

# Intercalation and Ion Exchange Properties of Hydrotalcite $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2\text{A}_x \cdot n\text{H}_2\text{O}$ Derivatives (A = $\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{Br}^-$ , and $\text{I}^-$ )

---

**Ranko P. Bontchev, Shirley Liu, James L. Krumhansl,  
James Voigt and Tina M. Nenoff**

**Sandia National Laboratories,  
P.O. BOX 5800, Albuquerque, NM 87185-0755**



Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,  
for the United States Department of Energy under contract DE-AC04-94AL85000.





# Introduction

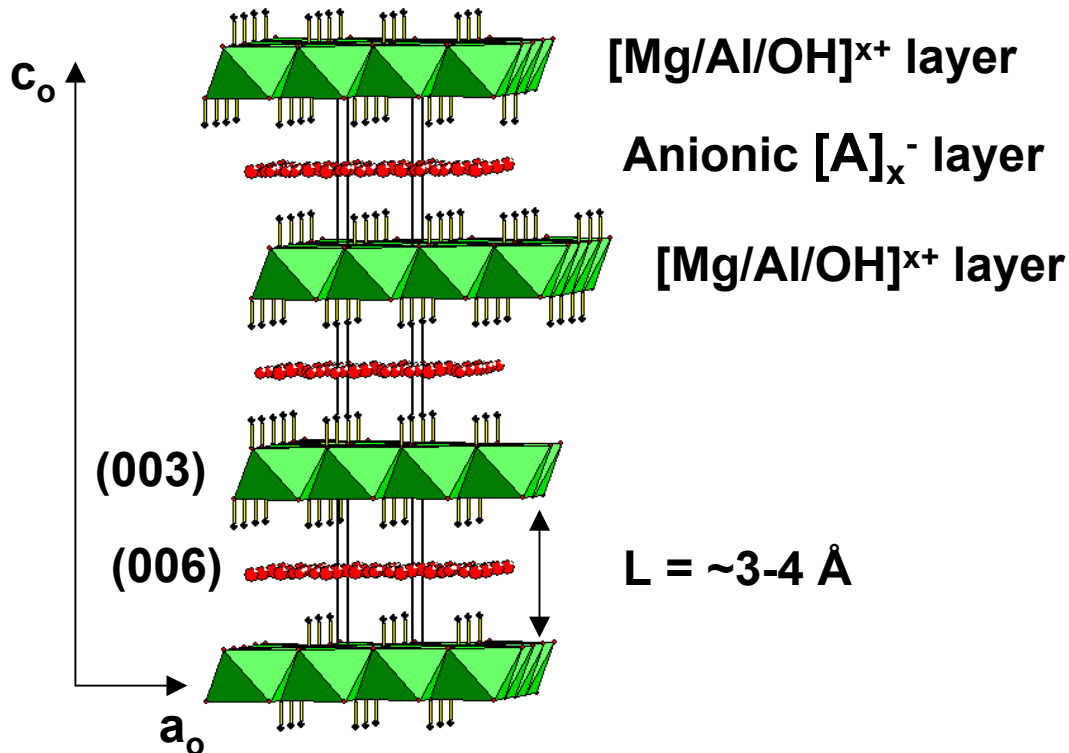
---

- **Current Research:** Precipitation of inert phases able to incorporate or exchange large amounts of anions
- **Target materials:** Anion “getters” ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , ...)
- **Most promising candidates:** Hydrotalcites (HTCs)

**Goal of this study: To evaluate the ability and selectivity of HTCs to incorporate a series of monovalent anions under different synthetic and ion-exchange conditions**

# Background

- HTC – double layered hydroxides with general formula  $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2\text{A}_x \cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  ...)
- Stacking of  $[\text{Mg}(\text{II})_{1-x}\text{Al}(\text{III})_x(\text{OH})_2]^{x+}$  and  $[\text{A}]_x^-$  layers
- Hexagonal (trigonal, R-3m) cell with  $a_0 \approx 3.05 \text{ \AA}$  and  $c_0 \approx 22\text{-}25 \text{ \AA}$



# Synthesis

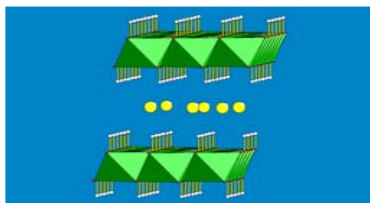
of pure and mixed AA'-HTCs:  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{A})_x(\text{A}')_{2-x}\cdot 4\text{H}_2\text{O}$   
(A, A' =  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ )

## I. One-pot synthesis:

1.  $\text{MgA}_2 + \text{AlA}_3 + \text{H}_2\text{O}$
2. Precipitation with  $\text{NH}_4\text{OH}$  (pH = 8.5)



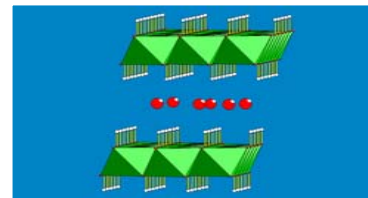
3. 12-24h @ 120°C ,  
Parr-reactor



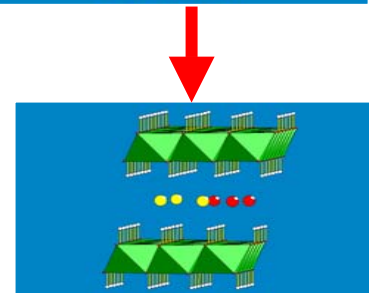
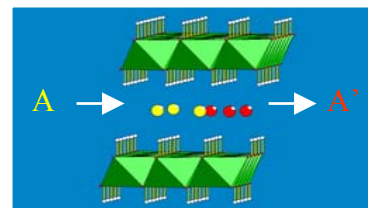
Crystalline A-HTC

