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Iodide Retention by Cinnabar (HgS) and Chalcocite (Cu₂S)*

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ABSTRACT

Sorption of iodide (I⁻) on cinnabar (HgS) and chalcocite (Cu₂S) was examined as a function of pH at 25°C in a series of batch experiments. Calculated distribution ratios (K_d) far exceed those reported for other minerals; maximal K_d 's of 1375 cc/g (Cu₂S) and 3080 cc/g (HgS) were observed between pH 4-5, but were substantial at all pH's measured (4 < pH < 10). Iodide sorption apparently occurs by the formation of an insoluble surface solid solution with exposed Hg and Cu sites. Surface solid solution formation is favored at low pH due to the lessened electrostatic repulsion of the iodide ion by the sulfide surfaces.

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MASTER

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Introduction

The results of several batch experiments show that iodide (I^-) sorbs strongly to cinnabar (HgS) and chalcocite (Cu_2S) surfaces, far in excess than that reported for other minerals (e.g., Sazarashi et al., 1994). Distribution ratios (K_d) as high as 3080 cc/g are reported for HgS and 1375 cc/g for Cu_2S . The surface chemistry of these minerals is dominated by exposed metal hydroxyl sites and sulfide groups, which are appreciably more acidic than aqueous hydrogen sulfide. Maximum iodide adsorption in the presence of 0.001 M NaCl occurs near pH 4, but is substantial ($K_d > 60$) at all pH's measured ($4 < pH < 10$). Marked increases in I^- adsorption are observed in $CaSO_4$ -saturated solutions at high pH (7-9) relative to SO_4 -absent solutions. Iodide retardation apparently occurs by the formation of an insoluble surface solid solution with exposed Hg and Cu sites. Surface solid solution formation is favored at low pH due to lessened electrostatic repulsion of the iodide ion by the mineral surface.

Experimental Methods

More than twenty experiments were conducted by batch method to investigate adsorptivities of I^- ions each mineral. Experiments were conducted with reagent grade cinnabar and chalcocite, which was used without prior washing or soaking. Test solutions were prepared using reagent grade chemicals and deionized water ($>18 M\Omega$). For each experiment, 0.1 g of mineral was added to 100 ml of solution containing 1 ppm I^- (10^{-5} M NaI) and 10^{-3} M NaCl; the solution was stirred until the pH stabilized. pH was adjusted using 0.1 M NaOH and 0.1 M HNO_3 . 5 ml of the charged solution was then removed by syringe, and pushed through a $0.45 \mu m$ filter. Iodide concentrations were measured with both an ion chromatograph (IC) and an ion-specific electrode (ISE). Typical precision on the IC at the 1 ppm level for I^- was ± 0.1 ppm. Machine drift was monitored with 1.3 ppm and 12.7 ppm I^- standards.

In early experiments utilizing the ISE, sorption of iodide was detected in almost all instances. Reproducibility, however, was inconsistent, both in terms

of exact millivolt readings, as well as the extent of millivolt changes (and therefore changes in iodide concentration). For these reasons, iodide concentrations were also measured by ion chromatography (IC). Several experiments were conducted in which iodide concentration was measured simultaneously by both techniques. The two techniques were compared during a titration experiment in which 0.1 g chalcocite was placed in 100 ml of a 0.1 ppm iodide solution (Figure 1). At low pH, the K_d as determined from IC is more than 15 times higher than that calculated from ISE (1233 vs. 78 cc/g). With increasing pH, the disparity decreases. Similar results were observed in several experiments with cinnabar as the sorbing agent. In general, we came to favor IC-based K_d values over those determined from ISE for the following reasons: (1) The ISE is subject to interferences from mercury, chlorine and pH. In particular, mercury buildup on the electrode surface requires the electrode be polished after every experiment, which eventually degrades its performance. (2) The IC may be calibrated with a standard solution and periodically checked over the course of several runs, therefore providing a level of analytical confidence not achievable with the ISE. Therefore, the results reported below pertain only to measurements made with the IC. In these experiments, 0.1 g of either HgS or Cu₂S was added to 100 ml of a 0.001 or 0.01 M NaCl, 10⁻⁵ M (1.3 ppm) iodide solution. In addition, two experiments (Cl absent, 1.3 ppm I⁻) were conducted under CaSO₄ saturated conditions. pH was measured at the time of sample extraction.

The distribution ratio, a measure of the sorptive character of a substance, was calculated from the following equation:

$$K_d \text{ (cc/g)} = \frac{c_o - c_1}{c_1} \times \frac{\text{volume of solution (cc)}}{\text{weight of adsorbent (g)}}$$

where c_o and c_1 are initial and equilibrium concentrations (ppm) of iodide ions, respectively.

Results and Discussion

Adsorption experiments for cinnabar and chalcocite were carried out in distilled water containing Cl^- and I^- ions ($[\text{Cl}^-]$ and $[\text{I}^-] = 10^{-3}$ and 10^{-5} M, respectively). Results are listed in Tables 1 and 2, and indicate that I^- ions are strongly adsorbed by both cinnabar and chalcocite. Figure 2 shows iodide K_d as a function of pH for HgS and Cu_2S in 0.001 M NaCl . Note first that K_d decreases with higher pH for both sulfide mineral surfaces. Iodide K_d 's define a concave curve, with a maximum K_d of just over 3000 cc/g at pH 4. Cu_2S -based K_d 's define a pattern somewhat antithetic to cinnabar at pH's < 8 ; at pH > 8 , the two curves converge. An increase in $[\text{Cl}^-]$ from 0.001 to 0.01 M was observed to have no effect on I^- adsorption. The apparent effect of CaSO_4 saturation on HgS adsorption is to increase K_d markedly at elevated pH (Table 3). At pH 8, an overall 97% increase in K_d was observed compared to the SO_4^{2-} -absent solution. The effect was similar, if not as dramatic, for Cu_2S (Table 4), with an approximately 58% increase in K_d within the saturated solution.

