

Efficient Recovery of Elemental Mercury from Hg(II)-Contaminated Aqueous Media Using a Redox-Recyclable Ion-Exchange Material

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The use of lithium-intercalated transition metal dichalcogenides, Li_xES_2 , as redox-recyclable ion-exchange materials for the extraction of the aqueous heavy metal ions Hg^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} was investigated ($0.25 \leq x \leq 1.9$; E = Mo, W, Ti, Ta). For Li_xTiS_2 and Li_xTaS_2 , hydrolysis produced $\text{S}^{2-}(\text{aq})$ ions, which precipitated Hg(II) as $\text{HgS}(\text{s})$. In contrast, the materials Li_xMoS_2 and Li_xWS_2 did not undergo hydrolysis to form 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 Li_xMoS_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 Hg^{2+} increased when the extractions were performed under anaerobic conditions. When Hg_yMoS_2 was heated under vacuum at 425°C , an entropy-driven internal redox reaction resulted in deactivation of the extractant, producing essentially mercury-free 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 1.5×10^{-4} . Samples of MoS_2 produced by heating Hg_yMoS_2 were reactivated to Li_xMoS_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 M HNO_3 with no loss in ion-exchange capacity. When the Mo/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 ppb) was detected in the filtrate after the extraction step. The highest observed capacity of Li_xMoS_2 for $\text{Hg}^{2+}(\text{aq})$ was 580 mg of mercury/g of $\text{Li}_{1.9}\text{MoS}_2$.

Introduction

Mercury and other highly toxic heavy metals such as cadmium and lead are present in many aquatic environ-

ments, and the remediation of such environments or the avoidance of heavy metal contamination in the first place is an area of active interest (1). A number of processes have been described for extracting mercury from aqueous media (2), including two significant recent reports (2a, b). In one of these, a semisynthetic ion-exchange material named thiomont (a thioalkylated montmorillonite clay) was found to have a capacity of 65 mg of Hg/g of thiomont (2a). Treatment of the mercury-loaded thiomont with 0.1 M aqueous HCl resulted in exchange of H^+ for Hg^{2+} and regeneration of the original thiomont extractant. In the other report, a mesoporous silica with thioalkyl groups grafted to the surface had a capacity of 505 mg of Hg/g of material for the first extraction (2b). In this case, treatment of the mercury-loaded material with concentrated aqueous HCl resulted in removal of mercury from the material, but the recovered material had only 40% of its original capacity for mercury. For comparison, the capacity of activated charcoal is only 1 mg of Hg/g of charcoal (2h). Although these thioalkylated materials have a high capacity for mercury, their reuse would generate a significant volume of secondary waste consisting of an acidic aqueous solution of mercury.

The generation of secondary waste is a major consideration for a remediation process such as the decontamination of primary waste containing low concentrations of pollutants (e.g., $\leq 10^{-3} \text{ M}$ mercury). In general, waste management using separation technologies becomes more difficult and more expensive as feed concentrations in the wastestream decrease. For example, it has been shown that the volume of secondary waste produced per mole of pollutant recovered is inversely related to the feed concentration (3). Furthermore, in recent years tougher environmental regulations and the high initial cost of new, more effective, and more selective extractants have made the reuse of the extractant an increasingly important issue. For these reasons, the reuse of the extraction materials and the minimization of secondary waste volume must become the focus of scientific efforts in the near future. Therefore, in addition to (1) a large capacity for the target pollutant, a modern and effective extractant must simultaneously satisfy three other design criteria: (2) it must have a high selectivity for the target species; (3) it must allow for the recovery of the target species in a minimal volume of secondary waste; (4) it must be reusable (recyclable).

We are investigating the use of redox-active transition metal containing extractants for the separation and recovery of specific pollutant ions (4-6). A generic scheme for a complete redox-recyclable extraction and recovery (R^2ER) process is shown in Figure 1. Our strategy is based on the seminal electrochemical-switching work of Porter et al. (7), Martin et al. (8), Fabbrizzi et al. (9), Echegoyen, Gokel et al. (10), Shinkai et al. (11), and Beer et al. (12), but with an added emphasis on recovering the target ion in a minimal volume of secondary waste. These groups as well as others have shown that the binding of ions can be enhanced by electrochemically switching (or redox switching) an extractant molecule. However, when one considers practical factors such as duty-cycle time, extractant effectiveness over many cycles, extractant cost, and secondary-waste volume, much work remains to be done before useful R^2ER schemes can be developed and reduced to practice.

