U.S. DEPARTMENT OF ENERGY | Nuclear Energy

SAND2010-0959C

Fuel Cycle Research and Development

Use of Nanocomposite Materials (SNL-NCP) to Entrap and Immobilize Highly Volatile/Soluble Radionuclides

Yifeng Wang, *Jeffrey Brinker, Yongliang Xiong, Kathleen C. Holt, Phil Pohl & Kevin A. McMahon*

Sandia National Laboratories

Materials Challenges in Alternative & Renewable Energy

Feb. 23, 2010

U.S. DEPARTMENT OF ENERGY

Nuclear Energy

The needs

Front-end needs

- Off-gas treatment
  - *Existing technologies: Ag-impregnated materials, e.g. AgZ*
  - *No disposition pathway available for those materials*
- Direct/easy conversion of adsorbing materials to waste forms

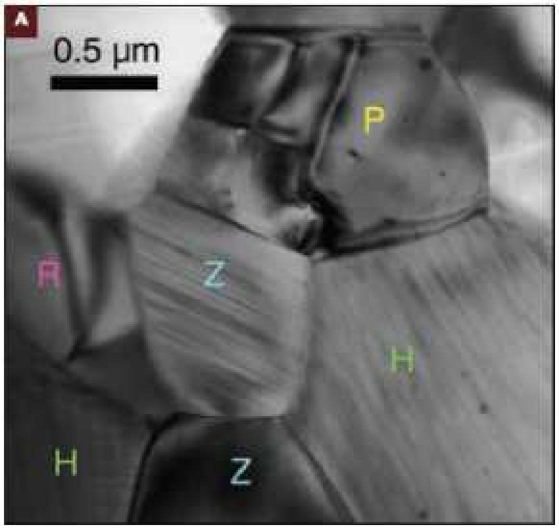
Back-end needs

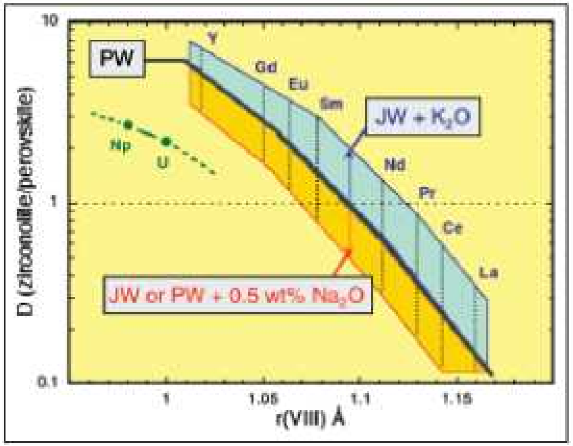
- Flexibility to accommodate various radionuclides
- Durable waste forms

Radionuclides of concern

- ^{129}I, ^{99}Tc & other volatile/soluble radionuclides

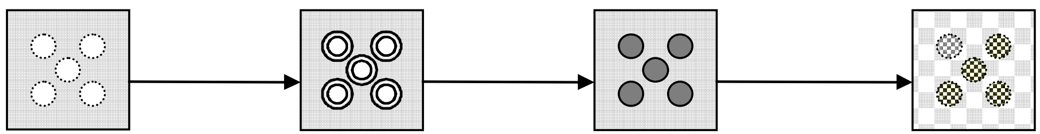
Limitations of Existing Waste Forms



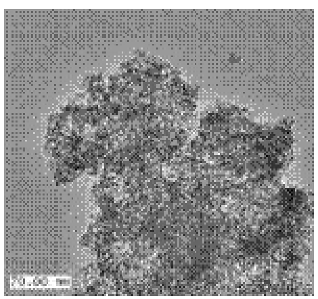


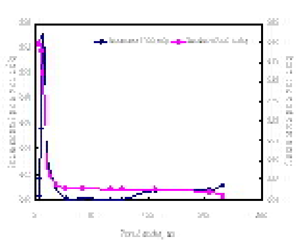
- **Immobilization Mechanism**
  - Incorporation of radionuclides (RNs) into mineral structure sites
- **Limited ability to accommodate different radionuclides**
- **Limited waste loading factors**
- **Dilemma in Durability**
  - Soluble RN vs. durable WF
    - *Changing stability of hosting minerals*
  - Dissolution kinetics vs. long term (1 My)
    - *Metal/alloy for Tc*
- **Thermodynamically stable waste forms?**

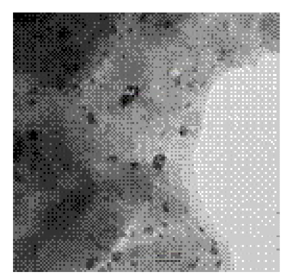
Development of New Generation of Waste Forms: Nano-immobilization & Nano-encapsulation



Nanoporous material | Functionalized pore surface | Sorption & immobilization | Fixation & encapsulation





