IO_3^- and I^- Sorption from Groundwater by Layered Double Hydroxides

Abbey Rickelmann[1], Emily Campbell[2], Natasha Pence[2], Tatiana Levitskaia[2], Sayandev Chatterjee[2], Frances Smith[2]
[1]California Polytechnic State University-San Luis Obispo [2]Pacific Northwest National Laboratory, Richland, Washington 99352

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Background

Several subsurface water plumes are found at the Hanford U.S. DOE site. These plumes contain many different types of hazardous components, including radioactive iodate (IO_3^-) and iodide (I^-), which pose environmental and health concerns. Inorganic layered double hydroxide (LDH) compounds remove IO_3^- and I^- through selective uptake. IO_3^- and I^- are mobile ions and the LDH compounds immobilize these ions. LDHs are mixed transition metal hydroxides that contain positively charged layers that undergo anion exchange.

Layered Double Hydroxide Synthesis

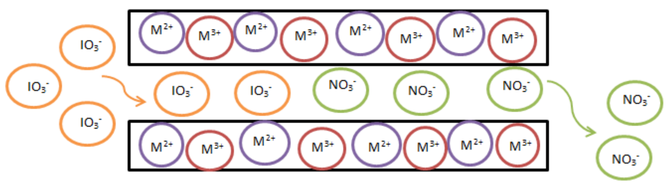
$$M^{2+} + M^{3+} + 2OH^- + 3NO_3^- \rightarrow \left[M^{2+}M^{3+}(OH)_2\right](NO_3^-)_3 \bullet mH_2O$$

M^{2+}= Ni^{2+}, Co^{2+}, Sn^{2+}, Cu^{2+}, Zn^{2+}
M^{3+}= Al^{3+}, Cr^{3+}, Fe^{3+}

- Mixed transition metal salts in 50 mL of water
- NaOH was added until the solutions were at the desired pH
- Solutions were heated at 110 °C for 3 days
- Solutions were filtered and washed with water, then left to air dry
- After drying, solids were ground into a fine powder, washed again with water, and left to air dry
- The solids were weighed and put into labeled vials

Photograph of synthesized LDH compounds

Scheme for IO_3^- Uptake

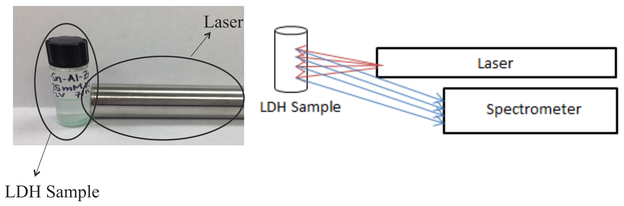


- When introduced to a solution containing IO_3^-, the NO_3^- in the LDH compounds is replaced by IO_3^- ions

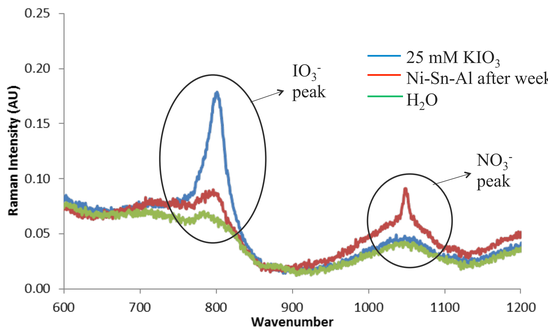
Raman Spectroscopy

- 150 mW 670 nm laser was used to monitor the uptake of IO_3^- by the LDHs

Raman Spectroscopy Schematic



Analysis of LDH by Raman Spectroscopy



Raman spectrum for Ni-Sn-Al LDH in contact with IO_3^- solution. The replacement of NO_3^- with IO_3^- is apparent from the decrease in intensity of the IO_3^- band and the increase in intensity of the NO_3^- band.

