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International High Level Radioactive Waste Management Conference

INORGANIC METAL FLUORITE MATERIALS AS NOVEL ADSORBENTS FOR GASEOUS RADIOIODINE CAPTURE

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The needs for nuclear Fuel cycle

- 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
- Material specifications and requirements
  - High capacity & selectivity
  - Fast sorption
  - Inorganic materials (e.g. alumina and its derivatives)
  - Easy to synthesis and scale up
  - Cost
- Not limited to nuclear fuel cycle

Development of High Performance Nanostructured Inorganic Adsorbents

- More than 10 years
- ~ $ 4 M invested
  - 2 LDRD projects
  - 1 DOE NE project
  - 1 DOE OCRWM S&T project
- Patents
  - 2 US patent issued
  - 4 patent pending
  - 1 patent in preparation
- Publications
  - ~ 20 peer-reviewed publications
- Materials, testing & applications
  - A broad set of materials
    - Nanoporous materials, layered materials, etc.
  - Alumina materials have been intensively tested for iodine sorption.
  - Applications covers the adsorption of cations, anions and gaseous species .

- Nanostructured double metal oxide-carbon composite
- High-performance nanoporous alumina & its derivatives
- Nanostructured waste form
- Fire resistant advanced activated carbon
- Fluorite-based materials & its nanostructured derivatives.
- Silicate materials for Kr sorption & separation

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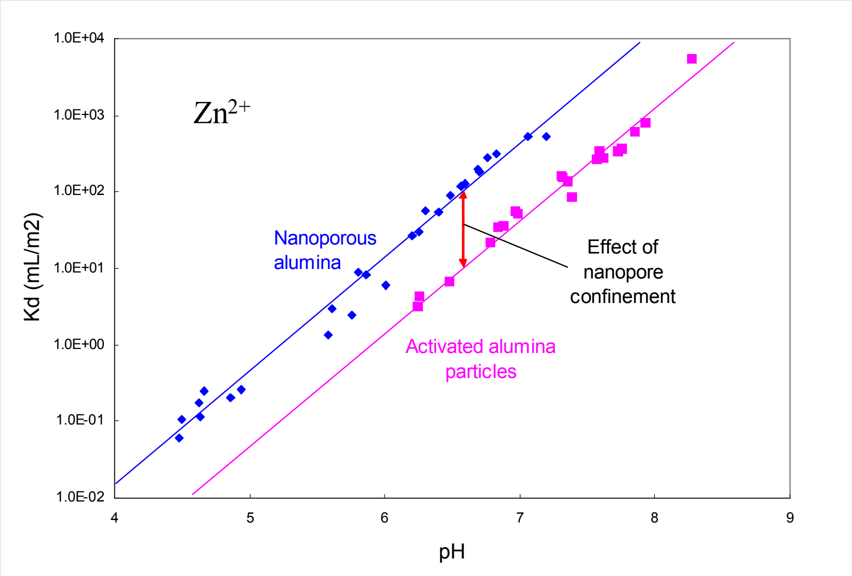
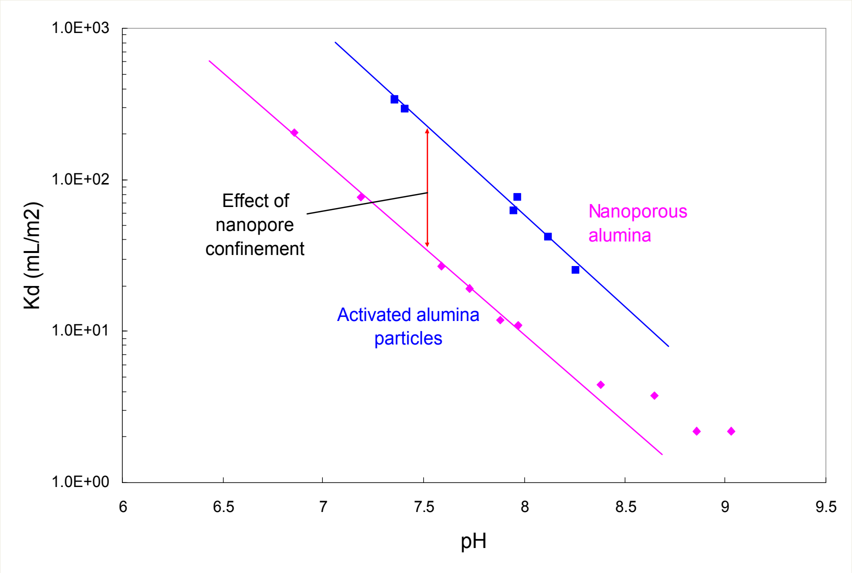
Why nano-scale?

