

# **Environmental Management Science Program**

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## **Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams Using Redox-active Layered Metal Chalcogenides**

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## Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams Using Redox-active Layered Metal Chalcogenides

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### Research Objective

Mercury and other highly-toxic heavy metals such as cadmium and lead are present in many aquatic environments, and the remediation of such environments or the avoidance of heavy-metal contamination in the first place is an area of active interest. In recent years tougher environmental regulations and the high initial cost of new, more effective, and more selective extractants has made the reuse of extractant materials and the minimization of secondary waste volume a focus of our scientific effort. Our research has involved the investigation of redox-active layered metal chalcogenides as selective, effective, and redox-recyclable extractants for heavy metals from aqueous solution.

### Research Progress and Implications

The use of lithium-intercalated transition-metal dichalcogenides,  $\text{Li}_x\text{MS}_2$ , as redox-recyclable ion-exchange materials for the extraction of the aqueous heavy-metal ions  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$  was investigated ( $0.25 = x = 1.9$ ;  $\text{M} = \text{Mo}, \text{W}, \text{Ti}, \text{Ta}$ ). For  $\text{Li}_x\text{TiS}_2$  and  $\text{Li}_x\text{TaS}_2$ , hydrolysis produced  $\text{S}^{2-}(\text{aq})$  ions which precipitated  $\text{Hg}(\text{II})$  as  $\text{HgS}(\text{s})$ . In contrast, the materials  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$  did not undergo hydrolysis to form  $\text{S}^{2-}$  ions. Instead, ion-exchanged materials such as  $\text{Hg}_{0.50}\text{MoS}_2$  and  $\text{Pb}_{0.15}\text{MoS}_2$  were isolated. The selectivity of  $\text{Li}_x\text{MoS}_2$  for the heavy-metal ions was  $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ . The affinities for the latter three ions, but not for  $\text{Hg}^{2+}$ , increased when the extractions were performed under anaerobic conditions. When  $\text{Hg}_y\text{MoS}_2$  was heated under vacuum at  $425^\circ\text{C}$ , an entropy-driven internal redox reaction resulted in deactivation of the extractant, producing essentially mercury-free  $\text{MoS}_2$  and a near-quantitative amount of mercury vapor (collected in a cold trap). The ratio of the volume of metallic mercury (secondary waste) to the volume of  $10.0 \text{ mM Hg}^{2+}(\text{aq})$  (primary waste) was  $1.5 \times 10^{-4}$ . Samples of  $\text{MoS}_2$  produced by heating  $\text{Hg}_y\text{MoS}_2$  were reactivated to  $\text{Li}_x\text{MoS}_2$  by treatment with *n*-butyllithium. Some samples were used for three cycles of extraction, deactivation/recovery, and reactivation with a primary waste simulant consisting of  $10 \text{ mM Hg}^{2+}(\text{aq})$  in  $0.1 \text{ M HNO}_3$  with no loss in ion-exchange capacity. When the  $\text{Mo}/\text{Hg}$  molar ratio was  $5.0$  and the initial  $[\text{Hg}^{2+}(\text{aq})] = 1 \text{ mM}$ , only  $0.033(2) \mu\text{M}$  mercury ( $6.5 \text{ ppb}$ ) was detected in the filtrate after the extraction step. The highest observed capacity of  $\text{Li}_x\text{MoS}_2$  for  $\text{Hg}^{2+}(\text{aq})$  was  $580 \text{ mg mercury per g Li}_{1.9}\text{MoS}_2$ . Initial experiments have indicated that  $\text{Li}_x\text{WS}_2$  is also a redox-recyclable extractant for  $\text{Hg}^{2+}(\text{aq})$ .

Since two of the lithium-intercalated transition metal dichalcogenides,  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$ , investigated showed promise as effective, selective, and redox-recyclable extractants for heavy metal ions from aqueous solution we decided to study of the mechanisms of activation, extraction, deactivation, and recovery of the extractant and the target ion. This investigation has involved the use of powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and X-ray absorption spectroscopy (XAS). Based on our results, we believe that heavy-metal ions are removed from solution by a reversible ion-exchange process with the negatively charged metal chalcogenide layers. The extracted heavy-metal ions are present in the interlayer space of the layered solid-state extractant. We have also determined that the metal ions are present, in the heavy-metal-loaded extractant, in a sulfur rich coordination environment and that the heavy-metal ions are in an oxidized form. The

XAS investigation indicated that the selectivity of the extractants may be based on the ability of certain heavy-metal ions to stabilize the negatively charged (reduced) metal-chalcogenide layers (that have a distorted geometry relative to the neutral (oxidized) metal-chalcogenide layer). The stabilization ability of the metal ions appears to correlate strongly with their degree of soft-Lewis acid character. The softer Lewis acids, such as  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ , are very effective at stabilizing the reduced chalcogen layers and are hence removed to a large extent. However, metal ions such as  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mn}^{2+}$ , that are harder Lewis acids than  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ , are not as effective at stabilizing the reduced chalcogen layers and hence are removed to a far lesser extent than both  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ .

## Planned Activities

We are actively investigating both the optimization of the  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$  extractants and the development of new redox-active layered extractants. Both the  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$  extractants do generate some hydrogen gas during the extraction process. Naturally, we would like to eliminate this potentially dangerous side product and are currently synthesizing  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$  extractants that will generate no hydrogen and are still effective extractants. We have shown that  $\text{Li}_x\text{MoS}_2$  is an effective, selective, and redox-recyclable extractant for  $\text{Hg}^{2+}(\text{aq})$  through at least three complete cycles of activation/extraction and reactivation/recovery. We would like to study both of the  $\text{Li}_x\text{MoS}_2$  and  $\text{Li}_x\text{WS}_2$  extractants through many more cycles of activation/extraction and reactivation/recovery. We are also interested in studying the feasibility of using electroactive conducting polymer films containing  $\text{MoS}_2$  and  $\text{WS}_2$  particles for effective, selective, and redox-recyclable extraction of heavy-metal ions from aqueous solution.

There are new alkali-metal-intercalated metal chalcogenides that remain to be investigated. Three such materials that will be studied are the lithium-intercalated  $\text{SnS}_2$ ,  $\text{VS}_2$ , and  $\text{NiPS}_3$  compounds. All of these materials have been synthesized previously as  $\text{Li}_x\text{MS}_2$  or  $\text{Li}_x\text{MPS}_3$  and will be tested by the methods we have developed for our  $\text{Li}_x\text{MS}_2$  ( $\text{M} = \text{Mo}, \text{W}, \text{Ti}, \text{Ta}$ ) studies.

## Other Access To Information

Gash, A.E.; Spain, A.L.; Dysleski, L.M.; Flaschenriem, C.J.; Kalaveshi, A.; Dorhout, P.K.; Strauss, S.H. *Environ. Sci. Technol.* 1998, 32, 999.

## Web Access

<http://www.chm.colostate.edu/>