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ENVIRONMENTAL APPLICATION OF MINERAL SULFIDES FOR REMOVAL OF GAS-PHASE HG(0) AND AQUEOUS HG²⁺

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ABSTRACT

Synthesized and commercially available metal sulfides were evaluated for their ability to adsorb elemental and ionic mercury. The coinage group metal sulfides adsorb elemental Hg(0) vapor stoichiometrically. The mechanism of Hg(0) uptake by the copper and gold sulfides is a redox process resulting in the formation of HgS. The mechanism in the case of Ag₂S involves redox but there is no HgS formation. The relative rates of Hg(0) adsorption increases in the order CuS > Ag₂S > Au₂S > Au₂S₃ corresponding to the metal ion reduction potentials.

The relative rate of Hg(0) adsorption for commercial grade CuS is increased by an activation process which involves making a slurry of the metal sulfide in concentrated oxalic acid followed by drying and then exposure to Hg(0). Relative rates of Hg(0) adsorption were also increased by decreasing the particle size of the metal sulfides. Particle sizes were decreased by synthesis of the metal sulfide in the presence of the particle-size mediating agent CTAB.

The metal sulfides remove ionic mercury from acidic solutions by precipitation with the dissolved sulfide forming HgS. In acidic solution there was no evidence of physical or chemical adsorption between Hg(0) and the metal sulfide. The quantity of ionic Hg²⁺ removal from aqueous solutions is correlated with the solubility of the metal sulfide. Cu₂S was the most soluble metal sulfide tested and thus removed the most ionic mercury from solution by precipitating HgS.

INTRODUCTION

Mercury can have adverse affects on the environment and human health, thus reduction of its environmental concentration coupled with removal is of great importance. Hg poses a serious problem whether it is elemental, aqueous, or present in ligated forms. (1) The emission of waste from incinerators, fossil fuel burning power plants, smelters, and other industrial processes is a serious concern for both private industry and government facilities. Because of the volatility of Hg it exists in the gas phase in the emissions of these processes. The environmental problems associated with Hg are numerous with the long-term bioaccumulation of Hg being one of the most significant concerns. Aqueous and ligated forms of Hg are generated from various industrial and government facilities and are no less of a concern than Hg generated from emission type sources. Today's technology provides no practical and cost effective measure for Hg abatement. Current scrubbing systems only remove 90% of airborne Hg. The development of a more effective scrubbing system is needed and would result in significant benefits not only for the waste producers but also the consumers that utilize finished products from Hg producing processes. Additionally it is important that the Hg removal process does not generate additional waste. The Hg removal reagents or processes must either be regenerative or the end product needs to be usable, marketable, or stable enough for immediate disposal for cost effective Hg abatement. (1-5)

These concerns have spurred the research and testing of various processes designed for the removal of effluent Hg vapor and aqueous Hg²⁺ waste. (4-7) There has been significant progress in the development of processes for the removal of Hg from waste sources. One innovative technology for the removal of Hg from both gaseous and aqueous sources involves use of metal sulfides. A Russian patent describes a process utilizing a metal sulfide that has Hg adsorbing abilities for airborne elemental Hg vapors. (8) Several transition metal sulfides have shown evidence of the ability to adsorb Hg vapor. (9-11) Metal sulfides have also been shown to have the ability to remove Hg²⁺ from aqueous waste sources. (12) The main reason for the interest in the testing and development of metal sulfides



in gas phase Hg abatement is cost related. One effective technique is the removal of Hg with activated carbon and sulfur, but that is prohibitively expensive. (13)

Understanding the mechanism for Hg adsorption into a solid state metal sulfide would greatly help in the further development and exploration of compounds with better Hg adsorbing properties. The metal sulfide chosen for Hg removal will depend on the chemical state and environment of the Hg waste. For example Strauss and Dorhout have shown aqueous Hg^{2+} to be removed by an intercalation mechanism. (14) They have shown Hg^{2+} will intercalate into a non-stoichiometric molybdenite compound. Since the removal by intercalation of the Hg^{2+} ion does not involve conventional covalent bonding between the Hg and the metal sulfide, the layered structure of the solid state compound is important. Early transition metal sulfides such as molybdenite have multiple bonds to sulfur resulting in less ability for the sulfur to bond with other atoms. The tendency for metal-sulfur multiple bonding of the early transition metal sulfides in each row render them more substitutionally inert than the late transition metal sulfides in each row. This would suggest that the removal of Hg by the early transition compounds would probably occur via an intercalation type mechanism.

