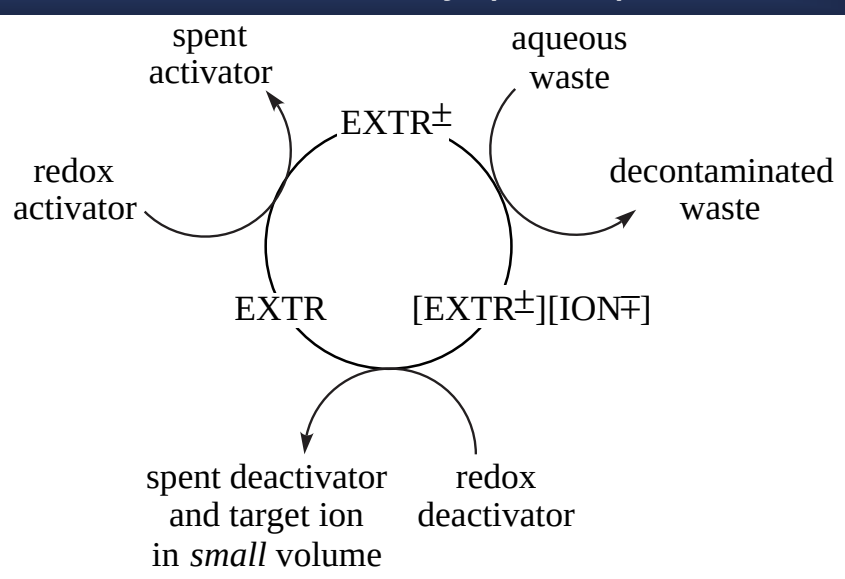
Abstract

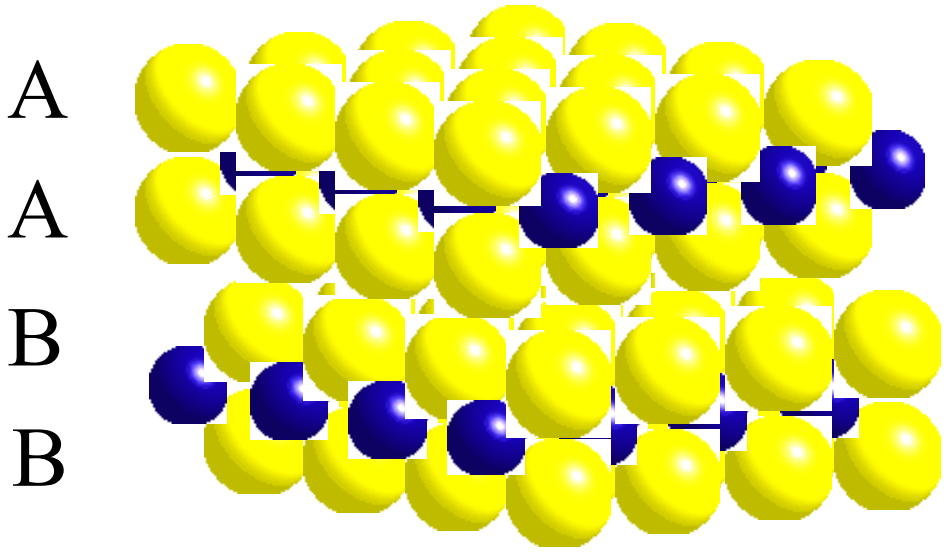
We are investigating the design and synthesis of redox-recyclable chalcogenide-based materials that are active as selective ion-exchange materials for the extraction and recovery of soft heavy-metal ions from aqueous solutions. These investigations have included exploring known extraction precursors based on the MoS_2 structure type and new materials based on the $H_2Zr(PO_4)_2$ structure. Redox-active extraction materials such as A_xMS_2 (A = Li, Na, K; M = Mo, W, Ti, Ta, Sn) have been prepared by literature methods. All of the redox-recyclable extraction materials displayed unique selectivities for ions such as Hg^{2+}, Ag^{+}, Pb^{2+}, and Cd^{2+}, in the presence of competing cations in aqueous acidic solution. Synthetic procedures will be discussed as will the analyses of the heavy-metal-loaded materials using XRD, EXAFS, XANES and ICP-AES.

Scheme of Redox-Recyclable Extraction and Recovery (R^2ER)[†]:



[†]Strauss, S. H. *Abstract of Papers*, 214th National ACS Meeting, Las Vegas, NV; ACS:Washington, DC, 1997; Abstract I&EC060.

Stacking in 2H-MoS_2



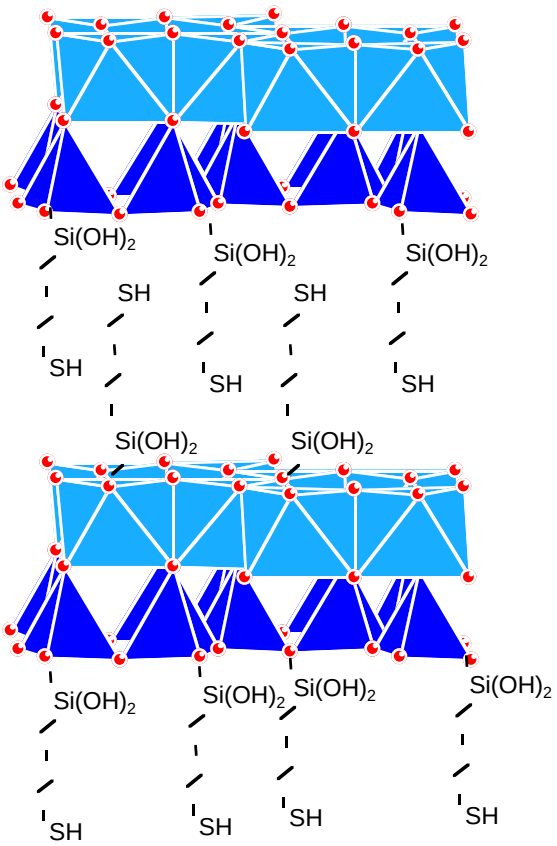
» T_d and O_h holes present between layers

