



## Soil Cation Exchange Capacity for Mercury

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### Abstract

Mercury is one of the most hazardous air and water pollutants. Before the issuance of the U.S. Clean Air Mercury Rule (CAMR) for coal-fired electric boiler utilities in 2005, much of scientific research focused on mercury atmospheric fate and transport. Presently, large quantities of mercury-laden fly ash and other flue gas adsorbents are being stored in lagoons and landfills because fly ash supply exceeds its demand. Mercury aqueous transport became its principal environmental transport mode. As demonstrated in the previous author's class, mercury in fly ash leachate may exceed the Maximum Contaminant Level of 2  $\mu\text{g/l}$ . This paper shows the derivation of mercury soil cation exchange capacity (CEC) and selectivity sequence as parts of mercury aquatic transport mechanism. The same or similar methodology can be applied to other metals.

### 1. Introduction

Mercury is one of the trace metals in coal than can occasionally be found in groundwater contaminated with fly ash leachate. Compliance with the CAMP has resulted in a tenfold increase in the amount of fly ash mercury. Consequently, there is an increased scientific interest in quantifying the extent of groundwater contamination if it is mixed with fly ash leachate.

A groundwater plume delineation entails both aquifer and plume characterization. The latter requires the knowledge of the initial plume concentration that, in the case of fly ash leachate, is the average leachate concentration. Mercury distribution within the plume depends on the aquifer's physical and chemical characteristics. An aqueous metal transport mechanism entails complexation reactions with aquatic ligands and condensation reactions on soil aluminosilicates. The former can be described using Mass Law for the dominant aquatic mercury species (as  $\text{Hg}^{2+}$ )

and the latter using the Freunlich or Langmuir isotherm, provided convincing soil adsorption data. Concentrations of mercury species adsorbed onto soil particles and those remaining in solution are independent of mercury (II) ion concentration. Whilst they are a function of the number of hydroxyl groups on the surfaces of alumino-silicate particles, free  $\text{Hg}^{2+}$  concentration is a function of soil CEC.

Assuming negligible biodegradation and volatilization rates, mercury plume retardation by soil consists of two independent steps. The first step, called initial retardation, entails mercury II ( $\text{Hg}^{2+}$ ) ion exchange through electrostatic diffuse layer on soil particle surfaces. The second step is governed by physical adsorption of mercury (II) complexes with aquatic ligands such as sulfate, sulfite, chloride, phosphate, nitrate, etc. on alumino-silicate surfaces. The extent of adsorption is heavily dependent on aquafer pH.

In unpolluted aquifers, the dominant aquatic ligand is chloride and, to a lesser degree, sulfate. Whilst mercury complexes with sulfur are insoluble and precipitate once formed, mercury chloride passes through aquafer. Free mercury as an ion is adsorbed according to the soil selectivity sequence for metals where each metal has its fixed position relative to other metals.

## 2. The Constant Charge in Clays

Soil cation exchange capacity (CEC) is one of the most important factors influencing the extent of metal cation adsorption on soil particles. The difference between adsorbed metal and that remaining in aqueous solution defines the amount of free metal available for further reactions such as hydrolysis, complexation, precipitation, radioactive decay, volatilization, oxidation,

reduction, and biological consumption. Metal-ligand complex concentration can be predicted if chemical composition, temperature, hydrogen ion activity and reaction product formation constants are known.

Free aqueous  $\text{Hg}^{2+}$ , unlike  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , normally presents in minute amounts because mercury compound solubility products are much larger than those for  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . It is retarded by soil depending on soil CEC.

Isomorphous substitution of one cation for another within soil crystal structure leads to charge imbalance in silicate clays and defines the constant clay charge. This imbalance accounts for the ability of clays to attract ions to particle surfaces.

The net negative charge is found in minerals where there has been an isomorphous substitution of a lower-charged ion (e.g.  $\text{Mg}^{2+}$ ) for a higher-charged ion (e.g.  $\text{Al}^{3+}$ ). Such a substitution commonly occurs in aluminum-dominated dioctahedral sheets. This results in an unbalanced negative charge which is an important source of negative charges on smectite, vermiculite, and chlorite clay micelles. Another example is a substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in a tetrahedral sheet, which also leaves one unbalanced negative charge. Such a substitution is common in several of soil silicate clay minerals such as fine-grained micas, vermiculites and some smectites [4]. Generally, soils in temperate regions tend to be dominated by the constant clay charge described as follows [7,8]:

$$\sigma_p = \left( \frac{2c\epsilon RT}{\pi} \right)^{0.5} \sinh \frac{zF\psi}{2RT} \quad (1)$$

where

$c$  – electrolyte concentration, mol

$\varepsilon$  – medium dielectric constant,  $C^2/J$

$R$  – universal gas constant, 8.314 J/K mol

$T$  - absolute temperature, K

$z$  – valence of potential determining ion

$F$  – Faradey constant, 96,485 J/V mol

$\psi$  – surface potential, V.