In this paper we report that (i) lithium-intercalated metal chalcogenides such as Li_xMoS_2 and Li_xWS_2 ($0.25 \leq x \leq 1.9$) will remove Hg^{2+} from aqueous solution; (ii) the capacity of Li_xMoS_2 can be as high as 580 mg of Hg/g of Li_xMoS_2 ; (iii) the concentration of mercury in an aqueous waste simulant

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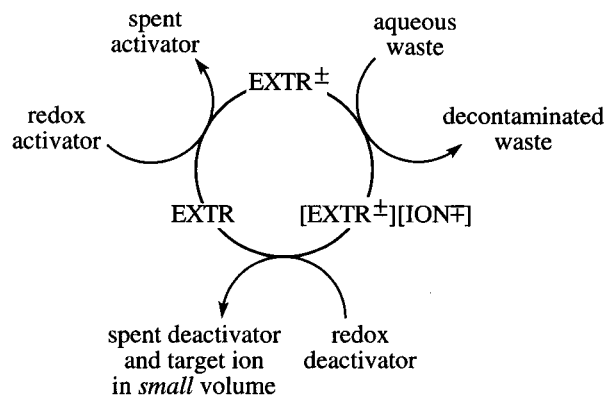


FIGURE 1. Complete, repeatable cycle of extraction, deactivation/recovery, and reactivation with a redox-recyclable extractant (EXTR). The EXTR species is oxidatively activated to EXTR^{\pm} if anions are to be extracted or reductively activated to EXTR^{-} if cations are to be extracted.

can be reduced from 1 mM $\text{Hg}^{2+}(\text{aq})$ (200 ppm) to 0.033(2) μM mercury (6.5 ppb) after one extraction with 5.0 equivalents of Li_xMoS_2 ; (iv) Li_xMoS_2 is more selective for $\text{Hg}^{2+}(\text{aq})$ than for $\text{Pb}^{2+}(\text{aq})$, $\text{Cd}^{2+}(\text{aq})$, or $\text{Zn}^{2+}(\text{aq})$; (v) greater than 94% of the ion-exchanged mercury in Hg_yMoS_2 is efficiently recovered in a cold trap, as metallic mercury, when Hg_yMoS_2 is heated under vacuum at 425 °C; and (vi) the molybdenum-containing material recovered after the heat-induced recovery step is essentially MoS_2 , which can be reactivated (recycled) to Li_xMoS_2 with *n*-BuLi in hexanes for another extraction-recovery cycle. Therefore, MoS_2 , WS_2 , and potentially other redox-active layered metal chalcogenides represent selective, redox-recyclable, cation-exchange materials that could be used in closed extraction-deactivation/recovery-reativation cycles similar to those reported by us for the extraction and recovery of $^{99}\text{TcO}_4^-$ and its nonradioactive surrogate ReO_4^- in a minimal volume of secondary waste using a redox-recyclable organometallic anion extractant (5). Our results suggest that R²ER of soft heavy metal ions is a viable concept and that redox-recyclable ion-exchange materials such as alkali metal-intercalated metal chalcogenides should continue to be developed and tested (obviously an activating agent that does not pose a safety hazard when used with large volumes of aqueous media would have to be used for an actual waste-remediation process).

Experimental Section

Distilled water was purified and deionized (to 18 M Ω) with a Barnstead Nanopure purification system. Nitric acid, hydrochloric acid, and metal nitrate salts were reagent grade or better. Schlenk, glovebox, and high-vacuum techniques were employed for some experiments (13). Purified, anhydrous hexane was prepared by stirring over H_2SO_4 (Mallinckrodt), flowing through activated basic alumina (Aldrich; 150 mesh), and distillation from sodium metal.

The concentrations of metal ions were determined by inductively coupled-plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer P400 ICP atomic emission spectrometer equipped with a high-salt nebulizer (the emission lines monitored were 670.781 nm for lithium, 202.030 nm for molybdenum, 194.227 nm for mercury, 220.353 nm for lead, 214.438 nm for cadmium, 213.856 nm for zinc, 334.941 nm for titanium, 226.230 nm for tantalum, and 207.911 nm for tungsten). Calibration curves, which were linear in concentration over the range 2.50–0.0500 mM were constructed using known concentrations of metal salts in each particular aqueous solution studied (i.e., matrix matching was used for all experiments). One standard was reanalyzed for at least every five samples during the course

of data collection. For each sample, five readings of the ICP-AES intensity were recorded and averaged. Selected samples were analyzed for mercury by cold vapor atomic absorption spectroscopy (Quest Diagnostics Biomonitoring, Ft. Collins, CO).

The black compounds Li_xMoS_2 , Li_xWS_2 , Li_xTiS_2 , and Li_xTaS_2 were prepared using literature procedures (14). In a typical experiment, 25 mL of *n*-BuLi (62.5 mmol; 2.5 M in hexanes; Aldrich) was added to a Schlenk flask containing 2.00 g of MoS_2 (12.5 mmol; Aldrich) and a Teflon-coated magnetic stir bar. The mixture was then stirred at 25 °C for 48 h under a nitrogen atmosphere. The solid product was recovered by filtration and was washed with two separate aliquots of dried hexanes. Samples of the lithium-intercalated materials were digested in aqua regia and analyzed for lithium and molybdenum by ICP-AES using standard procedures (15). For a fixed set of conditions (5 equiv of 2.5 M *n*-BuLi in hexanes per equiv of MoS_2 , 3 equiv of *n*-BuLi per equiv of WS_2 , TiS_2 , and TaS_2), the four black, nonstoichiometric materials $\text{Li}_{1.3}\text{MoS}_2$, $\text{Li}_{0.25}\text{WS}_2$, $\text{Li}_{1.5}\text{TiS}_2$, and $\text{Li}_{1.2}\text{TaS}_2$ were obtained (the lithium stoichiometry for $\text{Li}_{1.3}\text{MoS}_2$ was reproducible to within $\pm 7\%$). The concentration of commercial *n*-BuLi was determined by titration (13b).