In the case of the late transition metal sulfides that undergo gas phase Hg(0) removal the Hg is removed by bonding to the sulfur on the metal sulfide. The late transition metals of the metal sulfides are electron rich and are regarded as having metal-sulfur single bonds. Unlike the metal sulfur double bond character of the early transition metals the single bond of the late transition metal sulfides leaves the sulfur with lone electron pairs thus facilitating bonding with Hg.

The studies described here have attempted to advance previous work by not only studying the capacities and rates of Hg(0) vapor adsorption by the metal sulfides but also understanding the mechanism of Hg adsorption.

EXPERIMENTAL METHODS

Reagent grade metal nitrate was utilized for each synthesis except in the case of iron the dichloride was used. All reagents were used as received without further purification including, metal nitrates, $Na_2S \cdot 9H_2O$, oxalic acid, cetyltrimethylammoniumbromide (CTAB), $Hg(NO_3)_2 \cdot H_2O$, and ethanol. Elemental Hg was spectrophotometric grade that was on hand and used as received. Acidic solutions were made from concentrated reagent grades and used without further purification. Water was purified to $17M\Omega$ on an E-pure system. 325 mesh Cu_2S (chalcocite), 100 mesh CuS 99+% (Covellite), Au_2S_3 99.9%, Au_2S 99.9%, Ag_2S 99.9% were purchased from Aldrich chemical and were used as received.

All metal sulfides that are termed synthetic were prepared at the Idaho National Engineering and Environmental Laboratory (INEEL). The general procedure for the aqueous precipitation synthesis of the metal sulfides was taken from the literature method. (15)



Activation of the Metal Sulfides

Activation of the metal sulfide was accomplished by stirring the metal sulfide in a saturated aqueous solution of oxalic acid at room temperature. The metal sulfide was then filtered and allowed to dry at room temperature before exposure to Hg(0).

Removal of Hg(0) Vapor using Metal Sulfides

The metal sulfide was weighed and placed into a small recrystallization dish. The dish containing the metal sulfide was then placed into a closed container (desiccator) which also contained a separate dish with elemental Hg. The metal sulfide samples were periodically removed from the desiccator and the change in mass was measured. When there was no longer an increase in mass of a sample with further exposure to Hg(0) vapors the powder x-ray diffraction pattern (XRD) was obtained. The mole equivalents of Hg(0) incorporated into the sample is also calculated from the total mass increase of the metal sulfide sample. The x-ray diffraction pattern was used to indicate if structural changes have occurred to the metal sulfide and the total mass of mercury incorporated indicates the Hg(0) saturation concentration of the metal sulfide. The rates of adsorption are only relative rates as a result of the apparatus and data obtained. Temperature was maintained by placing the desiccator inside an oven, which was accurate to within $\pm 1^{\circ}\text{C}$. Hg concentrations inside the desiccator are 720ppm at 42°C , 1120ppm at 68° and 2500ppm at 90°C .

Removal of Hg^{2+} from aqueous solutions using Metal Sulfide

Ionic Hg^{2+} removal was determined using $5.0 \times 10^{-3}\text{M}$ (40ppm) standard solutions of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in $.1\text{M HNO}_3$. To the standard solutions 5 mole equivalents of each metal sulfide was added. The mole equivalents of metal sulfide to ionic Hg^{2+} were calculated based on the assumption of a 1:1 reaction. The mixtures were stirred for 2 hours, the solids were filtered off, and the resulting filtrate was analyzed using Atomic Absorption Spectrophotometry (AAS).