### 3. The Variable Charge in Clays

There is a second source of charges on some silicate clays such as kaolinite, humus, allophone, and Fe and Al hydroxides. Because these charges are dependent on the soil pH, they are termed the variable or pH-dependent, in contrast to the constant or more permanent charges resulting from isomorphous substitution. All soils contain a mixture of both the constant and the variable charge surfaces, even though one type might tend to dominate over the other. The total net surface charge density in a mixed system is a sum of the constant and the variable surface charge densities and is given as

$$\sigma_t = \sigma_p + \sigma_v \quad (2)$$

The variable surface charge density is defined as follows [4]:

$$\sigma_p = \left( \frac{2c\varepsilon RT}{\pi} \right)^{0.5} \sinh 1.15z(pH_0 - pH) \quad (3)$$

where

$c$  – electrolyte concentration, mol

$\varepsilon$  – medium dielectric constant,  $C^2/J$

$R$  – universal gas constant, 8.314 J/K mol

$T$  - absolute temperature, K

$z$  – valence, dimensionless

$F$  – Faraday constant, 96,485 J/V mol

$pH_0$  – hydrogen ion activity when surface potential  $\psi_0 = \psi$

$pH$  – soil hydrogen ion activity, s.u.

The soil cation exchange capacity is defined as the sum of all exchangeable cations that soil can adsorb. If clay mineral structure is known, the charge density per unit mass of soil can be determined using Eq. (1), (2), (3). For example, in montmorillonite one  $Mg^{2+}$  ion is substituted for every sixth  $Al^{3+}$  ion which means that a higher replacing power cation such as  $Cu^{2+}$ ,  $Fe^{3+}$  or  $Th^{4+}$  can replace one  $Mg^{2+}$  ion in a montmorillonite octahedral sheet. Using the Avogadro number, the number of  $Cu^{2+}$  ions in a soil-water mixture adsorbed into montmorillonite octahedral sheets can be calculated for a known  $Cu^{2+}$  aqueous concentration. The calculation assumes that every montmorillonite layer is saturated with water.

Based on the soil selectivity sequence for  $Hg^{2+}$  ion (Table 2),  $Hg^{2+}$  is not capable of replacing the octahedral layer cation metals in many clays except for hectorite (smectite subgroup) where one  $Li^+$  is substituted for every tenth  $Mg^{2+}$ . Theoretically, one  $Hg^{2+}$  can be substituted for every twentieth  $Mg^{2+}$  in hectorite if there are no competing cations in solution. On the other hand, the charge deficiency in hectorite, montmorillonite and many other clays is 0.66 C/unit cell which means that approximately 3 unit cells of clay is needed for one  $Hg^{2+}$  ion. This stoichiometry is a function of concentration of competing aqueous cations.

This discussion shows that soil CEC affects free  $\text{Hg}^{2+}$  groundwater movement to the extent determined by the soil type and concentration of competing aqueous cations. In variable charge clays such as kaolinite, soil pH is a factor that may affect  $\text{Hg}^{2+}$  ion mobility and needs to be taken into consideration.

CEC is measured by displacing all the bound cations with a concentrated solution of another cation, and then measuring either the displaced cations or the amount of added cation that is retained. Barium ( $\text{Ba}^{2+}$ ) and ammonium ( $\text{NH}_4^+$ ) are frequently used as exchanger cations, although many other methods are available. CEC measurements depend on pH, and therefore are often made with a buffer solution at a particular pH value. If this pH differs from the natural pH of the soil, the measurement will not reflect the true CEC under normal conditions. Such CEC measurements are called "potential CEC". Alternatively, measurement at the native soil pH is termed "effective CEC", which more closely reflects the real value, but can make direct comparison between soils more difficult. Table 1 lists effective CEC and surface areas for several soil types.

Table 1. Soil CECs and Surface Areas.