The extraction experiments were performed as follows. Samples of the lithium-intercalated solid extractants were weighed, in a glovebox, into reaction flasks containing Teflon-coated stir bars. The stoppered flasks were then removed from the glovebox. For anaerobic extractions, the flasks were moved into an oxygen-free "wet" glovebox where samples of a deoxygenated aqueous solution containing 0.1 M HNO_3 and 1.00 mM $\text{M}(\text{NO}_3)_2$ were added. For aerobic extractions, the reaction flasks were opened immediately before the addition of the aqueous samples. In both cases, the mixtures, which contained black solids suspended in colorless supernatants, were vigorously stirred at 25 °C for 2 h and then filtered through a fritted-glass funnel. The filtrates, all of which could be exposed to air at this point, were collected, diluted to a constant volume, and analyzed for metal ions by ICP-AES. In some cases, the filtered black solids were digested in aqua regia until all of the solids had dissolved. The resulting homogeneous solutions were also analyzed by ICP-AES.

Hydrogen evolution experiments were performed using a specially designed vacuum-tight flask with two chambers. The inner chamber was loaded with the appropriate aqueous solution and thoroughly degassed by three freeze (−196 °C)–pump–thaw cycles. The outer chamber of the apparatus was then loaded with a weighed sample of Li_xES_2 in the glovebox. After nitrogen gas was removed from the outer chamber by evacuation on a high-vacuum line ($\leq 10^{-4}$ Torr), the two chambers were connected by opening a Teflon valve connecting them, and the solid and liquid phases were vigorously mixed by shaking at 25 °C. The apparatus was reattached to the vacuum line, and the pressure inside the apparatus, due to hydrogen gas and water vapor, was measured using a Baratron Model 122A electronic manometer. The pressure of hydrogen in the apparatus was determined by subtracting the known vapor pressure of water at 25 °C from the total pressure (the solubility of hydrogen in water is negligible; 16), and the amount of hydrogen gas evolved was calculated using the ideal gas law. Identical hydrogen evolution results were obtained in an experiment using a Toepler pump attached to two cold traps (−196 °C) in line with the apparatus. The captured noncondensable gas was identified as H_2 by gas chromatography.

Powder X-ray diffraction (XRD) measurements were recorded with a Philips diffractometer using $\text{Cu K}\alpha$ radiation. Powder patterns were compared with those on the PDF database. Scanning electron micrographs were obtained with a Philips 505 scanning electron microscope (SEM) using an accelerating voltage of 20 keV. Differential scanning calo-

TABLE 1. Extractions of Soft, Divalent, Heavy Metal Ions from 0.1 M Aqueous HNO₃ Using the Redox-Recyclable Ion-Exchange Materials Li_xES₂ (E = Mo, W, Ti, Ta)^a

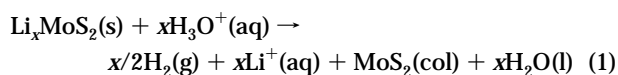
M ²⁺ (aq)	Li _x ES ₂ (s) ^b	initial E/M ²⁺ mol ratio	conditions	[M ²⁺ (aq)] _i , mM	M _y ES ₂ recovered ^c	([M ²⁺ (aq)] _i - [M ²⁺ (aq)] _f)/ [M ²⁺ (aq)] _i ^{d,e}
Hg ²⁺	Li _{1.3} MoS ₂	5.0	anaerobic	≤ 3.3 × 10 ⁻⁵ ^f	Hg _{0.20} MoS ₂	1.00(1)
Hg ²⁺	Li _{1.3} MoS ₂	5.0	aerobic	3.3 × 10 ⁻⁵ ^f	Hg _{0.20} MoS ₂	1.00(1)
Hg ²⁺	Li _{1.3} MoS ₂	4.4	aerobic	0.06	Hg _{0.24} MoS ₂	0.94(1)
Hg ²⁺	Li _{1.3} MoS ₂	3.0	aerobic	0.14	Hg _{0.29} MoS ₂	0.86(1)
Hg ²⁺	Li _{1.3} MoS ₂	2.0 ^g	aerobic	2.35	Hg _{0.32} MoS ₂	0.76
Hg ²⁺	Li _{0.25} WS ₂	2.0 ^g	aerobic	8.16	Hg _{0.09} WS ₂	0.18 ^h
Hg ²⁺	Li _{1.5} TiS ₂	2.0 ^g	aerobic	< 0.05 ⁱ	<i>j</i>	1.00
Hg ²⁺	Li _{1.2} TaS ₂	2.0 ^g	aerobic	< 0.05 ⁱ	<i>j</i>	1.00
Pb ²⁺	Li _{1.3} MoS ₂	5.0	anaerobic	0.26	Pb _{0.15} MoS ₂	0.74(1)
Pb ²⁺	Li _{1.3} MoS ₂	5.0	aerobic	0.59	Pb _{0.08} MoS ₂	0.41(2)
Cd ²⁺	Li _{1.3} MoS ₂	5.0	anaerobic	0.59	Cd _{0.08} MoS ₂	0.41(1)
Cd ²⁺	Li _{1.3} MoS ₂	5.0	aerobic	0.91	Cd _{0.008} MoS ₂	0.04(2)
Zn ²⁺	Li _{1.3} MoS ₂	5.0	anaerobic	0.87	Zn _{0.03} MoS ₂	0.13(1)
Zn ²⁺	Li _{1.3} MoS ₂	5.0	aerobic	0.98	Zn _{0.004} MoS ₂	0.02(1)

