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ANION ADSORPTION ONTO CLAY MINERAL SURFACES USING RADIOISOTOPE TECHNIQUES

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CHAPTER I

INTRODUCTION

Any reaction that occurs between two substances will depend initially on the reaction, or lack of reaction, of the various atoms or molecules that are on the surfaces of the substances being brought into contact with each other. When reactions involving substances of very small particle size are investigated the actual detailed composition of the surface layer of these particles becomes of paramount importance.

Use is made of particular surface properties of various substances in many aspects of chemistry. Catalysis often involves the reaction of molecules or atoms of two substances reacting at the surface of a third substance. In this case the composition of the surface layer of the catalyst particles is of far greater importance than the actual chemical composition of the catalyst as a whole.

The chemical composition of a material of small particle size may be markedly influenced by the presence of adsorbed atoms (or molecules) on the surface of individual particles. This influence may be such that chemical analysis would lead to the belief, from stoichiometric composition, that the actual compound was different from a similar compound without excess material adsorbed onto its surface. A large number

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of samples of apatite (a basic calcium phosphate mineral) which have been shown by X-ray analysis to have similar crystal structures, have a very wide range of chemical composition (Hendricks and Hill, 1950 ; Neuman and Neuman 1953). It has been calculated by Carlström (1955) that the adsorption of only two or three excess phosphate or calcium ions per unit cell on the surfaces of crystallites of synthetic apatite, of theoretical formula $Ca_5(OH)_2 \cdot 3Ca_3(PO_4)_2$ could cause variations in the Ca/P ratio from 1.5 to 2.0. Thus it can be seen that sorbed materials may markedly affect the chemical composition of a substance while having little effect on its basic crystal structure.

Many of the phenomena of soil chemistry are related to effects occurring on the large areas of the surfaces of clay minerals, hydrous oxides etc. which make up the soil. Plants growing in the soil obtain a large amount of their nutrient requirements from nutrients which include phosphate, nitrate or sulphate ions present in the soil solution. As these materials are removed by the plants they are replaced with fresh material by the desorption or dissolution of the nutrients from either the surfaces of the soil particles or the surfaces of various, relatively insoluble compounds present in the soil either naturally occurring or added as fertilizers.

The availability of the various anionic nutrients (sulphate, phosphate etc.) to plant roots is a matter of

great importance in determining the ability of particular soils to support various crops. Knowledge of this availability of nutrients to plants is largely empirical, often being based on the amount of nutrient removed by various chemical and plant extractants in relation to the total amount present in a particular soil sample. The elucidation of the nature of the various anion-soil surface complexes that are present in soils could become important in the design of means to increase the availability of these anionic nutrients to plants and thus to increase soil fertility.

The proportion of material involved in surface complexes between anions such as sulphate and phosphate and the individual soil particles is very small in relation to the soil as a whole. Because of this it is difficult to investigate the properties of these complexes by conventional means. Any reactions involving these complexes are likely to be hidden by the reaction of the soil (or those parts of it that react in some way with the reagents used) which makes up such a great proportion of the system being studied.

This difficulty of studying the reactions of only a very small proportion of a soil sample, or any other system wherein the total amount of any particular surface complex is very small in relation to the whole sample, can be overcome with the use of radioisotopes. If the anion involved in

a surface complex with soil, or a particular fraction of the soil, is radioactively labelled in some way, the total amount of such a complex can be measured very readily. If the phosphate anion was studied, using radioactive phosphorus (^{32}P) an amount of 5×10^{-14} gms. of phosphate could be detected readily if the phosphate was "carrier-free" (i.e. no ^{31}P present). (The above amount assumes 10% counting efficiency and a countrate of 10^3 counts per minute). Even if the radioactive phosphate used was only 0.01% ^{32}P the detectable amount would still be as low as 5×10^{-10} gms.

Studies on the total amount of phosphate, or other anions, on the surface of soil particles could be carried out by the use of radioactively labelled ions, as could the amount of readily exchangeable anion. The amount of a particular anion present in the soil that was readily exchangeable with a solution of that anion in contact with the soil could be determined by adding a minute amount of radioactively labelled anion to an equilibrium between the soil and a solution of the inactive anion. From the amount of radioactive anion adsorbed by the soil over a period of time it would be possible to calculate the amount of the surface complexed anion that had exchanged with the anion in the solution in that time. Such information would be useful in obtaining a measure of the availability of this anion, from the surface complex with the soil, to plants or other

substances in the soil solution capable of removing the anion from solution.

From exchange studies using radioactive anions the existence of different adsorption sites has been deduced (e.g. Shmo, 1963). Exchange has been found to occur at a number of different, simultaneously occurring, rates between soil and solution. From this it has been concluded that there are different types of sites in soils at which the various anions being studied are complexed, the different sites being characterised by different rates of release of the anions into solution. After radioactive exchange with the soil has taken place it is possible to study the various amounts of radioactively labelled anion that can be extracted from the soil with different extractants. Such amounts may then be compared with the amounts extracted with different reagents in the conventional methods of determination of the availability of nutrient anions in the soil. Some of the results that have been obtained by these radioactive techniques are discussed elsewhere in this thesis (see section on application of radioisotopes to soil problems p. 20).

Owing to the complexity of soil it is not readily possible to obtain information as to the exact nature and position of anion-soil surface complexes. Because of the large number of different types of sites in the

soil at which such complexes could exist it is extremely difficult to assign any particular complex (as characterised by an exchange rate from solution for instance) to a particular type of site. In order to overcome this difficulty it is desirable that studies be made on the anion-surface complexes of the various individual constituents that make up a soil sample. Once the nature of the surface complexes formed by the various anions with soil constituents has been elucidated, the complete picture of the complexes formed by anions with the soil particle surfaces may be obtained by testing combinations of the various soil constituents in controlled amounts. In this way an understanding of all the ways in which the various nutrients required by plants are held by the soil may eventually be obtained. Such knowledge would be valuable in working out means of overcoming various nutrient shortages in soils, either by addition of missing nutrients or by some treatment of the soil to render more readily available nutrients already present.

A large proportion of the various anionic nutrients required by plants seems to exist in the soil as surface complexes with various clay minerals. Unfortunately it is difficult to obtain individual clay minerals free from other minerals. Separation procedures are not completely efficient, and attempts to remove final amounts of impurities

often cause at least partial destruction of the clay mineral being sought. However one group of clay minerals that can be obtained in a "pure state" is the mica group.. Because of this it was decided to study the adsorption of an anion (phosphate was the anion chosen) onto the surface of this mineral group.

The presence of micas in clays has been recognised since the first microscope studies of argillaceous materials. It is now known to be widely distributed also among the fine grained fractions of clays (cf. Brown, 1961). The structure of mica was among the first of the clay minerals to be elucidated, chemical compositions and structural determinations being carried out by Winchell (1925 a, 1925 b) Mauguin (1927, 1928a, 1928 b), Pauling (1930) and Jackson and West (1930, 1933).

It was early recognised as a result of these studies that the structure of the non-swelling mica group was very similar to that of the swelling montmorillonite group of clay minerals (Hofmann, Endell and Wilm, 1934). Both groups of clay minerals have a layer structure composed of two tetrahedral silica sheets with a central octahedral alumina sheet, as shown diagrammatically in figure I;

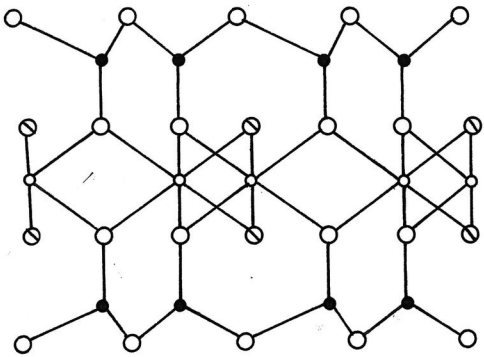


Figure 1 Montmorillonite (or mica structure)

The two main differences between these two classes of clay minerals are in the interlamellar cations and in the charge on the layers due to isomorphous substitution. The micas have considerable isomorphous substitution, especially of aluminium for silicon in the tetrahedral sheet, having a negative charge per unit cell of about 2 as opposed to the usual negative charge on montmorillonite minerals of about 0.7 per unit cell. The interlamellar cations present in the micas are usually the alkali metal ions potassium or sodium (calcium is present in the brittle mica, margarite) whereas a wide range of cations may be associated with montmorillonite minerals.

Hendricks and Jefferson (1939) have established that there exists a complex polymorphism in the micas based on the alternative orientations of successive equal layers.

There seem to be six simple ways in which the mica layers may be stacked on top of each other in an ordered manner (Smith and Yoder,1956).

The structure of mica is well known and it is possible to obtain large, pure samples of the various mica minerals. Mica exhibits perfect basal cleavage,splitting along the 001 plane (c axis) into very thin, smooth plates which are flexible and elastic. The surface of these plates is almost completely smooth even at a molecular level. As a result of this it is possible to obtain a sheet of mica, the surface of which has only a very small proportion of edges to the surface area. Thus it is possible to study phenomena occurring only on the surface of a piece of mica, providing the outside edges are suitably shielded (e.g. with paraffin wax). This enables the adsorption of anions onto a known clay mineral surface to be studied in isolation from other, possibly competing, reactions.

The surface of mica is a hexagonal sheet of oxygen atoms. This surface is similar in structure to that of a number of other clay minerals such as montmorillonite (both surfaces of the particles), vermiculite(both surfaces) halloysite and kaolinite(one surface) and others.

In all micas there is a net negative charge associated with each unit cell because of isomorphous substitution

within the lattice. This substitution is of two types, in the tetrahedral sheet where quadrivalent silicon atoms are replaced by trivalent aluminium ions (Beidellite substitution), and in the octahedral sheet where aluminium is replaced by ions of lower valency, particularly magnesium (Montmorillonite substitution). Examples of these two types of substitution are shown in figure 2. p. 10a. Most of the substitution in mica is of the Beidellite type, well crystallized mica having 25% of the silicon atoms replaced by aluminium (Grim, 1953).

All the experiments performed in this thesis on mica surfaces were carried out using muscovite mica. Muscovite is a dioctahedral mica, that is only two thirds of the possible octahedral positions are filled, and the octahedral sheet is populated only by aluminium atoms. Thus there would be very little, if any, of the Montmorillonite substitution in the mica samples actually studied. The structural formula for muscovite is $(OH)_4 K_2 (Si_6 Al_2) Al_4 O_{20}$ and the theoretical composition K_2O = 11.8%, SiO_2 =45.2%, Al_2O_3 = 38.5% and H_2O = 4.5%. Muscovite is a monoclinic mineral and the unit cell, which has dimensions a= 5.2 Å, b= 9.0 Å, c =20.0 Å, β =95° 30' is composed of two silica-alumina-silica layers. Because of isomorphous substitution each layer of the unit cell has a net negative

ORIGIN OF EXCHANGE SITES IN THE LAYER SILICATES

Jackson (1963)

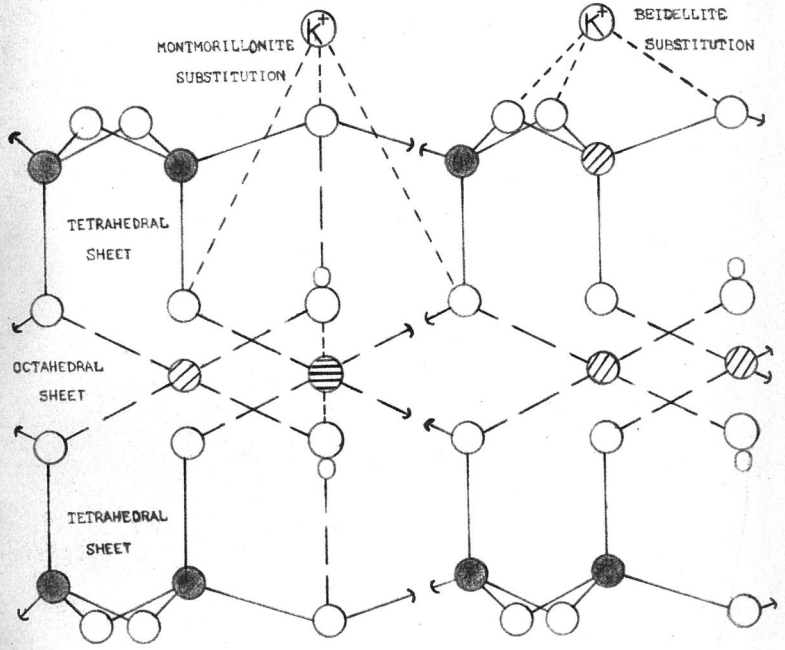


FIGURE 2

charge of about 2. As each layer has two surfaces the negative charge associated with the surface area of one side of the unit cell will be 1. That is, there will be about one negative charge per 45 -50 sq. Å on each mica surface.

One of the aims of this thesis was to study the amount of radioactively labelled phosphate that was adsorbed onto the surfaces of mica sheets. Mica which can be split into very thin sheets is very satisfactory for this purpose because the radioactive phosphate present can be measured through the mica sheet itself, the sheet being sufficiently thin to transmit readily the β particles emitted in the decay of the radioactive phosphorus. Commercial end-window geiger counters are made with mica end windows, and this mica is thin enough to transmit much weaker β particles than those emitted by phosphorus -32. The β particle emitted by sulphur -35, which is only one tenth as energetic as that from phosphorus -32, is detected readily with these geiger counters. Some of the work done in this thesis was carried out using the actual mica end-window of an end-window geiger counter as the surface for radioactive phosphate adsorption and desorption. Other work was done with mica sheets that were placed over this end window, the β particles from the radioactive phosphorus being readily transmitted through the two

thicknesses of mica into the sensitive volume of the geiger counter. The anion chosen for the sorption studies on mica surfaces in this thesis was the orthophosphate anion PO_4^{3-}. Phosphorus is one of the major requirements for plant nutrition, and consequently the fixation of phosphate by soils is a major problem in soil science. Many workers have investigated the fixation of phosphate by soils using both radioactive and non-radioactive phosphate. Some work has also been carried out on the fixation of phosphate by particular clay minerals such as mica (Perkins and King, 1943) vermiculite (Mitra and Prakash,1955) and montmorillonite (Martin and Laudelout,1959; 1961). Perkins and King found that most phosphate fixation depended on structural aluminium, only a small percentage of the total fixation being due to cations present on the mica surface. In the present thesis only adsorption by the surface of mica is considered, the edges of the mica sheets, at which adsorption onto structural aluminium and silicon could occur, being largely eliminated from the reaction system (cf. p. 37).

Phosphate fixation by the hydrous oxides of iron and aluminium has been investigated by Swenson,Cole and Sieling (1949), Wild (1950), Kanwar and Grewal (1960) and others. Studies on these oxides are complicated by their variable composition and specific surfaces, the

importance of which has been emphasised by Perkins and King (1944), Graham and Thomas (1947) and Colwell (1959).

The actual method of phosphorus fixation, whether by precipitation of insoluble phosphates on the surfaces of the various soil constituents or by adsorption, either physical or chemical, onto these surfaces, seems to be a largely unresolved problem. Numerous workers have offered evidence in favour of both these methods, and it seems possible that different constituents in the soil may cause both methods of fixation to occur at different sites. Ivanov (1955), Blanchet (1959), Colwell (1959), Schell and Jordan (1959) and others deduced that phosphate was held on various clay mineral and oxide surfaces by an adsorption mechanism. Kittrick and Jackson (1956) working on aluminium, iron and calcium compounds and Martin and Laudelout (1959) who carried out studies on the fixation of phosphate by the clay mineral montmorillonite said that phosphate fixation was a chemical precipitation.

Studies by Kanwar and Grewal (1960) led them to the belief, from a consideration of the molecular ratios of PO_4/R_2O_3 (R= Al or Fe) that fixation involved the formation of basic phosphates of iron and aluminium. However they also calculated from the much lower ratio of $PO_4/CaCO_3$ that phosphate is only adsorbed and not precipitated on the surface of calcium carbonate particles. Were

recently Bache (1964) has obtained results that seem to indicate that the fixation of phosphate by iron and aluminium hydrous oxides occurs in stages; precipitation, chemisorption and physical adsorption all occurring in the same system.

The composition of precipitates of phosphate with iron and aluminium hydrous oxides is given by a number of authors in the literature. There seems to be not more than one phosphate group associated with each aluminium (or iron) hydroxide molecule in these precipitates. Swenson, Cole and Sieling (1949) found that the precipitates formed had the composition $Al(H_2O)_3(OH)_2H_2PO_4$ even when the ratio of H_2PO_4 : Al = 9:1. They postulated a mechanism for the formation of the precipitate as:

$$Al(H_2O)_3(OH)_3 + H_2PO_4^- \rightleftharpoons Al(H_2O)_3(OH)_2H_2PO_4 + OH^-$$

The stability of the right hand side of this equation is greater at low pH values. As the pH value of the soil increases equilibrium is displaced to the left and phosphate is released. The composition of the precipitate given by Bache (1964) which is $Al(H_2PO_4)_n(OH)_{3-n}$ is also dependent on the pH value of the solutions from which it is formed. In his formula n=1 for pH values less than 3.5

and is less than 1 for higher pH values. In the analogous compound of iron phosphate, $Fe(H_2PO_4)_n(OH)_{3-n}$, n is less than 1 for all pH values greater than 1.5. It has been reported by Beatz (1954) that, from studies on the equilibria between aluminium and iron phosphates ($AlPO_4$ and $FePO_4$) abd radioactively labelled phosphate in solution, it appears that there is not much phosphate held in soils at $Al:PO_4$ or $Fe:PO_4$ ratios of 1:1. However at other ratios phosphate may be held more strongly.

It is clear that the exact mechanism whereby phosphate is fixed in the soil has not been completely resolved as yet. Because of the importance of the availability (or non-availability) of phosphate in the soil to plants growing therein any work that can help to elucidate the exact mechanism of phosphate fixation may be expected to be of considerable benefit to soil science.

The present investigation has been carried out on the adsorption of phosphate onto the surfaces of a clay mineral, namely mica. Mica has a net negative charge resulting from isomorphous replacement within the unit cell. This negative charge is neutralized by the adsorption of cations onto the surfaces of the mica particles. From the literature it is evident that the amount of adsorption by negatively charged clay minerals of phosphate (and other anions) is influenced by the nature of the adsorbed cation

present in association with these clay minerals.

It has been found that the presence of multivalent cations associated with clay minerals causes more phosphate adsorption (or fixation) than does the presence of monovalent ions. Ragland and Seay (1957) found that aluminium saturated clay minerals retained more phosphate than did the same clays when saturated with calcium ions. Similarly Schmalz (1953) observed that calcium saturated bentonite adsorbed more phosphate than did ammonium ion saturated bentonite from the same phosphate solution. He also found that more phosphate was required to saturate calcium bentonite than ammonium bentonite. Russell and Low(1954) found that the greatest amount of phosphate adsorbed by kaolinite was observed in the presence of aluminium ions. Martin and Laudelout (1959,1961) found that, although considerable phosphate fixation occurred with aluminium saturated montmorillonite suspensions, none occurred when the montmorillonite was saturated with sodium ions.

Studies on the effect of the exchangeable cation on the retention of sulphate by clay minerals have also revealed the greater efficiency of multivalent ions in increasing adsorption. Chao,Harward and Fang (1963) obtained an order of cation efficiency in aiding sulphate retention. It was $Al^{3+} > Ca^{2+} > K^{+} > NH_4^{+} > Na^{+}$. They

said that the influence of the different cations was due to two factors; the actual cation itself and the pH value of the solutions containing it, the lower the pH value the more sulphate adsorption occurred. Chang and Thomas (1963) found similarly that divalent cations caused more anion adsorption than did monovalent cations that were associated with the clay mineral net negative charges. They pointed out that the use of the trivalent cation aluminium gave adsorption results that were complicated by the lower pH value caused by aluminium solutions. They postulated that the neutral system of, for example, yttrium (Y^{3+}) ions should give higher anion retention than would a system with a divalent cation.

Wild (1953) studied the retention of phosphate by clays, subsoil containing clay materials, aluminium sulphate ($Al_2(SO_4)_3$) and aluminium saturated ion exchange resins. He established that the exchangeable cations influenced the amount of phosphate adsorbed by the aluminium in these systems. Two alternative explanations were advanced to explain these results, Wild maintaining that either, or both, could apply. He thought that either various cations released various amounts of aluminium, the aluminium itself causing the retention of phosphate, or else that the exchangeable cations affected the distribution of phosphate ions in the Gouy layer and this factor determined the amount

of phosphate sorption.

This last explanation of the effect of different cations on the retention of phosphate by clay minerals in terms of the Gouy electrical double layer has been discussed by Verwey and Overbeek (1948) and also referred to by Chang and Thomas (1963). Verwey and Overbeek state that greater adsorption of anions is possible for clay systems containing divalent cations than for those containing monovalent cations because with larger cationic charges the liquid charge is concentrated closer to the surface of the clay mineral particles. The corresponding increase of the double layer capacity implies a larger repulsion for small distances from the particle surfaces. However the corresponding contraction of the double layer has the result that the repulsive potential for anions decays more rapidly with increasing distances and will thus be diminished for greater distances from the particle surfaces. Thus there is less screening effect for anions, at a distance, from the clay mineral particle surfaces when the surfaces are saturated with multivalent ions than when they are saturated with monovalent ions, and, consequently more opportunity exists for anionic adsorption onto the clay surfaces.

Some studies have been made on the adsorption of various cations onto clay mineral surfaces. Cook, Cutler,

Hill, Wadsworth and Oblad (1953) and Coates and Anderson (1955) found evidence for the presence of two different types of sodium adsorption sites on montmorillonite. It was suggested that these different sites may be due to 6-coordinate and 4- coordinate aluminium in the montmorillonite. Nye, Craig, Coleman and Ragland (1961) have shown, from exchange isotherms, that aluminium ions are sorbed more strongly onto exchange sites in montmorillonite and kaolinite than are potassium, sodium and calcium ions. The relative strength of bonding of cations in the alkali and alkaline earth series (lithium, sodium, potassium, rubidium, caesium, calcium, strontium and barium) onto the surfaces of various mica minerals has been investigated by McDowell and Marshall (1962).

In the present work studies have been made of the adsorption and desorption of radioactive phosphate from cation saturated mica surfaces, using sodium saturated and aluminium saturated mica surfaces, over a wide range of pH values (3.0 to 9.0). In addition desorption experiments have been performed with mica surfaces saturated with other cations, and also with aluminium oxide surfaces. The effects of drying, temperature changes, adsorption times and desorption times on experimental results have been investigated and some studies carried out on the effects on the desorption of radioactive phosphate from aluminium saturated mica surfaces, and aluminium oxide surfaces, of different reagents used in soil phosphate extraction procedures.

CHAPTER 2.

APPLICATION OF RADIOISOTOPES TO SOIL PROBLEMS

A study has been made in this thesis of the sorption of radioactive phosphate onto the surface of a soil mineral, namely muscovite mica. The first use of radioactive phosphate in the problems of soil science was by Hevesy, Linderstrom-Lang and Olsen(1936) who studies phosphorus uptake by plants. Since then much work has been done in investigating the problems associated with soil and fertilizer research using this and other isotopes as radioactive tracers. (See for example reviews by Herbst,1953; Mattingly,1957; Mattingly and Talibudeen, 1961).

A number of different types of problem in soil science have been investigated by the use of radioisotopes as tracers. One of the most basic investigations that has been made in this way has been the determination of the total amount of potassium in a soil sample by measurement of the amount of the naturally occurring radioactive isotope ^{40}K present in the soil (See for instance Rodriguez and Mattingly,1960; Kogan,Nikiforov and Fridman,1961). Trace amounts of radioactive silver (^{110}Ag) have been used by Baranowski and Bors (1961) in order to study the amount of soil dislocation caused by cultivation. As the silver does not take part in any plant-soil interactions, it is a very

good means of following the amount of soil movement with time.

Use of the radioactive isotopes of strontium (^{89}Sr and ^{90}Sr) to study the adsorption of strontium by some of the clay minerals present in soils has been made by Spitsyn and Gromov (1959) . By using these radioisotopes they were able to study the effects of the presence or absence of calcium ions on the amount of adsorption by clay minerals of very small amounts of strontium from the soil solution. This is of particular importance because of the amount of ^{90}Sr formed in nuclear tests. Once it becomes adsorbed onto the soil in a similar manner to calcium it would be available to plants growing on such soil, and thus , ultimately, to higher forms of life where accumulation in bone structures could cause considerable radiation damage.

A considerable amount of work has been done on plant uptake of those radioisotopes that are deposited on the soil surface as a result of nuclear fallout from atomic tests. Scheffer and Ludwig (1961), from their work on the uptake of radioactive caesium (^{137}Cs) and strontium(^{90}Sr) by plants, concluded that these isotopes are strongly fixed in the soil, and thus not readily assimilated.

Much use has been made of the radioisotopes of various elements that are adsorbed on soil surfaces. By studying the exchange between ions in solution and those of the same species adsorbed onto the surface of either the soil as a

whole, or its constituents, it is possible to gain some insight into the actual methods of such adsorption. Studies on actual soils have been made in this manner with a number of different elements such as sodium (^{22}Na) (Babcock,1960; Fisher,1963), manganese (^{54}Mn) (Weir and Miller,1952) and calcium (^{45}Ca) (Borland and Reitemeier,1950; Smith,Blume and Wittaker,1953; Talibudeen, 1956; Hende,1960 and Fisher,1963). Some exchange studies have also been carried out on the adsorption of cations such as cobalt,using ^{60}Co(Spencer and Olieseking,1954), onto individual clay minerals and also onto cation exchange resins.

A number of workers have endeavoured to study the relationship between the amounts of various adsorbed cations and anions detected by isotopic methods and by the conventional physical and chemical methods of analysis. Such studies have been conducted by Hende (1960) for calcium (^{45}Ca), sulphate($^{35}SO_4$) and phosphate ($^{32}PO_4$) ions, and by Fisher (1963) for calcium (^{45}Ca), magnesium (^{27}Mg), potassium(^{42}K) and sodium (^{22}Na) ions.

Talibudeen (1956) has given an account of methods for estimating the specific activity of calcium,carbon,nitrogen, potassium,phosphorus and sulphur in the soil. He also discusses the general uses of isotopically labelled compounds in soil and fertilizer research. Studies with nitrogen are

carried out using compounds containing enriched amounts of the heavier isotope ^{15}N as there are no radioactive isotopes of nitrogen with sufficiently long half-lives for use in soils experiments.

The use of radioisotopes has enabled studies to be made on the uptake by soils from solution of very small amounts of trace elements. Rhodes (1957) has studied the uptake from solutions containing less than 1×10^{-9} moles per litre of a number of elements not normally found in soils in appreciable amounts. The elements that he has studied and the radioactive isotopes used were : caesium (^{137}Cs); cerium (^{144}Ce); niobium (^{95}Nb); plutonium (^{239}Pu); ruthenium (^{106}Ru); strontium (^{90}Sr); yttrium (^{91}Y) and zirconium (^{95}Zr).

Radioisotopes have been used in the elucidation of basic structural problems dealing with soils. Jacobs and Tamura (1960) have, using a radioactive isotope of caesium (^{137}Cs), investigated the method of fixation of caesium by expanding lattice clay minerals in relation to the collapse of the clay mineral lattice. They have been able to detect whether the caesium is entrapped within the expanded lattice, or merely fixed on the outer surface or edges of clay minerals.

The radioactive isotope of phosphorus, ^{32}P, has been used in the investigation of a number of the problems involving soils and phosphate fixation, release, etc. In experiments using isotopes one of the assumptions made is that the compound

incorporating the radioactive isotope reacts at the same rate as does the corresponding compound which contains inactive atoms only. A number of workers have investigated this assumption in relation to the adsorption and exchange of phosphate groups onto numbers of different sites. Arriaga e Cunha, Simões and Grácio (1960) studied the adsorption of both radioactive ($^{32}PO_4$) and non-radioactive ($^{31}PO_4$) phosphate onto ion exchange resins, the specific sites of which are comparable to many of the adsorption sites found in soil systems. They found that there was no difference in the rates of adsorption of the two different species ($^{31}PO_4$ and $^{32}PO_4$). Similar studies have been made by other workers on different systems. Olsen and Watanabe (1959) studied the adsorption of phosphate by glass and by a number of different soils. They found no difference in the rates of adsorption of $^{31}PO_4$ and $^{32}PO_4$.

The total surface area of naturally occurring phosphate minerals such as apatite has been determined by isotopic exchange (Rickson, 1952; Cano Ruiz and Talibudeen, 1957;and Scheffer,Ulrich and Benecke, 1961). The same method has also been applied to the determination of the total surface area of artificially prepared phosphates such as dicalcium phosphate (Olsen, 1952; Rickson, 1952; Scheffer,Ulrich and Benecke 1961), and of bone and other allied materials (Neuman and Mulryan,1950; Neuman,Weikel and Feldman,1954).

The actual procedure followed is to equilibrate the phosphate mineral with a phosphate solution of known pH value. After equilibration is complete the solution phosphate concentration will not change with time. A small amount of carrier free radioactive phosphate (so as not to alter the amount of phosphate present in the solution significantly) is added to the equilibrium solution. This solution is then analysed at various time intervals, and the decrease in the amount of radioactive phosphate present noted. The resultant experimentally determined curve of the fraction of radioactive phosphate remaining in solution after various times, due to isotopic exchange between solution and solid at chemical equilibrium, is composed of two exchange processes. This process differs from that studied in this thesis where there is no attempt to preserve chemical equilibrium. The mathematical method of analysis of the equilibrium experiments described above has been given by a number of authors (MacKay, 1938; Betts,1948; Wahl and Bonner, 1951, etc.)

There are a great number of different methods of chemical analysis of the amounts of phosphate in soil or in various fractions of the soil reported in the literature. A number of these methods have been compared with the determination of the amounts of total or "available" (to plants) phosphate in the soil as calculated from radioactive exchange(Sapetti, 1959; Moskal and Barsyczak,1959). A considerable amount

of study on the amount of the different extractable phosphate fractions of the soil (Scatz,1954; Ducet and Vanderwalle, 1959; Máté, Lathovics and Kende,1960; MacKenzie 1962) and on the forms of extractable and non-extractable phosphate in the soil (Tendille,1959; Tendille and Pynard,1959)has been carried out. The last mentioned authors have also studied the diffusion of phosphate ions in soil systems with the use of radioactive phosphorus. Numerous studies,such as those by Arriaga e Cunha and Lopes (1960) and Egawa,Nagai and Sato(1951) have been carried out on the availability of phosphate in different soils. Talibudeen (1957a,1957b) has described a number of methods of determining the amount of isotopically exchangeable phosphorus in soils and their advantages.

One of the great advantages of the use of radioactive phosphate is that the mechanisms of anion adsorption onto soils can be readily studied under various conditions. A number of studies by McAuliffe,Hall,Dean and Hendricks (1947), Egawa,Nagai and Sato (1951), Ivanov(1955) and others have shown that most phosphate is adsorbed onto the surfaces of the various soil constituents. Studies were carried out on soils, peats, and various clay minerals such as kaolinite,halloysite,gibbsite,diaspore,goethite,etc.

Molnár, Máté and Kende (1957) have studied the kinetics of uptake of phosphate by soil samples from solution

containing radioactively labelled phosphate as a function of time. They found that there was a linear relationship between the amount taken up by the soil and the original concentration of the radioactive phosphate solution.

Recently Gunary (1963) has used ^{32}P to study the influence of temperature, and also the differences from soil to soil, on the amount of phosphate adsorbed by the soil and the time required to reach isotopic equilibrium. He found that lowering the temperature from 23°C to 3°C caused a 55% drop in the amount of isotopic dilution observed. He deduced that the slow rate of attainment of isotopic equilibrium may be due to a redistribution, on the micro scale, of unevenly applied radioactive phosphate to the soil.

The work undertaken in this thesis has been partly an attempt to elucidate the nature of some of the complexes formed between radioactive phosphate and the surface of a particular soil mineral, mica. A number of previous workers have, as a result of experiments with radioactively labelled phosphate, deduced the existence of a number of different phosphate-soil complexes. Barbier and Tyszkiewicz (1953) said that the exchange between phosphate present in the soil and phosphate added as fertilizer proceeds with two simultaneous rates, one faster than the

other. Similar results have been obtained for exchange with phosphate minerals such as apatite by Cano Ruiz and Talibudeen (1957). Máté, Latkovics and Kende (1960) obtained results that suggested that phosphate is fixed in the soil as a number of compounds of different solubility thus leading to a number of different velocities of exchange processes. Talibudeen (1957a, 1957 b) has said that the total amount of phosphate present in soil may be subdivided into four fractions. These conclusions are reached on the basis of the ability of the soil phosphate to exchange with phosphate ions (that have been radioactively labelled) present in the soil solution. From studies of the phosphate equilibria in acid soils Taylor and Gurney (1962) have deduced the presence of at least two forms of phosphate present in the soil with different degrees of lability.

Seatz (1954) has carried out studies with ^{32}P on the equilibrium between phosphate in solution and in soil samples, and performed a graphical analysis of the exchange data obtained. He plotted the ratio $\frac{\text{radioactivity in the soil}}{\text{total radioactivity}}$ against logarithm (time) and obtained a curve with two points of inflexion. From this he deduced the existence of three distinct phases to the exchange reaction, corresponding to the presence, on the soil sample, of three different phosphate-soil complexes.

The first mention in the literature of the use of

the method of isotopic exchange between ions on the surface of a particular compound and in solution was by Paneth and Vorwerk(1922). They prepared samples of various insoluble lead salts and equilibrated them with solutions containing the same ions as those constituting the salt. By the use of very small amounts of a radioactive isotope of lead(^{212}Pb) the specific surfaces of the insoluble lead salts were investigated from the exchange of the radioactive lead in the solution with inactive lead on the surface of the lead salt crystals.

Phosphorus ^{32} has been used in an analogous manner to study the adsorption of phosphate onto clay minerals by McAuliffe,Hall,Dean and Hendricks (1947). They used clay minerals and naturally occurring metal hydroxides that are found in the soil, and studied the exchange of phosphate ions adsorbed onto the hydroxide surfaces of these compounds. They observed two different reactions occurring. However the interpretation of their work is complicated by the presence of other specific sites on which phosphate ions might be expected to be complexed in some way. In studies on the clay mineral kaolinite for instance (which was one of the clay minerals studied by McAuliffe et al) there are three different sites on which phosphate may be expected to be "fixed" (i.e. forming some type of complex with the surface at that point) in some way. Kaolinite has a layer structure (see figure 3) with one surface consisting of a sheet of

hydroxyl groups and the other surface being a sheet of oxygen atoms.

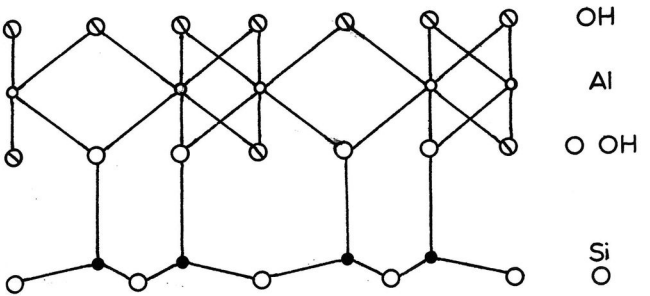


Figure 3.
Diagrammatic representation of kaolinite lattice structure (from Brown, 1961)

As can be seen from Figure 3 there are three different types of site to which phosphate may be attached in some manner. They are the hydroxyl group sheet (top of Figure 3), the oxygen atom sheet (bottom of Figure 3) and the edges of each kaolinite crystal. The actual available sites at these edges will depend on the broken bonds which may be present there, depending on just where the continuous lattice structure shown in Figure 3 is interrupted.

Because of these uncertainties as to the actual type of site on which the phosphate group is "fixed" there are considerable difficulties in the interpretation of the exact

nature of the various phosphate complexes formed. This difficulty is even more pronounced if any detailed investigation of the nature of the complexes formed between phosphate groups and soil samples is attempted.

A method of obtaining information about soil-phosphate complexes using anion exchange resins has been reported by Amer, Bouldin, Black and Duke (1955). They measured the rate of adsorption of phosphate by an anion exchange resin in contact with a soil sample. The rate of adsorption by the resin is controlled by the rate of release of the phosphate from the soil. A graph of quantity of phosphate versus time was prepared from the data obtained and resolved into three parts, corresponding to the existence of three simultaneously occurring processes of release of phosphate by the soil. These processes differed only in their rate, each being first order with respect to the phosphate concentration. These authors also studied the equilibration with phosphate solution using ^{32}P. They found the same three processes of phosphate release from the soil sample, except that the rate for the slowest reaction was apparently independent of time.

The mathematical method of analysis of the graph of the results obtained by Amer et al is somewhat similar to that developed in this thesis (cf. p. 72). It is assumed that, providing the reaction time is long enough, the two fastest rates have gone almost to completion whereas the complex with

the slowest rate of desorption is still present in appreciable amounts. The rate constant and initial amount of this complex present in the soil are calculated from data obtained after the first two complexes are assumed to have disappeared. These values are then used to help calculate the rate constant and initial amount of the middle and then lastly the fastest rate of removal or exchange of phosphate from the soil.

Similar methods for mathematical analysis of data obtained from the exchange of soil and solution phosphates using ^{32}P have been worked out by Scheffer,Ulrich,Benecke and Sendler (1960)(and also Benecke,1959.) They have obtained values for the rate constants and initial amounts of each soil-phosphate complex present. They also calculated the actual rate constants for the general case where there are n different complexes. One of the necessary conditions for the validity of their calculations is that the different phosphate fractions exchange at greatly differing rates. In other words if $R_1, R_2 \ldots\ldots R_n$ are the rates for the exchanges of the different phosphate fractions then $R_1 \gg R_2 \gg \ldots\ldots \gg R_n$. This enables the different exchange reactions to be considered to occur at different times, the first one being almost finished before the second one has appreciably commenced, the second one being almost finished before the third one has appreciably commenced etc.

The use of a graphical method of analysis,similar to

that of Amer, Bouldin, Black and Duke (1955), for the investigation of the forms of manganese present in the soil was reported by Weir and Miller (1962). They deduced that there were at least five forms of manganese-soil complex with different rates of exchange with manganese (labelled with ^{54}Mn) in solution. They actually distinguished and characterised four different manganese-soil complexes. From the fact that the remainder of their experimental graph was, after analysis, a ill curved they deduced that there were probably at least two more forms of soil-manganese complex present. If there had been only one other soil-manganese complex the remaining graph would have been a straight line. Because of the uncertainty of the exact time coordinate of the experimental points on their graphs and the fact that their final, partially resolved graph was only over a time co-ordinate span of 0 to approximately 5 minutes, it was not possible for them to proceed any further with the resolution.

One of the greatest difficulties, leading to uncertainty in their results, in their experiments was the fact that it was necessary to take an aliquot of the solution in contact with the soil and evaporate this to dryness before determining the quantity of radioactive manganese present. As this procedure took about ten seconds the actual time at which exchange would have stopped would be very uncertain for total exchange times of the order of one minute or less. From their quoted results it appeared that more than 97% of the radio-

active manganese in the solution had exchanged with the soil manganese in less than ten minutes. Thus the experimental results that they have obtained ap ly to less than 3% of the total exchangeable manganese on the soil. The accurate resolution of this amount into four different types of complex seems very difficult when the number of experimental points for the graphical analysis is relatively small because of the complex procedure required to obtain them. It seems that a system of continuous monitoring of the solution (or soil) such as has been developed in this thesis would give much greater prospects of successful interpretation of the whole exchange process.

Most studies of the adsorption or "fixation" of phosphate in relation to soil problems have been carried out with whole soil samples. This leads to great difficulties of interpretation if it is desired to elucidate the actual mechanism or position of adsorption, owing to the complex nature of the soil sample taken as a whole. Some work has however been done with various clay minerals and hydrous oxides found in the soil.

Perkins and King (1943) studied the fixation of phosphate by the mica group of clay minerals. They deduced that most phosphate fixation was due to structural or anionic aluminium groupings, only a minor part being played by cationic aluminium or magnesium and possibly by the hydroxide

radicle. Other clay minerals have been used as model compounds for phosphate studies, notably bentonite (Döring, 1956) and the kaolinite family of clay minerals (McAuliffe, Hall, Dean and Hendricks, 1947 and also Döring.) Döring studied the amount of phosphate fixation by these model systems as a function of solution phosphate concentration, time of contact of these clay minerals with the phosphate solution, and change in the pH value of the phosphate solution. McAuliffe et al studied the adsorption of radioactive phosphate onto the hydroxylic surfaces of both clay minerals and of a number of hydrous oxides (gibbsite, diaspore and goethite) as a function of time and deduced the existence of two different reaction rates for this adsorption.

The reaction between phosphate and hydrous oxides of iron and aluminium has been studied by Fiskick and Jackson (1956), Blanchet (1959) Colwell(1959) Eache (1964) and others, and a number of different conclusions drawn as to the method or methods, of fixation of phosphate by these compounds.

Studies on the adsorption or fixation of phosphate by individual constituents of soils lead to results that are more readily interpreted than results obtained from the soil as a whole. However most of the individual constituents (clay minerals, hydrous oxides) with which work

has been undertaken have possessed more than one possible type of reaction site for phosphate fixation. Thus there is still some room for speculation in these experiments as to just which type of reaction site is responsible for the fixation of all, or some part of the total amount, of the phosphate adsorbed by the compound being studied. The method of studying one particular surface only that is described in this thesis overcomes this difficulty and can lead to more definite conclusions as to the actual sites for phosphate adsorption in various soil constituents.

CHAPTER 3

MATERIALS USED

This thesis has been an investigation into techniques for studying the adsorption of various materials such as anionic groups (in particular phosphate) onto known solid surfaces. The actual Solid surfaces investigated were (a) the 001 surface of muscovite mica sheets and (b) the oxidised surface of metallic aluminium.

3·1 Mica

Two different sources of mica have been used, (1) muscovite mica which forms the end window of the Twentieth Century Electronics mica end-window Geiger-Muller counter type [illegible]3H, and (2) sheets split from a piece of muscovite mica supplied by Professor H.W. Wellman of the Geology Department, Victoria University of Wellington.

The majority of the work done for this thesis has been on the study of the desorption of radioactively labelled ortho-phosphate solution from the surface of mica sheets. In the present thesis no attempt has been made to study the desorption of phosphate from the edges of the mica sheets, as this would lead to a more complex picture which could be considerably more difficult to interpret. In order to eliminate the possibility of any adsorption (and thus any subsequent desorption) of phosphate onto the edges of the mica sheets, these edges were coated with paraffin wax. As mentioned above the mica studied was obtained from two sources, and before experimentation they

were prepared in different ways.

The mica forming the end window of the end-window geiger counter is cemented into a metal frame which forms the bottom of the geiger counter. (A diagrammatic representation of the geiger counter is presented elsewhere (Figure 6 p. 50)). To eliminate the possibility of adsorption onto the edges of the mica sheet, or onto the metal frame into which the mica had been cemented, a coating of wax was applied around the edges of the mica sheet, leaving all but the outside $\frac{1}{4}$" clear of wax. This wax coating was continued over the metal frame and up the side of the glass outside of the geiger counter for about one inch. This ensured that nothing other than the mica sheet under study and the surface of the paraffin wax came in contact with any solutions (both radioactive and non-radioactive) being studied.

In order to ensure that no radioactive phosphate was adsorbed by the paraffin wax, a geiger counter was treated as above except that the mica window was completely waxed over. After determining the background count rate ($\sim$50 counts per minute (c.p.m.)) the geiger counter was immersed in radioactive phosphate solution for 30 minutes. The observed count rate at this stage was $\sim$ 2,000 c.p.m. On removing the geiger counter from the radioactive phosphate solution and rinsing it in distilled water to remove any excess drops of radioactive phosphate adhering to the wax coated end window of the geiger counter the count rate was found to be still $\sim$50 c.p.m. thus showing that there had been no adsorption of radioactive phosphate onto the wax.

Some of the later work was done with mica sheets. The mica, which was muscovite mica obtained from the Geology Department, Victoria University of Wellington, was split in a stream of distilled water. A piece of mica about two inches square was taken, and one side was completely coated with wax. The other side, which was the side that had been freshly split under distilled water, was also completely coated with wax except for a circular area of approximately one inch diameter in the centre of this side, which was left uncoated. A short length of wire was attached to the mica sheet with wax, and waxed for about 1 - 2 inches along each side away from the mica sheet. This wire was used to attach the mica sheet to an end-window geiger counter of the type used in the rest of the work (see figure 4)

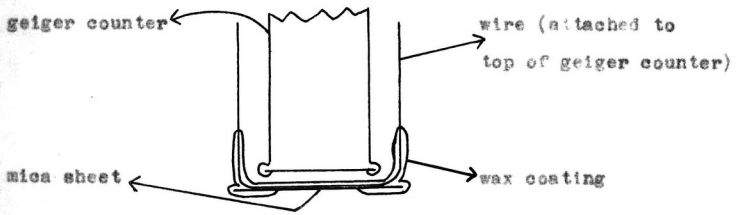


Figure 4

The mica end-window of this geiger counter was completely covered with wax as described above in the control experiment to establish the non-adsorption of phosphate by wax. It was

found that radioactive phosphorus could readily be detected through this thickness (two mica sheets plus two layers of paraffin wax plus one small air gap) of material. In order to obtain reproducible conditions from one experiment to another the area unwaxed on the surface of the mica sheet was made to coincide as closely as possible with the effective counting area of the end-window geiger counter.