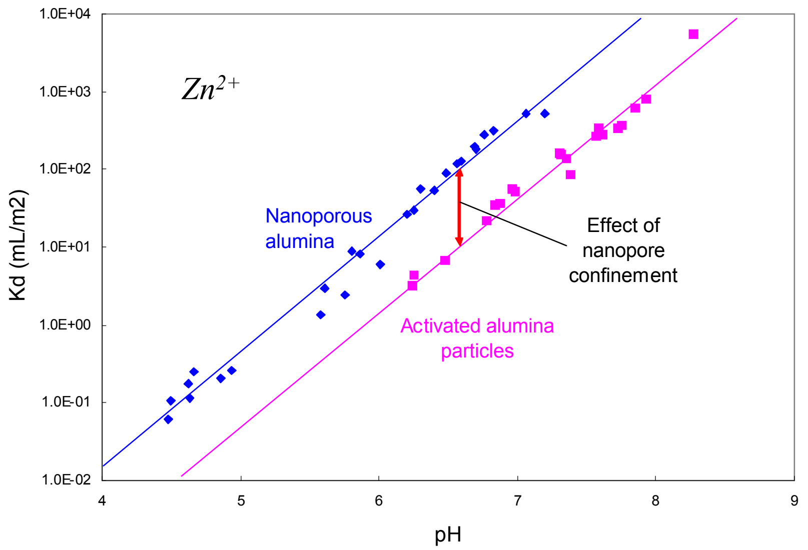


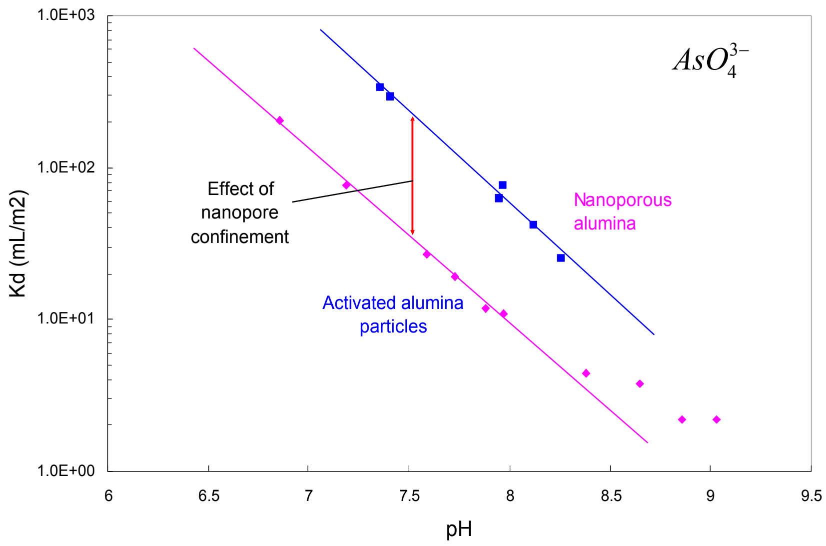
- 1 patent issued
- 2 patents pending
- 2 Technical advances
- Funding
  - LDRDs
  - FOA

Why Nano-scale?

- **Novel sorption capability: e.g. I-129, Kr & Xe**
- **Fast sorption kinetics**
  - Getter materials
  - Membrane separation
- **Easy to engineer material chemistry**
  - Surface modification & grafting
- **Easy to encapsulate**
  - Durability: host minerals
  - Flexibility
- **Chemical durability**
  - Thermodynamically stable
- **Mechanic strength**

Nanopore Confinement & Sorption





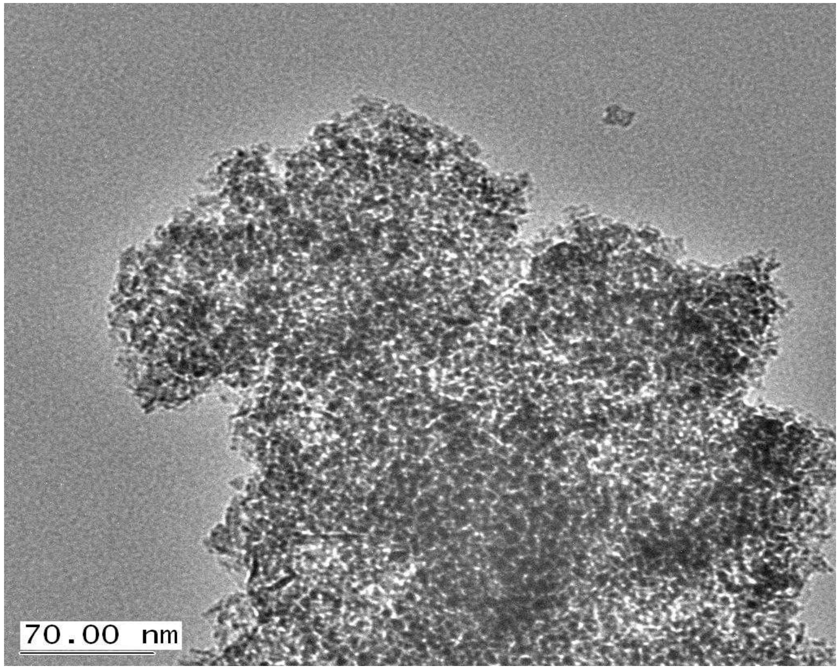
Nanopore confinement enhances ion sorption onto a solid-water interface for both cations and anions.