Synthesis of MnS , Ga_2S_3 , FeS , NiS , ZnS , Ag_2S , In_2S_3 , and CuS

CTAB (0.02 moles) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.02 moles) were dissolved in a 250ml beaker containing a mixture of 25ml of ethanol and 25ml of water. The beaker was warmed to 50°C to facilitate dissolution of the solids. In a separate vessel a stoichiometric quantity of the metal salt (0.02 moles $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, 0.02 moles $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.04 moles AgNO_3 etc.) was dissolved in 25ml of water. For the



MnS, Ga₂S₃, and FeS synthesis, 7M HCl was added dropwise to the CTAB/Na₂S solutions to lower the pH to 8. The two solutions were then combined, and an immediate dark precipitate was observed. The solution pH was monitored and adjusted to about 7.5 in the case of MnS, Ga₂S₃ and FeS. The solutions were then allowed to stir for 10 minutes and filtered. The resulting solid was dried and recombined with 50mL of water, placed in a sonication bath (Fisher Scientific FS-14) for 10 minutes, followed by a second filtration. The solid was collected and the sonication/filtration process repeated two more times to remove excess CTAB. The solid product was thoroughly air dried and calcined under a 4% H₂S/Argon mixture. Calcining was done at 300°C for all metal sulfides except CuS was calcined at 250°C. Confirmation of product was made using XRD. All reaction methods for the syntheses of the corresponding non-mediated metal sulfides were performed similarly to those described for the mediated metal sulfides with the exclusion of the CTAB and ethanol.

Synthesis of CuFeS₂

3.65g CTAB (0.01 moles) and 4.8g of Na₂S·9H₂O (0.02 moles) were dissolved in 25ml of ethanol and 25ml of water. In separate vessels (0.01 moles) each of Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·3H₂O were dissolved in 25ml water. The three solutions were combined, and the resulting black precipitate washed three times and calcined at 350°C for 2 hours under a H₂S/Ar atmosphere.

Instrumental

(XRD) patterns were performed on a XDS2000 Scintag XRD equipped with a solid state detector and a Phillips PW1710 Cu K α radiation. X-ray data was collected from 20 θ to 80 θ .

Atomic absorption spectrophotometry (AAS) was performed using a Buck Scientific Spectrophotometer Model 210 V6P with the Hg monitored at 253.7nm, slit width 0.7A; Cu monitored at 324.7nm slit width 0.7A. The flame was generated from an Air/Acetylene mixture.

RESULTS AND DISCUSSION

Relative Rate of Hg(0) Vapor Adsorption for Unactivated Metal Sulfide and Oxalic Acid Activated Metal Sulfide

Evaluation of metal sulfide adsorption for elemental mercury vapors was initially done at 42°C with commercial grades of MoS₂, CuFeS₂, Cu₂S, and CuS.



Only CuS adsorbed significant quantities of Hg(0) vapor. For example the relative rate of Hg(0) uptake for Cu₂S is 0.07 mmole/day compared with 1.7 mmole/day for CuS. The Hg(0) uptake for CuS is presented in Fig 1.

The Hg saturation concentration for the metal sulfide is the concentration in mole equivalents of Hg incorporated into the sample at the point that further exposure of the metal sulfide to Hg vapors results in no additional increase in the mass of the metal sulfide. The saturation concentration for Cu₂S is only 9.1×10^{-5} mole equivalents of Hg. The CuS sample on the other hand continually adsorbed Hg until it reached a saturation concentration of 0.5 mole equivalents of Hg.

