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The Advanced Fuel Cycle Initiative

Novel Bismuth-based Inorganic Oxide Waste Forms for Iodine Storage

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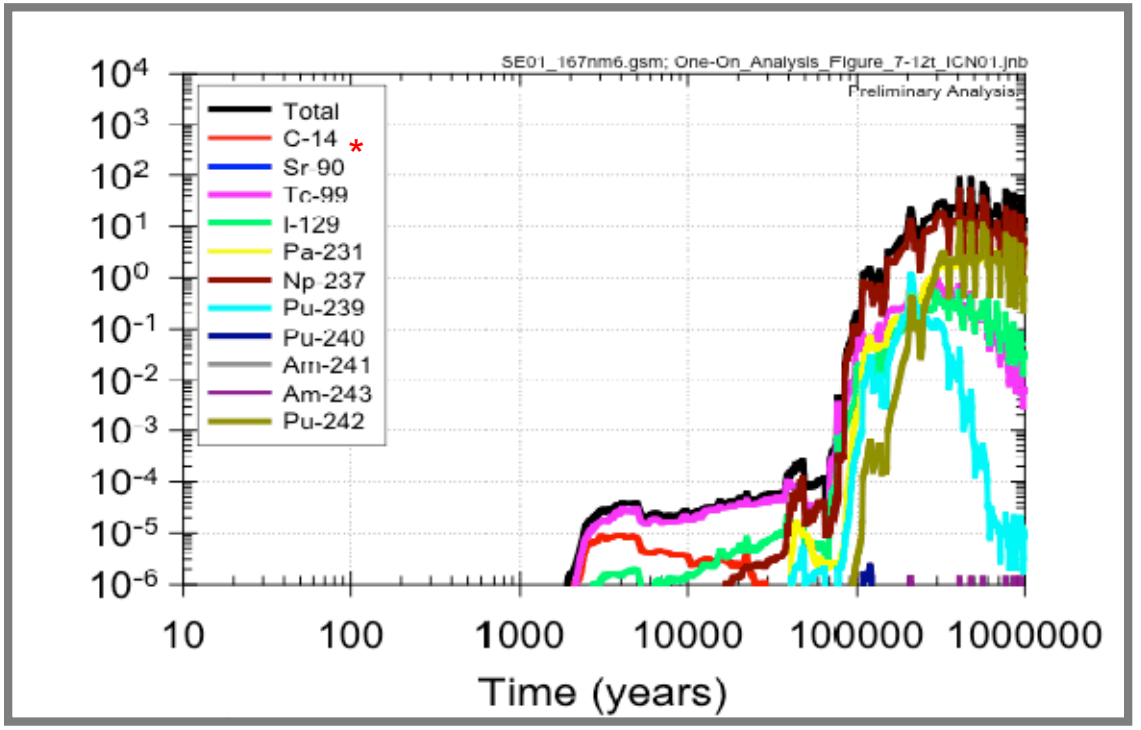
Why Iodine Is Important To Store

Among the various waste steams, volatile gases / long-lived fission products pose unique scientific issues with regards to long term storage. Understanding their interactions with capture and storage materials may ensure a technical basis for predicting stability with time.

2002 SR/FEIS analyses:

1 million year performance studies for Possible *Nuclear Repositories* (*eg.*, Yucca Mt)

- 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.



Courtesy of P. Swift, SNL

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

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On-going SNL I_2 Separations and Waste Form Research

1. Study/Optimize Loading of Iodine into Separations Material and Transition to Waste Form
   - Characterization of Baseline MOR (from ORNL)
   - Characterization of MOR (from INL reactor)
   - Analytical Procedure Development for all MOR Separations Materials

2. Bismuth Oxide Waste Forms – research into
   - in-situ precipitation of layered waste forms from caustic streams
   - durable low temperature encapsulation waste
     - Composition effects (oxide)
     - Weight loading
     - Encapsulation of AgI
     - Durability studies

3. Alternative Waste Forms
   - Effects of Decay on Waste Form Durability
   - Novel Metal-Organic Frameworks for I_2 Separations and Storage
   - AgI structure in MOR (correlation of ANL/APS data w/NEAMS modeling)

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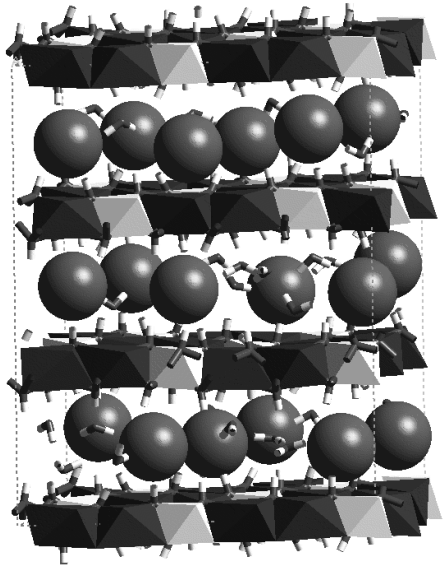
I. In-situ Bi-compounds for Iodine storage



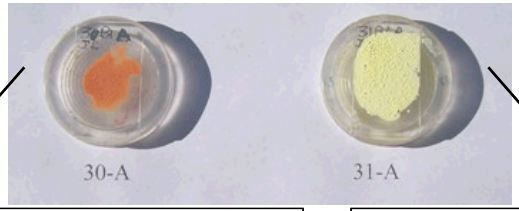
In-situ waste form:
Oxides (HTCs)
Bi-Cmpds