Wang et al., 2003, Mat. Res. Soc. Symp. Proc.; 2003, Geology

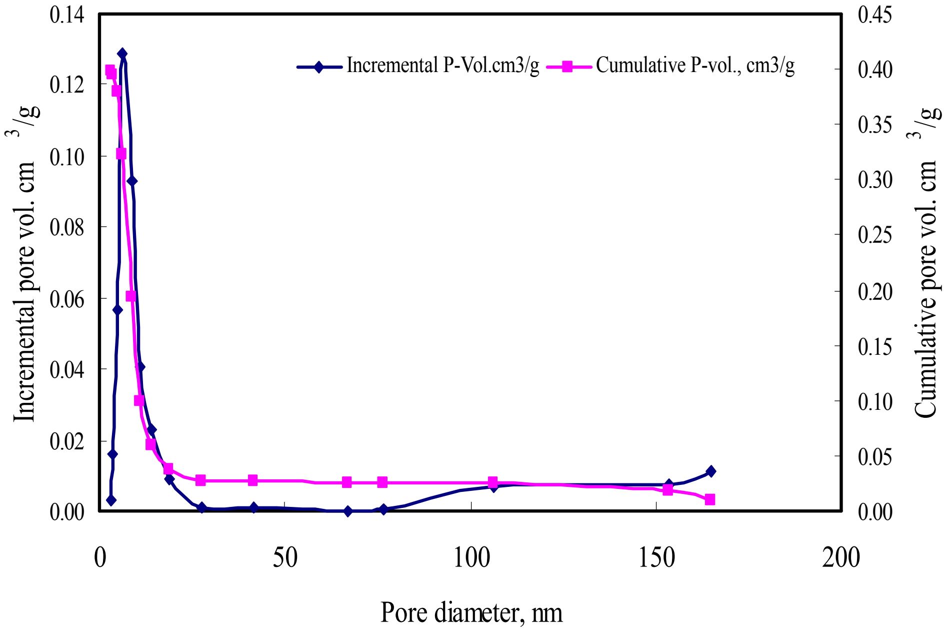
Material Synthesis

- **General route for synthesizing nanostructured metal oxides**
  - Based on a sol-gel method
  - Inorganic precursors & block copolymer (as a structural template)
  - Inexpensive, scalable for a large quantity production
- **One-pot synthesis**
  - Multiple metal oxides
  - Compositional & structural homogeneity ensured
- **Formation of monolith**
  - Preferred for material handling
- **U.S. Patent No. 7,238,288; two pending patents**

Material Synthesis (cont.)



TEM image of nanoporous double metal oxide synthesized using the one-pot route, showing worm-like pore structures.



BET measurements of nanoporous double metal oxide

Iodine Sorption on Nanoporous Alumina and Its Derivatives

Material	I/(m-Al) ratio	Sample wt, g	[I] uptake, ppm	
Nanoporous alumina w/ Ag	0.114	0.2036	35674	
Monolithic Nanoporous alumina w/o Ag	0.107	0.2035	66245	
BET measurements				
Material	Surface area, m^2/g	Pore vol. cm^3/g	Pore size, nm	Micropore vol. cm^3/g
Nanoporus alumina w/ Ag	215	0.706	12.7	0.006644
Monolithic Nanoporous alumina w/o Ag	354	1.75	19.15	0.014549

No silver is needed for I sequestration!

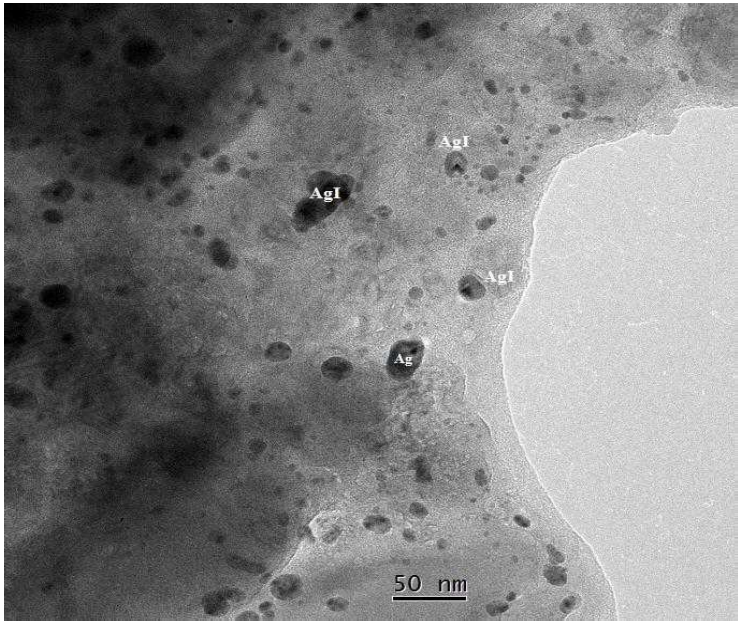
Ag-zeolite (?): Zeolite itself is not a good adsorbent for.

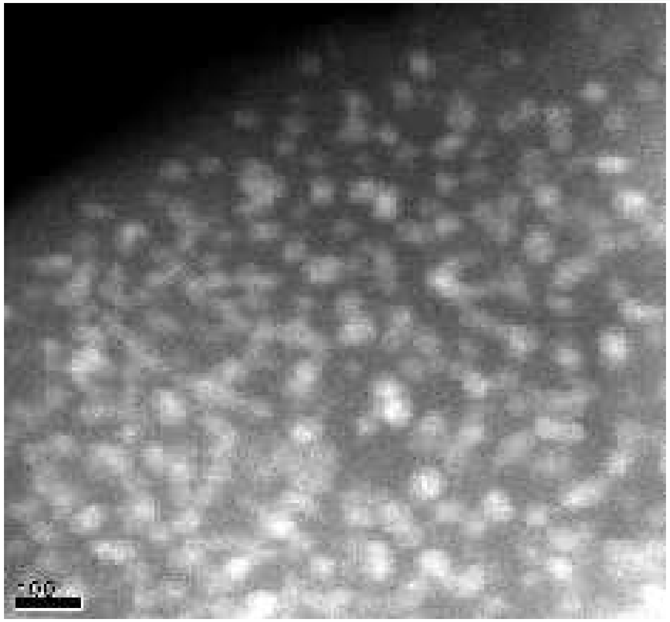
Nanopore Structures & Radionuclide Retention