## II. Direct ion exchange

1. Pre-synthesized A'-HTC



2. A'/A exchange in NaA sln.

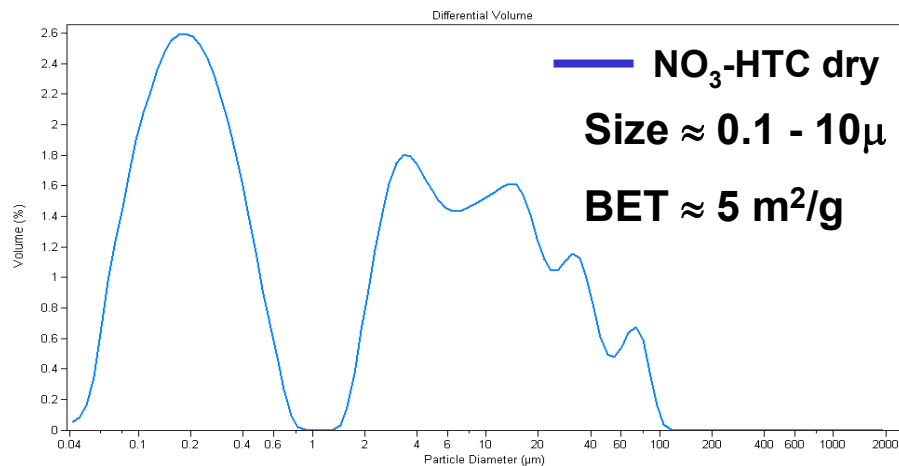
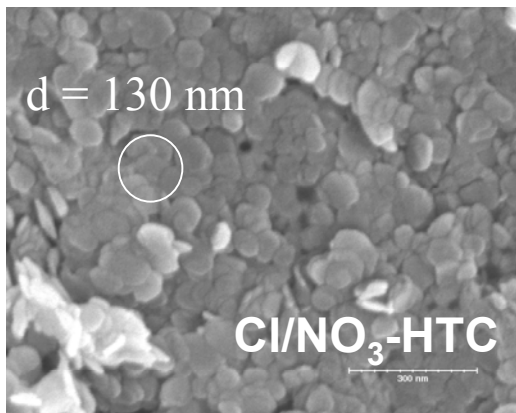
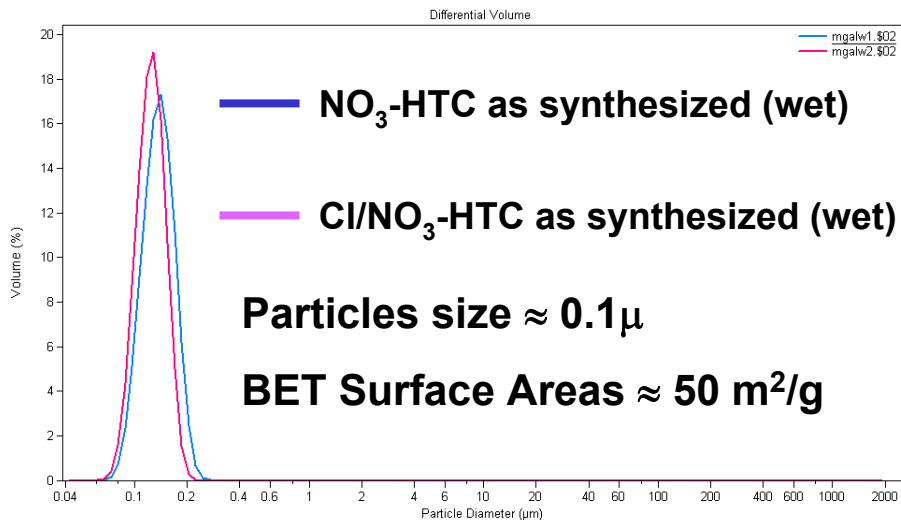
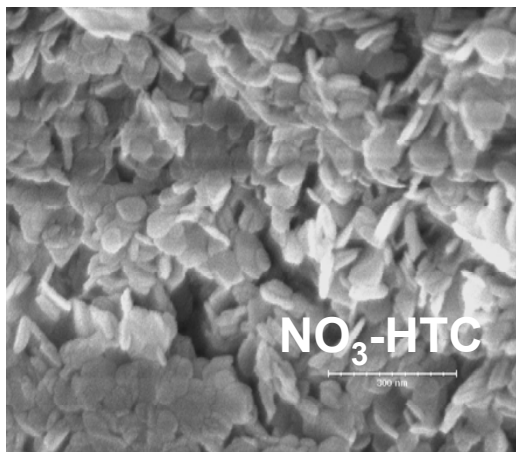


Crystalline AA'-HTC

Characterization: XRD, SEM, BET, DMLS, IC, FTIR

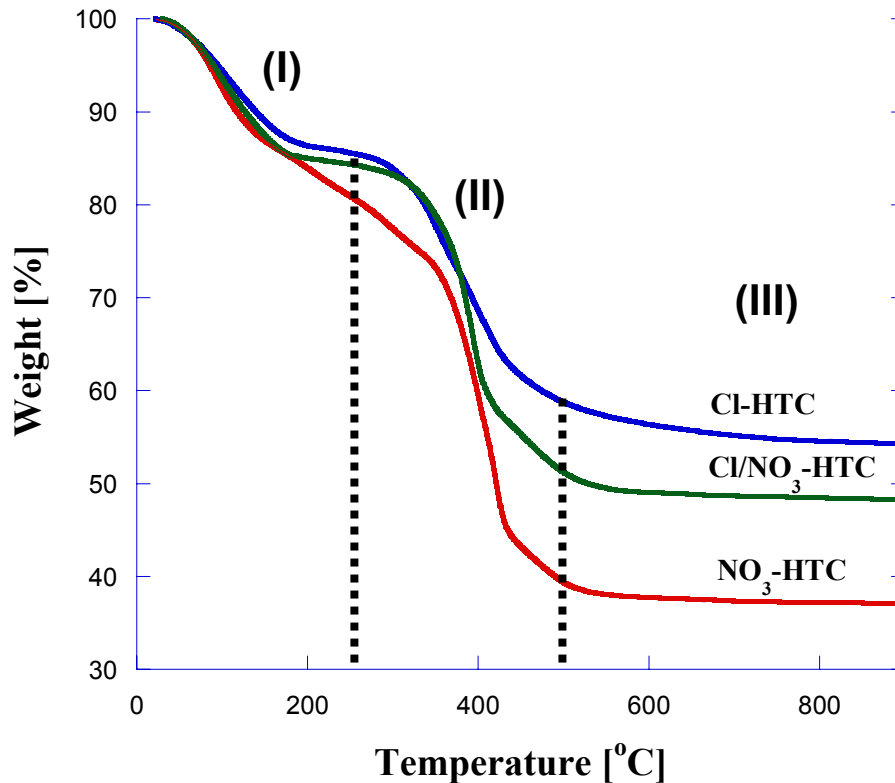
# Results

## Morphology, particles size and surface area of HTCs



# Results

## TGA / XRD of HTC



TGA:  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$

(I)  $25 < T < 250^\circ\text{C}$

$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{Cl}_2 \cdot 5\text{H}_2\text{O} - 5\text{H}_2\text{O}$   
(Calc. Wt. Loss = 14.20 %)