^a Unless otherwise noted, the extraction experiments consisted of (i) vigorously stirring a weighed quantity of solid Li_xES₂ with an aliquot of an aqueous solution containing 0.100 M HNO₃ and 1.00 mM M(NO₃)₂ for 2 h at 25 °C, (ii) filtering the extraction mixtures, and (iii) analyzing the filtrate for various metal ions by ICP–AES. ^b The values of *x* were determined by digesting samples of Li_xES₂ in aqua regia and analyzing the resulting solutions for lithium by ICP–AES. ^c The values of *y* were determined from the difference in initial and final aqueous concentrations of M²⁺, [M²⁺(aq)]_i, and [M²⁺(aq)]_f, respectively, which were determined by ICP–AES. ^d Unless otherwise noted, the theoretical maximum value of ([M²⁺(aq)]_i - [M²⁺(aq)]_f)/[M²⁺(aq)]_i for each experiment was 1.00. ^e One estimated standard deviation in the least significant digit is shown in parentheses. ^f Mercury concentration determined by cold vapor atomic absorption spectroscopy. ^g [Hg²⁺(aq)]_i = 0.0100 M. ^h The theoretical maximum value for this experiment was 0.25. ⁱ 50 μM mercury is the detection limit of our ICP atomic emission spectrometer under the conditions used in this study. ^j Li_{1.5}TiS₂ and Li_{1.2}TaS₂ were hydrolyzed under these conditions; the S²⁻ ions formed caused the precipitation of HgS (*K*_{sp} ~ 10⁻⁵⁰).

rimetry (DSC) measurements were performed with a Rheometric Scientific DSC Plus module.

Results and Discussion

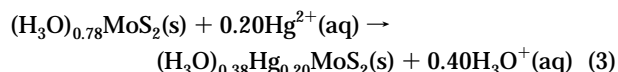
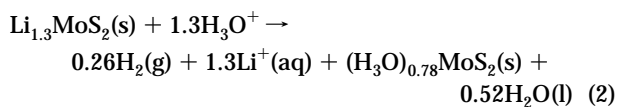
Extraction of Hg²⁺(aq) Using MoS₂. It is well-known that lithium-intercalated layered metal chalcogenides such as Li_xMoS₂ and Li_xWS₂ undergo exfoliation when treated with water (17). It is believed that H₂ gas formed in the interlamellar spaces forces apart the metal chalcogenide layers, producing high-surface-area colloids that are stable above pH 7. Note that 1 equiv of Li_xMoS₂ contains *x* equiv of reducing capacity relative to MoS₂ (i.e., one electron has been added to the MoS₂ conduction band for each intercalated lithium ion). Some investigators have claimed that all of the *x* reducing equiv in Li_xMoS₂ go into forming H₂, as shown in eq 1 (17a, 18). We measured the amount of H₂ gas



produced when samples of Li_{1.3}MoS₂ that had been stored in a nitrogen-filled glovebox were treated with aqueous 0.1 M HNO₃ under anaerobic conditions. The amount of H₂ collected, 0.26(5) equiv based on Mo (average of eight experiments), was less than the theoretical maximum of 0.65 equiv. Under these conditions (pH ~ 1), a flocculant black solid was formed instead of a metastable colloid. The solid exhibited a XRD pattern with a larger interlamellar spacing than MoS₂. Interestingly, the flocculant black solid did not contain any measurable Li⁺ (ICP–AES analyses of digested samples). On the basis of these results, we tentatively conclude that the flocculant black solid consists of small particles of (H₃O)_{0.78}MoS₂ or (H(H₂O))_{0.78}MoS₂. Therefore, eq 1 is incorrect in that it does not represent the fact that negatively charged molybdenum disulfide particles, which retain some ion-exchange capacity, are produced instead of a colloid of neutral MoS₂ particles. Complete characterization of the flocculant black solid and related materials will be reported in a subsequent paper (6a).

When 5.0 equiv of Li_{1.3}MoS₂ was treated with 1.0 equiv of 1.00 mM Hg(NO₃)₂ in 0.1 M HNO₃, the same amount of H₂ was collected as when mercury was absent (0.27(2) equiv;

average of three experiments). Furthermore, the observed decrease in the concentration of mercury in the aqueous supernatant corresponded to a Hg/Mo molar ratio of 0.20. Therefore, in this case, the flocculant black solid should be formulated as (H₃O)_{0.38}Hg_{0.20}MoS₂. Its formation can be represented by eqs 2 and 3, although the mechanism of

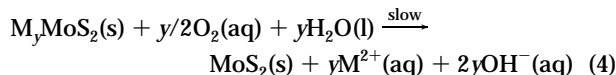


mercury intercalation (i.e., mercury extraction) may be more complex than shown in these idealized reactions. For the sake of brevity, the presumed hydronium component of (H₃O)_{0.38}Hg_{0.20}MoS₂ will be omitted for the remainder of this paper (e.g., (H₃O)_{0.38}Hg_{0.20}MoS₂ will be abbreviated Hg_{0.20}MoS₂). The driving force for the second reaction is undoubtedly the greater affinity of the soft Lewis acid Hg²⁺, relative to the hard Lewis acid H₃O⁺, for the soft Lewis base MoS₂^{-0.78}. Under these conditions, the final aqueous concentration of was ≤ 0.033(2) μM mercury (6.5 ppb). When the experiment was repeated in the presence of air, the final concentration of mercury was 0.033(2) μM (6.5 ppb). This value is slightly above the SDWA (19) acceptable level of 0.025 μM mercury (5.0 ppb). These experiments demonstrate that Li_xMoS₂ is capable of removing large amounts of mercury from aqueous solution to levels that are very close to those acceptable for drinking water.

