DESIGN AND SYNTHESIS OF NEW MATERIALS FOR HEAVY ELEMENT WASTE REMEDIATION

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Abstract

The design and synthesis of materials for the extraction of heavy element ions from aqueous waste streams has involved the synthesis of extractants, the extraction of target ions and the recovery of those waste contaminants by an efficient cycle that minimizes secondary waste volumes and provides efficient decontamination of the primary waste stream. The feasibility of using lithium-intercalated transition metal dichalcogenides, Li_xMS_2 as recyclable ion-exchange materials for the extraction of heavy metal ions Hg(II), Pb(II), Cd(II), Zn(II), Au(III), Ag(I), and Cu(I) was investigated ($0.25 \leq x \leq 1.9$, M = Mo, W) in acidic, nitrate-rich tank-waste simulants. The materials Li_xMoS_2 and Li_xWS_2 removed significant amounts of the heavy metal ions in question, down to ~ 5ppt. The selectivity of Li_xMoS_2 for heavy-metal ions was Hg(II) > Pb(II) > Cd(II) > Zn(II). Heating Ag_y and Hg_yMoS_2 solids under vacuum at 425 °C initiated an entropy-driven internal redox reduction that resulted in the deactivation of the extractant, producing essentially metal-free MoS_2 and elemental Ag or Hg. Samples of Li_xMoS_2 were used for three complete activation/ extraction/deactivation cycles with no loss in ion-exchange ability. The maximum measured capacity of the extractants for mercury is 580 mg Hg/g extractant. Other, newly developed ion-exchange materials have been developed and are being studied.

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Project Overview

» DOE Areas of Need - Hg, Pb, Cd
- Heavy metal waste streams
- Current heavy metal remediation research
- INEEL, Oak Ridge

» Extraction strategy
- Redox-recyclable extraction and recovery (R^2ER)
- Intercalated transition metal chalcogenides
- New materials development
  - Metal $[PSO_3]^{3-}$
  - $NaCuMnSn_3S_8$ electroactive spinels

» Results
- Extraction data
- Recyclability studies
- Extraction mechanism
- Competition reactions

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The Design Concept

Waste Remediation

- Acidic waste streams (pH ≤ 1.0)
- Heavy element contamination
- Competing with other metals
  - Alkaline
  - Alkaline earths
  - Early transition metals

Design of Materials

- Redox active / robust
- Selective for “soft metal” cations
  - Hg, Pb, Cd
  - Au, Ag, Tl
- Stable in low pH media
- Easily regenerated

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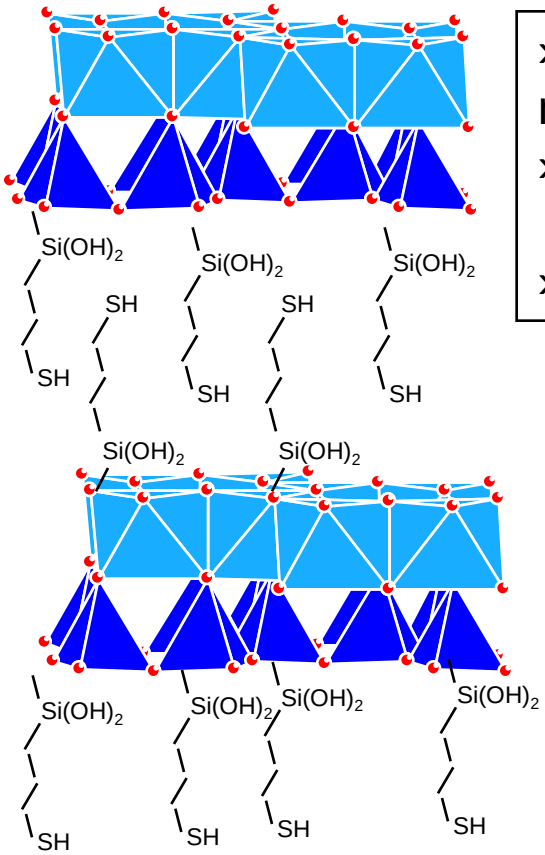
Rationale

Layered metal sulfides had been chosen for initial studies because they displayed the following characteristics:

- MS_2 solids were known to reversibly intercalate metal guest ions;
- MS_2 solids can be partially reduced, thereby providing a driving force for the intercalation of charge compensating metal ions;
- the chalcogenides are soft donor atoms so the selectivity of chalcogenide-based materials for soft charge-compensating metal ions such as the target pollutants (Hg^{2+}, Pb^{2+}, etc..) would be high;
- deactivation and regeneration of the guest-host material back to the activated host material would provide for recovery of the pollutant metal ions, the reuse of the solid extractant, and a minimum waste volume.

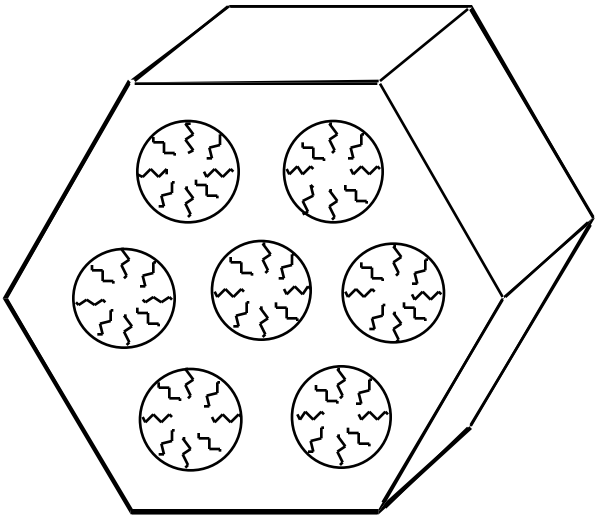
Current Heavy Metal Extractants:



»Functionalized kaolinite or montomorillonite: Thiomont†
»Capacity: 65 mg Hg/g material
70 mg Pb/g material
»Material can be reused

Kaolinite

»Functionalized mesoporous silica††
»Capacity: 600mg Hg/g
»Recyclable
»Capacity decreases 40% after first use



