Silver Removal from Aqueous Solution by Adsorption on Concrete Particles

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The ability of concrete to remove silver from its aqueous solutions was studied. Silver removal is favored by low concentration and high pH at room temperature. The intrinsic acidity constants, average pK_{a1}^{int} and average pK_{a2}^{int} were determined. The calculated pH_{PZC} (5.4) is in agreement with the pH_{PZC} values determined from zeta potential measurements, indicating that the concrete particulate behaves amphoterically.

The total acidity capacity for the negative and positive surface was $0.5 \frac{\mu C}{cm^2}$. A surface complex formation model (SCFM) was used to describe the adsorption of silver onto concrete particles. In general the equilibrium constants, the pK_S^i values, decrease as the silver loadings increase.

Key Words: Concrete, Equilibrium constants, Intrinsic acidity constants, Silver adsorption, Surface acidity.

Introduction

The major industrial use of silver is as silver halide in the manufacture of photographic film. In 1983, approximately 44% of silver was used in the manufacturing of chemicals for photographic products in the USA. Other industrial uses of silver include the production of electrical contacts and switching gear, batteries, catalysts and mirrors. It has also been used for jewelry, coins and indelible inks[1]. These industries emit discharges, which not only contribute to water deterioration but also adversely affect the aquatic ecosystem. Sorption is considered the dominant process in silver partitioning in water and its mobility in soils and sediments[2]. Silver accumulations in marine algae have been reported mainly because of adsorption rather than uptake. Free silver ion is hazardous to representative species of sensitive aquatic plants and invertebrates. In humans, serious toxic effects have resulted only from overdoses of medicines containing silver. However, skin contact with silver compounds can cause allergic reactions such as rashes, burning and swelling[3]. Very little is known about the chemical interactions between silver and concrete in the aqueous system. Published data concerning the interaction of silver with soil are rare. However, silver is very

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strongly adsorbed by clays and organic matter[4]. Some investigators[5] have used kaolin as a filter element for the removal of active silver from water. In the present investigation, a comprehensive study was undertaken to follow the adsorption of silver on concrete. Parameters such as pH and silver concentrations, which may affect the chemical interactions, were studied. The surface acidity of hydrous concrete was determined using electrophoretic mobility measurements. A surface complex formation model (SCFM) originally developed by Huang and Stumm[6] was used to describe the adsorption of silver onto concrete particles.

Experimental

All the chemicals used were of analytical reagent grade and were supplied by Fisher Scientific Company, Springfield, NJ, or Aldrich Chemical Company, Milwaukee, WI.

Concrete Particles: Concrete blocks were obtained from Yardville Supply Co, NJ. These were manufactured from ordinary Portland cements. The concrete blocks were crushed by a compressive testing machine (Tinius Olsen Testing Machine Co., Willow Grove, PA) and then finely ground. The powdered concrete was passed through an ASTM standard sieve no. 200. A size fraction of 0.18 mm-0.54 mm was used for batch equilibrium experiments. The concrete pH was measured in deionized water suspension with a pH meter. The pH was 11.0, indicating that the concrete was a highly alkaline material. The unwashed concrete particles contained chlorides, which form precipitate with silver. Before being subjected to adsorption processes and experimental techniques, the concrete was treated to remove chlorides.

Characterization of concrete particulates

The specific surface area of the concrete particles was 3.36 m^2/g, as determined by a Quanta Chrome Corporation Nova 2200 High Speed Gas Sorption analyzer.

The pH $_{PZC}$ of the concrete particles was 5.4, as determined by a Zeta-meter (Lazer Zee Meter, Model 500 Pen Kem Inc, Bedford Hills, NY) (Figure 1).

SEM-EDAX and XRD Analysis: The (SEM-EDAX) (Phillips 501 scanning electron microscope and Phillips EDAX 9100) results revealed that the major chemical components of the concrete material were Al, Si, Ca, Fe and Mg. X-ray diffraction analysis (Phillips Semi-automatic X-ray diffractometer) identified the crystal phases of the concrete particles as calcite ($CaCO_3$), quartz (SiO_2) gehlenite ($Ca_2 Al_2 SiO_7$), orthopyroxene (($Fe Mg SiO_3$) and olivine (($Fe, Mg)_2 SiO_4$).