When the initial mole ratio of Mo/Hg²⁺(aq) was changed from 5.0 to 4.4, 3.0, and 2.0, the fraction of mercury removed from solution ([M²⁺(aq)]_i - [M²⁺(aq)]_f)/[M²⁺(aq)]_i changed from 1.00(1) to 0.94(1), 0.86(1), and 0.76, respectively. The fractions 0.94, 0.86, and 0.76 correspond to flocculant black solid stoichiometries of Hg_{0.24}MoS₂, Hg_{0.29}MoS₂, and Hg_{0.32}MoS₂ respectively. These and related results are listed in Table 1. When the black, mercury-loaded solid from an extraction experiment for which the initial Mo/Hg²⁺(aq) mole ratio was 2.0 was digested in aqua regia and analyzed by

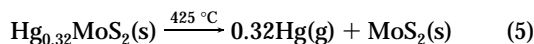
ICP–AES for mercury and molybdenum, the stoichiometry was found to be $\text{Hg}_{0.35}\text{MoS}_2$ instead of $\text{Hg}_{0.32}\text{MoS}_2$. Therefore, we conclude that the stoichiometries listed in Table 1 are probably accurate to within $\pm 10\%$. Note that 0.32 is less than 0.65, the theoretical maximum based on complete $\text{Li}^+/\text{Hg}^{2+}$ ion exchange for $\text{Li}_{1.3}\text{MoS}_2$, and is less than 0.39, the theoretical maximum based on complete $\text{H}_3\text{O}^+/\text{Hg}^{2+}$ ion exchange for $(\text{H}_3\text{O})_{0.78}\text{MoS}_2$. If $\text{Hg}_{0.32}\text{MoS}_2$ is the limiting stoichiometry for divalent mercury extraction by $\text{Li}_{1.3}\text{MoS}_2$, then the capacity of the lithium–intercalated molybdenum disulfide under these conditions is 380 mg of Hg/g of $\text{Li}_{1.3}\text{MoS}_2$. Therefore, $\text{Li}_{1.3}\text{MoS}_2$ is a very effective ion-exchange extractant for aqueous Hg^{2+} . Control experiments showed that the unactivated extractant MoS_2 extracted only a negligible amount of Hg^{2+} from an identical waste simulant.

Extraction of Other Heavy Metal Ions Using MoS_2 . In a series of extraction experiments, samples of $\text{Li}_{1.3}\text{MoS}_2$ were vigorously stirred at 25 °C for 2 h with aliquots of oxygen-free 0.1 M HNO_3 containing 0.20 equiv of $\text{M}(\text{NO}_3)_2$ (i.e., initial $\text{Mo}/\text{M}(\text{NO}_3)_2$ mole ratio = 5.0; $\text{M}^{2+} = \text{Hg}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+},$ or Zn^{2+} ; $[\text{M}^{2+}(\text{aq})]_i = 1.00$ mM). After separating the supernatants from the flocculant black ion-exchanged M_yMoS_2 solids by filtration, the final concentration of $\text{M}^{2+}(\text{aq})$ in each of the filtrates was determined by ICP–AES analysis. The ratios $([\text{M}^{2+}(\text{aq})]_i - [\text{M}^{2+}(\text{aq})]_f)/[\text{M}^{2+}(\text{aq})]_i$, listed in Table 1, were 1.00(1) for Hg^{2+} , 0.74(1) for Pb^{2+} , 0.41(1) for Cd^{2+} , and 0.13(1) for Zn^{2+} . When these experiments were repeated in the presence of air, the corresponding ratios were 1.00(1) for Hg^{2+} , 0.41(2) for Pb^{2+} , 0.04(2) for Cd^{2+} , and 0.01(1) for Zn^{2+} . Clearly, the presence of oxygen reduced the capacity of $\text{Li}_{1.3}\text{MoS}_2$ for lead, cadmium, and zinc but not for mercury. We tentatively conclude that O_2 must oxidize solid M_yMoS_2 ($\text{M} = \text{Pb}, \text{Cd}, \text{Zn}$), as shown in eq 4. Note that the selectivity



of the $\text{Li}_{1.3}\text{MoS}_2$ for the four ions, $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$, was qualitatively the same whether or not air was present. Note also that the slow reaction with O_2 represents a potential method for redox-recovering Pb^{2+} , Cd^{2+} , and Zn^{2+} from the heavy metal loaded solid extractants and for redox-recycling MoS_2 .

