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$^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ Scavengers for Low Level Radioactive Waste Backfills

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$^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ Scavengers for Low Level Radioactive Waste Backfills

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ABSTRACT

Minimization of $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ transport to the biosphere is critical to the success of low level radioactive waste (LLRW) storage facilities. Here we experimentally identify and classify optimal sorbent materials for inclusion in LLRW backfills. For low pH conditions (pH 4-5), Cu-sulfides and possibly imogolite-rich soils provide K_d 's (surface-solution partition coefficients) of roughly 10^3 ml g^{-1} for iodide, and 10^2 ml g^{-1} for technetium. At near neutral pH, hydrotalcites, Cu-oxides, Cu-sulfides and lignite coal possess K_d 's on the order of 10^2 ml g^{-1} for both iodine and technetium. At high pH (pH > 10), such as might occur in a cementitious LLRW facility, calcium monosulfate aluminate K_d 's are calculated to be roughly 10^2 ml g^{-1} for both iodine and technetium.

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Introduction

Demonstrably safe storage of low level radioactive waste (LLRW) is an important public health priority. In general, because of its large volume but relatively low activity, LLRW is stored in near-surface facilities (e.g., shallow trenches). An increasing emphasis has been placed on buried engineered structures, such as concrete vaults with backfills, which might diminish the risk of radionuclide releases into the biosphere. Because it is impossible to assure vault integrity over the hundreds to thousands of years required for decay of LLRW to benign daughter products, there is considerable interest in the development of chemically reactive backfills that might sorb and sequester those radionuclides that are soluble and otherwise non-sorbing in soils. In the cementitious systems called for in most current designs, many of the longer-lived radionuclides (^{241}Pu , ^{241}Am , ^{234}U and ^{232}Th) form insoluble salts and/or sorb strongly, so much so that the integrated dose to the biosphere is predicted to be low (Brady and Kozak, 1995). Nuclides $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ are two exceptions. They constitute a significant fraction of the radioactivity in LLRW inventories, yet neither forms insoluble salts nor sorbs appreciably to common soil minerals. Consequently, a substantial obstacle to the ultimate success of planned LLRW facilities is the uncertainty of I^- and TcO_4^- retention. An obvious way to mitigate this problem is to add sorbing agents to the backfill that specifically scavenge iodine and technetium. This is not a simple task, however, as the negative charge of most mineral surfaces causes both nuclides to be repelled.

Here we experimentally examine a wide variety of minerals (metal sulfides, copper oxides, hydrotalcites, lignite coal, etc.), which have previously been suggested and/or investigated as potential anion sorbers. We identify those materials that have the highest sorptive capacity for I^- and TcO_4^- in the types of aqueous solutions likely to be present in LLRW facilities.

Synthetic and Natural Sorbent Materials

Calcium Monosulfate Aluminate (CMSA)

CMSA has previously been suggested as a potential anion sorber (Glasser and Atkins, 1994). Two separate batches of CMSA (1 and 2) were synthesized. CMSA 1 was made from a 40:30:30 mixture of $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and CMSA 2 was made from a 60:22:18 mixture of $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, and H_2SO_4 . Salts were dry mixed then added to 1 liter of deionized (DI) water ($>18 \text{ M}\Omega$) and stirred for 15 minutes. The slurry was transferred to sealed polypropylene containers and heated to 90°C for 24 hours. After the slurry cooled, it was filtered, rinsed with DI water, and dried at 90°C for 4 hours. The material was then rehydrated with 1000 ml of DI water and replaced in a 90°C oven for four days after which it was again filtered, rinsed in DI water, and dried at 90°C for ~6 hours. X-ray diffraction (XRD) confirm the material's crystallographic properties. Because diffraction patterns varied slightly with the degree of hydration, and reference patterns are incomplete, we could not confirm that CMSA was 100% pure.

