

**Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams
Using Redox-Active Layered Metal Chalcogenides
P. K. Dorhout and S. H. Strauss - DE-FG07-96ER14696**

(1) Brief Summary of Progress (for the period September 15, 1996 - September 14, 1997)

(a) Objectives of the Grant. With support from the Department of Energy Environmental Management Science Program, Professors P. K. Dorhout and S. H. Strauss have begun to examine the extraction and recovery of heavy elements from aqueous waste streams using redox-active metal chalcogenides. They have been able to prepare extractants from known chalcogenide starting materials, studied the efficacy of the extractants for selective removal of soft metal ions from aqueous phases, studied the deactivation of extractants and the concomitant recovery of soft metal ions from the extractants, and characterized all of the solids and solutions thus far in the study.

The study was proposed as two parallel tasks: Part 1 and Part 2 emphasize the study and development of known metal chalcogenide extractants and the synthesis and development of new metal chalcogenide extractants, respectively. The two tasks were divided into sub-sections that study the extractants and their chemistry as detailed below:

- **Preparation and reactivity of metal chalcogenide host solids**
- **Extraction of target waste (guest) ions from simulated waste streams**
- **Examination of the guest - host solids**
- **Recovery of the guest metal and reuse of extractant**

Each section of the two tasks was divided into focused subsections that detail the specific problems and solutions to those problems that were proposed. The extent to which those tasks have been accomplished and the continued efforts of the team are described in detail below.

(b) Progress and Results. The DOE-supported research has proceeded largely as proposed and has been productive in its first 12 months. Two full-paper manuscripts were submitted and are currently under peer review. A third paper is in preparation and will be submitted shortly. In addition, 5 submitted or invited presentations have been made. These publications and presentations are listed below (and reprints are included):

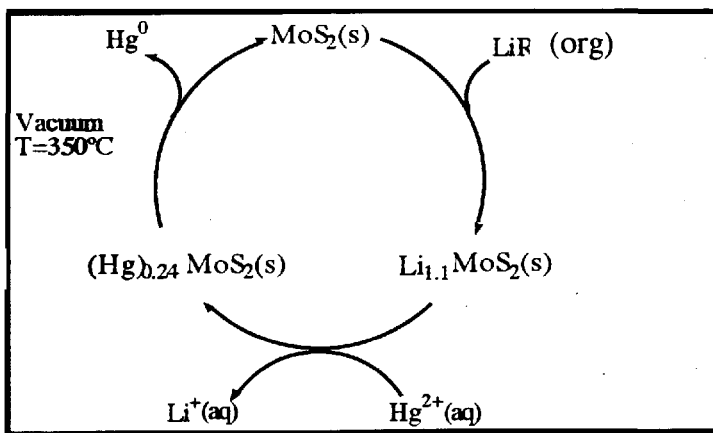
Manuscripts submitted.

1. A. E. Gash, A. L. Spain, L. M. Dysleski, C. J. Flaschenriem, A. Kalaveshi, P. K. Dorhout, and S. H. Strauss, "Efficient Recovery of Elemental Mercury from Hg²⁺-Contaminated Aqueous Media Using A Redox-Recyclable Ion-Exchange Material" *Environ. Sci. Tech.* **1997**, submitted.

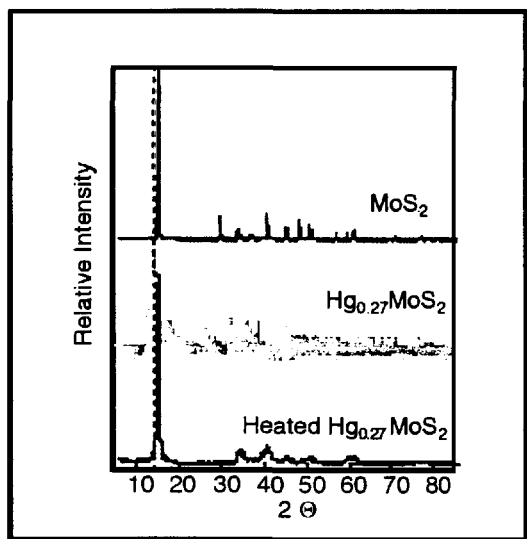
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Manuscript 1. *Efficient Recovery of Elemental Mercury from Hg^{2+} -Contaminated Aqueous Media Using A Redox-Recyclable Ion-Exchange Material.* This manuscript focuses on Task 1 and three sub-tasks (extraction of target ions, synthesis of activated extractants, and the recovery of waste contaminants). The