Recovery of Mercury from Hg_xMoS_2 . As discussed in the Introduction, extractant capacity and selectivity are only two of the four important design criteria for modern extractants. The other two criteria are the feasibility of recovering the pollutant in a minimal volume of secondary waste and the feasibility of reusing the extractant once the pollutant has been recovered. Since mercury could not be recovered from $\text{Hg}_{0.32}\text{MoS}_2$ by oxidation with O_2 , another method was investigated. When $\text{Hg}_{0.32}\text{HgS}_2$ was heated under vacuum to 425 °C, the entropy-driven internal redox reaction depicted in eq 5 resulted in the formation of mercury vapor and



polycrystalline MoS_2 (confirmed by XRD). The Hg vapor was collected in a cold trap at -196 °C. This procedure resulted in the recovery of $>94\%$ of the mercury originally present in $\text{Hg}_{0.32}\text{MoS}_2$ as elemental mercury. Only a trace amount of mercury was detected by ICP–AES when the recovered MoS_2 was digested in aqua regia (specifically, the stoichiometry of the recovered compound was $\text{Hg}_{0.02}\text{MoS}_2$). Note that elemental mercury represents the smallest possible volume for mercury-containing secondary waste, although its liquid and volatile nature might pose disposal problems that would not arise with a solid, nonvolatile waste form. However, it is possible that the elemental mercury recovered in a mercury

TABLE 2. Use of a Sample of Li_xMoS_2 for Three Consecutive Mercury Extraction-Deactivation/Recovery-Reactivation Cycles^a

$$\text{Li}_x\text{MoS}_2 \xrightarrow[0.1\text{ M HNO}_3(\text{aq})]{\text{Hg}^{2+}(\text{aq})} \text{Hg}_y\text{MoS}_2 \xrightarrow[-\text{Hg}^0]{\text{heat, vacuum}} \text{Hg}_z\text{MoS}_2$$

$$\uparrow \qquad \qquad \qquad \downarrow$$

$$\qquad \qquad \qquad n\text{-BuLi}$$

cycle	x value ^b		y value ^c		z value ^d
	n-BuLi titration	Li/Mo ratio from digestion	digestion	filtrate	
1	1.4	1.3	0.35	0.32	0.02
2	1.7	1.6	0.39	0.50	<0.01
3	2.0	1.8	0.50	0.50	<0.01

^a Samples of Li_xMoS_2 were prepared by treating weighed samples of MoS_2 with a 5-fold excess of 2.5 M $n\text{-BuLi}$ in hexane. Extraction consisted of (i) vigorously stirring a weighed quantity of solid Li_xMoS_2 with 0.5 equiv of 10.0 mM $\text{Hg}(\text{NO}_3)_2$ (based on Mo) in 0.1 M aqueous HNO_3 for 2 h at 25 °C in the presence of air; (ii) filtering the extraction mixtures; and (iii) analyzing the filtrate and the solid for lithium, mercury, and molybdenum by ICP–AES. Deactivation (recovery of mercury) consisted of heating the solid samples of Hg_yMoS_2 under vacuum at 425 °C for 6 h. Reactivation consisted of treating Hg_zMoS_2 with a 5-fold molar excess of $n\text{-BuLi}$ (based on Mo) as above. ^b The values of x were determined by (i) titrating the $n\text{-BuLi}$ that remained after activation of MoS_2 or Hg_yMoS_2 with 2-butanol and (ii) digesting samples of Li_xMoS_2 in aqua regia and analyzing the resulting solutions for lithium and molybdenum by ICP–AES. ^c The values of y were determined by (i) digesting samples of Hg_yMoS_2 in aqua regia and analyzing the resulting solutions for mercury and molybdenum by ICP–AES and (ii) determining the difference in initial and final concentrations of mercury for the extraction step. ^d The values of z were determined by digesting samples of Hg_zMoS_2 in aqua regia and analyzing the resulting solutions for mercury and molybdenum by ICP–AES.

remediation process based on chemistry similar to that described above might be recycled or sold, not discarded.

The thermal removal of mercury from $\text{Hg}_{0.32}\text{MoS}_2$ and regeneration of MoS_2 was monitored using differential scanning calorimetry (DSC). The DSC of $\text{Hg}_{0.32}\text{MoS}_2$ displayed an endothermic peak at 340 °C upon heating from 25 to 600 °C. The endothermic peak may correspond to the vaporization of elemental mercury (bp = 357 °C) (16). This observation is consistent with our explanation that mercuric ion, present in $\text{Hg}_{0.32}\text{MoS}_2$, is first reduced by an internal redox reaction and then vaporized as metallic mercury from the host MoS_2 layers.