Imogolite and Imogolite-Bearing Soil

Imogolite is a naturally occurring, one-dimensional, tubular aluminosilicate consisting of a curled sheet of gibbsite formed by the replacement of an hydroxyl layer by orthosilicate anions (Wada and Yoshinaga, 1969). Imogolite has a large anion exchange capacity even at neutral to high pH's, and has been shown to retain Cl, F, SO_4 , PO_4 and other anions. It is therefore probable that a permanent positive charge is present within the tubular portion of the mineral structure that acts as a strong anion sorbing surface (Theng et al., 1982; O'Donnell et al., 1993). Two forms of imogolite were obtained from Professor R. A. Dahlgren (Dept. of Land, Air and Water Resources- Univ. California at Davis): (1) a natural imogolite-bearing soil, (2) and a small, purified sample of imogolite gel from the Kitakami Pumice bed, Japan.

Hydrotalcite

The hydrotalcite mineral group has the general formula:

where $M^{+2} = Mg^{+2}, Zn^{+2}, Ni^{+2}, Fe^{+2}$

$M^{+3} = Al^{+3}, Fe^{+3}$

$X^{m-} = OH^-, Cl^-, NO_3^-, CO_3^{=}, SO_4^{=},$ and

subscript "x" is the formal positive charge of the mineral lattice. The metal cations are coordinated octahedrally by hydroxide ions, forming a framework of individual sheets which are decoupled from one another. Individual layers typically incorporate more metal cations than can be accommodated by the negative charges on the layer hydroxide. This charge deficiency is compensated by placing additional anions between layers. These anions however, are not strongly held and can be replaced by other ions from solutions that come in contact with the material. Hydrotalcites are therefore similar to the common silicate clays, except that clays, due to negative charges in the interlayer, tend to sorb cations, as opposed to anions. Hydrotalcites show promise as anion sorbers, due to the large number of specific stoichiometries (each with unique charges), hence sorptive capacities, which can be engineered.

We produced an Mg-Al version of hydrotalcite (Miyata, 1975; Miyata and Okada, 1977) and a Zn-Al analogue of the material. The latter was done because both Al and Zn are amphoteric, so both would be mobile in the pH 10 solution generated at the end of the synthesis procedure. Solutions consisting of 0.5 M zinc nitrate $[Zn(NO_3)_2 \cdot 6H_2O]$ and aluminum nitrate $[Al(NO_3)_3]$ were prepared and mixed in the ratio 3:1 (60 ml Zn/40 ml Al) and slowly added to 100 ml of a third solution consisting of 0.2 M sodium hydroxide

(NaOH) and 0.125 M sodium carbonate (Na_2CO_3) at 80°C in a beaker using a magnetic stirrer/hot plate. Concentrated NaOH was added dropwise to maintain pH at 10 ± 0.1 . The mixture was stirred for 15 minutes then allowed to cool. The solution was then filtered and rinsed several times with DI water. Drying cycle was 2 hours at 60°C followed by 3 hours at 90°C . Dried materials were analyzed with a scanning electron microscope (SEM) equipped with an x-ray energy dispersive spectrometer (EDS), as well as by XRD.

Chloride and sulfate-exchanged hydrotalcites were also synthesized and examined. The hydrotalcite lattice can withstand short exposure to mildly acidic solutions ($\geq \text{pH } 4.5$). Thus, to replace the CO_3^{2-} and OH^- initially present, the materials were soaked in weak acids of the appropriate anion at pH ~ 4.5 . Subsequent to such treatment, samples were washed, dried, and X-rayed to verify that the hydrotalcite had survived the treatment. SEM/EDS analysis of the dried materials verified the presence of chloride and sulfur (sulfate) on the treated materials. The Cl-exchanged hydrotalcite was made by adding a 5 gram sample of the above Zn-hydrotalcite to 25 ml DI water and stirring with a magnetic stirrer. The pH was monitored continuously using a Corning combination pH probe. Dilute HCl was added dropwise until a pH of about 4.5 was reached (beyond this pH the hydrotalcite begins to disappear rapidly). The slurry was filtered and rinsed with DI water then dried at 60°C for two hours. The sulfate-exchanged hydrotalcite was made similarly except dilute H_2SO_4 was added dropwise until a pH of about 4.0 was reached.

