

FINAL REPORT

Studies funded by the DOE-Environmental Management Program - DE-FG07-96ER14696 "Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams using Redox-Active Layered Materials" P. K. Dorhout, S. H. Strauss, PI's. Colorado State University.

PARTS OF THIS REPORT CONTAIN PROPRIETARY INFORMATION DISCLOSED IN A PATENT DISCLOSURE TO COLORADO STATE UNIVERSITY.

The goals of this program have been to develop a series of new compounds that act as redox-recyclable heavy metal ion selective materials. This has been a preliminary exploration into the viability of creating materials that act as selective exchange media. We have historically been involved in the separation of ionic pollutants such as radionuclides or toxic heavy metal ions from water by designing extractants with high selectivities and large capacities. We have also recognized that there is a more urgent need to develop processes that allow the target pollutants to be recovered in a minimal volume of secondary waste and that allow the extractants to be reused or recycled. We have been studying redox-active transition-metal-containing extractants that undergo reversible electron transfer activation and deactivation as the target ions are extracted and recovered or that undergo efficient, selective ion exchange.

The redox-recyclable extractants investigated so far include molecular organometallic complexes such as substituted ferrocenes and layered metal chalcogenides or oxochalcogenides such as MoS_2 and $\text{Zr}(\text{HSPO}_3)_2$. The molecular complexes can be dissolved in water-immiscible organic solvents for solvent-extraction processes or can be immobilized on inert supports for ion-exchange chromatography. The bulk metal chalcogenide solids themselves function as redox-recyclable or ion-exchangeable materials. We have thus demonstrated in the laboratory the viability of design and function of new compounds that are ion-selective solids or selective composites. The proposed work herein will demonstrate the applicability that these materials possess and will study the effectiveness of these and newly developed materials in complex mixtures of ions and organics.

Using activated MoS_2 , greater than 99% of mercury was selectively extracted from an aqueous phase containing 1 M HNO_3 and 10^{-3} M Hg^{2+} , reducing the mercury concentration to ppt levels ($k_D = 10^7$). Greater than 94% of the mercury could be recovered in elemental form after stripping giving an overall reduction in waste volume of more than 10^4 . These are just a few examples of how we have been able to effectively design and test materials for selective ion removal from simulated contaminated waste streams.

New compounds developed in our laboratories provide clear-cut evidence that continued efforts in new materials design and synthesis are effective means to solving mixed waste problems. For example, the reaction between aqueous solutions of zirconium or hafnium chlorides and Na_2SPO_3 result in the formation of a high surface-area gel that can be dried into a powder with a composition $\text{M}(\text{HSPO}_3)_2$ where $\text{M} = \text{Zr}$ or Hf . These layered materials provide a surface of HS^- within the interlayer gallery of the solids that are selective for soft metal cations such as lead, mercury or cadmium when in competition with alkali or alkaline earth ions. A view of these layered galleries is shown in Fig 1.

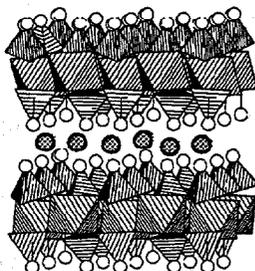


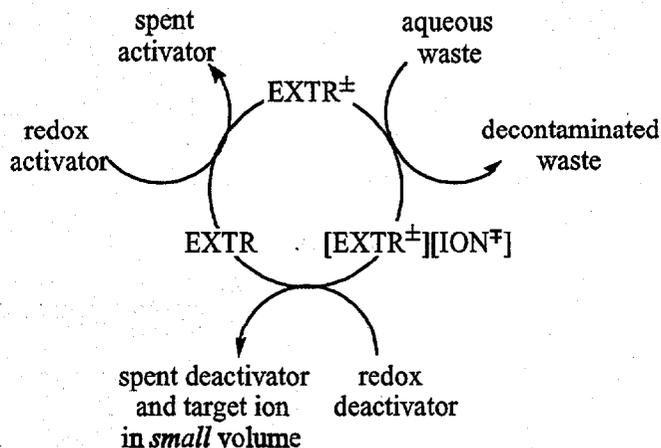
Fig. 1. Cd intercalated $\text{Zr}(\text{PSO}_3)_2^{2-}$.

