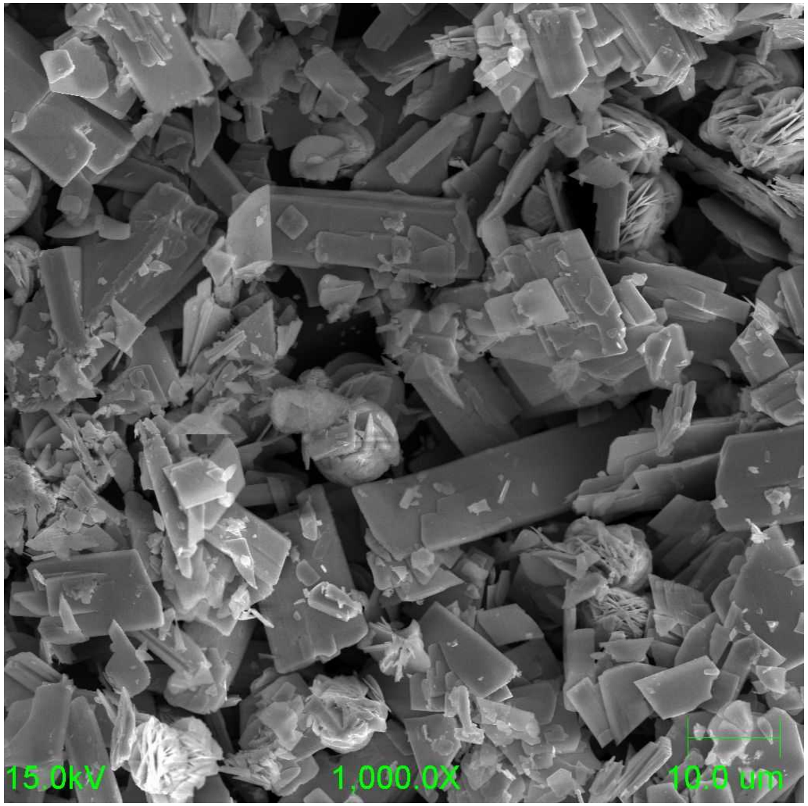


Bi-I-O: High Surface Area Layered Materials with highly tuned solubility



PCT Testing

SEM: Low Solubility Bi-O-I Phase Mixture



High surface area material that can be tuned to low solubility in ground water.

Future Plans (pg 1)

- **To maintain Iodine/Zeolite Encapsulation - next steps**

Pretreatment of I_2 loaded Zeolite:

*Base exchange can diminish evolution of HI on heating:

$$AgI + H^+_{(from\ zeolite)} \rightarrow Ag^+ + HI \quad vs. \quad AgI + Na^+_{(from\ zeolite)} \rightarrow Ag^+ + NaI$$

*Treatment with formate reduces I_2 in pores forming AgI, allowing the zeolite to be heated to ~ 500^o C without significant iodine vaporization.

Develop binders for the I_2-loaded zeolite which are both compatible with the AgI in the zeolite and do not cause significant iodine loss during fabrication.

* Multiple possible low melting point glasses are under investigation.
* Other binders is also being assembled and evaluated for testing.

The relative merits of two types of Ag-Zeolite, are being assessed experimentally: Mordenite and Faujasite

Future Plans (pg 2)

- **Address future changes in iodine capture methods (caustic scrub, etc.)**
  - Wet chemical loading of Ag-zeolites (KI_{aq} vs. I_2 gas);
  - Bi oxide based waste form characterization and development
- **CETE studies with Optimized Waste Forms**

Acknowledgement

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