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Kinetics of Chloride Desorption from Soils

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Chloride spreads with depth of penetration in soils resulting in an increasing vertical distribution and a diminishing average concentration. If adsorption occurs, the distribution of chloride becomes skewed rather than normal, and the length of the trailing edge is dependent upon the amount of adsorption. The peak itself does not shift, however. Washing a quantity of chloride out of a soil begins at the same rate whether the soil is a chloride adsorber or not. A break in chloride concentration vs. milliliters of wash water occurs only with materials which adsorb chloride. If the data are plotted as first-order reactions, there is a distinct break in the curve with chloride adsorbers; this second curve, if extrapolated, gives an intercept corresponding to adsorbed chloride. The intercept varies as factors influencing adsorption are varied. Plotting elution curves as first-order reactions gives the same results. Such a plot shows that the position of the peak will not shift unless all chloride is adsorbed.

WHEN a salt of chloride is placed on a soil surface and then eluted with water, its distribution in the soil at some later time will depend on a number of factors. The general tendency will be for the anion to follow the moving water front in a soil, but because velocity of the water is not uniform throughout the soil, some of the chloride will move ahead of the predicted water front and some will lag behind. In a system where saturated water flow occurs and in which the velocity of water flow is relatively fast, thus minimizing diffusion, the chloride will tend to spread out both on the leading edge and on the trailing edge. The form of the spread is like that of a normal curve and is described by the Day and Forsythe equation (3).

$$C/C^{\circ} = \frac{x^{\circ}}{(2\pi\beta\bar{x})^{1/2}} e^{-\frac{(\bar{x}-x)^2}{2\beta\bar{x}}} \quad (1)$$

where C/C° = ratio of solution concentration to original concentration
 x° = depth of added Cl solution
 \bar{x} = depth where peak concentration occurs
 x = any depth of interest
 β = a constant, determined empirically

β is called an "Index of Dispersion" by Day and Forsythe (3). Figure 1 shows this equation applied to some data for chloride distribution on coarse sand.

A β value of 0.60 was used on both the 5.2-cm. column and the 40.4-cm. column. The resulting curves show fair agreement with experimental points. If the same β value can be used in both columns, then the amount of spreading is proportional to the square root of the depth to which the chloride has moved. Even in the short column, the maximum concentration of chloride has been cut to only one-third that of the original.

Superimposed on the spreading tendency already mentioned, there is in some soils adsorption of chloride. Soils which adsorb chloride are characterized by relatively high oxide content, low cation-exchange capacity, and low pH. In such a soil, the chloride would not be expected to move along with the water.

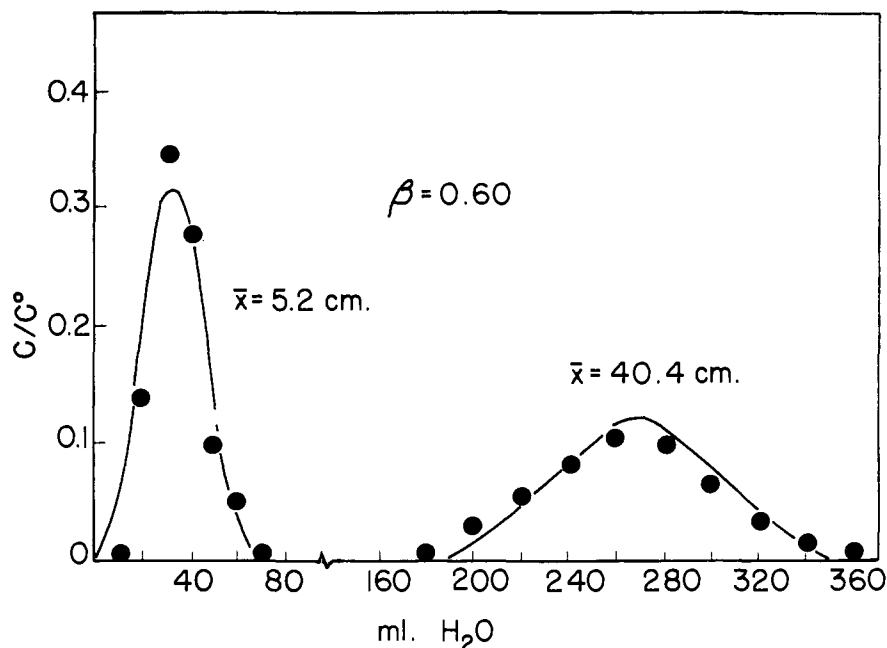


Figure 1. Chloride effluent curves from two sand columns of different lengths
Circles are experimental points and curves are calculated from Equation 1

The distribution coefficient expression of Kettle and Boyd (4) is

$$K_d = \frac{(V - 1)}{\rho} f \quad (2)$$

where

$$K_d = \frac{\text{meq. chloride/gram of soil}}{\text{meq. chloride/gram of H}_2\text{O}}$$

$$V = \frac{\text{volume of effluent at chloride peak}}{\text{pore volume of column}}$$

f = void fraction of column

ρ = bulk density of soil in the column.