Metal Sulfides, Copper Oxides

Cinnabar (HgS) has been identified as a highly effective sorbing agent for iodide (e.g., Allard et al., 1980; Strickert et al., 1980; Torstenfelt and Allard, 1984; Ikeda et al., 1994; Sazarashi et al., 1994). Because mercury is both toxic and expensive, other materials that might form stable sulfides having sorptive behavior similar to cinnabar, but lower toxicity, were examined. Copper and silver were obvious choices because, like mercury, both form strong aqueous complexes with halogen anions, and both metals also

form iodide salts with very low solubilities. In an empirical sense, these factors suggest that the metal sites exposed on the surfaces of solid particles should also have a strong affinity to sorb iodide. Although silver-loaded zeolites have a track record of scavenging iodine, copper was chosen as a less expensive alternative. In all experiments, reagent grade forms of both cinnabar and chalcocite (Cu_2S) were used without further purification or cleaning. Although copper sulfides are common minerals in supergene enrichment zones of primary hydrothermal copper deposits, both tenorite (CuO) and cuprite (Cu_2O) are well represented in the more oxidizing portions of supergene enrichment zones. Because oxidizing conditions are likely to prevail in most LLRW facilities, two scoping experiments were performed to evaluate the long-term iodide retention capacity of the copper oxides.

Coals

Several workers report that organic-rich soils effectively scavenge iodide (e.g., Whitehead, 1973; Whitehead, 1974; Muramatsu et al., 1989). Although sorption is ascribed to both organic and inorganic components in the soil, tests on the inorganic soil components in pure form (e.g. quartz, feldspar, various clays) seldom show significant iodide sorption. Consequently, we used coal as an analogue for refractory soil organic material and measured its affinity for iodide and pertechnetate. Two reference coal samples from the Argonne Petroleum Coal Sample Program (Vorres, 1993) were examined: (1) "Beulah-Zap" lignite, and (2) "Wyodak-Anderson" sub-bituminous coal. Both samples were pulverized and packed under an inert atmosphere. Low-rank coals were selected because they retain a greater number of organic functional groups that might potentially scavenge anions from solution.

Experimental Methods

Surface-solution partition coefficients (K_d 's) were calculated for iodide from the following formula:

$$K_d (\text{cc/g}) = [(C_o - C_e)/C_e] \times [V_{\text{sol}}(\text{cc})/\text{mass of adsorbent (g)}]$$

where C_o and C_e are initial and equilibrium concentrations of iodide ions, respectively.

K_d 's are system specific and, therefore not completely portable, as they can lump together a number of parallel surface reactions (e.g., Kent et al., 1988). K_d 's are used here in a relative sense to identify sorption trends from mineral to mineral and as a function of pH. Linearity was not demonstrated, therefore K_d 's as discussed here are effective in the sense that they are specific to the experimental setup. All titrations were carried out at 25°C ($\pm 2^\circ$) with an automated Mettler DL 12 titrator. pH was monitored with an AgCl Mettler glass electrode (Model DG-111SC). All test solutions were prepared with reagent grade chemicals and DI water.

Batch Sorption Measurements

Iodide sorption experiments were performed in semi-sealed 200 ml reactors containing 0.1 to 2.0 g of material added to 100 ml of a 0.001 M NaCl and 1.3 ppm I⁻ matrix solution. The powders were continuously suspended by vigorous stirring using an overhead polyethylene propeller. Nitrogen gas was continuously bubbled through the reactor in order to prevent CO₂ and O₂ adsorption from atmosphere. pH adjustments were made using 0.1 M NaOH and 0.1 M HNO₃. Solution-powder contact times varied from one minute to several minutes according to the time required for pH to stabilize. At the end of each contact period, approximately 5 ml of the suspension was transferred into a syringe and impressed into a 0.45 micrometer Acrodisc™ filter attached to the luer-lock tip of the syringe.