Difficulty was experienced in stopping the mica sheet from further splitting around the edges even after it had been waxed around them. It was found that it was not possible to seal permanently the edges with wax, as on prolonged soaking in water (or a dilute solution of the cation under study) splitting of the mica occurred with consequent splitting of the wax sealing the edges. In order to counteract this and thus to eliminate the undesirable possibility of radioactive phosphate penetrating to the interior of the mica and thus being trapped there it was eventually found necessary to seal the edges of the mica sheet by coating around them with glue. After it had dried, this glue was then covered with paraffin wax like the rest of the mica sheet (except for the central circle for adsorption studies on one face). This was thenfound to last satisfactorily.

A further necessity for reproducibility is that the mica sheets be placed in the same position relative to the geiger counter for each experiment. In order to obtain this condition it was considered necessary to place the mica sheet as close to the geiger counter end-window as possible (i.e. pressed hard up against and parallel to it) and to fill the gap caused by

the projecting flanges of the geiger counter with water. It was necessary to introduce water into this gap because if this was not done any subsequent leakage of water into the air gap would lead to a change in the observed count rate which would upset the results being obtained.

Unfortunately it was found that the introduction of a layer of water between the geiger counter end-window and the mica sheet caused a considerable lowering of the count rate, owing to the fact that even a thin layer (the actual thickness introduced would be 3- 5 mm) of water was enough to stop all but the most energetic fraction of the β particles emitted by radioactive phosphorus. An activity of $\sim$4,000 c.p.m. when measured with an air gap between the mica sheet and the geiger counter end-window appeared to be only $\sim$400 c.p.m. when water was introduced into the gap.

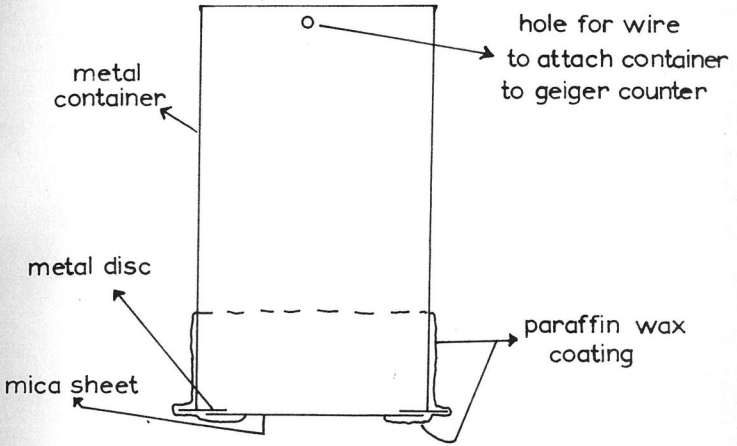
In an endeavour to increase the detectable count rate after the introduction of water into the gap between the mica sheet and the geiger counter end window, a higher specific activity of radioactive phosphate was used, giving an initial count rate of $\sim$ 25,000 c.p.m. On addition of water however the count rate was still reduced to a low value ($\sim$500 c.p.m.) It was therefore decided that a system would have to be designed to overcome the necessity of introducing water between the geiger counter end window and the mica sheet, without introducing any factor likely to affect the reproducibility of the results.

In order to do this it was decided to fit a shell around the geiger counter with a mica window in it, so that the geiger counter was completely removed from contact with the water.

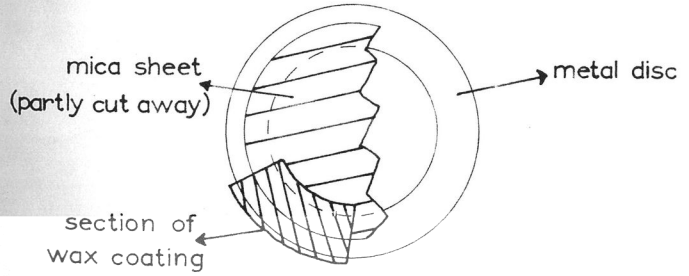
A piece of metal tubing of slightly greater internal diameter than the widest part of the end-window geiger counter(i.e. the metal ring onto which the mica end window is cemented) was taken, and a metal disc was attached to one end of the metal tube. A hole of diameter slightly greater than the effective counting area of the geiger counter was then cut in this metal disc. In the upper end of the tube (i.e. the end away from the metal disc) two holes were bored. Wire threaded through these holes was used to attach the tube to the geiger counter. A diagram of this metal container is shown in Figure 5 . p.42a.

The outside of the remainder of the metal disc, and the outsides of the metal tube for 1 - 1½ inches above the disc ,were coated with paraffin wax. A mica sheet was obtained and split as described previously (p. 39) A roughly circular piece of mica slightly smaller than the outside diameter of the metal disc, but greater than the diameter of the hole in the disc, was cut from a sheet, and laid on the disc with the freshly split face outwards. The edges of this mica were then coated with wax, and thus the mica sheet was sealed onto the metal disc on the end of the metal tube. A sufficient amount of the mica sheet was coated with wax so that the remaining,uncoated area was less than the effective counting area of the geiger counter.

After the mica sheet had been attached to the metal container it was immersed in water for 24 hours to see if there were any leaks. These leaks could be due to either incomplete sealing of the mica sheet onto the metal container with paraffin wax or to a crack in the piece of mica sheet selected. If a leak was detected the



Side View



End View

Metal Container for Mica Sheet (see p.42)

Figure 5

edges of the mica sheet were recoated with wax and the mica window of the container immersed in water for a further 24 hours. If there was still a leak the piece of mica was rejected and replaced with a fresh piece, and the leak testing procedure repeated.

When it had been ascertained that there was no leak, i.e. that the mica sheet was properly sealed onto the metal disc on the end of the container, the other side of the mica sheet inside the container was coated with wax also. The advantage of waxing the inside surface of the mica sheet (i.e. that surface that will face the geiger counter) is that the possibility of the mica sheet developing a leak which will admit solution into the metal container, and thus around the end of the geiger counter, is minimised. This is desirable because, although there is a wax coating all over the end of the geiger counter and for 1-1½ inches up the sides, it is possible that in inserting the geiger counter into the metal container a part of this wax coating may be rubbed off. There is a deliberately tight fit in order to facilitate the accurate placement of the geiger counter end window relative to the mica sheet being studied.

The geiger counter sides are only waxed for 1 - 1½ inches from the end window upwards because there is no chance of any solution that may penetrate inside the metal container coming into contact with the sides any further away from the end window than this. The outside of the metal container is

immersed to a depth of no greater than half an inch into the various solutions used, and the gap between the walls of the metal container and the geiger counter is large enough to eliminate the possibility of capillary attraction causing the level of the water inside (if any) to be significantly greater than the level outside the metal container. The inside surface of the metal disc on the bottom of the metal container was also coated with paraffin wax, as were the inside walls from the metal disc upwards to a distance of about one inch.

Another advantage of coating the inside surface of the mica sheet is that the thickness of the wax coating is usually greater than that of the mica sheet. Thus, provided this wax coating is kept of constant thickness (as was endeavoured to be the case), the effective total thickness of the window will be more nearly constant if the mica sheet thickness varies slightly from experiment to experiment. Wherever possible, this thickness variation was eliminated by cutting a number of sheets for the metal containers from the same large freshly split mica sheet before each series of experiments. However, when one(or more) sheet leaked at any stage it was not necessarily replaced by a sheet of the same thickness.

3.2 Aluminium

Experiments were also carried out on the desorption of radioactive phosphate from aluminium. The same mica end-window geiger counters as were used for the desorption of radioactive phosphate from mica surfaces were used in these experiments. A roughly circular flat piece of aluminium sheet was cut from a large sheetof aluminium of thickness 0.05 mm. Most of the experiments carried out with the aluminium sheet were performed using the metal tube around the geiger counter as described above. Instead of a mica sheet being waxed over the hole in the metal disc on the end of the tube an aluminium sheet was used. This was cut with a slightly smaller diameter than the outside diameter of the metal disc, placed over the disc, and the outside edges waxed onto the already waxed face of the metal disc with paraffin wax. In this way the aluminium sheet was sealed on to the metal container. The inside surface of the aluminium sheet was not coated with wax as were the mica sheets used in the same way. It was thought that as the aluminium sheet would,because of its greater effective weight (weight of mica used was 1-3.3 mgm.per square cm; weight of aluminium sheet was 14 mgm. per square cm.),transmit a lower percentage of the β particles emitted by the radioactive phosphorus. Thus, if a layer of wax was placed on top of the aluminium sheet, the total thickness might lead to too low an observable count rate. Also it would not be expected

that a crack would develop in the aluminium sheet thus allowing the penetration of radioactive phosphate solution to the inside of the metal container.

For an experiment on the desorption of radioactive phosphate from aluminium using solutions with a pH value of 9.0 it was necessary to use the totally enclosed apparatus (cf. p. 91). For this experiment a piece of aluminium sheet was placed on the end of an end-window geiger counter, and was cut so as to be only just less in diameter than the outside diameter of the metal disc that held the mica end window. The edges of the aluminium sheet were coated with wax so as to seal it onto the already wax coated geiger counter end-window. This geiger counter was then inserted in the rubber stopper as described in the section on high pH value experiments (p. 92)

3.3 Ion Exchange Resins

Some of the experiments performed in this thesis necessitated the use of ion exchange resins. The cation exchange resin used was Permutit Ion Exchange Zeo-Karb 225 (1) Hydrogen form cation exchange resin 14-52 mesh. From this was prepared hydrogen cation exchange resin and sodium cation exchange resin. The ion exchange resin was backwashed through an ion exchange column to remove impurities. To prepare the hydrogen resin approximately 2 N "Analar" hydrochloric acid was passed through the resin in the column to ensure that it was completely in the hydrogen form. Distilled water was then passed down the column until the issuing water was free of all traces of acid, to remove all excess hydrochloric acid.

The sodium resin was prepared by passing approximately 2N "Analar" sodium chloride solution down a backwashed ion exchange column of resin until well after the issuing solution was no longer significantly acid. The column was then washed with distilled water, as described above, to remove all excess sodium ions.

When the ion exchange resins had been prepared in the above manner they were stored in distilled water in stoppered flasks until required.

(1) Manufactured by the Permutit Company Limited, Permutit House, Gunnersbury Avenue , London, W.4.

In the preparation of deionised water, and for some of the experiments carried out, the mixed cation and anion exchange resin Biodemineralit was used. This ion exchange resin,which is also manufactured by the Permutit Company, consists of an equal mixture of a strong cation exchange resin (Zeo-Karb 225) and a strong anion exchange resin (De Acidite FF). Because it was not possible to remove any impurities that might have been present by backwashing, as this procedure would separate out the two different resins used in the mixture, the mixed resin was used as obtained from the makers.

3.4 Radioactive Phosphorus

The radioactive phosphate used in this thesis was obtained from The Radiochemical Centre, Amersham, Buckinghamshire, England. It was in the form of orthophosphoric acid adjusted to a pH value of 2-3 with dilute hydrochloric acid. It was quoted as being of high specific activity (> 1,000 curies/gm.P) and had a code number PBS 1. Twenty millicurie (mc.) quantities were obtained at a time as this was found to be the most economical way of purchase, owing to the relatively short half-life (14.30 days).

The twenty mc. were supplied in a total volume of about one millilitre. Stock solutions were made up from this by diluting about 4-10 or more drops (depending on how old the purchased solution was) to 150-200 ml. with a 10 ml. syringe. The syringe was stored in a plastic beaker in distilled water, and came into contact with nothing except the original radioactive phosphate solution and distilled water, in order to ensure that there was no contamination of the radioactive phosphate.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Apparatus

The work done in this thesis has been concerned with the adsorption and desorption of radioactive phosphate from mica surfaces. The amounts of this radioactive phosphate present at various times were studied with the use of end-window geiger counters.

4.11 Geiger Counters

The geiger counters used in this thesis were manufactured by Twentieth Century Electronics Limited. They were type No.EW3H. These geiger counters consisted (see figure 6) of a cylindrical glass envelope which had a thin sheet of mica across one end and which was sealed at the other end.

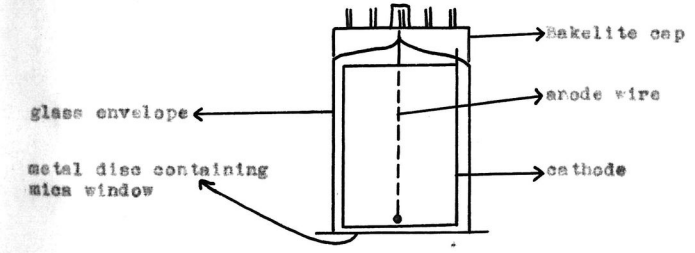


Figure 6

The cathode consisted of a stainless steel cylinder placed concentrically inside the glass envelope. A wire attached to the cathode was sealed through the top end (i.e. the end away from the mica window) to provide the negative terminal for the voltage supply. The anode was a central tungsten wire sealed

through the top of the glass envelope. The bottom end of the anode wire was a glass ball of about 2 mm. diameter suspended about 0.5 cm. above the mica end-window of the geiger counter. The top of the glass envelope had a bakelite cap, with eight small metal plugs protruding from it, on it. The cathode and anode wires were joined to two of these plugs which were all insulated from each other.

A metal disc was attached to the bottom of the glass envelope of the geiger counter, and to this disc a thin sheet of mica was cemented. The mica sheets were cut from 5 cm. square sheets of mica and were split so that the thickness of the sheets used corresponded to a weight of 1 to 3.3 milligrams per square centimetre. The mica was checked for even thickness over the window area in a polarised light strain viewer. The mica was cut into circles of diameter 3½±0.5 mm.,being held between two pieces of clean paper during the cutting operation. Finally the mica circle was cleaned with ether before being cemented into position inside the metal disc (1).

All the outside of the glass envelope between the bottom metal disc and the cap surmounting the top of it was painted with black paint in order to ensure that no light penetrated into the geiger counter through the sides and caused an effect on the count rate observable during the use of the geiger counter. At times during the present work the geiger counters were operated in air,with nothing surrounding the end window,

(1) Twentieth Century Electronics Ltd.Data sheet for E.M.3H

Window No.A 35-84

and then it would be possible, if they were light sensitive, for the count rate to be affected by the amount of light falling on the mica end window. However, other things being equal it was not found that there was any change in the count rate detected between day and night-time with all lights in the room extinguished. Therefore it would seem that these geiger counters are not light sensitive at least through their mica windows.

On some of the geiger counters used it was found that the top cap was slightly loose to the touch. Where this was found epoxy-resin glue was applied to the joint between the glass and the cap in order to promote a good seal. It was feared that if this was not done, constant handling, with consequent relative movement of the cap and the remainder of the geiger counter, might cause the joint between either the cathode or anode wire and the respective metal plug in the cap to weaken. If this joint broke, movement might give rise to an intermittent contact, with the effect that the geiger counter would only function intermittently also. This could be very undesirable in the middle of an experiment, as, when adsorption of radioactive phosphate onto the mica surface of the geiger counter end-window was being studied, it would not be possible to replace the faulty geiger counter with a new one.

One experiment was performed using a different type of geiger counter to that used for all the other work, the aim being to study the adsorption and desorption of radioactive phosphate from aluminium. This geiger counter was a type 1 B85 Thyrode counter tube made by the Victoreen Instrument Co.,United States of America. It consisted of a cylindrical aluminium case one end of which was sealed over. This case itself was the cathode for the geiger counter. The anode was a central wire inside the geiger counter with a connection through to the top of the geiger counter (cf. Figure 7)

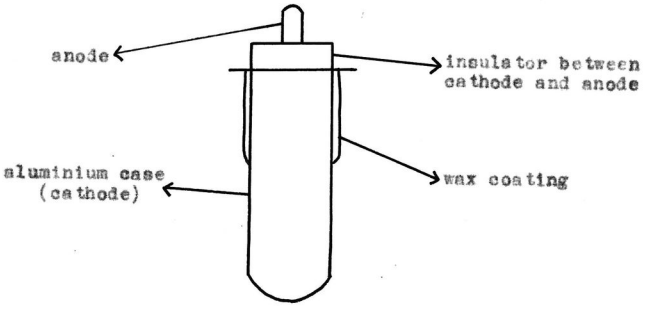


Figure 7

The cathode and anode terminals were insulated from each other as shown in Figure 7 .

Before use the top part of the cathode of the geiger counter was coated with paraffin wax. Thus, providing the geiger counter was immersed in the various solutions used

to such an extent that some of the bottom of the wax coating was always in the solution, a constant, reproducible area of aluminium would be in contact with all solutions used.

The background count rate for this geiger counter was determined with the bottom, unwaxed, part immersed in distilled water. It was found to be considerably higher under these conditions ($\sim$ 350 c.p.m.) than the background count rate usually found with the mica end-window geiger counters. The adsorption, and subsequent desorption, experiment was performed in a similar manner to that when the end-window geiger counters were used. The experimental results are described in the section on the desorption of radioactive phosphate from aluminium surfaces (p. 208)

4.12 Detecting and Recording Apparatus

The electronic apparatus used in conjunction with the geiger counter was as follows (see Plate [1])

(a) A Philips High Voltage Supply/Amplifier No.P.W.4022

(b) A Philips Rate Meter No.P.W.4042

(c) A Philips Electronic Counter No.4032

(d) A strip chart recorder

and

(e) An electronic quench circuit (Q).

The Electronic Counter, Rate Meter and High Voltage Supply/Amplifier (top to bottom) are shown in Plate [1]. Voltage to the geiger counter (G) is supplied by the High Voltage Supply/Amplifier through the electronic quench unit.

Whenever a geiger counter was used for the first time it was tested to ensure that it had reliable counting characteristics. The geiger counter was connected to the High Voltage Supply/Amplifier through the electronic quench unit, and the voltage increased slowly until it began to count. This was usually found to occur at about 450-500 volts. This value is known as the threshold voltage. It was found that after a number of desorption experiments had been performed with the same geiger counter, the threshold voltage often rose up to about 600 volts.

Once the geiger counter had commenced to count the voltage was raised and the plateau length determined.

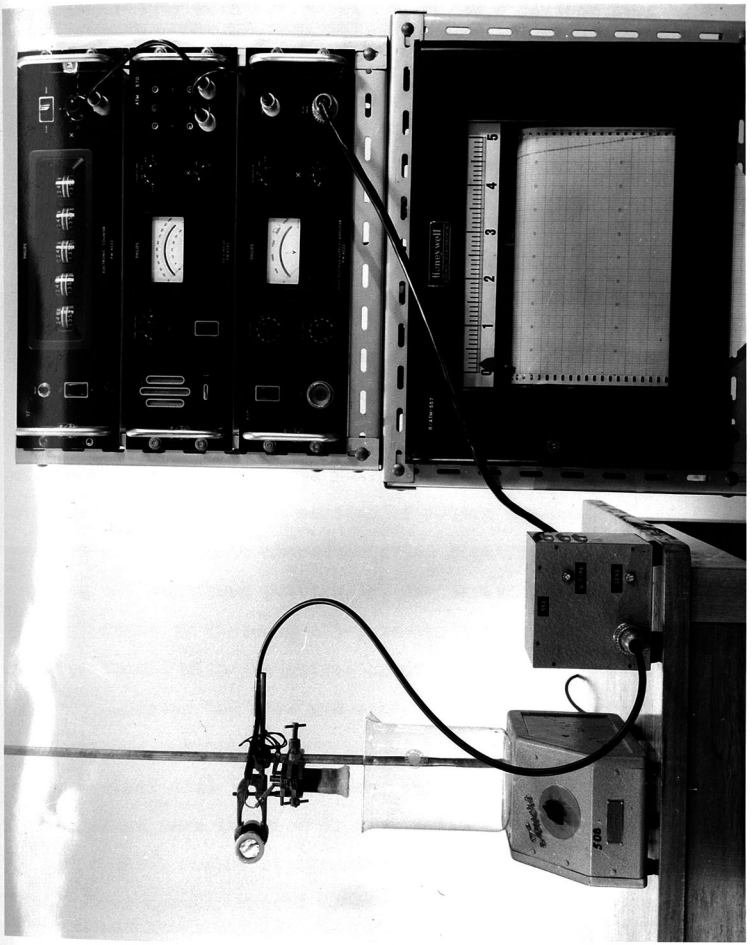


PLATE 1

Most new geiger counters of this type had a plateau length of 200-300 volts. The average background count rate (in air) was then determined and this was usually found to be approximately 40-50 c.p.m. If the background was excessively high, or the plateau length very short, the geiger counter would be rejected as unsatisfactory for the type of work carried out.

If both the background count rate and plateau length criteria were satisfactory the geiger counter was then coated with wax as described earlier (p.[38]). The plateau length and background count rate were checked once more after the geiger counter had been coated with wax. This was to ensure that the heating, to which the geiger counter had been subjected while the coating of molten wax was applied, had not altered these characteristics significantly.

As was mentioned previously, the threshold voltage was usually found to increase after desorption experiments had been performed with the geiger counter. These experiments involved placing the mica end-window of the geiger counter into aqueous solutions for considerable periods of time. It is assumed that this procedure was responsible for the threshold voltage increase in some way.

The total number of experiments that were performed with each geiger counter varied considerably. All the geiger counters used for the purpose of studying the adsorption and desorption of radio-active phosphate from the surface of their

mica end windows eventually failed to be of further use. This failure was of two types. Some of the geiger counters suddenly stopped counting for no apparent reason. It was found that even when the applied voltage was increased to as high as 1,500 volts no count rate was observed. In the other type of failure the plateau length was found to decrease to a very small value, usually less than 20 volts. Thus any attempt to operate the geiger counter sent it into continuous discharge.

All geiger counters that had failed in either manner were stored away for further testing. It was sometimes found that after a long period (three to six months or more) the geiger counters appeared to recover and be ready for use again.

When they were first obtained, the geiger counters had a background count rate of 40-50 c.p.m. in air. After they had been used for an experiment, all the adsorbed radioactive phosphate was not always removed. This led to the result that the background count rate for subsequent experiments varied considerably, ranging up to about 100 c.p.m. in some cases. It was felt that as prolonged soaking of the mica end-window of the geiger counter in a variety of solutions had not removed this last amount of activity, the subsequent experiment was unlikely to do so either. Thus it would not be expected that the background count rate would change sufficiently during the course of an experiment to

upset the results obtained. It was also possible that the increase in the background count rate was not due to a very small amount of remaining adsorbed radioactive phosphate. The increase may have been caused by a change in the characteristics of the geiger counter due to its prolonged immersion in the solutions used. In this case no significant change would be expected in the background count rate during a further experiment.

The resolving time for the electronic quench unit was determined by the use of the "paired source" method (Cook and Duncan,1952). All electronic quench units used were adjusted so that their resolving time was approximately 500 microseconds.

The geiger counters were operated during the experiments at approximately 100 volts greater than the threshold voltage. The signals from the geiger counter were fed from the electronic quench unit through the high voltage supply/ amplifier to the rate meter. The rate meter is connected to a strip chart recorder (shown on the bottom right of Plate 1), and also to an electronic counter. The electronic counter was used to obtain accurate values for the count rate by counting for a much longer time interval than that over which the rate meter averages out the count rate. The longest time constant available on the rate meter was 100 seconds, which can be considered to be equivalent to a counting period of 200 seconds

(Friedlander and Kennedy,1957; Crotty,1962), whereas the background count rate,for example, could be determined over a period of one hour with the use of a stop watch. This longer counting period would enable a more accurate value for the background count rate to be determined. The electronic counter was also useful for giving an approximate,but rapidly determined, value of the count rate at the beginning of an experiment, thus enabling the rate meter to be set at almost the right position immediately. This enabled the very beginning of the desorption experiments to be studied with greater accuracy.

Some of the later experiments were studied over a very long period of time (of the order of 500 hours). For the latter part of these experiments the count rate was decreasing very slowly. In order to determine accurately the slight difference in count rate over periods of 24 hours, the count rate was determined on the electronic counter for periods of approximately 1-2 hours. The actual change in count rate over the counting period was almost negligible at this stage, and any decrease in the count rate would be the same over the first half of the counting period as over the second half. Thus a very accurate value of the count rate was obtained for the time corresponding to the midpoint of the counting period by use of the electronic counter.

Two different strip chart recorders were used in the course of the work done for this thesis. The first was a continuous recording Brown recorder, and the second was a six channel Honeywell Brown recorder. Before use (and frequently thereafter) the recorder used was calibrated. In the case of the multichannel recorder each channel that was used was calibrated independently. First the recorder was adjusted to read zero with no external connection to the rate meter. Then it was connected to the rate meter, and the adjusting screws on the rate meter were adjusted so that the recorder read zero when the rate meter was reading zero, and read $^{30}/_{100}$ when the rate meter was switched to "calibrate" that is when exactly 50 cycles per second were being fed through it to the recorder.

It was not possible to obtain a reading on the recorder with the rate meter switched to "calibrate" and actually connected simultaneously to the high voltage supply/amplifier. Previous work by the author (Furkert,1962) has shown that the actual method used does,however,give valid results with respect to the whole electronic arrangement.

4.2 COUNTING PROCEDURE

At the commencement of each experiment the mica end-window of a geiger counter which had been waxed and tested and found to be satisfactory was equilibrated with various solutions to the required extent. The details of this equilibration are discussed elsewhere in this thesis (cf. p. 116). After equilibration the geiger counter end-window is immersed in the appropriate required solution in a two-litre beaker (or polythene container) as shown in Plate 2 .

On the bottom of the beaker is a glass enclosed magnet. This acts as a follower for the magnetic stirrer (s) which is under the beaker (see Plate 2). The solution in the beaker is slowly stirred by the rotation of the follower under the influence of the rotating magnet below. This procedure eliminates the need to have anything externally placed into the slution (apart from the follower itself) where it could become radioactively contaminated.

Stirring is carried out fairly slowly to avoid the creation of too deep a vortex in the solution. Care is needed to see that this vortex does not become so great that a bubble of air becomes trapped under the mica end-window of the geiger counter. If this occurs then not all of the mica surface may be in contact with the solution. This will have the effect of altering the count rate slightly, due to a difference in the backscattering effects of air and

PLATE 2

water for phosphorus -32, if this bubble formation occurs during the subsequent desorption experiment. Also, if there is an air bubble covering some of the mica surface, desorption of radioactive phosphate from the affected area will not occur.

The background countrate for the geiger counter, with its mica end-window immersed in the two litres of solution, was determined. After this had been done, the geiger counter end window was removed from the solution, and placed in a radioactive phosphate solution for a definite time, while radioactive phosphate was adsorbed onto the mica surface.

Depending on the amount of radioactive phosphate in the adsorbing solution, the count rate when the geiger counter end-window was immersed in this solution was sometimes greater than could be measured by the rate meter. When this was the case the voltage applied to the geiger counter was lowered below the threshold voltage during the time that the geiger counter end-window was in the radioactive phosphate slution.

After removal from the radioactive phosphate solution the threshold voltage for the geiger counter was checked to ensure that no unobserved variation had occurred. If necessary the switch positions on the high voltage supply/amplifier were altered so that the geiger counter was still operating 100 volts above the threshold voltage.

When the required adsorption period had elapsed the mica surface of the geiger counter end-window was removed from the radioactive phosphate solution, rinsed in desorbing solution and then replaced in the two litres of desorbing solution wherein the background count rate had been determined. Care was taken to ensure that no air bubbles were trapped against the mica surface of the end-window of the geiger counter in the process of insertion of this surface into the two litres of desorbing solution.

The exact time of introduction of the mica end-window of the geiger counter into the two litre beaker containing the desorbing solution was noted on the strip chart recorder. The recorder was run at a speed of 4 inches per hour during the initial portion of the desorption, while the count rate was dropping rapidly. After some time (usually 3-4 hours) when the rate of decrease of the count rate was slower, the recorder chart speed was changed to 1 inch per hour.

It was found that after about 40 hours the rate of decrease of activity as a function of time was, after suitable mathematical analysis, resolvable as a straight line. In order to ensure that there was a reasonable amount of time when there was only this straight line in the analysed curve, most experiments were allowed to run for approximately 100- 150 hours.

Once the radioactive phosphate has been desorbed from the mica end-window of the geiger counter into the

beaker of desorbing solution it will make no significant contribution to the count rate as determined by the geiger counter. This statement involves the assumption that the volume of desorbing solution is so great that there is no chance of enough radioactive phosphorus atoms disintegrating sufficiently close to the geiger counter to have a significant effect on the observed count rate. In order to ensure that this was so, after considerable time for desorption had elapsed, and the count rate was no longer decreasing rapidly, the volume of desorbing solution, in which the mica surface of the geiger counter end-window was immersed, was replaced with another, equal, fresh volume of desorbing solution. If this change had any effect on the observed count rate then the volume was insufficient to eliminate the effect of desorbed radioactive phosphate on the count rate. This effect was not observed with desorbing solution volumes of greater than one litre, and so all desorption experiments were carried out in two litre beakers.

As a further check that there was no contribution to the measured count rate from radioactive phosphate desorbed into the desorbing solution, some of the desorbing solution was taken and the count rate due to it determined. The "infinite thickness" for the β radiation from phosphorus -32 in water is approximately eight millimetres. In order to see how radioactive the desorbing solution was, the

following procedure was carried out.

A Philips lead castle was used with a mica end-window EW3H geiger counter inserted into it, so that the end window protruded through into the counting area. The mica end-window of the geiger counter was coated with a thin layer of paraffin wax. It has already been shown (p. 38) that radioactive phosphate is not adsorbed onto paraffin wax. The end window of the geiger counter was then placed in a beaker with a diameter twice that of the end window of the geiger counter. There was a depth of 3½ cm.(i.e. approximately four times the "infinite Thickness" for ^{32}P) of solution below the window of the geiger counter.

The background count rate was determined with the end window of the geiger counter immersed in distilled water (see figure 8).

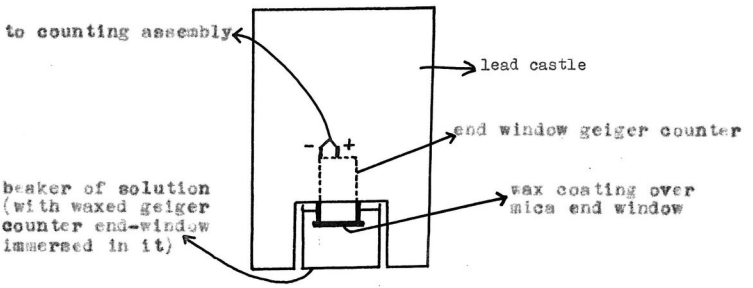


Figure 8

After the background count rate had been determined the

beaker was filled with some of the two litres of solution into which the radioactive phosphate from a mica sheet had been desorbed. After standing for some minutes, the solution was discarded and replaced with another filling from the two litres of desorbing solution. This was done a number of times to ensure that the count rate of the solution would not be unduly low due to adsorption of radioactive phosphate onto the walls of the beaker. It is reasonable to assume that this adsorption does not remove all radioactive phosphate from the solution as if this was so there would be no activity in the solution anyway as it would have all been adsorbed onto the walls of the two litre beaker into which the original desorption experiment took place.

Finally the count rate was determined with the wax coated mica end window of the geiger counter immersed in the beaker full of some of the original desorbing solution. It was found that the actual count rate of the solution (equals observed count rate - background count rate) was about 1% or less of the lowest count rate observed in the original desorption experiment. Thus it is apparent that within the limits of the experiment it is possible to ignore any effect on the actual detected count rate during the experiment by the solution into which desorption is carried out.

4.3 Processing of Data

At the completion of each experiment the recorder chart is used to obtain the count rate at suitable intervals of time. The value given by the recorder chart is taken, a coincidence correction is added, and then the value of the background count rate for the particular experiment is subtracted. As the half life of ^{32}P is only 14.30 days (Friedlander and Kennedy 1957) decrease in the actual count rate due to radioactive decay will have a significant effect for periods of time greater than about 10-20 hours. Thus it is necessary to correct each count rate calculated as above for radioactive decay. A table of factors was constructed from a semilogarithmic plot of percentage activity remaining versus time elapsed (after zero time when the mica surface of the geiger counter end window is first immersed in the desorbing solution), the percentage activity remaining after 14.30 days being 50.0. The series of values obtained by these various steps are given for a typical experiment in Table 1 .

The values that are finally obtained (Column 5, Table 1) are plotted on semilogarithmic graph paper such that a plot of log (count rate) versus time is obtained. It is found that, after a certain time, a straight line can be drawn through all the remaining points on the graph. This line is drawn and is extrapolated back until it cuts

the time = 0 axis at a point "Z".

This extrapolated line is found to lie below the remaining points that have been plotted on the graph. The value given by the line at the same time as each point already plotted is subtracted from the point already plotted, and a new series of points obtained.

TABLE 1

Time (hours)	Observed count rate	+ Coincidence - Background correction	x Correction for decay of ^{32}P
1/6	15,150	18,650	18,600
1/3	14,000	16,900	16,850
1/2	13,200	15,800	15,750
2/3	12,520	14,770	14,720
5/6	12,000	14,100	14,050
1	11,500	13,450	13,400
1 1/6	11,150	12,950	12,900
1 1/3	10,850	12,550	12,510
1½	10,550	12,150	12,110
1 2/3	10,350	11,850	11,820
1 5/6	10,150	11,580	11,550
2	10,000	11,350	11,320
2 1/3	9,600	10,900	10,880
2 2/3	9,410	10,650	10,630

TABLE 1 cont.

Time (hours)	Observed count rate	+Coincidence correction	-Background	x Correction for decay of 32_P
3	9,180	10,380	10,310	10,370
3 1/3	9,080	10,220	10,150	10,210
3 2/3	8,960	10,050	9,980	10,040
4	8,800	9,850	9,780	9,850
4 1/3	8,720	9,740	9,670	9,750
4 2/3	8,620	9,630	9,560	9,650
5	8,500	9,480	9,410	9,510
5 1/3	8,390	9,370	9,300	9,410
5 2/3	8,300	9,260	9,190	9,310
6	8,220	9,170	9,100	9,220
6 1/3	8,150	9,080	9,020	9,140
6 2/3	8,100	8,980	8,910	9,030
7	8,010	8,890	8,820	8,950
8	7,850	8,650	8,580	8,730
9	7,620	8,400	8,330	8,490
10	7,470	8,230	8,160	8,340
11	7,330	8,050	7,980	8,180
12	7,160	7,860	7,790	7,990
13	6,970	7,620	7,550	7,750
14	6,810	7,420	7,350	7,570
16	6,640	7,220	7,150	7,390
18	6,450	7,020	6,950	7,220
20	6,290	6,800	6,730	7,030

TABLE 1 cont.

Time (hours)	Observed count rate	+ Coincidence correction	- Background	x Correction for decay of ^{32}P
24	5,940	6,390	6,320	6,650
28	5,690	6,100	6,030	6,400
32	5,550	5,940	5,870	6,280
36	5,420	5,790	5,720	6,170
40	5,300	5,660	5,590	6,080
44	5,150	5,500	5,430	5,950
48	5,000	5,330	5,260	5,820
52	4,910	5,220	5,150	5,730
56	4,900	5,210	5,140	5,760
60	4,820	5,130	5,060	5,720
64	4,750	5,050	4,980	5,690
68	4,680	4,970	4,900	5,640
72	4,650	4,930	4,860	5,640
76	4,540	4,810	4,740	5,580
80	4,470	4,740	4,670	5,510
84	4,430	4,700	4,630	5,510
87	4,390	4,655	4,585	5,490

These new points are then plotted on the same graph on the same time abcissae as the original points.

It is then found that it is possible to draw a straight line through a number of the newly obtained points with the greatest time coordinate. On extrapolation

of this line back to the time = 0 axis (cutting it at a point "Y") it is found that some of the points with the shorter time coordinates lie above this line "Y". The subtraction process is repeated with the line "Y" and a line drawn as before through the points obtained. This process is repeated until a line is drawn which passes through all the remaining points including those with the shortest time coordinates. The total number of straight lines obtained by the above process of graphical analysis varied with different experiments. In a large number of these experiments three straight lines were obtained.

The resolved graph from the data given in Table 1 is shown on p. 294. It will be seen that three straight lines were obtained from this experiment, corresponding to three different desorption processes of radioactive phosphate from the mica surface.

The process being studied is one of desorption of the radioactive phosphate from the mica surface of the geiger counter end-window, or from the surface of a mica sheet. This desorption will begin to occur immediately the desorbing solution comes into contact with the mica surface, and thus there will be no elapsed time while diffusion or other undesirable initiating processes occur.

CHAPTER 5.

MATHEMATICAL ANALYSIS OF DATA.

Preliminary experiments on the desorption of radioactive phosphate from cation saturated mica surfaces showed that the amount of radioactive phosphate remaining on the mica surface decreased with time. The amount of radioactive phosphate remaining on the mica surface was measured continuously and plotted on a strip chart recorder as a function of time. After suitable processing of this data (see Processing of Data p. 67) a series of actual count rates, corresponding to amounts of radioactive phosphate remaining on the mica surface, at various time intervals after the commencement of the desorption experiment were obtained.

Desorption of radioactive phosphate was carried out into aqueous solutions. These solutions were stirred continuously so that once radioactive phosphate groups had been desorbed they were removed from the counting volume of the end-window geiger counters used. Thus the only radioactive phosphorus atoms whose radioactive disintegrations were measured were those actually present (as phosphate ions) adsorbed onto the surfaces being studied.

The desorbing solutions used in the experiments performed in this thesis contained no phosphate groups

(radioactive or inactive) except those that had already been desorbed from the surfaces under study. The amount of such phosphate groups was so small that it was not necessary to consider the possibility of readsorption of any of the groups onto the surface being studied in the mathematical interpretation of the results obtained.

The radioactive phosphate groups adsorbed onto the surfaces under study would be expected to be adsorbed onto some particular type of site or possibly a number of different types of site. It was assumed in this thesis that the radioactive phosphate associated with the surfaces being studied was present as some type of adsorption complex (or complexes) and not as a precipitate (see Discussion of Results p. 337).

On placing the surfaces studied in contact with various solutions (after adsorption of radioactive phosphate had occurred) it was observed tht the radioactive phosphate groups were desorbed into the desorbing solutions used.

It was not considered that the desorption of the radioactive phosphate groups from the adsorption sites on the surfaces studied was accompanied by any other necessary occurrence such as the replacement of these groups by some other species such as hydroxide. As it was believed that the radioactive phosphate groups were merely

adsorbed onto these surfaces it was not necessary that any other group (phosphate or other ionic species) be present at these adsorption sites. Thus the likelihood of any particular radioactive phosphate group being desorbed at any time would be dependent only on the strength of the linkage between the radioactive phosphate group and the particular adsorption site that it was associated with. Consequently the desorption of radioactive phosphate groups from any particular type of adsorption site would be a first order process, the rate depending only on the number of radioactive phosphategroups attached to adsorption sites of this particular type. If there was more than one type of adsorption site for radioactive phosphate on the surface studied then the overall desorption rate would be equal to the sum of the individual first order desorption rates for each type of adsorption site present.

If therewas more than one type of adsorption site for radioactive phosphate from which desorption was occurring simultaneously the mathematical analysis of the desorption process would be the same as that of the resolution of a mixture of radioisotopes decaying simultaneously with first order kinetics. The mathematical analysis of this last process (decay of a mixture of radioisotopes) has been described by a number

of authors (e.g. Friedlander and Kennedy,1957; Cook and Duncan,1952).

A necessary condition for successful mathematical analysis is that the half-lives of the mixture of radioisotopes be widely differing in time. If this is not so, reliable separation of the components is very difficult. This condition would also apply to a similar mathematical analysis of the problem of desorption of radioactive phosphate from a number of different types of adsorption site. That is the half-lives for each of the types of radioactive phosphate -surface complex (the half-life of one of these complexes is the time required for half of the amount of radioactive phosphate present at a given time to be desorbed) would need to be widely separated in time, e.g., 1 hour, 10 hours, 100 hours.

Another condition required before the above-mentioned method of mathematical analysis would be valid was that there was no interaction between radioactive phosphate groups adsorbed onto different types of adsorption site, or between groups adsorbed onto the same type of adsorption site, and adjacent to one another. In the work carried out on cation saturated mica surfaces the number of cations present was only one every 50 sq.Å, that is one cation every

7 Å in each direction. It seemed most unlikely that there would be more than one radioactive phosphate group per cation as the residual positive charge on one aluminium ion (the highest charged cation used) would not be expected to attract two phosphate groups when the total surface was not saturated with phosphate groups.

It was believed that some of the adsorbed radioactive phosphate ions were associated with the mica surface itself. However the amount of this type of adsorbed radioactive phosphate complex was always less than half of the total amount of radioactive phosphate adsorbed at all pH values studied. Therefore there would not be more than one radioactive phosphate group between each cation, and it seemed that such a number could be accommodated on the mica surface without necessarily being so close to one another as to lead to an interaction between them that would affect their desorption rate. Thus it seemed that this condition would be satisfied, at least for mica surfaces.

By analogy with the mathematical analysis of the decay of a mixture of radioisotopes the plot of the logarithm of the amount of radioactive phosphate remaining adsorbed (on the surface under study) against time might be expected to be analysable into a number of straight lines, one for each type of adsorption site.

The desorption curves obtained from the experiments performed in this thesis were in fact resolved into a number of straight lines. From this it has been concluded that there were actually a number of different types of adsorption sites for radioactive phosphate groups on the surfaces studied, from which these radioactive phosphate groups can desorb with first order kinetics. The actual mathematical method of analysis is as follows:

Assume that there are n different types of adsorption site on the surface being studied. If the radioactive phosphate groups desorb from these sites with first order kinetics then the rate constants for desorption will be $k_1, k_2, \ldots k_n$.

Let the initial amounts of each complex (that is the amount of radioactive phosphate associated with each type of adsorption site) be $A_1, A_2, \ldots A_n$. These are the amounts present at T = 0.

The amounts of each complex present after a desorption time t has elapsed will be:

$$A_1 e^{-k_1 t}, \quad A_2 e^{-k_2 t}, \quad \ldots\ldots\ldots A_n e^{-k_n t}.$$

It is assumed that the specific activity of each complex is the same and also that only radioactive phosphorus atoms disintegrating on the adsorbed surface are detected. Thus the measured count rate

will be proportional to the total amount of radioactive phosphate present adsorbed on the surface under study. The initial count rate will be proportional to A where

$A = A_1 + A_2 + A_3 + \ldots\ldots + A_n$.

The total amount of radioactive phosphate present at time T=0 is equal to A, and the amount present at time T= t will be:

$$A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + \ldots\ldots + A_n e^{-k_n t}$$

If the proportion of the amount of radioactive phosphate present that is detected by the geiger counter is B then the initial count rate will be B.A. and the count rate after time t will be:

$$B.A_1 e^{-k_1 t} + B.A_2 e^{-k_2 t} + \ldots\ldots\ldots B.A_n e^{-k_n t}$$

The logarithm of the count rate will be

$(\log_e B.A_1 - k_1 t) + (\log_e B.A_2 - k_2 t) + \ldots\ldots + (\log_e B.A_n - k_n t)$

i.e. $2.303 \log (\text{count rate}) = (2.303 \log B.A_1 - k_1 t)$

$+ (2.303 \log B.A_2 - k_2 t) + \ldots\ldots\ldots + (2.303 \log B.A_n - k_n t)$ (1)

As can be seen from equation (1) the count rate (which is proportional to the total amount of adsorbed radioactive phosphate present) can be resolved into a series of

logarithmic terms which on a plot of log (count rate) versus time will be represented as a series of straight lines.

The proportions of the total initial count rate that represent the amounts of each complex present initially will be given by the intercepts of each of these straight lines with the time =0 axis. The actual values obtained will be $B.A_1$, $B.A_2$, ... $B.A_n$. Thus it will be possible to obtain the relative amounts of each complex present as a fraction of the total amount of radioactive phosphate present. It will not be possible to calculate the actual amounts of each complex, or the actual total amount of radioactive phosphate present unless the proportion B of the amount present that is actually detected by the geiger counter is known.