Material	I sorption (ppm)	% of I lost during fixation	% of I lost during vitrification
Particles	98	~100%	~100%
Activated particles	8700	45	65
Nanoporous material	25000	~ 0	~ 0

- **Nanoporous structures not only enhance I sorption but also help to retain I during the fixation and encapsulation.**
- **Silver is not needed either for iodine retention!**

Waste Form Formation by Encapsulation

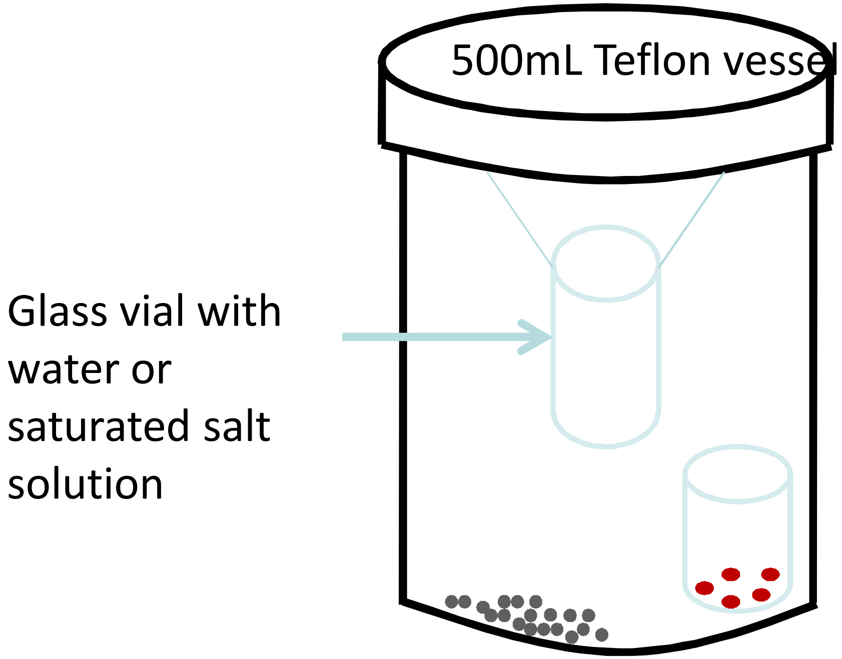




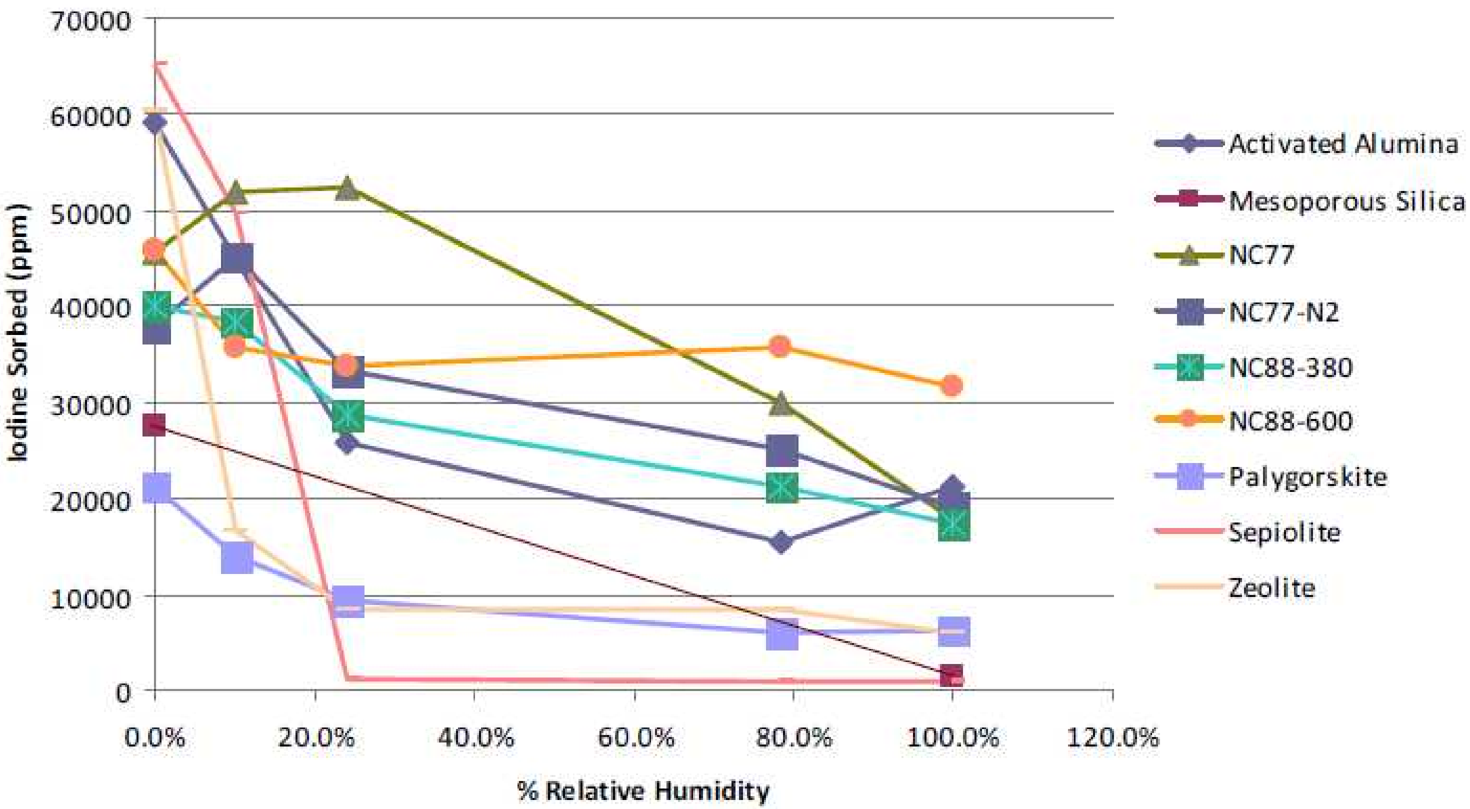
- Optimal conditions for vitrification
- Formation of nanocrystals
- Durability of waste forms