Equation 2 predicts that as K_d becomes greater than zero, the chloride peak will lag behind the water front. Curves obtained by Berg and Thomas (7) were found not to be symmetrical when chloride adsorption occurred. Studies by Chang (2) showed that the chloride peak size diminished and the trailing edge of the curve became more pronounced as chloride adsorption increased, but in no case was the peak position changed from a value approximating the pore volume of the exchanger.

This paper represents an attempt to interpret these deviations from behavior predicted by the equations of Day and Forsythe (3) and Kettle and Boyd (4) by resorting to the methods of chemical kinetics.

Materials and Methods

Exchangers used in the study included montmorillonite from Upton, Wyo., kaolinite from Dry Branch, Ga., and a Cecil subsoil clay ($< 2\mu$ diameter) taken

from a well-known site at Dixie, Va. Georgia kaolinite was treated for two different periods of time with solutions of 1*N* FeCl_3 at 80° C. to produce clays with iron contents of 1.65 and 4.55% in addition to the untreated sample which contained only 0.15% iron.

Potassium or calcium chloride solutions were added to the tops of columns and eluted with water, as was done by Berg and Thomas (7). In one experiment, 1*N* calcium chloride or hydrochloric acid was added three times to centrifuge tubes containing Georgia kaolinite, and the suspension centrifuged and the supernatant discarded. Thereafter, these samples were washed with water by successive stirring and centrifugation. Chloride was determined in all cases using a silver-silver chloride electrode in conjunction with a Beckman Model G pH meter.

Results and Discussion

If a quantity of soil is equilibrated with a chloride solution then washed with distilled water, the chloride content of the wash water will, of course, diminish with time. The pattern of this diminution, however, will vary considerably depending on whether or not adsorption of chloride occurs. As an example, consider Wyoming bentonite, a clay which adsorbs no chloride, and Georgia kaolinite which has been treated with FeCl_3 to obtain an iron content of 4.5%, a chloride adsorber. Figure 2 shows that although the columns of bentonite and kaolinite lost chloride similarly at first, the last bit of chloride (5 or 6 meq./100 grams) was exceedingly hard to re-

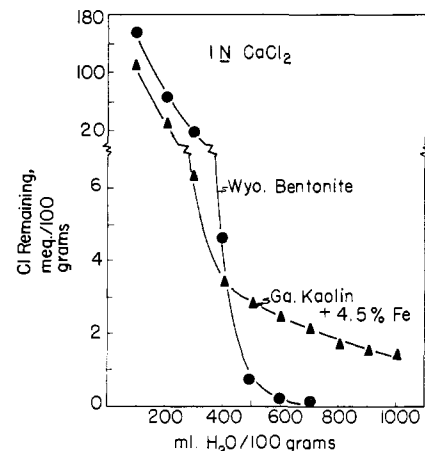


Figure 2. Chloride elution curves for columns of Wyoming bentonite and iron-treated Georgia kaolinite

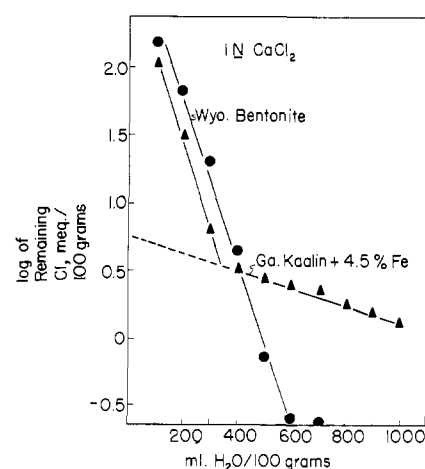


Figure 3. First-order reaction plot of chloride elution curves from Wyoming bentonite and iron-treated Georgia kaolinite

move from the Georgia kaolinite. The sharp deviation in slope at about 400 ml. strongly suggested that a simple first-order reaction was not being followed. If these data are plotted as a first-order reaction curve (log of chloride remaining vs. volume of H_2O , where volume is proportional to time), the results shown in Figure 3 are obtained. This shows that the removal of chloride from bentonite is simply proportional to volume of H_2O run through the column and thus is a first-order reaction. With the Georgia kaolinite, however, it becomes even more clear that, although the first reaction (washing) is about the same as that in bentonite, there is a second reaction, also first-order, which proceeds at a very slow rate. This, apparently, is hydrolysis of chloride from the hydrous iron oxide.