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

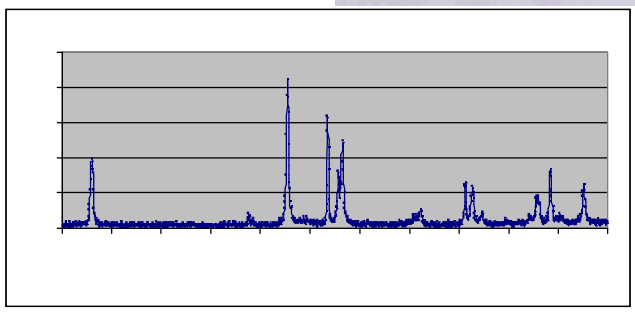
Experimental: Low temperature aqueous crystallization synthesis; Bi/M/I/O compounds. Variation of synthetic procedure: reactants, reactant ratios, order of mixing, time

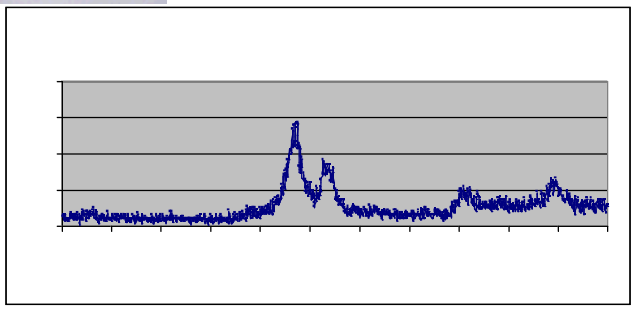
Characterization: X-ray diffraction (XRD), elemental analysis, leach testing and thermal studies (TGA/DTA); Stability testing in aqueous solutions, carbonate and chloride solutions, with temperature

Crystalline Phase



"Amorphous" Layered Phase





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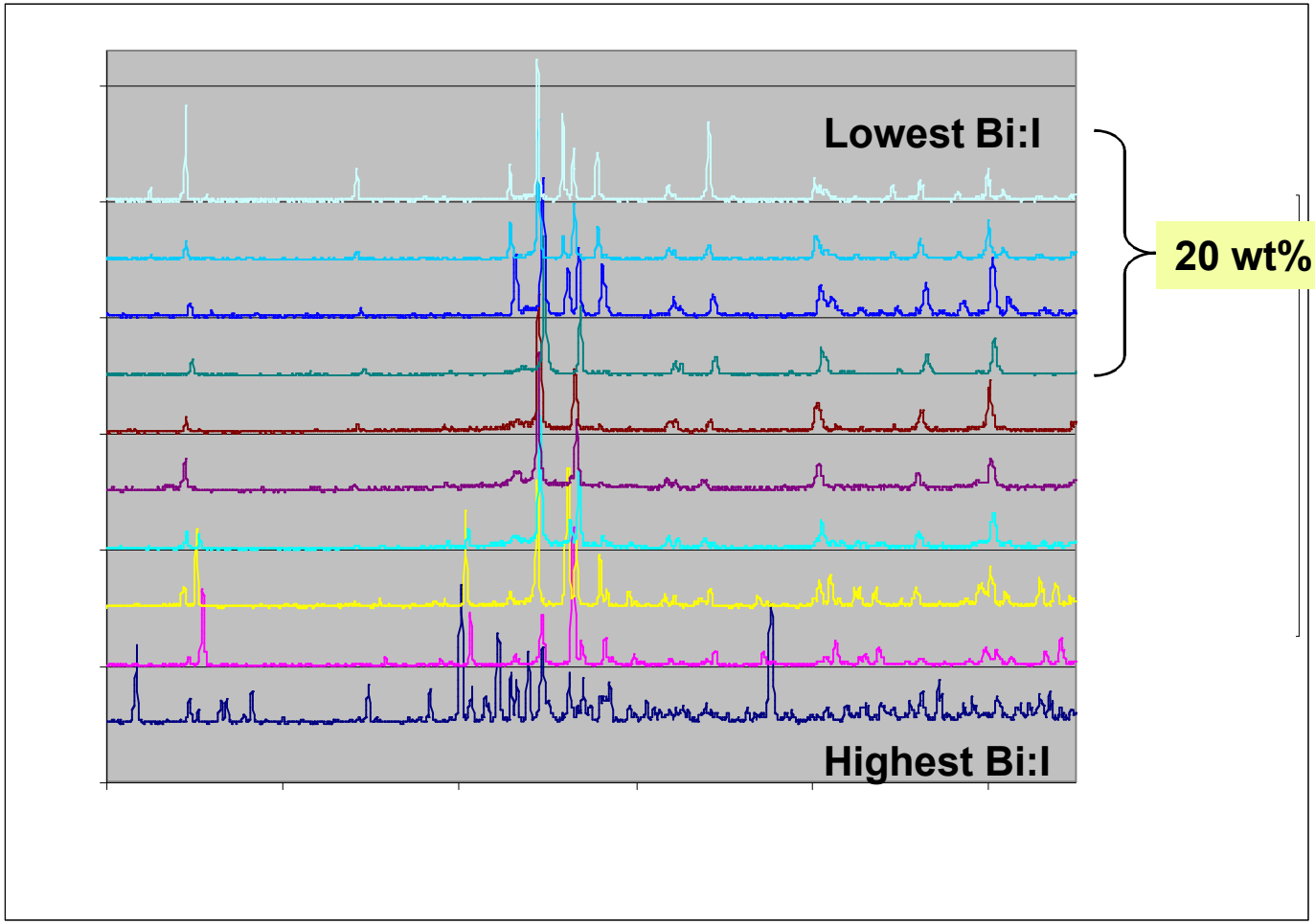
Bi-O-I Compounds Identified