Relative Humidity Testing

- **Control of relative humidity**
  - Saturated Salt Solutions
    - *LiCl = 10.23% RH*
    - *$MgCl_2$ = 24.12% RH*
    - *KCl = 78.5% RH*
  - DI Water = 100% RH

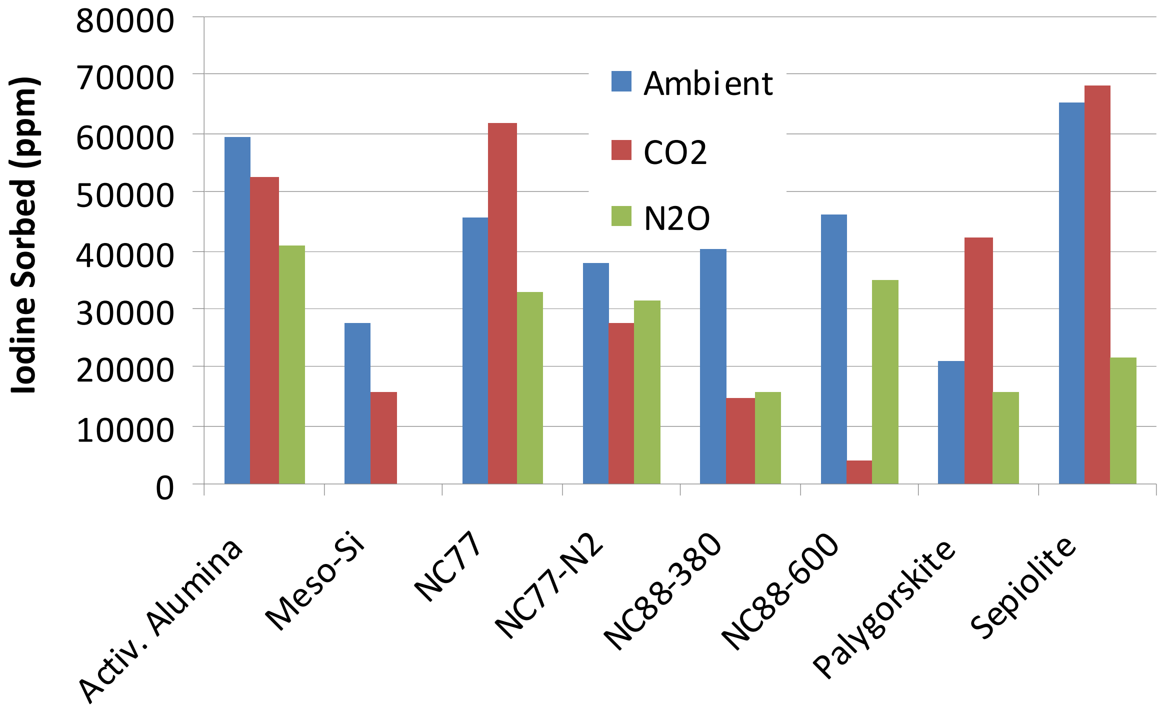


I_2 Sorption: Effect of Humidity



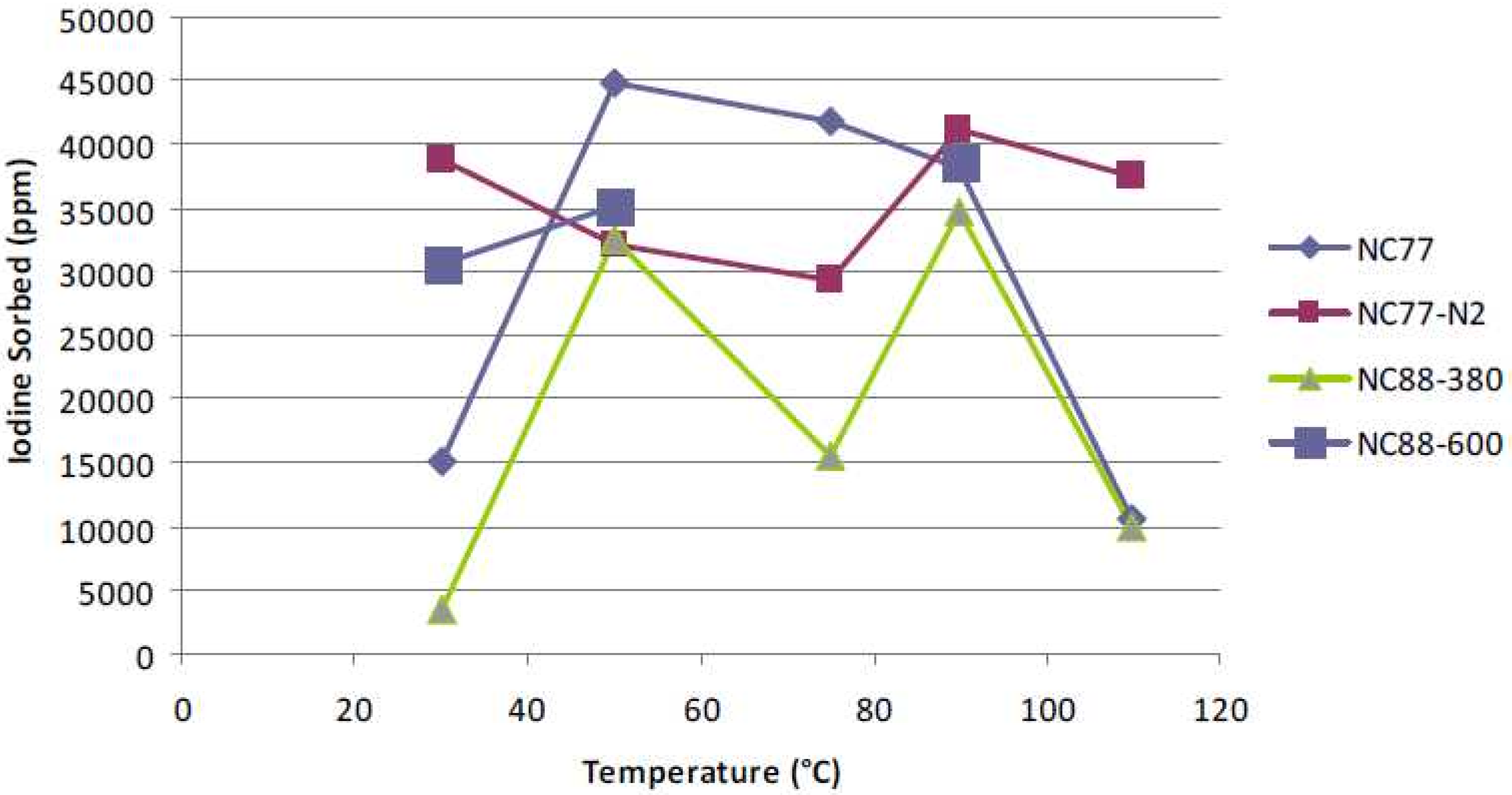
SNL-NCP (NC77) is the least sensitive to water vapor.