(II)  $250 < T < 500^\circ\text{C}$

[(I)] –  $[2\text{HCl} - 7\text{H}_2\text{O}]$

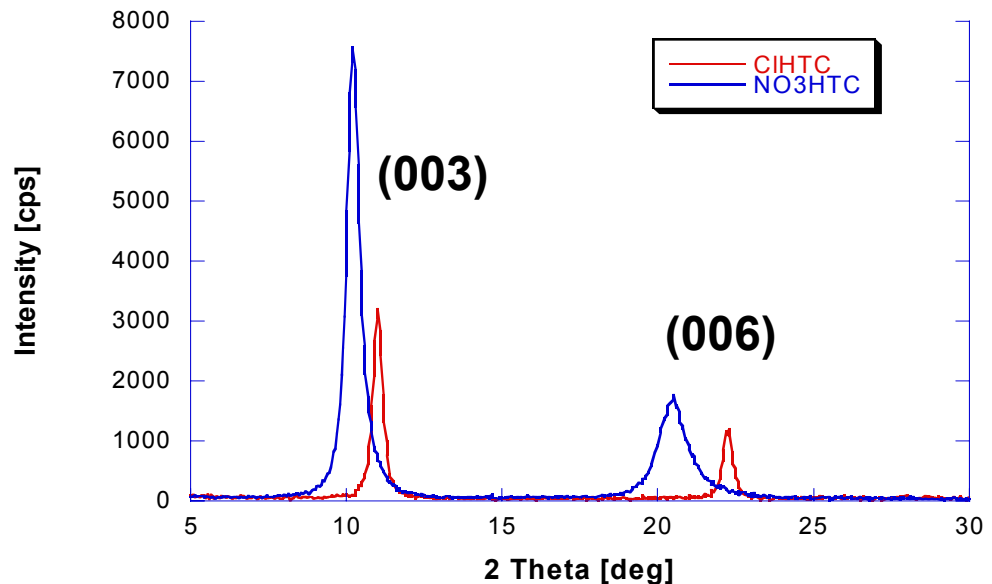
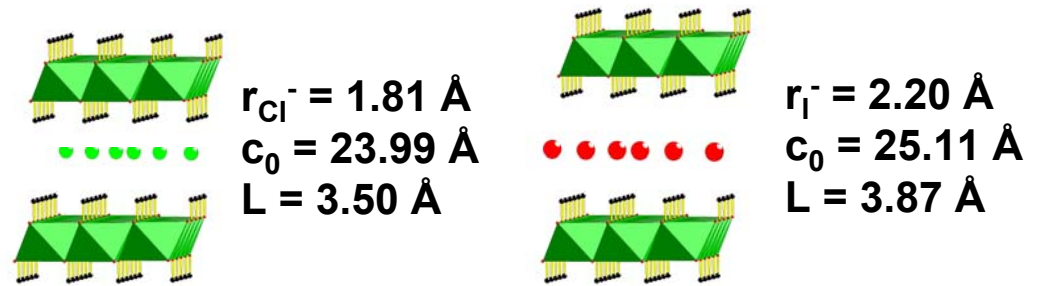
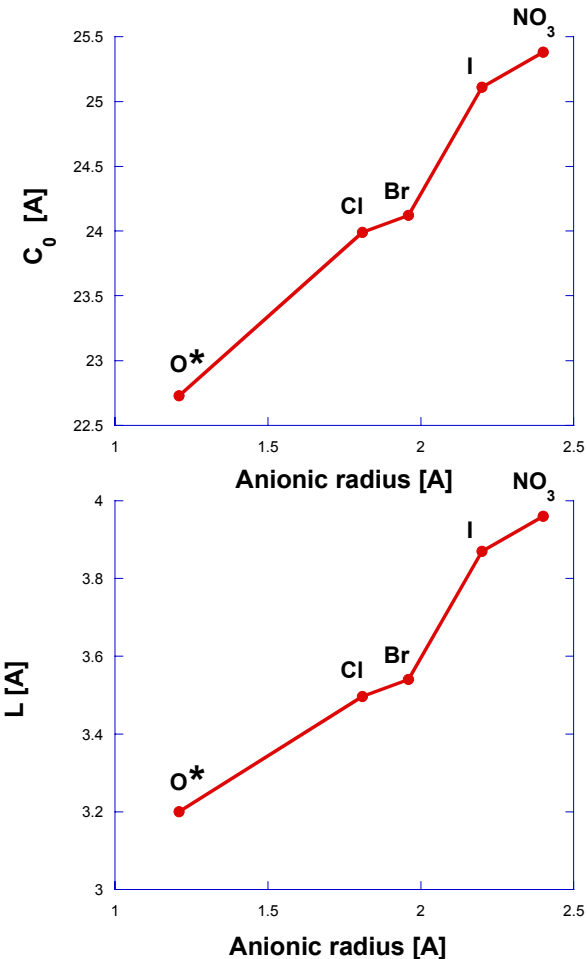
(Total Calc. Wt. Loss = 45.66 %)

XRD: (I) crystalline  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{A}_2 \cdot n\text{H}_2\text{O}$   
(II) amorphous  $\text{Mg}_6 / \text{Al}_2 / (\text{OH})_{18}$   
(III) crystalline  $\text{MgO} + \text{Al}_2\text{O}_3$