- 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





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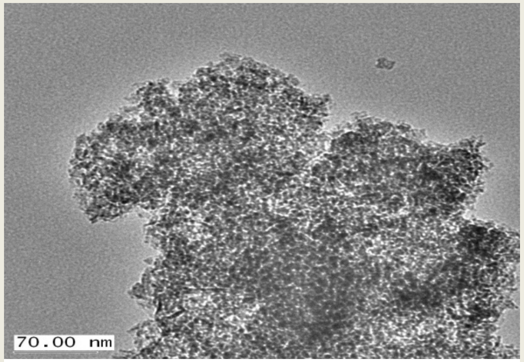
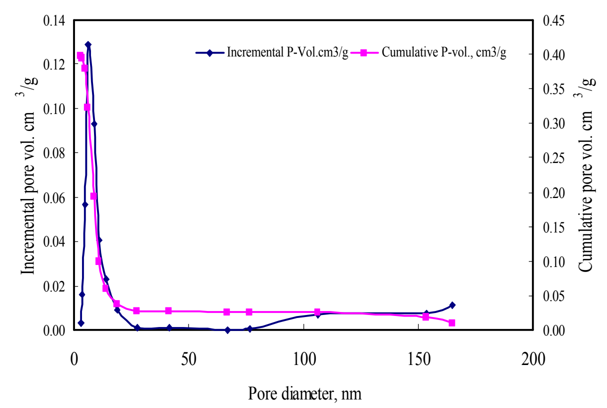
Material synthesis

- 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



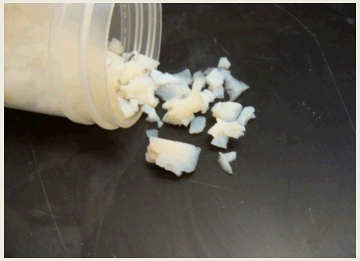
TEM image of nanoporous double metal oxide synthesized using the one-pot route, showing worm-like pore structures.



BET measurements of nanoporous double metal oxide

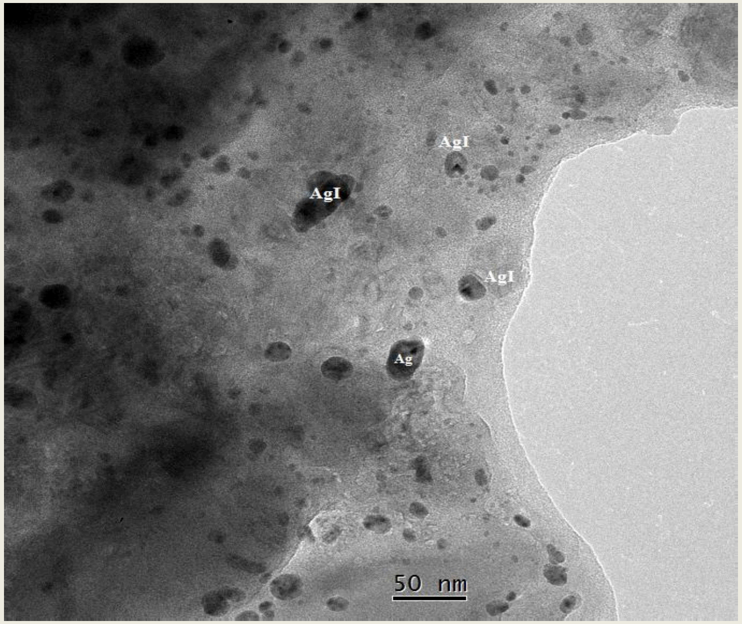
Iodine Sorption on Nanoporous Alumina and Its Derivatives