To summarize, maximum I^- adsorption was observed at low pH values, where sulfide surface charge is least negative (Dekkers and Schoonen, 1994); this may be caused by lessened electrostatic repulsion between the mineral surface and the ion. The metal sulfide surfaces consist of 2 site types, hydroxylated metal sites and sulfide groups that are negatively charged above pH 3. Because of electrostatic considerations, we assume that I^- adsorbs to the exposed, hydrated Hg and Cu centers at the mineral surfaces, displacing hydroxyls. For HgS , this process may be conceptualized as:

Because cinnabar and chalcocite are highly insoluble metal sulfides (solubility products: $[\text{Hg}^{++}] [\text{S}^{--}] = 10^{-52.4}$, $[\text{Cu}^{+}]^2 [\text{S}^{--}] = 10^{-48}$; Krauskopf, 1967), the surface solid solutions between HgS-HgI_2 and $\text{Cu}_2\text{S-Cu}_2\text{I}$ may account for the observed high retention of I^- by metal sulfides. The relative insolubility of HgI_2 and Cu_2I , and their solution with highly insoluble metal sulfides, probably causes the anomalously high limiting K_d , only after I^- becomes electrostatically

attracted to the mineral surface. These results suggest that radioactive iodide, though commonly perceived to be mobile in nature, may be successfully sequestered in some select natural settings where reducing conditions prevail and sulfides of certain metals are present.

References

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Figure 1. Relationship between K_d and pH for the adsorption of I^- ions on chalcocite as determined by ion chromatography and ion-specific electrode. Temperature = 25°C. Weight adsorbent in both experiments is 0.1 g/100 ml.

Figure 2. Relationship between K_d and pH for the adsorption of I^- ions on cinnabar (HgS) and chalcocite (Cu_2S). Temperature = 25°C. Weight adsorbent in both experiments is 0.1 g, charged into 100 ml of a 0.1 ppm I^- solution. Data may be found in Tables 1 and 2.

Table 1.
Cinnabar Adsorption Experimental Results*

Notes	Time Elapsed	Time	pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on HgS	Moles/cc I in Soln	K _d (cc/g)
	0:00	13:15	5.25	1.02				
Add HgS	0:14	13:29	5.28	0.83	19%	1.90E-06	8.10E-08	235
	0:21	13:36	4.01	0.25	75%	7.55E-06	2.45E-08	3080
	0:28	13:43	9.88	0.95	6%	6.47E-07	9.35E-08	69
	0:33	13:48	5.89	0.86	16%	1.58E-06	8.42E-08	187
	0:36	13:51	8.18	0.91	10%	1.05E-06	8.95E-08	117
	0:41	13:56	4.06	0.72	29%	2.92E-06	7.08E-08	413

* 0.1g cinnabar in 100 ml solution with 0.001 M NaCl. Initial [I⁻] = 10⁻⁵ M.

Table 2.
Chalcocite Adsorption Experimental Results*

Notes	Time Elapsed	Time	pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on Cu ₂ S	Moles/cc I in Soln	K _d (cc/g)
	0:00	9:28	5.58	0.97				
Add Cu ₂ S	0:08	9:36	6.62	0.76	22%	2.16E-06	7.84E-08	275
	0:10	9:38	7.20	0.76	22%	2.21E-06	7.79E-08	283
	0:13	9:41	9.63	0.90	8%	7.53E-07	9.25E-08	81
	0:17	9:45	9.94	0.92	5%	5.47E-07	9.45E-08	58
	0:23	9:51	4.02	0.43	55%	5.52E-06	4.48E-08	1233
	0:31	9:59	5.81	0.42	56%	5.62E-06	4.38E-08	1285

* 0.1g chalcocite in 100 ml solution with 0.001 M NaCl. Initial [I⁻] = 10⁻⁵ M.

Table 3.
CaSO₄ Saturation Effect on I⁻ Adsorption on Cinnabar

Notes	Time Elapsed	Time	pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on HgS	Moles/cc I in Soln	K _d (cc/g)
	0:00	15:05	4.31	0.98				
Add HgS	0:01	15:06	4.29					
	0:03	15:08	7.96	0.22	77%	7.73E-06	2.27E-08	3399

Table 4.
CaSO₄ Saturation Effect on I⁻ Adsorption on Chalcocite

Notes	Time Elapsed	Time	pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on Cu ₂ S	Moles/cc I in Soln	K _d (cc/g)
Before CaSO ₄	0:00	14:52	5.58	1.23				
After CaSO ₄	0:02	14:54	4.38					
Add Cu ₂ S	0:08	15:00						
	0:09	15:01	5.73					
	0:15	15:07	8.09	0.74	40%	4.01E-06	5.99E-08	669

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