feasibility of using lithium-intercalated transition-metal dichalcogenides, Li_xES_2 , as recyclable ion-exchange materials for the extraction of the heavy-metal ions $Hg^{2+}(aq)$, $Pb^{2+}(aq)$, $Cd^{2+}(aq)$ and $Zn^{2+}(aq)$ was investigated ($0.25 \leq x \leq 1.9$; E = Mo, W, Ti, Ta). For Li_xTiS_2 and Li_xTaS_2 , hydrolysis produced $S^{2-}(aq)$ ions which precipitated $Hg^{2+}(aq)$ as $HgS(s)$. Although these two materials removed

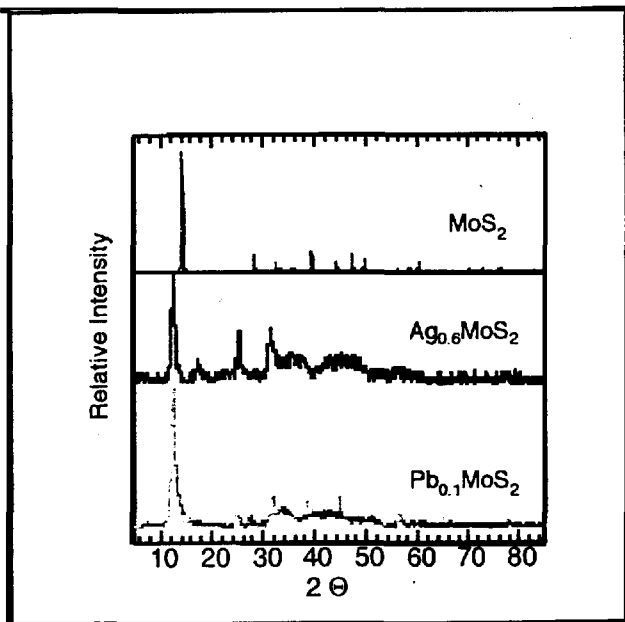


significant amounts of $Hg^{2+}(aq)$, their hydrolysis precluded their use as recyclable extractants. In contrast, the materials Li_xMoS_2 and Li_xWS_2 , which also removed significant amounts of the heavy-metal ions, did not undergo hydrolysis to form S^{2-} ions. Instead, ion-exchanged materials such as $Hg_{0.50}MoS_2$ and $Pb_{0.15}MoS_2$ were isolated. The selectivity of Li_xMoS_2 for the heavy-metal ions was $Hg^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$. The affinities for the latter three ions, but not for Hg^{2+} , increased when the extractions were performed under anaerobic conditions. When Hg_yMoS_2 was heated under vacuum at $425^\circ C$, an entropy-driven internal redox reaction resulted in deactivation of the extractant, producing essentially mercury-free MoS_2 and mercury vapor, illustrated in the powder diffraction data below. The mercury vapor was collected in a cold trap. In some experiments the heat treatment resulted in near-quantitative (>99%) recovery of mercury



