In the course of some studies on the effects of anions on the viscosities of clay suspensions, it was observed that anions such as pyro- and metaphosphate, oxalate and fluoride were much more effective in reducing the viscosity of kaolin suspensions than were chloride and nitrate. There is relatively little information available regarding the specific adsorption of anions by clay minerals; it is known, however, that soils take up considerable quantities of orthophosphate from acid solutions. Whether the active component of the soil, in this respect, is the clay mineral or hydrated iron and aluminium oxides, the adsorbed phosphate may be readily released by shaking the soil with neutral or acid solutions containing fluoride, oxalate, citrate or malonate. In addition, a soil which is normally capable of taking up appreciable quantities of phosphate will not do so if fluoride is present in the phosphate solution. It has been recognized that the ability of this group of anions to form soluble complexes with iron and aluminium is responsible for their effectiveness in this respect.

Detailed investigations by Thomas and Vartinian (1935) and Graham and Thomas (1947) into the nature and properties of hydrated alumina have shown that this material is especially reactive towards acids and salts of the anions listed above. Those studied in particular were F, PO₄, P₂O₇, C₂O₄ and SO₄. For example, it was found by Graham and Horning (1947) that on addition of hydrated alumina to neutral solutions of KF, K₂C₂O₄ and K₂SO₄, the magnitude of the rise in pH of the solution was in the same order as the complexing ability of the anion (F > C₂O₄ > SO₄). The interpretation of these results was briefly as follows. The increase in pH was due to displacement of surface OH groups by co-ordinative binding between the anion and the surface Al ions. Fluorine is of special interest in that it forms a very stable complex ion with aluminium (AlF₆)₃⁻, and has the same ionic radius as hydroxyl. Dickman and Bray (1941) report experimental results which indicate a stoichiometric replacement of the lattice OH of kaolinite by fluorine. Accordingly it was decided to investigate the adsorption of fluoride ion by pure clay minerals and hydrated alumina. Preliminary experiments with kaolinite and montmorillonite showed that they react with a solution of NH₄F in the same way as does hydrated alumina. When a portion of the powdered solid is shaken with a neutral solution of NH₄F, the suspension centrifuged and the supernatant liquid analyzed, it is observed that
1. The solution is alkaline.
2. The concentration of $F^-$ is reduced, i.e. $F^-$ has been adsorbed.
3. Aluminium may be detected in solution.

**Materials Used.**

*Kaolinite.*—A sample supplied by Merck and Company was examined by X-ray diffraction, and found to be free from mica, montmorillonite and quartz.

*Montmorillonite.*—From Wyoming bentonite.

*Hydrated Alumina.*—White, granular material, supplied by B.D.H. Ltd., and marked “for chromatographic adsorption analysis.” Ignition to 1300° resulted in a loss in weight corresponding to the composition $\text{Al}_2\text{O}_3 \cdot 2 \cdot 3\text{H}_2\text{O}$. Samples were dried at 105°C before use. The clay minerals were either K+-saturated or NH$_4$+-saturated, by leaching with N KC1 and N NH$_4$C1 respectively then washing out excess salts, and likewise dried at 105°C.

**Experimental.**

The pH effects were first investigated by adding K+-kaolinite and K+-montmorillonite to neutral 0·25 M KC1, KF, K$_2$C$_2$O$_4$ solutions, and the pH measured every 15 minutes. A progressive rise was observed with KF and K$_2$C$_2$O$_4$; the values attained after three hours are given in Table 1.

**Table 1.**

*pH attained by 0·25 M salt solutions originally pH 7·0 after contact with clay minerals.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight in gm.</th>
<th>Salt Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KCl</td>
</tr>
<tr>
<td>K+-kaolinite</td>
<td>2</td>
<td>6·6</td>
</tr>
<tr>
<td>K+-kaolinite</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>K+-kaolinite (&lt; lμμ)</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>K+-montmorillonite</td>
<td>2</td>
<td>7·0</td>
</tr>
<tr>
<td>Hydrated alumina</td>
<td>0·5</td>
<td>7·3</td>
</tr>
</tbody>
</table>

The figures for hydrated alumina are those given by Graham and Horning (1947). Their KCl and KF solutions were 0·1 M, K$_2$C$_2$O$_4$ 0·25 M.

