DETERMINATION OF METAL ADSORPTION CAPACITY OF SOILS FOR DISPOSAL OF MINING PROCESS SOLUTIONS BY LAND APPLICATION[1]

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Abstract: During mining and processing of precious metals it is often necessary to dispose of treated process solutions to manage the on-site water balance. The solutions typically have elevated levels of trace metals and possibly cyanide. Land application, where solution is applied to soils at a controlled rate, can be an effective means of treatment and disposal. Treatment of the solution occurs as metals are attenuated by soils. Important mechanisms of removal include adsorption by clays, organic matter, and hydroxide and oxide minerals.

Adsorption batch tests using synthetic treated mine process solution were performed on a 0 to 6 inch loam soil from a proposed land application area at a western U.S. precious metals mine to characterize the adsorption behavior of silver, cadmium and copper. Results of testing were used to construct adsorption isotherms to predict the maximum adsorptive potential of, and metal loads to, the soil. The results indicate that the soils were effective at reducing silver, cadmium and copper levels in the process solution and that soil had ample adsorption capacity for these metals, suggesting periodic land application of treated mining process solutions can be a safe, effective management tool.

Introduction

This paper addresses the determination of cadmium (Cd), copper (Cu) and silver (Ag) adsorption capacity of soils collected from a proposed land application area at a precious metal mine located in an alpine environment in the western United States. A discussion of the principles of land application and modeling of the mobility and attenuation of metals in natural soils precedes the discussion of experimental results.

Principles of Land Application

During mining and processing of precious metals it is often necessary to periodically dispose of treated process solutions to manage the on-site water balance. The solutions typically have elevated levels of trace metals and possibly cyanide. Land application, where solution is applied to soils at a controlled rate, can be an effective means of treatment and disposal. Process solutions are typically treated with strong oxidants (hydrogen peroxide, calcium hypochlorite, or sodium hypochlorite) to reduce cyanide to acceptable levels. Treatment may occur in lined ponds or in sophisticated treatment plants, which may utilize other means (e.g. lime addition) to lower metal levels prior to land application. Treated solutions are typically applied to gentle to moderate slopes using a sprinkler, mister or drip emitter distribution system. Areas chosen are typically grass and shrub meadows, although forested areas can also be utilized.

The purpose of land application is to utilize the ability of natural soils to attenuate the migration of metals and other deleterious substances in wastewater. Important mechanisms of removal include adsorption by clays, organic matter, and hydroxide and oxide minerals. Soil characteristics important to the use of an area for land application treatment include hydraulic conductivity, soil thickness, heterogeneity and metal adsorption capacity of

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soils, and the uniformity of these features. Additional factors considered in the siting of a land application area include site physiography, hydrology, vegetation and proximity to mine facilities. Important concepts integral to the use of land application treatment systems are:

- The <u>rate</u> of solution application and <u>total load</u> of metals are controlled to prevent runoff and migration of metals at unacceptable levels;
- Long-term uses of land application area soils are not unduly restricted.

Mobility and Attenuation of Metals in Natural Soils

The soil system is a complex, dynamic three-phase system composed of a skeleton of solids with pore space filled with liquids and gases. Chemical equilibria of soil systems differ from those of lakes and streams in that the reactive surface area of soil solids in contact with soil solution is many times greater than in aqueous systems (Dragun 1988). The mobility of many dissolved ions is strongly affected by interaction with the surfaces of solids in soils.

Although the mobility of metals in soils is controlled by many factors, including dissolution and precipitation reactions, chemical diffusion, and microbial activity, the primary mechanism governing the behavior of metals in many soils is the surface reaction (adsorption) of ions onto the surfaces of clay minerals, metal hydroxyoxides, and organic matter (Lindsay 1979, Bohn et al 1985).

Most metals are similar in that they exist as positively-charged ions that can be adsorbed by negatively-charged clays and minerals in soils and that their solubility generally increases as solution pH decreases. Notable exceptions to this trend are arsenic (As), mercury (Hg), molybdenum (Mo) and selenium (Se), which show an increase in solubility at circumneutral pH values. The solubility of some metals has been ascribed to the formation of sparingly soluble secondary minerals (Lindsay 1979). While this is almost certainly the case for iron, aluminum, and manganese, most researchers agree that sorption of many trace metal ions on the surfaces of iron, aluminum, and manganese oxides, organic matter, and clay minerals governs their solubility in soils (Salomons and Forstner 1988).