All HTCs preserve their crystal (layered) structure up to about 250-300°C

# Results

XRD:  $c_0$  and  $L$  as a function of the anionic radii ( $r_i$ ) of  $A^-$

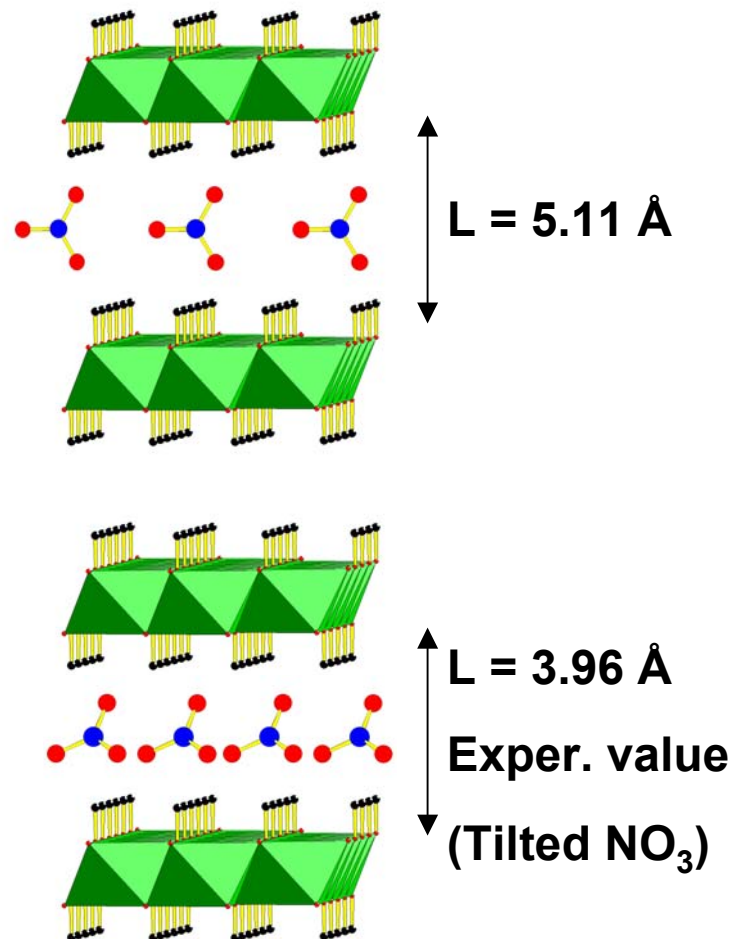
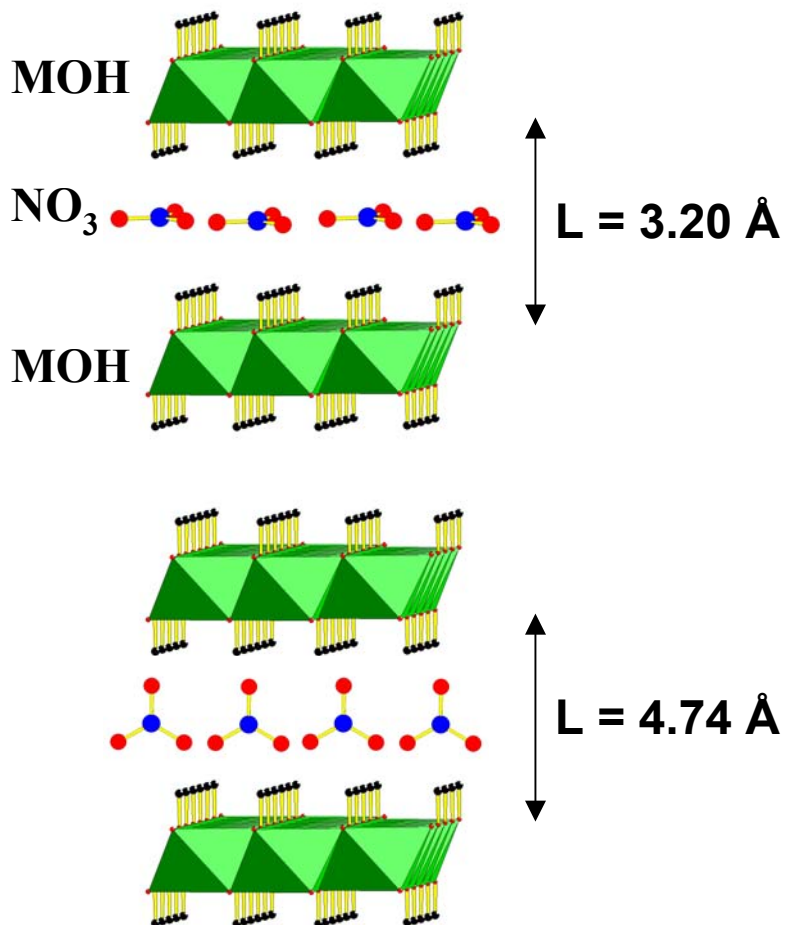


The bigger the ionic radius of  $A^-$ , the bigger  $L$  and  $c_0$

\* Determined from CO<sub>3</sub>-HTC (CO<sub>3</sub> in “flat configuration”)

# Results

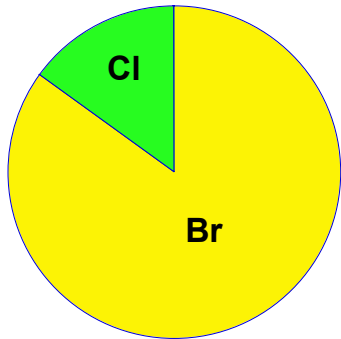
Possible orientations of the  $(\text{NO}_3)^-$  anions and resulting interlayer MOH - MOH distances [L] in  $\text{NO}_3$ -HTC



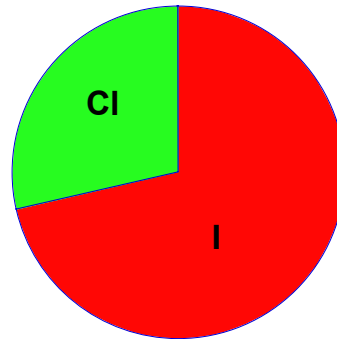


# Results

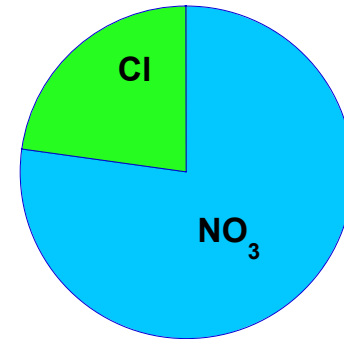
## Ion Exchange at Room Temperature: Cl-HTC + 1.0M NaA Solutions ( $A^- = Br^-, I^-, NO_3^-$ )