To prevent calcium monosulfate aluminate powder from dissolving, a 150 ml aliquot of iodide-free matrix solution was saturated with approximately 10 g of calcium monosulfate aluminate and quickly extracted and impressed through a 0.45 μm Acrodisc™

filter. Iodide was added to the saturated filtrate to a concentration of 1.3 ppm, and this was used as the matrix solution for subsequent batch experiments.

The filtered solutions were analyzed for dissolved iodide by ion chromatography using a Dionex™ model 2000i ion chromatograph. Good peaks were observed down to the 0.1 ppm level. Instrument calibration was achieved prior to each run with iodide standards (matrixed according to the solutions used in potentiometric titrations) derived from a stock 0.1 mol/L NaI standard (Orion stock # 945306). Fourteen analyses of a 12.7 ppm iodide standard yielded a mean value of 12.6 ppm with a population standard deviation (σ) of 0.4 ppm. Subsequent measurements on a 1.3 ppm standard ($n=10$) resulted in a mean value of 1.3 ppm and $\sigma = 0.1$ ppm. K_d error bar estimations (Figures 1-4) represent $\pm 1 \sigma$ as calculated from the 1.3 ppm iodide standard. Standards analyzed as unknowns prior to, during and following each lot of samples were consistent with the levels of accuracy and precision stated above.

"Hot Cell" Tc Measurements

The distribution of technetium was measured at Los Alamos National Laboratory using 61-day ^{95}Tc recovered by the Los Alamos Medical Isotopes Section from the Los Alamos Meson Physics Facility targets. This carrier-free radiotracer was present at extremely low concentrations. Typically, each absorber/solution experiment contained 3×10^9 atoms of ^{95}Tc .

Immediately after the radiotracer was added, a set of six tubes was placed on a 48 rpm rotator for dynamic contact periods of 2 hours, 6 hours, and 24 hours. At the end of each contact period, approximately 1.5 milliliters of the contacted solution was transferred into a 3-milliliter syringe that had a 0.45 μm Acrodisc™ filter attached to the luer-lock tip. The postcontact solution was expelled through this filter into a tared counting vial from which the solution weight was determined.

Each portion of postcontact solution was assayed by gamma spectrometry using the characteristic 240 keV and 106 keV gamma rays of ^{95}Tc . The fraction of radionuclide sorbed was determined indirectly from the difference in the measured gamma activity before and after each contact period. K_d values were calculated at Los Alamos in a manner similar to ours for iodide, except that grams of solution are substituted for cc's:

$$K_d = [(\text{Pr}-\text{Po})/\text{Po}][\text{S}/\text{A}]$$

where Pr = measured precontact activity per milliliter

Po = measured postcontact activity per milliliter

S = grams of solution contacted

A = grams of absorber contacted

Calculated minimum peak area values that could be detected with a 95% confidence level were used to calculate K_d values in terms of *greater than* (>) the computed minimum K_d values. Appropriate corrections were made to account for the fact that the liquid-to-solid ratio and the remaining activity of each radionuclide decreased as successive assay portions were removed.

Experimental Results - Iodide

Calcium Monosulfate Aluminate (CMSA)

A summary of results for the iodide retention experiments is presented in Table 1. On the basis of cement performance assessments, Glasser and Atkins (1994) suggested CMSA as a potential anion sorber. Our experimental results confirm the potential of CMSA as an I⁻ selective material. Maximum iodide K_d 's for both types of CMSA are in the pH 5-6 range (118 for CMSA-1 and 100 for CMSA-2), with steep drop-offs at higher pH's (Fig. 1).