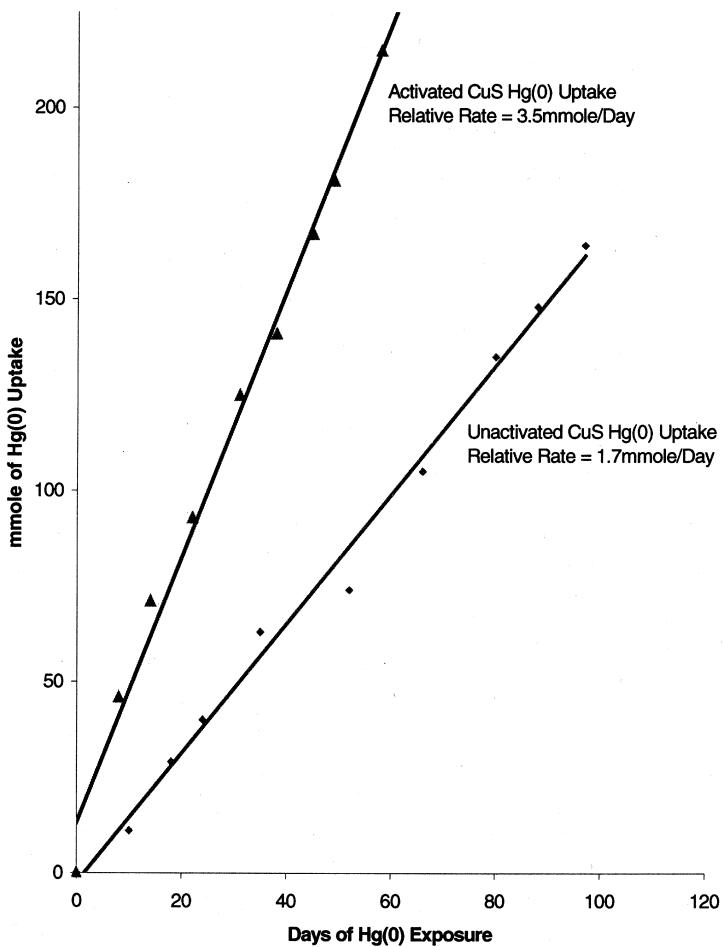


Figure 1. Relative rates of Hg(0) uptake by oxalic acid activated and unactivated CuS at 42°C.



As Hg was incorporated into the CuS, it changed color from dark blue to gray. When the gray Hg(0) saturated CuS sample is placed in a vial and agitated a red solid is observed on the walls of the vial. The color change suggested formation of a new compound. The stoichiometry of 0.5 mole equivalent Hg corresponds to the adsorption of 1 mole of Hg vapor by 2 moles of CuS. Powder XRD analysis of the gray solid revealed HgS. The stoichiometric formation of HgS showed that the removal of gas phase elemental Hg using CuS is not achieved by an intercalation process nor adsorption alone but is the result of an adsorption followed by a solid state electron transfer reaction involving the CuS and Hg(0). This is expressed in reaction 1.



The XRD pattern also shows the presence of Cu₂S. The powder pattern resulting from reaction 1, after the Hg saturation concentration of 0.5 mole equivalents revealed the absence of CuS. Therefore, the saturation concentration of Hg(0) into CuS indicates that reaction 1 goes to completion. Further analysis of reaction (1) and its products was done by combining the Hg saturated solids with a concentrated solution of HNO₃ which immediately discharged a yellow gas leaving behind a red solid and green solution. The red solid was washed with water, collected, and the XRD pattern proved to be that of the hexagonal phase of HgS. This phase of HgS is the source of the reddish color observed when the solid is agitated in a vial. The resulting green solution and yellow gas discharge after the addition of nitric acid are attributed to the dissolution of Cu₂S in reaction 1.

The MoS₂, CuFeS₂, Cu₂S, and CuS were each activated with oxalic acid and exposed to Hg(0) vapor. MoS₂ showed no evidence of Hg(0) adsorption at the temperatures studied. The Cu₂S and CuFeS₂ showed very little mass gain as a result of Hg adsorption in both the activated and unactivated cases. The rate of Hg(0) adsorption increased for the activated CuFeS₂ and Cu₂S however the error bars are large due to the small quantity of Hg(0) adsorption and their data are not presented here.

On the other hand the relative rate of Hg(0) adsorption by CuS is doubled with oxalic acid activation. Both activated and unactivated CuS adsorption rates are represented graphically in Fig. 1. Comparison of the relative rate data in Fig. 1 shows the large difference in the quantity of Hg(0) that has reacted with CuS after about 50 days. The unactivated form of CuS adsorbed 74 mmole Hg(0) after 52 days, contrasting sharply with the oxalic acid activated CuS that adsorbed 181 mmole Hg(0) after 49 days of exposure to Hg(0) at 42°C. The relative rate of Hg(0) uptake is 3.5 mmole/day for the activated CuS compared to 1.7 mmole/day for the unactivated CuS. The Hg(0) saturation concentration for activated CuS is also 0.5 mole equivalents.

Because the activated and unactivated CuS have Hg(0) saturation concentrations of 0.5 mole equivalents the activation process is a kinetic effect and does



not alter the Hg(0) saturation concentration of the CuS. In addition to both having saturation concentrations of 0.5 mole equivalents Hg(0) the activated and unactivated CuS show identical XRD patterns both before exposure to Hg(0) vapors and after saturation with Hg(0). Additionally the powder XRD patterns of the CuS before exposure to Hg(0) vapor shows no changes in its structure as a result of the activation process.