With the use of semilogarithmic graph paper a plot of count rate versus time is prepared and graphically analysed into a series of straight lines. The actual detail of this graphical analysis is given in the preceding section on the processing of the experimental data (p. 67). From the slopes of the straight lines obtained on the semi-logarithmic plot it is possible to calculate the half-lives of each complex. The half-life for a complex is the time required for the amount of the complex of radioactive phosphate with the surface being studied to decrease to half.

As the desorption of radioactive phosphate from each complex is a first order process the rate constants for desorption k_1, k_2 .....k_n are inversely proportional to the half-lives in the same way as for radioactive decay, namely,

$$k_1 = \frac{\log_e 2}{(t_{\frac{1}{2}})_1}\ ; \quad k_2 = \frac{\log_e 2}{(t_{\frac{1}{2}})_2}\ ; \quad \ldots k_n = \frac{\log_e 2}{(t_{\frac{1}{2}})_n}$$

Thus it is possible from the analysed data to calculate the rate constants for the desorption of each complex from the surface being studied. These rate constants will be characteristic of the ease of desorption of the radioactive phosphate from the surface, the higher the rate constant the more readily desorption will occur.

As was mentioned previously the relative amounts of each of the complexes present is given by the intercepts of the resolved straight lines with the time = 0 axis. If the complexes detected account for all the radioactive phosphate adsorbed onto the surfaces being studied, the sum of the initial count rates of each complex should be equal to the total initial count rate detected. In the experiments conducted for this thesis this was found to be the case, the total amounts of the different complexes detected adding up to the same value (within about 1%) as was obtained by graphical extrapolation of the original curve, from the desorption experiment, back to zero time. Thus it can be seen that there are no

other radioactive phosphate-surface complexes present in significant concentrations on the surfaces being studied.

CHAPTER 6.

EXPERIMENTAL.

In this thesis an attempt has been made to study the mica surface - cation - phosphate system. Preliminary experiments were conducted using mica surfaces saturated with aluminium and sodium ions. In order to do this the mica surface of an end-window geiger counter was soaked in a 0.5N solution of the required cation. This was done at least four times, the geiger counter end-window being left in the solution for at least thirty minutes each time.

It was found that the mica surface saturated with aluminium ions adsorbed considerably more radioactive phosphate (in the same period of time) than it did when it was saturated with sodium ions. On placing the mica end-window of the geiger counter (after adsorption of radioactive phosphate) in a beaker of water, the amount of radioactive phosphate adsorbed on the end-window was found to decrease with time. The amount of radioactive phosphate remaining on the geiger counter end-window was plotted, as a function of time, on a strip chart recorder. The count rate/time data was processed and mathematically analysed as indicated elsewhere (see section on mathematical analysis of data p. 72).

Analysis of experiments with both sodium saturated and aluminium saturated mica surfaces gave desorption curves

which indicated that there were three different types of adsorption site from which the radioactive phosphate was being desorbed. The desorption rates varied widely, indicating that the various types of adsorption site bound the radioactive phosphate with different strengths. The stronger the linkage between the radioactive phosphate and the adsorption site, the less readily desorption of the phosphate into the water would occur. The total amount of radioactive phosphate present was observed to be greater in the case of aluminium than when sodium was used as the exchangeable cation on the mica surface.

6.1 Control of the pH Value of Experiments

The preliminary experiments that have just been described were carried out without any steps being taken to control the pH value of either the radioactive phosphate solution or the ions adsorbed onto the mica surface. Once it had been established that the radioactive phosphate was adsorbed onto the mica surface in some manner, and that the desorption of this phosphate could be resolved into a number of components, it was decided that these components would be studied over a range of pH values. To avoid the possibility of there being any effect on the state of either the radioactive phosphate or the ions (especially the aluminium ions) adsorbed onto the mica surface, by their interaction when at different pH values, both the radioactive phosphate solution and the adsorbed ions on the mica surface were brought to the same pH value.

Adjustment of the radioactive phosphate solution to the required pH value was a relatively simple procedure, as phosphate ions in solution are buffered to a considerable extent by means of the following equilibria:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

At any pH value all four of the species, i.e. H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} will be present simultaneously although no more than two will be present in significant concentrations at any one pH value. Table 2/ p.85a gives the relative concentrations (in moles per cent) of the four orthophosphate species over a range of pH values.

The pH value of the radioactive phosphate solutions was adjusted to the required value by the addition of either approximately 0.1 N hydrochloric acid or approximately 0. 1N sodium hydroxide as required. These reagents were prepared by dilution of "analar" grade hydrochloric acid (or sodium hydroxide) with deionised water, the reagents being prepared and stored in plastic containers to avoid the introduction of any other ions into the solutions. As the radioactive phosphate was obtained as sodium orthophosphate in hydrochloric acid at pH 2-3 it can be seen that the reagents used for the adjustment of the pH value do not introduce any further species into the radioactive phosphate solution.

The pH value of all solutions used in this work was measured with a Radiometer Type 23 pH meter (1). A separate set of electrodes was used for all measurements of the pH value of radioactive solutions, and a special set of beakers for standard buffer solution, distilled water rinse, sample

(1) Manufactured by the Radiometer Company, 72 Emdrupvej Copenhagen N.V.Denmark.

TABLE 2

The Proportion of Phosphate ions in Solution per 100 Mols. of Dissolved Phosphate.

(Calculated from Buehrer, 1932)

pH	3	4	5	5·5	6	7	8	9
Mols. of H_3PO_4	9	0·9	0.1	3×10^{-2}	8×10^{-3}	3×10^{-4}	4×10^{-6}	5×10^{-8}
Mols. of $H_2PO_4^-$	91	98·9	98	94	82	33	3	0·5
Mols. of HPO_4^{2-}	2×10^{-2}	0·2	2	6	18	67	97	99·5
Mols. of PO_4^{3-}	6×10^{-12}	7×10^{-10}	7×10^{-8}	6×10^{-7}	6×10^{-6}	2×10^{-4}	3×10^{-3}	4×10^{-2}

solution,etc., was kept solely for use with these electrodes. Also, for each pH value measurement, an aliquot was removed from the solution having its pH value adjusted, and,after measurement, this was discarded. Thus the possibility of radioactive or other contamination of the prepared solution was eliminated.

It was found to be satisfactory to use only 0.1N acid or alkali for the adjustment of pH values. The actual concentration of phosphate in the radioactive phosphate solution is extremely small, and with the volumes of solution usually used as stock solutions for the radioactive phosphate (of the order of 100 ml. or less) it was found that only a few drops of either acid or alkali were ever required over the range of pH values studied (3 to 9).

The adjustment of the pH value of the ions adsorbed onto the mica surface under study was a more difficult task than for the radioactive phosphate solution. In order to maintain the pH value that had been obtained throughout the course of an experiment it was necessary to carry out the desorption into a solution of the same pH value as that of the radioactive phosphate solution and the ions on the mica surface.

Unfortunately, it was realised that it would not be possible to use buffer solutions as desorbing solutions for the experiments being performed. Any solution that

contained any positive or negative ions that were different from those under study (i.e. aluminium,sodium,hydrogen, hydroxyl,phosphate or chloride) would lead to results, the interpretation of which would be open to question. This is because, during the time that the mica surface is in contact with the desorbing solution,while the background count rate for the system is determined before the commencement of the adsorption of radioactive phosphate, any other ions present would be capable of displacing the ions under study, and leading to effects relating to the adsorption and desorption of these other ions.

Any positive ions present might replace the ions adsorbed onto the mica surface, neutralizing the net negative charge thereon, to a greater or lesser extent. This would lead to the possible formation of some complex between the radioactive phosphate and the newly introduced positive ions. The desorption of the radioactive phosphate from a complex with these ions would be expected to be in some way characteristic of the actual ion. Thus, if the amount of such an ion present on the mica surface was not known, it would be extremely difficult, if not impossible, to correctly interpret the results obtained from the desorption experiments.

Any negative ions,other than phosphate,present could possibly be themselves adsorbed onto the mica surface in some way thus either completely blocking some sites from

radioactive phosphate adsorption or else at least causing the radioactive phosphate adsorption to take place at a considerably slower rate. This latter case would be expected if the competing anion was less strongly complexed with the mica surface than the radioactive phosphate ions would be. If this was so then the other ions would be displaced by the radioactive phosphate used in the experiment. However, the ease of this displacement would depend on the nature of the initially complexed ion. Unless it was known just how readily the replacement of the initially complexed ion by the radioactive phosphate could take place it would not be possible to form any conclusions from the amount of radioactive phosphate actually adsorbed onto the mica surface.

If the buffer solution used to obtain the required pH value in the desorbing solution contained any phosphate ions another difficulty would arise. These phosphate ions could be adsorbed onto the mica surface during the preliminary soaking of the mica surface while the background count rate for the experiment was being determined. Then, when the mica surface was soaked in the radioactive phosphate solution, all possible adsorption sites would have already been satisfied by the adsorption of inactive phosphate ions from the buffer solution. Thus the only phenomenon that would occur would be the exchange between inactive and radioactive phosphate on the mica surface. Therefore

the subsequent desorption experiment would only be observable in respect of that fraction of radioactive phosphate which had exchanged with inactive phosphate during the time that the mica surface was in contact with the radioactive phosphate solution. It would not be possible from such an experiment to conclude anything about the actual or relative amounts of the various [phosphate] - [mica surface] (or [phosphate] -[adsorbed cation on mica surface]) complexes, unless some data were obtained about the rate of exchange between the inactive and radioactive phosphate ions adsorbed onto the mica surface.

Another difficulty that the use of a buffer solution would have created is that almost, if not all, of the solutions regarded as buffer solutions contain at least one chelating agent. This would be expected to attach itself so strongly to any possible adsorption site as to be incapable of displacement by the radioactive phosphate solution when this came in contact with it. This would lead to the observation of either no radioactive phosphate adsorption at all, or else to the adsorption only onto the chelating agent itself. Consequently, in either case it would not be possible to obtain any data relating to the adsorption of radioactive phosphate onto the mica surface, which had been the object of the experiment.

Thus it can be seen that it is not possible to use

a buffer solution to obtain a desorbing solution of the required pH value. As a consequence of this, to obtain the required pH value for the desorbing solutions, solutions of the chloride of the cation under study were prepared where possible. This solution was then adjusted to the required pH value with approximately 0.1N hydrochloric acid or approximately 0.1N sodium hydroxide as required. For aluminium saturated mica surface experiments it was not possible to prepare solutions of aluminium chloride (or any other aluminium salt) with a pH value greater than about 4.5, owing to precipitation of aluminium hydroxide. Therefore, for experiments on aluminium saturated mica surfaces, solutions of distilled water were used, the required pH value for the experiment being obtained as above using hydrochloric acid or sodium hydroxide.

It was found that for pH values of 5.5 or less, the actual pH value of solutions prepared in the above manner remained constant for a number of days. The pH value of such slutions was checked at times during experiments, and from time to time fresh amounts of solution were used to replace the original solution without any significant change in the pH value being observed.

6.11 Problems of Experimentation at High pH Values

Some experiments were performed with an aluminium saturated mica surface at a pH value of 9.0. Solutions of distilled water plus a small amount of approximately 0.1N sodium hydroxide were prepared having a pH value of 9.0. However, after standing overnight, it was found that the pH value had dropped to approximately 6.0 due to the adsorption of carbon dioxide from the air. Thus it was apparent that, in order to maintain the pH value of the solution at 9.0 for the length of time required for an experiment (usually of the order of 100 hours), steps would have to be taken to exclude air from the experimental system, or alternatively perform the experiment in an atmosphere devoid of carbon dioxide.

As it seemed more practicable to exclude air altogether, apparatus was designed to enable this to be done. The easiest way to do this seemed to be to use a container that was sealed apart from the hole necessary for the geiger counter. Then, on introduction of the geiger counter to the system, there would be no remaining gaps for air to penetrate through. After some experimentation the final apparatus designed was as shown in Plate 3. This consists of a two litre flat-bottomed flask with a widened neck into which is inserted a rubber stopper containing a number of holes. A solid rubber stopper was taken, and a hole drilled in it that was only just wide

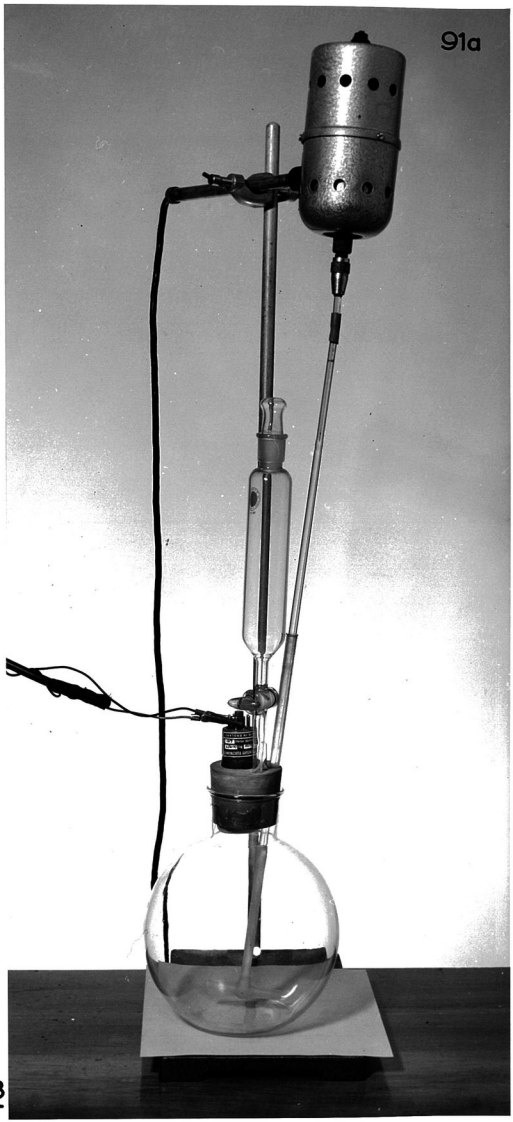


PLATE 3

enough to fit an end-window geiger counter at its narrower part (i.e. not including the greater diameter around the end-window).

A geiger counter was taken and in the usual way the edges around the end window and the sides of the geiger counter were coated with paraffin wax. After coating the sides of the end window geiger counter with paraffin wax it required considerable effort to insert it into the hole in the rubber stopper. When this had been done it was found that water did not leak between the sides of the geiger counter and the interior walls of the hole in the rubber stopper. Thus it would not be expected that much carbon dioxide would diffuse down between the sides of the geiger counter and the rubber stopper into the solution below. Any small amount of carbon dioxide that did so diffuse would not be enough to alter the pH value of the solution significantly. After the geiger counter had been inserted into the hole in the rubber stopper, the wax coating on it was checked, and,if it appeared to have been cracked in any way, a fresh layer of paraffin wax was coated over the waxed area still accessible.

As well as the large hole in the rubber stopper,through which the end-window geiger counter was inserted, three more smaller holes were bored through the rubber stopper,

around the side of the large hole. Through one of these holes a 100 ml. separating funnel with extended square-cut out let tube was inserted. This was arranged with the square-cut end fitting flush with the bottom of the rubber cork (i.e. the end at which the window of the end-window geiger counter was placed). The second of these holes was bored parallel to the sloping side of the rubber stopper as shown in figure 9 :

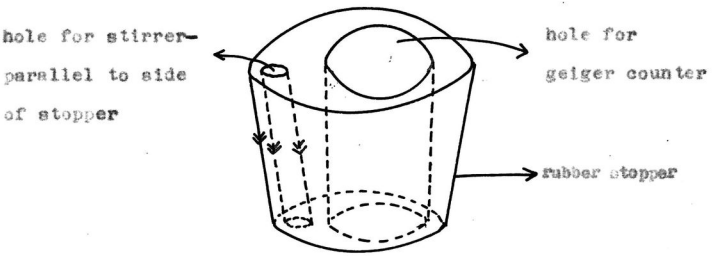


Figure 9

Into this hole a piece of glass tubing of external diameter equal to the internal diameter of the hole was inserted. This was placed so that it was flush with the bottom of the rubber stopper. The other end was made to protrude for approximately 10 cms. past the top of the rubber stopper. Through this glass tube a centrifugal stirrer was inserted. Because of the

angle of the hole in the rubber stopper, the bottom of this centrifugal stirrer was almost directly below the mica end window of the end-window geiger counter that was in the middle of the rubber stopper. The centrifugal stirrer was driven by a "Towers" brand overhead stirrer motor.

The centrifugal stirrer consisted of a glass rod onto one end of which was joined a piece of glass tubing. This tubing ended in a hollow "T" piece (see figure 10). At the upper end of the glass tube, just below where it was joined onto the glass rod, there was a hole with a lip which protruded to one side of it.

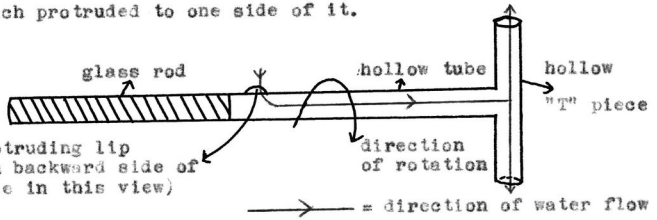


FIGURE 10

When the tube rotated in the direction indicated by the arrow water was caught by the hole (the protruding lip helping to force more water down the hole) and was sucked in at the top of the hollow section of the centrifugal stirrer, forced down the tube, and out both, rotating, ends of the "T" piece. The direction of water flow is indicated by the red arrowed, line.

It was necessary to use a centrifugal stirrer of this type, rather than an otherwise preferable magnetic stirrer and follower as was used in the rest of the desorption work in this thesis. (The magnetic stirrer would have the great advantage that it would eliminate the need for any direct connection with the outside of the otherwise totally enclosed apparatus). The reason for this is that the apparatus is totally enclosed and there is no air gap above the solution. As a result of this there would not be a vortex formed in the solution. Thus the liquid present would only be stirred in a horizontal plane, and there would be no mixing from top to bottom of the solution. This would be most unsatisfactory, as, when some of the radioactive phosphate began to be desorbed into the solution, it would not be removed to a great distance away from the end window, and thus the sensitive volume of the geiger counter. Thus some, at least, of the desorbed radioactive phosphate would still be counted by the geiger counter.

If this situation arose it would lead to erroneous results, as the actual loss of count rate would be less than the true loss of radioactive phosphate from the mica surface of the end window of the geiger counter. Also there would be the possibility that some of the

radioactive phosphate, if it stayed in close enough proximity to the mica surface for a sufficient length of time, could be readsorbed onto the mica surface. This would make the observed results even more difficult to interpret, as there would be more than one phenomenon being observed simultaneously (i.e. both desorption and readsorption).

A third small hole was also bored through the rubber stopper, smaller than the holes for either the stirrer or the separating funnel. This was to allow air to escape from the apparatus as it was filled with solution after the rubber stopper had been inserted into the neck of the two litre flask.

After the separating funnel, end-window geiger counter and glass tube to hold the centrifugal stirrer had been fitted to the rubber stopper, the bottom and sides of the stopper were coated with wax. This wax served a twofold purpose. Firstly it eliminated the possibility of any radioactive phosphate that might have come in contact with the rubber stopper being adsorbed thereon. This radioactive phosphate might have, subsequently, either directly increased the amount of radioactivity detected by the geiger counter, or, on being desorbed into the solution in the two litre flask, be sufficient to increase the background count rate due to the surroundings of the

geiger counter, and thus invalidate the data obtained.

Such a possibility existed because, once the geiger counter had been inserted in the rubber stopper, the background count rate was determined with the end window of the geiger counter, as well as the bottom of the rubber stopper, covered with solution in the two litre flask. The mica end window of the geiger counter was then placed in radioactive phosphate solution for a suitable time, and then, after rinsing in a portion of desorbing solution, the geiger counter and rubber stopper were reinserted in the neck of the two litre flask which was then completely filled with solution, and the desorption experiment performed. The geiger counter was not removed from the rubber stopper during the period of the immersion of its mica end window in the radioactive phosphate solution, and while endeavours were made to immerse only the very end of the geiger counter containing the mica end window into the radioactive phosphate solution, it was possible that the bottom of the rubber stopper came into contact with the radioactive phosphate solution at least for a short time during the insertion or removal of the mica end window from the solution.

A second reason for coating the rubber stopper with wax is that there could be impurities in the rubber which

could be desorbed on prolonged contact with the desorbing solution. These impurities could then possibly be readsorbed onto the mica window to some degree thus possibly affecting the results obtained. A wax coating would prevent the rubber of the stopper actually coming in contact with the desorbing solution. Such a coating would therefore eliminate the possibility of the desorbing solution (and possibly subsequently the mica surface of the geiger counter end window from its contact with this solution) being contaminated by any impurities that might be on the surface of the rubber stopper.

The whole apparatus for use at high pH values is shown assembled in Plate 3 p.91a . The two litre flask was filled to about one inch below the neck with the required solution. Then the rubber stopper, with the end-window geiger counter, separating funnel and centrifugal stirrer fitted, was inserted into the neck of the flask. The separating funnel was filled with more of the solution having the required pH value. This solution was then run into the two litre flask until the solution level was almost up to the bottom of the rubber stopper.

At this stage the centrifugal stirrer was spun rapidly by hand a number of times until all air bubbles trapped inside it were forced out the bottom of it

through the "T" piece. More of the solution in the separating funnel was then run into the two litre flask until it began to overflow through the air-escape hole. A visual examination was then conducted for bubbles remaining on the surface of the mica end-window of the geiger counter, or on the undersurface of the rubber stopper. If any bubbles were observed the whole apparatus was tilted slightly and rotated until they all vanished up the air escape hole. A little more solution was added until the air escape hole was again full. This hole was then tightly stoppered with a glass stopper. On opening the separating funnel stop cock once more the solution was made to rise up the gap between the centrifugal stirrer and the glass tube through which it was to rotate, to a height of about 5 cm. above the top of the rubber stopper. This was the only seal between the air and the solution inside the two litre flask. The total area of solution exposed to the air in this manner would be less than 0.05 $cm.^2$ and the air above this solution would not exchange with the rest of the atmosphere very readily, as it would be trapped between the stirrer shaft and the glass tube containing it, and could only diffuse in and out relatively slowly. Thus it can be seen that the amount of carbon dioxide adsorption by the solution through this seal would be very small, and would not be expected to affect the pH value of the solution significantly.

As a test of the ability of the apparatus to maintain a solution consisting only of distilled water plus a small amount of sodium hydroxide at a pH value of 9.0 for a lengthy period of time, a solution was prepared and the apparatus assembled as described above. The initial pH value of the solution used was 8.9 ($\pm$ 0.05), and after constant stirring for one week the pH value was found to have dropped only to 8.7 ($\pm$ 0.05). This was considered satisfactory for the experiments to be performed, as it was felt that, as long as the pH value was maintained at 9.0 $\pm$ 0.1 during the course of an experiment, there would be very little, if any, effect on the results obtained.

The solution, which had been freshly made up with the pH value adjusted to 9.0, which was placed in the separating funnel was usually more than was required to fill up the two litre flask as described above. After the background count rate had been determined, the rubber stopper was removed from the flask and the mica end-window of the geiger counter soaked in the radioactive phosphate solution for a suitable period of time. Before replacing the rubber stopper in the neck of the two-litre flask some of the solution was emptied out, and then the filling procedure repeated once more. The solution remaining in the separating funnel from the time the background count rate measurement was commenced until the time the actual desorption experiment

commenced was not found to exhibit any change in pH value during this period of time. It was left exposed to the air in the separating funnel, but the insertion of a ground glass stopper into the top of the separating funnel acted as a barrier to the air outside. After the actual desorption experiment had commenced any surplus solution remaining in the separating funnel was removed with a pipette and discarded. If the solution in the two litre flask was replaced with a fresh amount during the course of an experiment (for example to check that there was no contribution to the observed count rate from desorbed radioactive phosphate in the solution) the separating funnel was refilled with freshly made up solution.

For the start of the actual desorption experiments in the totally enclosed apparatus, zero time was taken as the moment when the desorbing solution first completely covered the mica surface of the end window of the geiger counter. At this time exactly the strip chart in the recorder was marked at zero hours, and then the remainder of the air space inside the apparatus eliminated in the previously described manner as quickly as possible.

It was found that considerable care was needed in placing the two litre flask so that the centrifugal stirrer rotated evenly in the centre of the glass tube through which it passed when it was connected to the

overhead stirrer motor. If the lining up of the stirrer motor, stirrer and glass tube containing the stirrer was not almost perfect it was not possible to cause the centrifugal stirrer to rotate. It was often found that considerable manipulation was required before a satisfactory stirring speed could be obtained.

6.12 Control of the pH Value of the Species on the Mica Surfaces

As well as the radioactive phosphate solution and the desorbing solution it was necessary to adjust positive ions adsorbed onto the mica surface under study to the pH value at which it was desired to perform the desorption experiment. It seems unlikely that this would be quite as important for monovalent cations such as sodium as it would be for multivalent cations such as aluminium. In the case of sodium ions for instance, there is only one positive charge per cation, and this will be fully neutralized by the residual negative charge on the mica surface . Thus it would not be expected that a change in the pH value of the environmental solution would have much effect on the nature of the sodium ions considered as adsorption sites for phosphate ions.

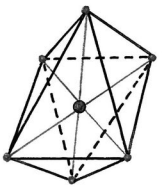
In the work that has been undertaken for this thesis, adsorption sites for phosphate related to the edges of the mica sheets have not been considered for study. In fact, steps have been taken to eliminate, or at least to minimise, the amount of the edges of the mica sheets positioned where adsorption could occur. While it would be expected that differences in pH values would have a profound effect on any sites such as these edge sites, which would probably be due to broken bonds, and so

capable of existing as either positive or negative sites according to the pH value (for an account of this type of behaviour see for example Fieldes and Schofield(1960)), it does not seem probable that there would be very much effect on adsorption sites related to the actual face of the mica sheets. Thus it does not seem very likely that, in the case of sodium (or other monovalent cation) saturated mica surfaces, the pH value of the solution in contact with the mica surface would be very important.

When the case of a multivalent cation, such as aluminium, neutralizing the net negative charge on the mica surface is considered however, a different picture presents itself. If only one positive charge per cation is used in the neutralization of the net negative charge on the mica surface, then there will be one or more (two if aluminium is the cation considered) positive charges remaining unneutralized by the mica surface. Depending on the pH value of the solution, these might be expected to exist either as positive charges or, if the pH value was sufficiently high, to have hydroxyl groups attached to them. If there were other negative ions present in the surrounding solution then these ions could also possibly be attached to the remaining positive charges on the cation.

6.121 The Effect of Changes in pH value on the Nature of Aluminium Ions

The multivalent cation on which most work has been done in the present thesis is aluminium, and the effect of changes in the pH value on this cation will now be considered. In solution, at sufficiently low pH values the aluminium is present as the hydrated ion $(Al(H_2O)_6)^{3+}$ the water molecules being present in octahedral coordination around the central aluminium atom:

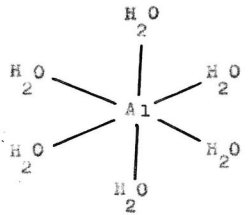


• = H_2O molecule

● = Al atom

—— = Al - H_2O bond

which will be represented by:



As the pH value is increased a gradual change takes place through a number of steps until eventually a precipitate of aluminium hydroxide $Al(OH)_3$ is formed. The precise nature of these changes does not seem to have been established with finality. Most of the available literature data

seems to favour the first step as being one of two processes:

either $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$

which may be written more simply (leaving out the water molecules associated with the aluminium)

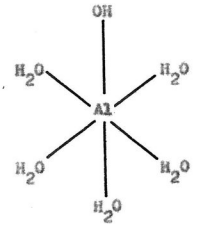
$$Al^{3+} + H_2O \rightleftharpoons [AlOH]^{2+} + H^+ \quad \ldots\ldots\ldots(1)$$

or $2Al(H_2O)_6^{3+} + 2H_2O \rightleftharpoons [Al(H_2O)_4OH]_2^{4+} + 2H^+ + 4H_2O$

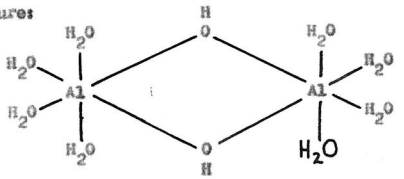
which may be written as

$$2Al^{3+} + 2H_2O \rightleftharpoons [AlOH]_2^{4+} + 2H^+ \quad \ldots\ldots\ldots(2)$$

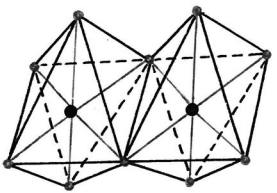
The structure of the aluminium complex formed by (1) may be represented as



while the aluminium complex dimer in (2) has the structure:



the aluminium coordinate octahedra being linked along one edge as shown below, the two hydroxyl groups each sharing their single negative charge between the two aluminium atoms.



• = O H group

• = H_2O molecule

● = Al atom

—— = Al——H_2O bond

—— = Al——(OH) bond

The first process postulated for the first hydrolysis step (1) is the simpler of the two and would be the first of a number of similar steps if there was no tendency for condensation of the complex ions formed. These steps would be:

$$Al^{3+} + H_2O \rightleftharpoons (AlOH)^{2+} + H^+ \ldots\ldots\ldots\ldots (1)$$

$$(AlOH)^{2+} + H_2O \rightleftharpoons \left[Al(OH)_2\right]^+ + H^+ \ldots\ldots\ldots (3)$$

$$\left[Al(OH)_2\right]^+ + H_2O \rightleftharpoons Al(OH)_3 + H^+ \ldots\ldots\ldots (4)$$

$$Al(OH)_3 + H_2O \rightleftharpoons \left[Al(OH)_4\right]^- + H^+ \ldots\ldots\ldots (5)$$

There seems to be no mention anywhere in the literature of the existence of step No. (4). Although no references to its formation by equation (3) were found, the existence of the species $\left[Al(OH)_2\right]^+$ has been postulated by Treadwell and Lien (1931), Treadwell and Zürcher (1932) and by Lepin and Vaivade (1953). The existence of this species is, however, refuted by Küntzel, Riess and

Königfeld (1935) and also by Souchay (1948).

Steps (5) which is perhaps better written as:

$$Al(OH)_3 + OH^- \rightleftharpoons \left[Al(OH)_4\right]^-$$

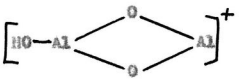
is the dissolution of solid aluminium hydroxide to form the aluminate ion. This step is fairly well established and has an equilibrium constant for the above equation

$$K = \frac{\left[Al(OH)_4^-\right]}{\left[Al(OH)_3\right]\left[OH^-\right]} \simeq 10^2$$

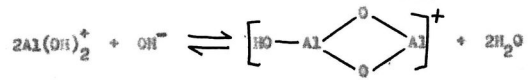
the actual values quoted ranging (at 25°C) from $10^{1.54}$ by Heyrovsky (1920) to $10^{2.78}$ by Fricke and Meyring (1933).

The phenomena occurring during the initial stages of hydrolysis have been investigated by a number of workers. Treadwell and Zürcher (1932) prepared basic soluble chloride of aluminium by dissolving aluminium in insufficient hydrochloric acid. They also showed that it was possible to prepare these basic soluble chlorides by dissolving aluminium in 1N aluminium chloride solution. Solutions with the same properties result from dissolving freshly precipitated aluminium hydroxide ($Al(OH)_3$) in either insufficient hydrochloric acid or insufficient aluminium chloride solution. However these last two methods of preparation tended to give cloudy solutions and so were not recommended. Titrations of the prepared basic

chlorides with alkali were performed electromerically using a platinum electrode with a 0.1N calomel electrode as reference electrode. Working with carbon dioxide free alkali, and in an inert atmosphere, they obtained results that they interpreted as giving evidence for the existence of the species $Al(OH)_2^+$, $Al_2(OH)_5^+$ and the complex:

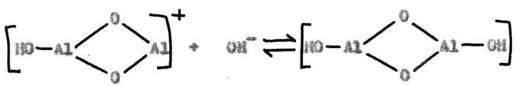


formed by the elimination of water thus:



although the above equation is almost certainly only the end result of a number of steps.

This complex is interesting because of the apparent presence of an oxygen bridge between two aluminium atoms. Treadwell and Zürcher also found that on addition of more alkali the above complex is converted to a hydrated oxide:



which they say is four times more soluble in alkali than the usual $Al(OH)_3$.

The two successively formed complex ions $Al(OH)_2^+$ and $Al_2(OH)_5^+$ are also described as being prepared

in a similar fashion in the earlier paper of Treadwell and Lien (1931).

Küntzel, Riess and Königfeld (1935) believed that the process of hydrolysis is more complex than did Treadwell and Zürcher. They suggest the existence of two processes (a) Primary hydrolysis with consequent formation of a basic salt; and (b) Polymerization of the basic salt to give a new form that is resistant to acids. This hypothesis would help to explain why the titration of aluminium salts with alkali is so difficult if not impossible to reverse once any precipitate, supposedly of aluminium hydroxide is formed. This precipitate is very readily formed, even at low pH values (less than 5) and no amount of agitation of the solution seems to completely redissolve it.

These conclusions, as to the formation and polymerisation of a basic salt of aluminium, are in agreement with similar conclusions reached by Bjerrum (1910) as a result of his work with chromium salts.

Souchay (1948) found, by cryoscopic measurements on eutectic potassium nitrate/ice mixtures, definite evidence for the existence of the species $(AlOH)_2^{4+}$. He said that there must be a continual aggregation of the species from x=1 to x= 2.2 (x = number of moles OH^- ions per mole

aluminium salt) at which point precipitation was observed to occur on allowing the solutions to stand for some time. This theory is slightly different from that of Jander and Winkel (1931) who believed that condensation occurred progressively from x=0 onwards.

It has been postulated by Faucherre (1948), (1954) that the hydrolysis of aluminium nitrate proceeds by two distinct processes. Which of these processes is predominant depends upon the concentration of the aluminium ions. Three concentration ranges are considered.

(1) For an aluminium ion concentration of greater than 1×10^{-2} moles per litre. The predominant reaction here is:

$$2Al^{3+} + 2H_2O \rightleftharpoons (AlOH)_2^{4+} + 2H^+$$

and the hydrolysis constant K_1 is given by

$$K_1 = \frac{\left[(AlOH)_2^{4+}\right]\left[H^+\right]^2}{\left[Al^{3+}\right]^2}$$

(2) For an aluminium ion concentration of less than 5×10^{-3} moles per litre. The predominant species produced in this concentration range is the monomer $(Al\ OH)^{2+}$:

$$Al^{3+} + H_2O \rightleftharpoons (AlOH)^{2+} + H^+$$

with the hydrolysis constant K_2 for this reaction being

$$K_2 = \frac{\left[(AlOH)^{2+}\right]\left[H^+\right]}{\left[Al^{3+}\right]}$$

(3) In the concentration range (for aluminium ions)

between 5×10^{-3} moles per litre and 1×10^{-2} moles per litre the two ions $(Al\ OH)^{2+}$ and $(Al\ OH)_2^{4+}$ coexist in equivalent proportions.

The hydrogen ion concentration $[H^+]$ is given by the equation:

$$[H^+] = 2K_1 \frac{c^2}{[H^+]^2} + K_2 \frac{c}{[H^+]}$$ where c = concentration of aluminium ions

From this equation it is possible to calculate K_1 and K_2. The values quoted by Faucherre are:

$K_1 = 5.82 \times 10^{-9}$ for ionic strength $\simeq 0.60$

$K_1 = 8.72 \times 10^{-9}$ for ionic strength $\simeq 0.12$

and

$K_2 = 1.07 \times 10^{-6}$ for ionic strength $\simeq 0.60$

$K_2 = 1.83 \times 10^{-6}$ for ionic strength $\simeq 0.12$

The actual results obtained by Faucherre did not completely agree with the theory expressed above, and he assumed that this was because of the presence of small amounts of higher species even at an early stage in the titrations.

Evidence for the formation of condensed complex ions in more concentrated solutions is also available for other ions than aluminium. An example of this is the work of Geloso and Faucherre (1948) on the hydrolysis of lead nitrate. They found that at concentrations of lead (plumbous) nitrate greater than 1×10^{-2} moles per litre the predominant species was $(Pb\ OH)_4^{4+}$

while at concentrations less than 5×10^{-3} moles per litre predominantly $(Pb\ OH)^{+}$ was formed. At intermediate concentrations a mixture of the two species was obtained.

More recently, a detailed study of possible mechanisms for the hydrolysis of the aluminium ion in dilute aqueous solutions has been performed by Brink and Peech (1963 a). They studied the hydrolysis of aluminium chloride solutions in the concentration range 10^{-2} to 10^{-5} moles per litre. After consideration of a number of postulated reaction mechanisms they came to the conclusion that the most probable was the simple formation of the uncondensed complex $(Al\ OH)^{2+}$ i.e.

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5OH^{2+} + H_3O^{+}$$

Because the hydrolysis constant was found to be too high on dilution the explanation was offered that some aluminium hydroxide had been precipitated. This aluminium hydroxide was presumably present by the more extensive hydrolysis of a small portion of the aluminium ions present. The hypothesis used was that the solution was supersaturated with aluminium hydroxide and on dilution some of this was precipitated out thus upsetting the equilibrium and causing an increase in the hydrogenion concentration and thus in the hydrolysis constant.

Further work has been carried out by the same authors

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(Frink and Peech, 1963 b) on the hydrolysis of the aluminium ion in hectorite and montmorillonite suspensions. They believed that initial hydrolysis proceeded as they described above, and, from solutions of aluminium in sodium chloride, they have calculated a value for the hydrolysis constant of $10^{-4.9}$. On soil materials aluminium is present as Al^{3+} ions. Some other aluminium is retained as aluminium hydroxide and does not lower the exchange capacity of the soil. The amount of hydrolysis of aluminium was stated to be lower on the clay surface than when the aluminium was present in solution, according to the calculations made.

The presence of a number of other species of aluminium complex ions has been reported by various workers. Some of these for which evidence has been brought forward are:

$Al_2(OH)_{10}^{4-}$, $Al_2(OH)_8O_2^{6-}$,

$Al_n(OH)_{3n+1}^{-}$, $Al_4(OH)_8^{4+}$,

$Al_6(OH)_{15}^{3+}$, $Al_3(OH)_8^{+}$,

$Al_{13}(OH)_{32}^{7+}$

and many others. A number of these are referred to in the publication of Bjerrum, Schwarzenbach and Sillen (1958) pp. 20-21.

The immediately preceding discussion has been on the effect of changes in the pH value of the solution on aluminium ions therein. However, in this thesis, studies have been made on the adsorption of radioactive phosphate ions onto the surfaces of mica sheets saturated with aluminium ions. Thus, the aluminium ions that have been involved in the work that has been carried out have not been in the same environment as they would have been in an aluminium salt solution.

These ions, that are adsorbed onto the surface of a mica sheet, neutralize the net negative charges residual on the mica surface. These negative charges occur approximately once every 50 sq. Å on the surface of the mica sheet. This means that, if aluminium ions are adsorbed onto the surface of the mica sheet to neutralize the negative charges thereon, the individual aluminium atoms would be approximately 7 Å away from each other. As a result of this distance of separation it seems very unlikely that any polynuclear complexes of aluminium will be formed on the mica surface due to hydrolysis of the aluminium ions with increase in the pH value of the environmental solution. Thus the only likely changes, on change in the pH value, will be in the presence and number of the free charges remaining on each aluminium atom over and above that required for neutralization of the net negative

charge on the mica surface. The various possible configurations that might be expected at various pH values have been discussed elsewhere in this thesis (p 122).

The actual method of bringing the mica surface, with its adsorbed cations, to the required pH value for the desorption experiment to be undertaken varied with the different adsorbed cations. When a monovalent cation was being studied it was possible to ensure the presence of this cation in all solutions in which the mica surface was placed. When sodium saturated mica surfaces were being studied they were prepared by soaking the mica surface in repeated amounts of 1N sodium chloride solution. The mica surface was then placed in contact with a 0.2N solution of sodium chloride. This solution was at the desired pH value for the experiment, adjustment of the original pH value to the desired pH value being accomplished with 0.1N hydrochloric acid or 0.1N sodium hydroxide as required. The soaking of the mica surface in the solution of the required pH value was carried out at least six times with fresh amounts of solution, each soaking being of at least 30 minutes duration. It was considered that by this time all alterable species would be in the form they normally assumed at the pH value under study.

The use of multivalent cations, such as aluminium, as the adsorbed cations on the mica surfaces presents more

difficulties however. It is not possible to prepare, experimentally, solutions containing aluminium ions with a pH value greater than about 4.5. When a solution of an aluminium salt (such as the chloride, nitrate or sulphate) in water has its pH value determined this is found to be approximately pH 3 to pH 3.5 for a concentration of salt of the order of 0.1 moles per litre. This is due to the hydrolysis of the salt of a weak base (aluminium hydroxide) with a strong acid (hydrochloric, nitric acid, etc.) in aqueous solution. Addition of small amounts of alkali (e.g. sodium hydroxide) to the aluminium salt solution raises the pH value of the solution slightly, but above a pH value of about 4.0 - 4.5 precipitation of aluminium hydroxide occurs. It is believed that the reason for this is that addition of the alkali, even in small amounts, causes the pH value to rise very sharply at the point of first contact of the two solutions (added alkali and aluminium salt solution). This leads to the precipitation of aluminium hydroxide at this point. Unfortunately, contrary to the situation in most titrations, the aluminium hydroxide does not redissolve on shaking of the solution mixture. It seems that, although definite values are quoted in the literature for the solubility product of aluminium hydroxide (values given at 20°C range between

$10^{-29.92}$ according to Korenman, Frum and Kudinova (1953) and $10^{-32.90}$ according to Szabó, Csányi and Kávai (1955) addition of alkali to a solution of aluminium ions gives a precipitate that is not soluble even over a long period of time. The most likely explanation of this phenomenon is that the precipitate formed has colloidal properties and has not properly crystallized out.

As a consequence of the impossibility of preparing aluminium solutions with suitably high pH values for a great proportion of the work that it was desired to undertake, it was necessary to adjust the pH value of the aluminium ions adsorbed onto the mica surface in some other way. The mica surface was repeatedly (at least four times, for not less than 30 minutes each time) soaked in 0.5N solution of a suitable aluminium salt. Distilled water was taken and, by the addition of either 0.1N hydrochloric acid or 0.1N Sodium hydroxide, its pH value was adjusted to that at which it was desired to perform the subsequent desorption experiment from the aluminium saturated mica surface. The mica surface, which had been saturated with aluminium ions by the above procedure, was then soaked in this solution of distilled water with the desired pH value at least six times for 30 minutes or more each time. The aluminium ions present on the

mica surface to neutralize the excess negative charge thereon will have the two remaining positive charges not associated with the mica surface either free, or associated with some anion, probably hydroxide. The only change in the state of the aluminium that would be expected with a change in the pH value of its surrounding solution would be in the species, if any, that were associated with the two remaining unneutralized , positive charges. It has already been shown previously (p. 117) that it would not be expected that there would be any interaction between adjacent aluminium atoms on the mica surface. It is considered that the amount of soaking in solutions of the required pH value that was given each aluminium saturated mica surface would be enough to bring about the equilibrium situation, of the aluminium ions present, at that required pH value.

Although it would have been possible to use solutions of aluminium salts at the pH value of the subsequent desorption experiment where the required pH value was 4 or less, it was decided to do all experiments on aluminium saturated mica surfaces using the procedure as described above.

An experiment conducted with all species brought to a pH value of 3.0 was performed in which the pH value of the aluminium saturated mica surface was adjusted with

0.1M aluminium nitrate solutions. This experiment produced the same results as did experiments performed at a pH value of 3.0 with the pH value of the aluminium saturated mica surface controlled by the use of distilled water (containing hydrochloric acid) in the manner described above. Thus it appears that, at least at pH values of 4.0 or less, it makes no difference whether the aluminium saturated mica surface is soaked in solutions containing aluminium ions or not when the pH value is being adjusted.

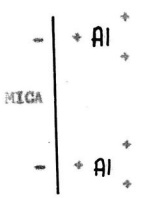
6.2 Adsorption of Radioactive Phosphate onto Cation Saturated Mica Surfaces

The preliminary experiments that had been carried out on the desorption of radioactive phosphate from aluminium saturated and from sodium saturated mica surfaces were repeated with all the relevant solutions, and the mica surfaces, controlled to the same pH value. The results obtained were similar to those obtained previously, that is, there appeared to be more radioactive phosphate adsorbed by the aluminium saturated mica surface of a geiger counter end-window than by a similar but sodium saturated mica surface. Desorption experiments from both systems indicated the existence of three different complexes as characterised by different desorption rates from the cation saturated mica surface. From the differences in the total amounts of radioactive phosphate adsorbed by the mica surface when it was saturated with different cations (aluminium and sodium) it appeared that the nature of the cation must play some part in some at least of the different complexes formed.