Metal ions in soils also form a number of ion pairs, especially at higher pH levels (8 to 11) typical of many treated mining process solutions. Ion-pairing is especially prevalent with hydroxyl (OH^-), sulfate (SO_4^{-2}), and chloride (Cl^-) ions (Stumm and Morgan 1979), which are often present in elevated concentrations in treated process solutions. Metal ions can also "complex" with soluble organic ligands, in a process similar to ion-pairing (Stevenson 1982). Thus, as the abundance of soluble hydroxide (i.e. high pH), sulfate, chloride, and organic carbon increases, metal ion solubility also tends to increase. This fact underscores the utility of site specific testing of soils in a proposed land application area.

The most "reactive" component of the soil system is that portion less than 2 microns in size. The clay-sized fraction is composed mostly of clay minerals, metal hydroxyoxide minerals, and amorphous organic material or humus. Each of these compounds have surface functional groups, primarily consisting of exposed hydroxyl groups or oxygen along surfaces. The large surface area of the clay-sized material and the presence of negatively-charged surface functional groups allows clay-sized particles to react with soluble positively-charged metals and remove them from solution. Surface complexation refers to the process of a surface functional group reacting with a soluble ion to form a covalent bond. This process is known as *specific* adsorption and the resulting complex is often referred to as an "inner-sphere" complex (Sposito 1984). This is the primary reaction affecting sorption of metals in soil. When the bond is electrostatic attraction, an "outer-sphere" complex is formed. Metals are not bound as strongly in an outer-sphere complex as in an inner-sphere complex. Outer-sphere complexation is readily reversible and is also referred to as ion exchange. This is the predominant binding mechanism affecting major cations like calcium, magnesium, and sodium.

Adsorption Modeling

Adsorption of metals in soils has been intensively studied to provide a means of predicting metal behavior in soil systems. The capacity of soils to adsorb most metals appears to be inversely related to pH and to be affected by competition between ions (Salomons and Forstner 1988). For example, the adsorption of cadmium is reduced by addition of calcium. Metal ions also differ in their affinity for specific adsorption surfaces (Sposito 1984).

Adsorption isotherms are used to describe the adsorption of metals by soils. An adsorption isotherm plots the amount of metal adsorbed per unit mass of adsorbate on the y-axis versus the equilibrium solute concentration on the x-axis. The shape of the curve of this plot provides information regarding the adsorptive behavior of the adsorbate (metal), and several mathematical models have been developed to explain this behavior. The most commonly employed are the Freundlich and the Langmuir. The Freundlich equation employs two empirical constants and is plotted on a log-log scale. It is thus very robust. However, it does not allow for the calculation of an adsorption maximum for a given metal. For this reason, it is often useful to employ the Langmuir equation. The Langmuir equation assumes (1) a constant energy of adsorption independent of surface coverage (i.e. a homogeneous surface), (2) adsorption on specific sites with no interaction between adsorbate molecules, and (3) a maximum adsorptive capacity determined by a complete monolayer of molecules on all adsorbent surfaces. Although constant energy of adsorption is rare in natural systems, there typically is significant interaction with molecules already adsorbed. Thus the two factors tend to compensate one another and a relatively constant energy of adsorption is yielded. Given the theoretical limitations, the Langmuir isotherm is best viewed as an empirical description of actual adsorption processes (Bohn et al 1985).

The common form of the Langmuir equation is given as

$$\frac{x}{m} = \frac{KCb}{1 + KC} \tag{1}$$

where C is the equilibrium concentration of adsorbate in question, x/m is the mass of adsorbate per unit mass of adsorbent, K is a constant related to the binding strength, and b is the maximum amount of adsorbate that can be adsorbed on a single complete monomolecular layer. If adsorption conforms to the Langmuir model, the equation defines a limit to adsorption where the amount of material adsorbed fails to increase despite increasing solution concentration, yielding a logarithmic curve with a strong inflection at the point of maximum adsorption.