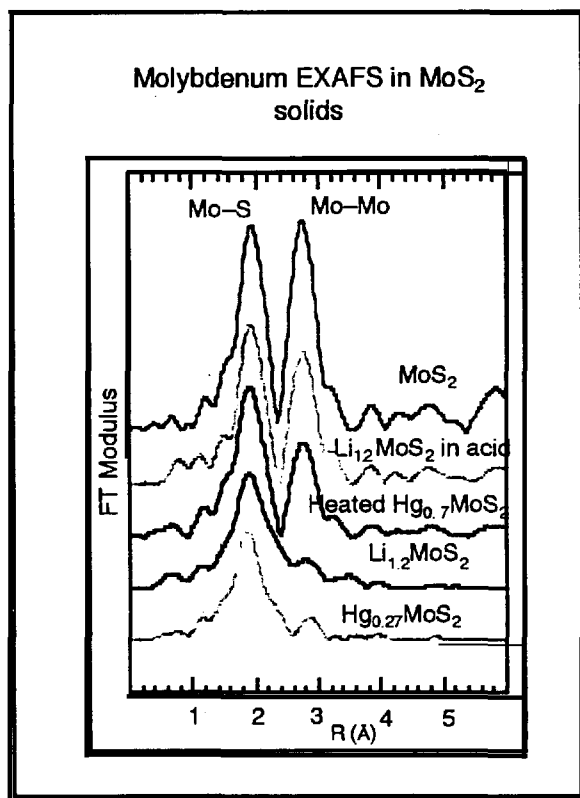
from Hg_yMoS_2 . The ratio of the volume of metallic mercury (secondary waste) to the volume of 10.0 mM $Hg^{2+}(aq)$ (primary waste) was 1.5×10^{-4} . Samples of MoS_2 produced by heating Hg_yMoS_2 were reactivated to Li_xMoS_2 by treatment with *n*-butyllithium. Samples of Li_xMoS_2 were used for three complete cycles of extraction, deactivation/recovery, and reactivation with a primary waste simulant consisting of 10 mM $Hg^{2+}(aq)$ in 0.1 M nitric acid with no loss in ion-exchange capacity giving the cycle illustrated above. When the initial molybdenum/mercury molar ratio was 5.0, no $Hg^{2+}(aq)$ was detected after the extraction step. The highest observed capacity of Li_xMoS_2 for $Hg^{2+}(aq)$ was 580 mg of mercury per g of $Li_{1.9}MoS_2$. The effect of mercury intercalation on solid is seen in the powder diffraction pattern of MoS_2 on the left.

Summarizing this work, we have developed a general process that may be applied to all of our redox-recyclable materials. This may be represented by the scheme shown above. The extractant is activated by a reducing agent, organolithium reagents in this example, which yields an activated Li_xMoS_2 solid. The activated solid contacts the contaminated waste stream containing mercury in this case, which releases the lithium ion into solution and extracts mercury ions from the waste stream. The extractant is recovered in a heating step to yield the deactivated extractant and elemental mercury; the contaminant in its smallest volume.



Manuscripts in preparation.

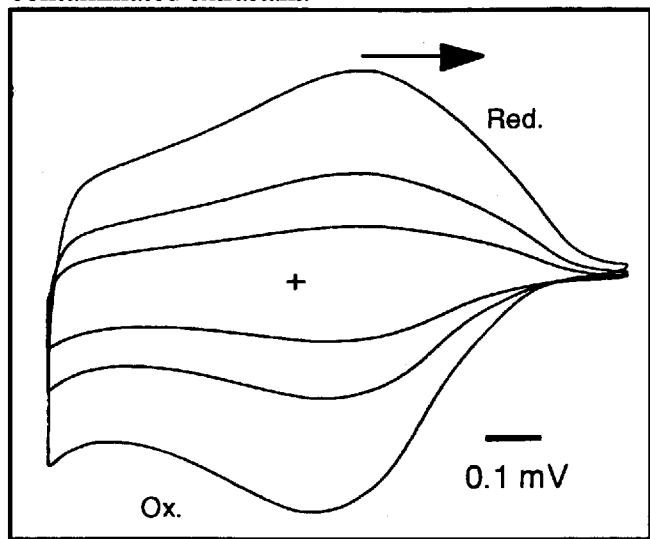
Our manuscript in preparation involves a detailed study of the local structure of the guest ions within the extractant host matrix. This work expands on Task 1 to include the sub-task of examination of the guest - host solids. To accomplish this, we have developed a collaboration with Dr. Patrick G. Allen at the Lawrence Berkeley Laboratory (LBL), Berkeley, California. Dr. Allen has employed the general class of techniques known as Extended X-ray Absorption Fine Structure, EXAFS, to study the guest ion *in situ*. This cannot be accomplished by any other method we have been able to find. The results of these experiments are outlined below.