- The following equation was applied to calculate the IO_3^- uptake

$$\%\ IO_3^- = 1 - \left(\frac{\text{Final } IO_3^- \text{ Intensity}}{\text{Initial } IO_3^- \text{ Intensity}}\right) \times 100$$

$\%\ IO_3^-$ sorption by select LDH compounds

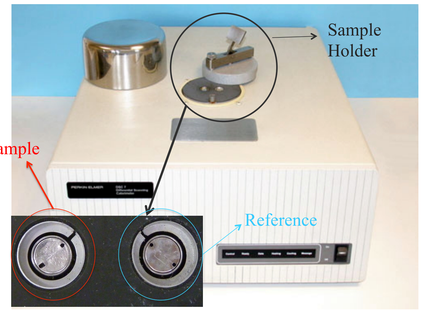
LDH Compound	Initial Intensity	Final Intensity	% Sorption
Ni-Sn-Al	0.093	0.016	82
Ni-Sn-Al-Mn	0.115	0.075	35
Zn-Al-Mn	0.112	0.097	14
Mn-Cr	0.107	0.072	33
Co-Cr	0.115	0.016	86

Differential Scanning Calorimetry

Thermodynamic properties of the LDH compounds were determined by using differential scanning calorimetry (DSC)

Procedure:
- Samples were placed in sealed aluminum pans
- Heated from 30 °C to 450 °C at 5 °C/min then cooled to 100 °C at 5 °C/min
- Stability of the LDH compounds as a function of temperature were obtained

Instrumentation



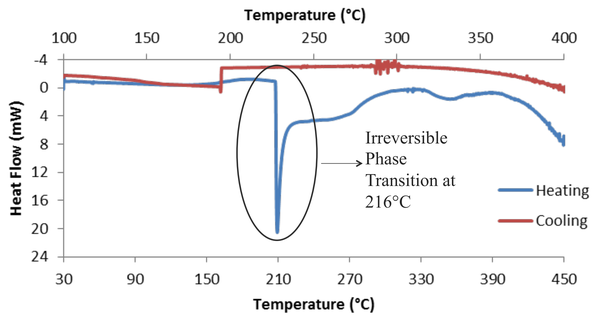
Calibration

- Four metals with known melting points (T) and enthalpy of fusion (ΔH) were used to calibrate the DSC

Metal	$T_{melting}$ (°C)	ΔH_{fusion} (J/g)
Indium	156.6	28.5
Tin	231.9	60.2
Lead	327.5	23.0
Zinc	419.5	108.1

DSC Results

DSC Thermogram of Ni-Al-Zr LDH



DSC Analysis ofResults

LDH Compound	$T_{Transition}$ (°C)	$\Delta H_{Transition}$ (J/g)	% Mass Loss
CaHyapp-Sn	212	287	7.8
Co-Cr	194	224	22.2
Ni-Al	219	77	29.1
Ni-Al-Zr	216	157	27.7
Ni-Cr	185	326	34.8
Ni-Sn-Al	195	154	21.6
Ni-Sn-Al-Zr	203	269	19.6

Discussion

- Raman spectroscopy was used to determine relative IO_3^- uptake
- DSC analysis indicated that each LDH was found to lose bound water between 180-220°C

Future Work

Further experiments will be performed to determine IO_3^- and I^- sorption of LDH compounds in groundwater. Similar technology can then be applied to radioactive waste where interferences from other compounds are present.

Acknowledgements

- STAR Program Directors
- This work was supported by Washington River Protection Solutions (WRPS) and conducted at the Pacific Northwest national Laboratory operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.
- Radiochemical Science Group

This material is based upon work supported by the S.D. Bechtel, Jr. Foundation, National Marine Sanctuary Foundation, Carnegie Corporation of New York, and/or National Science Foundation under Grant Nos. 0952013 and 0833353. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the funders.

The STAR program is administered by the Cal Poly Center for Excellence in Science and Mathematics Education (CESaME) on behalf of the California State University.

PNNL-SA-97503

www.pnnl.gov

File Name // File Date // PNNL-SA-#####