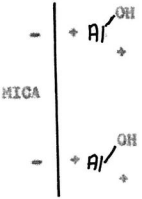
The cations adsorbed on to the surfaces of mica particles neutralize the net negative charge present due to isomorphous replacement within the mica structure. As these negative charges effectively occur approximately once every 50 sq.Å

there will be about 7 Å between negative charges. Thus any adsorbed positive monatomic species will netralize only one negative charge on the mica surface.

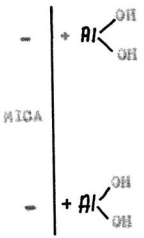
When the mica surface is saturated with sodium ions there will not be any excess positive charge, as each sodium ion will be completely neutralized by one of the residual negative charges on the mica surface. In the case where the mica surface is saturated with aluminium ions however, the negative charge on the mica surface will only neutralize one of the positive charges on the aluminium ions, which are trivalent. This means that the aluminium ions will have two positive charges remaining. Depending on the pH value of the solution in which the aluminium saturated mica surface is placed, each aluminium ion may be associated with 0, 1 or 2 hydroxyl groups, such that the total of hydroxyl groups plus positive charges equals two (as the third charge on each aluminium is associated with the mica surface). The three possibilities may be represented diagrammatically as:



(1)



(2)



(3)

If the above possibilities are correct it would be expected that at suitable intermediate pH values (and even possibly at all pH values studied) there might be a mixture of some, or all, of (1), (2) and (3) above on the same mica sheet.

If other negative ions were present in the experimental system being studied it would be possible for some of these ions to be preferentially associated with some of the positive charges of the aluminium that remain unneutralized by the mica surface. However the amount of such negative ions was minimised as much as possible, and those present were mostly the monovalent anions chloride and nitrate which are not regarded as readily forming

complexes with aluminium ions in dilute solutions. Thus it seems unlikely that any such aluminium - anion (other than hydroxyl or phosphate) complexes would form a significant part of the experimental system being investigated.

From the above discussion it would be expected that there would be little or no phosphate associated with the sodium ions of sodium saturated mica surfaces. While it was possible that there could be some association between the phosphate group and the sodium ions adsorbed onto the mica surface, such an association would not be expected to be very strong. The sodium ions, having their only positive charge neutralized by the negative charges on the mica surface, would not have any particular attraction for the negatively charged phosphate groups. Thus any bond between the phosphate group and the sodium ions which were bound onto the mica surface would be expected to be considerably weaker than the bonds formed between phosphate groups and aluminium ions which still possessed a residual positive charge not neutralized by the mica surface.

Providing there was not a large activation energy factor to be considered for the desorption of radioactive phosphate groups associated with the sodium ions it would be expected that the rate of desorption of any phosphate associated with the sodium ions present on the mica surface

would be considerably faster than any other rates of desorption of the other complexes formed between phosphate groups and aluminium ions. As there was no evidence for any such faster desorption process it would not seem that there could be any phosphate associated with the sodium ions that were neutralizing the excess negative charge on the mica surface.

However, from the results obtained, the absence of a phosphate - sodium complex did not seem to be supported, there appearing to be three types of phosphate adsorption site on both the sodium saturated and aluminium saturated mica surfaces. If there was actually no phosphate associated with the sodium ions on the mica surface then all three types of adsorption complex would have to be associated with the mica surface. The three types of adsorption complex found with aluminium saturated mica surfaces were found to have similar rate constants for desorption as were the three complexes with phosphate associated with sodium saturated mica surfaces. Thus it seemed reasonable to assume that the three desorption complexes are of a similar nature in both sets of experiments. If this was the case, then the conclusion would be that if there was no phosphate associated with the sodium ions on sodium saturated mica surfaces, then similarly there would be no phosphate

associated with the aluminium ions present neutralizing the net negative charge on mica surfaces.

The possibility of there being different adsorption processes with the same rate constants in the two types of mica surface -cation system being studied seemed remote. If there was, for instance, one process associated with the aluminium ions present that had the same rate constant for desorption of phosphate as did one of the desorption processes from the mica surface itself, then the amount of this phosphate - substance (i.e. mica surface plus aluminium ions) complex as characterised by the particular rate constant would be considerably higher, relative to the other types of complex than when observed in experiments with sodium mica. This phenomenon was not observed in the initial experiments, and so other explanations were considered for the similarity in appearance of the results from the experiments on sodium and aluminium saturated mica surfaces.

From the general knowledge of the role of aluminium in soil- phosphate systems (see introduction p. 16) it would be expected that aluminium would form very readily one or more complexes of some type with phosphate ions adsorbed onto the surface of mica. Thus it seemed that the explanation of the similarity of the initial series of experiments was very unlikely to be that there was no

phosphate associated with the aluminium ions which were bound to the mica surface and neutralizing the excess charge thereon.

The only other reasonable explanation for the initial results that readily suggested itself was that for some reason the mica surface was not saturated with sodium ions, but that there were still some aluminium ions remaining on the mica surface and neutralizing the net negative charge thereon. As it had been observed that the total amount of radioactive phosphate adsorbed by the aluminium saturated mica surface was greater than that adsorbed by what was believed to be a sodium saturated mica surface, it would seem that only some of the aluminium ions had been replaced with sodium ions. If there was no phosphate associated with the sodium ions present on the mica surface then it would be expected that the total amount of radioactive phosphate adsorbed onto the mica surface would be reduced relative to the amount adsorbed when the surface was completely saturated with aluminium ions.

6.21 Preparation of Aluminium Free Sodium Saturated Mica Surfaces

As the immediately preceding hypothesis seemed the most reasonable explanation of the initial results obtained, further experiments were designed to test it. The difficulty that had to be overcome was the ensuring of the removal of all the aluminium ions present on the mica surface being studied and their replacement with sodium ions. The most likely method for success in this undertaking appeared to lie in the use of ion exchange resins. It would be expected that either the sodium form or the hydrogen form of cation exchange resins would be equally effective in the removal of aluminium, or other multivalent ions, from the surface of a mica sheet.

The sodium form of a cation exchange resin (sodium resin) would replace these ions directly with sodium ions. The hydrogen resin would replace any ions present with hydrogen ions, and these could in turn be replaced readily with sodium ions by soaking the mica surface in concentrated sodium chloride solution.

The use of sodium resins would have the advantage that the ions on the mica surface have sodium ions substituted for them in one step thus lessening the possibility of any outside contamination of the mica surface after the removal of all unrequired ions. If hydrogen resin

was used to remove all other cations from the mica surface, it was then possible to saturate the surface with any desired cation such as sodium readily. Thus it was not necessary, by using this resin, to prepare a large number of different cation forms of ion exchange resins to study a series of different cations adsorbed onto mica surfaces.

It is possible to remove the positive ions, present neutralizing the negative charge on the surface, from layer structure clay minerals that have a residual negative charge on the surface of the layers due to isomorphous replacement, by the use of the hydrogen form of cation exchange resins. In this way all other positive ions are replaced by hydrogen ions. These hydrogen ions may be replaced by any other ion by taking the freshly treated clay mineral and bringing it into contact with concentrated solutions of the required ion. (The method of treatment of the clay mineral montmorillonite in this manner is described by Purkert, 1962).

When the hydrogen forms of clay minerals are prepared in the above manner it is necessary to treat them immediately with other cations. The hydrogen form is not stable, and if, after preparation, the

clay mineral is left to stand, breakdown of the clay mineral begins to occur. Aluminium ions are liberated by this breakdown, and replace the hydrogen ions present neutralizing the residual negative charge on the clay mineral surfaces. Breakdown of the clay mineral only occurs until sufficient aluminium ions have been liberated to replace the hydrogen ions present. The rate of this breakdown decreases with increasing removal of hydrogen ions and their replacement by aluminium ions, and after 50% of the hydrogen ions have been replaced the rate of clay mineral breakdown is extremely slow.

This breakdown of the clay minerals and their subsequent release of aluminium ions occurs at the edges of individual surface layers. In the work undertaken for this thesis mica was the clay mineral used. As it was desired to study adsorption and desorption phenomena related only to the surface of the mica, the edges of the sheets were, as far as possible, eliminated from the experimental system by coating them with wax. Therefore, if the mica surfaces being studied were to be saturated with hydrogen ions it would seem unlikely that breakdown of the mica could occur with time. This would mean that the hydrogen saturated mica surface would be reasonably stable with time. An eventual partial

breakdown of the structure would occur at those few edges that it is assumed would be present across the area of surface under study (approximately 6 sq.cm.) but these would not be a very large amount of breakdown over a reasonable period of time (e.g. two to three weeks).

The hydrogen resins and sodium resins used in the treatment of the mica surface have been described earlier (p. 47).

In an endeavour to prepare a mica surface that was almost entirely free from aluminium (or other multivalent) ions a number of procedures were investigated. Success was believed to have obtained when almost all radioactive phosphate adsorbed was found to desorb with only the one rate constant. (It was not found that it was possible to completely eliminate other desorption rates. However these made a very small contribution to the total activity. cf. Graph of desorption experiment p. 285) It was believed that this rate constant was related to radioactive phosphate adsorbed onto the mica surface itself, and so found to be present regardless of which cation was adsorbed onto the mica surface.

The experiments concerning preparation of aluminium free sodium saturated mica surfaces were carried out on the mica end-windows of end-window geiger counters.

A new geiger counter was obtained for the first

attempt to prepare an aluminium free sodium saturated mica surface. After being prepared and coated with paraffin wax in the usual way (cf. p. 38) the mica surface was placed in two litres of distilled water containing hydrogen saturated ion exchange resin. A polythene contained was used for this solution, which was stirred continuously, by means of a magnetic stirrer and a polythene and paraffin wax coated follower, for a period of three days. After this time the mica surface was taken and soaked in a solution of 0.5 *N* sodium chloride, which was contained in a polythene beaker. This soaking was repeated four times, and lasted for at least 30 minutes each time.

The geiger counter mica end-window was then placed in two litres of decinormal sodium chloride in a polythene container. This sodium chloride solution had been prepared by dissolving "analar" sodium chloride in deionised water, prepared by passing distilled water through a column 30 cm. high and 3 cm. in diameter which was filled with the mixed cation and anion exchange resin "Biodemineralit" All deionised water prepared in this manner was stored exclusively in polythene containers.

After the geiger counter mica end-window had remained in the sodium chloride solution for some time, during which time the background count rate of the geiger counter

with its end-window immersed in the solution was determined, it was removed. The mica end-window was then placed in a solution containing radioactive phosphate for a suitable time (in this experiment ten minutes) and then replaced in the polythene container full of sodium chloride solution. The loss in the radioactivity from the mica end-window was then followed as a function of time on the strip chart recorder in the usual manner.

Upon graphical analysis of the results it was found that there still appeared to be three desorption processes whose rate constants were comparable to those obtained with an aluminium saturated mica surface as the adsorber surface for the radioactive phosphate. Thus it was concluded that aluminium ions had not been removed from the mica surface of the geiger counter end-window, or at least not completely. It was not possible to ascertain what percentage of radioactive phosphate had been adsorbed by the mica surface in this experiment, relative to the amount that would have been adsorbed by a completely aluminium saturated mica surface. This would have required the adsorption of the same radioactive phosphate solution onto the same mica end-window which had been completely saturated with aluminium ions, and this experiment was not carried out.

The mica end-window of a geiger counter that had

been used for a previous experiment was taken and soaked for some hours in a solution containing 1 gm. of sodium dithionite ($Na_2S_2O_4$) in 50 ml. of 0.3 M Sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) solution. This solution was used in an endeavour to remove all ions from the mica surface. In the stepwise procedure for the removal of phosphate from soild described by Chang and Jackson (1957) it is stated that the use of the sodium dithionite/sodium citrate reagent removes all iron bound and reductant soluble phosphate. The mica end-window of the geiger counter was then placed in a polythene beaker containing a stirred "Biodemineralit" - water mixture for 12 hours. It was expected that this would remove any excess ions whether positive or negative from the mica surface. After this treatment the mica surface of the geiger counter end-window was soaked in 1.0N sodium chloride solution five times for at least 30 minutes each time.

The sodium chloride solution was prepared by dissolving the required weight of "analar" sodium chloride in two litres of deionised water in a polythene container. A suitable amount (10-20 grams) of hydrogen form ion exchange resin was added and the solution stirred continuously for 24 hours. The hydrogen resin was used in order to remove any traces of other positive ions that might be present in the sodium chloride solution. These

might be due either to impurities in the sodium chloride used or else be traces introduced in the chemical manipulations , e.g. weighing and use of metal spatula.

The hydrogen resin would also remove some of the sodium ions from the solution and replace them with hydrogen ions. This had the effect of lowering the pH value of the solution to between 2 and 3. However when the experiments were performed at a constant pH value, the pH of the finally used sodium chloride solutions was adjusted to the required value by the use of either 0.1N hydrochloric acid or 0.1N sodium hydroxide ,both of which reagents were prepared by dissolving the "analar" compound in deionised water and storing in polythene bottles. Thus the lowered pH value of the 1N sodium chloride solution would not lead to the subsequent introduction of any ions likely to cause any interference with the experiments. The actual amount of sodium ions replaced by hydrogen ions would not have been very great. As the strength of the sodium chloride solution was not a critical factor in the experiment, the slight lowering of this strength (with respect to the sodium ions) would not affect the results obtained.

After soaking in the sodium chloride solution, the mica surface of the geiger counter end-window was placed

in two litres of deionised water in a polythene container. The deionised water had had its pH value adjusted to 5.5 by means of the solutions described above. After a suitable length of time, the background count rate of the geiger counter having been determined, the mica surface was removed and soaked in a radioactive phosphate solution for 30 minutes, and then replaced in the polythene container as before. The desorption experiment was then followed and the data obtained analysed in the usual manner.

Analysis of the results obtained from this experiment showed that there were still three different, simultaneously occurring, desorption rates of radioactive phosphate from the mica end-window of the geiger counter. This seemed to suggest that aluminium, or some other cation which was capable of forming some type of adsorption complex with phosphate, was still present on the mica surface of the geiger counter end-window.

At the conclusion of this last experiment the same geiger counter was taken and soaked in 0.5N aluminium nitrate solution fourtimes for at least 30 minutes each time. In this way all the adsorbed cations would be expected to be replaced by aluminium ions. The mica window was then soaked six times in distilled water having a pH value of 5.5. After this procedure (to bring the mica surface of the geiger counter end-window

to the same state as in the previous experiment except for the replacement of any sodium ions with aluminium ions) had been followed, the mica window was immersed in two litres of distilled water with a pH value of 5.5, and the background count rate determined. The mica window was then soaked in a further portion of the same radioactive phosphate solution as was used in the above experiment on what was supposed to have been a sodium saturated mica surface.

Subsequent desorption of the radioactive phosphate appeared to occur with three simultaneous rates as had been expected for aluminium saturated mica surfaces. After a correction had been applied to the total amount of radioactive phosphate adsorbed by the aluminium saturated mica surface because of the radioactive decay of the ^{32}P isotope (half-life = 14.30 days) in the interval between the commencement of the two experiments, the total amounts of radioactive phosphate adsorbed by the mica window of the geiger counter in each experiment were compared. It was found that the amount adsorbed by the mica window in the second experiment, with aluminium only being the saturating cation, was slightly less than twice the amount (3,900 c.p.m. = 2.000 c.p.m.) adsorbed by the mica window when attempts had been made to eliminate all aluminium ions from it, and replace them with sodium ions.

The differences in initial count rate between experiments on aluminium saturated mica surfaces and sodium saturated mica surfaces that had been observed in the experiments initially performed in this thesis had been of this order of magnitude. Thus it would seem that the last procedure described for the removal of aluminium ions had not met with any particular success, over and above that obtained by the more usual processes.

As a further check that the first method tried for the preparation of aluminium ion free sodium saturated mica surfaces (p.132) was not successful, the procedure was repeated on another fresh geiger counter with unused mica end-window. While it seemed unlikely, it was thought that the reason for failure to prepare a sodium saturated mica surface might lie in the technique of handling used, rather than in the method itself. However the results obtained from this experiment were the same as before, that is there were three desorption rates of radioactive phosphate from the mica surface observed.

After this, a further experiment was performed with the same geiger counter and the same radioactive phosphate solution, in the way which has been described above, wherein the mica surface of the geiger counter end-window is first saturated with aluminium ions. It was found that the

relative amounts of radioactive phosphate adsorbed in the two experiments were, once again, approximately in the ratio 2:1 for aluminium saturated mica surface :sodium saturated mica surface. The actual initial count rates calculated for the two experiments were 1,000 c.p.m. and 450 c.p.m., and while this ratio was slightly higher than that observed when the second procedure had been followed the difference did not appear very significant.

As success had not been obtained by either of the above procedures a third method was investigated. A further new geiger counter was taken, prepared for experimentation in the usual way, and the mica surface of its end-window soaked in a solution of sodium form ion exchange resin for 12 hours. The mica window was then taken and soaked in 1.0N sodium chloride solution four times, and then in 0.2N sodium chloride solution which had been adjusted to have a pH value of 5.5 in the usual manner. This last treatment was carried out six times. The mica surface of the geiger counter end-window was placed in two litres of 0.2 N sodium chloride solution with a pH value of 5.5. All the above steps were carried out in polythene beakers and containers. The sodium chloride solutions were prepared with "analar" sodium chloride and deionised water and hydrogen resin as described in the account of the previous method attempted(p.[134])

After determination of the background count rate for the geiger counter, the mica end-window was placed in a solution of radioactive phosphate for 30 minutes and then rinsed twice in 0.2% sodium chloride solution of pH value 5.5. Following this procedure, the mica window was reimmersed in the two litres of sodium chloride solution in the polythene container and the desorption curve for the radioactive phosphate recorded and analysed.

As a further precaution against the possibility of introduction of any cations other than sodium to the system under study, the radioactive phosphate solution, which had always been stored in a polythene container to minimise the adsorption of the radioactive phosphate groups (which were present in extremely small concentration) on to the walls of the container, was also stored over a small amount (approximately one gram) of sodium resin. It was hoped that this ion exchange resin would remove any traces of aluminium or other multivalent ions that might have originally been present in the radioactive phosphate solution.

While these ions would not be expected to have a great effect on the system being studied, it was thought that they could possibly exchange with, and so displace, some of the sodium ions present on the mica surface of the geiger counter end-window during the time of adsorption of the radioactive phosphate onto this mica surface. If

this phenomenon actually occurred it would be possible for radioactive phosphate groups also present in the solution to be adsorbed onto these newly created sites thus giving a false, and unduly high, picture of the amount of adsorption actually occurring onto the sodium saturated mica surface. A polythene container was also used for the radioactive phosphate solution during the actual time of adsorption onto the mica surface.

It was considered that a possible complicating factor, leading to a slightly high initial count rate for the desorption experiment, might be the presence of a small amount of radioactive phosphate solution adhering to the surface of the mica end-window of the geiger counter. Any radioactive phosphate so present would be rapidly washed into solution. This would give rise to an anomalously high count rate for the first minute or so of the desorption experiment. Accordingly it was decided that it would be more satisfactory if the mica surface of the end-window of the geiger counter was washed in a portion of solution of the same composition as the eventual desorbing solution. This would ensure the removal of any adhering drops of radioactive phosphate solution that had not been detached from the mica surface on its removal from the radioactive phosphate solution it had been placed in for the purposes of adsorption. This washing procedure was carried out

twice.

As the total time for the washings was less than 10 seconds, there does not seem to be any possibility that any significant amount of radioactive phosphate would be desorbed by this procedure. Even if a complex existed with a half-time of desorption as short as 20 seconds, the majority of the amount of such a species present would not be removed by this washing procedure, and so its presence would still be detected readily on analysis of the subsequently obtained desorption curve.

The most rapidly desorbed species actually detected in any of the desorption experiments performed had a half-life of desorption of 0.5 to 0.6 hours. That is, it was desorbed approximately 100 times as slowly as the hypothetical species above. Also it was shown (see mathematical analysis p. 80) that the actual species detected accounted for all the radioactive phosphate initially adsorbed on the mica surface under study. Thus, if a very rapidly desorbed species does exist it must be present in very small concentration relative to all the other species detected.

If there was any radioactive phosphate solution left adhering to the mica surface of the end-window of the geiger counter this would give an apparent initial count rate that was higher than the true initial count rate

due solely to the total amounts of the various radioactive phosphate - cation saturated mica surface complexes formed. The amount of increase of the count rate due to the adhering radioactive phosphate solution would probably be comparable for all the experiments performed with the same radioactive phosphate solution. Thus the relative effect on the initial count rate of an experiment using a sodium saturated mica surface would be greater than when an aluminium saturated mica surface was used as the adsorbing surface. This could lead to a considerable alteration in the ratio of the initial count rates for the two experiments.

Another possible disadvantage of the presence of adhering radioactive phosphate solution on the mica surface would be that if it was left for any length of time before the commencement of the desorption experiment (or before being rinsed off with desorbing solution) further adsorption of radioactive phosphate ions could occur onto the mica surface. As is shown elsewhere in this thesis (p. 197) the relative amounts of the various species adsorbed over a range of time does not alter. However the total amount adsorbed increases with increasing time of adsorption from the radioactive phosphate solution. Thus the relative amounts adsorbed in two experiments can only be calculated where both adsorption times are the same. This might not effectively be so if in one

experiment a longer time elapsed between removal of the mica surface from the adsorbing solution and subsequent desorption or washing, than was the case in the second, comparative experiment.

Analysis of the data obtained from the experiment just described gave different results from those obtained previously. The total amount of radioactive phosphate initially adsorbed was lower than had been observed for previous experiments. It was found that almost all the radioactive phosphate was desorbed with a rate constant similar to that of the least readily desorbed species observed on aluminium saturated mica surfaces.

This data led to the conclusion that almost all aluminium or other multivalent ions had been removed from the surface of the mica end-window of the geiger counter. The most likely explanation of the single species present on both sodium and aluminium saturated mica surfaces was that the radioactive phosphate was adsorbed in some way directly onto the mica surface. If this was so then the species would be present no matter what cation was adsorbed onto the mica surface. Later repetition of the above experiment gave the same results, and so it was assumed that, at least at the pH value of these experiments (5.5) there was some type of complex formed between phosphate ions and the actual surface of the mica, independent of any cations also present

to neutralise the net negative charge on the mica surface.

Over 80% of the total adsorbed radioactive phosphate was present on the sodium saturated mica surface as the one species with a low rate constant. The remainder of the activity was not sufficient to analyse reliably into any components, but it had an approximate half-time for desorption that indicated that it might be due to adsorption of radioactive phosphate onto a relatively small amount of aluminium or other multivalent ions still present on the mica surface.

After completion of the desorption experiment on the sodium saturated mica surface of the geiger counter end-window, the geiger counter was taken and the procedure described on p. 136 was followed. Thus it was possible to ascertain the ratio of the total amounts of radioactive phosphate adsorbed onto the same mica surface when saturated with aluminium ions, and when saturated with sodium ions. After correction for radioactive decay of the ^{32}P atoms the ratio of the two total amounts was found to be 2,450 c.p.m. : 230 c.p.m. That is $\frac{2450}{230}$ or between 10 and 11 times as much radioactive phosphate was adsorbed by the aluminium saturated mica surface as by the sodium saturated mica surface.

This pair of experiments on the same mica surface was subsequently repeated twice on other geiger counter mica

end-windows. Similar results to the above were obtained in both cases. The ratios of the total amounts of radioactive phosphate adsorbed by the aluminium and sodium saturated mica surfaces were observed to be 8:1 and 9:1. It is considered that these figures are in satisfactory agreement with each other in view of the difficulties involved in the preparation of the aluminium ion free sodium saturated mica surfaces.

6.22 Sodium Saturated Mica Surfaces

Sodium saturated mica surfaces which had been prepared free of aluminium ions in the way indicated in the preceding section were also studied at other pH values. At a pH value of 3.0 it was found that when an aluminium free sodium saturated mica surface was allowed to adsorb radioactive phosphate, the subsequent desorption experiment yielded on analysis very similar results to those obtained in the previously described work at a pH value of 5.5. Over 90% of the total amount of radioactive phosphate adsorbed by the sodium saturated mica surface appeared to be complexed with the mica surface in the one type of complex. The rate constant for this species was 9×10^{-5} minutes^{-1} which is of comparable magnitude to that of the species found on sodium saturated mica surfaces at a pH value of 5.5 (5×10^{-5} minutes^{-1}).

An attempt was made to obtain a value for the ratio of the amounts adsorbed by sodium saturated mica surfaces and by aluminium saturated mica surfaces at a pH value of 3.0. The procedure described in the previous section for sodium and aluminium saturated mica surfaces at the same pH value was followed for one of the successful experiments on a sodium saturated mica surface (that is an experiment in which it appeared that almost all of two of the species normally present on aluminium saturated mica surfaces at a pH value of 3.0 were absent).

Unfortunately the total initial amount of radioactive phosphate that was adsorbed onto the sodium saturated mica surface was approximately 13,000 c.p.m. As it was expected that the amount of radioactive phosphate adsorbed by an aluminium saturated mica surface at the same pH value of 3.0 would be considerably more than this, a period of approximately two half-lives of the ^{32}P (approximately one month) was allowed to elapse before commencement of the experiment using radioactive phosphate and the aluminium saturated mica surface.

Even after this period of time had elapsed it was still found that the total amount of radioactive phosphate initially adsorbed was greater than could be plotted on the strip chart recorder. The strip chart recorder was marked accurately for zero time for the desorption experiment, that is when the mica surface was first placed in the desorbing solution, and left running while the desorption took place. It was found that after about 4½ hours the count rate had dropped to a measurable amount which was then followed out on the strip chart recorder.

As this experiment had been performed on an aluminium saturated mica surface at a pH value of 3.0 it was thought that the actual desorption curve would be expected to have

the same shape as the other experiments carried out on the same system but with a lesser specific activity of radioactive phosphate. Two other experiments on aluminium saturated mica surfaces with pH values of 3.0 were therefore considered. For each of these experiments the ratio of the initial count rate to the count rate observed after 5 hours and after 10 hours was calculated. The values obtained are given in Table 3, the two experiments being labelled "A" and "B".

TABLE 3

Ratio of Count Rates	Experiment "A"	Experiment "B"
$\frac{\text{Initial count rate}}{\text{Count Rate after 5 hours}}$	2.06	2.10
$\frac{\text{Initial count rate}}{\text{Count Rate after 10 hours}}$	2.37	2.41

The ratios given in Table 3 were taken and multiplied by the observed count rates, for 5 hours and 10 hours, of the experiment that was being studied, to ascertain the initial count rate. The count rate after desorption had proceeded for 5 hours was observed to be 36,300 c.p.m., and after 10 hours to be 31,900 c.p.m. With the four values given for the ratios in Table 3 these two observed count rates gave values for the initial count rate of :

(over)

36,300 x 2.06 ≏ 75,000 c.p.m.

36,300 x 2.10 ≏ 76,000 c.p.m.

31,900 x 2.37 ≏ 76,000 c.p.m.

31,900 x 2.41 ≏ 77,000 c.p.m.

Average value = 76,000 c.p.m.

Thus from the above calculations it seemed that the initial count rate in the comparison aluminium saturated mica surface desorption experiment would have been about 76,000 c.p.m.

For this experiment the aluminium saturated mica surface had been prepared by soaking the mica surface of a geiger counter end-window in 0.5M aluminium sulphate ($Al_2(SO_4)_3$) solutions. Subsequent work (see p. 183) has shown that mica surfaces saturated with aluminium sulphate solutions adsorb approximately three times as much radioactive phosphate as do mica surfaces saturated with either aluminium nitrate or aluminium chloride. However, apart from the initially high adsorption of radioactive phosphate, the desorption rates and the relative amounts of the different species present are the same.

As all comparison experiments with sodium and aluminium saturated mica surfaces at a pH value of 5.5 had been carried out using aluminium nitrate solutions, in

order to have a basis of comparison between the two pH values (3.0 and 5.5) it was felt that the calculated initial count rate of 76,000 c.p.m. for the aluminium sulphate saturated mica surface with a pH value of 3.0 should be divided by three. This gave an equivalent initial count rate of 25,300 c.p.m.

When the initial count rate of 25,300 c.p.m. for the aluminium saturated mica surface was corrected for the radioactive decay of the ^{32}P atoms during the elapsed time between commencement of the sodium saturated mica surface - radioactive phosphate desorption experiment and commencement of the similar experiment on the aluminium saturated mica surface, the value obtained was 108,000 c.p.m. The ratio of this count rate to the initial count rate of radioactive phosphate adsorbed by the sodium saturated mica surface was $\frac{108,000}{13,000}$ or between 8:1 and 9:1. While this figure is very uncertain, owing to the number of assumptions involved in its calculation, it can be seen that, if these assumptions are basically valid, then the ratio of the total amounts of radioactive phosphate adsorbed by aluminium saturated mica surfaces and by sodium saturated mica surfaces is comparable at pH values of 3.0 and 5.5.

Endeavours were made to study the adsorption and

subsequent desorption of radioactive phosphate onto a sodium saturated mica surface with a pH value of 9.0. Owing to the difficulties already described involved in working at high pH values (cf. p. 91) it was necessary to use the totally enclosed apparatus that had been designed for work at these pH values. Unfortunately this apparatus is made of glass which would not be satisfactory for experiments with sodium saturated mica surfaces, because of the necessity to exclude all traces of aluminium from experiments with this system. As it did not seem practicable to make a similar piece of apparatus out of polythene materials, some way had to be devised to eliminate all contact between any glass and the solutions which the sodium saturated mica end-window of the geiger counter was to be immersed in.

The centrifugal stirrer was coated with paraffin wax both inside and outside as far up as the point at which it entered the glass tube through the rubber stopper. Although the desorbing solution would rise up this glass tube some distance (about 10 c.m. past the bottom of the stopper) it was not possible to coat either the outside of the stirrer shaft or the inside of the glass tube in which the stirrer rotated with paraffin wax. This was because the amount of clearance was such that the introduction of any wax would stop the stirrer rotating.

In an attempt to exclude the glass of the walls of the two litre flask which held the desorbing solution from contact with this solution, a polythene bag was inserted into the flask, and the desorbing solution placed inside this bag. This polythene bag was big enough to protrude through the neck of the two litre flask, and the rubber stopper containing the geiger counter, stirrer, etc, was inserted inside it. When filled with solution the bag swelled out to hold almost the same volume as the two litre flask would have held had the bag not been present. There was a small volume around the sides that did not have anything but air filling it.

Even though the polythene bag was checked for leaks before use, it was found that the empty space between the walls of the two litre flask and the outside of the polythene bag gradually filled with liquid when the bag (inside the two litre flask) had been filled with solution and allowed to stand for some time. If this was to happen during a desorption experiment, the level of the desorbing solution in the polythene bag inside the two litre flask would drop. This would have the effect of breaking the contact between the mica surface of the geiger counter end-window and the desorbing solution. Such a happening would cause interference with the desorption of the radioactive phosphate, thus invalidating

the data obtained after this point, as even if more liquid was added the time scale would be meaningless unless the exact time that the mica surface was out of contact with the solution was known.

In order to stop the desorption solution level falling away from the mica surface under study during an experiment, the volume between the polythene bag and the walls of the two litre flask was also filled with desorbing solution. Provided the rate of movement of the solution through the walls of the polythene bag was slow enough it would not be expected that a significant amount of aluminium ions from the glass could penetrate into the polythene bag in the period of time required for a desorption experiment. As the rate of leakage of solution through the polythene bag into the air gap between it and the two litre flask was observed to be slow (a period of some days being required to fill the gap), and as the rate would be expected to be slower with solution on both sides of the polythene bag it did not seem likely that contamination of the solution would occur in this way.

Care was taken to ensure that the bottom end of the rubber stopper which would be in contact with the desorbing solution was coated with wax. The protruding edges of the two glass tubes that came through to the

bottom of the rubber stopper were also coated with wax. These two tubes were the end of the separating funnel through which some of the desorbing solution was added and the tube inside which the centrifugal stirrer rotated. One of the steps in the operation of the enclosed apparatus was the addition of the remainder of the desorbing solution required to completely fill the space around the geiger counter end-window inside the two litre flask. This was done through a glass separating funnel.

No method of overcoming the necessity of using this glass separating funnel was devised. To minimise any undesirable effect that the use of this glass separating funnel might have on the experiments with sodium saturated mica surfaces, as much solution as possible was added directly into the polythene bag inside the two litre glass flask before the rubber stopper plus geiger counter, etc., was inserted. The separating funnel was rinsed out several times with the desorbing solution, and then, after the rubber stopper had been inserted in the two litre flask, desorbing solution was poured into the separating funnel and rapidly run into the flask until all the space below the rubber stopper was full of the desorbing solution. If any of the desorbing solution remained in the separating funnel after this procedure had been carried out it was immediately withdrawn and discarded.

All the solutions used were prepared in the same manner as described earlier (p.139) for experiments on aluminium ion free sodium saturated mica surfaces at a pH value of 5.5, except that they were all adjusted to a pH value of 9.0.

Although experiments on the sodium saturated mica surface of a geiger counter end-window were carried out more than once in the manner described above, it appeared that success in obtaining aluminium ion free sodium saturated mica surfaces had not been achieved at this pH value. The experimental results indicated the presence of three complexes between radioactive phosphate and the mica surface being studied. These complexes had the same rate constants for desorption as those observed for aluminium saturated mica surfaces at a pH value of 9.0. The total amount of radioactive phosphate adsorbed by the prepared mica surface was about half of that adsorbed by aluminium saturated mica surfaces under the same conditions.

These results were similar to those obtained at first with sodium saturated mica surfaces that were subsequently shown to have a considerable amount of aluminium ions still present adsorbed onto their surfaces. Thus it seemed reasonable to conclude that, during the experiments performed on sodium saturated mica surfaces with a pH value of 9.0, aluminium ions were still present adsorbed onto the mica surfaces, in about half the concentration

normally found with prepared aluminium saturated mica surfaces.

6.23 Aluminium Saturated Mica Surfaces

After the initial experiments had shown that mica surfaces saturated with aluminium ions adsorbed radioactive phosphate that could subsequently be desorbed into solution, further studies on the radioactive phosphate/aluminium/mica surface system were carried out. The adsorption and subsequent desorption of radioactive phosphate from an aluminium saturated mica surface were studied over a range of different pH values. A considerable amount of work was done at a pH value of 5.5 as this was a pH value comparable to that found in many soils. Experiments were also performed at considerably higher (9.0) and lower (3.0) pH values than 5.5, in order to study the change in the desorption phenomena with change in pH value.

Desorption experiments performed at pH values of 5.5 and 3.0 were carried out in the usual way into two litre beakers containing distilled water with the required pH value. The preparation of the aluminium saturated mica surfaces at these pH values is described previously (p.118). Experiments on aluminium saturated mica surfaces with a pH value of 9.0 were performed using the specially designed, totally enclosed apparatus (see "Problems of Experimentation at high pH values p. 91) For the experiments at a pH value of 5.0 equilibration of the mica surface was carried out in the same way as for

the experiments at lower pH values except that solutions of distilled water having a pH value of 9.0 were used that had been prepared immediately prior to being required.

One of the assumptions that had been made in this work was that in the desorption of radioactive phosphate from aluminium saturated mica surfaces only the phosphate group was desorbed. Because there is far more radioactive phosphate adsorbed onto aluminium saturated mica surfaces than onto sodium (or other monovalent ion) saturated mica surfaces it is believed that the phosphate groups are associated with the aluminium ions in some way. After adsorption of phosphate the situation at the mica surface can be represented as in figure 11

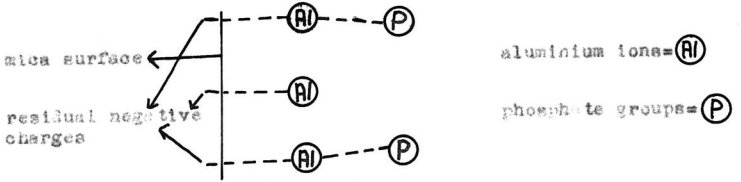


Figure 11

The aluminium ions and the phosphate groups are shown diagrammatically. The linkages between phosphate and aluminium, and between aluminium and the mica surface are shown as (— — — —) there being no implication as to what sort of linkage may actually exist. When desorption occurs it is known that, because of the loss

of radioactivity, the radioactive phosphate must be removed from the mica surface in some way.

There are two possible ways in which this removal of the radioactive phosphate could occur. One is the breaking of the aluminium-phosphate linkage, the result of which is shown in figure 12, the same symbols being used as those used in the preceding figure 11 above.

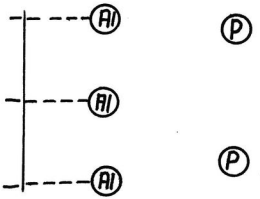


Figure 12.

The other possibility involves the breaking of the aluminium-mica surface linkage, with consequent release of an aluminium-phosphate complex. This is illustrated in figure 13.

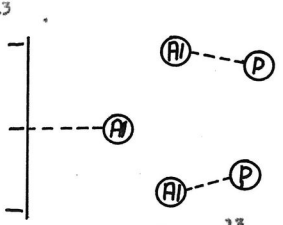


Figure 13.

If the second possibility occurred (figure 13), the residual negative charges on the mica surface would be

left unsatisfied when the aluminium ions were removed into solution with the radioactive phosphate groups. As a result of this, other positive ions present in the surrounding solution would be adsorbed onto the mica surface to satisfy the net negative charge thereon.

If there were any aluminium ions present in the desorbing solution these would be more likely to be adsorbed onto the mica surface than monovalent ions. Even if the desorbing solution used was not made up with any aluminium ions it would be expected that there would be some aluminium ions present from the glass walls of the beaker used. It seemed unlikely that there would be many free aluminium ions present from breakdown of the aluminium-phosphate complexes released into the solution by the desorption process. If these complexes were unstable enough to dissociate readily, the aluminium phosphate linkage could have broken originally on the mica surface, leading to the first possibility suggested (Figure 12).

Thus, although it might be expected that some of the residual negative charges on the mica surface left unsaturated by the desorption of the aluminium-phosphate complexes would be saturated with fresh aluminium ions, some of these charges would probably be saturated with other positive ions. The only positive ions that would

be present in any significant concentration in the desorbing solutions used would be sodium and hydrogen ions. Some of the residual negative charges on the mica surface would therefore be neutralized by these monovalent ions. It had already been established that mica surfaces saturated with monovalent ions adsorbed far less radioactive phosphate than when they were saturated with aluminium ions (or other multivalent ions). Consequently if radioactive phosphate was adsorbed onto the mica surface for a second time, without any preliminary treatment of the mica surface, it would be expected that less would be adsorbed, owing to the lesser amount of aluminium ions present.

If, however, the first possibility for the desorption of the radioactive phosphate that was discussed (see figure 12) was correct, it can be seen that the mica surface is finally (after desorption of all radioactive phosphate) in the same condition as it was initially, before any adsorption of radioactive phosphate had occurred. Thus a further treatment with radioactive phosphate should lead to the same amount of adsorption as occurred the first time the mica surface was placed in the radioactive phosphate solution.

To test which of the two possibilities was correct, two consecutive desorption experiments were performed.

A mica end-window geiger counter was taken, and, after preparation in the usual way (cf.p. [38]) the mica end window was soaked in 0.5N aluminium nitrate solution four times for at least 30 minutes each time. The mica window was soaked in distilled water having a pH value of 3.5 six times in order to adjust the pH value of the aluminium ions saturating the mica surface to 3.5. The background count rate of the geiger counter was determined while the mica end-window was immersed in two litres of distilled water at a pH value of 3.5.

After the background count rate had been determined and the mica surface of the geiger counter end-window had equilibrated with the two litres of solution, the geiger counter was removed and the mica end-window placed in a solution of radioactive phosphate with a pH value of 3.5 for a suitable length of time (10 minutes). The mica surface was then rinsed with distilled water having a pH value of 3.5 and replaced in the two litres of distilled water for desorption of the radioactive phosphate.

After desorption of the radioactive phosphate from the mica end-window of the geiger counter had occurred, the mica window was soaked again in distilled water having a pH value of 3.5. The geiger counter was placed with the mica surface of its end-window in two litres of distilled water with a pH value of 3.5. The mica surface was allowed to equilibrate with the two litres of distilled water, and

the background count rate was determined. The mica surface was then removed from the two litres of distilled water and soaked in radioactive phosphate. The radioactive phosphate used was another portion of the same solution, with a pH value of 3.5, as was used for the first adsorption. The adsorbing time was the same as for the first experiment (10 minutes). The mica surface was, after removal from the radioactive phosphate solution, rinsed with distilled water having a pH value of 3.5 and replaced in the two litre beaker full of distilled water also with a pH value of 3.5, into which the radioactive phosphate was desorbed as before.

The initial count rate, due to the adsorbed radioactive phosphate, for the first experiment was found to be 730 c.p.m. For the second experiment, after the first amount of radioactive phosphate had been desorbed, the initial count rate was found to be 570 c.p.m. As there was a considerable time interval between the commencement of the two experiments (139 hours) it was necessary to correct the second observed increase in count rate for the radioactive decay of the ^{32}P atoms in the radioactive phosphate solution. When this was done the second count rate became 750 c.p.m. This is seen to be in good agreement with the increase in count rate observed in the first experiment of 730 c.p.m.

From the above data it seems that the same amount of radioactive phosphate was adsorbed onto the mica surface

of the geiger counter end-window in e ch experiment. This result is in agreement with the first desorption possibility, that is, that the bond which breaks on desorption is between the aluminium ion and the phosphate group, and not between the aluminium ion and the mica surfaces. Thus the results obtained above are in agreement with the assumption that has been made.

Over the range of pH values studied there appeared to be three different desorption rates for the radioactive phosphate adsorbed onto the aluminium saturated mica surface. Typical experiments at each pH value studied are shown in the section of this thesis wherein some actual experimental results are given (p. 282). From a study of the rate constants associated with each of the desorption rates it seemed that the same three different desorption rates, and hence, presumably, the same three types of adsorption complex were present at all pH values. Table 4 gives the rate constants (k_a, k_b and k_c) for each of the three desorption rates for some of the experiments that have been performed at various p^H values.

TABLE 4

pH value at which experiment was conducted	Rate constants for the three desorption rates		
	k_a (minutes^{-1})	k_b (minutes^{-1})	k_c (mins.$^{-1}$)
3.0	1.7×10^{-2}	2.2×10^{-3}	8.8×10^{-5}
3.0	2.1×10^{-2}	2.4×10^{-3}	5.7×10^{-5}
3.0	2.1×10^{-2}	2.3×10^{-3}	11.0×10^{-5}
5.5	2.3×10^{-2}	1.7×10^{-3}	3.6×10^{-5}
5.5	1.7×10^{-2}	2.3×10^{-3}	4.8×10^{-5}
5.5	1.7×10^{-2}	1.9×10^{-3}	4.8×10^{-5}
5.5	1.9×10^{-2}	1.7×10^{-3}	5.8×10^{-5}
9.0	2.3×10^{-2}	1.8×10^{-3}	3.9×10^{-5}
9.0	2.3×10^{-2}	2.3×10^{-3}	5.0×10^{-5}

The values of k_a were all approximately constant with repeated experiments at the same pH value, and also over the range of pH values studied. It seemed reasonable to assign a value of 2×10^{-2} minutes^{-1} to k_a for all pH values (at least in the pH range 3 -9) from the above data. Similarly all the values quoted for k_b, both in repeated experiments at the same pH value, and

over the pH range studied were close to 2×10^{-5} minutes^{-1}.

The experiments conducted at pH values of 5.5 and 9.0 all had approximately the same value for k_c the average value being 4.6×10^{-5} minutes^{-1}. The experiments which were performed with a pH value of 3.0 however, gave rise to a rather wide range of values for k_c (see Table 4). The average value of k_c at this pH value is 8.3×10^{-5} minutes^{-1} which is comparable in magnitude to the value calculated for this rate constant at other pH values. As the values for k_a and k_b at a pH value of 3.0 are in good agreement with the values of k_a and k_b at other pH values it seems that the rate constant k_c represents the same(or a very similar) desorption process at all pH values. The value of k_c will be taken as 5×10^{-5} minutes^{-1}.

The rate constants listed in Table 4 were obtained directly from the measurement of the half-life of each different mica surface-radioactive phosphate complex (as characterized by the different desorption rates). The actual method of calculation is given in the section on the mathematical analysis of data (p.72) As has been shown the half-lives are obtained from the slopes of the various components of the overall desorption rate which have been resolved graphically. Owing to the almost horizontal position of the straight line corresponding

to the slowest desorption rate, considerable possibility of inaccuracy in the determination of the half-life of the complex existed. As this half-life was inversely proportional to the rate constant $\left(K_c = \frac{\log_e 2}{(t)_{\frac{1}{2}c}}\right)$ a relatively wide variation in the values for K_c was not unexpected.