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



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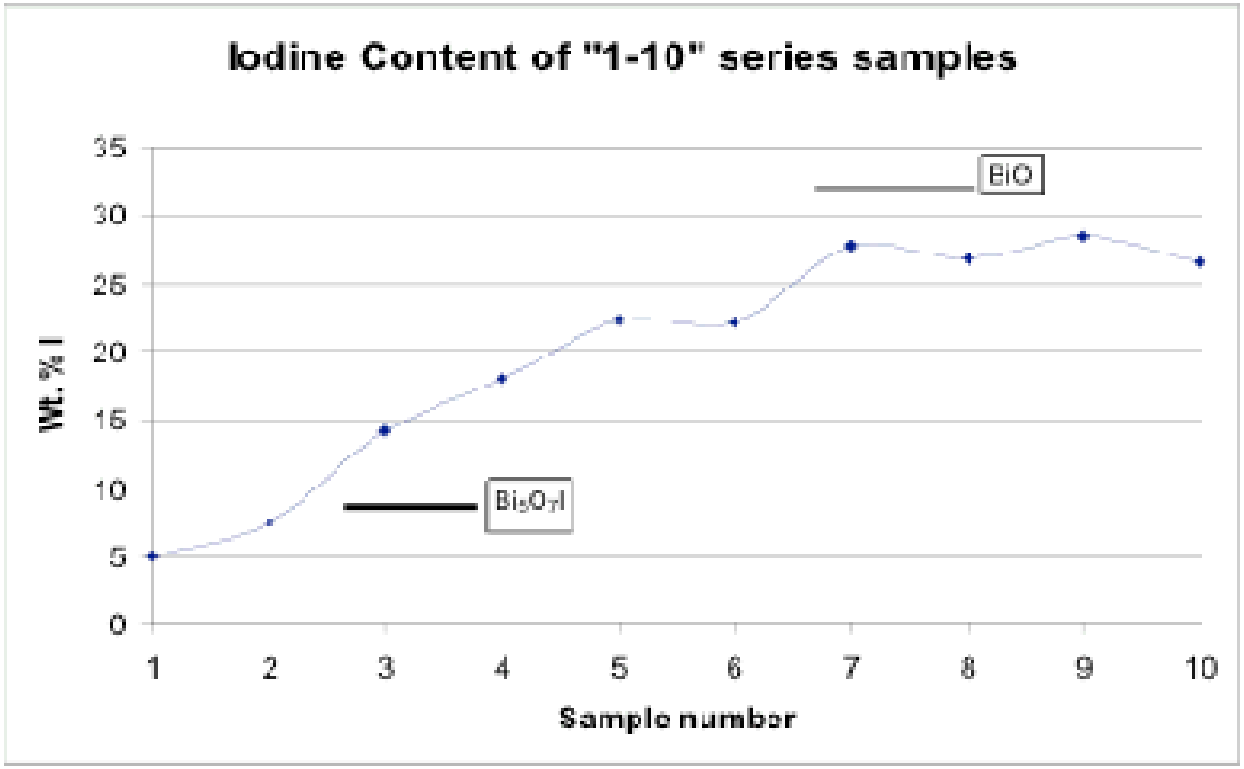
Mixture of Phases for Optimized Iodine Uptake

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



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

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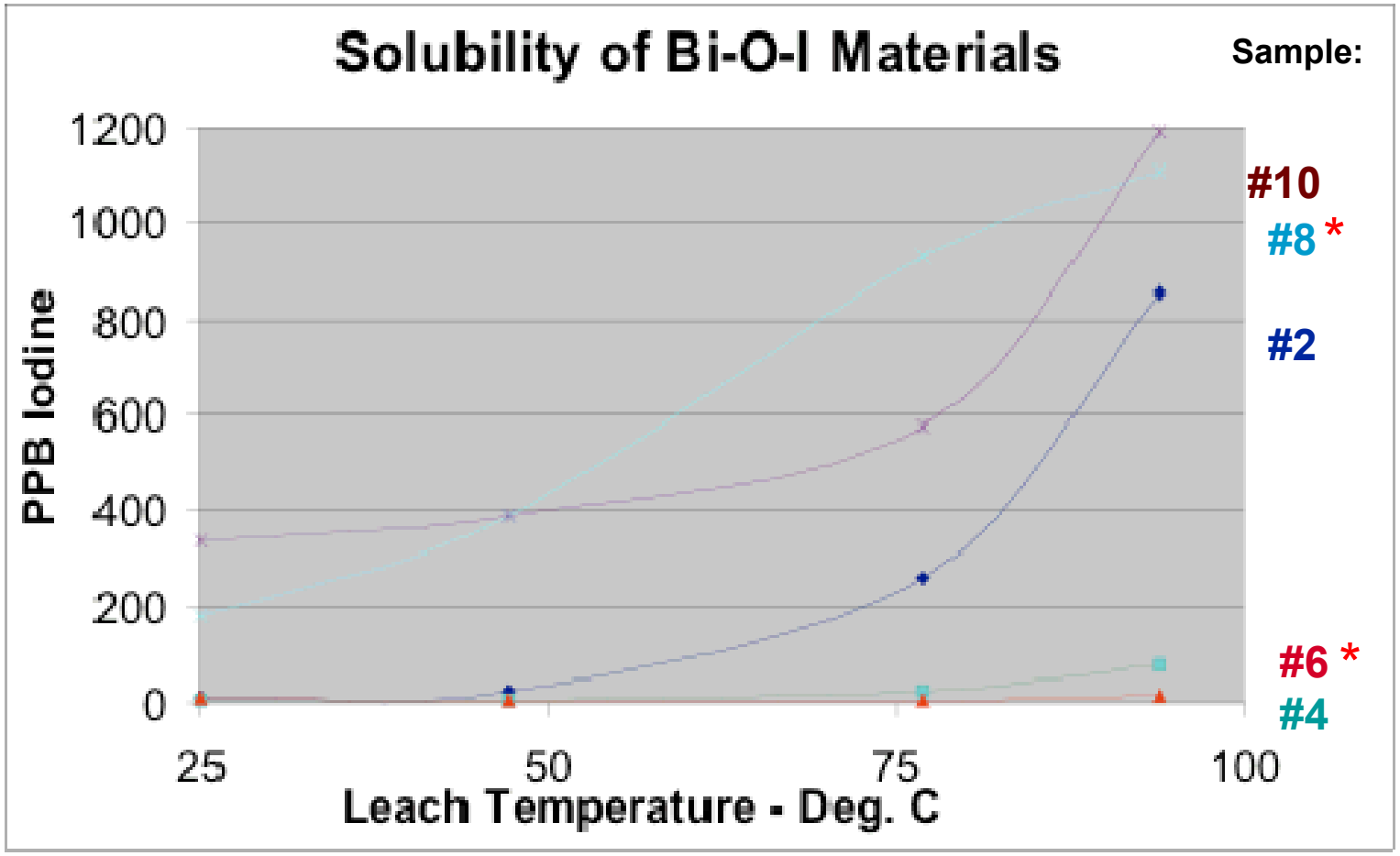
Solubility of Bi-O-I Phases in Accelerated Testing