Higher temperatures were utilized not only to study the increase in rate with temperature but also to determine the feasibility for Hg(0) removal at higher temperatures with CuS. The unactivated CuS showed no phase changes besides those in reaction 1 at 42°C over the entire Hg(0) exposure time of 195 days. Samples were then monitored for degrading phase changes in the unactivated CuS at 68°C and 90°C. The resulting powder patterns of the Hg(0) saturated CuS at all temperatures were identical. It is important that these materials be robust so they do not lose their adsorption properties in Hg(0) sorption applications at higher temperatures. Table 1 shows the relative rate increase for the uptake of Hg(0) by both the activated and the unactivated forms of CuS at each of the temperatures studied. At all temperatures the relative rate of Hg(0) sorption is at least doubled by the oxalic acid activation process.

After the CuS samples reached the Hg saturation concentration at each temperature the presence of HgS was observed using powder XRD identical to reaction 1 at 42°C. Additionally the peaks due to HgS can be observed appearing with time.

Hg(0) Vapor Sorption by Mediated and Unmediated Synthetic Metal Sulfide

The synthetic metal sulfides described in the experimental section were made with and without the particle size mediating agent cetyltrimethylammoniumbromide (CTAB). The smaller particles obtained from the mediated synthesis were desired for their greater reaction surface area. Out of all the metal sul-

Table 1. Relative Rates of Hg(0) Uptake at each Temperature Studied for Both Activated and Non Activated CuS

Temperature (°C)	Relative Rate of Hg(0) uptake	
	Unactivated CuS (mmole/Day)	Activated CuS (mmole/Day)
42	1.7	3.5
68	2.5	6.0
90	13.0	32.0



fides synthesized only CuS and Ag₂S adsorbed Hg(0). Both of these metal sulfides adsorbed Hg(0) stoichiometrically. All of the synthesized metal sulfides in this study excepting the coinage metals have negative reduction potentials. This suggests that redox is, if not entirely then at least partially responsible for Hg(0) removal using metal sulfides. The relative rate of Hg(0) adsorption increases with the positive increase in the reduction potential between CuS and Ag₂S.

The much smaller particle sizes from the mediated synthetic metal sulfides result in much faster Hg(0) adsorption rates than commercial grade and non-mediated metal sulfides. For example the commercial grade CuS has a particle size on the order of 5 μ m compared with <1 μ m for the synthetically mediated CuS. The relative rate of Hg(0) adsorption is increased five-fold for particle sized mediated CuS. The rates of Hg(0) uptake increase in the order commercial grade < non-mediated < mediated.

In the case of Ag₂S the relative rate of Hg(0) adsorption is nearly doubled when the Ag₂S is synthesized compared with commercial grade Ag₂S. Additionally the relative rate of Hg(0) uptake is increased five fold for particle size mediated Ag₂S compared with commercial grade Ag₂S. A similar rate increase is observed for the mediated CuS. The Hg(0) adsorption by Ag₂S occurs according to reaction 2 where an amalgam Ag₂Hg and the silver mercury sulfide are formed. The Ag₂S does not form HgS with Hg(0) as CuS does in reaction 1. However, reaction 2 still occurs by a redox process. All batches of the Ag₂S were obtained with 100% purity and had saturation concentrations of 1.0 mole eq of Hg(0) which agrees with the stoichiometry indicated in reaction 2.



The purity of the metal sulfides was determined by XRD. In each case the purity of the metal sulfide and the saturation concentration must agree with the proposed reaction stoichiometry. For example pure phase CuS gives a saturation concentration of 0.5 mole equivalent, which agrees with reaction 1. However, XRD of the mediated CuS indicated the sample was 70% CuS and 30% Cu₂S. The mediated CuS reached a saturation concentration of 0.33 mole equivalents Hg(0) which would be expected for a sample containing about 70% CuS and 30% Cu₂S. The relative rate of reaction between synthetic CuS and Hg(0) would be significantly higher than those reported here if the CuS was obtained with 100% purity.