Mineral	Type	CEC (surface charge cmolc/kg <sup>-1</sup> )	Surface area (external m <sup>2</sup> /g <sup>-1</sup> )
Smectite	High activity clay	-80 to -150	80 to 150
Vermiculite	High Activity clay	-100 to -200	70 to 120
Fine Mica	High activity clay	-10 to -40	70 to 175
Chlorite	High activity clay	-10 to -40	70 to 100
Kaolinite	Low activity clay	-1 to -15	5 to 30
Gibbsite	Al-oxide	+10* to -5	80 to 200
Goethite	Fe-oxide	+20 to -5	100 to 300
Allophane	Amorphous	+10 to -150	100 to 1000
Humus	Organic	-100 to -500	Variable

\* Positive sign indicates that the minerals no longer exhibit a cation exchange capacity, but rather an anion exchange capacity.

Base saturation expresses the percentage of potential CEC occupied by the cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  or  $\text{Na}^{+}$ . These are traditionally termed "base cations" because they are non-acidic, although they are not bases in the usual chemical sense. Base saturation provides an index of soil weathering and reflects the availability of exchangeable cationic nutrients to plants.

Positive charges of soil minerals can retain anions by the same principle as cation exchange. The surfaces of kaolinite, allophane and iron and aluminum oxides often carry positive charges. In most soils the cation-exchange capacity is much greater than the anion-exchange capacity, but the opposite can occur in highly weathered soils, such as ferrosols.



The CEC is expressed in terms of moles or equivalents of positive charge adsorbed per unit mass of soil ( $1 \text{ meq}/100\text{g} = 1 \text{ cmol}_c/\text{kg}$ ). Thus, if a soil has a CEC of  $10 \text{ cmol}_c/\text{kg}$ , 1 kg of the soil can adsorb 10 cmol of  $\text{H}^+$  which can be exchanged for 10 cmol of another monovalent cation such as  $\text{K}^+$  and  $\text{Na}^+$ , 5 cmol of a divalent cation such as  $\text{Hg}^{2+}$ , or 3.33 cmol of  $\text{Al}^{3+}$ .

The soil CEC in  $\text{meq}/\text{kg}$  for  $\text{Hg}^{2+}$  ion can be described by the following expression:

$$CEC = \frac{10^3 \sigma_t}{2\rho F \cdot MW_{hg}} \quad (4)$$

where

$\sigma_t$  – total soil negative charge, Eq. (2)

$\rho$  – soil density, approximately  $2.65 \text{ kg}/\text{L}$

$F$  – Faraday constant,  $96,500 \text{ Coulomb}/\text{mole electrons}$

$MW$  – molecular weight of  $\text{Hg}^{2+}$ ,  $200.6 \text{ (g/mol)} = 200.6 \text{ mol H}^+$ .

The Faraday constant for 1 mole of protons is  $96,500 \text{ C}$  [6]. From the point of view of fundamental particles, the charge of one proton equals to the charge of one electron. The molecular weight of  $\text{Hg}^{2+}$  equals the molecular weight of a proton times 200.6. One liter of soil volume is assumed to weight  $2.65 \text{ kg}$  [4].

After a substitution of the values above in Eq. (3,4), the CEC expression for  $\text{Hg}^{2+}$  ion takes the following form:

$$CEC(\text{meq}/\text{kg}) \approx 10^{-5} \cdot \left( \frac{2c\varepsilon RT}{\pi} \right)^{0.5} \cdot \left( \sinh \frac{zF\psi}{2RT} + \sinh 1.15z(pH_0 - pH) \right) \quad (5)$$

where all parameters are as specified previously.

**4. Soil Selectivity Sequence for Mercury II Ion**

The relative affinity of aqueous  $\text{Hg}^{2+}$  for soil depends on the soil composition and pH. As a rule of thumb, the relative affinity (selectivity) of soil for a free metal cation will increase with the ability of the cation to form inner-sphere surface complexes. For a series of metal cations, this ability is a function on their ionic radii and valence. Table 2 shows the mercury II adsorption affinity series (selectivity sequence) for Hg II based on the ionic radii for the most common metals.

Ionic radius and valence are the two most important atomic properties of elemental metals in soil minerals. Valence is the ratio of the electric charge to the charge of a proton. The standard ionic radii calculated from crystallographic data are listed in Table 2 [8]. The radii depend on the valence ( $Z$ ) as well as the coordination number ( $\text{CN}$ ) of metal cations. Radius decreases as the valence increases and increases with an increase in the  $\text{CN}$  for a constant valence. The quantity  $s = Z/\text{CN}$  determines the strength of the ionic bond between a cation and an anion.