Sample treatment

Four bottles each containing 25 g of concrete with 100 ml of 0.1 N HNO_3 were placed on a shaker for two h and then centrifuged for 30 min at 2000 rpm. The same material was then shaken with deionized water a few times and centrifuged. The resistance and pH of the supernatants were measured (Table 1). The temperature was kept constant at 20°C. After treatment and drying at 95°C the weight of the sample was 96.4 g. The total loss in the 100 g of concrete was less than 3%.

Testing of the samples

Ten grams of treated concrete was shaken with 100 ml of 0.05 M $NaNO_3$ at pH 0.5 for 24 h. The suspension was centrifuged for 30 min and the supernatant titrated with (0.01-1 M) $AgNO_3$ solution. No detectable

precipitate with chloride was observed.

Batch adsorption experiments

The batch adsorption experiments were carried out using pH as a master variable. Silver nitrate (AgNO$_3$) was chosen as the form in which to deliver silver ion. The experiments were conducted by shaking 10 g of the treated adsorbent with 100 ml of silver nitrate solution of desired concentrations i.e. 1 E-4, 5 E-4 and 1 E-3 M/L, containing the appropriate amount of 0.1 or 1 N HNO$_3$ in different polyethylene bottles. The ionic strength was kept constant at 0.05 M NaNO$_3$. The samples were shaken on a shaker (Eberbach Co., Ann Arbor, MI) at 150 excursions per minute for 24 h, the ideal period for reaching equilibrium. The final pH was recorded and aliquots of the suspensions centrifuged. The residual concentration of metal was analyzed with a flame atomic absorption spectrophotometer (Perkin-Elmer, Model Zeeman 5000).
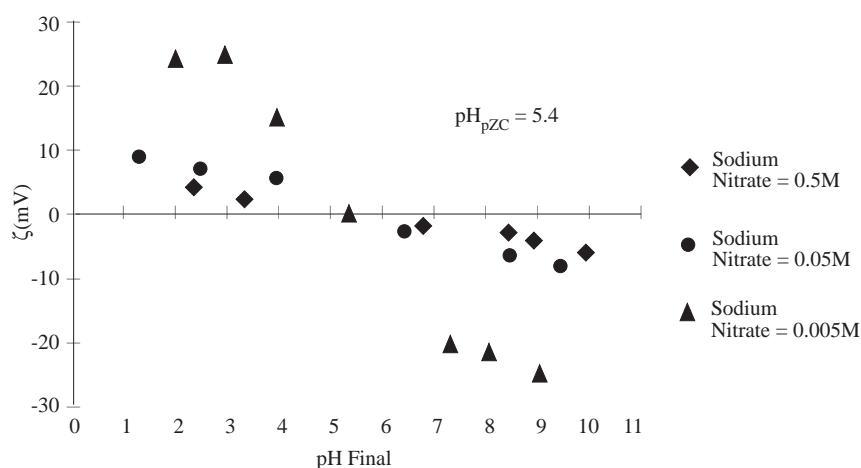

Figure 1. Zeta Potential for the Treated Concrete.

Table 1. The Resistance and pH of the Supernatants After Treating the Concrete.

Supernatants	Resistance (Ω)	pH
0.1 N HNO$_3$	33.42	7.47
Deion. Water	51.23	8.97
Deion. Water	52.44	9.26
Deion. Water	46.96	9.25
Deion. Water	46.55	9.25

Results and Discussion

Table 1 shows that the resistance of the supernatants is affected first by nitrates and then by chlorides. After washing with deionized water most of the chlorides and acids are removed and the resistance and pH become constant.