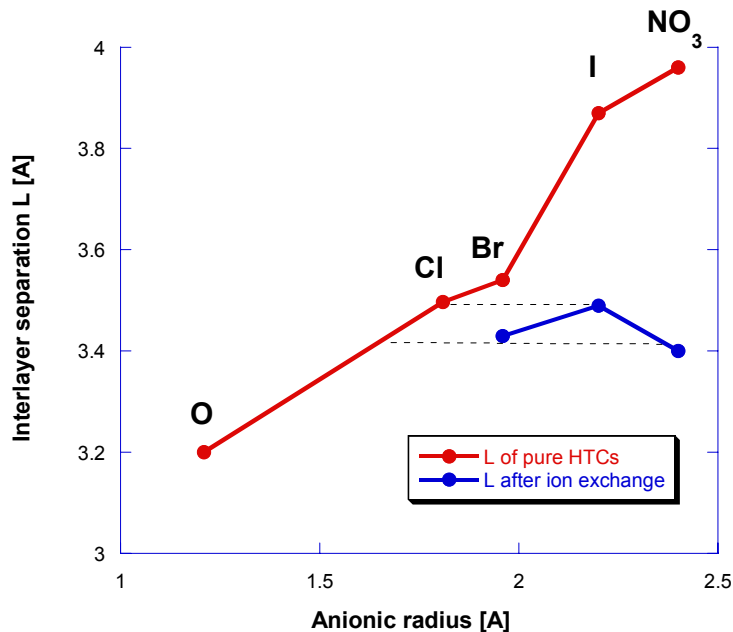
Br : Cl = 5.62 : 1



I : Cl = 2.50 : 1



NO<sub>3</sub> : Cl = 3.40 : 1

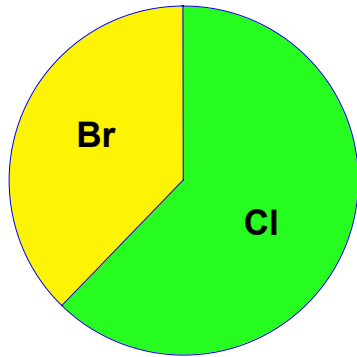


Cl-HTC shows highest selectivity for Br<sup>-</sup>

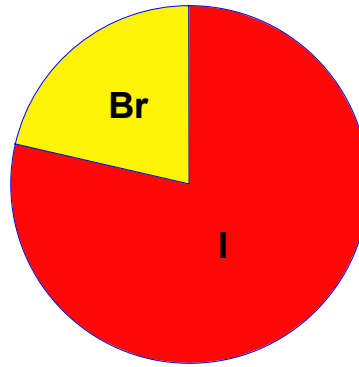
In all cases the interlayer spacing L is determined by Cl<sup>-</sup>

# Results

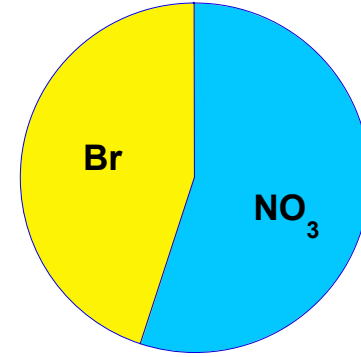
## Ion Exchange at Room Temperature: Br-HTC + 1.0M NaA Solutions ( $A^- = Cl^-, I^-, NO_3^-$ )



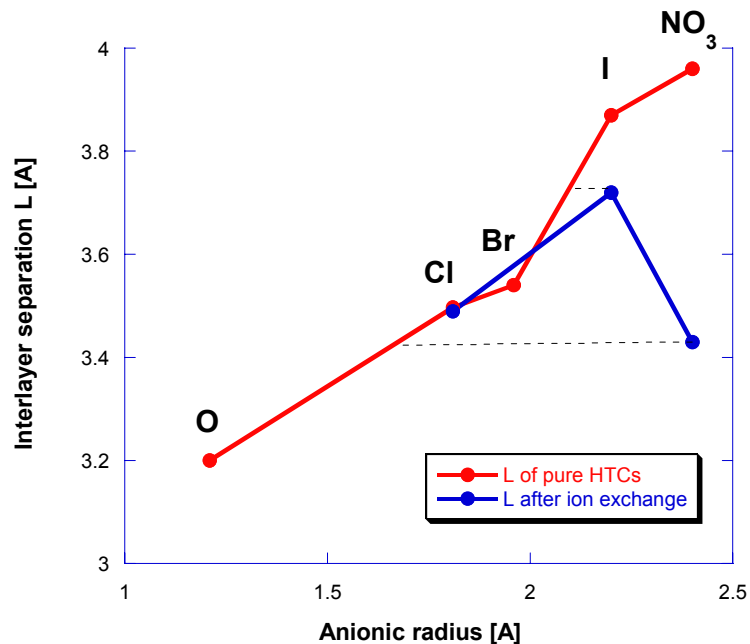
Cl : Br = 1.64 : 1



I : Br = 3.69 : 1



NO<sub>3</sub> : Br = 1.22 : 1



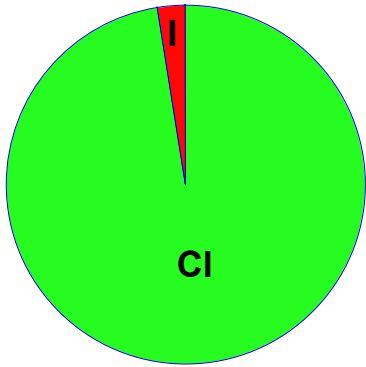
Br-HTC shows highest selectivity for  $I^-$

$Cl^-$  and  $NO_3^-$  determine the interlayer spacing  $L$  in  $Cl^-/Br-HTC$  and  $NO_3^-/Br-HTC$