Solubility Studies: 50mg of sample and 50 ml H_2O,for 5 days
Temperature: 25, 48, 75, and 94°C
Analyzed: 0.2 micron filters and diluted to concentrations for analysis by ICP-MS

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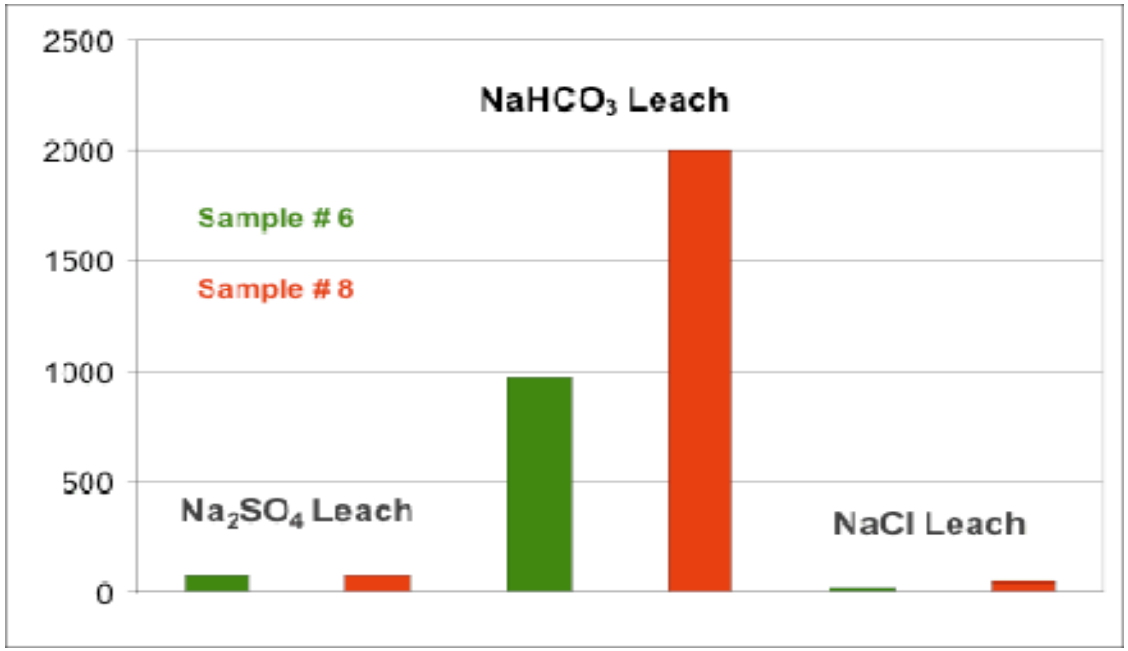
Solubility of Bi-O-I mixture in Simulant Groundwater



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).

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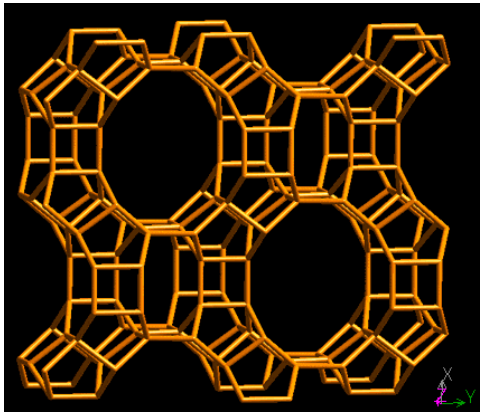
II. Low Temperature Glass Encapsulants for Iodine

- ^{129}I is present in the off-gas stream.
- It is separated by passing the vapor through a bed of Silver-Zeolite molecular sieves.
- Silver-Mordenite (Ag-MOR) is the leading candidate: $Ag_2Al_2Si_{10}O_{24}\cdot 7(H_2O)$.

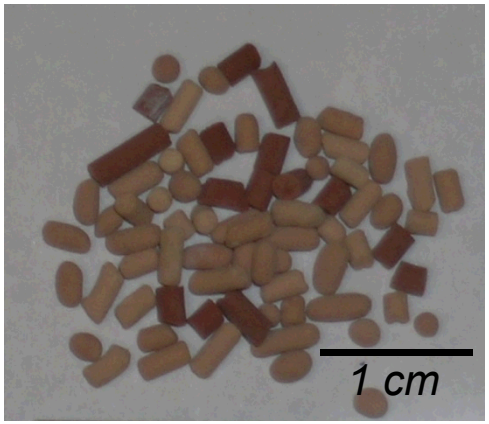
•Options for Waste Form Research:

leave Iodine in AgI-MOR

remove AgI from MOR and store AgI (sublimation temp ≈550°C)



MOR structure



Ag-MOR (IONEX)