At pH 1.5 the solid is insoluble (Figure 2). The solubility diagram was constructed by taking the equilibrium constant as

$$\log k = \frac{-\Delta G}{2.303RT} \tag{1}$$

Below pH 2, silver in Ag_2O_3 form in the aqueous medium reaches its least soluble state and allows us to greatly simplify construction of the diagram by plotting log [AgO] vs pH according to the equation

$$\log[AgO] = -12.52 + 14 - pH \tag{2}$$

For the different equations, log c against each pH has been plotted. Ivanova et al.[7] have also observed that with the addition of nitric acid to pH 1.5-2, the silver containing solution is precipitated. Therefore, a pH range of 2 to 11 was considered for most of the adsorption experiments. Figure 3 shows the percent removal as a function of final pH after the 24-h reaction span. The results show an increase in percent removal at basic pH. It is assumed that the surface sites for silver are anionic and can act as weak Brønsted bases.

When pH is decreased, there is a greater concentration of H^+ to compete with Ag^+ for these anionic sites, resulting in lower percent removal.

By increasing the dose of adsorbent to 10 g, the maximum removal of silver at a concentration of 1 E-4 M/L was achieved, indicating that silver is only minimally adsorbed onto concrete.
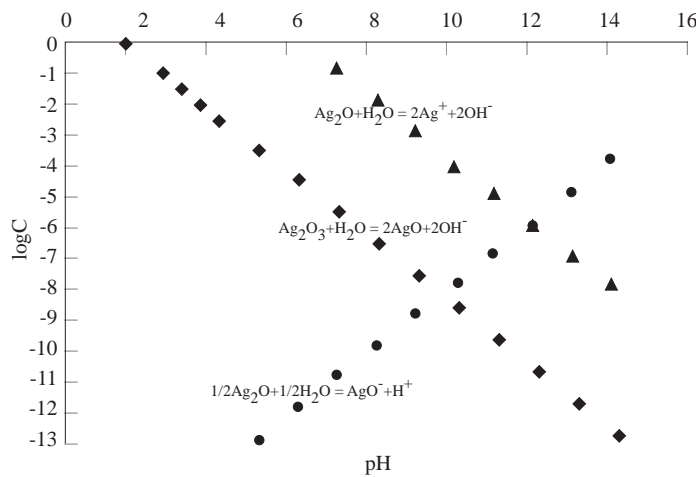

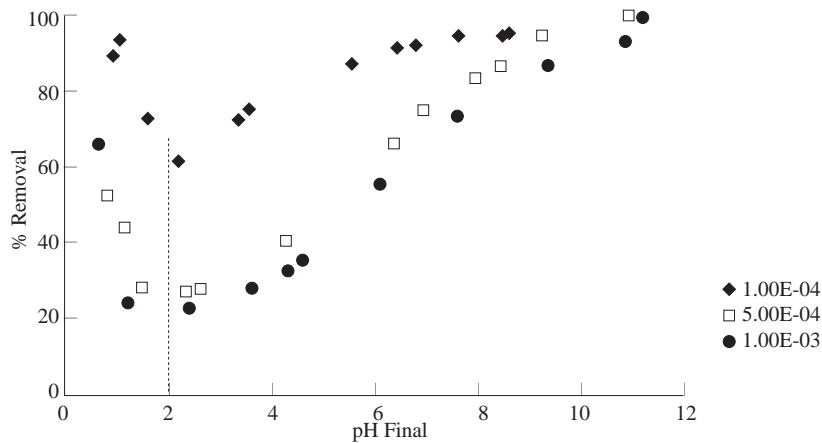**Figure 2.** Solubility Plot for Soluble Silver in Water.

Figure 3. Percent Removal of Silver Nitrate at Various Concentrations on 10 g Concrete.

Surface acidity

After ionic dissolution, the solid surface develops hydroxyl groups, which behave amphoterically.

$$SOH_2^+ = SOH + H^+; \quad K_{a1}^{int} = \frac{(SOH)(H^+)}{(SOH_2^+)} \tag{3}$$

$$SOH = SO^- + H^+; \quad K_{a2}^{int} = \frac{(SO^-)(H^+)}{(SOH)} \tag{4}$$

Where S stands for the Brønsted sites. The protonated (SOH_2^+), neutral (SOH) and ionized (SO^-) surface hydroxyl groups may not be structurally or chemically fully equivalent[6], although to follow the reaction equilibrium we considered a single hydroxyl group in the chemical reaction.