The relative amounts of each of the different complexes between the radioactive phosphate and the aluminium saturated mica surface were obtainable from the experimental data. These relative amounts were obtained from the intercepts of the resolved straight lines with the time =0 axis. Further details of the method involved in the calculation of these relative amounts is given in the mathematical analysis section(p. 72).

The relative amounts of the three different complex species were found to vary somewhat with change in the pH value of the system. All species were found to be present in significant amounts at all pH values studied. Representative values of the different relative amounts of each species for some of the experiments performed are given in Table 5 . The various complexes formed between the radioactive phosphate and the aluminium saturated mica surface are designated as "A" (with rate

constant k_a), "B" (k_b) and "C" (k_c).

TABLE 5

pH value at which experiment was conducted	Relative amount of "A" (%)	Relative amount of "B" (%)	Relative amount of "C" (%)
3.0	51	19	30
3.0	39	23	38
3.0	45	20	35
5.5	44	25	31
5.5	43	24	33
5.5	42	27	31
5.5	43	26	31
9.0	36	16	48
9.0	29	27	44

It will be seen from the above table that the relative amounts of each complex "A", "B" and "C" are approximately reproducible constant for each pH value studied. As was mentioned previously a considerable amount of work was carried out at a pH value of 5.5, and the values given in Tables for the relative amounts of the three different species at this pH value are in very good agreement. Other

experiments at this pH value gave relative amounts for each complex within about 5% of the average values of the experiments listed above, and so the best values as selected above are a reasonable representation of all the results obtained.

The average percentage of each of the three different species at the various pH values studied are given in Table 6 .

TABLE 6 .

pH value	Average relative amount of "A"(%)	Average relative amount of "B"(%)	Average relative amount of "C" (%)
3.0	~45	~20	~35
5.5	40 -45	~25	30 -35
9.0	30-35	20-25	~45

From a study of Table 6 it can be seen that the relative amount of "B" was least at all the pH values studied. There was less of this species than the amounts of "A" or "C" present. Between one fifth and one quarter of the total amount of radioactive phosphate adsorbed onto the aluminium saturated mica surface seemed to have a rate constant for desorption of 2×10^{-3} minutes^{-1} ($= k_b$).

At pH values of 5.5 and below the predominant complex species present seemed to be type "A", the amount of this species present being slightly less than half of the total amount of radioactive phosphate adsorbed onto the aluminium saturated mica surface. When the pH value was increased to 9.0 however, the relative amounts of "A" and "C" were altered. At this pH value "C" was the most predominant species present, the ratio of the amounts of "C" and "A" being the reverse of that observed at lower pH values.

The amounts of each of the complexes "A", "B" and "C" calculated above are only known relative to one another. Another interesting problem worthy of investigation is the manner in which the total amount of adsorbed radioactive phosphate, and hence the amount of each of the three different complexes, varied as the pH value of the system under study (that is, the radioactive phosphate solution, the mica surface and the equilibrating and desorbing solutions) was varied. A necessary prerequisite for any studies of this nature would be the preparation of radioactive phosphate solutions having different pH values but the same concentration of phosphate present in them. This would not be an easy task, for it was necessary to add small amounts of acid or alkaline solution to the radioactive phosphate solution in order to alter its pH value. Unless the total amounts of solution added to each portion

of the radioactive phosphate solution were equal, having regard to the total amount of solution present in each portion, the concentrations of the different portions would become different from one another.

A comparison was made of the total amounts of radioactive phosphate adsorbed by an aluminium saturated mica surface at two different pH values. A stock radioactive phosphate solution was prepared and divided into two parts. These parts were made as equal in quantity as could be judged, and stored in separate polythene containers. As both solutions were about 100-150 ml. in volume an error of about a millilitre would not have greatly upset the equality.. It was desired only that the two solutions have the same phosphate concentration within $\pm$ 1 or 2%, as the aim of the experiment was merely to see if there was any significant difference in the total amounts of radioactive phosphate adsorbed onto the aluminium saturated mica surface at different pH values. It was not considered that an initial experiment justified the use and subsequent radioactive contamination of pipettes, etc.

The pH values of the two solutions of radioactive phosphate were adjusted to the required values in the usual way (cf. p. 85) Both solutions were adjusted at the same time, and considerable care was taken to ensure

that the same amounts of solution were added to each of the radioactive phosphate solutions. When a drop of acid (or alkali) was not required for one of the two solutions a drop of distilled water was added to keep the solution volumes equal. In this way two solutions having the same total phosphate concentrations, but different pH values, were prepared. The pH values of the two solutions were 5.5 and 3.5.

An end-window geiger counter was taken and after preparation for use the mica end-window was saturated with aluminium ions in the way which has been described earlier (p. 118). The aluminium ions adsorbed onto the mica surface were adjusted to a pH value of 3.5 and then the mica end-window of the geiger counter was equilibrated with two litres of distilled water with a pH value of 3.5. While the mica surface was in the two litres of solution the background count rate for the geiger counter was determined. The mica surface of the geiger counter end-window was then soaked in the radioactive phosphate solution having a pH value of 3.5 for a suitable period of time (10 minutes). After this period of time had elapsed the mica window was removed from the radioactive phosphate solution, rinsed in distilled water having a pH value of 3.5, and then

replaced in the two litres of solution at a pH value of 3.5, into which the radioactive phosphate then desorbed.

When the radioactive phosphate had been desorbed from the mica end-window of the geiger counter, the mica window was soaked in an aluminium solution and then in distilled water as before, until an aluminium saturated mica surface with a pH value of 5.5 had been obtained. This window was then placed in two litres of distilled water having a pH value of 5.5, and the background count rate for the geiger counter determined. The mica end-window was removed from the two litres of solution and placed in the radioactive phosphate solution that had been adjusted to a pH value of 5.5. The mica window was left in this radioactive phosphate solution for the same time as for the previous adsorption at a pH value of 3.5 (10 minutes). It was then removed, rinsed in distilled water having a pH value of 5.5, and replaced in the two litres of distilled water with a pH value of 5.5 into which the adsorbed radioactive phosphate was desorbed.

From analysis of the desorption-curves of radioactive phosphate at the two pH values, the initial count rates for the two experiments were calculated. As the second experiment had of necessity been commenced some time after the first experiment, the observed initial

count rate for this experiment was corrected for the natural radioactive decay of the radioactive phosphate solution used during the time interval between the commencement of the two experiments. The initial count rate observed in the experiment conducted at a pH value of 3.5 was approximately 730 c.p.m. The corrected initial count rate for the experiment performed with all solutions, etc., at a pH value of 5.5 was 5,300 c.p.m.

The ratios of the total amounts of radioactive phosphate solution adsorbed onto the aluminium saturated mica surface of a geiger counter end-window at the two pH values studied can be calculated from the above data. The ratio

$$\frac{\text{amount adsorbed at a pH value of 5.5}}{\text{amount adsorbed at a pH value of 3.5}} = \frac{5,300}{730} \simeq \frac{7}{1}$$

As the relative amounts of the three different complex species which were present at all pH values (3 -9) were approximately the same at pH values of 3.0 and 5.5 it would not be expected that there would be much difference in the relative amounts present at a pH value of 3.5 to the relative amounts present at the other two pH values. The actual experiment performed at a pH value of 3.5 was not satisfactorily analysed, partially owing to the relatively low initial count rate (730 c.p.m.) However

the desorption species type "C" was detected with a rate constant of 3.6×10^{-5} minutes^{-1} and an amount of radioactive phosphate, relative to the total amount present initially, of 39 per cent, these two figures being in reasonable agreement with those observed for type "C" at pH values of both 3.0 and 5.5. Thus it can be said that the total amounts of each of the three species "A", "B" and "C" of radioactive phosphate - mica surface complexes were one seventh (approximately) as great at a pH value of 3.3 as at a pH value of 5.5.

6.231 Experiments at Very High and Very Low pH Values

The range of pH values over which most of the experimental work on aluminium saturated mica surfaces has been carried out was 5.0 - 9.0. At higher pH values the aluminium present would be in a similar form to the aluminate ion $Al(OH)_4^-$. Any radioactive phosphate associated with this form of aluminium would be very weakly held owing to the repulsion of the negative charges between the phosphate groups and the aluminate-like groups.

The actual form of the aluminium adsorbed onto mica surfaces at such high pH values (10-11) is not known. By analogy with the species postulated for lower pH values (see p. 122) the actual situation might be as shown in figure 14

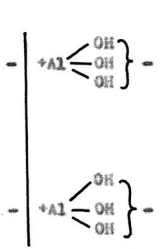


Figure 14.

In the above figure one of the positive charges on the aluminium neutralises the net negative charge on the mica surface, and three hydroxyl groups associated with

the aluminium give rise to an effective single negative charge. Any phosphate groups present at very high pH values (10-14) would be either HPO_4^{2-} or PO_4^{3-}. Both of these ions are highly negatively charged, and consequently any association between these ions and the aluminate-like ions shown in Figure 14 would be very readily broken in solution leading to very rapid desorption.

No experiments were performed at these very high pH values as this thesis was concerned mainly with the adsorption of radioactive phosphate onto sites that could possibly be found in the soil. Some work has been done on the removal of radioactive phosphate from the mica surface under the influence of various reagents (see "Effects of Various Substances on the Desorption of Radioactive Phosphate" p. 230).

One of the more effective reagents for this purpose was found to be 0.1N sodium hydroxide. The pH value of this solution was 13 and contact of this solution with the aluminium saturated mica surface would be expected to raise the pH value of the surface somewhat. As this occurred the attraction between the aluminium ions and the adsorbed radioactive phosphate ions would be considerably diminished owing to increased repulsion between the now negatively charged aluminium groupings and the already negative phosphate groups. It was found that on placing the mica surface into a sodium hydroxide

solution the radioactive phosphate was rapidly desorbed thus showing that the tendency for the complex to dissociate was greater in this solution.

At very low pH values (0-2) any phosphate groups would exist as predominantly H_3PO_4 molecules. As H_3PO_4 is a neutral molecule it would not be as strongly bonded to positively charged aluminium groups as any of the other, negatively charged orthophosphate groups $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. Thus it would not be expected that, in an experiment performed at very low pH values, there would be as much adsorption of radioactive phosphate as had been observed to occur at higher pH values.

Experiments were carried out at pH values of 0.0 and 1.0 on the adsorption and subsequent desorption of radioactive phosphate from an aluminium saturated mica surface. The experiments were carried out in the same manner as was followed at higher pH values, the pH value of the mica surface and of the desorbing solutions being adjusted with 1.0N and 0.1N hydrochloric acid solutions respectively.

In both experiments relatively little radioactive phosphate was adsorbed onto the mica surface. The radioactive phosphate solution for the experiment conducted with a pH value of 1.0 was obtained by the addition

of a small number of drops of concentrated (2N) hydrochloric acid to an approximately 20 ml. portion of a stock radioactive phosphate solution that had been used previously for experiments with a pH value of 5.5. Thus the concentration of radioactive phosphate used was not much less than that used for the experiments at the higher pH value.

The initial increase in the count rate due to the adsorption of radioactive phosphate, at a pH value of 1.0, onto the aluminium saturated mica surface was approximately 1500 c.p.m. After making a suitable correction for the radioactive decay of the $^{32}_{15}P$ atoms in the radioactive phosphate solution it was found that the amount adsorbed by the aluminium saturated mica surface at a pH value of 1.0 was about $\frac{1}{50}$ of that adsorbed by an aluminium saturated mica surface, in the same time interval, at a pH value of 5.5.

It would be expected that there would be the same or less amount of radioactive phosphate adsorbed onto the mica surface at a pH value of 0.0 than at a pH value of 1.0. Because of the very small amount of radioactive phosphate adsorbed onto the aluminium saturated mica surface in the first experiment (pH value 1.0) a fresh, more highly concentrated solution of radioactive phosphate was prepared for use in the experiment at a pH value of 0.0. Thus it was not possible to estimate the amount

of radioactive phosphate actually adsorbed in this experiment, relative to the amount adsorbed in the other experiments that had been performed at pH values of 1.0 and 5.5. Experiments performed with the same radioactive phosphate solution which had been adjusted to other pH values, indicated that the total amount of radioactive phosphate actually adsorbed at a pH value of 0.0 was even less than the amount adsorbed in the experiment at a pH value of 1.0.

The desorption curves for the two low pH value experiments are shown in the section of experimental data on pp.300-1 . It can be seen there that the experiment performed at a pH value of 1.0 appeared to give rise to only one desorption rate with a rate constant of about $1 - 1.5 \times 10^{-4}$ minutes^{-1}. Detailed analysis of the desorption graph cannot be performed satisfactorily owing to the low initial count rate (see graph p.300). Analysis of the experimental desorption curve (see p.301) for the experiment performed at a pH value of 0.0 showed the presence of three desorption rates with rate constants in the same range as had been observed for experiments conducted at higher pH values.

Neither of the experiments at the very low pH values have been repeated, and this would be necessary, using much more concentrated solutions of radioactive phosphate, before any definite conclusions as to the number of complexes

between the radioactive phosphate and the aluminium saturated mica surface present at these pH values could be drawn. It does seem, however, that the amount of radioactive phosphate adsorbed is very little at these pH values, relative to the amounts adsorbed at higher pH values.

6.232 The Effect of Different Aluminium Compounds Used

In all the experiments on aluminium saturated mica surfaces the mica surfaces studied were at some time soaked in aluminium ion solutions. The work that has been done in this thesis has been dealing with very small quantities of material on the mica surfaces. The greatest number of aluminium ions that would be expected to be present on the mica surface under study was one for each negative charge present on the mica surface due to interlayer isomorphous replacement. The number of negative charges present on an area of mica such as that studied (about 6 sq.cm.) was approximately 10^{15} (see p.275) This number of aluminium ions would be equivalent to $\frac{10^{15}}{6 \times 10^{23}} \times 27$ or 4.5×10^{-8} moles of aluminium. With such a small amount of aluminium present on the mica surface any impurities that were at all preferentially adsorbed onto the mica surface would have a marked effect on the relevance of the data obtained to the radioactive phosphate -aluminium-mica surface system under study.

The only readily available aluminium salt obtainable with a degree of purity corresponding to "analar" requirements was aluminium sulphate $(Al_2(SO_4)_3 \cdot 16H_2O)$ Consequently this salt was used for some of the experiments

on aluminium saturated mica surfaces. However a divalent ion such as sulphate might be expected to be more likely to have a tendency to form some sort of complexes with the aluminium ions, or with the mica surface itself than would a monovalent ion such as the nitrate or chloride ion. Most of the experiments performed were, therefore, carried out using aluminium nitrate $\left(Al(NO_3)_3.9H_2O\right)$ as this was more readily obtainable than hydrated aluminium chloride.

Anhydrous aluminium chloride, on addition of water, undergoes partial hydrolysis yielding hydrochloric acid and aluminium hydroxide.

As the possibility of some sort of anomalous behaviour existed with the use of aluminium sulphate solutions experiments were carried out to see if this was so. Analysis of experimental data for experiments in which aluminium sulphate and in which aluminium nitrate had been used had already shown that the qualitative data obtained from each experiment was the same. In both cases three different complexes were detected, with the same rate constants being obtained for the corresponding complexes, regardless of the aluminium salt used. The amounts of each of the three complexes, relative to the total initial amount present, were the same for both aluminium salts, providing the relevent experiments were

conducted at the same pH value. Thus the only possible difference caused by the use of aluminium sulphate rather than aluminium nitrate would be in the total amount of radioactive phosphate adsorbed initially onto the mica surfaces.

Two geiger counters were taken and prepared for experimentation in the usual manner (cf. p. 38). They were coated with paraffin wax such that the total area of the mica surface of the end-window covered was as equal as possible for the two geiger counters. One geiger counter had its mica end-window soaked in 0.5 N aluminium sulphate solution. The other geiger counter was soaked in 0.5 N aluminium nitrate solution. Both mica surfaces were brought to a pH value of 5.5 using distilled water, equilibrated in two litres of distilled water with a pH value of 5.5, and their background count rates determined. Each mica end-window was then soaked for the same period of time in portions of the same radioactive phosphate solution of pH value 5.5. After rinsing of the mica surfaces of the geiger counter end-windows the usual desorption experiments were performed.

It was found on analysis of the desorption curves so obtained that the mica surface saturated with aluminium sulphate adsorbed approximately three times as much radioactive phosphate as did the mica surface that had

been saturated with aluminium nitrate. Thus it appeared that the presence of sulphate ions in association with aluminium ions adsorbed onto the mica surface enhanced the subsequent adsorption of radioactive phosphate.

Similar duplicate experiments were performed using mica surfaces which had been saturated with aluminium ions using aluminium nitrate solutions and aluminium chloride solutions. The total amounts of adsorbed radioactive phosphate were found to be the same in both experiments. Also the desorption curves were analysed similarly, showing that there was no difference in the experimental results caused by the use of either aluminium nitrate solutions or aluminium chloride solutions. This seemed to be evidence for the hypothesis that the difference in the total amounts of radioactive phosphate adsorbed with aluminium sulphate and aluminium nitrate solutions was caused by the sulphate and not by the nitrate ions.

6.24 Other Cation Saturated Mica Surfaces

From a combination of available knowledge about mica surfaces, and the experimental results that have been obtained in this thesis, it was believed that there was no radioactive phosphate associated with sodium ions present on a mica surface neutralizing its net negative charge. The main reason for this was the fact that sodium is a monovalent ion and so, after neutralizing the excess negative charge on the mica surface, there would be no remaining positive charge capable of associating with any negatively charged radioactive phosphate groups present. In order to obtain confirmation of this belief experiments were performed in which other monovalent ions were used to saturate the mica surface.

Mica surfaces, saturated with potassium and ammonium ions and adjusted to a pH value of 5.5, were prepared by analogous procedures to that used in the preparation of sodium saturated mica surfaces (p. 139) Experiments on the adsorption of radioactive phosphate and its subsequent desorption into solution were performed on these mica surfaces in the same way as had been done with sodium saturated mica surfaces.

The experiment using the potassium saturated mica surface was performed first. It was found that the increase in count rate after adsorption of the radioactive phosphate was less than 100 c.p.m. Consequently

it was not possible to attempt an analysis of the desorption curve in order to obtain the rate constant (or constants) of desorption. An approximate calculation showed that the amount of radioactive phosphate adsorbed from the radioactive phosphate solution used was less than ten per cent of the amount that had been adsorbed onto an aluminium saturated mica surface, at the same pH value, from a portion of the same solution. From this it was clear that there could have been very little, if any, radioactive phosphate associated with the potassium ions present on the mica surface. When comparable amounts of radioactive phosphate had been adsorbed by sodium saturated mica surfaces it had been shown that all the radioactive phosphate had been associated with the mica surface itself.

For the experiment of adsorption of radioactive phosphate onto an ammonium ion saturated mica surface and its subsequent desorption into solution a radioactive phosphate solution of higher specific activity was used. The total amount of radioactivity adsorbed initially was approximately 1180 c.p.m., and the desorption curve was analysed in the usual way. It was found that there were three different complexes present with rate constants for desorption as follows:

1.9×10^{-2} minutes^{-1}

2.3×10^{-3} minutes^{-1}

and

4.6×10^{-5} minutes^{-1}

It can readily be seen (cf. p.166) that the first two rate constants quoted above are similar to those obtained in the case of experiments on aluminium saturated mica surfaces. The third rate constant, 4.6×10^{-5} minutes^{-1}, is approximately the same as that found in experiments on both sodium saturated and aluminium saturated mica surfaces. It is believed that this rate constant is characteristic of a complex between the radioactive phosphate and the mica surface itself.

By analogy with the experimental results obtained from sodium saturated mica surfaces, ammonium ion saturated mica surfaces would be expected to form only the one complex with radioactive phosphate, as ammonium and sodium ions are both monovalent. As there were actually three complexes formed, as characterised by the different rate constants of desorption, the other two complexes would be either associated with the ammonium ions present or else with some aluminium ions that had not been removed from the mica surface during the preparation of the ammonium ion saturated mica surface.

If the two other complexes present were associated with the ammonium ions adsorbed onto the mica surface their rate constants for desorption of the radioactive

phosphate would not necessarily be the same as the rate constants for desorption of radioactive phosphate from complexes with aluminium ions on an aluminium saturated mica surface. The total amount of radioactive phosphate adsorbed onto the ammonium ion saturated mica surface was far less than the amount that it was expected would have been adsorbed had the mica surface been saturated with aluminium ions.

The actual initial amount of radioactive phosphate present as a complex with the smallest rate constant of desorption was very similar (630 c.p.m. to 545 c.p.m.) to the amount adsorbed onto a sodium saturated mica surface in an experiment conducted with a portion of the same radioactive phosphate solution. This amount was 55% of the total amount of radioactive phosphate adsorbed onto the mica surface initially. These facts suggested that the radioactive phosphate present as complexes with rate constants of desorption of 1.9×10^{-2} minutes^{-1} and 2.3×10^{-3} minutes^{-1} was associated with a small amount of aluminium ions present adsorbed onto the otherwise ammonium ion saturated mica surface. Further evidence for this was the fact that the ratio of the initial amounts of the two complexes present (350 c.p.m. : 200 c.p.m. or 44:25) was the same as the ratio of the amounts of the complexes with the two

highest rate constants present initially in experiments on aluminium saturated mica surfaces at this pH value of 5.5 (cf. Table 5 p. 169).

The most likely conclusion from the above discussion seems to be that the ammonium ion saturated mica surface had a small proportion of aluminium ions adsorbed onto it. Apart from a small amount of radioactive phosphate associated with these aluminium ions the only radioactive phosphate associated with the ammonium ion saturated mica surface is actually associated with the mica surface itself.

From the above experiments it appeared that, as is the case with sodium ions, there was no radioactive phosphate associated with either ammonium or potassium ions when these ions were present neutralizing the excess negative charge on a mica surface, and this surface was brought into contact with a solution of radioactively labelled phosphate ions.

Experiments on hydrogen ion saturated mica surfaces were performed at pH values of 1.0 and 3.0. Very little radioactive phosphate was adsorbed onto the mica surface at a pH value of 1.0. This was not unexpected as, at this pH value, the radioactive phosphate would be present mainly as H_3PO_4 molecules, which are uncharged,

and so it would be unlikely to form a strongly bound complex with the mica surface itself or any ions that happened to be present adsorbed onto the mica surface. At a pH value of 3.0 however, as has been shown earlier, there is adsorption of radioactive phosphate onto the mica,surface itself. Also at this pH value any multivalent ions such as aluminium present adsorbed onto the mica surface will form complexes with the radioactive phosphate in contact with it.

A mica surface was placed in contact with hydrogen form ion exchange resin for four weeks. The surface was then adjusted to a pH value of 3.0 and an experiment performed with radioactive phosphate at a pH value of 3.0. All the solutions used for adjustment of the pH value, and the desorbing solutions, were made up with deionised water contained in polythene beakers and containers. Analysis of the desorption curve for this experiment showed the presence of three first order desorption processes for desorption of the adsorbed radioactive phosphate corresponding to three different complexes with the hydrogen ion saturated mica surface.

The rate constants that were obtained, 1.9×10^{-2} minutes^{-1}, 1.6×10^{-3} minutes^{-1} and 6.1×10^{-5} minutes^{-1}, gave rise to the belief that there were still some

aluminium ions present on the mica surface because of their similarity to the rate constants observed for the desorption of radioactive phosphate from aluminium saturated mica surfaces (cf. p. 166). If this was so, it could be because the method of preparation of the hydrogen ion saturated mica surface did not exclude all traces of aluminium ions sufficiently well.

Clay minerals in which a net negative charge on the surface of the clay particles is neutralized by hydrogen ions are not normally stable. A breakdown tends to occur with the liberation of aluminium ions which replace the hydrogen ions on the surfaces. However, as was discussed earlier (p. 130), this breakdown was considered unlikely to occur significantly in the present work, due to the almost complete shielding of the edges of the mica sheets used with wax. Thus it would not have been expected that much aluminium would have been present on the mica surface from such a breakdown.

It has previously been found (see for instance the description of the experiment on an ammonium ion saturated mica surface(p. 188)) that the presence of only a relatively small amount of aluminium ions is sufficient to give rise to a readily detectable amount of the complexes associated with these ions. It may well be that there was actually a small amount

of aluminium ions present in the above experiment, most of the ions present being hydrogen ions. It may not be possible to prevent the presence of such an amount of aluminium ions on a hydrogen ion saturated mica surface. Even the small amount of structural breakdown of the mica surface may release a sufficient quantity of aluminium ions so that the radioactive phosphate that becomes associated with them makes up a significant proportion of the total amount adsorbed. A series of further, rigorously performed (with regard to the exclusion of aluminium ions), experiments on hydrogen ion saturated mica surfaces could be performed to investigate this matter.

6.3 The Effect of Drying on Radioactive Phosphate - Mica Surface Complexes

The various types of adsorption complex between the radioactive phosphate and the cation saturated mica surface being studied in this thesis are formed in aqueous solution. It was not known whether the difference between the various complexes observed was related to the presence or absence of water molecules in association with some of them. If this was so, some or all of the complexes might be affected by the removal of any surplus water that was only loosely held on the mica surface in association with either the mica surface itself, the positive ions thereon, or the adsorbed radioactive phosphate molecules. Any change in the nature of the complexes present caused by removal of water, leading to the formation of a new complex or to an alteration of the relative proportions of the complexes already present, could be subsequently detected from analysis of the results of the desorption experiment. This change would be a change in, respectively, the rate constants obtained for each species of complex present, or the relative amounts of each complex present which are calculated from the intercepts of each species with the initial time axis in the desorption graph.

A mica surface was saturated with aluminium nitrate solution and then soaked in radioactive phosphate solution

after all the usual pH value adjustments and background count rate determination procedures had been carried out. After rinsing off any surplus radioactive phosphate solution, the mica surface was stored in a desiccator over freshly dried silica gel. The mica surface was left in the desiccator for three weeks. This drying time had elapsed the mica surface was placed in two litres of distilled water that had been adjusted to the same pH value (5.5) at which the initial part of the experiment had been carried out. The subsequent desorption of the radioactive phosphate from the mica surface into the two litres of distilled water was recorded and analysed.

No observable change in either the type, or number, of the complexes present were detected. It was found that the relative proportions of each complex present were unaltered. From these facts it appears that there was no effect on the complexes between the radioactive phosphate and the aluminium saturated mica surface on prolonged drying. Thus any water molecules that are associated with the complexes present must be sufficiently tightly bound to be stable under the drying conditions imposed.

The actual analysed desorption graph of the above experiment is shown in the experimental data section on pp.303-4. It will be seen to be very similar to experiments performed at the same pH value but without any drying (pp.292-3)

6.4 The Effect of Adsorption Time on the Amount of Radioactive Phosphate Adsorption

The length of time for which radioactive phosphate was adsorbed onto the mica surface under study was one of the factors determining the amount of adsorption occurring in an experiment. In most of the experiments carried out in this thesis the adsorption time has been kept constant at 30 minutes. Provided any series of experiments was carried out with the same adsorption time for each experiment, comparisons could be made between individual experiments in the series, without having to consider the effect of the adsorption time.

After an adsorption time of 30 minutes the subsequent desorption curve of radioactive phosphate from aluminium saturated mica surfaces was analysable into three different desorption rates. It was considered that these three different desorption processes corresponded to three different types of radioactive phosphate-aluminium saturated mica surface complex. These three different complexes had widely different half-lives of desorption in contact with aqueous solution. By half-lives in this context is meant the time required for half the amount of radioactive phosphate present at any one moment to desorb into solution.

These half-lives, which are inversely proportional to the rate constants associated with each complex species

present, are characteristic of the ease of desorption of the different complexes from the aluminium saturated mica surface. Because of the large differences in the magnitudes of these half-lives it might be expected that in a given adsorption time the actual amounts of each of the three complexes formed would be somehow related to the different complexes themselves. If this was so, then adsorption for a different length of time might be expected to lead to a change in the relative amounts of the three complexes present, as well as to a variation in the total amount of radioactive phosphate adsorbed. Consequently it was decided to investigate this possibility.

Two aluminium saturated mica surfaces were prepared and adjusted to a pH value of 5.5. Sheets of freshly split mica were used, together with the metal container that had been designed for use in conjunction with them (see p.41). The two mica surfaces were cut from the same mica sheet, adjacent to each other, so as to have the mica thickness as near to identical for the two pieces used as possible. The edges of the mica surfaces so cut were coated with paraffin wax so that as equal an area as possible was left unwaxed and ready for radioactive phosphate adsorption. A stock radioactive phosphate solution was prepared having a pH value of 5.5. Experiments were carried out on the two aluminium saturated mica surfaces

using portions of the same radioactive phosphate solution. The adsorption time for one experiment was 5 minutes, and for the other experiment 30 minutes.

Analysis of the two desorption curves showed that for both experiments the radioactive phosphate adsorbed had formed three distinct complexes with the aluminium saturated mica surface (as characterised by the rate constants for the three desorption rates). These complexes were the same in both experiments, and the relative proportions of each complex to the total amount adsorbed were the same in each experiment. This indicated that the rate of adsorption of radioactive phosphate onto the adsorption sites corresponding to each of the three complexes formed must be the same, or at least very similar.

The total amount of adsorption of radioactive phosphate onto the mica surface that had been soaked in the radioactive phosphate solution for 30 minutes was greater than the total amount adsorbed after only 5 minutes of soaking. The count rate at the commencement of the desorption experiment after 30 minutes soaking was 35,500 c.p.m., and the initial count rate after 5 minutes soaking was 20,000 c.p.m. Thus after 30 minutes soaking in radioactive phosphate solution

$\frac{35,500}{20,000}$ or 1.8 times as much radioactive phosphate

was adsorbed onto an aluminium saturated mica surface as after 5 minutes soaking.

The validity of the above ratio of the total amounts of radioactive phosphate adsorbed onto the aluminium saturated mica surface for two different time intervals of adsorption was dependent on there being no significant difference between the two mica sheets used for the experiments. In order to eliminate such a factor from consideration in the calculation of the ratio obtained, further experiments were carried out. After all the radioactive phosphate had been removed from the two mica surfaces they were prepared as above, being saturated with aluminium ions and then having their ph value adjusted to 5.5. For the sake of the following explanation the two mica surfaces used will be called "R" and "S".

In the first pair of experiments surface "R" was soaked in radioactive phosphate for 5 minutes and surface "S" was soaked for 30 minutes. The results already obtained had shown that the same adsorption processes had occurred with both the surfaces "R" and "S". Thus the only differences in the two surfaces that could have had an undetected effect on the ratio of the total amounts of adsorption would have been differences in the total area available for adsorption or in the effective thicknesses of the mica surfaces (that is, the thickness of the mica surface itself plus the

coating of wax that had been applied to the inside surface of the mica sheet (see p. 43)).

Another possible factor leading to a difference in the observed count rates caused other than by different times of adsorption of the radioactive phosphate could have been a difference in the counting efficiencies of the two geiger counters used. A separate geiger counter was used with each of the metal containers used so that removal and reinsertion of the geiger counters could not lead to a change in the counting characteristics of the geiger counter plus metal container (with mica surface waxed over one end) assembly.

As it was desired to ensure that none of the three abovementioned factors had any influence on the assumptions made from the experimental data obtained (that is the calculation of the ratio of the total adsorptions with different adsorption times) two further experiments were performed. First of all the two geiger counters associated with the mica surfaces "R" and "S" were exchanged with each other so that the geiger counter that was originally in the metal container with the mica surface "R" was now in the metal container with mica surface "S" and vice versa. Two further experiments on the adsorption and subsequent desorption of radioactive phosphate from the mica surfaces "R" and "S" were then carried out. However the relative adsorption times were

reversed in comparison with the first pair of experiments carried out. The mica surface "S" was soaked in radioactive phosphate for 5 minutes, and the mica surface "R" was soaked in radioactive phosphate for 30 minutes. Desorption experiments were then carried out on the two mica surfaces and the relevant desorption curves replotted in the usual way and analysed.

The increase in count rate of the system containing the mica surface "S" was found to be 2,800 c.p.m. after 5 minutes adsorption time. The increase in count rate of the mica surface "R" after 30 minutes adsorption time was 4,500 c.p.m. From these two figures the ratio of the total amount of adsorption of radioactive phosphate from the radioactive phosphate solution after 30 minutes adsorption time to the amount adsorbed after only 5 minutes adsorption time is seen to be $\frac{4,500}{2,800}$ or 1.6 to 1. This figure is in good agreement with that calculated from the first pair of experiments with these adsorption times of 1.8 to 1.

Considering the above experimental data, it seemed that the total adsorption of radioactive phosphate onto an aluminium saturated mica surface at a pH value of 5.5 was approximately 1.7 times as much after a 30 minute adsorption period as after a 5 minute adsorption period.

Adsorption of radioactive phosphate onto aluminium

saturated mica surfaces has been carried out for periods of time up to 60 minutes. It was found that more radioactive phosphate was adsorbed in experiments with longer adsorption times, but no evidence was obtained that suggested that there were other than three different complexes formed with the same relative amounts as were adsorbed after 30 minutes adsorption time.

From the above experiments it can be concluded that the adsorption of radioactive phosphate onto aluminium saturated mica surfaces seems to lead to the formation of three different radioactive phosphate - aluminium saturated mica surface complexes. The rate constants for the desorption of these complexes into aqueous solution, and the relative proportions of each complex present seem to be independent of the adsorption time, at lease for adsorption times of up to one hour. The actual amount of adsorption appears to increase with increasing adsorption time.

6.5 Relationship of Temperature to Radioactive Phosphate Adsorption

All the experiments that have been carried out in this thesis have been carried out at room temperature. All the desorptions of radioactive phosphate were carried out into two litres of solution that was continuously stirred. The temperature of these solutions was found to stay fairly constant at about 23± 1 °C for all the experiments during the course of the work done. This temperature was slightly above the room temperature which was usually about 20 °C. The increased temperature is believed to be due to the heat from the magnetic stirrer on which the two litres of desorbing solution were placed and also, possibly, due partially to the work done by the stirrer itself.

The three different desorption rates detected for the desorption of radioactive phosphate from aluminium saturated mica surfaces might be dependent on the temperature at which the desorption took place. In an endeavour to test the likelihood of this possibility an attempt was made to do an experiment at a markedly different temperature from that at which all the rest of the work had been done.

0°C, the temperature of melting ice, seemed the most easily obtainable temperature. A large, insulated, square box was obtained (actually a thermostat without

a central rotating spindle) and this was packed with an ice/water mixture. A two litre beaker almost full of water was immersed in this ice/water mixture so that the outside level (of the ice/water mixture) was slightly higher than the level of the internal solution. This two litres of water was stirred with an overhead stirrer motor and a centrifugal stirrer (the same one as was used in the experiments conducted at a pH value of 9.0 (see p. 91)). to ensure good circulation of the two litres of water. The temperature of the two litres of water was measured over a period of 12 hours and found to be constant at $+ 1.0 \pm 0.1^{\circ}C$. Thus by a twice daily renewal of the ice/water mixture the two litres of water could be kept at this constant temperature.

A geiger counter was taken and, after it had been checked and found to be functioning satisfactorily, the mica surface of the end-window was immersed in the two litres of water at $+ 1.0^{\circ}C$. The outside edges of the geiger counter end-window had already been coated with wax as usual. After some time had elapsed to allow the geiger counter to reach the temperature of the water it was connected to the electronic apparatus. It was found that the plateau of the geiger counter, which had previously been greater than 200 volts in length, was very short and the geiger counter readily went into continuous discharge.

As a check that a sudden bre kdown in the geiger counter had not occurred in some way it was removed from the solution and allowed to warm up to room temperature. It was then found to be functioning satisfactorily. While still connected to the electronic apparatus, the geiger counter end-window was once more immersed in the two litres of water at + 1.0°C. The plateau length of the geiger counter was observed to decrease with time, until it was impossible to measure the background count rate at all.

From the above experiments it appeared that the geiger counters used were not capable of being used at such a temperature with their mica end-windows immersed in water. As, according to the manufacturers, they were supposed to function satisfactorily over a wide range of temperature from below 0°C upwards, it seemed that immersion of the geiger counter end-window in solution reduced the temperature range over which they could satisfactorily be used. Because of the failure of this experiment an investigation of the effects of temperature change on either the nature or the amount of the various complexes of the radioactive phosphate on cation saturated mica surfaces has not been carried out.

The above experiments were carried out before the alternative method of experimentation using the metal

container, with a mica surface on one end, surrounding a geiger counter had been devised. It seems possible that a successful experiment at reduced temperatures would be performed using this apparatus. The end-window geiger counter, not being in actual contact with any solutions, might be found to function satisfactorily at these low temperatures. Further experiments might also be possible at higher temperatures (say 35 - 45°C) and thus activation energy data could possible be calculated.

6.6 Radioactive Phosphate Adsorption on to Hydrated Aluminium Oxide Surfaces

Most of the desorption experiments in this thesis have been carried out with mica surfaces. However the experimental method could be applied equally well to any other surfaces, providing suitable methods for the detection of the radioactive phosphate (or any other adsorbing group with a suitable radioisotope that it was desired to study) could be found. As a considerable amount of experimentation had been done on aluminium saturated mica surfaces it was also decided to study the adsorption and subsequent desorption of radioactive phosphate from aluminium surfaces.

The actual surface studied will not be pure aluminium. There will be a thin film of aluminium oxide on the surface of the aluminium studied and there may be some hydroxyl groups present as well.

For the first experiment on an aluminium surface a different type of geiger counter was used. This was a type 1 B 85 Thyrode Counter Tube. (For details of this geiger counter see p. 53). The outside of this geiger counter was an aluminium tube. As the geiger counter was designed for use in a portable monitor (Victoreen Thyac Survey Meter, Model 389C [1]) the aluminium wall (which

(1) Manufactured by The Victoreen Instrument Co. Cleveland, Ohio, U.S.A.

was actually the cathode) would have been thin enough to easily transmit the β particles emitted by ^{32}P.

The top of the aluminium tube was coated with paraffin wax so that a constant area of aluminium could be studied. This area of aluminium was soaked in distilled water with a pH value of 5.5 six times for at least 30 minutes each time. It was hoped by this procedure to bring any hydroxide or other groups, the nature of which might depend on the pH value, to the configuration that they would be expected to have at this pH value. The aluminium surface of the geiger counter was then immersed in two litres of distilled water having a pH value of 5.5 and the background count rate determined. After the background count rate of the geiger counter in the two litres of solution had been determined, the aluminium surface of the geiger counter was immersed in radioactive phosphate solution with a pH value of 5.5 for a suitable period of time (30 minutes), removed and rinsed in distilled water with a pH value of 5.5.

The count rate of the geiger counter due to the adsorbed radioactive phosphate was now determined. It was found to be about 50,000 c.p.m. (uncorrected for coincidence loss) which was too high to measure on the rate meter and strip chart recorder. If the oxide layer on the outside of the aluminium tube was not too tightly bound to the aluminium it might have been possible to rub some of this

coating off, together with the adsorbed radioactive phosphate associated with it. It was also possible that such rubbing would remove the adsorbed radioactive phosphate alone. In order to see if the above possibilities existed the aluminium surface was rubbed with sheets of filter paper, care being taken not to induce radioactive contamination of anything (except the filter paper). After prolonged rubbing it was found that the count rate was reduced to about 30,000 c.p.m. (uncorrected) at which stage the aluminium surface was reimmersed in the two litres of solution and the change in count rate with time measured as usual.

The observed count rate decreased very slowly with time, showing that there was no longer present any complexes between the radioactive phosphate and the the aluminium surface desorbing with a rapid rate. Owing to the high count rates involved, accurate calculation of the coincidence loss was very difficult, and because of the very slow rate of loss of the radioactive phosphate the count rate at each time interval needed to be known accurately if analysis of the desorption curve was to be attempted. The count rate calculated after desorption had occurred for 30 minutes was about 43,000 c.p.m. and after 420 minutes (7 hours) about 42,000 c.p.m. Because of this very slow fall in the count rate no attempt

was made to analyse the desorption curve into its components (if any) or to calculate any rate constants.

After desorption had occurred for some time (about 40 hours) the geiger counter became unstable and very readily went into continuous discharge. The plateau length was found to have diminished from greater than 200 volts to about 10-20 volts. Accordingly the geiger counter was put aside as being of no further use at the time.

Another way of studying the adsorption of radioactive phosphate onto aluminium surfaces employed was by use of thin sheets of aluminium instead of mica sheets as had been used for some of the work in this thesis with the metal containers. Thin sheets of aluminium (thickness = 0.05 mm.) were obtained and were attached to the metal containers in the same way as the mica sheets had been. The preparation of these aluminium sheets plus metal containers has been described earlier (see p. 45).

Experiments were performed on these aluminium sheets at a range of pH values (3.0 - 9.0). Experiments were not carried out at very high or very low pH values as aluminium is soluble in both acids and alkalis. The experiment performed at a pH value of 9.0 was carried out with the totally enclosed apparatus designed for work at this pH value (cf. p. 91). The aluminium sheet

was sealed over the end-window of the geiger counter used with this apparatus with wax, and the experiment performed in the same way as with the mica surface of the geiger counter end-window at this pH value.

Before commencing each experiment on the aluminium surfaces the surfaces were soaked in distilled water previously adjusted to the pH value at which the experiment was to take place by the use of hydrochloric acid or sodium hydroxide. This soaking was carried out six times for at least 30 minutes each time. The usual experimental procedure was then carried out and, after desorption of the adsorbed radioactive phosphate into distilled water with the same pH value as that at which the experiment was being performed, the resultant desorption curve was analysed.

The experiment conducted at a pH value of 3.0 was carried out twice. Reasonable agreement was obtained between the values calculated for the rate constants, and also between the relative amounts of each corresponding complex. The values obtained for the rate constants, and the relative amounts of each corresponding complex are given for the two experiments performed at a pH value of 3.0 in Table 7 .

TABLE 7.

	First Experiment	Second Experiment	Average
rate constant for first complex "E"($=k_e$)	1.9×10^{-2} mins.$^{-1}$.	1.6×10^{-2} mins.$^{-1}$.	1.7×10^{-2} mins.$^{-1}$
rate constant for second complex "F"($=k_f$)	1.7×10^{-3} mins^{-1}.	1.0×10^{-3} mins^{-1}.	1.3×10^{-3} mins.$^{-1}$
rate constant for third complex "G"($=k_g$)	3.7×10^{-4} mins.$^{-1}$.	3.3×10^{-4} mins.$^{-1}$.	3.5×10^{-4} mins.$^{-1}$
relative amount of "E" (as % of total amount)	41%	39%	40%
relative amount of "F" (as % of total amount)	44%	42%	43%
relative amount of "G" (as % of total amount)	15%	19%	17%

As can be seen from Table 7 there are apparently three different radioactive phosphate-aluminium complexes present at a pH value of 3.0.

The adsorption of radioactive phosphate onto an aluminium surface was also performed once at pH values of 5.5 and 9.0. From a study of the desorption curves of radioactive phosphate from aluminium at these pH values

there appeared to be three different complexes present at a pH value of 5.5 and only one complex at a pH value of 9.0. The rate constants and the relative amount of each complex detected at the two pH values are given in Table 8.

TABLE 8.

pH value	radioactive phosphate - aluminium complex	rate constant (minutes $^{-1}$)	relative amount of complex present
5.5	"H"	$k_h=0.8\times10^{-2}$	32%
5.5	"I"	$k_i=0.8\times10^{-3}$	21%
5.5	"J"	$k_j=3.9\times10^{-5}$	47%
9.0	"L"	$k_l=3.3\times10^{-5}$	100%

The rate constant k_l of the only detected complex "L" present at a pH value of 9.0 is in good agreement with the smallest rate constant k_j obtained from the desorption curve of the experiment performed at a pH value of 5.5. From this it may be considered that there is a possibility that both the complexes characterised by the rate constants k_j and k_l are of a similar nature. This similarity of rate constant, which is based on only one pair of experiments

cannot however be taken as conclusive evidence of such a similarity between the two complexes.

The two other rate constants found at a pH value of 5.5, k_h (=0.8 x 10^{-2} minutes^{-1}) and k_j(= 0.8 x 10^{-3} minutes^{-1}) are comparable in magnitude to the two largest rate constants calculated from the experiments conducted at a pH value of 3.0, namely k_e (= 1.7 x 10^{-2} minutes^{-1}) and k_f(= 1.3 x 10^{-3} minutes^{-1}). Although the agreement between the two sets of figures is by no means good, the two complex species present at these two pH values may be the same. More duplicate experiments would be needed to be done to investigate this point further.

If the two complex species were of the same type it would appear that the relative proportions of the two alter markedly with the change in the pH value. At a pH value of 3.0 there were approximately equal amounts of the two complexes "E" and "F", there appearing to be slightly more of "F" (see Table 7). At a pH value of 5.5 however, there was approximately one and a half times as much of "H", which may correspond to "E", as there was of "I" (corresponding to "F"). Also the percentage of the total adsorbed radioactive phosphate which was present as these two complexes altered with the change in pH value. "E" plus "F" accounted for about

80% of the total amount of adsorbed radioactive phosphate on the aluminium surface at a pH value of 3.0, while "H" and "I" made up only about 50% of the total adsorbed radioactive phosphate at a pH value of 5.5.