〰〰 = $Si(OH)_2(CH_2)_3SH$

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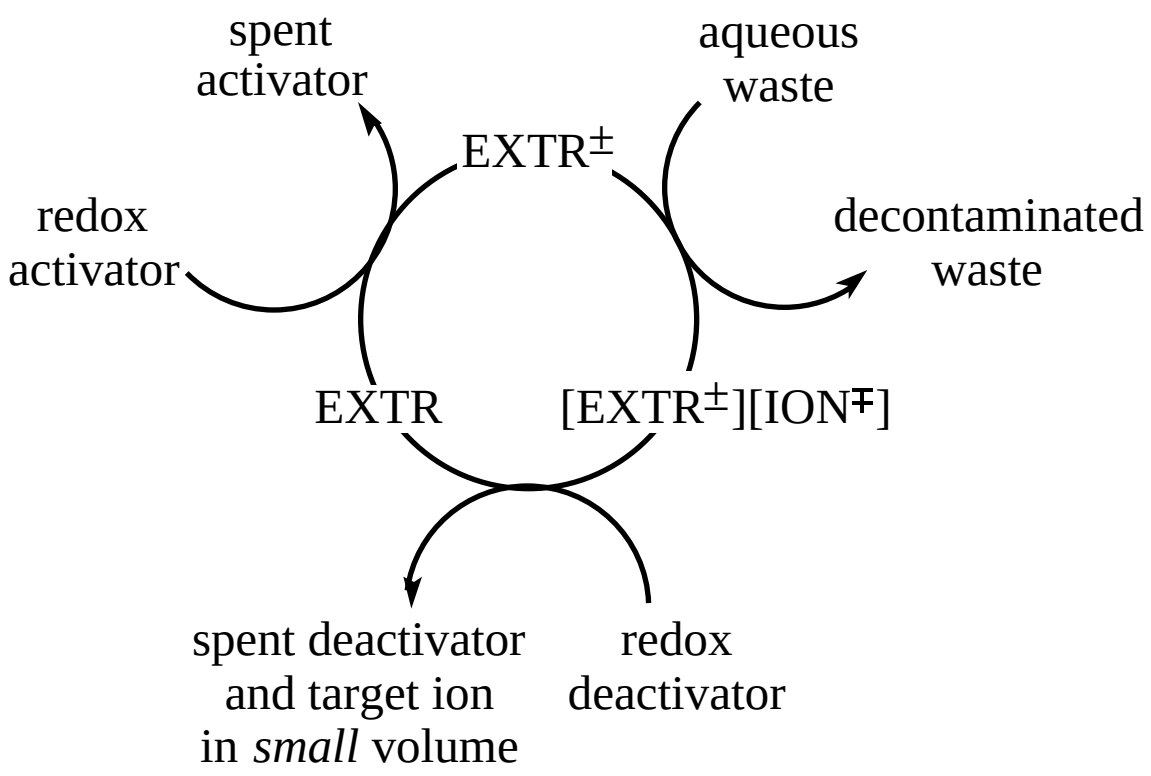
†Detellier *et al*. *Environ. Sci. Technol.* **1995**, *29*, 131.
††Feng *et al*. *Science* **1997**, *276*, 923.

Our Strategy for Redox-Recyclable Extraction and Recovery (R^2ER)



Requirements of Extractant:

» Effective - high K_d values
» Selective - competition
» Recovery of target species
» Recyclable
» Stable
» Non-Toxic
» Minimal waste volume

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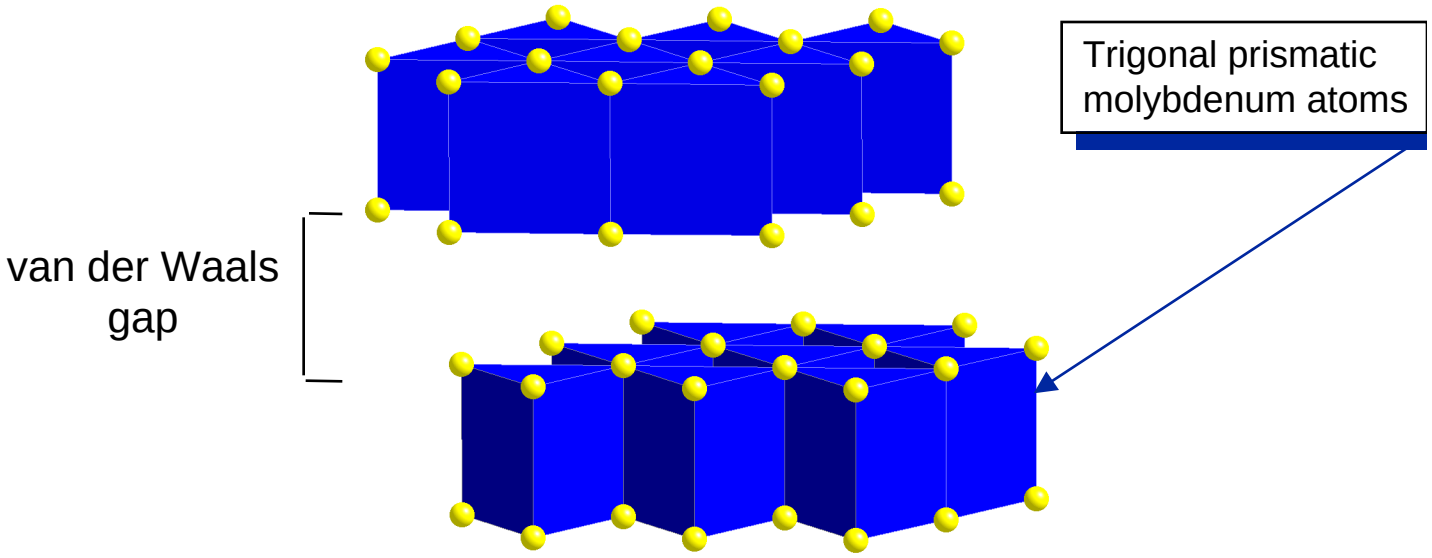
The First Material of Choice: Hexagonal (2H) MoS_2



- Many different species can be intercalated into the van der Waals gap of layered transition metal chalcogenides.

Reductive Intercalation Reaction:

$$\underset{\text{2H phase}}{MoS_2(s)} + 5\ BuLi(org) \xrightarrow[25\ \ C]{48\ hr.} \underset{\text{1T phase}}{Li_{1.3}MoS_2(s)} + 0.65\ C_8H_{18}(g)$$

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Intercalation Chemistry of Early Transition Metal Dichalcogenides