Cadmium can be removed from the solids by washing with mild acid solutions, for example, reconstituting the original solid for reuse. Further modifications of similar materials are under study.

In all of our studies, we have examined not only the ion exchange behavior of our compounds but the fundamental processes by which these compounds select, hold, and exchange the ions of interest. These studies have been critical to developing an understanding of the principles that govern the design of new materials for other problems such as mixed hazardous wastes - the focus of this program. For example, we have utilized not only X-ray diffraction techniques for structural elucidation, but we have employed Extended X-ray Absorption Fine Structure techniques to understand how selected contaminant ions such as Hg(II) interact with the host compound matrix. We now believe that the selectivity can be traced to the complex and intimate bonding relationship that exists between the soft cation of choice and the soft anionic matrix which includes coordination geometry and metal oxidation state. Knowledge of these key features has led us to develop new solids such as the zirconium thiophosphate discussed above which is selective for cadmium. This demonstrated expertise will allow our proposed program to be successful at fine-tuning materials that will be selective for specific cations that reside within very complex mixtures.

We have shown, for example, that the complexed mercury in and EDTA-Hg(II) solution can be readily extracted into activated MoS₂ given that mercury ions will prefer the geometric constraints of the solid guest-host Hg_xMoS₂ composite over the organic complex. Indeed, it is likely that our solids will compete favorably over other organic contaminants and naturally occurring complexants that we will encounter in our target mixed waste solutions.

In all, we have been investigating a relatively underexplored strategy in waste remediation, the use of redox-active transition-metal containing extractants for the separation and recovery of specific pollutant cations or anions. We have named this strategy Redox-Recyclable Extraction and Recovery (R²ER). Our investigations have been based on the seminal electrochemical-switching work of Porter, Martin, Fabbri, Echegoyen, Gokel, Shinkai, and Beer, *but with an added emphasis on recovering the target pollutant 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 an extractant molecule. However, when one considers practical factors such as duty-cycle time, extractant stability under harsh conditions, extractant effectiveness over many cycles, extractant costs, and secondary-waste volumes, much work needs to be done before useful R²ER schemes such as ours can be developed and reduced to practice.



Organic Polymer Matrix Studies. The goal of organic polymer matrix processing has been to develop a polymer/extractant mixture that will act to disperse the extractant so as to increase the overall surface area of the absorbing material and to facilitate the regeneration of that material. We have targeted both electrochemically active and inert polymer matrices so as to test the viability of employing

electrochemistry as a potential redox-active material switch. Our group has the electrochemical equipment and experience to explore these materials in house.

Recently, we have electrochemically grown films of polypyrrole from a mixture containing a colloid of activated H_xMS_2 particles. This procedure resulted in the encapsulation of layered H_xMS_2 solids within the polymer matrix, as shown in Fig. 2. The encapsulation of materials within polymer matrices is known to occur but no one has studied the ion-exchange ability of these encapsulated materials. We have grown polymer films of polypyrrole from various mixture concentrations of pyrrole and MS_2 suspensions on platinum foil electrodes. The redox activity of the finely-divided extractant on the electrode is currently being established through routine electrochemical methods, and the activity toward our target cations will be determined. The recyclability of the materials will also be demonstrated by electrochemical means. The viability of the electrochemical redox methods will also be demonstrated in solutions that contain mixtures have the organic components of the target systems. Finally, K_D values for the cations of interest will also be determined, where K_D is the ratio of mmole contaminant absorbed per gram of extractant to the mmole of contaminant remaining in solution by volume. These studies will be extended into modified polypyrroles, polyaniline, and polythiophene, each of which has a unique redox couple and region of electrochemical stability, in a given pH range.