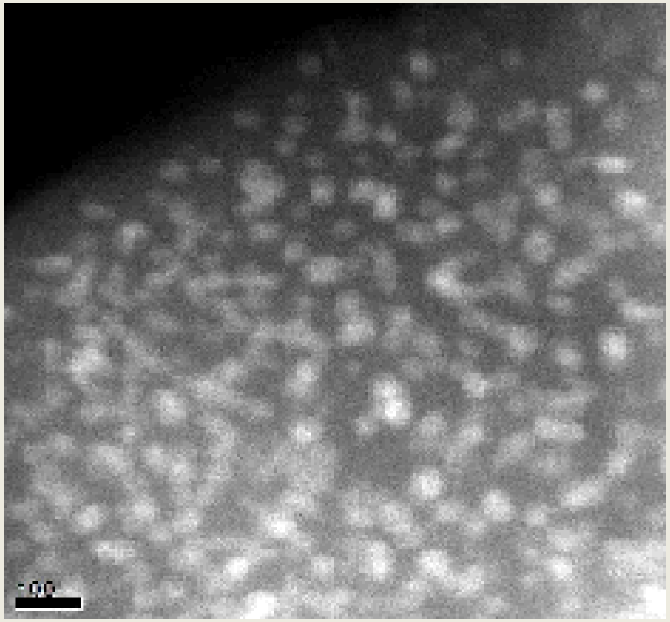
Material	I/(m-Al) ratio	Sample wt, g	[I] uptake, ppm	
Nanoporous alumina w/ Ag	0.114	0.2036	35674	
Monolithic Nanoporous alumina w/o Ag	0.107	0.2035	66245	
BET measurements				
Material	Surface area, m^2/g	Pore vol. cm^3/g	Pore size, nm	Micropore vol. cm^3/g
Nanoporus alumina w/ Ag	215	0.706	12.7	0.006644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



No silver is needed for I sequestration!

Waste Form Formation by Encapsulation





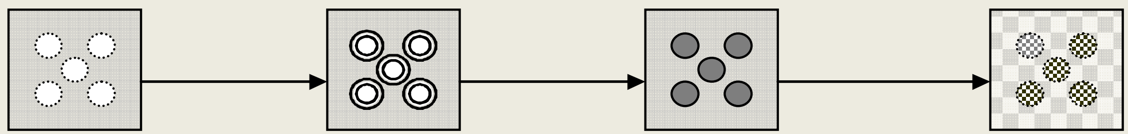
- Optimal conditions for vitrification
- Formation of nanocrystals
- Durability of waste forms

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!