IVB	VB	VIB
Ti	V	Cr
Zr	Nb	**Mo**
Hf	**Ta**	**W**

» 2 D-layered structures

» MS_2 are redox-active

»Chalcogens are “soft” donors

» TiS_2 and TaS_2 decompose in H_2O

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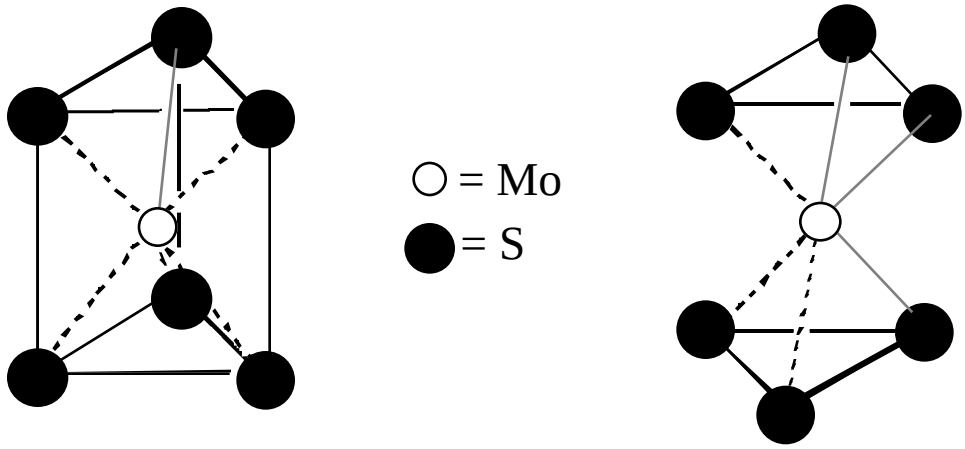
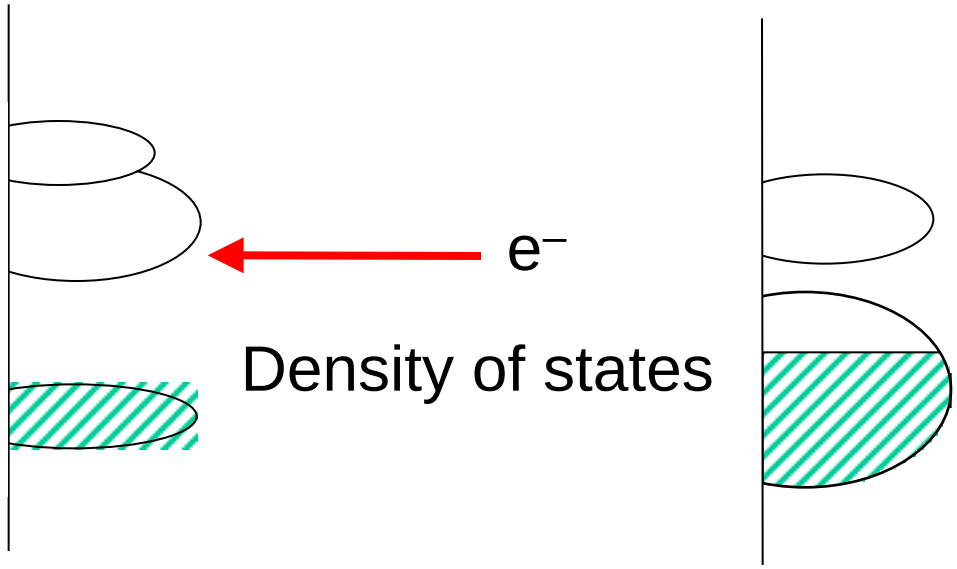
Two Polymorphs of MoS_2 Driven by Electronic Stability



2H-Phase
T.P. coor. (d^2)

1T-Phase
Octahedral coord. ($d^{(2+x)}$)



Reduction of MoS_2 will result in high lying electrons unless the structure distorts to an octahedral coordination. The guest must stabilize this or it will not be accepted into the structure.

Py, M. A.; Haering, R. R. *Can. J. Phys.*, **1983**, *61*, 76.

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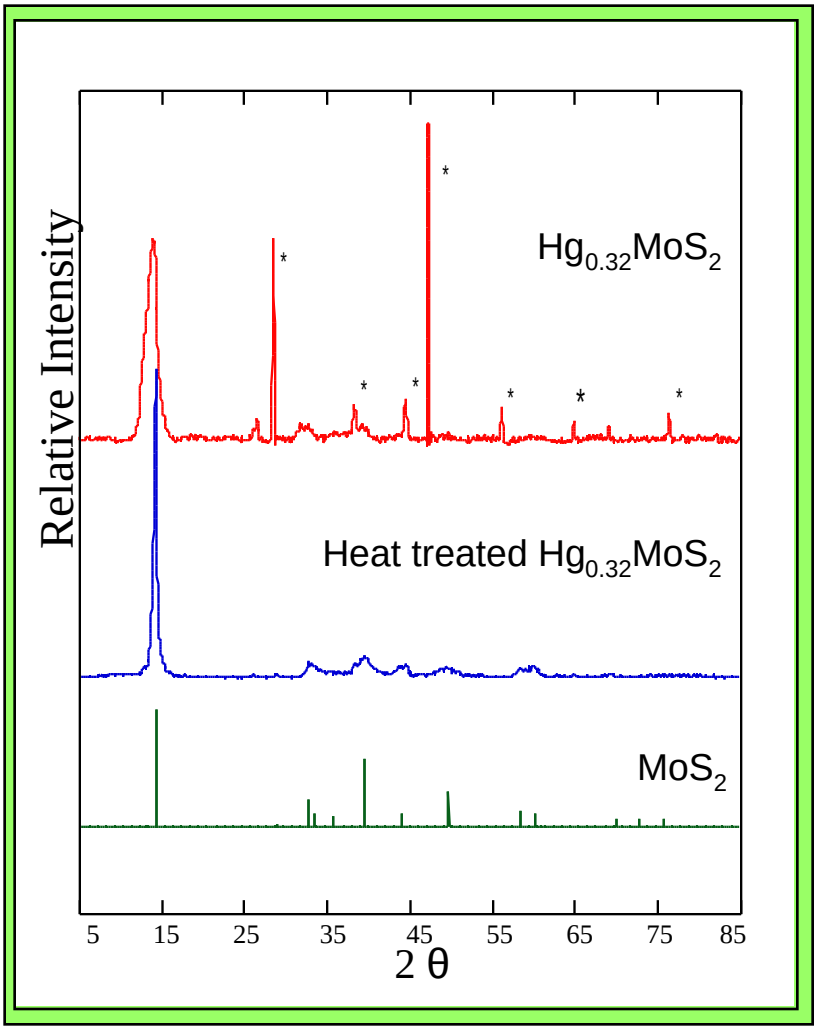
Powder X-ray Diffraction Studies



Powder X-ray diffraction is used to determine that the solid has absorbed the contaminant from solution based on the shift in the interlayer spacing peak near 15°. Heat treatment of the solid containing Hg reveals a reconstitution of the un-intercalated solid and expulsion of the guest ion as elemental mercury in a cold trap.