The total number of surface sites available for adsorption, $N_t(\mu \ C/cm^2)$, is defined as "surface acidity capacity" and is therefore the sum of these three hydroxo groups.

$$N_t = (SOH_2^+) + (SOH) + (SO^-) \tag{5}$$

The surface concentration of proton [H^+] is related to its bulk phase, [H^+], by the Boltzmann equation:

$$[H^+] = [H^+]_{bulk} e^{\frac{-F\Psi_0}{RT}} \tag{6}$$

where F, Ψ_0, R and T are the Faraday constants, surface potential, gas constant and absolute temperature.

According to the Graham equation derived from the Gouy-Chapman electrical double layer theory, in the absence of specific adsorption the surface charge density, σ, can be related to the surface potential, Ψ_0 (mv) for a 1:1 electrolyte. For simplicity, the zeta potential ζ, can be expressed as the surface potential Ψ_0 (mv).

$$\sigma(\frac{\mu C}{cm^2}) = 11.7\sqrt{C} sinh \frac{1}{0.05}\Psi_0 \times 10^{-3} \times 10^6 \tag{7}$$

At pH < pH$_{PZC}$, the surface is positively charged, therefore

$$N_t \cong (SOH_2^+) + (SOH) \tag{8}$$

And when pH > PH$_{PZC,}$ the surface is negatively charged, i.e.

$$N_t \cong (SOH) + (SO^-) \tag{9}$$

The surface concentration (in mole/g), (SOH_2^+) and (SO^-), is converted from the surface charge density (in C/cm^2), σ- (at pH > pH$_{PZC}$) and σ+ (at pH < PH$_{PZC}$), respectively, i.e

$$(SOH_2^+) = \frac{S_A}{F}\sigma^+ \tag{10}$$

And

$$(SO^-) = \frac{S_A}{F}\sigma^- \tag{11}$$

where S_A is the specific surface area (in m^2/g).

By substituting the above relationship into Equations 3 and 4 and with further mathematical rearrangement, one arrives at

$$\frac{1}{[H^+]} = \frac{N_t}{K_{a1}^{int}\sigma^+} - \frac{1}{K_{a1}^{int}} \qquad \text{For the positive charge surface} \tag{12}$$

$$[H^+] = \frac{N_t K_{a2}^{int}}{\sigma^-} - K_{a2}^{int} \qquad \text{For the negative charge surface} \tag{13}$$

By plotting H^+ vs. $\frac{1}{\sigma^-}$ (Figure 4) and $\frac{1}{H^+}$ vs. $\frac{1}{\sigma^+}$ (Figure 5), the average intrinsic acidity constants, pK_{a1}^{int}, pK_{a2}^{int} and N_t are determined. The average value of N_t ($0.5\frac{\mu C}{cm^2}$), average pK_{a1}^{int} (4.61) and average pK_{a2}^{int} (6.62) were obtained from these plots.

Theoretically, pH_{PZC} is a mean value of pK_{a1}^{int} and pK_{a2}^{int}. The calculated pH_{PZC} values are in agreement with the pH_{PZC} values determined from zeta potential measurements. This is a clear indication that the concrete particulate behaves amphoterically.
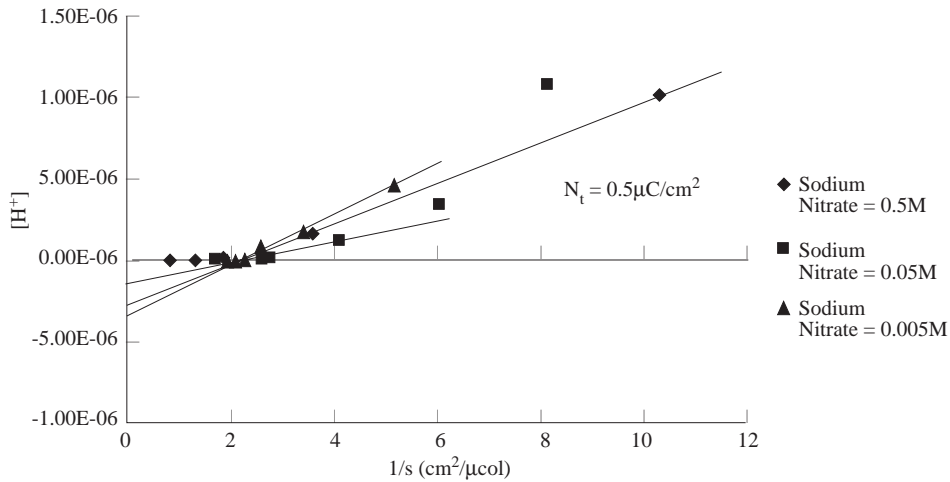