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

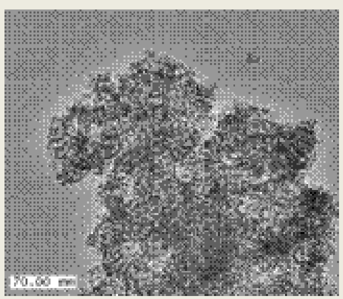


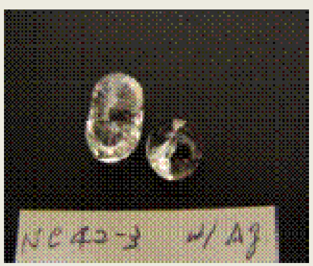
Nanoporous material

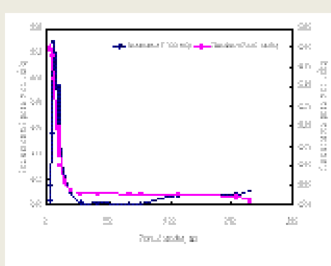
Functionalized pore surface

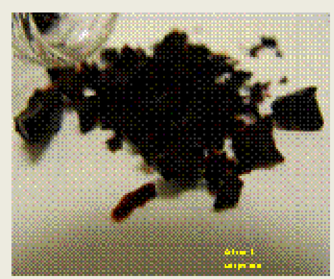
Sorption & immobilization

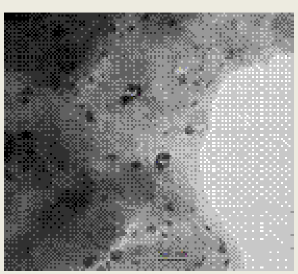
Fixation & encapsulation











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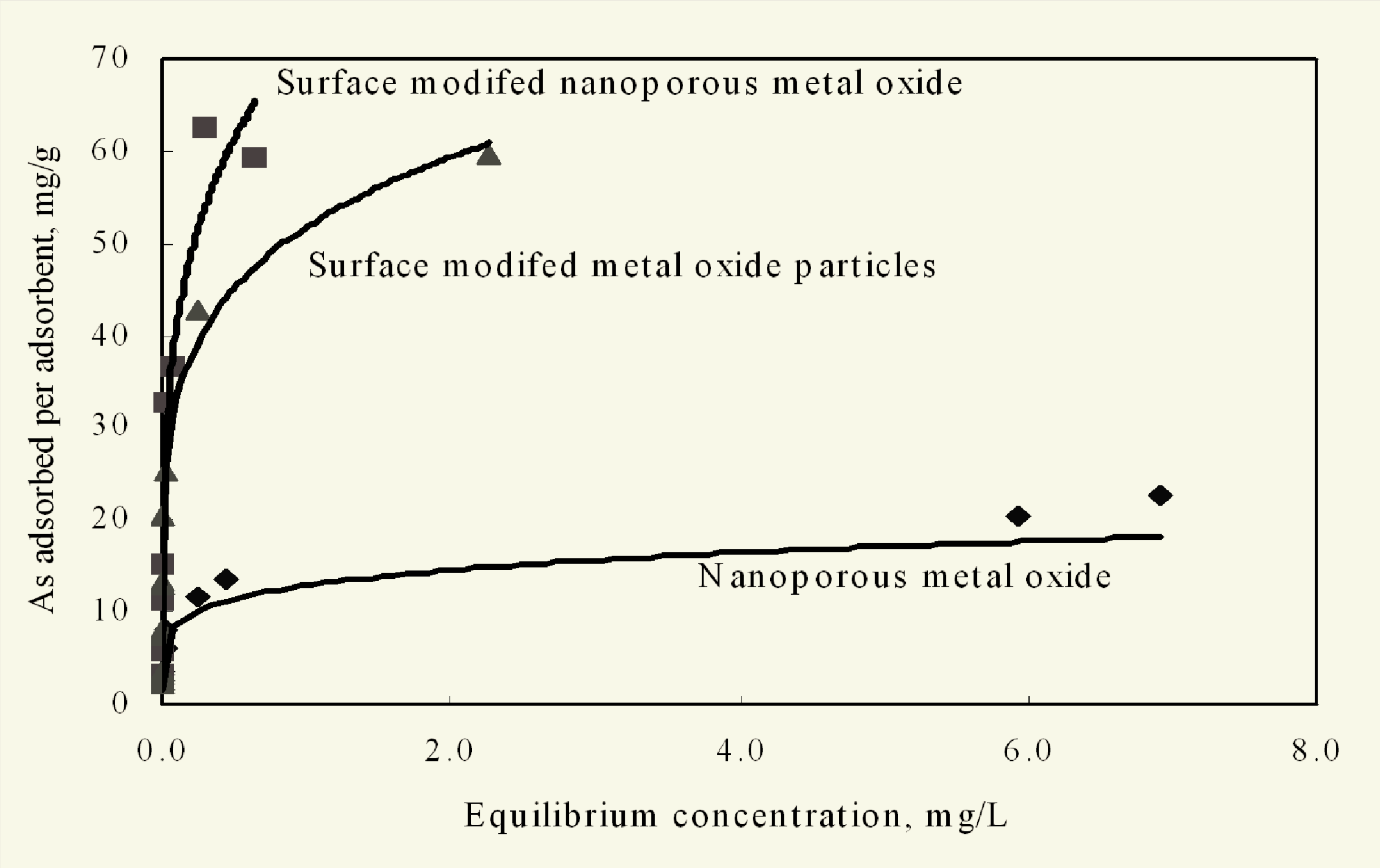
Surface Modification & its effect on ion sorption