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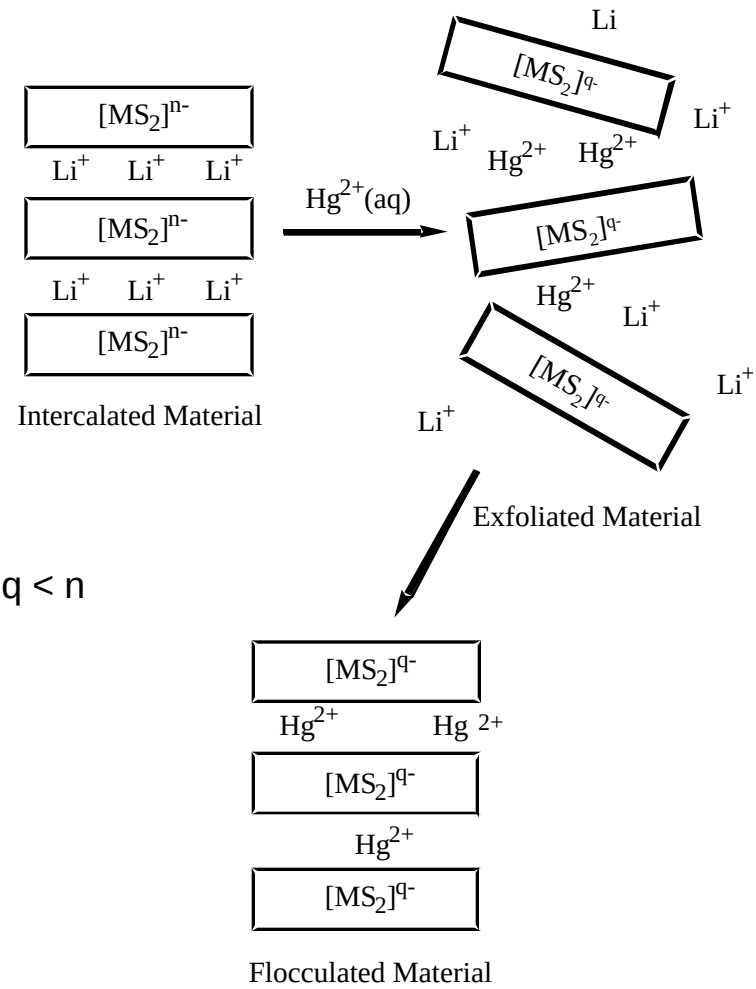
Mechanism of Extraction for MoS_2



q < n

- Some lithium intercalated transition metal chalcogenides† reduce H_20 to $H_2(g)$ upon contact with aqueous solution.
- Reaction with water causes exfoliation
- Exfoliation exposes sulfide surface
- Cations of interest can be captured in the flocculated material

Exfoliation Reaction:

$$Li_{1.3}MoS_2(s) + 1.3\ H_3O^+ \longrightarrow 0.26H_2 + 1.3\ Li^+ + (H_3O)_{0.78}MoS_2(s) + 0.52\ H_2O$$

Extraction Reaction:

$$(H_3O)_{0.78}MoS_2(s) + x\ M'^{2+}(aq) \longrightarrow (H_3O)_{(0.78-2x)}M'_xMoS_2(s) + 2x\ H_3O^+(aq)$$

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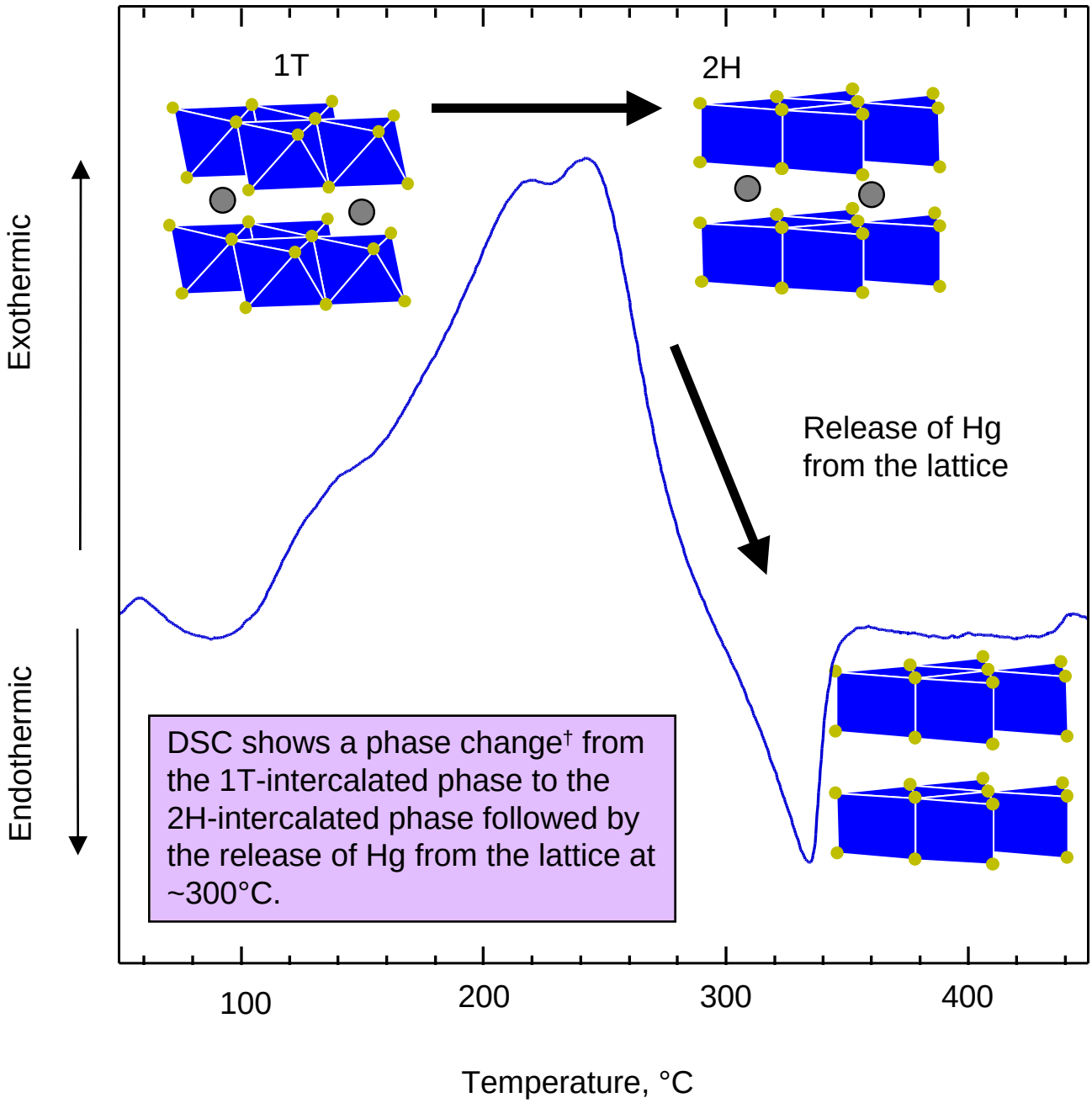
†Gee et al. *Mater. Res. Bull.* **1986**, *21*, 543. Yang et al. *J. Phys. Chem. Solids* **1996**, *57*, 1113.

Differential Scanning Calorimetry of $Hg_{0.3}MoS_2$ - Heat to release Hg°



DSC shows a phase change† from the 1T-intercalated phase to the 2H-intercalated phase followed by the release of Hg from the lattice at ~300°C.

† Schöllhorn et al. *J. S. C. Chem. Comm.* **1992**, 1386.