A single sample of $\text{Li}_{1.3}\text{MoS}_2$ was treated with 10.0 mM $\text{Hg}(\text{NO}_3)_2$ (Mo/Hg^{2+} mole ratio = 2.0) in 0.1 M HNO_3 , deactivated at 425 °C under vacuum and reactivated with $n\text{-BuLi}$ through three complete cycles. The conditions (temperature, time, initial molar ratios) were kept constant for all three cycles. The results are listed in Table 2, which also depicts the complete extraction-deactivation/recovery-reactivation cycle. No detectable mercury was found in Hg_zMoS_2 after the first cycle. Interestingly, more mercury was extracted for the second cycle than for the first and more was extracted for the third than for the second. This is apparently due to a greater value of x for Li_xMoS_2 as the material is cycled. We believe that the increase in x is due to faster reductive intercalation of lithium as the MoS_2 extractant is recycled. The increased rate of reductive intercalation is most likely due to a decrease in the particle size of the recycled material relative to native MoS_2 . Figure 2 shows the scanning electron micrographs of (a) native MoS_2 (before the first activation), (b) deactivated extractant after one complete cycle, and (c) deactivated extractant after two complete cycles. There appears to be a decrease in the average particle size as the material is cycled. The observed decrease in particle size is probably due to the several cycles of exfoliation and reflocculation that the material experienced during this procedure. A smaller MoS_2 particle size might increase the rate of reductive intercalation of MoS_2 by $n\text{-BuLi}$. This in turn would lead to a higher value of x (in Li_xMoS_2)

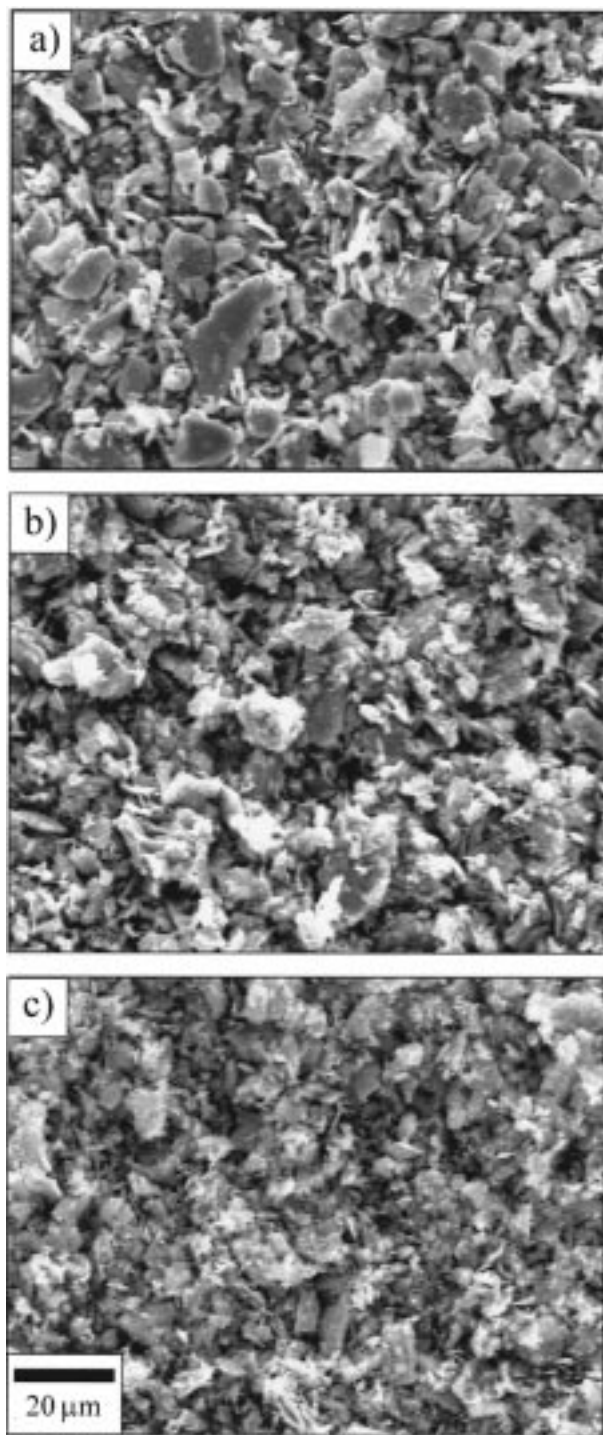


FIGURE 2. Scanning electron micrographs of a sample of molybdenum disulfide before activation and after one and two complete cycles of activation, extraction, and deactivation/recovery: (a) native molybdenum disulfide (before the first activation); (b) deactivated extractant after one complete cycle; (c) deactivated extractant after two complete cycles.

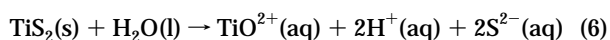
when MoS_2 is treated with *n*-BuLi for a fixed amount of time. In any event, the data in Table 2 clearly show that Li_xMoS_2 can be used for several complete extraction-deactivation/recovery-reativation cycles without a significant loss of activity. The average stoichiometries $\text{Li}_{1.9}\text{MoS}_2$ and $\text{Hg}_{0.50}\text{MoS}_2$ observed for the third cycle result in a calculated ion-exchange capacity of 580 mg of Hg/g of $\text{Li}_{1.9}\text{MoS}_2$. Recall that thioalkylated mesoporous silica takes up 505 mg of Hg/g of material for the first extraction cycle (2b).