Equation [1] is often rearranged to the linear form

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b} \tag{2}$$

By plotting C/x/m versus C, a straight line is yielded if the data conform to the Langmuir equation. This line has a slope of 1/b and intercept of 1/Kb. The value for K is the quotient of the slope and the intercept.

Thus, it can be seen that the Langmuir equation allows identification of a maximum adsorption capacity by soils for metals of concern.

This paper discusses the results of adsorption testing for Ag, Cd and Cu in a 0 to 6 inch soil sample collected from a proposed land application area at a precious metal mine located in an alpine environment in the western United States. The soil was exposed to a laboratory solution synthesized to represent the chemistry of a

239

treated process solution. Several additional metals and various soil depth increments were evaluated during the study but only the previously mentioned data are discussed owing to the large scope of the study. These data are sufficient to illustrate the principles of soil adsorption of metals and land application area evaluation.

Materials and Methods

Soil Collection

A series of adsorption batch tests were conducted on a representative sample collected from the A horizon at the 0 to 6 inch depth of a loamy-skeletal, mixed Dystric Cryochrept from the proposed land application area. The sample was retained at near-freezing conditions at field moisture content to prevent biological or physical changes that might affect chemical adsorption.

The soil was a loam with 16 %, 47% and 37 % clay, silt and sand, respectively; 4.5 % organic matter and a cation exchange capacity of 33.50 meq/100 g. Paste pH and conductivity (SC) values were 4.5 and 0.27 mmhos/cm, respectively. The soil was classified as a loamy-skeletal, mixed Dystric Cryochrept.

Adsorption Testing

Two batch solutions (stock and metal) were formulated to closely simulate the chemistry of treated process solution. The stock solution consisted of major ions added at concentrations similar to actual solution values including sulfate (1800 mg/l), calcium (2500 mg/l), sodium (450 mg/l), chloride (3500 mg/l), TDS (9400 mg/l), and specific conductance (11500 μmhos/cm). A second solution (metal) with identical major ion concentrations had trace metals added at roughly 10 times the levels in treated process solution including copper (9.43 mg/l), cadmium (0.122 mg/l), mercury (0.028 mg/l), lead (0.129 mg/l), selenium (0.101 mg/l), silver (0.240 mg/l), and zinc (4.91 mg/l). Metals were added using inductively coupled plasma (ICP) standards to insure accurate results.

The two solutions were mixed at stock:metal ratios of 0:1, 1:1, 2:1, 5:1, 10:1, 20:1, and 100:1. Forty gram subsamples of soil were added to 800 ml of each stock:metal dilution and agitated for 24 h in a rotary extraction apparatus. The extract was then filtered through 0.7 μm glass fiber filters. Silver and cadmium were analyzed using graphite furnace-atomic absorption methods at 0.0005 and 0.002 mg/l instrument detection levels. Copper was analyzed using the ICP method at a 0.15 mg/l instrument detection level. Table 1 shows the initial concentrations of silver, cadmium and copper for each dilution.

Table 1. Initial concentrations of metals in stock:metal solutions.

Metal	Stock:Metal Solution						
	0:1	1:1	2:1	5:1	10:1	20:1	100:1
Ag	0.33	0.17	0.11	0.06	0.03	0.015	0.001
Cd	0.12	0.06	0.04	0.02	0.01	0.005	0.001
Cu	9.43	4.72	3.14	1.57	0.86	0.45	0.09

Results and Discussion

Results of adsorption testing are presented in Table 2. Values for x/m are calculated by subtracting the value for a metal at a given dilution ratio in Table 2 from the corresponding value in Table 1. The amount of metal adsorbed by soil was plotted against the amount remaining in the extracted solution for each dilution. Cadmium adsorption (Figure 1) did not appear to fit a Langmuir curve, which may be in part because the equilibrium

Table 2. Equilibrium metal concentrations in soil extracts.