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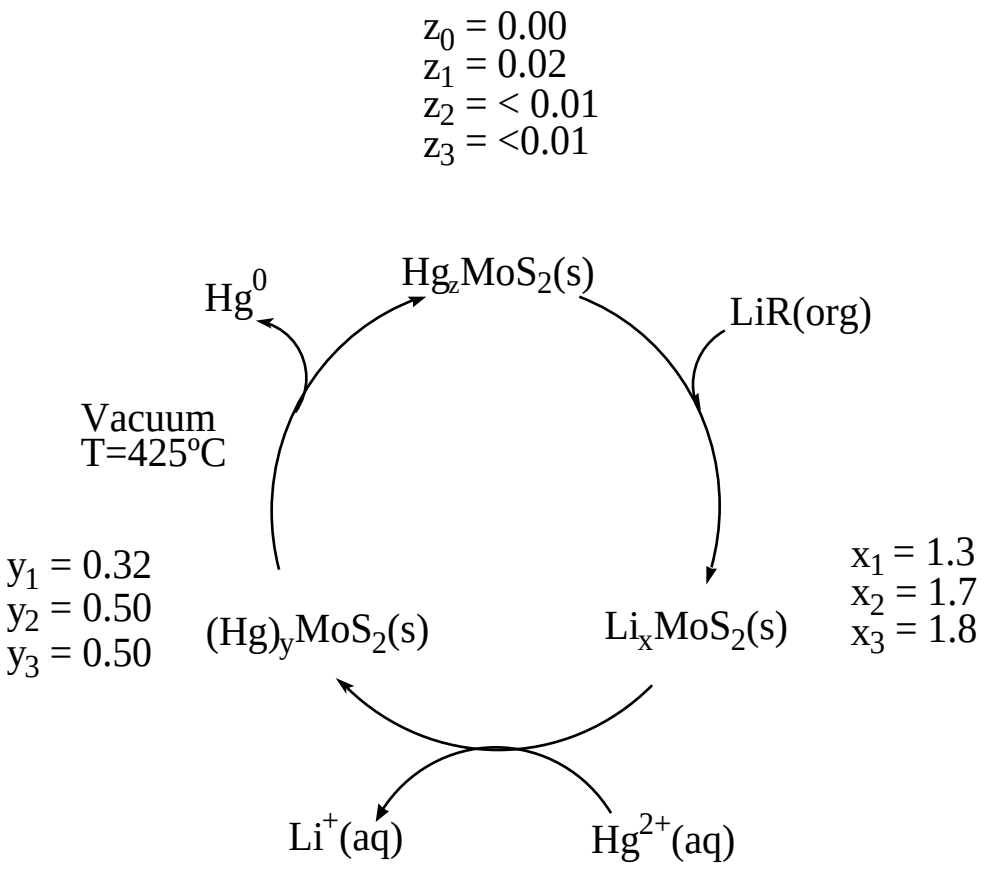
Li_xMoS_2 as a Recyclable Extractant: Activation - Contact - Deactivation



Shown here is an example of recycling of the MoS_2 extractant whose equilibrium capacity was found to be 580 mg Hg/g extractant. The increased capacity of MoS_2 for Li^+ is likely due to a decrease in particle size with each cycle. See images on the next page.

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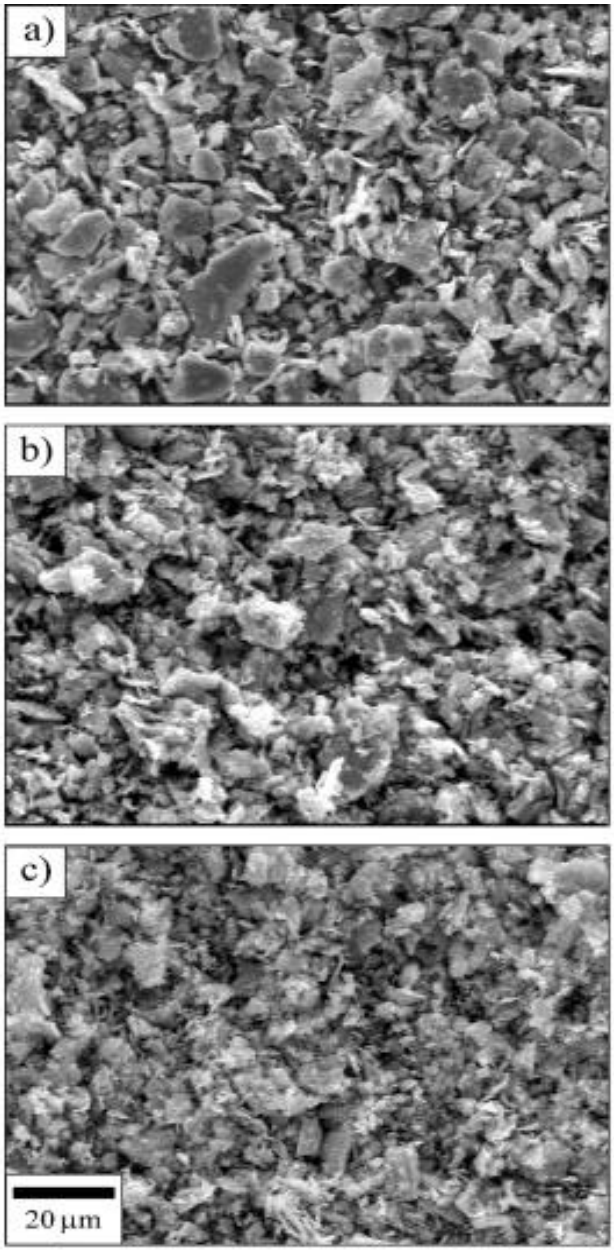
Recycling effects on particle size



MoS_2(Aldrich)

material cycled once

material cycled 3 times

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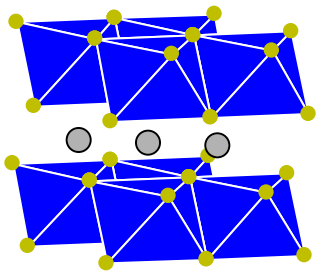
MoS_2 Extraction Data



Metal Ion	% Removed
Hg^{2+}	99(1)
Ag^{+}	99(1)
Au^{3+}	99(1)
Cu^{2+}	87(4)
Tl^{+}	63(3)
Pb^{2+}	42(5)
Cd^{2+}	7(2)
Zn^{2+}	2(2)
Mg^{2+}	0
Ba^{2+}	0
Sr^{2+}	0

Extractions from acidic solutions of target cations. K_d values for mercury, silver, gold are all above 10^4.

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Minimizing Secondary Waste

» Reduction of Hg^{2+} by $[MoS_2]^{n-}$ layers:

$$Hg_yMoS_2\,(s) \xrightarrow[\text{Vacuum}]{425\,^\circ\,C} y\,Hg\,(g) + MoS_2\,(s)$$

» Treat 100 L of waste containing $[Hg^{2+}(aq)] = 2 \times 10^{-3}$ M; recovered solid is Hg(*l*) ($\rho = 13.534$ g cm^{-3})

» 100 L of $[Hg^{2+}(aq)] = 2 \times 10^{-3}$ M contains 0.2 moles of Hg

» One contact with 5:1 extractant:metal ion ratio gives $[Hg^{2+}(aq)] = 3.3 \times 10^{-9}$ M (0.5 ppb)

» 0.2 moles of Hg corresponds to 40g of Hg = 2.95 ml of Hg

» This is an approximately **34,000** fold volume reduction

» In theory the recovered Hg could be reused

» MoS_2 could be recycled up to 5 times in our laboratory

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Extended X-ray Absorption Fine Structure Studies of M'MoS_2

- **EXAFS provides local coordination information**
- **Atom specific**
- **Need not be crystalline or solid**
- **Reliable to 0.01Å**
- **Requires synchrotron - SSRL**

» Used to understand the local coordination environment around interlayer guest atoms within the chalcogenide host framework.