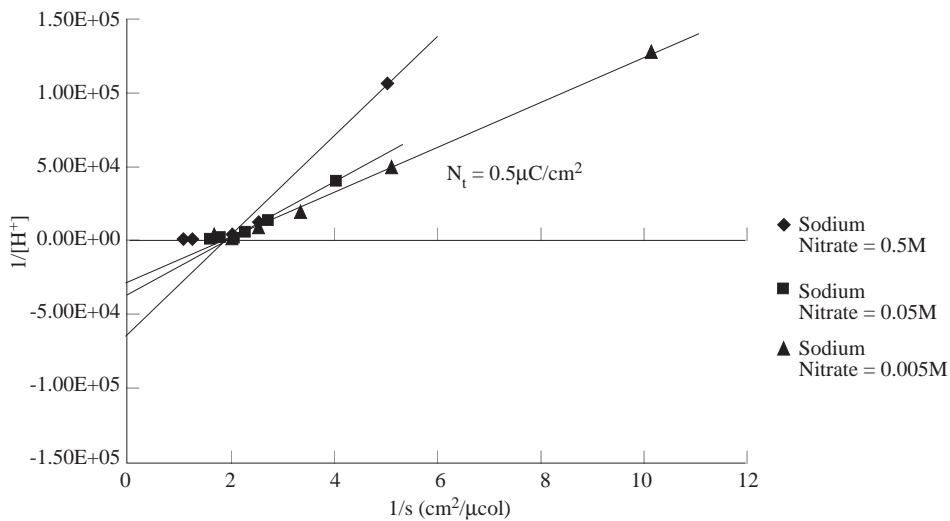**Figure 4.** Surface Acidity for Negative Surface.

Figure 5. Surface Acidity for Positive Surface.

Speciation diagram

The speciation of the hydrous concrete particle is defined as

$$\alpha^+ = \frac{[H^+]^2}{\left([H^+]\exp(-\frac{F\Psi_0}{RT})\right)^2 + K_{a1}^{int}[H^+]\exp(-\frac{F\Psi_0}{RT}) + K_{a1}^{int}K_{a2}^{int}} \tag{14}$$

$$\alpha^0 = \frac{K_{a1}^{int}[H^+]}{\left([H^+]\exp(-\frac{F\Psi_0}{RT})\right)^2 + K_{a1}^{int}[H^+]\exp(-\frac{F\Psi_0}{RT}) + K_{a1}^{int}K_{a2}^{int}} \tag{15}$$

$$\alpha^- = \frac{K_{a1}^{int}K_{a2}^{int}}{\left([H^+]\exp(-\frac{F\Psi_0}{RT})\right)^2 + K_{a1}^{int}[H^+]\exp(-\frac{F\Psi_0}{RT}) + K_{a1}^{int}K_{a2}^{int}} \tag{16}$$

where α^+, α^0 and α^-, are the fractions of the positive, neutral and negative surface hydroxyl groups, respectively $S(OH)_2^+$, $S(OH)^0$, and SO^- correspond to Ag^+, $AgOH$ and AgO^-H respectively.