» In close packed structure T_d = 0.36 Å; O_h = 0.66 Å

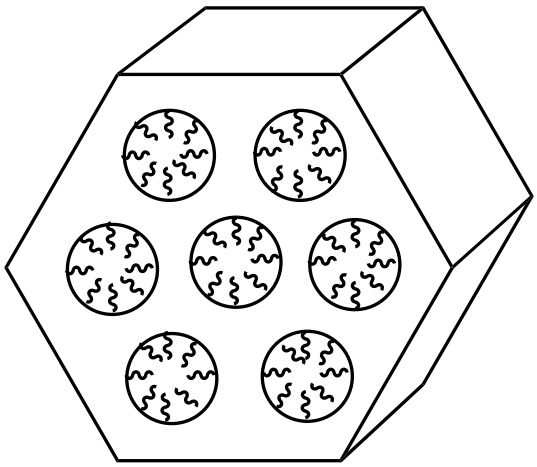
» In MoS_2 the holes are T_d = 0.42 Å; O_h = 0.76Å

Recent Literature on Heavy Metal Extractants:

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



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



〰 = $Si(OH)_2(CH_2)_3SH$

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

Anaerobic Extraction Results

Metal Ion	Anaerobic	Aerobic
Hg^{2+}	99(1)	99(1)
Ag^{+}	99(1)	99(1)
Cu^{2+}	99(1)	87(4)
Tl^{+}	99(1)	63(3)
Pb^{2+}	71(4)	42(5)
Cd^{2+}	41(2)	7(2)
Zn^{2+}	13(2)	2(2)

The % removal of Cu^{2+}, Tl^{+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} all decrease in the presence of oxygen. We postulate the oxidation of the metal-loaded-solid by O_2 as a possible explanation of the above data.

Proposed Oxidation of M_yMoS_2 by O_2:

$$M_yMoS_2(s) + y/2\ O_2 + y\ H_2O \xrightarrow{\text{slow}} MoS_2(s) + y\ M^{n+} + 2y\ OH^-$$

Aerobic Extraction Results

Batch extractions were done using $Li_{1.3}MoS_2$ the results of which are shown in the table at right. The filtrates from the extractions were then analyzed by ICP-AES to determine the % of metal ions removed. There appears to be a rough trend based on the degree of soft Lewis acidity of each metal ion. The softer Lewis acids are removed to a much greater extent than the harder Lewis acids.

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

Extraction Conditions:
$(Mo/M^{n+}) = 5$
$[M^{n+}] = 0.001$ M/ 0.1 M HNO_3

Rationale

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

- MS_2 solids are 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 and for the reuse of the solid extractant.

Conclusions

- One material, Li_xMoS_2, was found to be an effective, selective, and redox-recyclable ion-exchange material for Hg^{2+}(*aq*). Li_xMoS_2 displayed a capacity to remove 580 mg Hg/g extractant, a value that is comparable to other mercury extractants. Thermal treatment of the mercury-loaded material resulted in the generation of metallic mercury and MoS_2, which was reactivated for further use. Over three complete cycles of extraction-deactivation/recovery-reactivation Li_xMoS_2 showed no loss of capacity for Hg^{2+}(*aq*).

- XAFS results confirm that Hg^{2+} species are present and coordinated to sulfur atoms in the mercury-loaded molybdenum disulfide. These XAFS results coupled with those from hydrogen evolution experiments and mass balance studies suggest that Li_xMoS_2 removes heavy metal ions by an ion-exchange process.

- Mo EXAFS results indicated that the heavy metal ions Ag^+, and Hg^{2+} stabilize the reduced (1T phase) MoS_2. These results help explain the selectivity of Li_xMoS_2, for heavy metal ions.

- Although detailed study is still required, Li_xWS_2 appears to be a good candidate as an effective, selective, and redox-recyclable material for Hg^{2+}(*aq*).

- $Li_{1.5}TiS_2$, $Li_{1.2}TaS_2$, and Li_xSnS_2 showed a high capacity for Hg^{2+}(*aq*) however, there was considerable evidence that a reversible ion-exchange reaction was not the mechanism of ion removal, as was the case with Li_xMoS_2.

Other Waste Streams

We have tested the capability for $Li_{1.3}MoS_2$ to be an effective extractant for heavy metal ions in other relevant waste streams.

Photographic Fixer Solution: 1 mM Ag^+/0.1 M $Na_2S_2O_3$.

A Mo/Ag^+ ratio of 3.0 resulted in the removal of 99% of Ag+(*aq*).

"Brine" Solutions: Solution A (1 mM Hg^{2+}/ 2 M NaCl/ 0.1 M HNO_3) and Solution B (1 mM Hg^{2+} / 2 M $MgCl_2$/ 0.1 M HNO_3).

A Mo/Hg^{2+} ratio of 5.0 removed 65% of Hg^{2+}(aq) from Solution A and 55% of Hg^{2+}(*aq*) from Solution B.

Concentrated Phosphoric Acid (85%):

Heavy metals are common contaminants in H_3PO_4 because it is made from phosphate-based minerals.[†] A Mo/Pb^{2+} ratio of 5.0 resulted in the removal of 45% of Pb^{2+}(*aq*) from concentrated H_3PO_4 that was 1mM in Pb^{2+}(*aq*) .

[†]Schorr, M.; Lin, I.J. *Industrial Minerals* **April 1997**, 61.