» Hg exists as Hg(II), 80%, and Hg(I), 20%.

» Since powder X-ray diffraction could not disclose the nature of the bonding, models based on logical coordination configurations were established.

» Models such as HgS, $HgCl_2$, and Hg_2Cl_2

» The EXAFS data concludes that the solid and the selected guest have an intimate relationship with one another.

» Guest must stabilize the 1-T form of MoS_2

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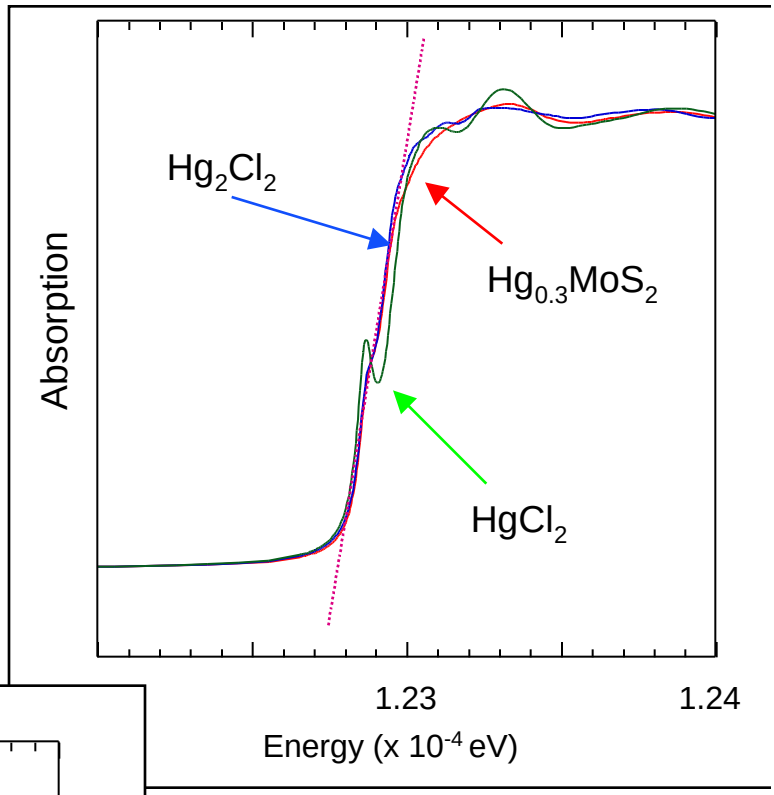
Hg EXAFS Data

Hg L_3-edge

- Curves fit to models that are consistent with published structures of Hg_2Cl_2 and $HgCl_2$.
- The intercalated $Hg_{0.3}MoS_2$ sample shows an environment more like that of Hg in Hg_2Cl_2.
- First shell coordination of 2 S at 2.38 Å and Hg-Hg interactions at 2.55 Å.



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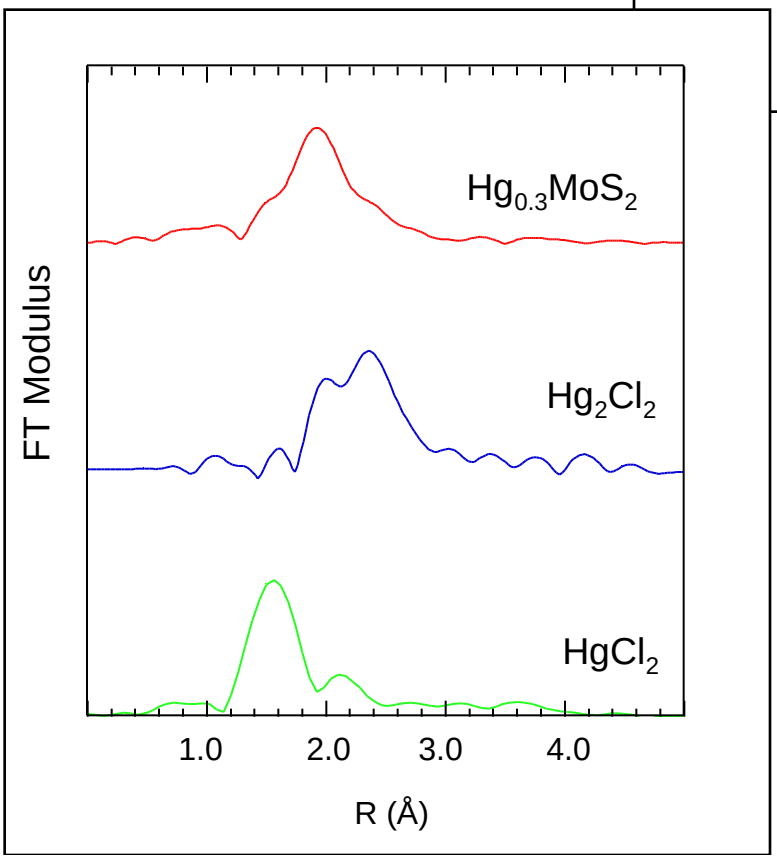

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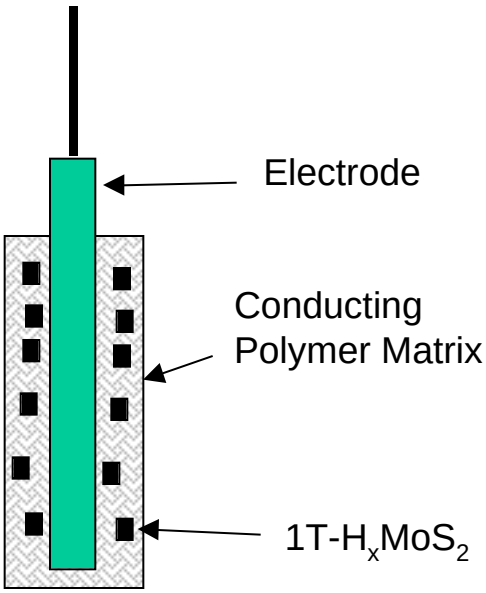
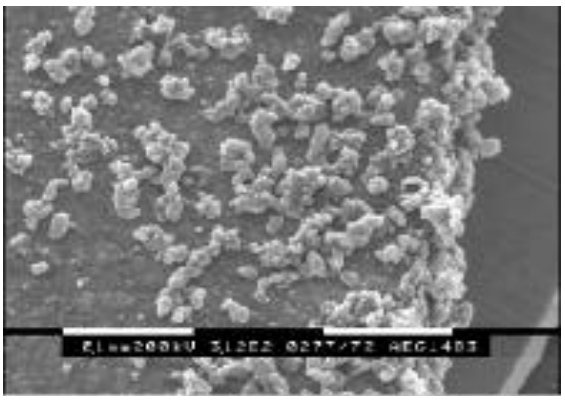
Electroactive MoS_2



Activated H_xMoS_2 can be imbedded within a conducting polymer matrix to create an electroactive material that is selective for Hg, Ag, and Pb ions. We are currently developing a completely recyclable MoS_2-based electrode.