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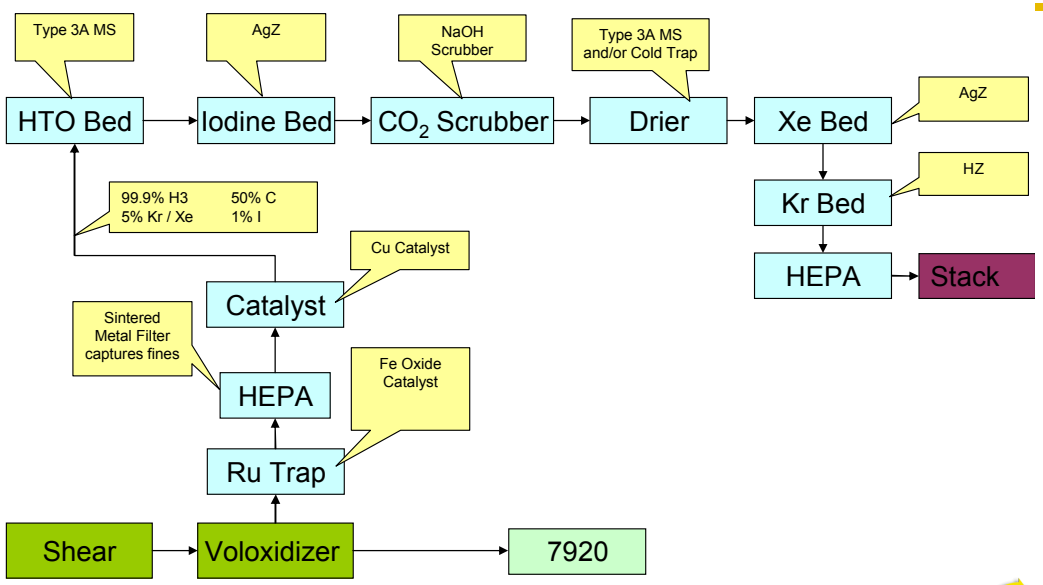
Voloxidation Off-gas Capture Systems

Courtesy of R. Jubin, ORNL



- For Iodine removal, Ag-MOR zeolite is used as the getter
- Samples sent to SNL for Waste Form Development
- Simulated Dissolver Off-Gas at INL
- Lab Test of Cycle Separations: Coupled End to End run (CETE) at ORNL (HOT Runs):
  - Close material balance for volatile components
  - Investigate release of volatile components during voloxidation

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Several other ^{129}I waste forms have been investigated

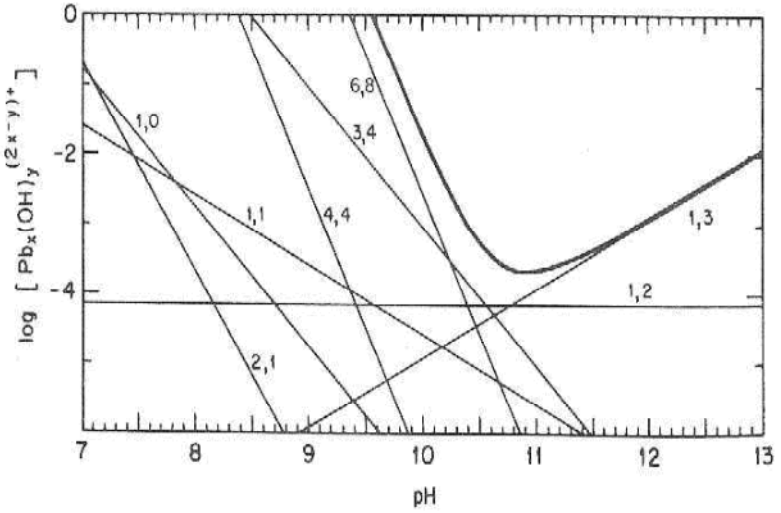
Low melting glasses of AgI with vanadium and lead oxide.

Low melting AgI/Ag pyro-phosphate glass (500˚C)
(T. Sakuragi et al, Mater. Res. Soc. Symp. Proc. Vol. 1107 (2008))

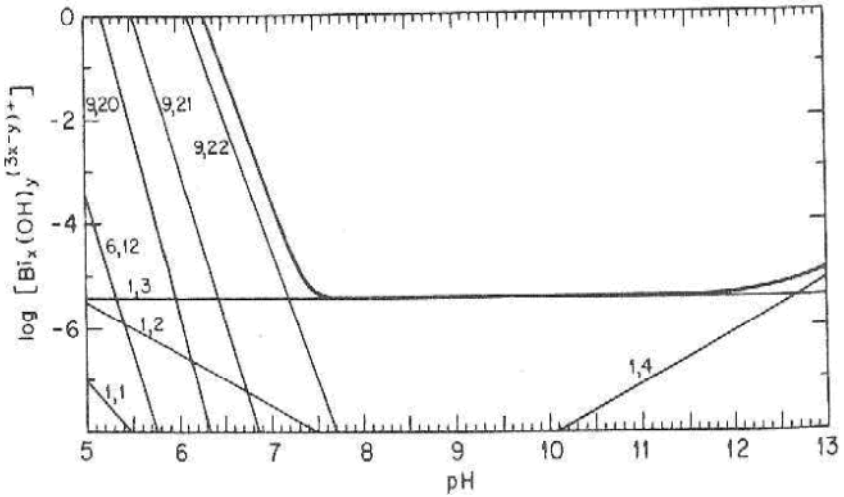
Encapsulation of AgI-MOR in grout (PNNL).