The activation process with oxalic acid was performed on the synthetic CuS in a similar manner as the commercial grade CuS. The activation process did not increase the rate of Hg uptake. The rate actually decreased for this sample but the small decrease is attributed to the sample having a lower concentration of CuS present. This is evident from the lower saturation concentration of the sample studied.



Hg(0) Vapor Sorption Properties of Commercial Grade CuS, Ag₂S, Au₂S and Au₂S₃

Fig. 2 compares the overall relative rates of Hg(0) adsorption for the four commercial grade metal sulfides CuS, Ag₂S, Au₂S and Au₂S₃. It is evident from Fig. 2 that the relative rates of Hg(0) uptake agree with the reduction potentials of the metal sulfides. An advantage that the metal sulfides have for uptake of Hg(0) vapors is the removal occurs by chemical reaction or chemisorption. Some Hg removal processes that occur via physisorption have diminished rates and capacities as temperature is increased. Processes, which involve chemisorption with sulfur on a solid support also, show decreased Hg(0) capacities with an increase in temperature. (13) On the other hand the metal sulfides show a continual increase in adsorption rate with increasing temperature and appear not to have any decreased

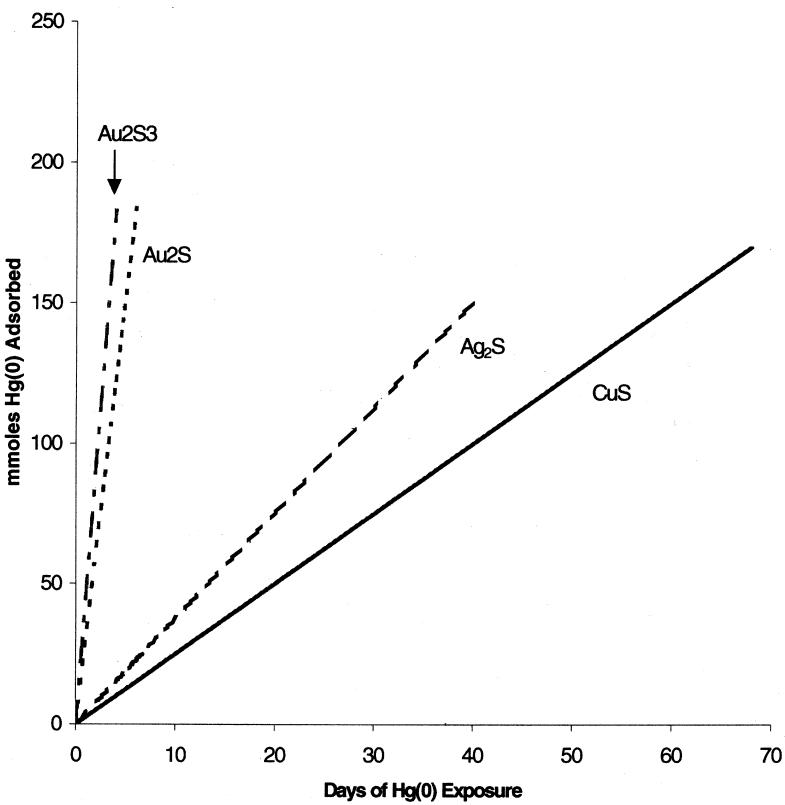


Figure 2. Relative rates of Hg(0) uptake for commercial grade CuS, Ag₂S, Au₂S, and Au₂S₃ at 70°C.

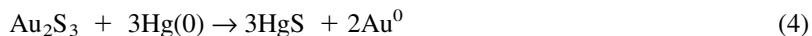


Table 2. Relative Rate of Hg(0) Uptake, Hg(0) Saturation Concentrations for the Commercial Grade Metal Sulfides and Reduction Potentials for each Metal. T = 70°C

	Hg(0) Saturation Concentration mole equivalents Hg(0)	Rate of Hg(0) Adsorption (mmole/day)	Reduction Couple and Potential for the MS in acidic solutions
CuS	0.5	2.5	Cu ²⁺ /Cu ¹⁺ 0.17
Ag ₂ S	1.0	3.8	Ag ¹⁺ /Ag ⁰ 0.79
Au ₂ S	1.25	31	Au ¹⁺ /Au ⁰ 1.68
Au ₂ S ₃	2.9	46	Au ³⁺ /Au ⁰ 4.26

capacities up to the temperatures studied here. Since Hg(0) is removed by a chemical reaction involving the formation of HgS the rate would increase continually with an increase in temperature. Table 2 lists the rates of Hg(0) uptake and saturation concentrations for the commercial grade metal sulfides at 70°C. Included in Table 2 is the reduction potential for the metal sulfides.