SEM image of MoS_2 imbedded in conducting polymer on an electrode.

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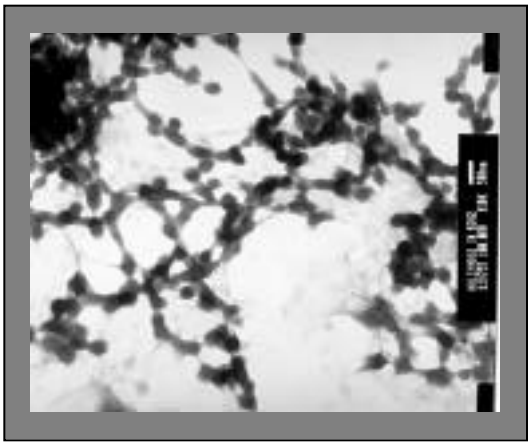
Xerogel-Imbedded MoS_2

To increase the surface area exposed to solutions and to prevent particle size reduction with recycle steps, activated MoS_2 can be placed within a silica xerogel monolith by reacting $Si(OEt)_4$ with acid in the presence of exfoliated H_xMoS_2. The dried xerogel composite can be used as an extractant for Hg, Pb, and Ag in acidic solutions with minimal filtration efforts. Suspensions of $M'MoS_2$ in water are difficult to filter and may clog pump-and-treat processes.



SEM image of a highly porous Xerogel with imbedded 1T-MoS_2 particles

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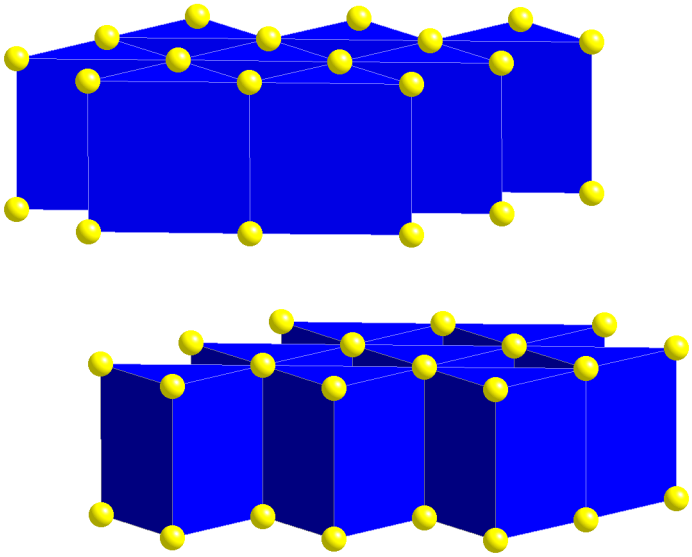
Conclusions about MoS_2

- MoS_2 acts as a selective and redox active material for waste remediation
- Can recycle material and extraction products - Ag, Hg
- EXAFS has helped understand the environment of Hg in the lattice
- Electroactive MoS_2 can be imbedded in conducting polymers on electrodes
- High surface area MoS_2 shows promise as an extractant in xerogel monoliths



MoS_2

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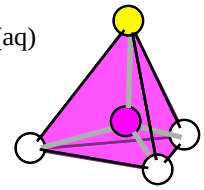
New Designer Extractants

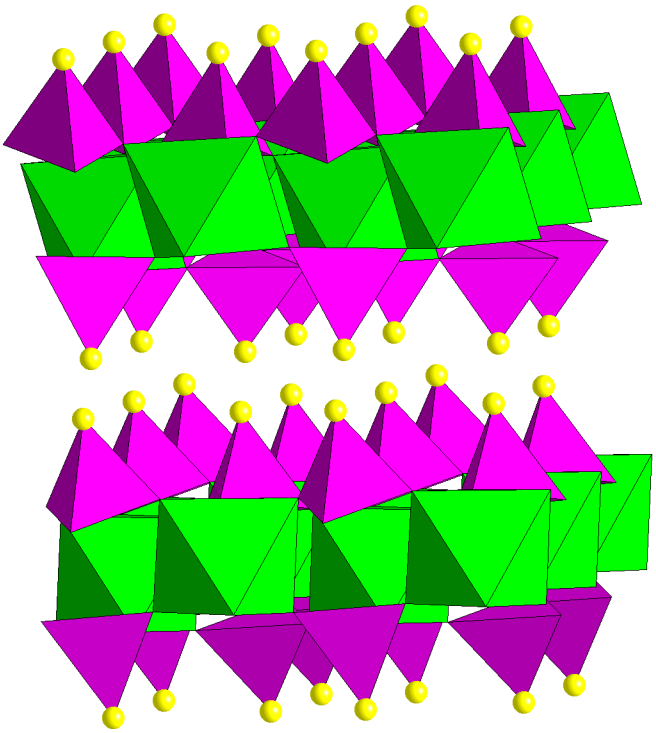
Inorg. Chem. **2000**, in press.

$$6\ NaOH_{(aq)} + PSCl_{3\ (l)} \xrightarrow{\text{Reflux}} Na_3PSO_{3\ (s)} + 3\ NaCl_{(aq)} + 3\ H_2O$$

$$ZrCl_4 + 2\ Na_3PSO_3 \xrightarrow[\text{Reflux 24h}]{\text{1 M HCl}} Zr(NaPSO_3)_{2\ (s)} + 4\ NaCl_{(aq)}$$



$[PSO_3]^{3-}$



A new thio-based zirconium phosphate solid ion exchange material. Based on Clearfield's zirconyl phosphates* – $H_2Zr(PSO_3)_2$

* *J. Inorg. Nucl. Chem.* **1964**, 26, 117

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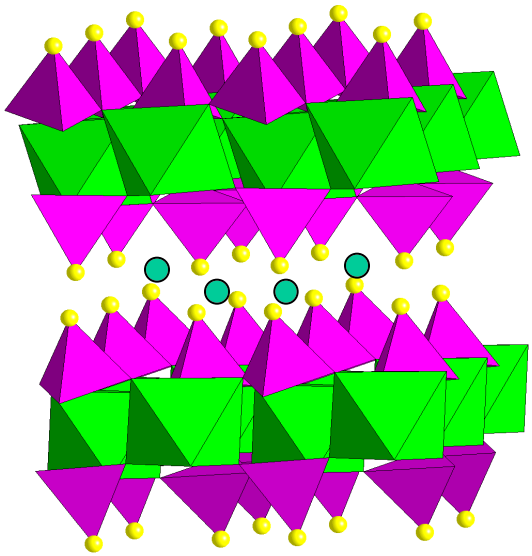
Extraction Data for $Na_2Zr(PSO_3)_2$