We have developed a different approach:
encapsulation with a low temperature sintering bismuth oxide based glass

Solubility of PbO in Water



Solubility of Bi_2O_3 in Water



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Samples were prepared by sintering mixtures of glass powder and AgI-MOR/AgI

- Non-radioactive iodine was used.
- AgI-MOR was ground to -400 mesh (<37 μm)
- AgI powder or ground AgI-MOR powder was mixed with Glass A powder
- Pellets (3.2 cm in diameter) were pressed without binder
- Pellets were heated in air at 5˚C/min to 500˚C for 1 to 3 hr

Properties of Glass A

Property	Value
Composition	BiZnB oxide
Recommended Sintering Conditions	500˚C for 15 min
Coefficient of Thermal Expansion	8.8×10^{-6}/˚C
Density	5.71 g/cm^3
Mean Particle Size	8 μm

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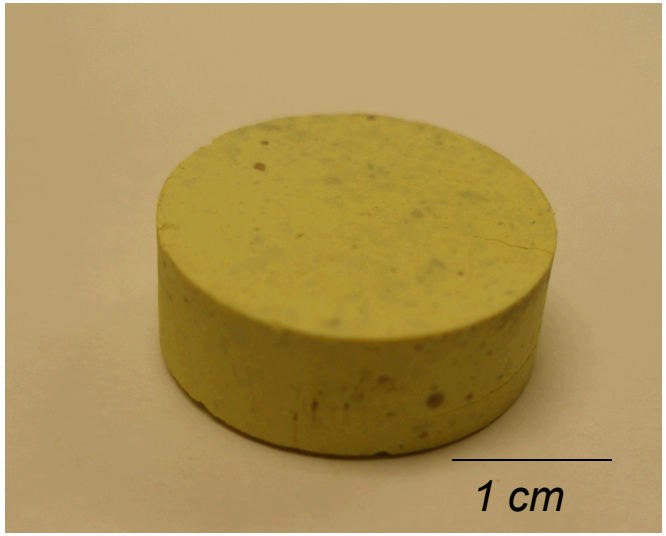
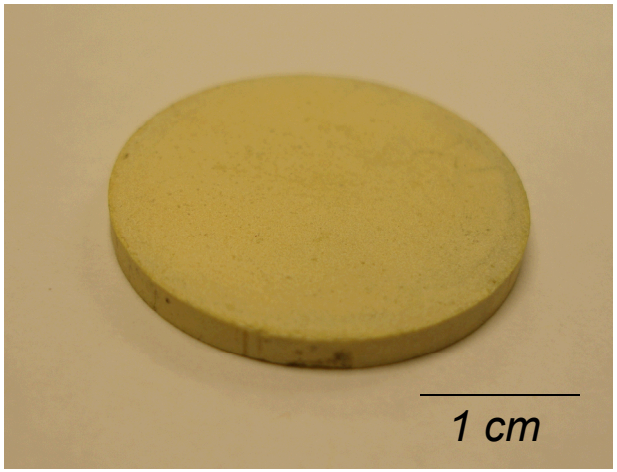
Low Temperature Glass Formation

After heating to 500C, the pellets were dense and crack-free.



20 wt% AgI- MOR/80 wt% Glass A
500˚C for 1 hr



50 wt% AgI/50 wt% Glass A
500˚C for 3 hr

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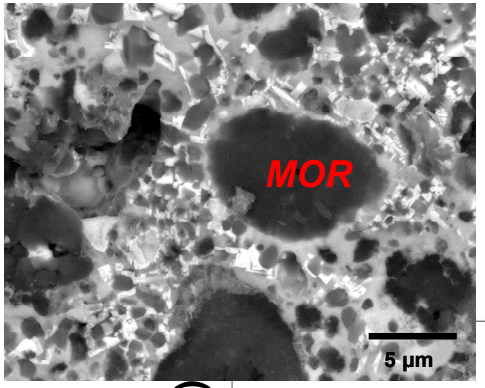
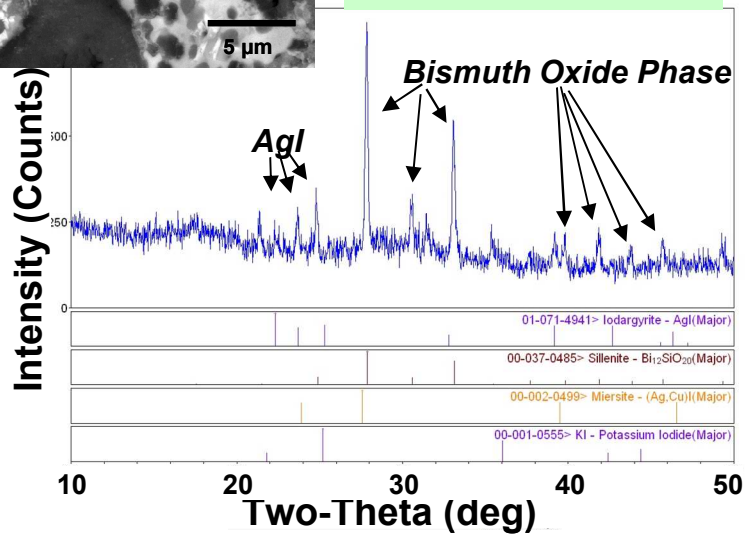
Analysis of Formed Glass Encapsulants