Powder X-ray diffraction displays evidence for the activity of the extractant. The powder diffraction data of the extractant, MoS_2 , was compared to the pattern of the mercury intercalated solid and the reconstituted, deactivated solid in the patterns on p. 3. The extractant also showed activity toward silver and lead ions in solutions as well as displaying selectivity in competition reactions. The powder patterns above display the structural changes observed for the respective solids. The powder data do not, however, offer any insight into the structural organization of the extracted contaminants or guests within the extractant host lattice. For this information, we turned to EXAFS measurements at LBL.

Shown at the left are representative fourier transform EXAFS data for the extractant, the

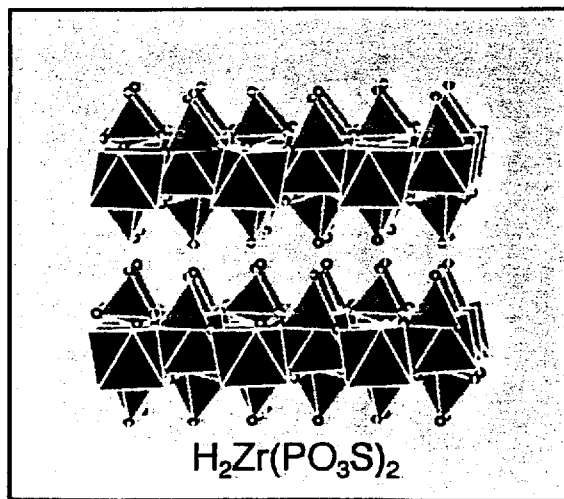
activated extractant, Li_xMoS_2 , guest-host solids, and deactivated, reconstituted extractant. The spectra reveal the coordination environments of the guest species and the host lattice. The mercury guest species are both Hg^{2+} and Hg^+ ions based on modeling known standards HgCl_2 , Hg_2Cl_2 , and HgS . The geometry of the molybdenum host atoms was transformed from trigonal prismatic to octahedral in the "activated" extractant as well as in the guest-host solids. This organization, however, is metastable and is "reorganized" to a less reducible form of MoS_2 upon heating above 100°C . From this information, we realized that the best host matrix consists of a MoS_2 lattice (known as the 1-T form) that is "pre-organized" into a particular coordination environment (for Mo) and based on literature precedent, this solid could be activated and deactivated using mild (with respect to $n\text{-BuLi}$) reducing agents. We have also used differential scanning calorimetry to study the thermally-activated phase transitions in the activated extractants as well as to follow the thermally-initiated removal of elemental mercury from the guest-host solid also known as the contaminated extractant.



We have been able to demonstrate that milder reducing agents could yield activated extractants that were very effective at soft metal ion extractions. For example, the preorganized MoS_2 can be reduced by NaBH_4 and NaS_2O_4 in aqueous solutions and shows an extraction only slightly less than that activated by $n\text{-BuLi}$ in hydrocarbon solvents. Still other reducing agents are being sought that will activate the extractant in aqueous solutions. For example, a composite matrix of polypyrrole and the metastable 1-T MoS_2 shows a shift (arrow) in the redox waves of a cyclic voltammogram

with respect polypyrrole, shown above, illustrating that the MoS_2 /polypyrrole composite can be electrochemically reduced and oxidized. Activation by electrochemical methods in aqueous solutions may afford an ion-selective/absorptive reversible electrode that could be used both as a detector and as an extractor of heavy element waste in large scale and remote operations.

Other Work of Note. We have begun work on Task 2 described in the proposal. This work has yielded a new solid of the tentative chemical formula $\text{H}_2\text{Zr}(\text{PO}_3\text{S})_2$ (structure at right) which was prepared by modifying a procedure for the preparation of $\text{H}_2\text{Zr}(\text{PO}_4)_2$ by Clear-field. The reaction required the preparation of $\text{Na}_3\text{PO}_3\text{S}$ followed by reaction with ZrCl_4 in acidic solution.