Imogolite and Imogolite-Bearing Soil

Approximately 0.5 g of the purified imogolite gel was dried, crushed to powder consistency and examined for iodide retention. Despite the reported large anion exchange capacity for imogolite (e.g., Theng et al., 1982; O'Donnell et al., 1993), in two separate experiments using 0.1 and 0.3 g of material, no loss of iodide was detected over a pH range 3 to 8. However, for the imogolite-bearing soil sample, significant sorption was observed between pH 4 and 5.5 (Fig. 2). Assuming that the imogolite fraction is not responsible for removal of the iodide, some component of the soil must be responsible, although it is unclear which one. The large number of functional groups present as organic molecules within the soil fraction may play an important role. Similar low iodide K_d 's for pure imogolite have been measured elsewhere (R.A. Dahlgren and W.H. Casey, personal communication).

HgS (Cinnabar), CuS (Covellite) and Cu₂S (Chalcocite)

The results of several batch sorption experiments confirm that iodide is strongly adsorbed to the cinnabar surface, with a maximum K_d of nearly 3400 cc/g at a pH of 8 in a calcium sulfate-saturated solution (Fig. 3). Under non-sulfate saturated conditions, maximum K_d measured is 3080 cc/g, decreasing linearly down to about 70 cc/g at pH 9.9. Our maximum K_d for cinnabar (non-sulfate saturated conditions) is in excess of two times greater than the next highest reported value (Ikeda et al., 1994). Similarly, substantial iodide K_d 's were experimentally determined for the copper sulfide minerals- 1375 for covellite and 1285 for chalcocite. Iodide retentive properties fell off with increasing pH, although between a pH of 10 and 4.5 the K_d never dropped lower than about 200 for chalcocite and 60 for covellite. We hypothesize that at higher pH, hydroxyls displace iodide from metal centers exposed at the respective mineral surfaces. Given the success of copper sulfide minerals for retaining iodide, we performed two simple K_d measurements utilizing a 24 hour contact time to determine the iodide retention properties of two copper

oxide minerals, CuO (cuprite) and Cu₂O (tenorite). In the near-neutral pH range, K_d's of 453 and 136 were calculated for tenorite and cuprite, respectively. Additional work is planned to document the pH dependence of iodide K_d's for these materials.

In general, for metal sulfide minerals, iodide sorption is greatest at low pH where surface charge is least negative and electrostatic repulsion between the surface and the ion is diminished (Balsley et al., in press). Under these conditions, we propose that iodide adsorbs to the exposed, hydrated metal centers ($\equiv M$) along the mineral surfaces and displaces hydroxyls in the process:

The observed high retention of iodide among the metal sulfide minerals is therefore attributed to surface solid solution between metal-sulfide and metal-iodide at low pH (Balsley et al., 1996).

Hydrotalcite

Although the potential for anion retention in hydrotalcite is recognized, we know of no experimental results outside of this study that confirms or denies this property. With carbonate/hydroxide, K_d's near 50 were calculated and little pH dependence was observed. For the Cl⁻ and SO₄⁼ treated materials, a slight pH dependence was observed and K_d's >100 were recorded when the pH was raised or lowered slightly from neutral. The nature of the anion initially present on the exchange site in hydrotalcite samples appears to control iodide sorption (Fig. 4), although we are at this time unsure about the exact retention mechanism.

Coals

A peak K_d of 844 was calculated for sub-bituminous coal. A K_d of 518 was observed for lignite coal (see Table 1). To our knowledge, these represent the only data

using coals as anion-sorbing materials. A second set of experiments was designed to test the long-term (24 hour) sorptive capacity at near neutral pH of both coals. Although the sub-bituminous coal still retained a significant proportion of iodide over the 24 h time period, the K_d declined from 662 (recorded after 10 minutes contact time) to 132 (24 hours contact time). The K_d for lignite coal dropped from 75 (12 minutes contact time) to 0 (24 hours contact time). Iodide sorption on coal appears to be a transitory phenomenon. A slow polymerization and elimination of surface functional groups may occur upon immersion in water, which might explain the observed K_d decrease. In any case, refractory organic material such as coal appears to be an unreliable sorbent for iodide.