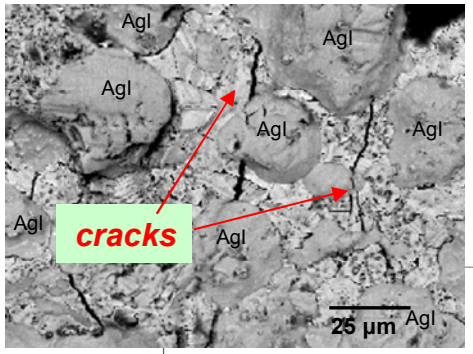


20 wt% AgI- MOR/80 wt% Glass A, 500˚C for 1 hr; dense pellets

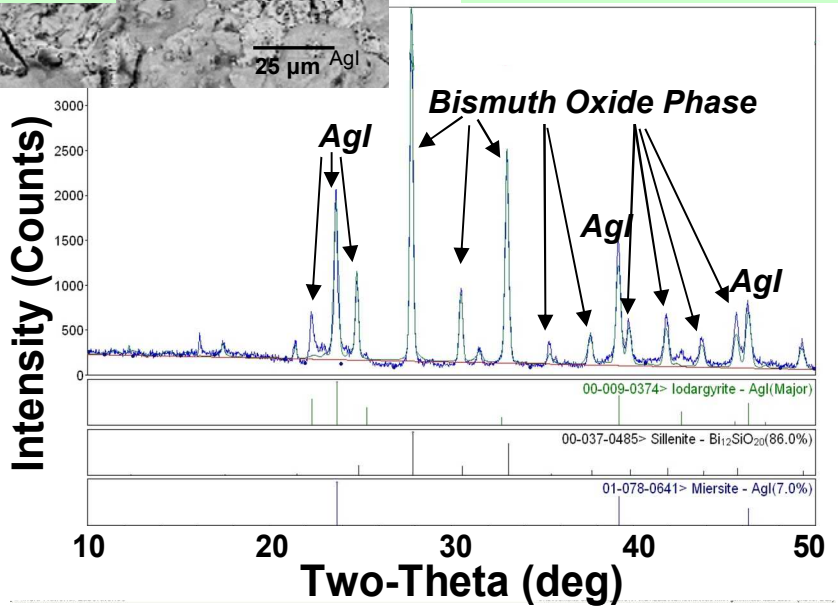


The remnants of MOR particles were no longer crystalline but were surrounded by crystallized Glass A.

The AgI was not located only in the MOR regions.



50 wt% AgI/50 wt% Glass A, 500˚C for 3 hr



The AgI particles are surrounded by a crystalline matrix

Cracks in the Glass - phase are most likely due to mismatch is thermal expansion coefficients.

No cracks propagating through the glass.

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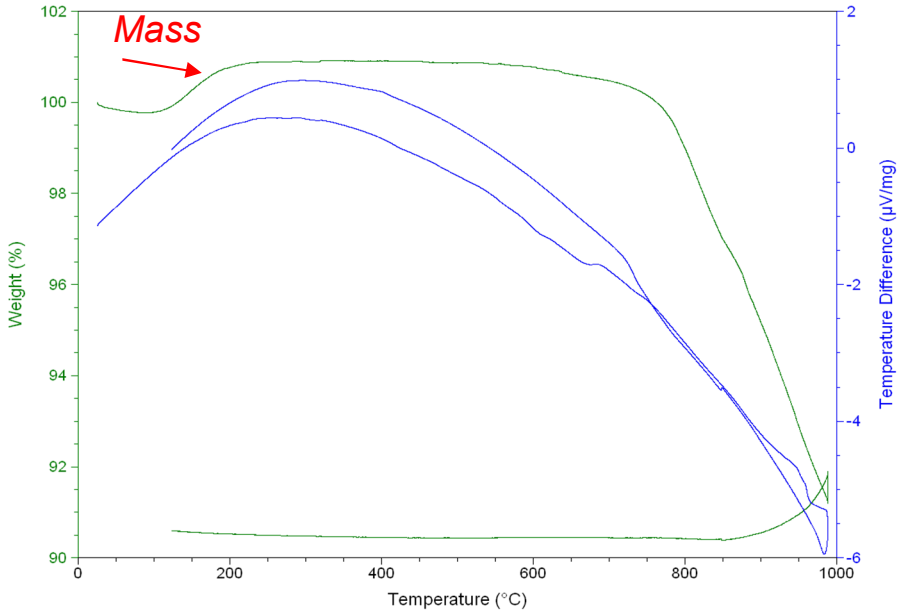
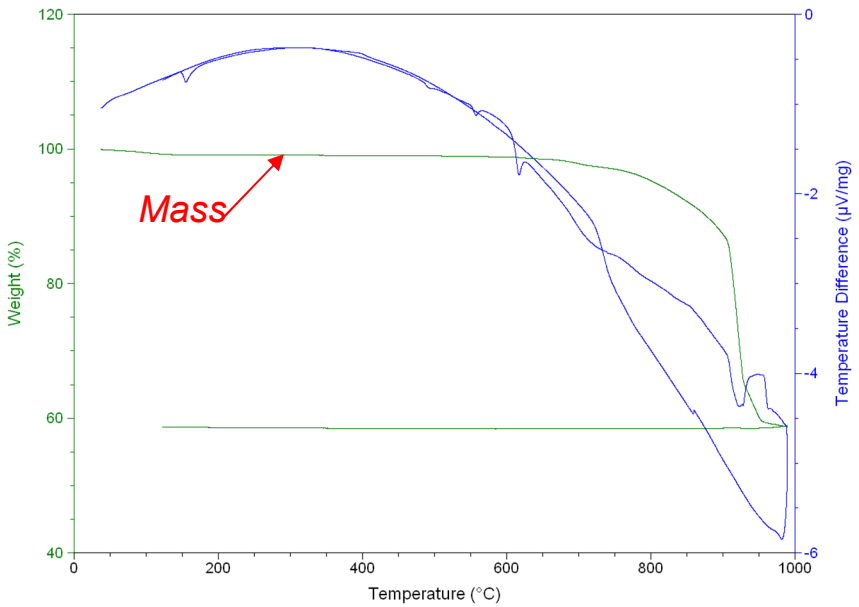
Thermal Studies on Glass A Encapsulant loaded with AgI or AgI-MOR

Thermogravimetric analysis of sintered samples indicated stability to > 700˚C.
Next Study: A slightly higher temperature sintering (thus less soluble glass) may result in a better performing glass.