A polycrystalline solid was isolated from a gel which was filtered and dried in vacuo. The diffraction pattern of the solid resembled that of the oxophosphate, $\text{H}_2\text{Zr}(\text{PO}_4)_2$, but our new solid shows a remarkable activity toward Cd^{2+} in aqueous solution. We are currently making modifications to the synthesis of the thiophosphate solid to afford single crystals for a structural study but a model based on the Clearfield oxophosphate is shown below. New synthetic targets include thiophosphates of tin, and vanadium that may display redox activity comparable to that of MoS_2 .

(2) Brief Summary of Work to be Performed During the Coming Year of Support.

This project is one that is of an *exploratory* nature into a practical, soluble problem. These first 12 months of the project have allowed us to develop an understanding about the relationships that exist within a family of metal chalcogenides, in particular, MoS_2 . The related family of solids will be our targets for the coming period. We plan to develop a similar detailed analysis of other related layered metal chalcogenides that may be selective for a variety of other target metal ions such as Ag, Au, Hg, Pb, Tl, and Cd. In addition, we will pursue the latest developments in the electrochemical activation, extraction, deactivation and recovery using our metal sulfide-based extractants. Finally, we will continue to follow the dual-task, four point program in the areas of extractant synthesis and development outlined in the introduction of this report

Technical Summary. Our DOE-supported research is going well and according to our initial plan of exploration. We have used our equipment allocation to purchase a new vacuum pump and dedicated furnaces and controllers for our synthetic efforts. We have initiated a successful dual-task initiative to explore the ion-selective ability of redox active metal-sulfide based solids and to prepare new, targeted solids for the selective removal of soft-metal cations from aqueous waste streams.

(3) Statement of Estimated Unobligated Funds.

The initial \$333,000 granted by the DOE-EMSP has been spent to \$231,911 based on an estimate of encumbered funds as of 9/15/97 by the chemistry department's accountant. A budget statement that reflects the expenditures can be found in section (7) below.

(4) Proposed Budget for the Coming Year.

No change from the \$333,000 award amount.

(5) Information About Other Current and Pending: Research Support of Senior Personnel.

The main senior researchers on the project are Professors Dorhout (1.0 month) and Strauss (1.0 month). We have made inquiries into qualified postdoctoral candidates but have not hired anyone to fill the position. We plan to hire an additional senior researcher (postdoc) this period.

Since the original funding of this proposal, Dorhout has received funding from the DOE-

BES-actinide program for the study of the solids state chemistry of actinide chalcogenide materials in conjunction with the G. T. Seaborg Laboratory at LANL. The proposed work is unrelated to the current project. In addition, since September, 1996, Dorhout has been the recipient of the Alfred P. Sloan Research Fellowship (\$35,000) and the Camille Dreyfus Teacher Scholar Fellowship (\$60,000) for accomplishments in solid state chemistry, some of which have been made possible through the funding of the DOE-EMSP.

Since the original funding of this proposal, Strauss has received a contract from APCI to study metal carbonyl chemistry (unrelated to the current project) as well as an unrestricted gifts from Central Glass, APCI, and DuPont for the study of weakly coordinating anions (unrelated to the current project). There are no changes to his (unrelated) NSF funding.

(6) Contribution of the Project to the Area of Education and Human-resource Development.

The DOE-EMSP project at Colorado State University has provided funding for the training of two graduate research assistantships (K. Gansel and A. Gash) in the area of environmental management as well as funding for two undergraduate summer traineeships (C. Flashenriom and A. Kalaveshi) and a summer predoctoral research experience (L. Disleski). The undergraduate and predoctoral students are coauthors on our submitted manuscripts (see above) and will be co-authors on at least one other manuscript (in preparation).

(7) Detailed Expenditures for the Reporting Period.

Category	Budgeted (\$) 9/97 - 9/00	Expenses (\$) 9/96 - 9/97
Salary	177,733	45,867
Travel	6,000	790
Materials and Supplies	19,501	8,855
Other	9,404	5,597
Tuition	11,725	5,124
Equipment	12,950	7,357
Total Direct Costs	237,313	73,590
Indirect	95,687	27,499
Total	333,000	101,089

(8) Attachments:

A. Reprints (preprints) of two manuscripts submitted for publication.