From the acidity constants, pK_{a1}^{int} and pK_{a2}^{int}, bulk proton concentration, $[H^+]$, and the surface potential Ψ_0 (at ionic strength of 0.05 M), the distribution diagram of surface hydroxyl groups as a function of pH was constructed (Figure 6).
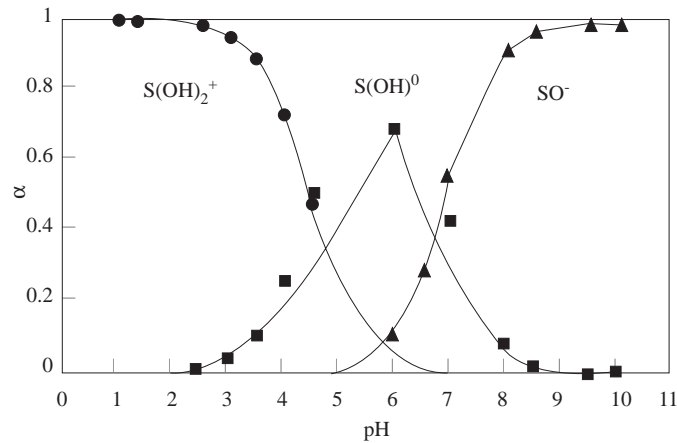

Figure 6. The Speciation Diagram of the Hydrous Concrete Particles as a Function of pH.

Surface complex formation model

At low metal concentrations, metal adsorption onto hydrous solids, such as metal oxides, is mainly a surface coordination process, which can be modeled thermodynamically as a complexation reaction between surface sites and adsorbates [8]. The surface complex formation model has been successfully used in describing the adsorption reactions at oxide-water interfaces [9−11].

The simplest possible surface complex reaction for silver adsorption onto hydrous concrete is expressed as follows.

$$SO^- + Ag^+ = AgOS \; ; \; K_S^i = \frac{(AgOS)}{(Ag^+)(OS^-)} \tag{17}$$
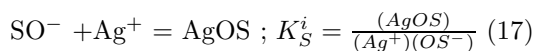
where $Ag^+ = Ag_{Total added}$ (Moles/g) - AgOS (Moles/L) x W (L/g)

OS^- = free sites (N_t-AgOS)

AgOS= sites occupied by Ag^+

W= Wt of adsorbent (g/L)

The average stability constants pK_S^i (Table 2 and Figure 7) for silver species complexed with concrete have been calculated. The version of SCFM provides good prediction of metal adsorption onto concrete. These constants have apparent dependence on the total of silver nitrate added. In general, the pK_S^i values decrease as the silver loadings increase.

Table 2. Modeled Silver-Concrete Stability Constants for Silver Uptake Experiments

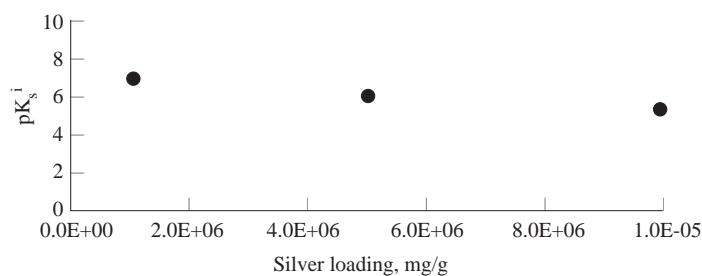| Equilibrium	Concentration $(\frac{Moles}{L})$ X W $(\frac{L}{g})$	Average pK_S^i
$SO^- + Ag^+ = AgOS$	1×10^{-6}	6.99
	5×10^{-6}	6.08
	1×10^{-5}	5.47

Figure 7. Stability Constants for Ag^+ onto Concrete Particles as a Function of Silver Loadings

Conclusion

Below pH 2, silver nitrate is insoluble. It is assumed that the surface sites for silver are anionic and can act as weak brønsted bases. When pH is decreased, there is a greater concentration of H^+ to compete with Ag^+ for these anionic sites, resulting in lower percent removal. Silver removal is favored by low concentration and basic pH. The calculated pH_{PZC} values are in agreement with the pH_{PZC} values determined from zeta potential measurements, indicating that the concrete particulate behaves amphoterically.

In general, the pK_S^i values decrease as the silver loadings increase. A greater amount of solid (10 g/100 ml) is required for maximum removal at low concentrations, indicating that silver is minimally adsorbed onto the concrete surface.

Acknowledgment

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