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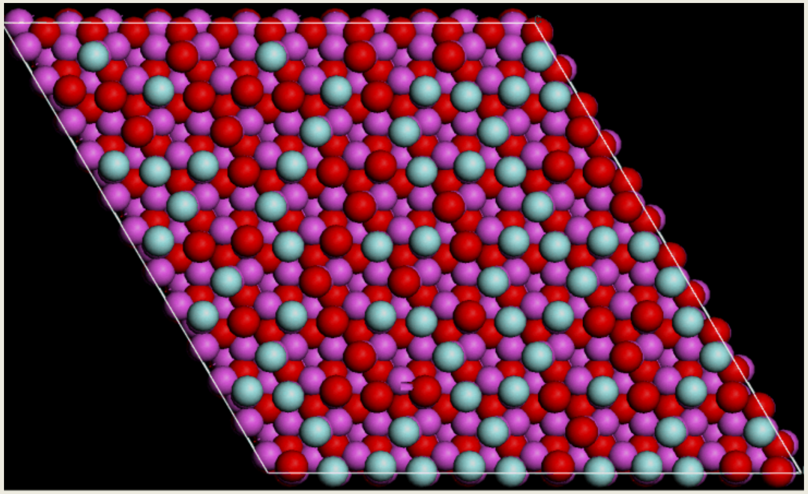
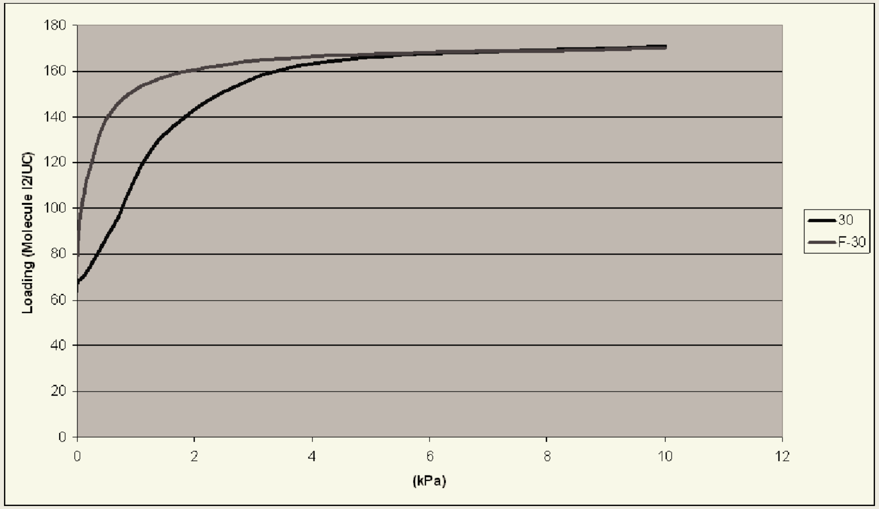
Molecular Design of Adsorbent Materials

- Surface terminating atoms
- Existing inorganic adsorbents
  - Oxide compounds
- Molecular dynamic modeling
  - Fluorine vs. oxygen





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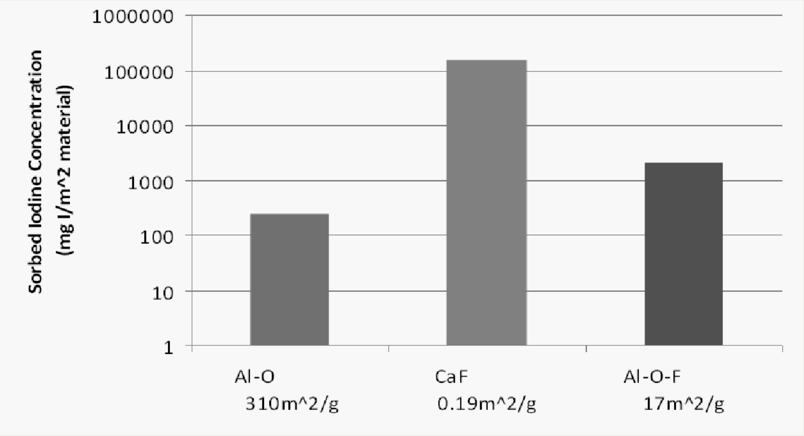
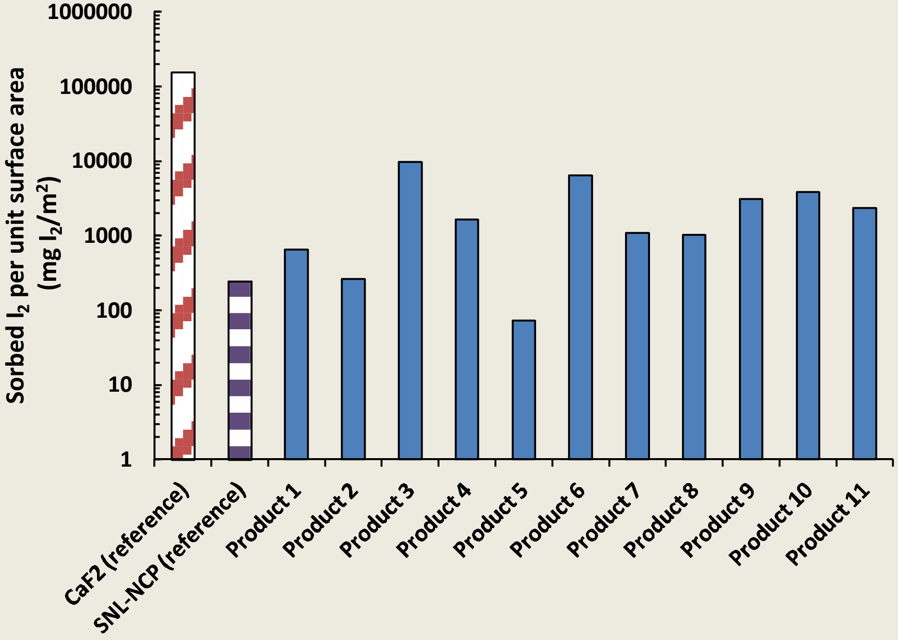
Fluorite-based materials (cont.)