20 wt% AgI- MOR/80 wt% Glass A, 500˚C for 1 hr



50 wt% AgI/50 wt% Glass A, 500˚C for 3 hr

On-going studies to determine max weight loadings and durabilities of waste forms

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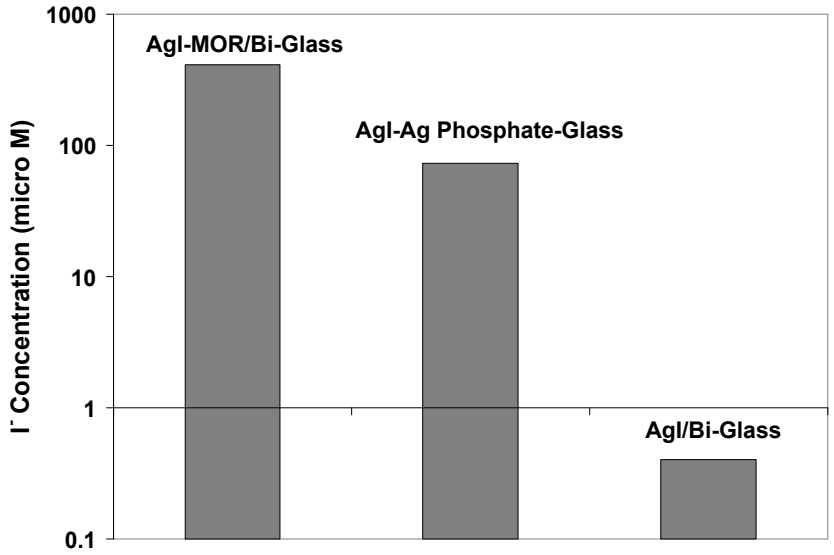
An accelerated aqueous leaching test was performed on the samples.

- PCT (Product Consistency Test, ASTM Designation: C 1285 – 02) test was done on crushed material: 90˚C for 1 week.
- I^- concentration measured with an I^- -specific electrode.
- High I^- concentration in AgI-MOR/Glass A sample due to loading method at SNL.
- The AgI/Glass A sample had a very low I^- concentration.



Conclusions

We have demonstrated two novel Bi-containing waste forms for Iodine from various streams.

1) in-situ precipitation from caustic streams of layered Bi-I-O high surface area phases with stability for low temperature repositories

2) a new waste form for ^{129}I that uses a low temperature sintering glass to encapsulate either AgI-MOR or AgI.

Both forms have high weight percent loading

(>20 wt% Iodine for Bi-I-O and 20wt% AgI-MOR, 50 wt% AgI for glasses).

Leach testing showed low iodide solubility for the AgI/Glass sample.

On-going research is into optimized glass compositions for increased weight loading and enhanced stability/durability.

Acknowledgement

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

This project is funded under the DOE/NE-AFCI Separations and Waste Form Campaigns.

EXTRA SLIDES

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Ag-MOR must be treated so that AgI is formed upon I_2 exposure

If the Ag in the Ag-MOR has not been properly reduced,
much of the I does not form AgI but is present as volatile elemental iodine.

Proper treatment involves:*
4 hr at 300°C in inert gas to remove residual air and moisture
24 hr at 500°C in H_2 to convert ionic Ag^+ to metallic Ag^0
purging with flowing Ar to remove residual H_2

In this work, we used a simpler loading technique in which the Ag-MOR is soaked for 1 hr in an aqueous KI solution, rinsed with deionized water and then dried.

This may lead to some residual KI present in the AgI-MOR.

*R.D. Scheele, L.L.Burger, and C.L. Matsuzaki, Methyl Iodide Sorption by Reduced Silver Mordenite. PNL-4489, Pacific Northwest Laboratory, Richland, Washington, 1983..

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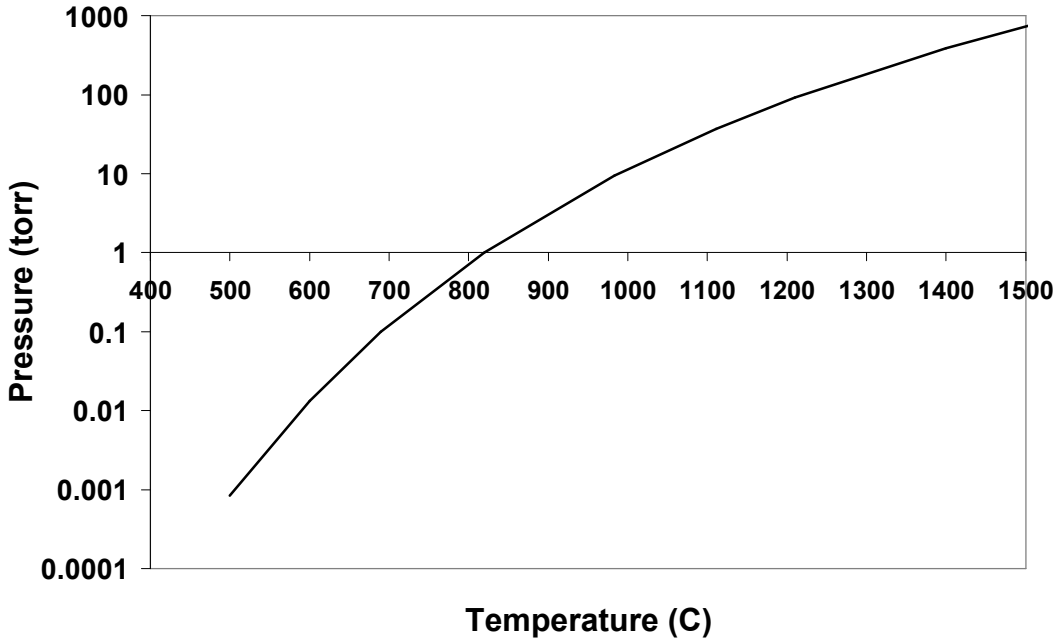
AgI Stability

- AgI has very low solubility but has a relatively high vapor pressure.
- The solubility in water at 20˚C is 3×10^{-6}g/L or 1.3×10^{-8} mol/L.
- It undergoes a β to α phase change at 147˚C and it melts at 558˚C.
- It has a vapor pressure of 10 mT at 600˚C.
- This limits the thermal processing temperature.



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The glass powder densified normally with 20 wt% AgI-MOR

Densification starts around 400˚C and is essentially complete by 500˚C.

Normal densification occurred with up to 50 wt% AgI.