Experimental Results - Technetium

Though a number of natural minerals can seemingly scavenge technetium from solution, most of the candidates depend on first reducing Tc (VII) to (IV) at the mineral surface (e.g., Fried et al., 1977; Vandergraaf et al., 1984; Huie et al., 1988; Winkler et al., 1988; Bock et al., 1989). We experimentally examined TcO_4^- sorption, initially using ReO_4^- as an analogue. Based on the results of these experiments, several samples were subsequently sent to Los Alamos National Laboratory to verify sorption of Tc to metal sulfides, and other candidate materials. Tc K_d 's are listed in Table 2. Among all of the materials tested, we observed the highest K_d 's for CMSA-1 and lignite coal (134 and 128, respectively). The lignite coal value is not unexpected due to the potential for attachment to exposed organic functional groups. There is substantial sorption of TcO_4^- to CMSA and SO_4^{2-} -substituted hydrotalcite. Because of the presence of sulfate in both materials, a reasonable first hypothesis is that TcO_4^- exchanges for exposed sulfate groups. Significantly, Tc sorption onto CMSA is substantial at the hyperalkaline pH where CMSA is most stable. CMSA is, therefore, a potentially ideal additive to cementitious LLRW backfills, as well as to backfills made alkaline by glass hydrolysis (e.g., Hanford). The

identification of sulfate-substituted hydrotalcite as a near neutral pH sorber of Tc is immediately relevant as well for: 1) use as a backfill additive, and 2) consideration as an active component in schemes for pre-treatment scavenging of Tc from LLRW.

Summary

The optimal iodide and technetium scavenging agent for implementation to LLRW backfills will depend on the ambient pH of the facility, a quantity that is difficult to predict. For low pH conditions (typical of saturated, organic-rich soils) Cu-sulfides, and possibly imogolite-rich soils, should provide the most efficient scavenging of I⁻ and Tc. For near neutral pH's (typical of unsaturated or alkaline soils) hydrotalcites, Cu-oxides, Cu-sulfides and possibly lignite (Tc only) are the most efficient sorbers. CMSA might be the most effective backfill additive at the high pH's likely to be found in a cementitious facility. All of the materials described above are well known in the geologic record and therefore likely to be durable over at least hundreds to thousands of years.

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Table 1. Iodide Sorption Data*

pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on solid	Moles/cc I ⁻ in sol ⁿ	K _d (cc/g)
Calcium Monosulfate Aluminate #1					17.8 m ² /g
4.0	1.11	10	9.8x10 ⁻⁷	9.0x10 ⁻⁸	108
6.3	1.10	11	1.1x10 ⁻⁷	8.9x10 ⁻⁸	118
8.0	1.13	8	8.1x10 ⁻⁷	9.2x10 ⁻⁸	88
10.0	1.19	3	3.3x10 ⁻⁷	9.7x10 ⁻⁸	34
Calcium Monosulfate Aluminate #2					17.8 m ² /g
4.2	1.26	5	5.5x10 ⁻⁷	9.5x10 ⁻⁸	58
5.6	1.21	9	9.1x10 ⁻⁷	9.1x10 ⁻⁸	100
8.3	1.25	6	5.9x10 ⁻⁷	9.4x10 ⁻⁸	63
10.9	1.29	3	2.8x10 ⁻⁷	9.7x10 ⁻⁸	29
Unsieved Imogolite-Bearing Soil					39.0 m ² /g
4.0	1.08	19	1.9x10 ⁻⁶	8.1x10 ⁻⁸	231
5.5	1.09	18	1.8x10 ⁻⁶	8.2x10 ⁻⁸	220
5.9	1.26	5	5.3x10 ⁻⁷	9.5x10 ⁻⁸	56
7.9	1.28	4	3.8x10 ⁻⁷	9.6x10 ⁻⁸	39
9.9	1.28	4	3.8 x10 ⁻⁷	9.6x10 ⁻⁸	39
Cinnabar (HgS)					1.99 m ² /g
4.0	0.25	76	7.6x10 ⁻⁶	2.5x10 ⁻⁸	3080
4.1	0.72	29	2.9x10 ⁻⁶	7.1x10 ⁻⁸	413
5.3	0.83	19	1.9x10 ⁻⁶	8.1x10 ⁻⁸	235
5.9	0.86	16	1.6x10 ⁻⁶	8.4x10 ⁻⁸	187
8.0	0.22	77	7.7x10 ⁻⁶	2.3x10 ⁻⁸	3399
8.2	0.91	11	1.1x10 ⁻⁶	9.0x10 ⁻⁸	117
9.9	0.95	7	6.5x10 ⁻⁷	9.4x10 ⁻⁸	69
Covellite (CuS)					0.75 m ² /g
4.0	0.40	58	5.8x10 ⁻⁶	4.2x10 ⁻⁸	1375
6.3	0.83	13	1.3x10 ⁻⁶	8.7x10 ⁻⁸	145
6.9	0.42	56	5.6x10 ⁻⁶	4.4x10 ⁻⁸	1273
7.2	0.62	51	5.1x10 ⁻⁶	4.9x10 ⁻⁸	1032 [†]
8.3	0.78	18	1.8x10 ⁻⁶	8.2x10 ⁻⁸	215
Chalcocite (Cu ₂ S)					1.11 m ² /g
4.0	0.43	55	5.5x10 ⁻⁶	4.5x10 ⁻⁸	1233
5.8	0.42	56	5.6 x10 ⁻⁶	4.4x10 ⁻⁸	1285
6.6	0.76	22	2.2x10 ⁻⁶	7.8x10 ⁻⁸	275
7.2	0.76	22	2.2x10 ⁻⁶	7.8x10 ⁻⁸	283
8.1	0.74	40	4.0x10 ⁻⁶	6.0x10 ⁻⁸	669
9.6	0.90	8	7.5x10 ⁻⁷	9.3x10 ⁻⁸	81
9.9	0.92	5	5.5x10 ⁻⁷	9.5x10 ⁻⁸	58

*BET (Brunauer et al., 1938) surface area given to the right of mineral name.

[†]24 hour contact time.