I_2 Sorption: Effect of Other Gaseous Components



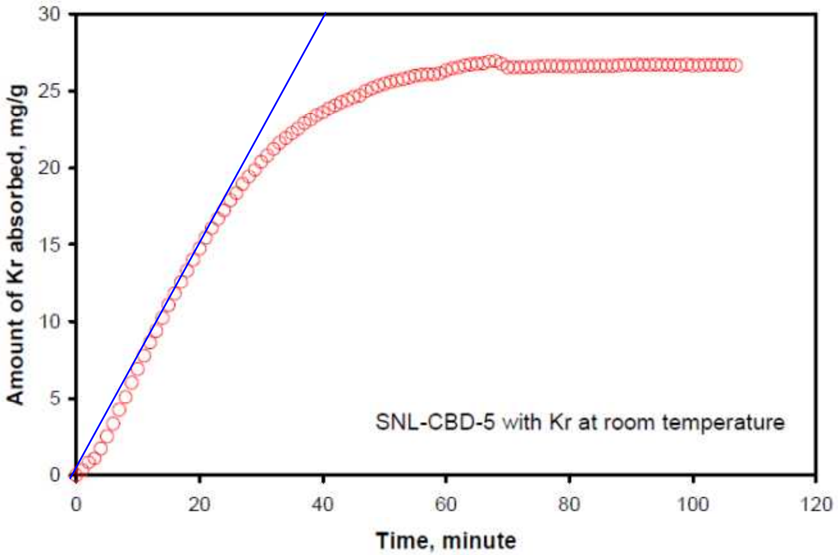
Enhancement of I sorption by CO_2?

I_2 Sorption: Temperature Effect



Kr & Xe Sorption Tests

- **TGA analysis**
- **Two stages:**
  - Heating & Degassing
  - Cooling & sorption



Ar & Kr Sorption @ Room Temperature & 0.9 atm

Table 1. Adsorption Experiments with Ar at room temperature and 0.9 atm (685 torr) pressure*

Adsorbents	Weight percentage of noble gas adsorbed (wt.%)
MP zeolite	0.00
Zeolite 13X	0.08
NC 77	0.33
NC 95 (unground)	0.23
NC 95 (ground)	0.31
S51HF	0.68
Hydromagnesite	0.02
DARCO	0.72
Activated Carbon (Alfar Aesar)	0.50
SNL-CBD-1	0.42±0.06
SNL-CBD-2	0.37±0.01
SNL-CBD-5B	0.24
Log#339	0.175±0.005 (average of un-ground and ground samples)
Log#355 (unground)	0.14
S159-2-B (unground)	0.20
Silicate-P	0.26
Silicate-S	0.36
Mordenite-N	0.27
Mordenite-A	0.12
Spectrum zeolite	0.03
Wako zeolite	0.07
Spectrum $Al(OH)_3$ (Spectrum Chemical MFG Corp)	0
S185-4	0.19
S185-5	0.13
S187	0.01
S188	0.05
S189-1	0.10
S189-2	0.02
Brucite (Fisher Scientific)	0.00
Nesquehonite (Synthetic)	0.00
Calcium citrate tribasic (earlandite) (ACROS ORGANICS)	0.00

*Samples are first subjected to 2 hours desorption at 90 °C, and then 2 hours adsorption at room temperature in the vacuum microbalance.