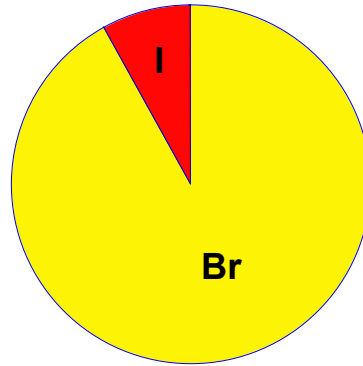
Both  $Br^-$  and  $I^-$  determine  $L$  in  $I^-/Br-HTC$

# Results

## Ion Exchange at Room Temperature: I-HTC + 1.0M NaA Solutions ( $A^- = Cl^-, Br^-, NO_3^-$ )



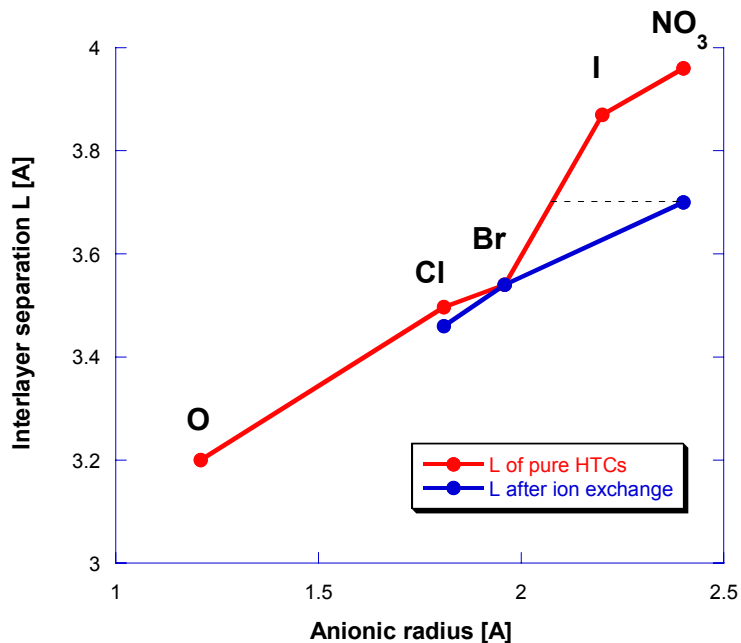
Cl : I = 40.00 : 1



Br : I = 11.30 : 1



NO<sub>3</sub> : I = 4.42 : 1



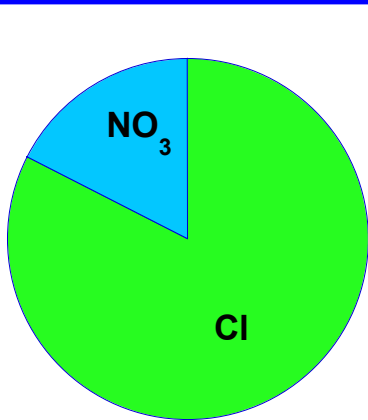
I-HTC shows highest selectivity for Cl<sup>-</sup>

Cl<sup>-</sup> and Br<sup>-</sup> determine the interlayer spacing  $L$  in Cl/I-HTC and Br/I-HTC

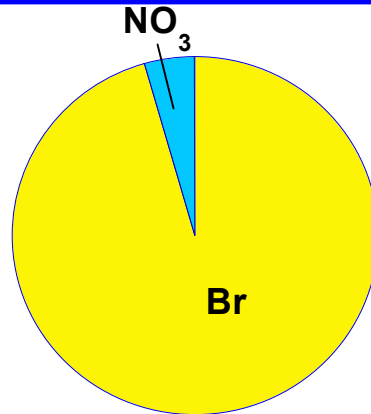
NO<sub>3</sub><sup>-</sup> determines  $L$  in NO<sub>3</sub>/I-HTC

# Results

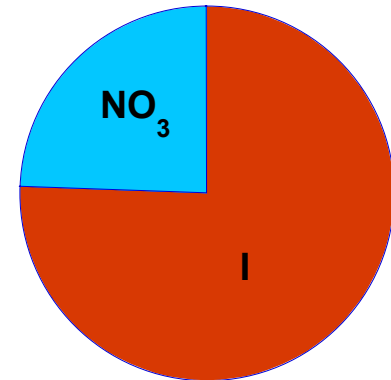
## Ion Exchange at Room Temperature: NO<sub>3</sub>-HTC + 1.0M NaA Solutions (A<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>)



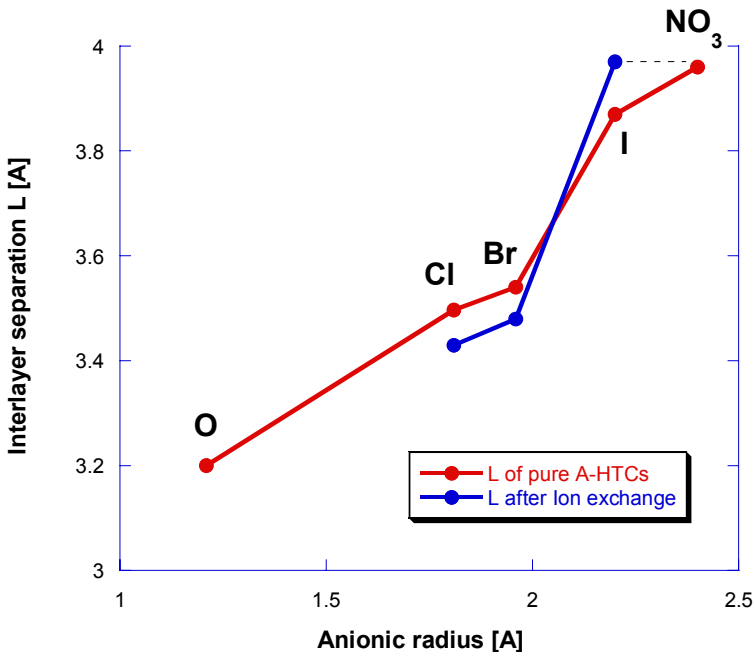
Cl : NO<sub>3</sub> = 4.75 : 1



Br : NO<sub>3</sub> = 21.40 : 1



I : NO<sub>3</sub> = 3.09 : 1



NO<sub>3</sub>-HTC shows highest selectivity for Br<sup>-</sup>

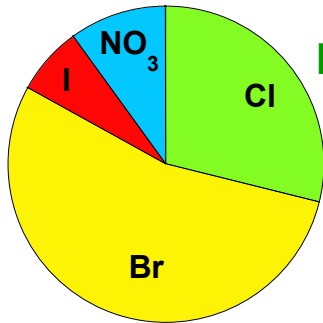
Cl<sup>-</sup> and Br<sup>-</sup> determine the interlayer spacing L in Cl/NO<sub>3</sub>-HTC and Br/NO<sub>3</sub>-HTC