As a further proof that this is not a result of capricious chance, the factors which affect chloride adsorption can be varied and the second reaction line (and

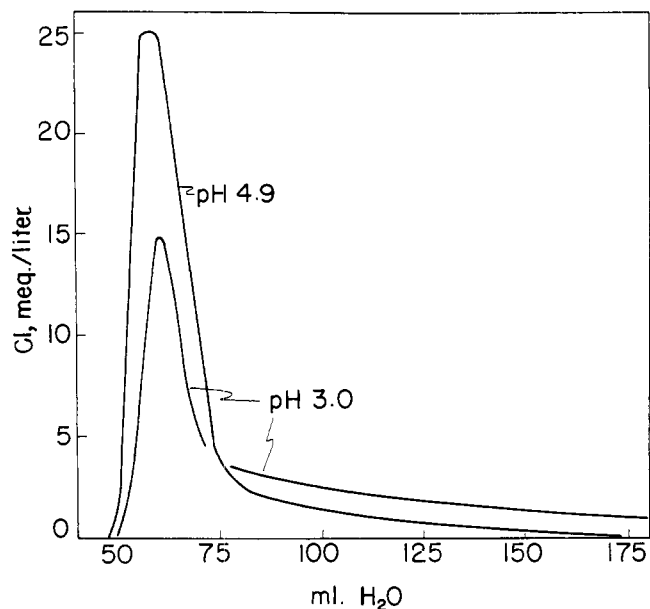


Figure 4. Chloride elution curves from Cecil clay at two pH values

Table I. The Effect of Iron Content and Cation Saturation on the Amount of Chloride Retained by Georgia Kaolinite

% Fe on Kaolin	Cl Retained, Meq./100 Grams	
	HCl-saturated	CaCl ₂ -saturated
0.15	1.38	0.64
1.65	2.57	0.83
4.55	6.60	2.21

its resultant intercept) moved up or down the log scale. Some results for Georgia kaolinite are shown in Table I. (These results were obtained by repeated centrifugation rather than by column leaching.) The increasing intercept values with lowered pH and increased iron confirm the expectations. Similar results can be obtained with a variety of soils; for example, a Cecil clay saturated with 1*N* HCl gave an intercept of 10.3 meq./100 grams, while one receiving 1*N* KCl gave only 2.5 meq./100 grams.

These facts help to explain the tailing effect and the immobility of the chloride peak. The peak comes through at a

void volume of one unless all the chloride is adsorbed by the column, a circumstance difficult to achieve unless a very small amount of chloride is added. Thus, the chloride which is unadsorbed merely moves through the column, spreading as it goes, and forms the expected normal curve on elution. The long tail arises from the hydrolysis of chloride off adsorption sites, and its length is dependent upon the amount of chloride adsorbed. Figure 4 shows elution curves for chloride from columns of Cecil clay. The peak position is the same in both cases, but the peak size is greatly reduced at the lower pH, showing that much of the chloride has been adsorbed. If these same data are plotted as a first-order reaction (Figure 5), the second (hydrolysis) reaction behaves as predicted, and calculations from the intercepts of the second slope show that 62% of the chloride was eluted in the normal curve at pH 4.9 and only 16% at pH 3.0. The rate of removal of unadsorbed chloride was the same in both cases as shown by the dashed lines in Figure 5. This indicates that the peak position will not be changed unless all the chloride is adsorbed.

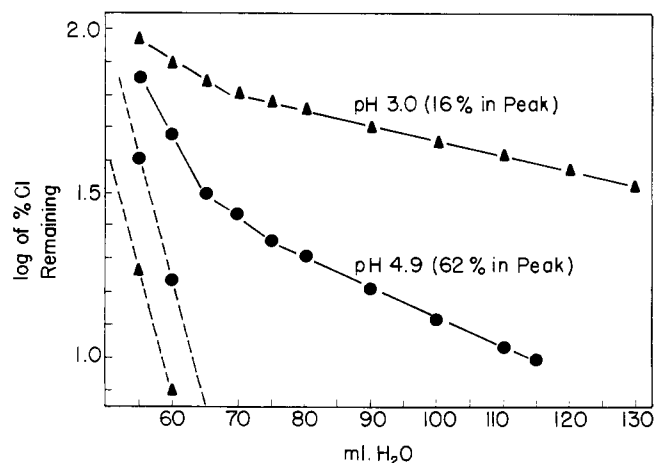


Figure 5. First-order reaction plot of chloride elution curves from Cecil clay at two pH values

The movement and distribution of chloride in soil is very similar to that of nitrate (5) and reasonably close to that of sulfate (7). Thus, these generalizations apply to those anions also. It should be emphasized that these experiments were performed under idealized conditions. In the field, unsaturated and lateral flow can change anion distribution greatly, but the basic patterns predicted above will still obtain.

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