Table 2. Adsorption Experiments with Kr at room temperature and 0.9 atm (685 torr) pressure*

Adsorbents	Weight percentage of noble gas adsorbed (wt.%)
MP zeolite	0.36±0.08
Zeolite 13X	0.64
NC 77	0.24
Hydromagnesite (Synthetic)	0.05
DARCO	3.60
SNL-CBD-1	3.01
SNL-CBD-2	2.51
Silicate-S	0.71
SNL-CBD-3[A]	1.93
SNL-CBD-3B[A]	1.97
SNL-CBD-3C	2.56
SNL-CBD-4	1.63
SNL-CBD-5	2.69
SNL-CBD-6	2.06
Mordenite-N	1.74
Mordenite-A	1.31
Silicate-P	1.03
Wako zeolite	0.99
Spectrum zeolite (Spectrum Chemical MFG Corp)	0.53
Calcium citrate tribasic (earlandite) (ACROS ORGANICS)	0.16
S159-2-B	0.30
S185-4	0.30
S185-5	0.42
S187	0.29
S188	0.39
S189-1	0.32
S189-2	0

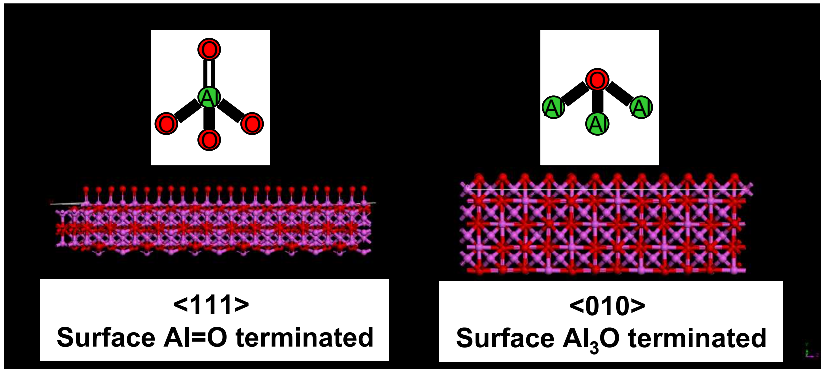
*Samples are first subjected to 2 hours desorption at 90 °C, and then 2 hours adsorption at room temperature in the vacuum microbalance.
[A] Sample spill outside of the crucible was observed; therefore true value should be higher than this.

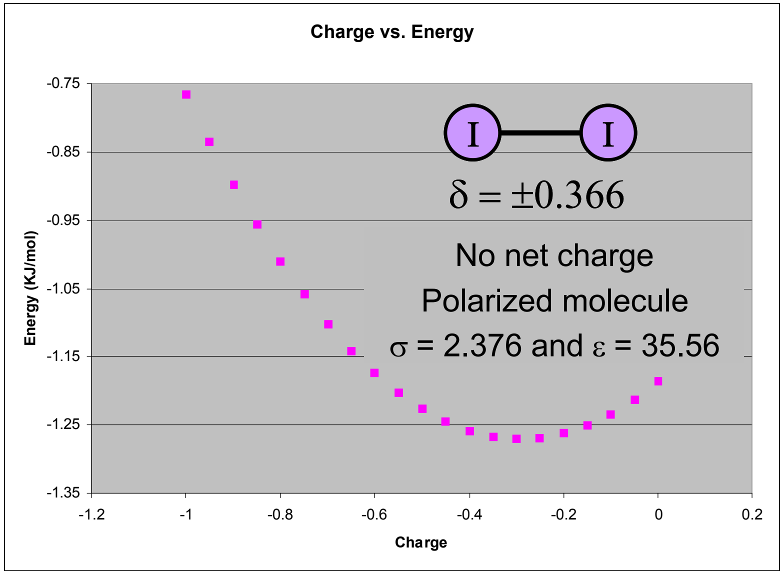
Testing Results: Ar and Kr adsorption

- Activated carbon materials have high adsorption capacities for Ar, followed by SNL-NCP and naturally occurring layered silicates. These samples have adsorption capacities higher than 0.30%.
- Activated carbon, SNL-NCP materials (SNL-CBD series), naturally occurring layered silicates have high adsorption capacities for Kr.
- New SNL-NCP materials (nanostructured C-inorganic composites) have high adsorption rates, comparable to activated carbon.

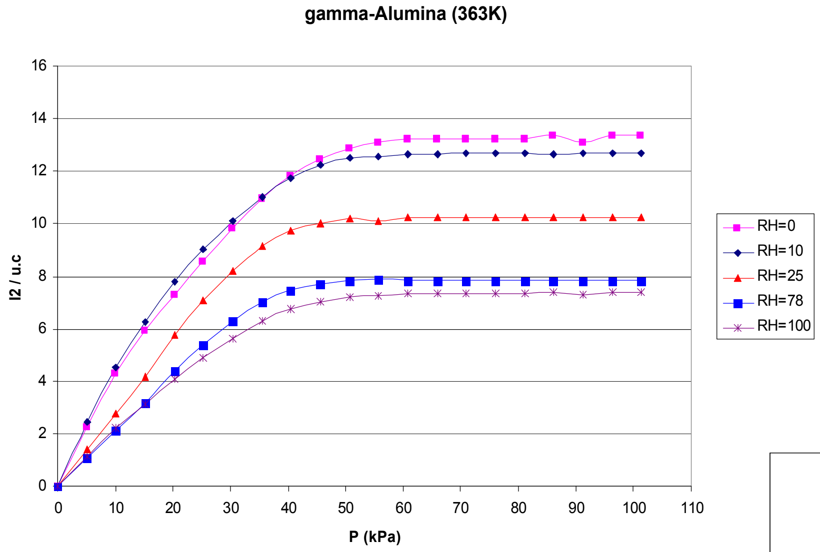
Molecular Dynamic Modeling: Model System for Iodine Sorption