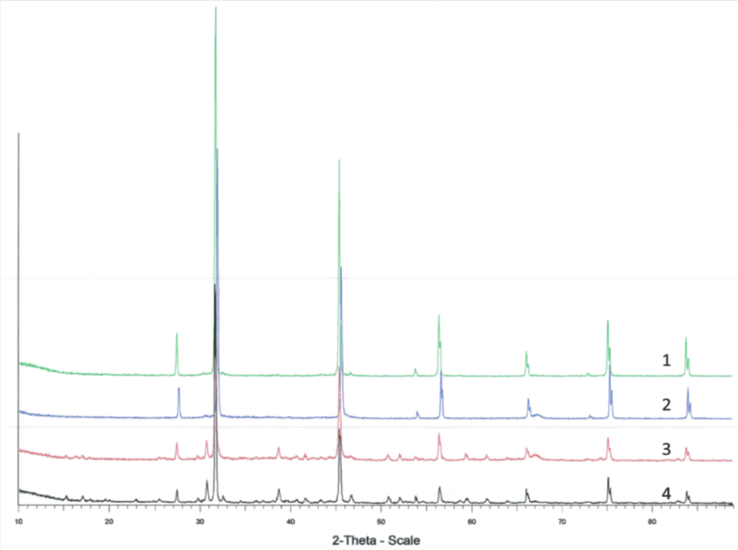
- New discovery
  - Fluorite material for gaseous iodine (normalized to surface area) is ~ 1,000 times higher than the conventional oxide materials
- Synthesis of nanoporous fluorite materials
  - Sol-gel method
  - Direct precipitation
  - Thermal decomposition



Product #	I_2 uptake (total, ppm I/g sample)	BET S.A. (m^2/g)	Stoichiometric Ratio
1	17,521	27.02	ND
2	10,462	39.83	$Al_1F_{0.61}O_{1.20}$
3	49,311	5.00	$Al_1F_{0.45}O_{1.28}$
4	10,291	6.26	ND
5	3663	50.20	ND
6	41,625	6.39	$Al_1F_{0.51}O_{1.25}$
7	28,906	26.22	$Al_1F_{0.75}O_{1.13}$
8	33,073	32.17	$Al_1F_{0.72}O_{1.14}$
9	36,970	11.85	$Al_1F_{2.0}O_{0.5}$
10	46,386	11.90	$Al_1F_{1.51}O_{0.75}$
11	29,815	12.56	$Al_1F_{2.22}O_{0.39}$
12	25,697	ND	$Al_1F_{2.31}O_{0.34}$
SNL-NCP	76,658	310.88	
CaF_2	29,585	0.19	

Structure & sorption capabilities of nanoporous fluorite materials





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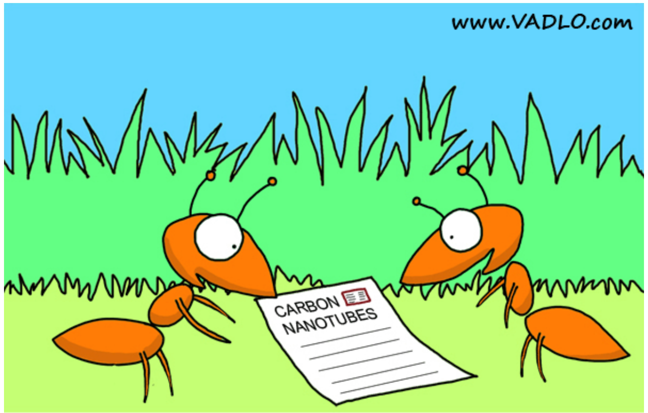
What's next?

- Continue to improve the performance of fluorite materials by increasing specific surface areas.
- Gain a better understanding of fluorite-water interface chemistry.
- Expand the work to other applications.



"Finally, we can drink Coke with a straw."

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Acknowledgments

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