Target	K_d "$(C_i-C_f)/C_fV/M$"
Cu^{2+}	10^4
Cd^{2+}	10^4
Zn^{2+}	10^4
Co^{2+}	10^1
Mn^{2+}	10^1
Ni^{2+}	10^1
Ca^{2+}	10^0
Mg^{2+}	10^0
Na^{+}	10^0



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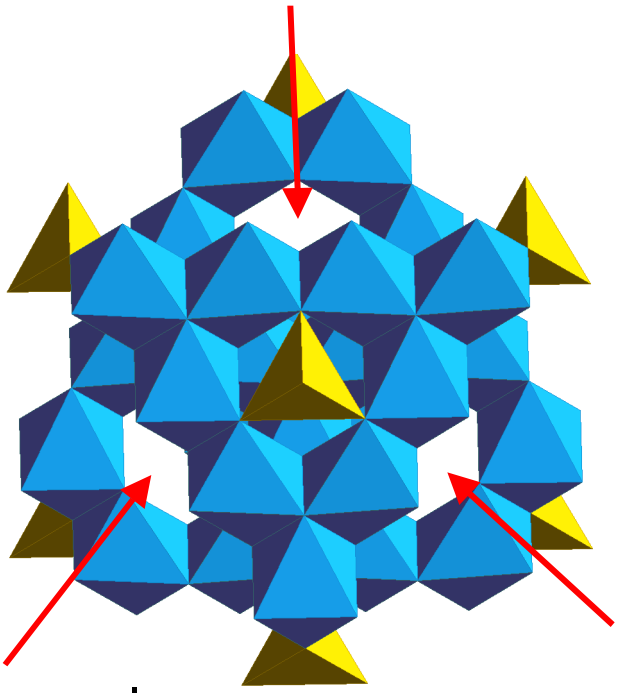
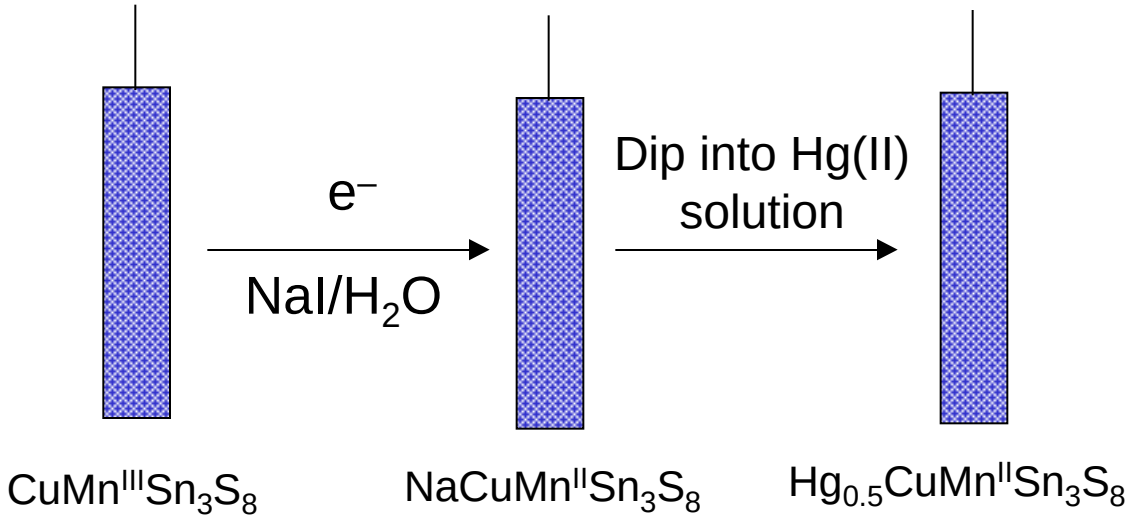
Thiospinels as Electroactive Selective Materials



$NaCuMnSn_3S_8$ can be prepared as an "activated" electrode by reducing or oxidizing the Mn(II) in the structure (blue octahedra). This activated electrode can sorb Hg(II) from solution in exchange for Na^+. The channels in the structure, shown by the red **arrows**, facilitate ion exchange. The Hg can be released thermally or electrochemically. We are currently optimizing this system.



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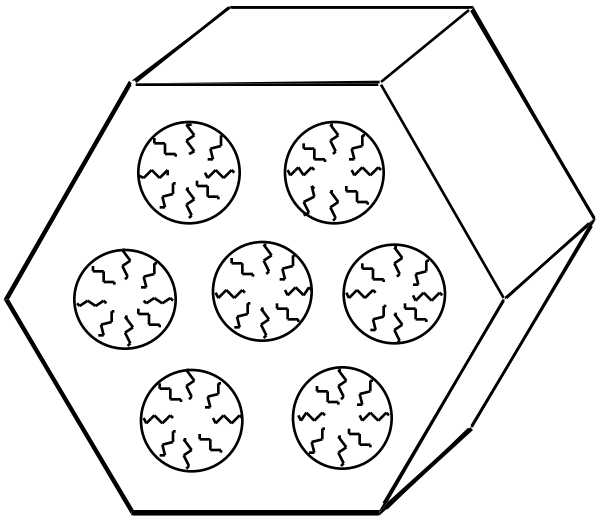
New Proprietary Materials

Functionalized Mesoporous Silica Solids
NOT organothiol-based solids
NO chance for organomercury formation



- Inorganic **Sulfur-based** building blocks
- Large pores - 4-5 nm
- High surface area
- Easily prepared and modified
- Reversibly bind heavy metals by ion exchange
- Highly robust and recyclable
- Disclosure filed with CSU in 1999

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Key Areas for Development

- New materials
- New redox chemistry
- New support materials - better surface area, higher throughput - proprietary
- Testing recyclability
- Understanding mechanisms

Educational Goals

- New synthetic methods
- Structure-property relationships
- Interdisciplinary education - chemistry and engineering
- Practical training opportunities
- Problem solving skills

Conclusions

New Materials from our laboratory

- Redox-active metal sulfides
  - Na_xMoS_2 and Li_xMoS_2
- Electrochemically active materials
  - MoS_2 Imbedded electrodes
  - Thiospinels
- Ion-exchange solids
  - Zirconium thiophosphates
  - Mesoporous materials- proprietary

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  - Ms. Christine J. Flashenriem - CSU undergrad

- Collaborators
  - Dr. Patrick G. Allen - LLNL

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- References
  - ES&T **1998**, *32*, 1007.
  - ACS Symp. Ser #727, **1999**, 53.
  - Inorg. Chem. **2000**, in press.

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