The smallest rate constant found at a pH value of 3.0, k_g ($= 3.5 \times 10^{-4}$ minutes^{-1}) was approximately ten times as large as the common rate constant found at pH values of 5.5 and 9.0 (average of k_j and k_l $= 3.6 \times 10^{-5}$ minutes^{-1}). Thus it seemed very unlikely that the radioactive phosphate-aluminium surface complex "G" associated with k_g was the same complex as was found at higher pH values ("J" and "L").

6.7 The Effect of Desorption Time on the Analysis of Results

The techniques devised by the author in this thesis have recently been applied by other workers to a study of mica saturated with some other cations. Some work has been done by Morris (1964) on iron saturated mica surfaces. He studied the desorption of previously adsorbed radioactive phosphate from iron saturated mica surfaces for very long periods of time. The results that he obtained were similar to those obtained in the present work with aluminium saturated mica surfaces with one significant difference. It appeared that there was a radioactive phosphate-iron saturated mica surface complex with an extremely small rate constant, about one tenth of the smallest rate constant observed in the present work of about 5×10^{-5} minutes^{-1}. The existence of this very slowly desorbed complex was detected only by carrying out desorption experiments for much longer periods of time than had been done in the author's work with aluminium saturated mica surfaces.

Analysis of desorption experiments has been carried out graphically in this thesis as has been explained earlier (p. 67). The information actually determined from the desorption graph was the half-lives of the complexes on the cation saturated mica surfaces. These

half-lives are inversely proportional to the rate constants for the desorption of each complex. When the desorption experiments were performed for up to 200 hours all the loss of radioactive phosphate from the mica surface could be satisfactorily accounted for by the existence of a complex with a half-life of about 250 hours (which is equivalent to a rate constant of 5×10^{-5} minutes^{-1}) plus two complexes with shorter half-lives. In the work done by Morris the existence of the complex with a very long half-life (equivalent to a very low rate constant) was only apparent after considerably more than 200 hours of the graph of the desorption experiment had been analysed. As a consequence of this it was decided to perform a desorption experiment with an aluminium saturated mica surface for a considerably longer period than had been done before.

An aluminium saturated mica surface was prepared in the usual manner and adjusted so that it had a pH value of 5.5. After adsorption of radioactive phosphate, desorption was carried out into two litres of distilled water with a pH value of 5.5. The first 120 hours were followed on the strip chart recorder. After this time the count rate was measured periodically with an electronic counter. As the change in count rate was very small after such a long desorption time an accurate value of the count rate at various times was most important.

The total number of counts over a long period of time (1 - 2 hours usually) was determinted, and thus the uncertainty in the count rate was reduced. The electronic counter was checked against the strip chart recorder and found to give the same value for a fixed count rate (using a uranium source) over a range of count rates. Thus the values of the count rate from both the strip chart recorder and the electronic counter could be satisfactorily used together on the same graph without the necessity for any correction of one relative to the other. The desorption experiment was followed for a total period of 770 hours.

Graphical analysis of this experiment revealed the presence of four complexes with different rate constants. Two of these rate constants, 2.3×10^{-2} minutes^{-1} and 1.9×10^{-3} minutes^{-1}, were approximately the same as two of the three rate constants that had been detected in the previous experiments on aluminium saturated mica surfaces. The other two rate constants were both different to the third rate constant of 5×10^{-5} minutes^{-1} which had been detected in previous experiments, one being greater and one less than this value. The actual values obtained were 2.4×10^{-4} minutes^{-1} and 10×10^{-6} minutes^{-1}. The smallest rate constant was within a factor of two of the values obtained by Morris (1964) of 4.5×10^{-6} minutes^{-1} for this very slowly desorbing complex on an iron saturated mica surface.

The above experiment involving desorption for a very long period of time was repeated in the same way. Four different rate constants were again obtained, their values being:

(1) 1.9×10^{-2} minutes^{-1}

(2) 2.1×10^{-3} minutes^{-1}

(3) 2.2×10^{-4} minutes^{-1}

and (4) 3.0×10^{-6} minutes^{-1}

The three largest rate constants were very similar to those obtained in the first experiment wherein the desorption was followed for such a long period of time. The smallest rate constant of 3×10^{-6} minutes^{-1} was somewhat different from that obtained in the first experiment, but it was still of the same order as the value first obtained, and also of the same order as the value obtained in the work with iron saturated mica surfaces.

Thus it appears that the radioactive phosphate-aluminium saturated mica surface complex which was previously thought to exist and to have a rate constant for desorption into distilled water of 5×10^{-5} minutes^{-1} was actually a mixture of two complexes with rate constants of about 2×10^{-4} minutes^{-1} and 5×10^{-6} minutes^{-1}. The actual value for the smallest rate constant was not obtained with great certainty. A slight difference in the graphical analysis could lead to a considerable variation in the actual value obtained, but it seems definitely to be between

10^{-6} and 10^{-5} $minutes^{-1}$.

As will be seen from the values quoted above for the two largest rate constants for desorption, which are very similar to the values obtained in the previous experiments of $2x10^{-2}$ $minutes^{-1}$ and $2x10^{-3}$ $minutes^{-1}$ (see p.166) the splitting of the complex associated with the third, smallest rate constant (as obtained in the previous experiments) into two parts has not had any effect on the first two, less strongly bonded, complexes.

The splitting up of the most tightly held complex into two complexes has only been performed at the one pH value of 5.5. As the original three complexes were detected over the range of pH values detected (3.0 -9.0), it seems probable that there are actually four complex species present at all the pH values in the range studied.

From the two experiments performed with very long desorption times the relative amounts of the two complexes with the smallest rate constants have been calculated at a pH value of 5.5. If the two complexes are called "C" and "D" then the amount of "C_1" plus "D" relative to the total amount of adsorption of radioactive phosphate will be the same as was originally found for the complex "C" that was believed to exist. This amount, at a pH value of 5.5, was 30-35 % of the total amount of radioactive phosphate present (see Table 6p. 170)

In the two experiments described above the ratio of "D" to "C_1" was found to be 1,870 c.p.m. ± 590 c.p.m. or 3:1 for the first experiment and 3,600 c.p.m. ± 1,760 c.p.m. or 2:1 for the second experiment. Thus it appears that there is between two and three times as much of the complex with the lowest rate constant as there is of the complex with the next lowest rate constant. The relative amounts of each of the four complexes "A","B","C_1" and "D" now believed to be present instead of the original three complexes "A", "B", and "C" are given in Table 9 for a pH value of 5.5.

TABLE 9 .

radioactive phosphate-aluminium saturated mica surface complex	rate constant of complex (minutes^{-1})	relative amount of complex (%)
"A"	2×10^{-2}	40-45
"B"	2×10^{-3}	~25
"C_1"	2×10^{-4}	~10
"D"	5×10^{-6}	20-25

As was mentioned above it seems probable that there are actually four complexes present at the other pH values studied (3.0 - 9.0). To obtain the relative amounts of each of these complexes it would be necessary to perform experiments at these pH values in which desorption

was carried out for some hundreds of hours as in the experiments described immediately previously at a pH value of 5.5.

When the desorption of radioactive phosphate from an aluminium saturated mica surface was carried out for a period of about 100-200 hours analysis of the desorption curve obtained indicated the presence of three complexes with rate constants for desorption of 2×10^{-2} minutes^{-1}, 2×10^{-3} minutes^{-1} and 5×10^{-5} minutes^{-1}. If however, the desorption experiment was carried out for 500-1,000 hours, subsequent analysis revealed the presence of four complexes whose rate constants were 2×10^{-2} minutes^{-1}, 2×10^{-3} minutes^{-1}, 2×10^{-4} minutes^{-1} and 5×10^{-6} minutes^{-1}. Examination of these two series of figures suggests an interesting possibility. From the data obtained there seems no reason why the complex with a rate constant for desorption of 5×10^{-6} minutes^{-1} does not actually consist of two complexes with rate constants of 2×10^{-5} minutes^{-1} and 5×10^{-7} minutes^{-1}. However with the radioactive counting techniques at present available there seems little hope of verification or otherwise of such a hypothesis.

In order to detect a rate constant of 5×10^{-7} minutes^{-1} it would seem, by analogy with the results obtained from the above desorption times, that it would be

necessary to follow the desorption for a period of time of the order of at least 5,000 hours. This does not seem possible owing to the magnitude of the necessary correction for the radioactive decay of the ^{32}P atoms. The maximum count rate that can be measured reliably with the present electronic arrangement is certainly not more than a corrected count rate of about 40,000 c.p.m. This corresponds to a measured count rate of about 30,000 c.p.m. before correction for coincidence loss.

The amount of the complex with rate constant 5×10^{-6} minutes^{-1} is only 20-25 % of the total amount of radioactive phosphate initially present on the aluminium saturated mica surface (see Table 9, p.222). The suspected complex with rate constant 5×10^{-7} minutes^{-1} would be only part of this, and so the maximum initial count rate due to this complex would be less than 10,000 c.p.m.. If this amount of radioactive phosphate was allowed to decay through eight half-lives the count rate would be then less than 40 c.p.m. above the background count rate, an amount that could be accurately measured only with difficulty. But eight half-lives for ^{32}P ($t_{\frac{1}{2}}$ = 14.30 days) is only 2,800 hours, and this would certainly not be long enough to enable analysis of the desorption curve to reveal the presence of a complex with a rate constant for desorption of 5×10^{-7} minutes^{-1}, if such a complex existed.

If the existence of such a complex were to be investigated it would be necessary to obtain counting

equipment that could measure, with some degree of accuracy, very high count rates. One possibility might be the use of a scintillation counter in some way, but this would give rise to technical problems owing to the describing arrangement necessary. Five thousand hours is equal to about fourteen half-lives for radioactive phosphorus. Consequently if it was desired to have a final count rate, after the passage of such a period of time, of 100 c.p.m. above the background count rate, the initial count rate would have to be greater than 1.6×10^{6} c.p.m..

One possible method of measuring such a high initial count rate would be by using the metal container plus mica surface designed during the course of this thesis and inserting accurately known thicknesses of lead between the mica surface and the geiger counter end-window during the earlier part of the experiment. If the count rate could be reduced by a factor of exactly 100 for instance, the actual initial count rate could be calculated from the observed initial count rate. When the count rate had dropped considerably (after about 1,500 hours) the lead could be removed, and the observed count rate would then become 100 times greater. In this manner it would be possible, theoretically, using the present electronic arrangement, to have

an actual initial count rate of 3×10^{6} c.p.m.

Five thousand hours is approximately seven months, and over such a long period of time difficulty might be encountered with the mica sheet splitting, or some such other factor upsetting the experiment. Because of this it seems that the hypothesis of the existence of such a radioactive phosphate-aluminium saturated mica surface complex will not lead to a practical investigation.

The experiments performed on the desorption of radioactive phosphate from aluminium saturated mica surfaces for long periods of time had shown that the complex with a rate constant for desorption of 5×10^{-5} minutes^{-1} was actually a combination of two complexes with rate constants for desorption of 2×10^{-4} minutes^{-1} and 5×10^{-6} minutes^{-1}. Previous experiments on sodium saturated mica surfaces had given rise to the belief that there was only one radioactive phosphate-sodium saturated mica surface complex present. It was believed that this complex had a similar rate constant for desorption to that observed with aluminium saturated mica surfaces, namely 5×10^{-5} minutes^{-1}. It therefore seemed pertinent to investigate the desorption of radioactive phosphate from a sodium saturated mica surface for a long period of time as had been done with the aluminium saturated mica surface.

An experiment was conducted with radioactive phosphate and a sodium saturated mica surface. The same precautions to ensure that the mica surface studied was free of aluminium ions were taken as has been described for the earlier experiments on sodium saturated mica surfaces (p. 139). The desorption of the radioactive phosphate was followed for 350 hours as it was felt that by this time it would be possible to ascertain if there was a complex species present with a rate constant for desorption of less than 5×10^{-5} minutes^{-1} or not. The experiment was conducted at a pH value of 5.5. The actual desorption graph may be found in the section of this thesis giving some actual experimental results (p. 312).

Analysis of the desorption curve showed the existence of only one complex accounting for the majority of the initially adsorbed radioactive phosphate present. This complex had a rate constant for desorption of the radioactive phosphate of approximately 6×10^{-6} minutes^{-1}. This was in good agreement with the smallest rate constant observed for the desorption of radioactive phosphate from an aluminium saturated mica surface. The little amount of adsorbed radioactive phosphate that was not desorbed with this rate constant appeared to have a fairly high rate constant ($\simeq 2 \times 10^{-2}$ minutes^{-1}) and was almost

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certainly due to the presence of a small percentage (relative to the number of sodium ions present) of aluminium ions.

There was no evidence for the existence of a complex with a rate constant comparable to that discovered in the long desorption experiments with aluminium saturated mica surfaces (2×10^{-4} minutes^{-1}) in the above experiment with a sodium saturated mica surface. This suggested that the three largest of the four rate constants for desorption found in the experiments with aluminium saturated mica surfaces were related to the presence of the aluminium ions. The other rate constant which appeared to be present in experiments with both sodium saturated and aluminium saturated mica surfaces seemed therefore to be related to a complex between the radioactive phosphate and the mica surface itself.

The above results obtained from the experiment with a sodium saturated mica surface suggest that the earlier experimental results on this system, which indicated the existence of only one complex species with a rate constant for desorption of 5×10^{-5} minutes^{-1}, may be in error. Further experiments with long desorption times would need to be done to obtain complete clarification of the results. However it does seem to have been established that there is very little radioactive phosphate associated with sodium

saturated mica surfaces, and what amount there is, is associated with the mica surface itself rather than the sodium ions. This complex between the radioactive phosphate and the mica surface has also been detected in experiments with aluminium saturated mica surfaces.

6.8. The Effects of Various Substances on the Desorption of Radioactive Phosphate

An investigation was carried out on the effects on the desorption of radioactive phosphate of conducting such a desorption into various solutions. Such studies can give an idea of the efficiencies of various substances for the removal of radioactive phosphate from the surfaces studied (mica and aluminium). There are many methods given in the literature for the extraction of phosphate from soil samples. The various portions of phosphate extracted by different reagents have often been attributed to different adsorption sites in the soil, e.g., aluminium bound phosphate, iron bound phosphate, organically bound phosphate, etc.

Most of the studies undertaken on the effects of various substances on the desorption rate of radioactive phosphate were carried out with aluminium saturated mica surfaces. Desorption into solutions of these substances was studied only after the usual desorption experiments had been allowed to continue for some time, usually about 100 hours. By this time all the radioactive phosphate present as complexes with rate constants 2×10^{-2} minutes^{-1} and 2×10^{-3} minutes^{-1} will have been desorbed into the desorbing solution. Thus what was actually being studied was the effect of these various reagents on the desorptior

of radioactive phosphate from the mica surface itself, as it is believed that the complex with the smallest rate constant for desorption of 5×10^{-5} minutes^{-1} is a complex between radioactive phosphate and the mica surface, not between radioactive phosphate and any cations adsorbed onto the mica surface. However it is thought that the presence of aluminium ions adsorbed onto the mica surface does have some relation to the amount of this radioactive phosphate - mica surface complex, as there is considerably more of this complex formed on aluminium saturated mica surfaces than on sodium saturated mica surfaces. This hypothesis is propounded in the section of this thesis discussing the experimental results (see p. 332)

The effects on the desorption rate of the various reagents studied may therefore possibly be related to the extraction of aluminium bound phosphate from soil samples. The effect of a number of reagents was studied. These reagents weresa follows:

1. Citric acid $HOOC.CH_2.C(OH)(COOH).CH_2.COOH, H_2O$ Concentration=0·2M
2. Tri-sodium citrate/citric acid buffer solution. Concentration of both reagents = 0·2M. pH value of buffer used=4·6
3. Distilled water saturated with carbon dioxide. The pH value of this solution was 4·7.
4. Sodium hydroxide NaOH. Concentration = 0·1N
5. Sulphuric acid H_2SO_4. Concentration = 0.5N

6. Hydrochloric acid HCl. Concentration = 0·5 N.

7. Ammonium fluoride NH_4F. Concentration = 0.5 M. The pH value of this solution was adjusted to 8·5 with concentrated ammonium hydroxide (NH_4OH)

The procedure followed with each of these reagents was the same. The amount of radioactive phosphate on the mica surface was measured in terms of the observed count rate while the mica surface was immersed in water. The actual count rate was falling gradually as the complex with the smallest rate constant (5×10^{-5} minutes^{-1}) was desorbed into the water. The mica surface was then immersed in a solution of one litre of the desorbing reagent being studied, and the rate of the decrease in the count rate as a result of the presence of this reagent was plotted on the stripchart recorder. In this way it was easy to see if the reagent used caused any increase in the rate of removal of the radioactive phosphate from the mica surface, over and above the rate of removal already being caused by the distilled water into which the desorption had previously been taking place.

It was found that citric acid solution, tri-sodium citrate/ citric acid buffer solution and carbon dioxide saturated water had little effect on the rate of removal of radioactive phosphate from an aluminium saturated mica surface. The rate of decrease of the observed count rate was only slightly enhanced by the presence of any

of these three reagents in the desorbing solution. The aforementioned three reagents were chosen because it has been suggested by some workers that the presence of carbon dioxide and of various organic acids, such as citric acid, in soils, due to root and fungal metabolism, influences the complexing of phosphate by iron and aluminium compounds (see for example Johnston, 1959; Paauw, 1955).

In the experiments in which the tri-sodium citrate/citric acid buffer solution and the carbon dioxide saturated water were used as desorbing agents the initial desorption experiment into distilled water was being conducted at a pH value of 5.5. Contact of the mica surface with these solutions of pH value 4.6 - 4.7 might have caused a lowering of the pH value of the mica surface which was saturated with aluminium ions, and which had some radioactive phosphate ions adsorbed onto it.

It has been shown previously in this thesis (p. 175) that the amount of radioactive phosphate adsorbed by an aluminium saturated mica surface for a 30 minute soaking time is considerably less at a pH value of 3.5 than at a pH value of 5.5. There is no reason to suppose that the amount of radioactive phosphate adsorbed onto an aluminium saturated mica surface does other than decrease continuously with a fall in pH value over this

range (5·5 - 3·5). Thus the amount of radioactive phosphate adsorbed at a pH value of 4·6 - 4·7 would be expected to be less than the amount adsorbed at a pH value of 5·5. The actual reason for the slight increase in the rate of removal of radioactive phosphate from aluminium saturated mica surfaces caused by these two reagents (tri-sodium citrate/citric acid buffer solution and carbon dioxide saturated water) has not been decided but it seems that it may be related largely to the lowering of the pH value that their use would cause.

The effect of an 0·2 M solution of citric acid on the desorption of radioactive phosphate from a mica surface was investigated during the preliminary experiments that were performed in this thesis. The experiments concerned had not been carried out at a controlled pH value, but the actual pH value would have been about 3·5. The effect of the citric acid would have been to lower the pH value of the mica surface and adsorbed radioactive phosphate. As was discussed above with the other reagents (tri-sodium citrate/citric acid buffer solution and saturated solution of carbon dioxide) this lowering of the pH value may be at least partially responsible for the enhanced rate of release caused by the use of citric acid solution.

The use of sodium hydroxide as a desorbing reagent for radioactive phosphate on aluminium saturated mica

surfaces was investigated. The use of 0·1N sodium hydroxide has been reported in the literature (e.g. by Ghani, 1943; Williams, 1950; Chang and Jackson, 1957) as a reagent for the extraction of phosphate from the soil. It is believed to extract all aluminium and iron bound phosphate from the soil. It was found that on placing the mica surface in 0·1N sodium hydroxide the rate of removal of radioactive phosphate was greatly accelerated. A large amount of the radioactive phosphate was desorbed almost immediately (within 30 minutes or less) and the remaining amount was removed fairly readily so that the observed count rate fell almost to background in a few hours.

The pH value of 0·1N sodium hydroxide is 13. Consequently the placing of the mica surface in this solution would be expected to raise considerably the pH value of all the various species associated with the mica surface, that, is the aluminium ions and the radioactive phosphate ions. As has been discussed earlier (p.177) , at high pH values, such as might be expected to exist on the mica surface when placed in contact with 0·1N sodium hydroxide, the aluminium ions on the mica surface would have a similar configuration to the aluminate ion, that is, have effectively one negative charge associated with them. Similarly any sites on the mica surface itself

that could be

affected by a change in the pH value would be negatively charged if at all possible.

The radioactive phosphate ions, under the influence of the 0·1N sodium hydroxide, would be expected to exist mainly as PO_4^{3-} ions. As these ions are highly negatively charged, and the mica surface would be effectively negatively charged also (at least because of the close proximity of the negatively charged pseudo-aluminate groups), it would be expected that there would be little if any attraction between the radioactive phosphate ions and the aluminium saturated mica surface under these conditions. Thus rapid desorption of radioactive phosphate from the aluminium saturated mica surface would be expected on placing this surface in contact with 0·1N sodium hydroxide solution.

This phenomenon was actually observed in a number of experiments carried out a range of pH values from 3.0-9·0. It thus appeared that the placing of aluminium saturated mica surfaces, on which radioactive phosphate had previously been adsorbed, into 0·1N sodium hydroxide solution raised the pH value of the surface to a value greater than 9·0, with consequent more rapid desorption of the radioactive phosphate.

The effect on the desorption rate of radioactive phosphate from aluminium saturated mica surfaces by placing these surfaces in strongly acidic media has also been investigated.

Half-normal sulphuric acid has been used by Dean (1938), Chang and Jackson (1957) and others to extract calcium bound phosphate from the soil. It has also been shown that this reagent will extract a considerable fraction of both aluminium bound and iron bound phosphate from the soil (Ghani, 1943; Williams, 1950).

The effect of placing a mica surface, which had been saturated with aluminium and on which radioactive phosphate had been adsorbed, into a 0.5N sulphuric acid solution would be to lower the pH values of these species to a fairly low value (at most to the pH value of 0.5 N sulphuric acid which is 0.7). At low pH values the radioactive phosphate groups would exist mainly as H_3PO_4 molecules. These molecules would not be bound onto the mica surface itself (or onto the aluminium ions adsorbed onto it) as tightly as if they were negatively charged as the mica surface will be either neutral or slightly positively charged (due to charges on the aluminium ions present) at low pH values. Thus it would be expected that the presence of 0.5N sulphuric acid as a desorbing solution would cause the radioactive phosphate to be desorbed more readily than a solution of somewhat higher pH value.

Experiments using 0.5 sulphuric acid as a desorbing solution showed a rapid loss of radioactive phosphate from

aluminium saturated mica surfaces, as would have been expected. It was found that most of the radioactive phosphate present was removed within a few hours. Not all of the radioactive phosphate was removed in a reasonable period of time (24 hours). It seemed that 0.5 N sulphuric acid did not remove all the radioactive phosphate present on aluminium saturated mica surfaces. This was in contrast to the use of 0.1N sodium hydroxide which had been observed to remove all adsorbed radioactive phosphate fairly rapid ly (24 hours or less).

These results were in agreement with the work of Chang and Jackson (1957), Ohani (1943), Williams (1950) and others who have found that while 0.1 N sodium hydroxide removed all aluminium bound phosphate in the soil, 0.5N sulphuric acid removed a consider ble fraction, but not all of this phosphate.

As has been shown elsewhere in this thesis (p. 183) the use of aluminium sulphate to form an aluminium saturated mica surface has been shown to lead to the retention of more radioactive phosphate (in 30 minutes) than the use of aluminium nitrate or aluminium chloride for the same purpose. Because of this it was thought that there could possibly be an effect on the desorption of radioactive phosphate caused by the sulphate ions in

0·5 N sulphuric acid. To test this possibility the effect of 0·5 N hydrochloric acid as a desorbing reagent was investigated.

The effect on the desorption rate of radioactive phosphate from aluminium saturated mica surfaces of 0.5N hydrochloric acid was found to be the same as the effect of 0.5N sulphuric acid. Most, but not all, of the radioactive phosphate was removed fairly readily by this reagent. Thus it can be seen that there is no apparent difference between the efficiency of these two reagents as desorbing reagents for radioactive phosphate from aluminium saturated mica surfaces.

The use of ammonium fluoride as a reagent for the extraction of phosphate from soil has been widely referred to in the literature (Bray and Kurtz, 1945; Swenson, Cole and Sieling, 1949; Seatz, 1954; Sinha and Mandal, 1955; Ginzburg, 1959 and others.) Turner and Rice (1954) found that neutral ammonium fluoride (pH7.0) dissolved aluminium phosphate but not iron phosphate, and this reagent (with a strength of 0.5 Molar) was used by Chang and Jackson (1957) in their procedure for the systematic fractionation of soil phosphorus. Later work (e.g. Fife, 1959) has shown that the use of 0·5 M ammonium fluoride at a pH value of 8.5 gives better results for the selective extraction of aluminium bound phosphate as opposed to iron

bound phosphate.

The use of this reagent (0.5 M ammonium fluoride, pH value 8.5) as a desorbing solution for the rapid removal of radioactive phosphate from both aluminium saturated mica surfaces and aluminium oxide coated surfaces was investigated in this thesis. It was found that this reagent caused the rapid removal of radioactive phosphate from both the surfaces studied. All the radioactive phosphate adsorbed onto an aluminium oxide coated surface was removed in a few hours by the ammonium fluoride. Radioactive phosphate was also removed almost completely from aluminium saturated mica surfaces in a short space of time by ammonium fluoride at a pH value of 8.5.

In the procedure of Chang and Jackson (1957) for the systematic fractionation of soil phosphorus, extraction of aluminium bound phosphorus with ammonium fluoride is carried out for one hour. In the present work the great majority of the radioactive phosphate adsorbed onto aluminium saturated mica surfaces, and onto aluminium oxide coated surfaces, is removed in one hour using this reagent.

From the above experiments it appeared that 0.5 M ammonium fluoride at a pH value of 8.5 was a good extractent for radioactive phosphate bound onto aluminium oxide coated surfaces, or aluminium ion saturated surfaces. This is in accord with the literature, and so it would be

interesting to see if any success at radioactive phosphate removal from either iron surfaces or iron saturated mica surfaces could be obtained with this reagent. From the literature it would not appear likely that much, if any, acceleration of the rate of removal of radioactive phosphate from the above iron containing surfaces would be obtained by the use of alkaline ammonium fluoride.

6.9 Studies of Phosphate Adsorption and Exchange

The three phenomena that may be studied in relation to the interaction between mica surfaces and orthophosphate groups, using radioactive phosphate, are the adsorption and desorption of radioactive phosphate from the mica surface, and the exchange of radioactive ($^{32}PO_4$) and non-radioactive ($^{31}PO_4$) phosphate groups adsorbed onto the mica surface. The great majority of the work undertaken in this thesis has been on the desorption of radioactive phosphate from mica surfaces after it has been adsorbed under certain conditions.

6.91 Adsorption of Radioactive Phosphate

The initial adsorption of radioactive phosphate onto the mica surface under study occurred during a period of time with the mica surface in contact with a solution containing radioactively labelled orthophosphate molecules. The actual species present would depend on the pH value of the solution and would be $H_3{}^{32}PO_4$, $H_2{}^{32}PO_4^-$, $H^{32}PO_4^{2-}$ or $^{32}PO_4^{3-}$.

Phosphorus -32 (or ^{32}P) is a pure β emitter having a radioactive half-life of 14.30 days and giving off β particles with a maximum energy of 1.701 Me_V (Friedlander and Kennedy, 1957). Owing to this high value for the energy of the β particles emitted by ^{32}P, an end-window geiger counter placed in a solution containing radioactive

phosphate would count all the radioactive disintegrations occurring in the solution closely surrounding the end window, as well as those of radioactive phosphate groups actually adsorbed onto the mica surface of the end window. Thus there would be no appreciable alteration in the observed count rate, as measured with the geiger counter, as the amount of radioactive phosphate adsorbed onto the mica surface of the geiger counter end window, which was immersed in the radioactive phosphate solution, changed with time. Consequently it is not possible to study the rate of adsorption of radioactive phosphate onto the mica end-window of a geiger counter as a function of time by monitoring the solution of radioactive phosphate continuously.

Similar work to that being done for this thesis with radioactive phosphate has been undertaken recently with radioactive sulphate (Rankin,1964). The isotope used in this research was sulphur -35 (or ^{35}S), which is also a pure β particle emitter. However the energy of the β particle of ^{35}S is only 0.167 Mev (Friedlander and Kennedy,1957). Because of this lower energy, the only radioactive disintegrations of ^{35}S atoms that are measured by an end-window geiger counter with its mica end-window immersed in a solution containing radioactively labelled sulphate groups are those occurring actually on the mica end-window or in very close proximity to it. It is

therefore possible to study the adsorption of radioactive sulphate onto the mica end-window of a geiger counter in a direct manner by merely measuring the increase in the count rate as a function of time, while the geiger counter end-window remains in contact with the radioactive sulphate solution.

As it was not possible to study the amount of radioactive phosphate adsorbed onto the mica end-window of a geiger counter as a function of time in the same way as could be done with radioactive sulphate, some other way would have to be found if it was desired to study adsorption phenomena. By finding out the total amount of each of the different complexes (as indicated by the desorption experiments) that were formed between the radioactive phosphate and the mica surface, it would be possible to calculate the total number of phosphate groups involved in each type of complex. This information would be very helpful in elucidating the exact nature of each type of phosphate-mica surface complex.

It seemed that a possible way to obtain some of this information would be by studying the total amount of radioactive phosphate adsorbed onto a mica surface, in a fixed period of time, from solutions containing different amounts of phosphate in them. If it was desired to find the relative amounts of each of the different complexes formed, the usual desorption experiments could be performed

with a number of similar mica surfaces, on which were radioactive phosphate adsorbed from different strengths of phosphate solution. From the information gained as a result of the above experiments, it would be possible to plot adsorption - concentration relationships for the total adsorbed phosphate and for each of the phosphate-mica surface complexes formed.

It was decided to conduct some preliminary experiments on the adsorption of radioactive phosphate onto aluminium saturated mica surfaces. The object of these experiments was to see what, if any, relationship existed between the concentrations of the radioactive phosphate solutions used and the amounts of radioactive phosphate adsorbed. The amount adsorbed would be expected to increase with increasing time of adsorption (experiments performed previously had already demonstrated this) and so adsorption from various radioactive phosphate solutions could only be compared if carried out for the same time interval.

These preliminary experiments would not lead to true adsorption isotherms as the amounts of radioactive phosphate adsorbed from the radioactive phosphate solutions used were not the total amounts that could be adsorbed from these solutions. These amounts would increase with time until an equilibrium was reached for each radioactive phosphate solution concentration. However it would be

possible to see what relationship, if any, existed between solution concentration and amount of adsorption of radioactive phosphate for a given, constant, time. Experiments could also be carried out to determine the amount of adsorption from a solution of constant radioactive phosphate concentration as a function of adsorption time.

A series of experiments was performed in order to see the effects of a series of adsorptions from increasing strengths of radioactive phosphate, for a fixed time, onto a mica surface. An end-window geiger counter was taken, prepared for use, and washed in 0.5 N aluminium nitrate solution four times, for at least 30 minutes each time. The background count was then determined in air, as it was intended to determine the count rate of the adsorbed radioactive phosphate in air. Only the total amount of adsorption was to be determined.

A stock solution of radioactive phosphate was prepared with a count rate of greater than 80,000 c.p.m. (on portable monitor). Ten ml. of this solution were taken with a pipette, and diluted to 100 ml. with distilled water (solution I). After stirring, 10 ml. of solution I were taken and diluted to 100 ml. in the same way (solution II). This procedure was repeated until four more solutions (III, IV, V and VI) had been prepared, all six solutions being in separate glass beakers. Thus a series of solutions

with a range of concentrations of radioactive phosphate of 10^5 was prepared. These solutions were stored in glass beakers, and it would be expected that some adsorption of the radioactive phosphate groups onto the glass might occur. However it would be expected that the more concentrated solutions of phosphate would have correspondingly more phosphate adsorbed onto the glass walls of the beakers, and so the effect would be comparable to the initial amount of radioactive phosphate present. Thus the relative proportions of radioactive phosphate in each solution might be expected to be more or less unaltered.

The geiger counter prepared as above was soaked for a short period of time (approximately 1½ minutes) in each of the solutions VI to I in that order. By starting with the weakest solution first, and working through to the strongest, it was not necessary to remove the adsorbed radioactive phosphate after each solution had been used. The total amount adsorbed onto the mica surface by solution III for instance would be the same if it was all adsorbed from solution III or if some was already adsorbed from solution IV .

It was found that no radioactive phosphate appeared to be adsorbed from solutions VI and V. The count

rate of the solution VI appeared to be not more than 3 c.p.m. above the background count rate, and this small amount may have been merely due to a statistical fluctuation as the counting time was only one minute. The count rate of solution V, out of which no radioactive phosphate appeared to have been adsorbed, was 30 c.p.m. above the background count rate and so it can be seen that there was an easily detectable amount of radioactive phosphate present in the solution.

On placing the geiger counter mica end-window in solutions IV,III,II and I increasing amounts of radioactive phosphate were observed to be adsorbed. The increases in the count rate above the background count rate are given in Table 10 (same time interval of adsorption, Solutions IV,III,etc., each with 10 times as much radioactive phosphate present as in the previous one):

TABLE 10.

Solution	Increase in Count Rate (c.p.m.)
IV	5
III	60
II	470
I	5,270

From the above figures it can be seen that the increase in the amount of adsorbed radioactive phosphate

is approximately a factor of ten with each tenfold increase in solution radioactive phosphate concentration. This is the same rate of increase as that of the solution concentrations, and so it seems that there is a linear relationship between the amount of radioactive phosphate present and the amount adsorbed by the mica surface, over the range of concentrations studied.

Phosphate groups that are adsorbed onto a mica surface are all negatively charged over the range of pH values studied. The only non-negatively charged species present could be H_3PO_4, of which there would be only a few per cent even at the lowest pH value studied extensively in this thesis (3.0). Therefore it would not be expected that there would be much, if any, multilayer adsorption of phosphate groups onto mica surfaces.

Weir and Soper (1962) have found that the total adsorption of radioactive phosphate by soils follows a Langmuir adsorption isotherm for amounts of up to 20-30 μ gm. of phosphorus per ml. Similarly Rennie and McKercher (1959) found a Langmuir adsorption isotherm for phosphate adsorption by soils up to a solution concentration of 20 μ gm. per ml. Adsorption experiments with phosphate and soils have been carried out by a number of other workers also, such as Molnár, Máté and Kende (1957), Olsen and Watanabe (1957) and Russell and Low (1954).

The last mentioned authors (Russell and Low) favoured the fitting of a Freundlich adsorption isotherm to the adsorption curve of phosphate on kaolinite, but Olsen and Watanabe stated that phosphate adsorption by soils showed a clearer agreement with the Langmuir adsorption isotherm than with the Freundlich adsorption isotherm. Thus from the above conclusions of other workers it would appear reasonable to expect that the present studies, if carried out at equilibrium, might lead to a Langmuir adsorption isotherm. If this was so, and sufficiently high concentrations of phosphate were used, monolayer saturation of the mica surface would occur, and no more phosphate would be adsorbed on increasing the phosphate concentration of the adsorbing solution.

Adsorption studies of phosphate onto X-ray amorphous "aluminium hydroxide" have been conducted by Hsu and Rennie (1962 a). They discuss the limitations of the Langmuir adsorption isotherm when applied to the adsorption of ions. One of the conditions for this isotherm is that there is a free space around the adsorbing particles, unaffected by other particles (in this case ions). They therefore conclude that the Langmuir adsorption isotherm is only valid when the interfering force due to inter-acting ions is negligible or constant. The initial fixation of phosphate by X-ray amorphous "aluminium hydroxide" is primarily due to an adsorption reaction.

This is rapid and is followed by a slow decomposition-precipitation process.

Further work has been done by the same authors (Hsu and Rennie, 1962 b) using aluminium saturated cation exchange resins. They believed that the exchangeable aluminium ions on the cation exchange resin precipitated phosphate from solution. However the precipitation data obtained corresponded to adsorption isotherms. From this they reached the conclusion that the close agreement between adsorption isotherms and phosphate fixation data may not necessarily imply an adsorption reaction in soils, owing to the restrictions on the validity of the adsorption isotherm discussed in their first paper(1962a).

In the present work it is believed that the radioactive phosphate-aluminium saturated mica surface complexes are adsorption and not precipitation phenomena. Evidence for this fact based on the similarity of the results of similar work using radioactive sulphate (Rankin,1964)is discussed elsewhere in this thesis (p. 337).

Owing to the solubility of aluminium sulphate ($Al_2(SO_4)_3$) it would hardly be expected to form a precipitate. If precipitation is not occurring in the present work with aluminium saturated mica surfaces and radioactive phosphate, then it seems most likely that the results obtained,and described, will actually be related to the amount of adsorption of radioactive

phosphate relative to the amount present in the adsorbing solutions.

In order to calculate any data from such adsorption-concentration relationships it would be necessary to know the actual amount of phosphate adsorbed onto the mica surface. The radioactive phosphate solution that was obtained from England contained 20 millicuries of ^{32}P of high specific activity. It was not possible to calculate the number of atoms of phosphorus actually present from this information, and the actual amount was far too small to be estimated by any of the conventional methods for the quantitative determination of phosphorus (20 millicuries of pure ^{32}P ("carrier free ^{32}P") would contain only 7.0×10^{-8} gms. of phosphorus).

The best way to find out the actual amount of phosphorus present in the radioactive phosphate solution seemed to be by diluting the solution with a known amount of inactive phosphate. As the increase in adsorption of phosphate with increasing solution concentration was linear over a range of concentration of at least 10^3, addition of a sufficiently small amount of inactive phosphate to the radioactive phosphate solution would not necessarily affect the observed count rate.

Suppose there are x gms. of phosphorus in the radioactive phosphate solution, and after adsorption

onto the mica surface of an end-window geiger counter the increase in the observed count rate is X_1 c.p.m. This count rate will correspond to the presence of X gms. of phosphorus adsorbed onto the mica surface. Therefore the fraction of the radioactive phosphate adsorbed onto the mica surface is $\frac{X}{x}$. If y gms. of inactive phosphate are then added to the radioactive phosphate solution the total amount of phosphorus present in the solution will be (x + y) gms. Assuming that the mica surface has not been saturated with phosphate groups, the same proportional amount of phosphorus will be adsorbed onto the mica surface. Therefore the actual amount of phosphorus adsorbed onto the mica surface will be $\frac{X}{x}.(x + y)$.

That is the amount of phosphorus adsorbed from the added non-radioactive phosphorus will be $\frac{X \cdot y}{x}$. The amount of phosphorus adsorbed from the phosphorus in the original radioactive phosphate solution will be $\frac{X \cdot x}{x}$ or X. As X gms. of phosphorus from the original radioactive phosphate solution gave rise, on adsorption onto the mica surface of the geiger counter end window, to a count rate of X_1 c.p.m. it can be seen that there will be no detectable effect on the adsorption experiment by the addition of inactive phosphate to the radioactive phosphate solution, providing that the total amount of phosphate in the solution is not sufficient to lead to

saturation of the mica surface.

The other possibility to be considered is when the total amount of phosphate present becomes more than sufficient to lead to saturation of the mica surface being studied. In this case there will be an effect on the observed count rate after adsorption. Using the same symbols as before, the amount of phosphate in the radioactive phosphate solution x gms. will give rise, after adsorption, to an observed count rate X_1 c.p.m. where X_1 is proportional to X. Let y_1 gms. be the amount of inactive phosphorus added so that there is just enough phosphorus, $(x + y_1)$ gms., present to lead to saturation of the mica surface. Then the actual amount adsorbed will be $\frac{X}{x}(x + y_1)$ gms. This value, $\frac{X}{x}(x + y_1)$ is therefore the amount of phosphate present on the mica surface after saturation with phosphate solution. This corresponds to a fraction adsorbed of $\frac{\frac{X}{x}(x + y_1)}{(x + y_1)}$ which $= \frac{X}{x}$, the same fraction as for non-saturation of the mica surface.

If y_2 gms. $(y_2 > y_1)$ of inactive phosphorus are added (as phosphate) to the radioactive phosphate solution the total amount of phosphorus present $(= (x + y_2)$ gms.) will be more than is required for saturation of the mica surface. The actual amount of phosphorus present on

the mica surface after adsorption will therefore still be $\frac{X}{x}(x + y_1)$ gms. The fraction of the total phosphorus present adsorbed onto the mica surface will now be $\frac{\frac{X}{x}(x + y_1)}{(x + y_2)}$. The total amount of phosphorus adsorbed will be partly from the original radioactive phosphate solution (containing x gms. phosphorus). The actual amount of phosphorus adsorbed from the original solution will be, as before, equal to the fraction of the total phosphorus adsorbed $\left(\frac{\frac{X}{x}(x + y_1)}{(x + y_2)}\right)$ multiplied by the amount of phosphorus in this original solution, x gms. That is, the actual amount will be equal to $\frac{X}{x}(x + y_1) \times \frac{x}{(x + y_2)}$ or $X \frac{(x + y_1)}{(x + y_2)}$ gms.

As $Y_2 > y_1$, $x + y_2 > x + y_1$ and therefore $\frac{(x + y_1)}{(x + y_2)} < 1$.

It can therefore be seen that the total amount of phosphorus adsorbed from the original radioactive phosphate solution, when the total amount of phosphorus present is more than enough to saturate the mica surface, is less than that adsorbed when there is either just enough, or less than enough, phosphate present to saturate the mica surface. Thus, as the observed count rate is proportional to the amount of

phosphorus adsorbed from the original radioactive phosphate, it will be lowered by a factor of $\left(\frac{x + y_1}{x + y_2}\right)$.

These calculations are all made for a constant adsorption time for each of the adsorption experiments. As is discussed elsewhere (p. 197) the amount of phosphate adsorbed by mica surfaces appears to increase with increasing adsorption time.

The above mathematical treatment involves the assumption that there is an equal tendency for radioactive and non-radioactive phosphate ions (or molecules) to adsorb onto the mica surface (apart from considerations of the relative concentrations of the two species). The only possible reason for any difference in adsorption rates would appear to be due to the different gram ionic weights of the two species. Assuming that the species are $H^{31}PO_4^{2-}$ and $H^{32}PO_4^{2-}$, the two gram ionic weights are respectively 96 and 97 grams. Thus it would be expected that any difference in their rates of adsorption onto a mica surface would be very small, and consequently unlikely to affect this work.

If the species present were PO_4^{3-}, $H_2PO_4^-$ or H_3PO_4 the ratios of the gram ionic weights for the respective compounds containing ^{32}P and ^{31}P would also be very close

to unity. The values for the individual ratios are:

$$\frac{^{32}PO_4^{3-}}{^{31}PO_4^{3-}} = \frac{96}{95} = 1.0105$$

$$\frac{H^{32}PO_4^{2-}}{H^{31}PO_4^{2-}} = \frac{97}{96} = 1.0104$$

$$\frac{H_2{}^{32}PO_4^{-}}{H_2{}^{31}PO_4^{-}} = \frac{98}{97} = 1.0103$$

and

$$\frac{H_3{}^{32}PO_4}{H_3{}^{31}PO_4} = \frac{99}{98} = 1.0102$$

Thus within the limits of the experimental work the above assumption seems to be quite justified and it is possible to neglect the existence of any isotope effect.

Some experiments were performed in an endeavour to saturate a mica surface with phosphate groups. The geiger counter mica end-windows were not used, but sheet mica was taken and split and used with the metal containers as described earlier (p. 42) The mica surfaces so prepared were soaked in 0.5N aluminium nitrate solution four times, for at least 30 minutes each time. They were then soaked indistilled water with a pH value of 5.5 six times in order to adjust the pH value of the aluminium

saturated mica surface to 5.5. The background count rate for each mica surface plus inclosed geiger counter was determined in air as it was intended to determine the amount of adsorbed radioactive phosphate in air, and not immersed into a solution and subsequently desorbed.

A stock solution of very highly radioactive phosphate solution was prepared (the count rate of this solution was later calculated to be of the order of 10^6 c.p.m.) and a series of solutions I,II,III.....VI, containing 10^{-1}, 10^{-2} ,.....10^{-6} times as much of the radioactive phosphate stock solution, prepared in the same way as has been described earlier (p. 246). These solutions were made up in polythene beakers to minimise the loss of phosphate from solution by adsorption onto the walls of the container. Immediately before use portions of these solutions were poured into glass beakers, but it seems unlikely that there would be as much adsorption onto the walls of these beakers as if the radioactive phosphate solutions had been left standing in them overnight.