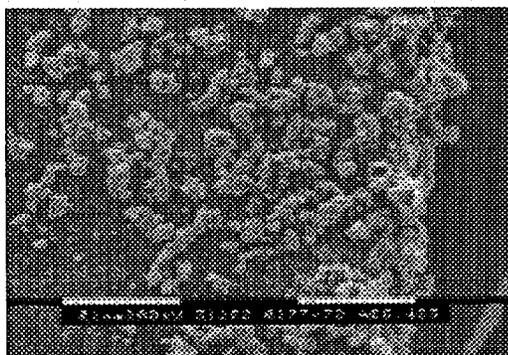


Fig. 2 SEM micrograph of MoS_2 in polypyrrole on a Pt electrode.

Inorganic Matrix Studies. The goal of sol-gel processing of materials has been to control the structure of that material on a nanometer (macromolecular) scale from the earliest stages of processing. Indeed, as precursors to high-surface area ceramics and monoliths, sol-gels offer the ability to prepare high-purity and high-integrity porous or dense ceramics. Sol-gel solids have been shown to be effective materials for supporting and retaining transition metal complexes. We have demonstrated that our MS_2 ($M=Mo, W$) solids can be encapsulated within a silica matrix and maintain their sorptive abilities. For example, hydrolysis of solution of activated H_xMoS_2 and $Si(OCH_3)_4$ yielded a highly porous material, shown in a transmission electron micrograph, Figure 3, that can readily sorb mercury from aqueous solutions. Figure 3 shows the dark spots, small particles of silicate, large objects, particles of MS_2 , and thin veils of silicate surrounding large pores through which solutions can flow unimpeded. Flow studies need to be performed to determine the extent of flow improvement over neat, activated Li_xMoS_2 .

In addition to providing a larger surface area for contact of the Li_xMS_2 solids with contaminated solutions, the sol-gel matrix provides stability of the solids by encapsulating the extractant within a matrix. We have shown that the extractant particle size changes over time with activation and deactivation. This is due to the kinetics of intercalation of the contaminant within the extractant matrix - a mechanism that pries apart the layered solids and results in partial exfoliation of the extractant. The gel- MS_2 matrix comprises very small particles of MS_2 , as seen in the micrograph, that are nearly single layer. Consequently, exfoliation of the extractant is minimized; thus, the materials do not degenerate with time and create flow and filter problems. It will be important to study the chemistry of these gel materials by selecting several different gels and gel precursors. This can be accomplished by changing the organic oxide in the silicon precursor - methoxy-, ethoxy-, neopentoxy-, for example. These

changes effect the gelation time which in turn effects the viscosity of the gel, hence the density of the solid that forms. The density of these sol-gel solids (in the solid phase they are called aerogels or xerogels, depending upon density and preparation) will determine the surface area and flow-through characteristics.

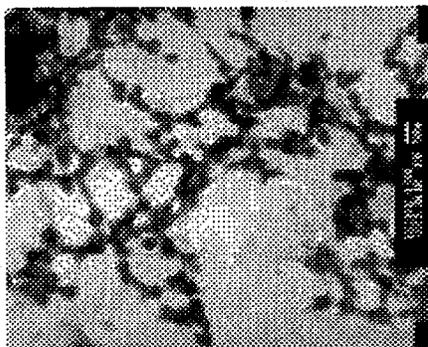


Fig. 3. TEM image of gel-MS₂ matrix showing a large MoS₂ particle in the upper left-hand corner.

THIS SECTION CONTAINS PROPRIETARY INFORMATION. Mesoporous Materials. Recently, we have demonstrated that the use of low-temperature template-assisted syntheses results in hexagonally ordered mesostructured zirconium thiophosphates. The surfactant cetyltrimethylammonium bromide, C₁₆H₃₃(CH₃)₃NBr, was used to template the formation of these materials. The exact conditions to prepare these materials has been disclosed in a patent disclosure in 8/99. The new material has proven to be an effective extractant for heavy metal cations in solutions of acidic media or neutral pH. A schematic diagram of these materials is shown below, based on TEM and XRD analysis. The structure is similar to the MCM-41 silicate materials.