NO<sub>3</sub><sup>-</sup> (“tilted”) determines L in I/NO<sub>3</sub>-HTC

# Results

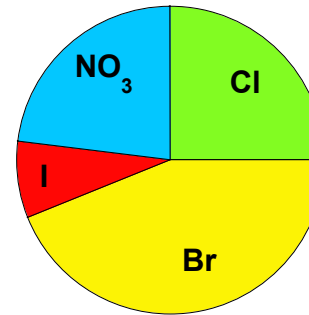
## Ion exchange of A-HTCs with 1 M NaA' solutions @ room temp.

Cl-HTC in NaBr/NaI/NaNO<sub>3</sub> sln



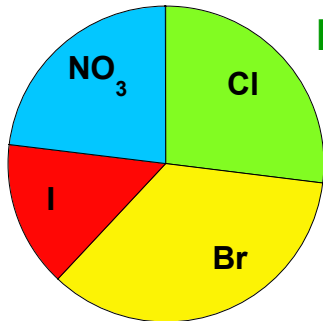
Final % Cl = 29  
Br = 54  
I = 7  
NO<sub>3</sub> = 10

I-HTC in NaBr/NaCl/NaNO<sub>3</sub> sln



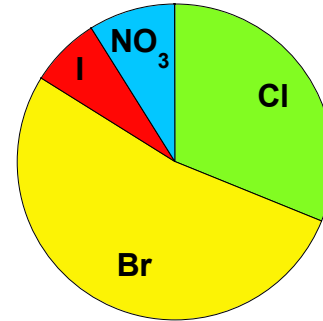
Final % Cl = 25  
Br = 44  
I = 8  
NO<sub>3</sub> = 23

Br-HTC in NaCl/NaI/NaNO<sub>3</sub> sln



Final % Cl = 27  
Br = 35  
I = 15  
NO<sub>3</sub> = 23

NO<sub>3</sub>-HTC in NaCl/NaI/NaBr sln



Final % Cl = 31  
Br = 53  
I = 7  
NO<sub>3</sub> = 9

All A-HTCs show highest selectivity for Br<sup>-</sup>

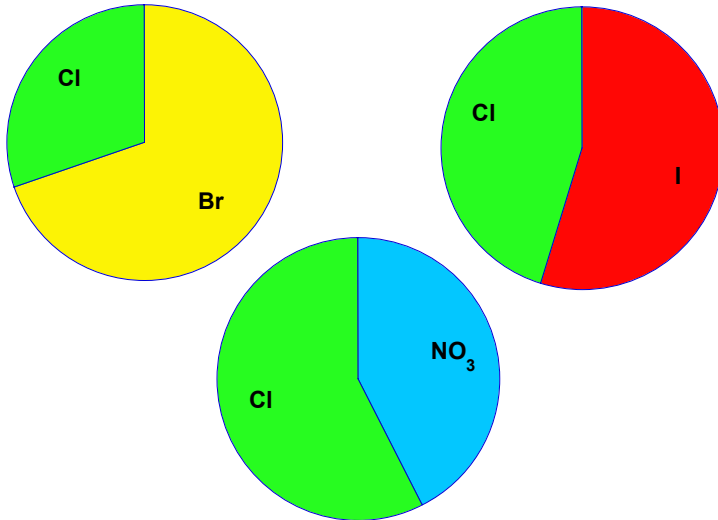
In all cases, the order of ion exchange preference is Br<sup>-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup>

Cl<sup>-</sup> determines the interlayer spacing L in all cases

# Results

One-pot synthesis of A'/Cl-HTCs ( $A' = Br^-, I^-, NO_3^-$ )  
( $MgA_2 + AlA_3$ ) +  $NaA' + H_2O$

Starting  $A' : Cl = 1 : 1$

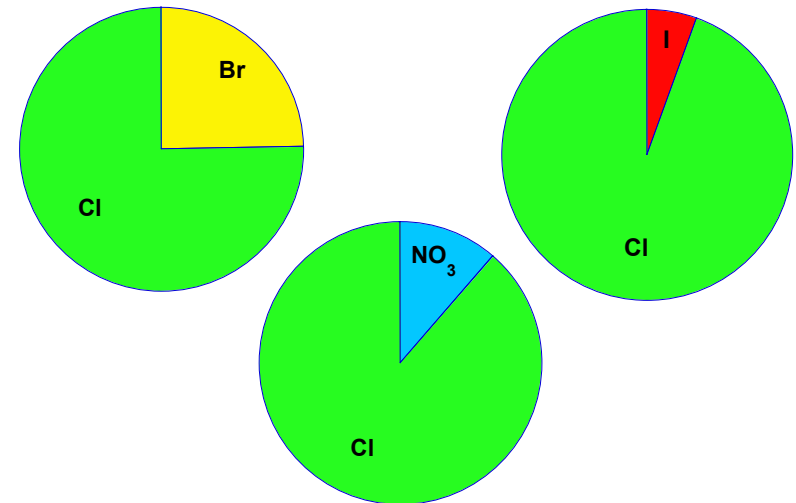


Final  $Br : Cl = 2.29 : 1$

$I : Cl = 1.21 : 1$

$NO_3 : Cl = 0.74 : 1$

Starting  $A' : Cl = 1 : 3$



Final  $Br : Cl = 0.33 : 1$

$I : Cl = 0.06 : 1$

$NO_3 : Cl = 0.13 : 1$

The higher the starting ( $A' : Cl$ ) ratio, the higher the incorporation of  $A'$  in the final  $A'/Cl$ -HTC