The pH rise was also recorded when twice the quantity of kaolin was added, and also when a fine fraction, possessing a larger specific surface, was employed.

In order to obtain quantitative information, portions of the materials, the clay minerals being first NH$_4$+-saturated, were weighed into paraffined flasks containing NH$_4$F solutions of varying concentration. The solutions had been previously adjusted to pH 7 using brom-thymol blue. The flasks were sealed and rotated end-over-end intermittently for five days, the contents centrifuged and
 aliquots of clear solution analyzed for OH, F and A1, in that order. Hydroxyl was estimated by titration with standard H₂SO₄, fluorine volumetrically after steam-distillation (Willard and Winter method), and A1 volumetrically as oxinate after fuming off most of the H₂SO₄.

Discussion.

It is evident from Figure 1 that hydrated alumina possesses by far the highest adsorptive capacity for fluorine, and that the amount taken up increases as the initial concentration of NH₄F increases. Kaolinite shows a similar behaviour, but the montmorillonite curve flattens out at a value of 17 m.e. F−/100 gm. It is of interest to note that this value is of the same order as that found for the maximum adsorption of polymetaphosphate anion, 18± 4 m.e./100 gm. of Na+-montmorillonite, from Calgon solutions (Van Olphen, 1950).

Figure 2 shows the amounts of aluminium dissolved by the fluoride solutions. This aluminium probably exists partly as (A1F₆)³⁻ and partly as (A1O₂)₄⁻; the amounts dissolved never exceed 1% of the total aluminium of the clay mineral.

The adsorption process appears to consist of an immediate displacement of surface hydroxyl groups, due to co-ordinative binding between fluoride ions and aluminium ions in the octahedral layer. Adsorption sites are thus available at the edges of clay mineral platelets. In addition, a kaolinite crystal has one basal surface composed of A1-OH linkages. The more accessible aluminium ions are evidently dissolved quite readily, and co-ordinate six F− ions in solution. The removal of these aluminiums at plate edges exposes OH ions for replacement by F−, especially in the kaolinite structure, where A1:OH = 1:2.

The process of solution and replacement does not appear to proceed indefinitely. When kaolinite is shaken up with neutral NH₄F, and the alkalinity continually neutralized with H₂SO₄, it is observed that the amounts of acid required decrease with time, until there is virtually no further reaction.

It is clear that the adsorptive capacity for fluorine depends on the extent of surface of exposed A1-OH linkages. Hydrated alumina, which posses a porous structure, provides a very large active surface, and the solution-replacement process would probably proceed until all the solid is dissolved.

From a consideration of the lattice structures, the kaolinitic minerals would appear to possess a greater inherent sorptive capacity for fluoride than montmorillonite.

<table>
<thead>
<tr>
<th></th>
<th>Si : A1</th>
<th>A1 : OH</th>
<th>m.e.OH−/100 gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>1 : 1</td>
<td>1 : 2</td>
<td>1550</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2 : 1</td>
<td>1 : 1</td>
<td>556</td>
</tr>
</tbody>
</table>

When comparing the curves for the two minerals in Figure 1, it must be remembered that the mean particle sizes differ enormously, and that if it were possible to carry out the experiments with clay
fractions possessing a comparable specific surface, kaolinite would probably exhibit by far the greatest adsorptive capacity.

The removal of aluminium from the edges of kaolinite plates and from hydrated alumina exposes more hydroxyl ions, i.e. additional adsorption sites for fluorine. The curves for these two materials are very similar in form. On the other hand, attack at the edges of montmorillonite platelets exposes a proportionately less number of adsorption sites for F−, and these positions are soon all occupied.

The clay particles presumably acquire a peripheral zone in which F− proxies for OH− in the octahedral layers.