Table 1. (Continued)*

pH	ppm I ⁻	% I ⁻ sorbed	Moles I ⁻ on solid	Moles/cc I ⁻ in sol ¹¹	K _d (cc/g)
Zinc Hydrotalcite (Cl Substitution)					28.61 m ² /g
4.1	0.97	22	2.2 x 10 ⁻⁶	7.8 x 10 ⁻⁸	289
5.8	1.08	14	1.4 x 10 ⁻⁶	8.6 x 10 ⁻⁸	157
6.1	1.08	14	1.4 x 10 ⁻⁶	8.6 x 10 ⁻⁸	157
8.0	0.98	22	2.2 x 10 ⁻⁶	7.8 x 10 ⁻⁸	276
10.0	1.22	2	2.4 x 10 ⁻⁷	9.8 x 10 ⁻⁸	25
Zinc Hydrotalcite (SO ₄ Substitution)					not measured
4.1	0.97	22	2.2 x 10 ⁻⁶	7.8 x 10 ⁻⁸	289
5.5	1.04	17	1.7 x 10 ⁻⁶	8.3 x 10 ⁻⁸	202
8.0	1.16	7	7.2 x 10 ⁻⁷	9.3 x 10 ⁻⁸	78
10.0	1.19	5	4.8 x 10 ⁻⁷	9.5 x 10 ⁻⁸	50
Zinc Hydrotalcite (CO ₃ Substitution)					not measured
4.8	1.12	7	7.4 x 10 ⁻⁷	9.3 x 10 ⁻⁸	80
6.0	1.17	3	3.3 x 10 ⁻⁷	9.7 x 10 ⁻⁸	34
7.6	1.16	4	4.1 x 10 ⁻⁷	9.6 x 10 ⁻⁸	43
7.9	1.15	5	5.0 x 10 ⁻⁷	9.5 x 10 ⁻⁸	52
10.5	1.14	6	5.8 x 10 ⁻⁷	9.4 x 10 ⁻⁸	61
Lignite Coal					4.72 m ² /g
3.9	0.85	34	3.4 x 10 ⁻⁶	6.6 x 10 ⁻⁸	518
6.1	1.17	9	9.3 x 10 ⁻⁷	9.1 x 10 ⁻⁸	103
7.8	1.32	0	--	--	0 [†]
8.1	1.20	7	7.0 x 10 ⁻⁷	9.3 x 10 ⁻⁸	75
9.9	1.24	4	3.9 x 10 ⁻⁷	9.6 x 10 ⁻⁸	40
Sub-Bituminous Coal					4.35 m ² /g
3.3	0.78	34	3.4 x 10 ⁻⁶	6.6 x 10 ⁻⁸	513
3.7	0.81	31	3.1 x 10 ⁻⁶	6.9 x 10 ⁻⁸	457
6.2	0.64	46	4.6 x 10 ⁻⁶	5.4 x 10 ⁻⁸	844
7.4	1.14	12	1.2 x 10 ⁻⁶	8.8 x 10 ⁻⁸	132 [†]
8.1	0.71	40	4.0 x 10 ⁻⁶	6.0 x 10 ⁻⁸	662
8.9	0.81	31	3.1 x 10 ⁻⁶	6.9 x 10 ⁻⁸	457
9.9	1.15	3	2.5 x 10 ⁻⁷	9.7 x 10 ⁻⁸	26

*BET (Brunauer et al., 1938) surface area given to the right of mineral name.

[†]24 hour contact time.

Table 2. Optimal Tc K_d Values

Material	K_d	pH
CuO	43	6.8
Cu ₂ O	55	7.1
CuS	67	5.4
Cu ₂ S	31	8.6
Imogolite Gel	23	6.4
Imogolite Soil	18	6.0
CMSA-1	134	11.7
ZnHt-Cl	17	5.3
ZnHt-SO ₄	84	6.7
ZnHt-CO ₃	1.3	7.7

Figure 1. K_d versus pH for synthesized calcium monosulfate aluminate in a 1.3 ppm (10^{-3} M NaCl) starting iodide solution. To monitor drift, a low- and high-concentration iodide standard were measured as unknowns throughout the run. In addition, a 1.3 ppm iodide standard was repeatedly analyzed at the start of the session ($n=10$) to determine machine error. Error bars represent $\pm 1 \sigma$.

Figure 2. K_d versus pH for the natural imogolite-bearing soil in a 1.3 ppm (10^{-3} M NaCl) starting iodide solution. Error bars represent $\pm 1 K_d \sigma$ as calculated from repeated measurement of a 1.3 ppm iodide standard.

Figure 3. Iodide K_d versus pH for cinnabar, covellite, chalcocite, tenorite and cuprite in a 1.3 ppm (10^{-3} M NaCl) starting iodide solution. A single experiment was also run under calcium sulfate saturated conditions for selected materials. Error bars represent $\pm 1 \sigma$ as calculated from repeated measurement of a 1.3 ppm iodide standard.

Figure 4. K_d versus pH for three varieties of synthetic hydrotalcite in a 1.3 ppm (10^{-3} M NaCl) starting iodide solution. Error bars represent $\pm 1 \sigma$ as calculated from repeated measurement of a 1.3 ppm iodide standard.

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