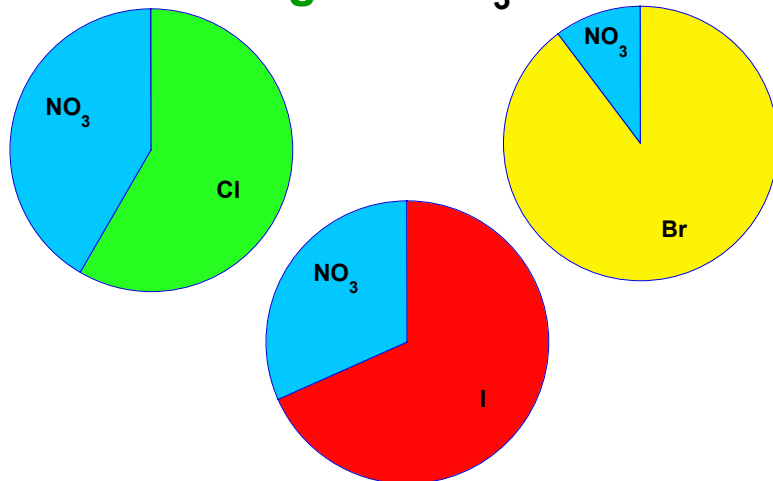
$A'/Cl$ -HTCs show highest selectivity for  $Br^-$  in all starting ( $A' : Cl$ ) ratios

$Cl^-$  determines the interlayer spacing  $L$  in all cases

# Results

## One-pot synthesis of A/NO<sub>3</sub>-HTCs (A<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>)

Starting A : NO<sub>3</sub> = 1 : 1

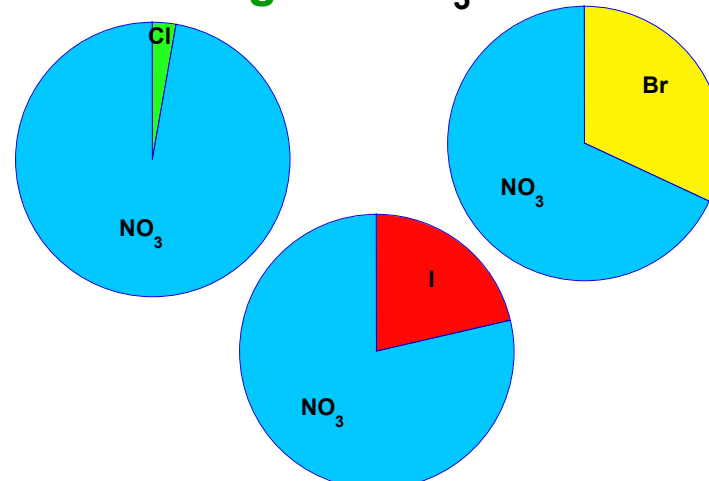


Final Cl : NO<sub>3</sub> = 1.40 : 1

Br : NO<sub>3</sub> = 8.86 : 1

I : NO<sub>3</sub> = 2.17 : 1

Starting A : NO<sub>3</sub> = 1 : 3



Final Cl : NO<sub>3</sub> = 0.03 : 1

Br : NO<sub>3</sub> = 0.47 : 1

I : NO<sub>3</sub> = 0.27 : 1

The higher the starting (A : NO<sub>3</sub>) ratio, the higher the incorporation of A in the final A/NO<sub>3</sub>-HTC

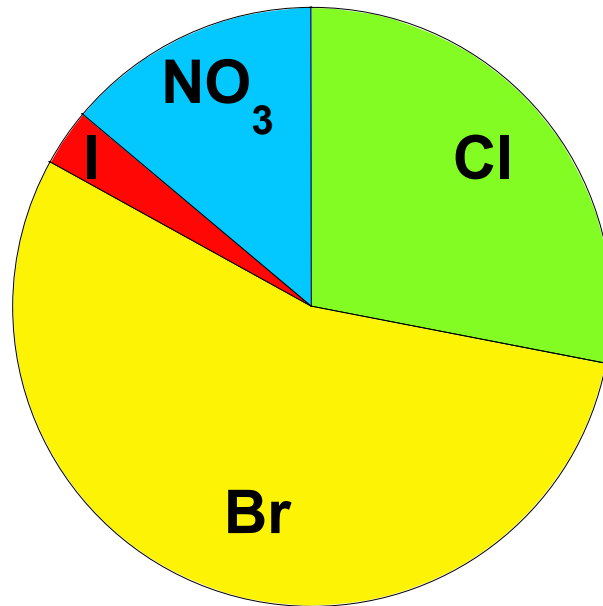
A/NO<sub>3</sub>-HTCs show highest selectivity for Br<sup>-</sup> in all starting (A : NO<sub>3</sub>) ratios

Cl, Br and I determine the interlayer spacing L when A : NO<sub>3</sub> = 1:1

NO<sub>3</sub> (“tilted”) determines the interlayer spacing L when A : NO<sub>3</sub> = 1:3

# Results

One-pot synthesis of HTC with **starting ratio**  $\text{Cl}:\text{Br}:\text{I}:\text{NO}_3 = 1:1:1:1$



**Final %** Cl = 28  
Br = 55  
I = 3  
NO<sub>3</sub> = 14

The as-synthesized HTC shows highest incorporation of Br<sup>-</sup>  
The order of ion incorporation preference is Br<sup>-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup>  
Cl<sup>-</sup> determines the interlayer spacing L





# Conclusions

---

All synthetic methods (one-pot synthesis, ion exchange) lead to mixed AA'-HTCs with virtually the same A : A' ratios

The final A:A' ratio in one-pot synthesized AA'-HTCs is proportional to and could be controlled by the starting A:A' ratio

There is no simple and straightforward correlation between the size of the incorporated A/A' anions and the interlayer spacing L

All A-HTCs show highest selectivity for Br<sup>-</sup>

In all mixed HTCs the order of anion incorporation preference is  
 $\text{Br}^- > \text{Cl}^- > \text{NO}_3^- > \text{I}^-$



# Acknowledgments

---

**Thanks to Diana Sipola for the particles size distribution, surface area determination and SEM images**

**Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000**