The extraction ratios for Hg^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} when 5.0 equiv of $\text{Li}_{1.3}\text{MoS}_2$ was used were 1.00(1), 0.74(1), 0.41(1), and 0.13(1), respectively. These extraction ratios correlate with the decreasing E° values for $\text{M}^{2+/0}$ redox couples, 0.85, -0.12 , -0.40 , and -0.76V , respectively (20). Since $\text{Li}_{1.3}\text{MoS}_2$ is a strong reducing agent (i.e., it reduces water to H_2), it is possible that it could also reduce the aqueous heavy metal ions to heavy metal atoms, which could adsorb to the surfaces of the MoS_2 particles. In other words, the oxidation states of the mercury and molybdenum in Hg_yMoS_2 could be $2+$ and $(4 - 2y)+$, respectively, 0 and $4+$, respectively, or any values between these limits. To elucidate the oxidation states and coordination environments of mercury and the molybdenum, we have started a X-ray photoelectron (XPS), X-ray near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) investigation of these compounds. A more detailed analysis and discussion of these results will be presented in a subsequent paper (6a). Here we simply note that $\text{Hg}_{0.32}\text{MoS}_2$ appears to contain mostly Hg^{2+} with a small amount of Hg_2^{2+} . Clearly, the presence of Hg_2^{2+} indicates that some reduction of Hg^{2+} , by a reduced form of molybdenum, has taken place. However, there was no evidence of elemental mercury in any of the compounds. Therefore, the elemental mercury recovered when Hg_yMoS_2 was heated was formed during the deactivation/recovery step, not during the extraction step.

Extraction of $\text{Hg}^{2+}(\text{aq})$ Using Other ES_2 -Based Extractants (E = W, Ti, Ta). We have also investigated other lithium-intercalated layered metal sulfides as extractants for $\text{Hg}^{2+}(\text{aq})$. Samples of $\text{Li}_{0.25}\text{WS}_2$, $\text{Li}_{1.5}\text{TiS}_2$, and $\text{Li}_{1.2}\text{TaS}_2$ were treated with 0.50 equiv of 10.0 mM $\text{Hg}(\text{NO}_3)_2$ in 0.1 M HNO_3 . The results are listed in Table 1. All three compounds remove substantial amounts of Hg^{2+} from aqueous solution. The results for $\text{Hg}_{0.09}\text{WS}_2$ indicate that solid $\text{Li}_{0.25}\text{WS}_2$ is very effective at taking up mercury. If one considers that the maximum amount of $\text{Hg}^{2+}(\text{aq})$ that could be taken up by $\text{Li}_{0.25}\text{WS}_2$ is 0.12 equiv, then the material is utilizing 75% of its total theoretical capacity. Control experiments showed that unactivated WS_2 extracted only a negligible amount of $\text{Hg}^{2+}(\text{aq})$ from an identical waste simulant.

The compounds $\text{Li}_{1.5}\text{TiS}_2$ and $\text{Li}_{1.2}\text{TaS}_2$ displayed a very high capacity for $\text{Hg}^{2+}(\text{aq})$. However, control extraction experiments showed that TiS_2 and TaS_2 removed essentially the same amount of $\text{Hg}^{2+}(\text{aq})$ as did their lithium-intercalated analogues. Several lines of evidence indicate that $\text{Hg}^{2+}(\text{aq})$ was not removed by a reversible ion-exchange process, as was the case with MoS_2 . For example, XRD patterns of solids present after $\text{Hg}^{2+}(\text{aq})$ was extracted using either $\text{Li}_{1.5}\text{TiS}_2$ or TiS_2 indicated the presence of only TiS_2 and HgS . The XRD patterns indicated that the HgS was present as a mixture of two polymorphs (21). The 001 line for $\text{Hg}_{1.24}\text{TiS}_2$ was not observed ($2\theta = 10.2^\circ$) (22). Similar results were obtained for $\text{Hg}^{2+}(\text{aq})$ extractions using either $\text{Li}_{1.2}\text{TaS}_2$ or TaS_2 : the 001 line for $\text{Hg}_{1.0}\text{TaS}_2$ ($2\theta = 9.9^\circ$) (23) was not observed. In addition, ICP-AES analysis showed that the filtrates from $\text{Li}_{1.5}\text{TiS}_2$ or TiS_2 extractions contained significant amounts of soluble titanium. Finally, the strong odor of H_2S was detected whenever $\text{Li}_{1.5}\text{TiS}_2$ or TiS_2 was used for aqueous extractions. In contrast, when $\text{Li}_{1.3}\text{MoS}_2$ is used to extract $\text{Hg}^{2+}(\text{aq})$ (i) the XRD pattern was consistent with Hg_yMoS_2 (6a) and was inconsistent with MoS_2 and/or HgS , (ii) ICP-AES analysis indicated a negligible amount of soluble molybdenum species, and (iii) the odor of H_2S was not detected.

The presence of HgS lines in the XRD patterns can be explained if S^{2-} anions are formed during the extraction process. Titanium disulfide is known to undergo a complicated set of hydrolysis reactions (24). One greatly simplified possible reaction is shown in eq 6. If this reaction or a



similar reaction occurred to an appreciable extent in our experiments, then a significant amount of S^{2-} anions would have been available for the precipitation of HgS ($K_{sp} \sim 10^{-50}$). According to Table 1, the $Hg^{2+}(aq)$ extractions using titanium-based solids extracted all of the available $Hg^{2+}(aq)$. The extractions were performed with an initial $Ti/Hg^{2+}(aq)$ ratio of 2.0; it is therefore possible that all of the $Hg^{2+}(aq)$ cations originally present could be converted to HgS by the hydrolysis of only one-fourth of the TiS_2 originally present.

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