The pH value of the original stock solution of radioactive phosphate was adjusted to 5.5, and all the dilutions were made with deionised water that had been adjusted to a pH value of 5.5 also. Thus it would be expected that the pH value of each of the diluted solutions would be reasonably close to 5.5. It was not possible

to adjust the pH value of the diluted solutions to exactly 5·5 by the addition of small amounts of acid or alkali as this would have altered the concentration of radioactive phosphate present by changing the solution volume.

Solutions of inactive phosphate were prepared having concentrations of 10^{-1}, 10^{-3} and 10^{-5} grams of phosphorus per litre in them. These solutions were prepared by dissolving sodium dihydrogen orthophosphate in distilled water and diluting to the required extent. As distilled water with a pH value of 5.5 was used for the dilutions, the pH value of the final solutions would have been between 5·0 and 5·5. The inactive phosphate solutions were prepared within 24 hours of their being required in order to minimise the time during which the very small concentrations of phosphate in these solutions could be further reduced by the action of micro-organisms.

A prepared mica surface was taken and soaked for a fixed period of time (5 minutes) in each of the six prepared radioactive phosphate solutions starting with the weakest, and then using the next strongest one, etc. After this period of soaking, the mica surface was rinsed with distilled water having a pH value of 5·5, and the increase in count rate, due to adsorption of radioactive phosphate onto the mica surface, was then determined. It was found that some radioactive phosphate seemed to be adsorbed from all six solutions. The increase

in count rate after adsorption from the weakest solution was not greater than the uncertainty in the count rate (see Table 11) and so little if any phosphate may have been adsorbed. The results of these experiments are summarised in Table 11 .

TABLE 11 .

Solution	Concentration of Phosphate relative to Stock Solution	Increase in Count Rate (c.p.m.)
VI	10^{-6}	3 ± 3.5
V	10^{-5}	8 ± 4
IV	10^{-4}	70 ± 5
III	10^{-3}	400 ± 10
II	10^{-2}	3,970 ± 20
I	10^{-1}	40,100 ± 30

It can be seen that the increase in count rate is approximately tenfold for Solutions III,II and I. The amounts of radioactive phosphate adsorbed for Solutions IV, V and VI are greater than might have been expected from the dilution of Solutions I,II and III. This may mean that the actual amounts of radioactive phosphate adsorbed onto the mica surface are slightly higher than would otherwise have been expected by extrapolation to these very low phosphate concentrations. However,

further more accurate work would be required in this concentration range before the results could be accepted with confidence as, especially with such low amounts, a small amount of extra radioactive phosphate introduced by means of, e.g., the 10 ml. pipette used for the dilutions would have a considerable effect on the observed count rates after adsorption had occurred.

The above experiments having served to verify the approximate linearity of the relationship between radioactive phosphate in solution and the amount of this phosphate adsorbed onto an aluminium saturated mica surface in a fixed time, further experiments were performed in which a mixture of radioactive and non-radioactive phosphate was used.

Ten millilitres of the stock radioactive phosphate solution were taken with 10 ml. of the inactive phosphate solution containing 10^{-5} gms. phosphorus per litre, and diluted to 100 ml. with distilled water having a pH value of 5.5. This new solution (I') contained the same amount of radioactive phosphate as did Solution I above, plus 10^{-7} gms. inactive phosphorus in 100 ml. This solution was repeatedly diluted tenfold as before, giving Solutions II', III', IV' and V'. The sixth dilution was not made as the amount of radioactive phosphate adsorbed from this solution was very small (see above Table 11).

The contents of each of the prepared solutions is given in Table 12 , the amount of phosphorus in 100 mls. of the original stock solution being designated as "A" gms.

TABLE 12.

Solution	Amount of Radioactive Phosphorus/100 ml.	Amount of Added Inactive Phosphorus /100 ml.
V'	10^{-5} A gms.	10^{-11} gms.
IV'	10^{-4} A gms.	10^{-10} gms.
III'	10^{-3} A gms.	10^{-9} gms.
II'	10^{-2} A gms.	10^{-8} gms.
I'	10^{-1} A gms.	10^{-7} gms.

A new freshly prepared mica surface was taken, and after the background count rate with it had been determined in air, it was soaked for the same time interval as before (5 minutes) in each of the solutions V' to I' in that order. The increase in the count rate over the background count rate due to adsorption from each solution is given in Table 13 . It will be seen that the relative amounts of radioactive phosphate adsorbed by the mica surface from each solution are approximately the same as those for the first series of adsorptions with no inactive phosphate added (cf. Table 11 p. 260). The actual amounts adsorbed from each solution are slightly higher than those observed for the

first series of experiments, but this is probably due to the second mica sheet being slightly thinner than the first sheet, and consequently allowing a higher proportion of the β particles emitted by the disintegrating radioactive phosphorus atoms through into the counting volume of the end-window geiger counter.

TABLE 43.

Solution	Total amount of Phosphorus in 100 ml. solution (gms.)	Increase in Count Rate (c.p.m.)
V'	$10^{-5}A + 10^{-11}$	16 ± 4
IV'	$10^{-4}A + 10^{-10}$	78 ± 6
III'	$10^{-3}A + 10^{-9}$	535 ± 10
II'	$10^{-2}A + 10^{-8}$	$4,550 \pm 20$
I'	$10^{-1}A + 10^{-7}$	$52,760 \pm 40$

It therefore appeared from the above results that the total amount of phosphate present in any of the solutions V' to I' was insufficient to lead to complete saturation of the mica surface under study during the adsorption time for the above determinations (5 minutes). As the greatest amount of phosphate used was in solution I', from the above experiments a lower limit for the amount of phosphate in 100 ml. of solution required for saturation of the aluminium saturated mica surface for a five-minute adsorption time could be set at $(10^{-1}A + 10^{-7})$ gms.

phosphorus where A gms. was the amount of phosphorus present in 100 ml. of the original stock radioactive phosphorus solution.

A further series of solutions were prepared by dilution of the stock radioactive phosphate solution and addition of more concentrated inactive phosphate solution. Only three solutions (I",II" and III") were prepared, solution I" consisting of 10 mls. of the stock radioactive phosphate solution plus 10 mls. of a solution containing 10^{-3}gms. inactive phosphorus per litre plus 80 mls. of distilled water. Solutions II" and III" were prepared by tenfold dilutions as before. It was not necessary to prepare any more dilute solutions than III".

The total amount of phosphorus per 100 ml. in solution III" ($(10^{-3}A + 10^{-7})$ gms. - see Table 14) was less than the lower limit for saturation of the mica surface of ($10^{-1}A + 10^{-7}$) gms. calculated from the second series of experiments. Thus the addition of the inactive phosphate to solution III" should not have had any effect on the observed increase in count rate, which should be the same as that found for the corresponding solutions (III and III') in the first two series of experiments. Consequently the actual amount of radioactive phosphate adsorbed onto the surface of the aluminium saturated mica sheet from solution III" would

enable the calculation of the amounts of radioactive phosphate that should be adsorbed onto the mica surface if phosphate saturation had not been reached with the amount of inactive phosphate added.

As the phosphate solutions I to VI and I' to V' had been prepared in the same polythene beakers(and used in the same glass beakers) the amount of radioactive phosphate that had become adsorbed onto the sides of these beakers had become quite considerable for the more radioactive solutions. In order to minimise the amount of adsorbed radioactive phosphate on the beaker walls relative to the phosphate concentration in solution, solutions I",II" and III" were prepared (and used) in the beakers that had been used previously for solutions IV,V and VI. It would not be expected therefore, that the experimental results obtained from the adsorptions of phosphate onto the aluminium saturated mica surface from these three solutions could be affected by the small amounts of phosphate already adsorbed onto the beaker walls.

The same experimental procedure used in the first two series of experiments was followed with solutions III",II" and I". The increases in the observed count rate due to adsorption of the radioactive phosphate in the solutions onto another freshly prepared aluminium saturated mica surface are given in Table 14.

TABLE 14

Solution	Total Amount of Phosphorus in 100 ml. solution (mgs.)	Increase in Count rate (c.p.m.)
III"	10^{-3} A + 10^{-7}	400 ± 5
II"	10^{-2} A + 10^{-6}	4,580 ± 15
I"	10^{-1} A + 10^{-5}	19,300 ± 30

It can be seen that the increase in count rate caused by adsorption from Solution III" was approximately the same as was observed with Solution III (cf. Table 11 p. 260) Solution II" caused an increase in count rate on the mica surface of slightly more than that caused by the comparable Solution II, the increase for which was only 3,970 c.p.m. The actual increase of 4,580 c.p.m. was more similar to that caused by Solution II' which was 4,550 c.p.m. (Table 13 p263) From this it seemed that the mica sheet used in the third series of experiments was of comparable thickness to the first two sheets used.

It also seemed that the total amount of phosphate in solution II" was not more than that required to lead to saturation of the mica surface. If the total amount present in the solution was more than that required for saturation the observed increase in count rate would be less than ten times as much as the increase caused by Solution III".

From the above conclusion another lower limit for the total amount of phosphorus (as phosphate) required to saturate the aluminium saturated mica surface with phosphate in an adsorption time of five minutes can be obtained. This new lower limit will be $(10^{-2} A + 10^{-6})$ gms. Whichever of these two lower limits $(10^{-2} A + 10^{-6})$ gms. or $(10^{-1} A + 10^{-7})$ gms. is the higher will depend on the value of "A" the amount of phosphorus in 100 mls. of the original stock radioactive phosphate solution. The difference between the later calculated lower limit, $(10^{-2} A + 10^{-6})$ gms. phosphorus, and the first calculated lower limit, $(10^{-1} A + 10^{-7})$ gms. phosphorus, is $(9 \times 10^{-7} - 9 \times 10^{-2} A)$ gms., that is, $9 \times 10^{-2} (10^{-5} - A)$ gms. Therefore, providing that "A" is less than 10^{-5} gms. the lower limit for the amount of phosphorus required for saturation of the mica surface will be $(10^{-2} A + 10^{-6})$ gms.

The total amount of radioactive phosphorus that was used to make up the stock radioactive phosphate solution was less than two millicuries. As was stated previously (p.$_{252}$) the amount of phosphorus in 20 millicuries of pure ("carrier free") ^{32}P is only $7{\cdot}0 \times 10^{-8}$ gms. Thus the amount of radioactive phosphorus in "A" (the actual volume of "A" prepared was about 100 mls.) would be less than 7×10^{-9} gms. Even if the number of radioactive phosphorus atoms was only one in a thousand non-radioactive phosphorus atoms in the originally obtained "high specific activity"

radioactive phosphate solution, the total amount of phosphorus in "A" would be only 7×10^{-6} gms., that is, still less than 10^{-5} gms. It seems unlikely that the proportion of radioactive phosphorus atoms would be as low as (or lower than) one in a thousand, and so "A" may be safely taken as less than 10^{-5} gms. The lower limit for the amount of phosphorus present in 100 mls. of adsorbing solution required to saturate the aluminium saturated mica surface in five minutes therefore can be placed at $(10^{-2}A + 10^{-6})$ gms.

From the increase in count rate caused by Solution II" it would be expected that the increase in the count rate of the mica surface due to adsorption of radioactive phosphate from Solution I" would be about 40,000-50,000 c.p.m., providing that the total amount of phosphate in solution was not more than that required for saturation of the aluminium saturated mica surface. As can be seen from Table 14 the actual increase in count rate caused by adsorption from Solution I" was only 19,300 c.p.m., or about half of the expected value. From this it seemed that the amount of phosphate in Solution I" was more than the amount required for saturation of the mica surface.

Previously (p. 256) it was shown mathematically that the count rate increase after adsorption from a phosphate solution containing a greater amount of phosphate

than that required for saturation would be reduced by a factor of $\left(\frac{x + y_1}{x + y_2}\right)$ relative to the increase observed with the same amount of radioactive phosphate but insufficient total phosphate to saturate the mica surface. In this case the increase in count rate has been reduced by a factor of $\frac{12,300}{40,000}$ or approximately $\frac{1}{3}$.

Thus the relationship is obtained: $\frac{x + y_1}{x + y_2} = \frac{1}{3}$

or $2x + 2y_1 = x + y_2$

$\therefore \quad y_2 = y_1 + (x + y_1)$

Now y_2 = amount of added inactive phosphorus=10^{-5}gms.

The total amount of phosphorus required

for saturation, $x + y_1 = y_2 - y_1$

$= 10^{-5} - y_1$

i.e. $x + y_1 = 10^{-5} - y_1$ .....(1)

Now y_1 = amount of inactive phosphorus required to be added to produce saturation, and it is known from the second series of adsorption experiments performed that this is greater than, or equal to, 10^{-7} gms.

i.e. $y_1 \geqslant 10^{-7}$

Thus (equation (1)) $x + y_1 = 10^{-5} - y_1$

$\leqslant 10^{-5} - 10^{-7} = 99 * 10^{-7}$

i.e. $x + y_1 \leqslant 99 * 10^{-7}$ .....(2)

Also as $y_1 \geqslant 10^{-7}$ and $x + y_1 > y_1$ (x a positive quantity)

then $x + y_1 > 10^{-7}$ .....(3)

The lower limit for the total amount of phosphorus required for saturation is $(10^{-2}A + 10^{-6})$ gms. As in the above calculations x is the amount of phosphorus present in the radioactive phosphorus solutions used, and the calculations are being made on the solutions giving the highest increases in count rate, $x = 10^{-1}A$ gms. Thus the lower limit can be written as $(10^{-1}x + 10^{-6})$gms. As the amount required for saturation is $(x + y_1)$ there results the relationship:

$$10^{-1}x + 10^{-6} \geqslant x + y_1$$

$$\text{or } 0.9\,x + y_1 \leqslant 10^{-6}$$

i.e. (multiplying by $\frac{10}{9}$) $(x + y_1) + \frac{1}{9}y_1 \geqslant \frac{10}{9} * 10^{-6}$....(4)

If the substitution 10^{-7} is used for y_1 $(y_1 \geqslant 10^{-7})$ there is an uncertainty introduced into the equation (4) above

For $\frac{10}{9} * 10^{-6} - \frac{1}{9}y_1 \leqslant \frac{10}{9} * 10^{-6} - \frac{1}{9} * 10^{-7}$

Thus the right hand side of equation (4) has been replaced by a larger value, and may no longer be less than the left hand side. If the substitution is made the result is:

$$(x + y_1) \geqslant \frac{10}{9} * 10^{-6} - \frac{1}{9} * 10^{-7}$$

i.e. $(x + y_1) \geqslant 11 * 10^{-7}$ .....(5)

The validity or lack of validity of equation (5) will depend on the relative values of x and y_1. It can be calculated that equation (5) and equation (4) also, are valid for all values of x providing y_1 is greater than or equal to 10^{-6} gms. If y_1 is less than 10^{-6} gms then it is necessary that x be sufficiently large, the actual value of x required for the validity of equation (5) increasing, as y_1 decreases, to a value of 1×10^{-6} gms. for $y_1 = 10^{-7}$ gms.

From the above calculations it can be seen that there is little value in using equation (5) to obtain an actual lower limit for the total amount of phosphorus required for saturation of the mica surface, unless more information is obtained about either x or y_1.

The range of possible values for the amount of phosphorus required for saturation can be calculated from equations (2) and (3). Combining these two equations one obtains:

$$99 \times 10^{-7} \geqslant (x + y_1) > 10^{-7} \quad \ldots\ldots\ldots\ldots (6)$$

Equation (6) specifies the possible range of the amount of phosphorus, in grams per 100 mls. of solution, required for saturation of the aluminium saturated mica surfaces under study with an adsorption time of five minutes. Considering the accuracy of the experimental data equation (6) may best be written as:

$$1 \times 10^{-5} > (x + y_1) > 1 \times 10^{-7} \quad \ldots\ldots\ldots\ldots (7)$$

that is the total amount of phosphorus required for saturation is between 10^{-5} and 10^{-7} grams.

Assuming that the great majority of the phosphorus present in the solutions from which adsorption is taking place is ^{31}P, it is possible to calculate the limits for the number of phosphorus atoms, and hence the number of phosphate groups, in these solutions.

The number of atoms of phosphorus in one gram-atomic weight, that is, in 31 gms. is 6.023×10^{23}. Therefore the number of atoms in 1×10^{-7} gms. will be $\frac{1 \times 10^{-7}}{31} \times 6.023 \times 10^{23} \simeq 2 \times 10^{15}$ atoms. Similarly the number of atoms in 1×10^{-5} gms. phosphorus will be 2×10^{17} atoms. The phosphate solutions used consisted of orthophosphate (PO_4) groups as the only phosphorus containing species present. The number of phosphate groups present is thus equal to the number of phosphorus atoms present in the solution. This gives the relationship:

$2 \times 10^{17} >$ number of phosphate groups present in solution for saturation $> 2 \times 10^{15}$.

As was mentioned elsewhere in this thesis (p. 121) there is a net negative charge on the mica surface under study. This charge isbalanced by the adsorption of positive ions such as aluminium onto the mica surface. There is effectively one negative charge every

50 sq. $\mathring{A}$. The mica surface studied had a diameter of about one inch and so a surface area of about 6 sq.cm. That is , the area of the surface was 6×10^{16} sq. $\mathring{A}$ (1 cm. = 10^{8} $\mathring{A}$). Thus the number of negative charges on the surface, which corresponds to the number of adsorbed cations (cf. p. 121), would be $\frac{6 \times 10^{16}}{50}$ or 1.2×10^{15} charges. This number of charges (and so adsorbed cations) on the mica surface is approximately half of the minimum number of phosphate groups present in the solution.

The increases in count rate observed on the mica surfaces under study were between one third and one quarter of the actual increases in the count rate measured with the mica surface plus geiger counter actually immersed in the adsorbing solution. The actual value for the two increases in count rate and the ratio of the two values are given for a number of the experiments performed in Table 15 .

TABLE 15.

Solution	Increase in Count Rate adsorbed onto mica surface. (= B c.p.m.)	Increase in Count Rate in desorbing solution (= C c.p.m.)	$\frac{B}{C}$	
IV	70	275	0.25	average for first series of experiments = 0.25
III	400	1,850	0.22	
II	3,970	15,000	0.27	
IV'	78	265	0.29	average for second series of experiments = 0.32
III'	535	1,520	0.35	
II'	4,550	14,660	0.31	
III"	400	1,350	0.30	average for third series of experiments = 0.32
II"	4,580	13,000	0.35	

The results from Solutions VI,V (Table 11) and V' (Table 13) are not given as, owing to the relatively small increase in count rate while the mica surface was immersed in the adsorbing solutions (approximately 100 c.p.m. or less), the value of this increase was determined very approximately. No attempt was made to determine the increase in count rate recorded by the mica surface plus geiger counter while the mica surface was immersed in Solutions I,I' or I". The actual count rate for these solutions would have been of the order of 10^5 c.p.m.,

which was too high to measure with the electronic arrangement being used.

From the available data it was not possible to calculate the actual number of phosphate groups adsorbed onto the mica surface. More information would be needed about the relationship between the actual disintegration rate of the radioactive phosphorus atoms adsorbed (as phosphate) onto the mica surface, and the observed count rate. It does appear however, from the above calculations, that the number of phosphate groups actually adsorbed onto the aluminium saturated mica surface at saturation is considerably less than the total number of adsorbed cations present.

The actual volumes of the adsorbing solutions used were about 20 ml. and so the saturating solution would contain between 4×10^{14} and 4×10^{16} phosphate groups. The count rate of the adsorbing solution, after soaking the mica surface in it for five minutes, was not greatly lower than before the soaking for the various adsorbing solutions used. Thus only a small percentage of the phosphate groups present in the solution can have been adsorbed onto the mica surface during the adsorption time.

From the preliminary experiments on the amounts of adsorption of radioactive phosphate onto aluminium saturated mica surfaces described above two conclusions can

be drawn. The actual amount of phosphate adsorbed in a fixed time is directly proportional to the amount of phosphate in the adsorbing solution over a wide concentration range. The actual concentration range is only known approximately as the exact amount of radioactive phosphate present in the adsorbing solutions was not calculated.

The linear relationship between the amount of phosphate adsorbed onto an aluminium saturated mica surface and the amount of phosphate in a fixed quantity of adsorbing solution exists over a concentration range of at least 10^{3}, for an adsorption time of five minutes. The upper limit for the concentration of phosphate is greater than 10^{-6} gms. of phosphorus ($= 3 \times 10^{-6}$ gms. phosphate) per 100 ml. of adsorbing solution. With higher concentrations of phosphate it is possible to saturate the mica surface with phosphate groups in an adsorption time of five minutes.

Providing the total concentration of phosphate in the adsorbing solution is insufficient to cause saturation of the mica surface, for the adsorption time studied, the amount of radioactive phosphate adsorbed is unaffected by the amount of inactive phosphate also present. Thus the amount of adsorption of radioactive phosphate is not dependent on the specific activity of the phosphate solution used for adsorption.

6.92 Exchange of Radioactive and Non-radioactive Phosphates

As was mentioned previously, another phenomenon that could be studied with the use of a geiger counter mica end-window and radioactive phosphate solution is the exchange between adsorbed phosphate on the surface of the mica and phosphate in a surrounding solution. These studies could be made in three ways, only two of which are practicable for the use of radioactive phosphate. The three possibilities are as follows:

1. The mica surface of the geiger counter end-window would be firstly soaked in inactive phosphate solution. After a suitable time for equilibration of the mica surface with the phosphate solution, a small amount of radioactive phosphate would be introduced into the solution which was in contact with the mica surface. The actual number of phosphate groups that were introduced would be very small in comparison with the amount of inactive phosphate already present in the solution. Thus there would be no significant effects due to the possibility of greater phosphate adsorption onto the mica surface because of an increased solution phosphate concentration. As long as the actual volume of the solution was great enough the increase in the background count rate of the geiger counter would not be very great initially.

The solution in which the mica surface was immersed

would be continuously stirred. The assumption is made that there is a continuous exchange between the phosphate groups adsorbed onto the surface and those in the surrounding solution. When any of the radioactive phosphate groups came sufficiently close to the mica surface it would be possible for them to exchange with inactive phosphate groups already adsorbed thereon. This would lead to an increase in the observed count rate. However considerable precautions would have to be taken because the geiger counter would also detect the radioactive disintegration of any radioactive phosphate groups in the solution close to the mica surface of the geiger counter end-window. It would be necessary to shield the solution from the face of the mica end-window in some way while still allowing sufficient contact for exchange to take place.

2. The geiger counter mica end-window could be soaked in radioactive phosphate solution for a suitable time. It could then be placed in a large volume of inactive phosphate solution. Desorption of the radioactive phosphate would occur as in the majority of the work described in this thesis. However there would be the simultaneous adsorption of inactive phosphate onto any vacant adsorption sites on the mica surface. If the mica surface had not been initially completely saturated with the radioactive phosphate then there would be adsorption sites immediately available for the inactive

phosphate groups.

Whether complete saturation of the mica surface had been achieved or not with the radioactive phosphate, as soon as some of this had been desorbed into the solution adsorption sites would be freed for the inactive phosphate in the solution. Such subsequent adsorption could possibly lead to a different pattern of desorption of the radioactive phosphate from the mica surface. Providing the amount of solution containing the inactive phosphate was large enough, and adequately stirred, there would be no readsorption of radioactive phosphate, or other effect on the observed count rate due to the presence of the desorbed radioactive phosphate close enough to the mica end-window of the geiger counter for its radioactive disintegration to be detected.

3. The opposite situation to that described under possibility 2. could also be studied, that is, the mica surface of the geiger counter end-window could be soaked in inactive phosphate solution and then placed in a container of radioactive phosphate. However, as, owing to the great energy of the β particle emitted by ^{32}P, the geiger counter could detect all the radioactive phosphate in the solution immediately surrounding the mica end-window (to a distance of almost 1 cm.) there would be no change in the observed count rate as the radioactive phosphate was adsorbed. Thus, this procedure would not be applicable

to experiments using radioactive phosphorus. It could perhaps be considered for use in studies on the phenomena of adsorption of different species such as sulphate, the radioisotope of sulphur (^{35}S) emitting a β particle of much less energy than that of ^{32}P.

An experiment was conducted following a procedure similar to that described in 1. Considerable difficulty would be experienced in securing a satisfactory method of eliminating the detection of any radioactive phosphate prior to its adsorption. Such a method would use very dilute solutions, which would lead to a very slow rate of radioactive phosphate/non-radioactive phosphate exchange. An experiment was carried out which gave an indication of the rate of exchange between radioactive and and non-radioactive phosphate groups adsorbed onto a mica surface.

A geiger counter which had been prepared and coated with paraffin wax in the usual way was taken and the mica end-window saturated with aluminium ions by cooking it in 0.5 N aluminium nitrate solution four times, for at least 30 minutes each time. The mica window was then placed in two litres of inactive phosphate buffer solution containing one milligram of phosphorus per millilitre of solution. The pH value of this buffer solution was 4.9. The geiger counter end-window was left immersed in this

inactive phosphate solution for some hours and during this time the background count rate for the geiger counter was determined. The mica window was then placed in radioactive phosphate solution, also with a pH value of 4.9 , for a suitable time, and then, after rinsing in some of the inactive phosphate buffer solution, replaced in the two litres of buffer solution.

The amount of radioactive phosphate adsorbed by the mica surface in this manner was very small ($\sim$150 c.p.m.). This amount was far less than was usually adsorbed by an aluminium saturated mica surface which had not been soaked in inactive phosphate solution. . From the results obtained in this experiment it can be seen that the rate of exchange of inactive and radioactive phosphate on the surface of an aluminium saturated mica sheet is considerably slower than the rate of adsorption of radioactive phosphate directly onto aluminium saturated mica surfaces.

CHAPTER 7.

EXPERIMENTAL RESULTS

The results of a number of desorption experiments, typical of those performed in this thesis, are represented in graphical form in the following pages. Only one experiment is shown for most of the pH values and surfaces studied. Pairs of experiments are shown for some of the systems on which a considerable amount of work was carried out (Aluminium saturated mica surfaces at pH values of 3.0, 5.5 and 9.0 and sodium saturated mica surfaces at a pH value of 5.5.) A number of experiments were performed with some surfaces (e.g.aluminium saturated mica surfaces at a pH value of 5.5) to study a number of phenomena such as the effect of adsorption time, the relationship of the relative amounts of radioactive phosphate adsorbed by sodium saturated and by aluminium saturated mica surfaces, etc., and the rate constants and relative amounts of the various complexes detected have been given for many experiments in the text (see for example Table 4, p. 166 and Table 5 p.169)

In the graphs on the following pages the surfaces from which the desorption of radioactive phosphate was studied are given (either as cation saturated mica or as hydrated aluminium oxide surface) together with the pH value at which the experiment was carried out and the rate constants for

each of the desorption complexes detected. The majority of experiments have, after partial analysis, had the initial portion of the desorption curve replotted on a larger time scale in order to enable more accurate calculation of the largest rate constants (corresponding to the shortest half-lives for desorption). In these experiments the various plots are shown on successive pages.

The relative proportions of the various radioactive phosphate-surface complexes "A", "B" etc. (corresponding to rate constants k_a, k_b etc.) are given by the intercepts of the straight lines, that were obtained by analysis, with the time=0 axis.

The actual graphs are as follows:

Sodium saturated mica pH 3·0 p.285

Sodium saturated mica pH 5·5 pp. 286 and 287

Aluminium saturated mica pH 3·0 pp.288-9 and 290-1

Aluminium saturated mica pH 5.5 pp.292-3 and 294-5

Aluminium saturated mica pH 9.0 pp.296-7 and 298-9

Aluminium saturated mica pH 1.0 p.300

Aluminium saturated mica pH 0.0 p.301

Ammonium ion saturated mica pH 5.5 p.302

Aluminium saturated mica dried over silica gel (see p.195) pH 5·5 pp.303-4

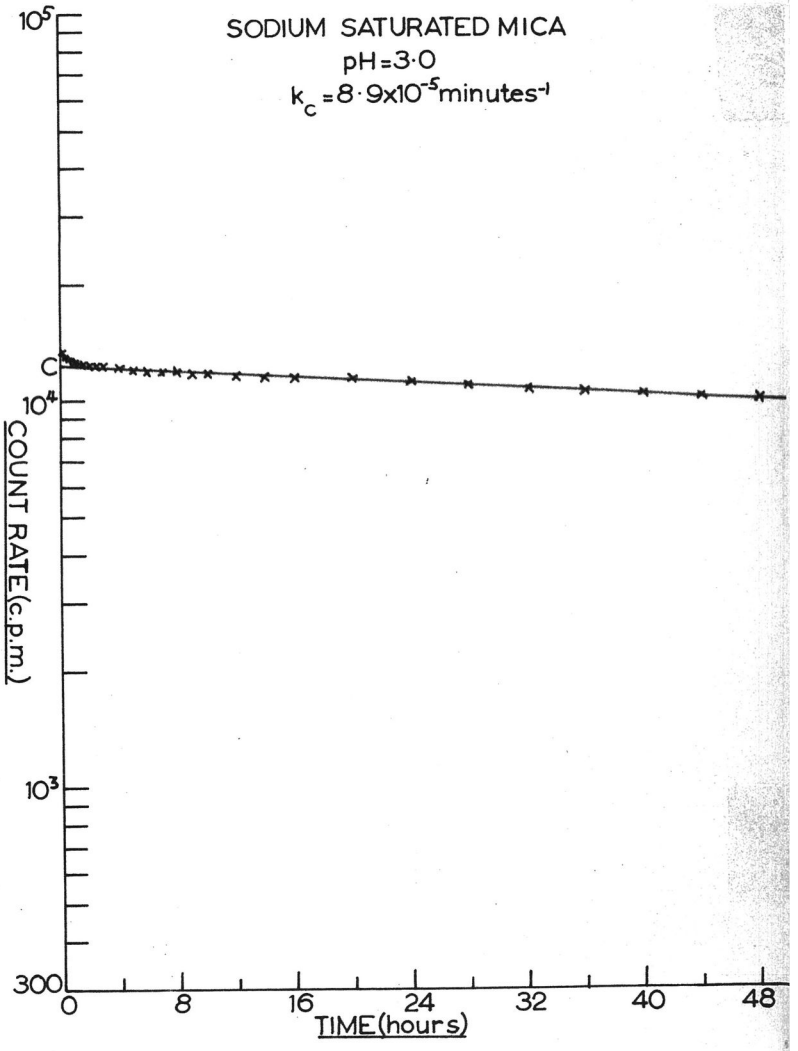
Hydrated aluminium oxide surface pH 3.0 p. 305-6

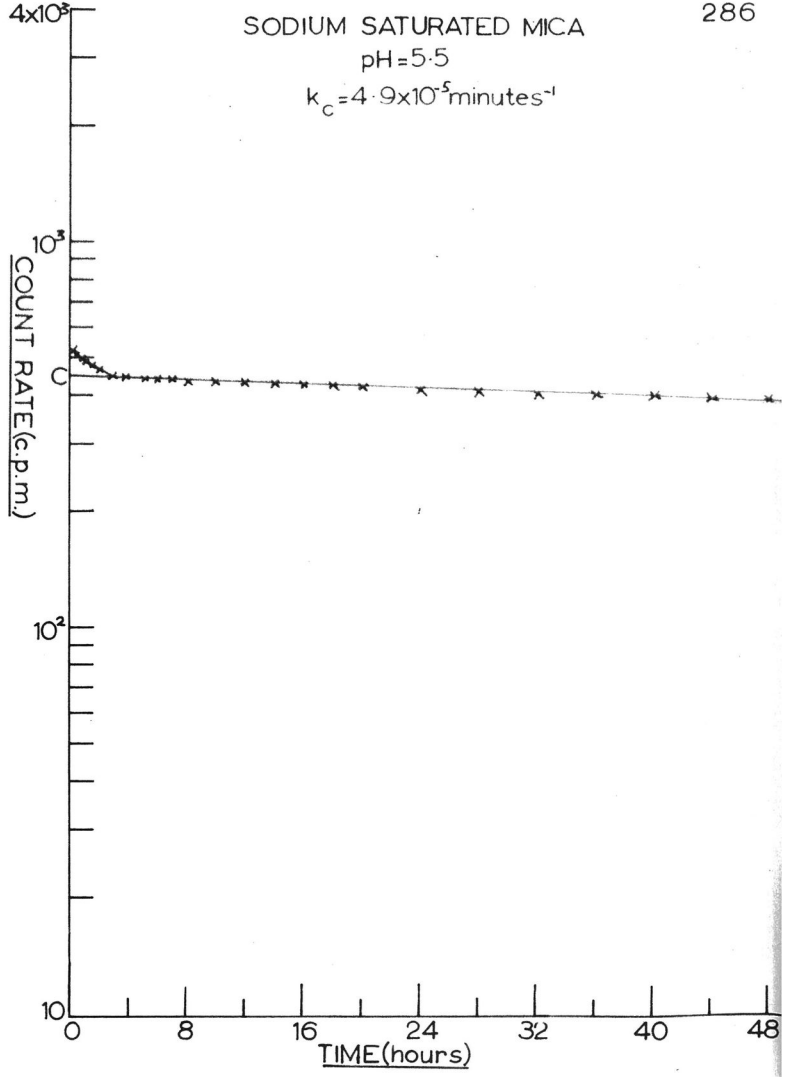
Hydrated aluminium oxide surface pH5·5 p.307

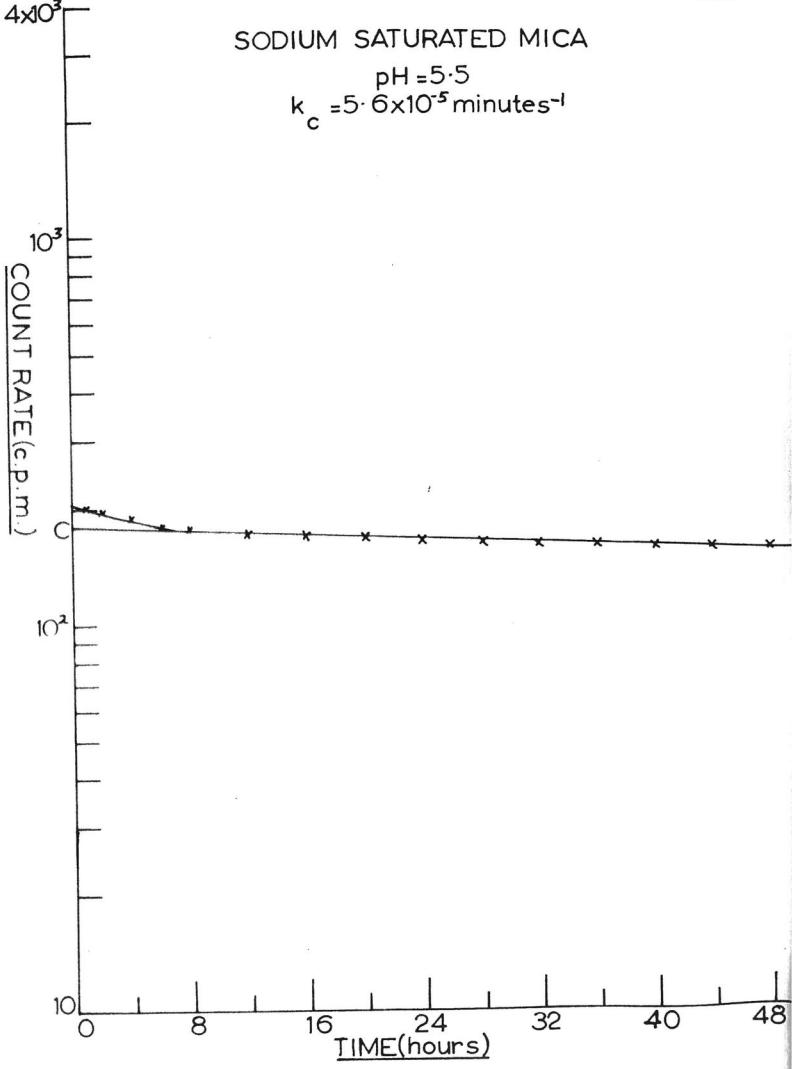
Hydrated aluminium oxide surface pH 9.0 P. 308

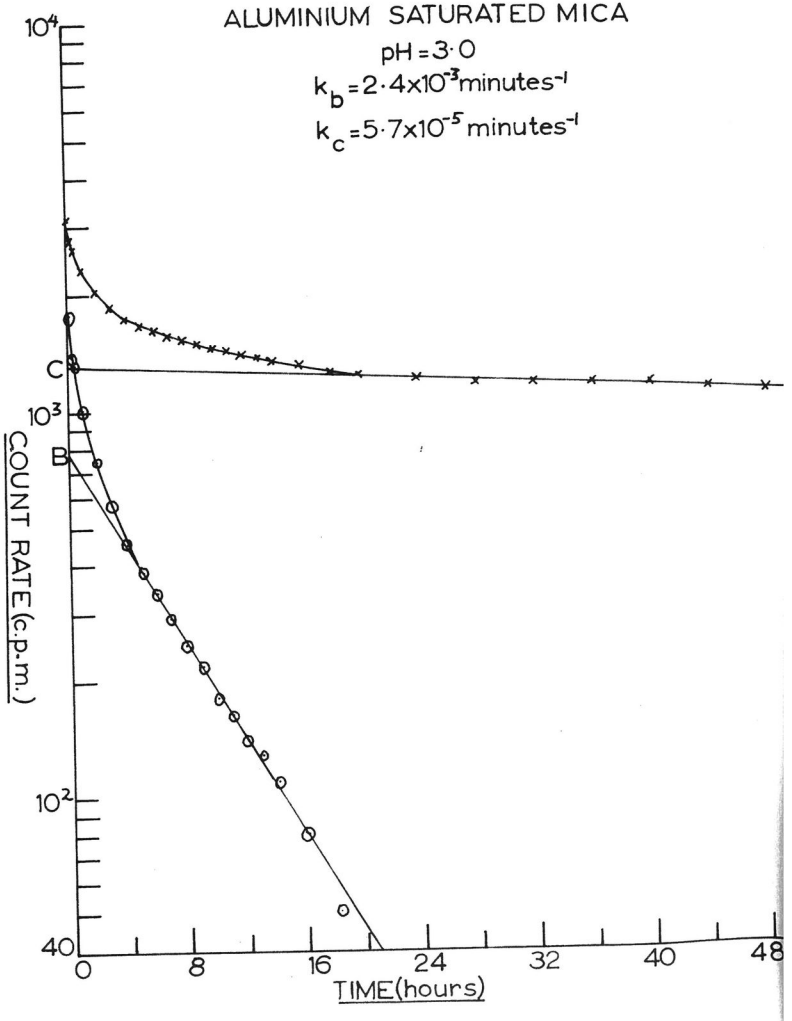
Aluminium saturated mica desorbed for a much greater period of time (see p.217) pH 5.5 pp.309-11

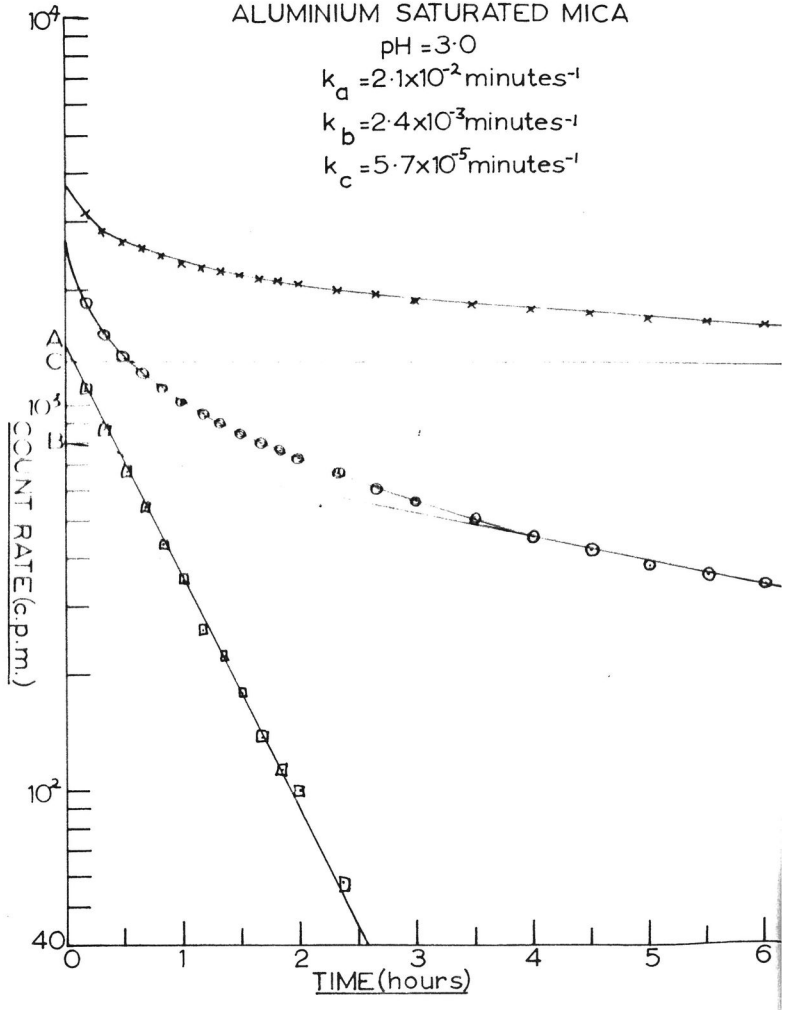
Sodium saturated mica desorbed for a much greater period of time (see p.217) pH 5.5 p.312

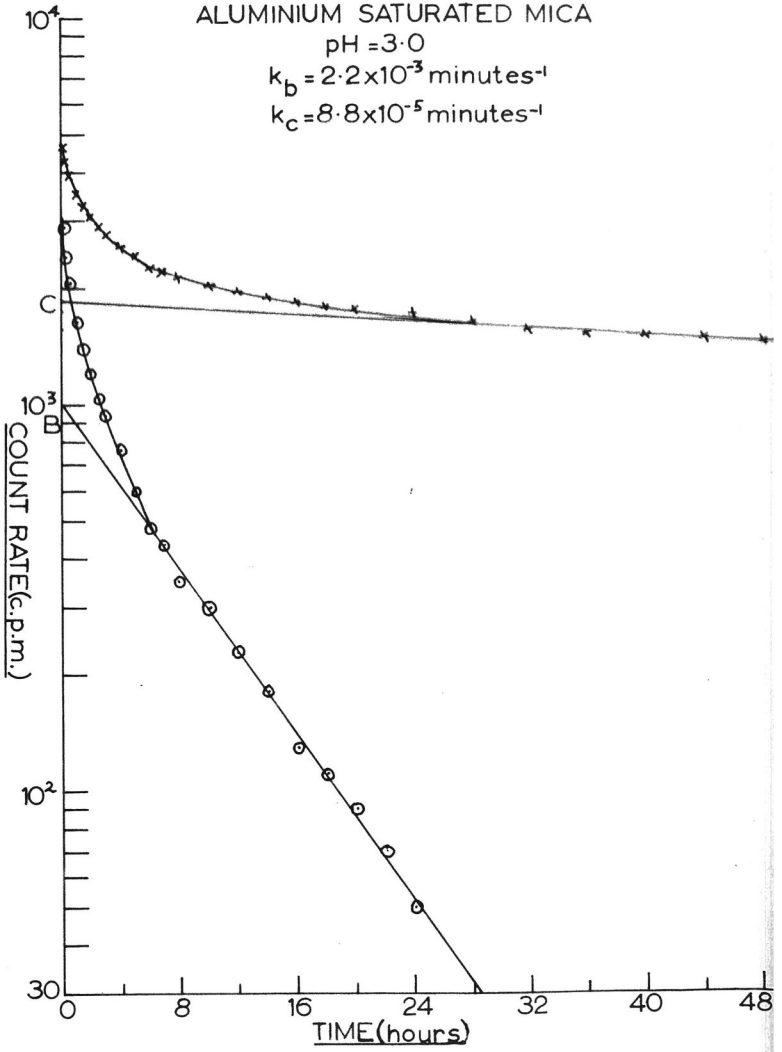

SODIUM SATURATED MICA
pH=3·0
$k_c = 8 \cdot 9 \times 10^{-5}$ minutes^{-1}
10^5
C
10^4
10^3
300
COUNT RATE(c.p.m.)
0
8
16
24
32
40
48
TIME(hours)