The soil adsorption selectivity coefficients for  $\text{Hg}^{2+}$  ion relative to other metal cations were calculated as  $(Z/\text{IR})^{\text{HgII}}/(Z/\text{IR})^{\text{metal}}$  and are listed in the last column in Table 2. The affinity coefficients for  $\text{Hg}^{2+}$  in this sequence range from 0.25 for  $\text{Al}^{3+}$  (low affinity) to 3.69 for  $\text{Cs}^+$  (high adsorption affinity). The average selectivity coefficient for  $\text{Hg}^{2+}$  is estimated as the midpoint in the selectivity sequence :  $(3.69 + 1)/2 = 2.345$ .

Table 2. Soil Adsorption Selectivity Sequence for  $\text{Hg}^{2+}$  [9].

Metal	Z	CN	IR (nm)	Z/IR	Z/CN	Metal/ $\text{Hg}^{2+}$	$\text{Hg}^{2+}$ /Metal
Cs	1	12	0.188	5.32	0.08	0.27	3.69
Rb	1	12	0.172	5.81	0.08	0.30	3.37
Cs	1	6	0.167	5.99	0.17	0.31	3.27
K	1	12	0.164	6.10	0.08	0.31	3.22
Rb	1	6	0.152	6.58	0.17	0.34	2.98
K	1	8	0.151	6.62	0.13	0.34	2.96
K	1	6	0.138	7.25	0.17	0.37	2.71
Hg	1	6	0.119	8.40	0.17	0.43	2.33
Ag	1	6	0.115	8.70	0.17	0.44	2.26
Na	1	6	0.102	9.80	0.17	0.50	2.00
Li	1	6	0.076	13.16	0.17	0.67	1.49
Ba	2	6	0.135	14.81	0.33	0.76	1.32
Pb	2	6	0.119	16.81	0.33	0.86	1.17
Li	1	4	0.059	16.95	0.25	0.86	1.16
Sr	2	6	0.118	16.95	0.33	0.86	1.16
Ca	2	8	0.112	17.86	0.25	0.91	1.10
<u>Hg</u>	2	6	0.102	19.61	0.33	1.00	<u>1.00</u>
Ca	2	6	0.1	20.00	0.33	1.02	0.98
Mn	2	6	0.083	24.10	0.33	1.23	0.81
Fe	2	6	0.078	25.64	0.33	1.31	0.76
Co	2	6	0.075	26.67	0.33	1.36	0.74
Cd	2	6	0.075	26.67	0.33	1.36	0.74
Zn	2	6	0.074	27.03	0.33	1.38	0.73
Cu	2	6	0.073	27.40	0.33	1.40	0.72
Mg	2	6	0.072	27.78	0.33	1.42	0.71
Ni	2	6	0.069	28.99	0.33	1.48	0.68
Cu	2	4	0.057	35.09	0.50	1.79	0.56
Mn	3	6	0.065	46.15	0.50	2.35	0.42
Fe	3	6	0.065	46.15	0.50	2.35	0.42
Zr	4	8	0.084	47.62	0.50	2.43	0.41

Co	3	6	0.061	49.18	0.50	2.51	0.40
Pb	4	6	0.078	51.28	0.67	2.62	0.38
Al	3	6	0.054	55.56	0.50	2.83	0.35
Ti	4	6	0.061	65.57	0.67	3.34	0.30
Mn	4	6	0.053	75.47	0.67	3.85	0.26
Al	3	4	0.039	76.92	0.75	3.92	0.25

## 5. Summary

Since coal combustion fly ash contains more mercury than before the CAMR and aqueous transport is the most probable mode for mercury release from fly ash into environment, there is a reasonable scientific interest in defining coal fly ash leachate mercury. For unpolluted groundwater mercury species, mercury loss via vapor transport mechanism and bacterial and fungal metabolism is negligible due to low vaporization and metabolic rates. Divalent mercury plume propagation in aquatic media is governed by sorption on soil particles which can be described using Mass Law for dominant aquatic mercury species. Concentration of mercury species remaining in aqueous solution is the difference between initial mercury in leachate and mercury available for sorption onto soil. For a series of metal cations, the relative affinity (selectivity) of soil to adsorb metal is a function of their ionic radii. This paper derives and presents the soil selectivity sequence for mercury (II) and a CEC expression for mercury (II). Similar expressions, derived for other metals, can be incorporated into groundwater fate and transport equations to define initial plume concentration.



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