Figure 3 shows the relation between F− taken up and OH− liberated. These results alone cannot be taken to indicate non-equivalence of F− and OH−, as the OH is estimated on the clear solution and takes no account of the buffer capacity of the clay. Hydroxyl will consequently be under-estimated. Dickman and Bray's results, which indicate a stoichiometric replacement of OH− by F−, are open to criticism, since their method for estimation of fluorine, gravimetrically as PbFCl, is not applicable when A1 is present in solution.

When allowance is made for the buffering action of Si-OH groups at the edges of the kaolinite particles according to the reaction

\[ >\text{Si-OH} + \text{OH} \rightarrow >\text{Si-O}^- + \text{H}_2\text{O} \]

the amounts of F− and OH− become more nearly equivalent, but not entirely so. The maximum buffering exhibited by the kaolin between pH 7 and pH 8.1, as determined in a separate experiment, amounts to less than 0.5 m.e./100 gm. The F− uptake is consequently still in excess of OH− liberated. The excess of F− over OH− for montmorillonite is even more marked.

Acknowledgement.—My thanks are due to Miss B. C. Terrell for assistance with analytical work.

Summary.

It has been found that fluoride ions are adsorbed by kaolinite, montmorillonite, and hydrated alumina from neutral fluoride solutions. Simultaneously, hydroxyl ions are replaced and surface aluminium ions dissolved. The increase in net negative charge on the kaolinite particles resulting from the excess of fluoride ions adsorbed over hydroxyl ions displaced may provide an explanation for the dispersion of kaolinite suspensions by dilute fluoride solutions. Furthermore, the action of fluoride in causing release of “fixed” phosphate from soils may be interpreted as a de-sorption process, which is accompanied by solution of aluminium.
References.

Discussion.
Professor C. W. Correns.—I believe that the adsorption of chloride ion by clay is not reversible. Can the speaker say if the adsorption of fluoride ion is reversible?

C. M. G. de Bruijn.—I would be interested in D.T.A. results on the fluoride-treated clay minerals, as these would throw light on the type of adsorption.

L. H. P. Jones.—Mr. Samson mentioned the use of fluoride solutions as extractants for soil phosphorus. In this connexion, some recent results by E. G. Williams at the Macaulay Institute are of interest. Commercial precipitated aluminium phosphate was found to be extensively and rapidly soluble in N/2 neutral NH_4F. This prompted an examination of the aluminium content of NH_4F extracts of soils. Considerable amounts ranging from 0.1 to 1.0% Al_2O_3 were found, and the values seem to be useful criteria of the phosphate sorption capacities of the soils. The amounts of iron extracted are much lower, in agreement with the fact that the FeF_6^{3-} complex is weaker than the AlF_6^{3-} complex. It seems probable that neutral NH_4F extracts mainly Al-bound phosphorus.

D. M. C. MacEwan.—In the case of montmorillonite, much F^- is taken up without much release of OH^- . Does this show that there must be positive charges on the edges of this mineral, as van Olphen supposes?

O. Talibudeen.—The release of Al from clays after NH_4F treatment may be due to the salt-like character of the AlF_3 formed and its preferential solubility in NH_4F solutions to form a double salt complex of the type NH_4AlF_4. The specific effect of the (NH_4)^+ ion in this connection may be noteworthy.

H. R. Samson.—No experiments on desorption of fluoride have been carried out. I would expect that the process would be even less likely to occur than for chloride, which has no specific attraction for a lattice constituent.

I do not think that the non-equivalence of F^- and OH^- for montmorillonite provides support for van Olphen's suggestion of positive edges. Direct evidence of the reversible exchange of "inert" anions, such as chloride or nitrate, would be required. Van Olphen's results with polymetaphosphate are inconclusive, since polyanions of this kind adsorb on to practically anything.

The stable complex ion is AlF_6^{3-}. As far as I know no complex of the type NH_4AlF_4 exists. A few experiments with NaF solutions appear to indicate that the effects are not specific for NH_4F.