- **Capturing the polarization effect of I_2 is the key to the simulation of iodine gas adsorption on metal oxide surfaces.**



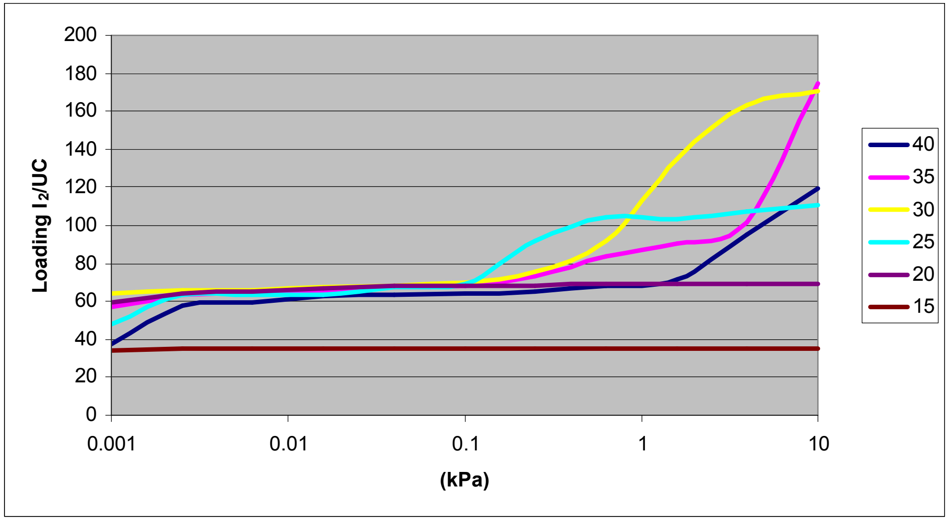


MD Simulations: Iodine Sorption on alumina surfaces



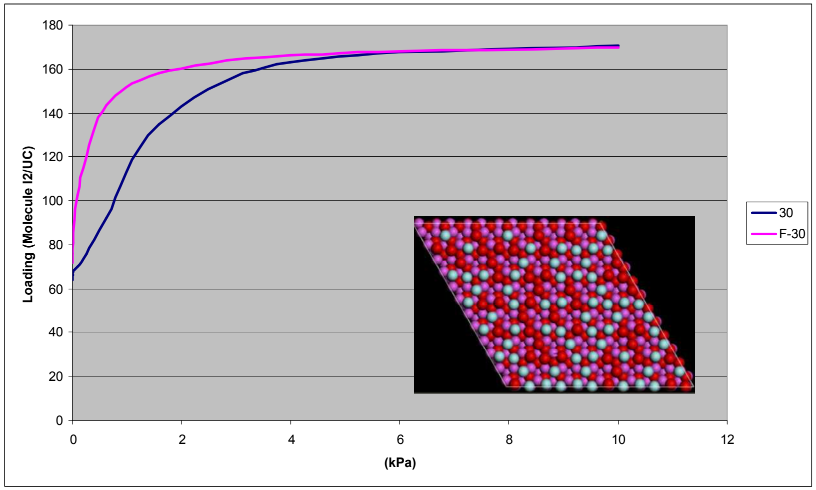
Unconfined

There existence of optimal pore sizes for iodine sorption onto nanoporous materials (2.5 – 3.5 nm).



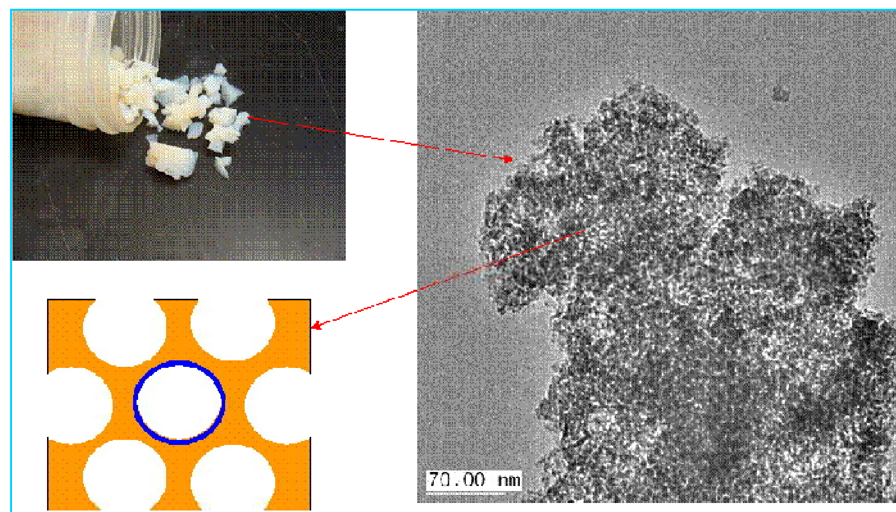
Confined

MD Simulations: Iodine Sorption on alumina surfaces (cont.)



- Material design & optimization
  - Surface modification
  - Control of pore sizes

Molecular design



Concluding Remarks

- **Performance of SNL-NCP materials**
  - Nanostructured
  - High sorption capability/selectivity
  - No Ag needed for entrapment and immobilization
  - Easily converted to durable waste forms
  - Applicable to a wide range of radionuclides
  - Inexpensive for synthesis
- **Future work**
  - Enhancement of Kr & Xe sorption
  - Functionalization of nanopore surfaces
  - MD modeling
  - Collaboration with other labs

Acknowledgement

Other contributors:

Huizhen Gao

Nate Ockwig

Yingbing Jiang (UNM)

Sandia is a multiprogram 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.