Metal	Stock:Metal Solution						
	0:1	1:1	2:1	5:1	10:1	20:1	100:1
Ag	0.18	0.08	0.04	0.01	0.006	0.002	<0.0005
Cd	0.10	0.05	0.04	0.02	0.01	0.009	0.005
Cu	2.20	0.64	0.30	<0.15	<0.15	<0.15	<0.15

concentrations of cadmium were far below the soil adsorption capacity. Hence, all soil cadmium adsorption data may lie along the lower linear portion of a Langmuir curve. Nonetheless, a minimum estimate of the soil adsorption capacity can be developed. At high cadmium loads, the soil appears to be able to retain a minimum of 1 mg Cd per kilogram soil, but maximum adsorption capacity may be much higher. At very low solution cadmium concentrations, the soil appears to desorb cadmium into solution, perhaps due to competition for adsorption sites between cadmium and more abundant ions like copper. The net effect is for soils to maintain a solution cadmium concentration of 0.02 mg/l even at cadmium loads far below 0.02 mg/l. The levels of cadmium in the treated solution (actual and synthetic at high dilution) appear to be very close to natural soil equilibrium values, hence little change in the soil cadmium system would be expected due to land application. Copper was added to batch solutions at higher concentrations than other constituents because it was more abundant in the treated process solution.
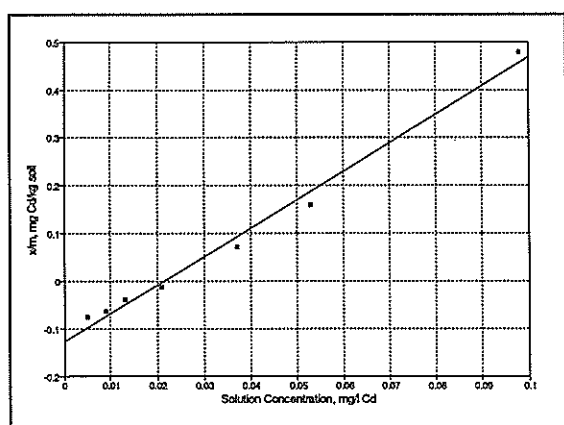
The linear isotherm for copper (Figure 2) indicates that it fits the Langmuir curve closely (Figure 3) with the exception of some data points that were below analytical detection (which were reported at the detection level).
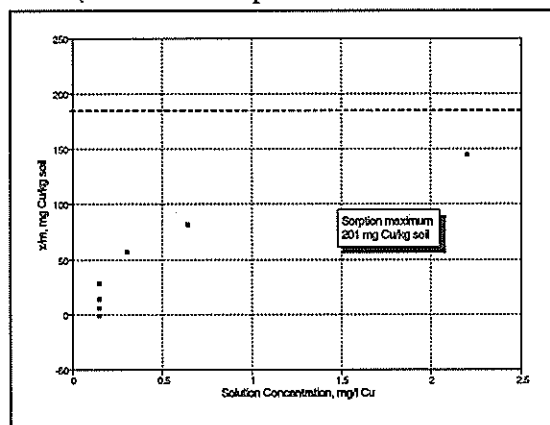

Figure 2. Linear adsorption isotherm for copper exhibiting a Langmuir-type curve of logarithmically decreasing adsorption of copper by soil with increasing solution concentration. Note effect of instrument detection limits on the curve at low C values.
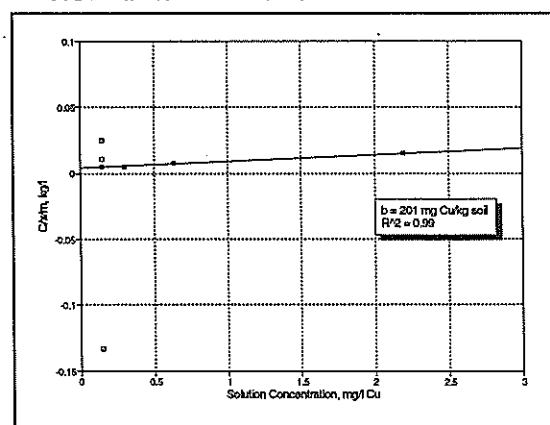

Figure 1. Linear adsorption isotherm for cadmium showing linear adsorption behavior of cadmium by soil with increasing solution concentration.

Figure 3. Langmuir isotherm for copper showing maximum adsorption of copper by soil at 201 mg Cu/kg soil.