The adsorption mechanism is different in the case of Ag₂S. The XRD patterns of Ag₂S reactions clearly show there is no HgS formation. However, there are still redox products formed such as the Ag₂HgS₂. The 1 mole equivalent Hg(0) saturation concentration of Ag₂S reaction would indicate a 1:1 reaction stoichiometry which is in agreement with the products determined by XRD patterns. The XRD pattern of the gold sulfides reveals HgS and metallic Au⁰. The saturation concentration of the gold sulfides agrees well with the stoichiometries indicated in reactions 3 and 4. The experimental saturation concentration for the Au₂S is 1.25 mole equivalents Hg(0) which is slightly higher than the actual reaction stoichiometry of 1:1. The XRD pattern shows two extra lines that have not been characterized but they are very low intensity and do not constitute a significant portion of the products formed. The saturation concentration for the Au₂S₃ is 2.9 mole equivalents Hg(0) which is 95% of that shown in reaction 4.



Adsorption of Ionic Hg²⁺ by Metal Sulfides

Removal of ionic Hg²⁺ from, acidic aqueous solutions was determined using atomic absorption spectroscopy (AAS) for detection. Initial adsorption experiments used 5 mole equivalents of the metal sulfides, stirred in 0.11 aliquots of 40 ppm ionic Hg²⁺ containing standard solutions. After stirring for two hours the solutions were filtered and analyzed using AAS. In each case the solutions



were monitored for the corresponding metal cation in addition to Hg. The AAS showed the lower the resulting Hg^{2+} concentration attained the higher the corresponding metal concentration. Cu_2S resulted in the greatest decrease in ionic Hg^{2+} from aqueous solutions. The Cu_2S studies were repeated to quantify the Hg removed and the dissolved solids in solution. This was done in order to determine if any sorption occurs on the surface of the metal sulfide. The experiments showed that the quantity of Hg^{2+} removed from solution corresponds directly with the quantity of Cu_2S dissolved. This indicates in acidic solutions there is no physical or chemical adsorption of Hg^{2+} to the metal sulfides.

Summary

The readily available coinage metal sulfides adsorb elemental Hg(0) vapor from the atmosphere. In the case of CuS, Au_2S and Au_2S_3 the removal occurs by a redox process forming HgS and a reduced form of the metal. The removal of Hg(0) with Ag_2S also occurs by a redox reaction but there is no formation of HgS. Activation of the commercial CuS with oxalic acid doubles the relative rate of Hg(0) adsorption in reaction 1. The particle size mediating of CuS and Ag_2S with the surfactant CTAB results in a smaller particle size and the greater surface area gives a five-fold relative rate increase compared with the commercial grade CuS and Ag_2S . It would be reasonable to expect the gold sulfides to behave similarly. The overall relative rates of Hg(0) removal for commercial grade sulfides increase in the order $CuS < Ag_2S < Au_2S < Au_2S_3$ which correlates with the increasing reduction potential for each metal ion.

The Hg(0) saturation concentration of CuS is 0.5 mole equivalent Hg(0) which correlates with the reaction stoichiometry of 2CuS to 1Hg in reaction 1. The powder XRD pattern confirms the HgS formation but it only shows weak reflections at the 2θ values that correspond with Cu_2S . Regrettably even when observing the pure phase of Cu_2S by XRD one does not observe very intense patterns like that of HgS. Therefore acid tests were also used to indicate the presence of Cu_2S . The XRD patterns clearly show the products from the gold sulfides and Hg(0) are HgS and metallic gold. In both cases the stoichiometric quantity of Hg(0) adsorbed agrees with the products determined by XRD patterns. In the case of silver sulfide the products formed are the amalgam Ag_2Hg and Ag_2HgS_2 which also agrees with the stoichiometric quantity of Hg(0) adsorbed.

Experiments showed ionic mercury is not sorbed onto any of the metal sulfides studied. All quantities of mercury removed from solution were precipitated with dissolved sulfide ion from the metal sulfide.



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