241

Using all data points above the detection level, the value of b, maximum adsorption capacity, in the Langmuir equation was 201 mg Cu per kilogram soil. Copper is known to have a strong affinity for soil organic matter and is typically retained strongly in surface soils.

Silver, like copper, has a very strong affinity for soil organic matter and also like copper appeared to follow a Langmuir curve (Figure 4) very closely. The linearized plot of silver on the Langmuir isotherm (Figure 5) indicates an adsorption maximum of 3.29 mg Ag per kilogram soil.
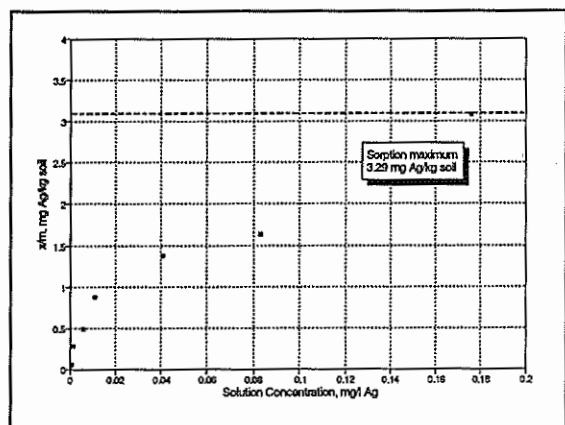

Figure 4. Linear adsorption isotherm for silver exhibiting a classic Langmuir-type curve of logarithmically decreasing adsorption of silver by soil with increasing solution concentration.
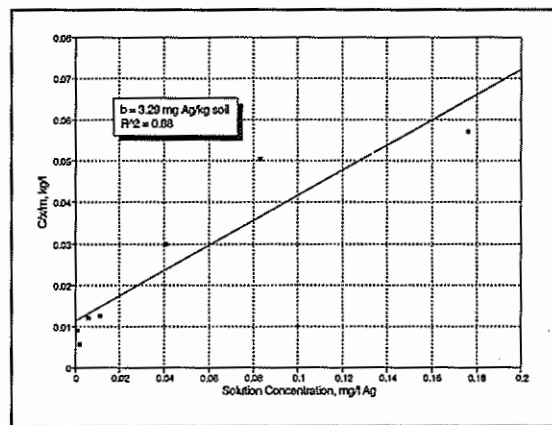
Figure 5. Langmuir isotherm for silver showing maximum adsorption of silver by soil at 3.29 mg Ag/kg soil.

Determination of Maximum Metal and Solution Loading

The maximum solution load can be calculated by dividing the maximum metal load (shown in kilograms metal per hectare of soil for convenience) by the average solution concentration for a given metal. These values are shown in Table 3.

Table 3. Maximum metal and solution loading to soilsbased on adsorption batch test data.

Metal	Maximum Metal Load[1] (kg/ha)	Average Metal Concentration of Treated Solution (mg/l)	Maximum Solution Load	
			(m/ha)	(l/ha)
Silver	12.83	0.15	8.55	8.55×10^7
Cadmium	3.90	0.02	19.50	1.95×10^8
Copper	783.90	4.0	19.60	1.96×10^8

[1] - Assuming a 30 cm treatment zone thickness, a bulk density of 1.3 g/cm^3, and uniform solution application.

Of the three metals shown in Table 3 it can be seen that silver would limit the amount of solution which could be applied per hectare (8.55×10^7 l). Values are also shown in meters of solution per hectare for convenience. In practice, the *rate* at which a solution is applied to a soil is limited by the hydraulic conductivity of the soil, the depth to groundwater and the evapotranspiration demand. Characterization and management of these

factors ensures that solution application rates are low enough to prevent ponding of solution, runoff, or significant migration to groundwater.

CONCLUSIONS

As part of a land application study for a precious metals mine, an evaluation of soil adsorption capacity was performed for a proposed land application area which would receive treated process solution. Adsorption isotherms were developed to characterize metal adsorption and to calculate maximum metal loads to soils. Results indicated that the 0 to 6 inch depth of soils in the proposed land application area would provide ample adsorption of silver, cadmium and copper if subjected to well-managed application of process solutions and provided the loading rate and capacity for adsorption are not exceeded.

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