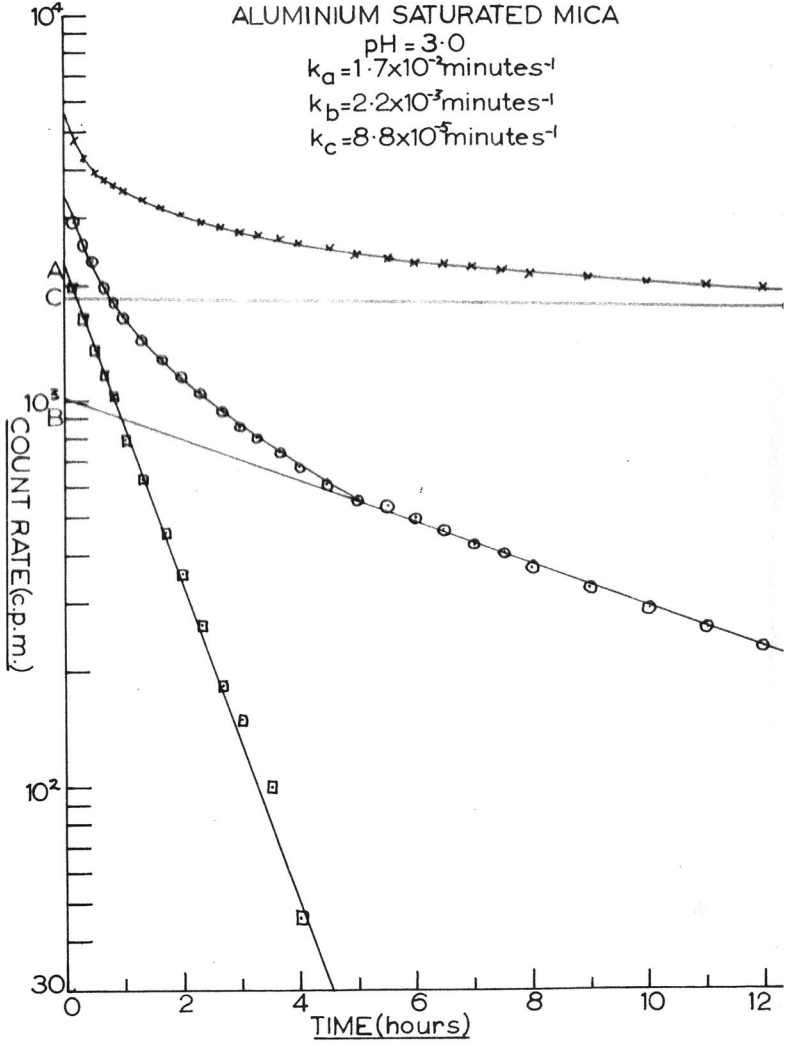

SODIUM SATURATED MICA
pH = 5·5
$k_c = 4 \cdot 9 \times 10^{-5}$ minutes^{-1}
4x10³
10³
C
10²
10
COUNT RATE(c.p.m.)
0
8
16
24
32
40
48
TIME(hours)

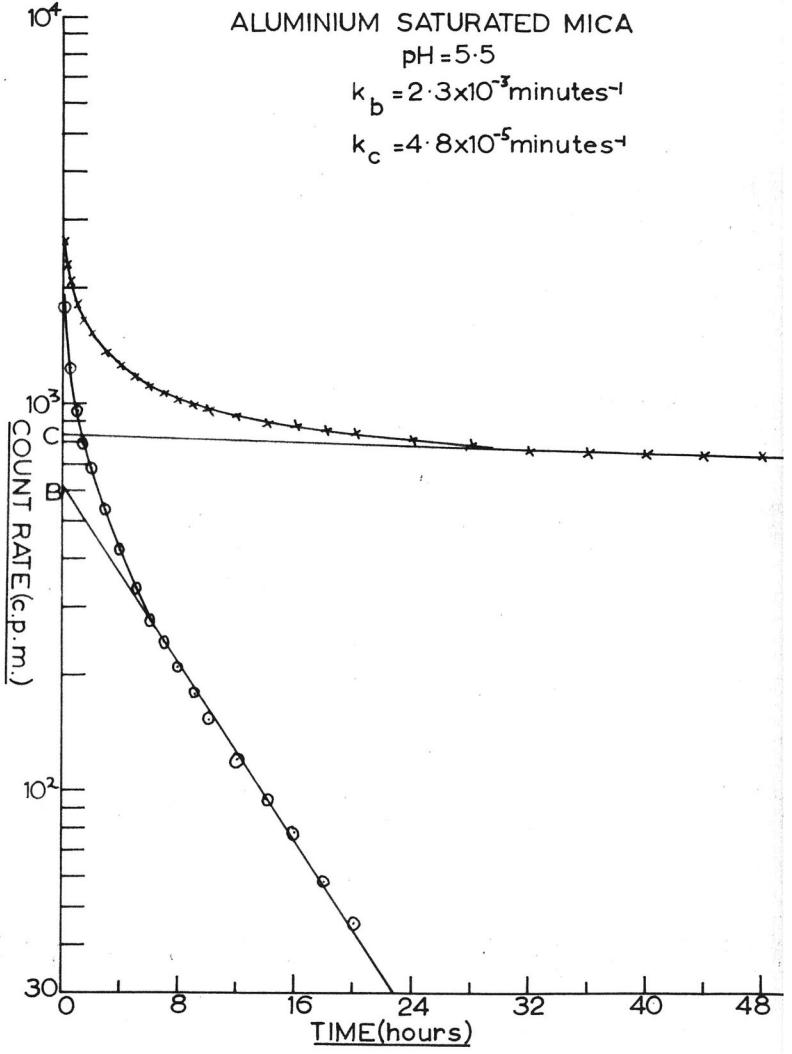

SODIUM SATURATED MICA
pH = 5·5
k_c = 5·6x10⁻⁵ minutes⁻¹
4x10³
10³
COUNT RATE(c.p.m.)
0
10²
10
0
8
16
24
32
40
48
TIME(hours)

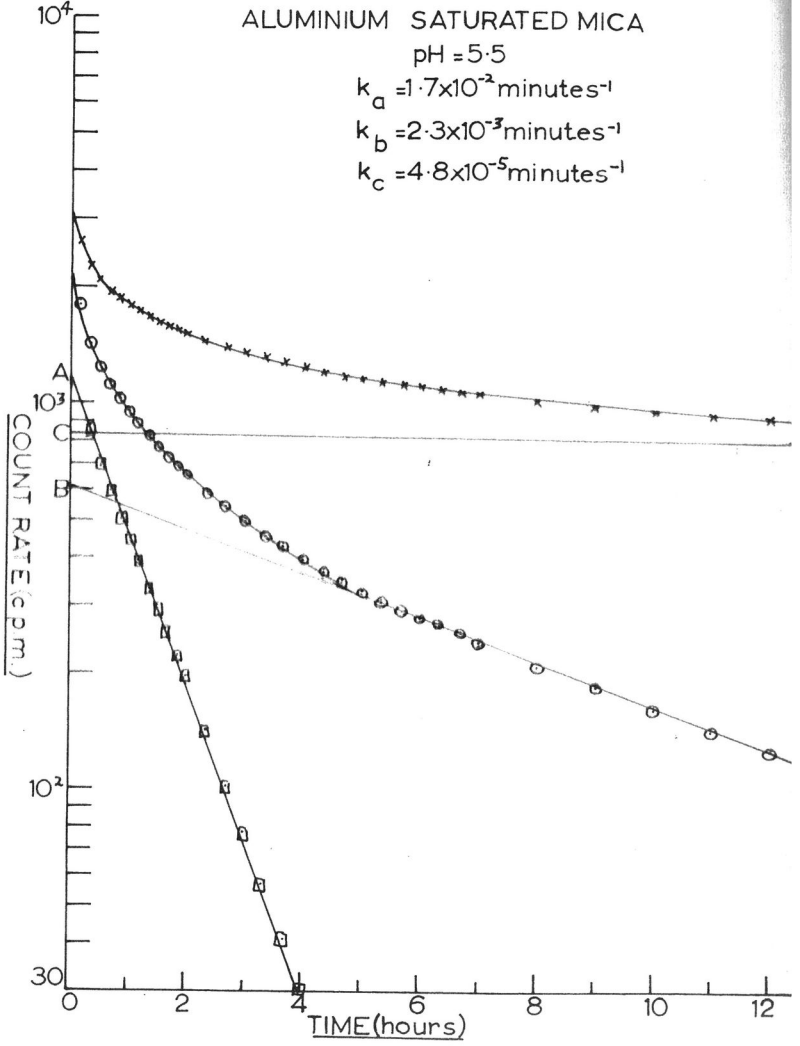

ALUMINIUM SATURATED MICA
pH = 3·0
$k_b = 2 \cdot 4 \times 10^{-3}$ minutes^{-1}
$k_c = 5 \cdot 7 \times 10^{-5}$ minutes^{-1}
10^4
C
10^3
B
10^2
40
COUNT RATE (c.p.m.)
0
8
16
24
32
40
48
TIME (hours)

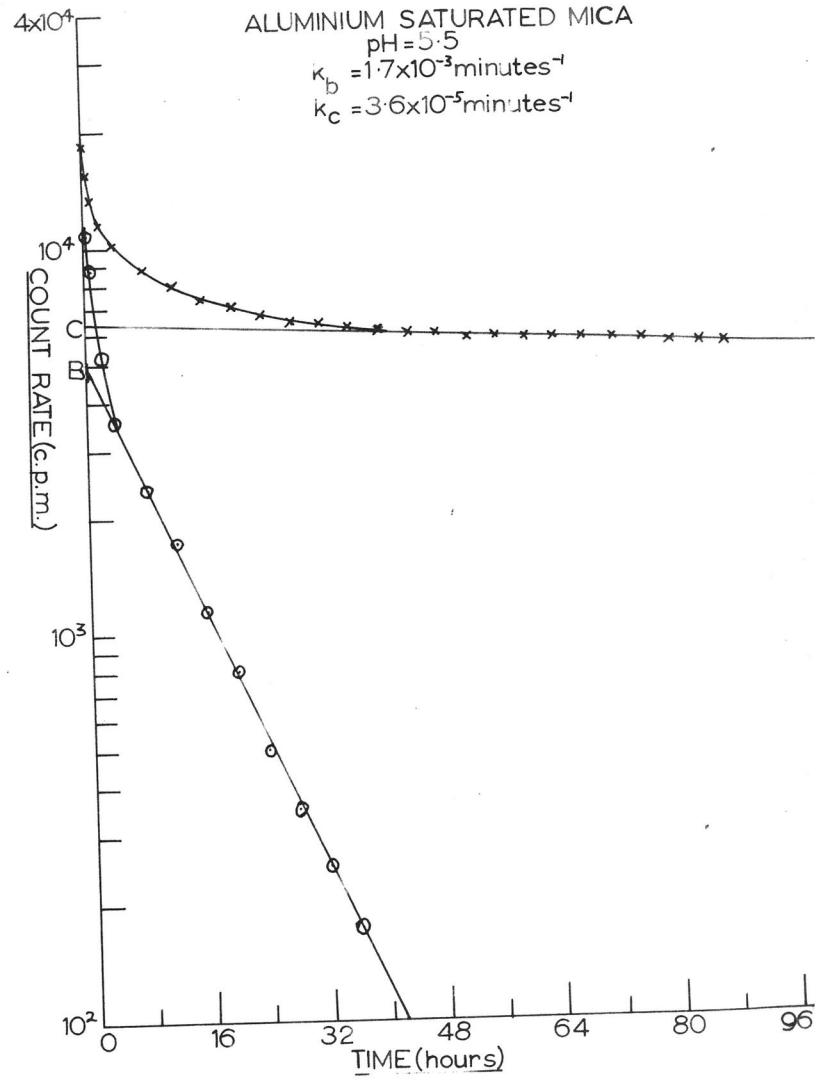

ALUMINIUM SATURATED MICA
pH = 3·0
k_a = 2·1x10^{-2} minutes^{-1}
k_b = 2·4x10^{-3} minutes^{-1}
k_c = 5·7x10^{-5} minutes^{-1}
A
C
B
COUNT RATE (c.p.m.)
TIME (hours)
10^4
10^3
10^2
40
0
1
2
3
4
5
6

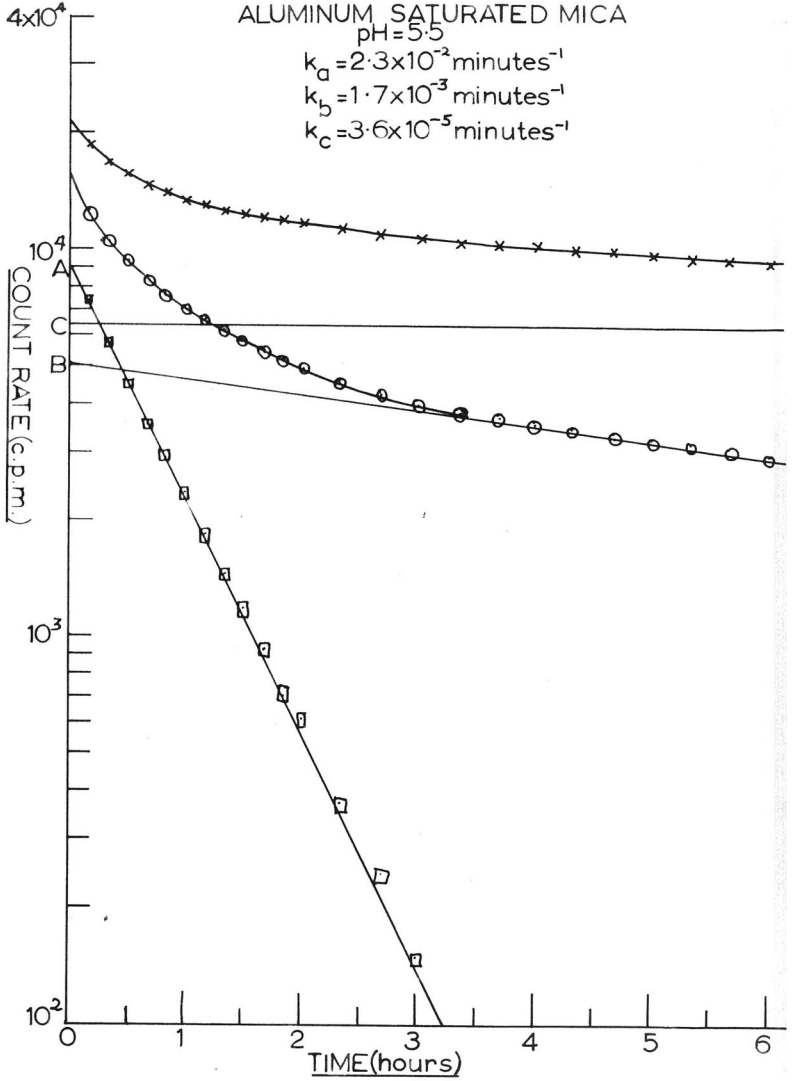

ALUMINIUM SATURATED MICA
pH = 3·0
$k_b = 2{\cdot}2 \times 10^{-3}$ minutes^{-1}
$k_c = 8{\cdot}8 \times 10^{-5}$ minutes^{-1}
10^4
C
10^3
B
COUNT RATE(c.p.m.)
10^2
30
0
8
16
24
32
40
48
TIME(hours)

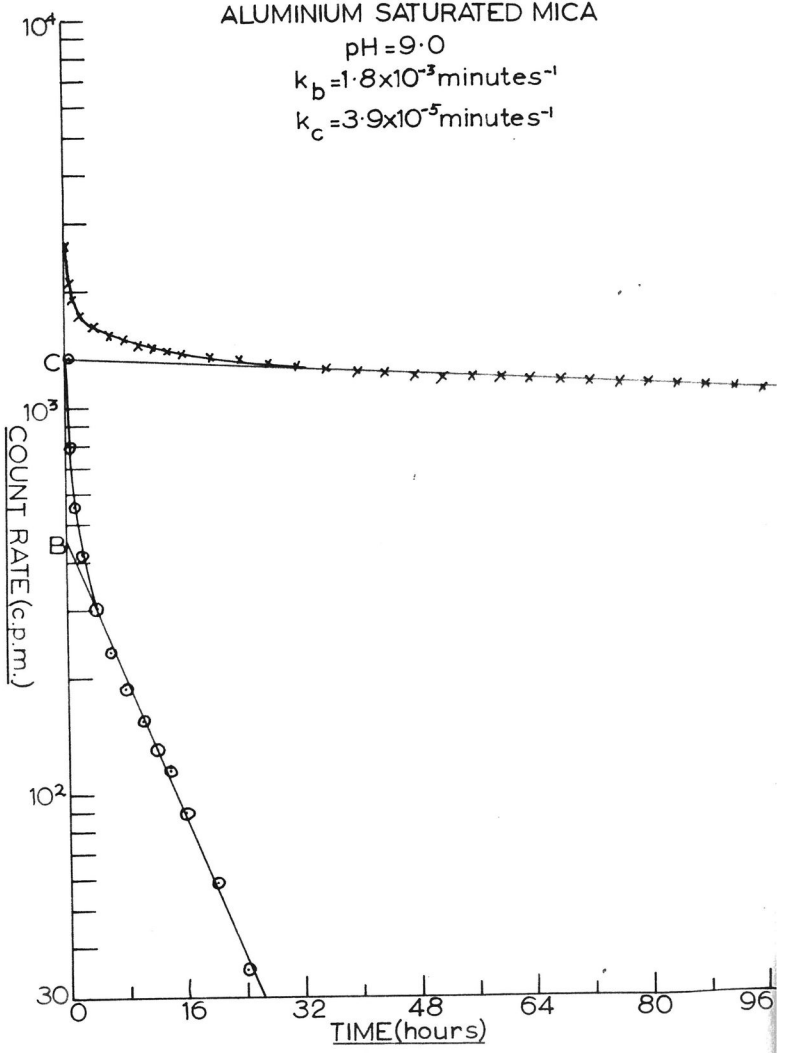

ALUMINIUM SATURATED MICA
pH = 3·0
$k_a = 1{\cdot}7 \times 10^{-2}$ minutes^{-1}
$k_b = 2{\cdot}2 \times 10^{-3}$ minutes^{-1}
$k_c = 8{\cdot}8 \times 10^{-5}$ minutes^{-1}
A
C
B
10^4
10^3
10^2
30
COUNT RATE(c.p.m.)
0
2
4
6
8
10
12
TIME(hours)

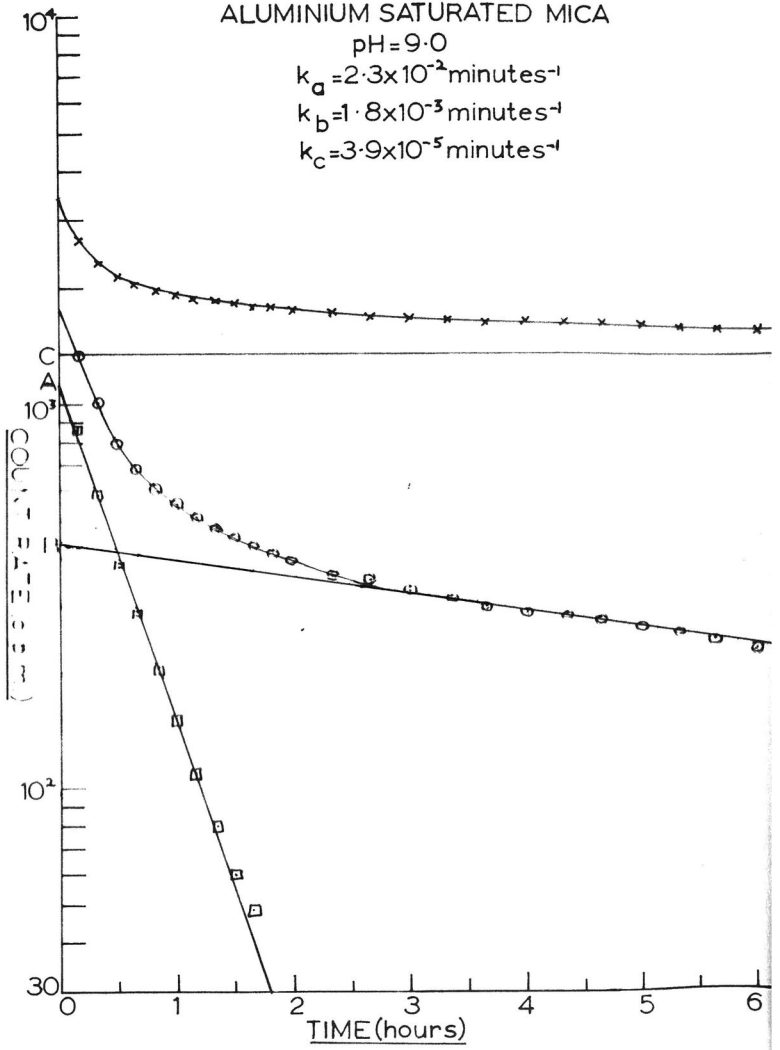

ALUMINIUM SATURATED MICA
pH = 5·5
$k_b = 2 \cdot 3 \times 10^{-3}$ minutes^{-1}
$k_c = 4 \cdot 8 \times 10^{-5}$ minutes^{-1}
10^4
10^3
10^2
30
C
B
COUNT RATE (c.p.m.)
0
8
16
24
32
40
48
TIME (hours)

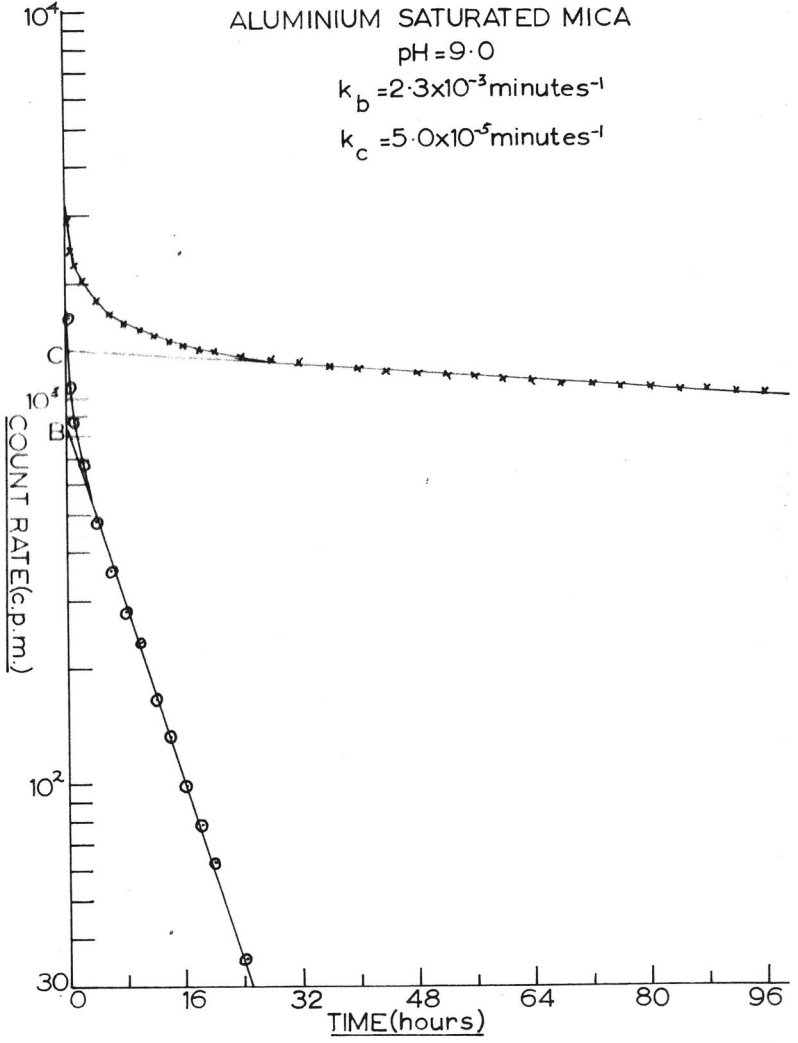

ALUMINIUM SATURATED MICA
pH = 5·5
k_a = 1·7x10^{-2} minutes^{-1}
k_b = 2·3x10^{-3} minutes^{-1}
k_c = 4·8x10^{-5} minutes^{-1}
A
B
C
COUNT RATE (c p m)
TIME (hours)

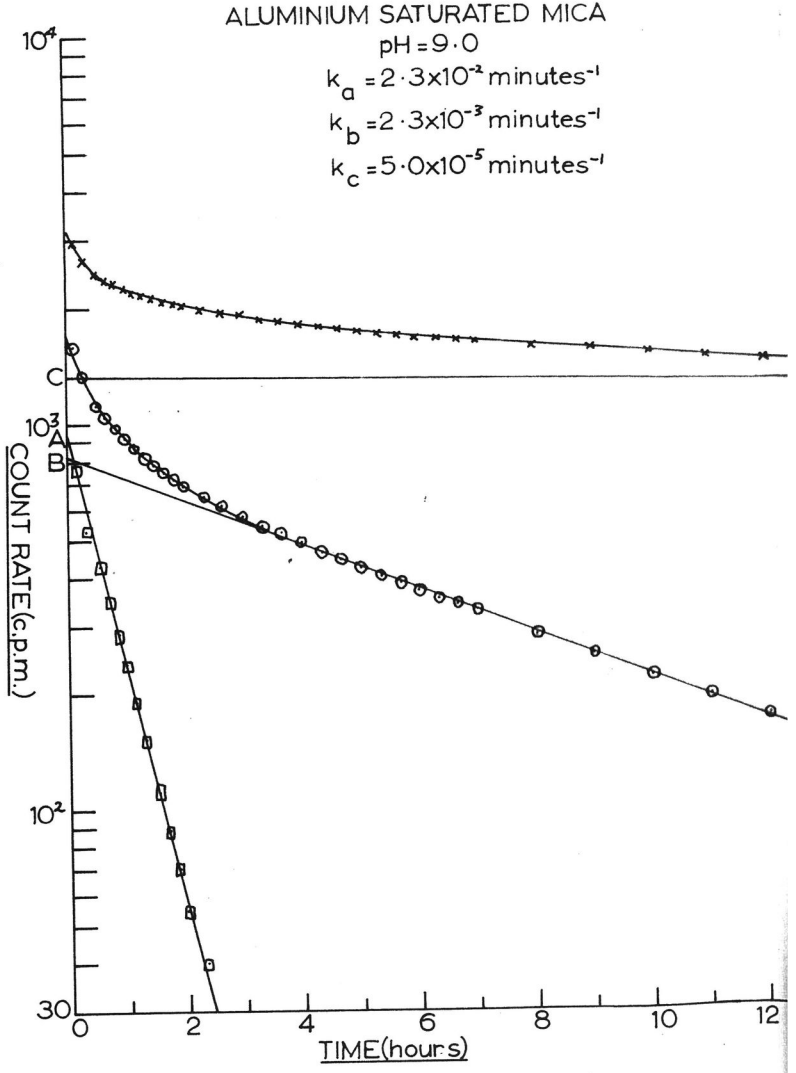

ALUMINIUM SATURATED MICA
pH = 5·5
k_b = 1·7x10^{-3} minutes^{-1}
k_c = 3·6x10^{-5} minutes^{-1}
4x10^4
10^4
10^3
10^2
C
B
COUNT RATE (c.p.m.)
0
16
32
48
64
80
96
TIME (hours)

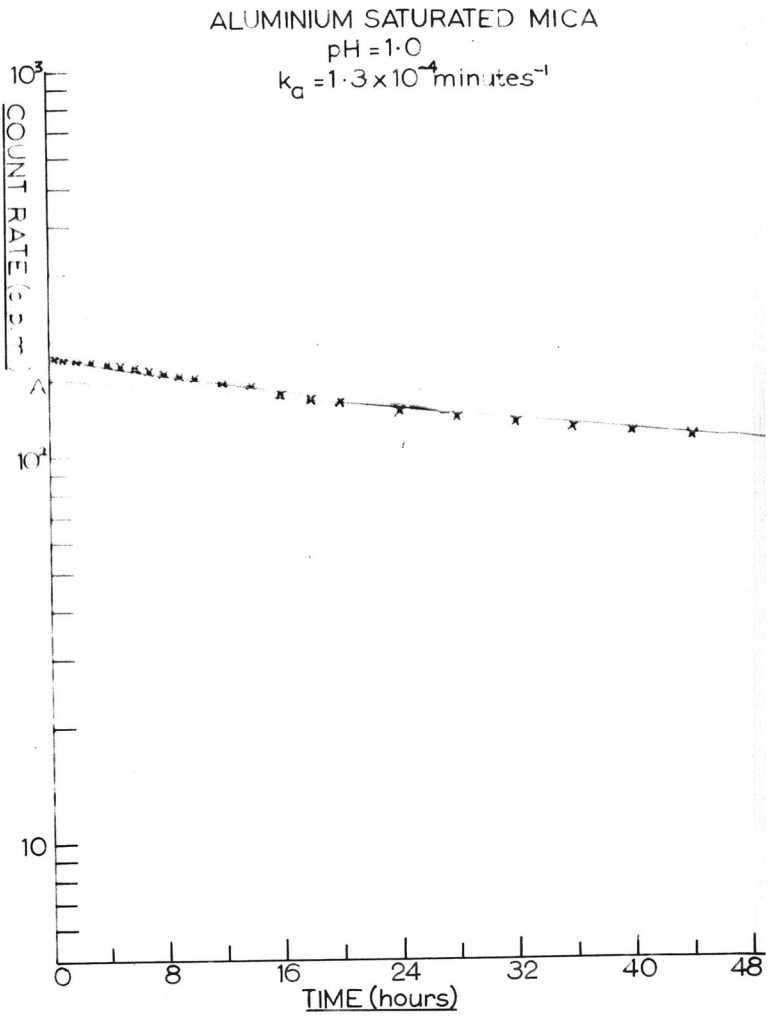

ALUMINUM SATURATED MICA
pH=5·5
$k_a = 2{\cdot}3\times10^{-2}$ minutes^{-1}
$k_b = 1{\cdot}7\times10^{-3}$ minutes^{-1}
$k_c = 3{\cdot}6\times10^{-5}$ minutes^{-1}
4x10⁴
10⁴
10³
10²
A
C
B
COUNT RATE (c.p.m.)
0
1
2
3
4
5
6
TIME (hours)


ALUMINIUM SATURATED MICA
pH = 9·0
$k_b = 1{\cdot}8 \times 10^{-3}$ minutes^{-1}
$k_c = 3{\cdot}9 \times 10^{-5}$ minutes^{-1}
10^4
C
10^3
B
10^2
30
COUNT RATE (c.p.m.)
0
16
32
48
64
80
96
TIME (hours)


ALUMINIUM SATURATED MICA
pH = 9·0
$k_a = 2{\cdot}3 \times 10^{-2}$ minutes^{-1}
$k_b = 1{\cdot}8 \times 10^{-3}$ minutes^{-1}
$k_c = 3{\cdot}9 \times 10^{-5}$ minutes^{-1}
C
A
10^4
10^3
1
10^2
30
0
1
2
3
4
5
6
TIME (hours)


ALUMINIUM SATURATED MICA
pH = 9·0
k_b = 2·3x10^{-3} minutes^{-1}
k_c = 5·0x10^{-5} minutes^{-1}
C
B
COUNT RATE(c.p.m.)
10^4
10^3
10^2
30
0
16
32
48
64
80
96
TIME(hours)


ALUMINIUM SATURATED MICA
pH = 9·0
$k_a = 2 \cdot 3 \times 10^{-2}$ minutes^{-1}
$k_b = 2 \cdot 3 \times 10^{-3}$ minutes^{-1}
$k_c = 5 \cdot 0 \times 10^{-5}$ minutes^{-1}
10^4
C
10^3
A
B
COUNT RATE(c.p.m.)
10^2
30
0
2
4
6
8
10
12
TIME(hours)


ALUMINIUM SATURATED MICA
pH = 1·0
$k_a = 1 \cdot 3 \times 10^{-4}$ minutes^{-1}
10^3
COUNT RATE (c.p.m.)
10^2
10
0
8
16
24
32
40
48
TIME (hours)

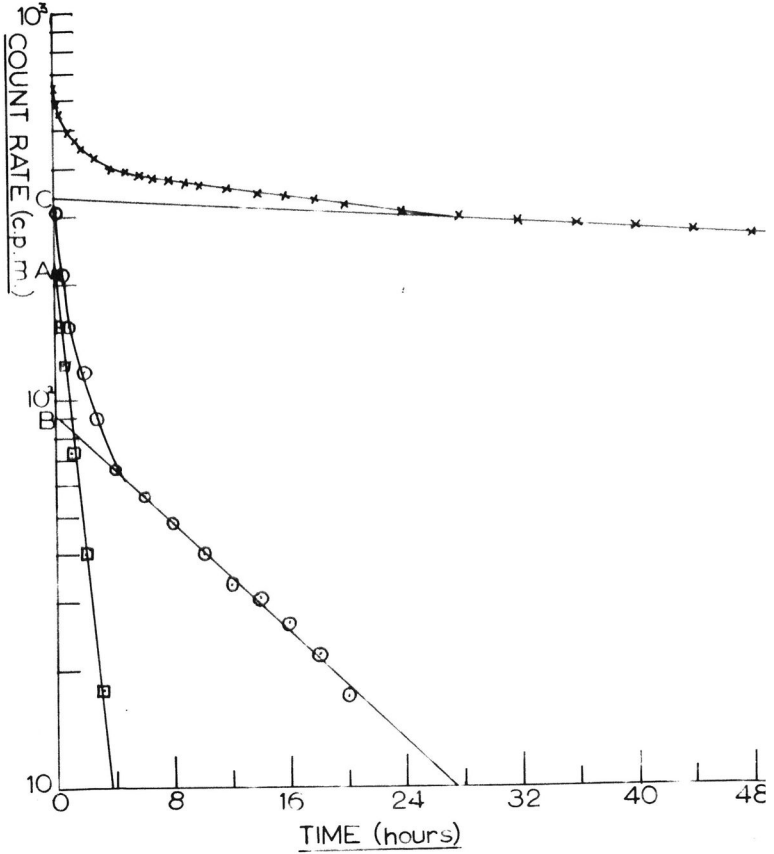
ALUMINIUM SATURATED MICA

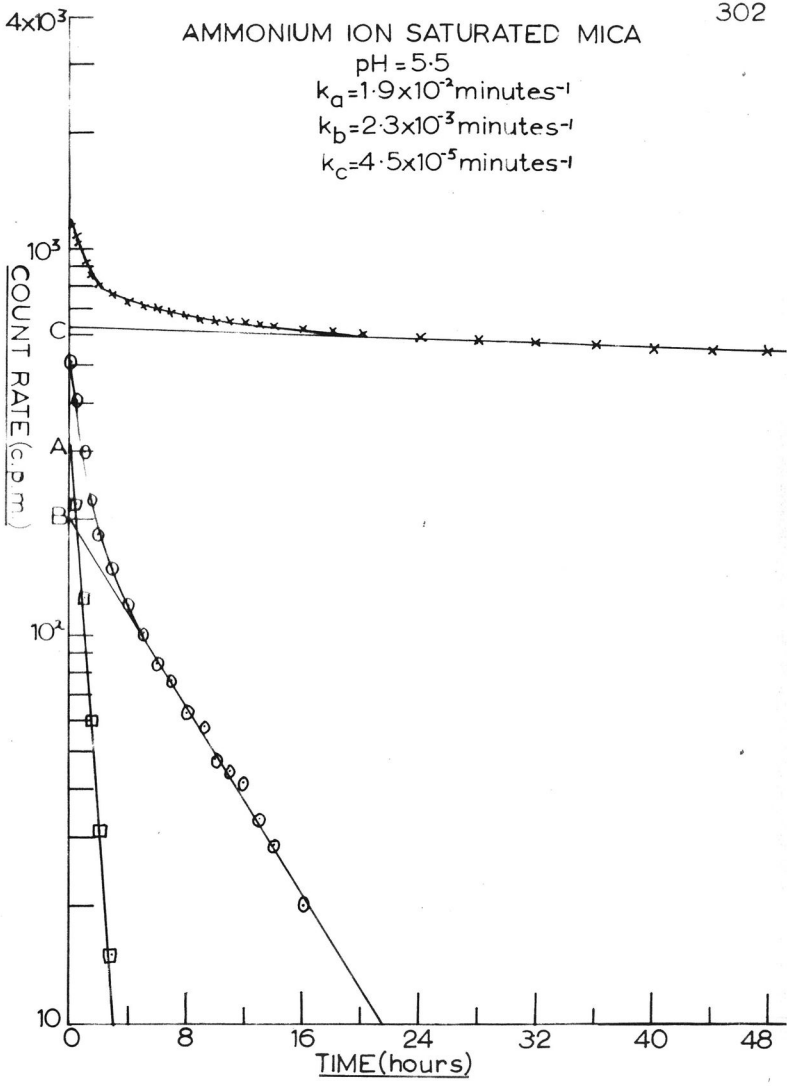
pH = 0·0

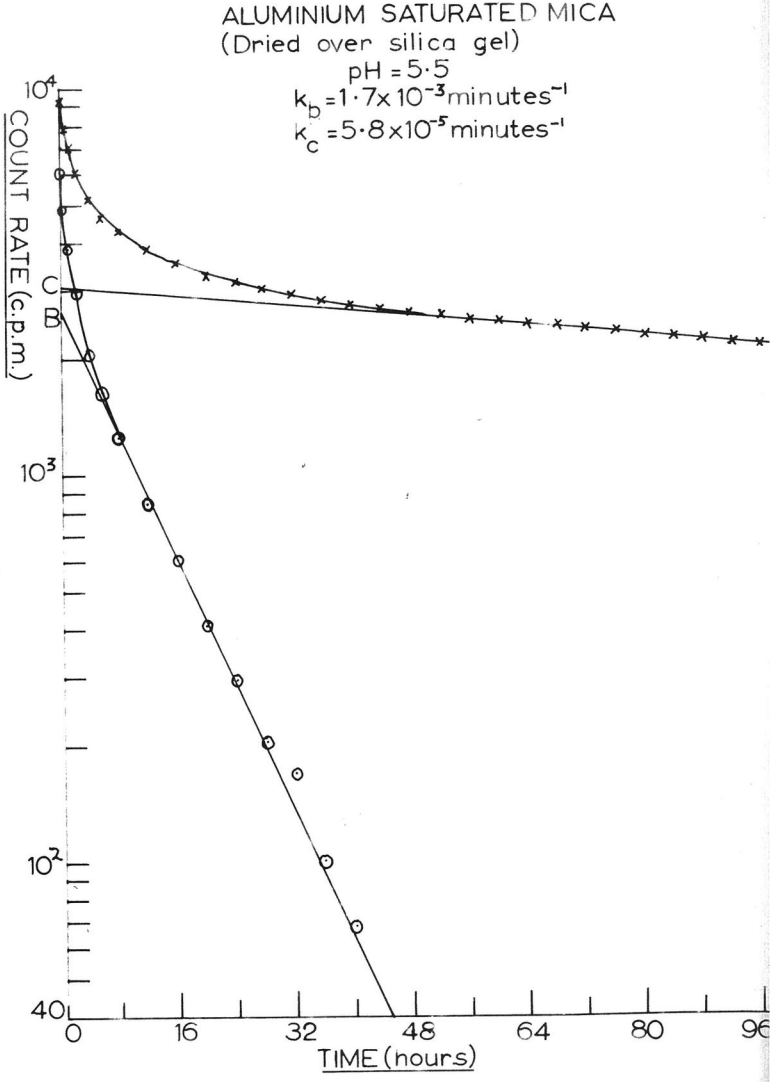
$k_a = 1{\cdot}5 \times 10^{-2}$ minutes^{-1}

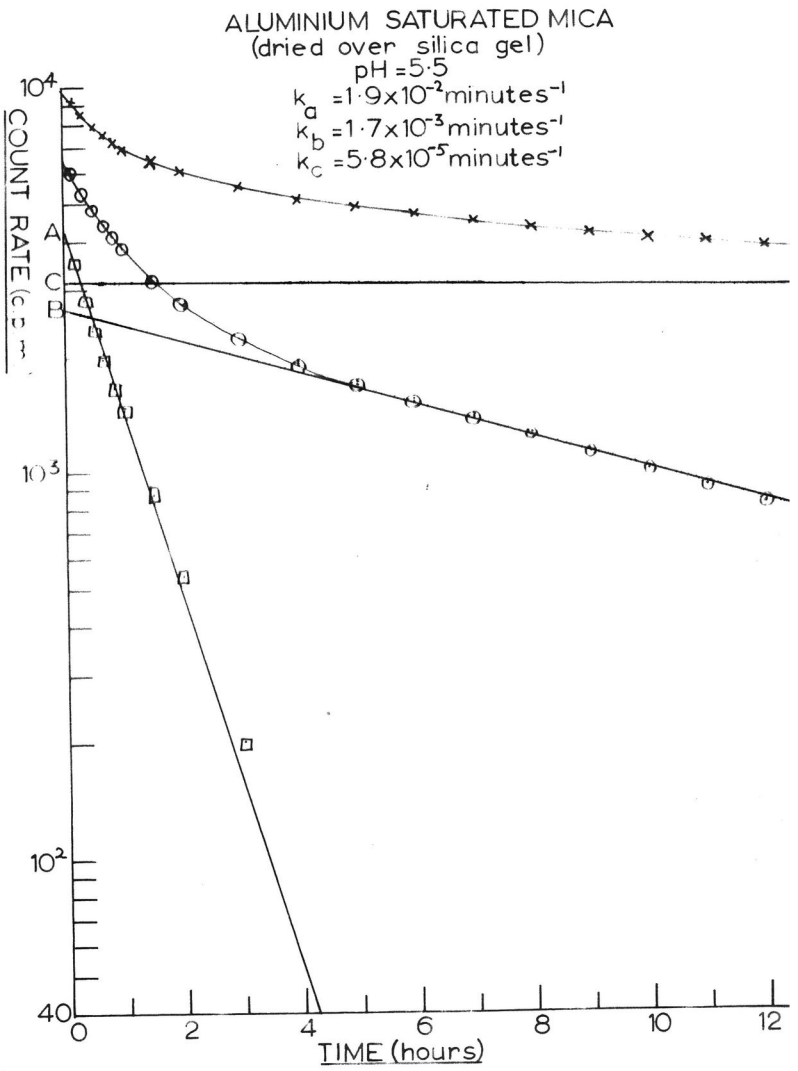
$k_b = 1{\cdot}4 \times 10^{-3}$ minutes^{-1}

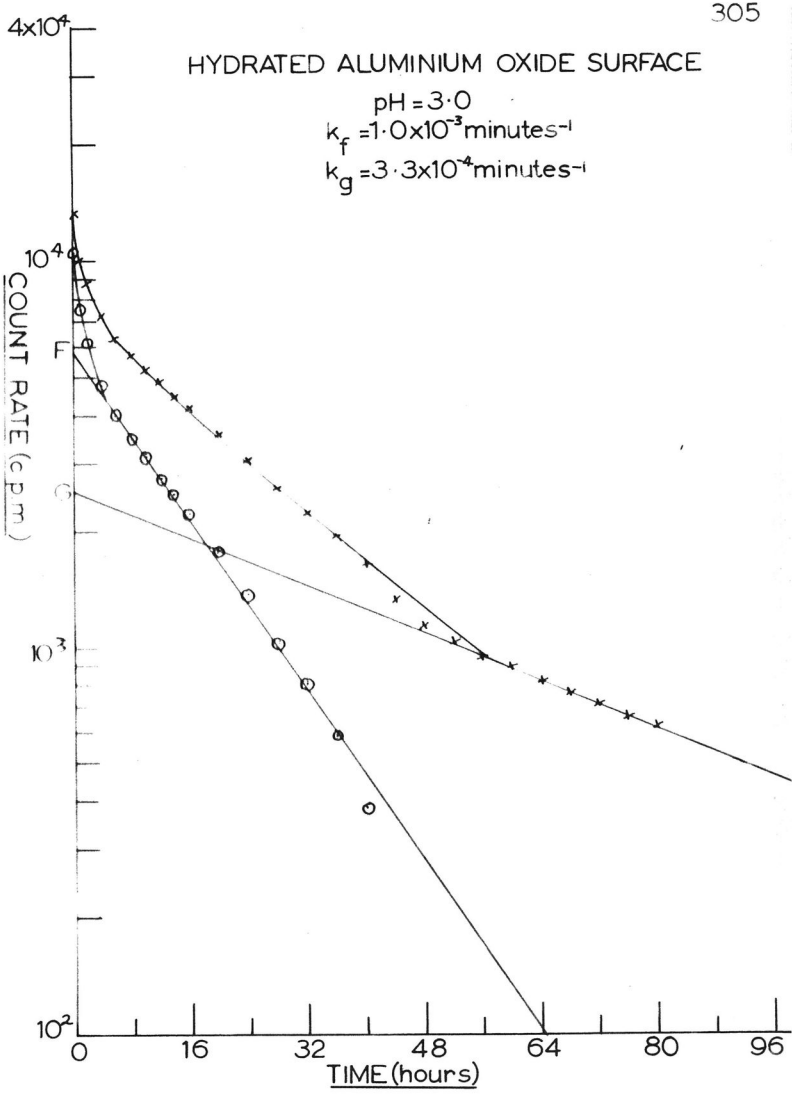
$k_c = 9 \times 10^{-5}$ minutes^{-1}

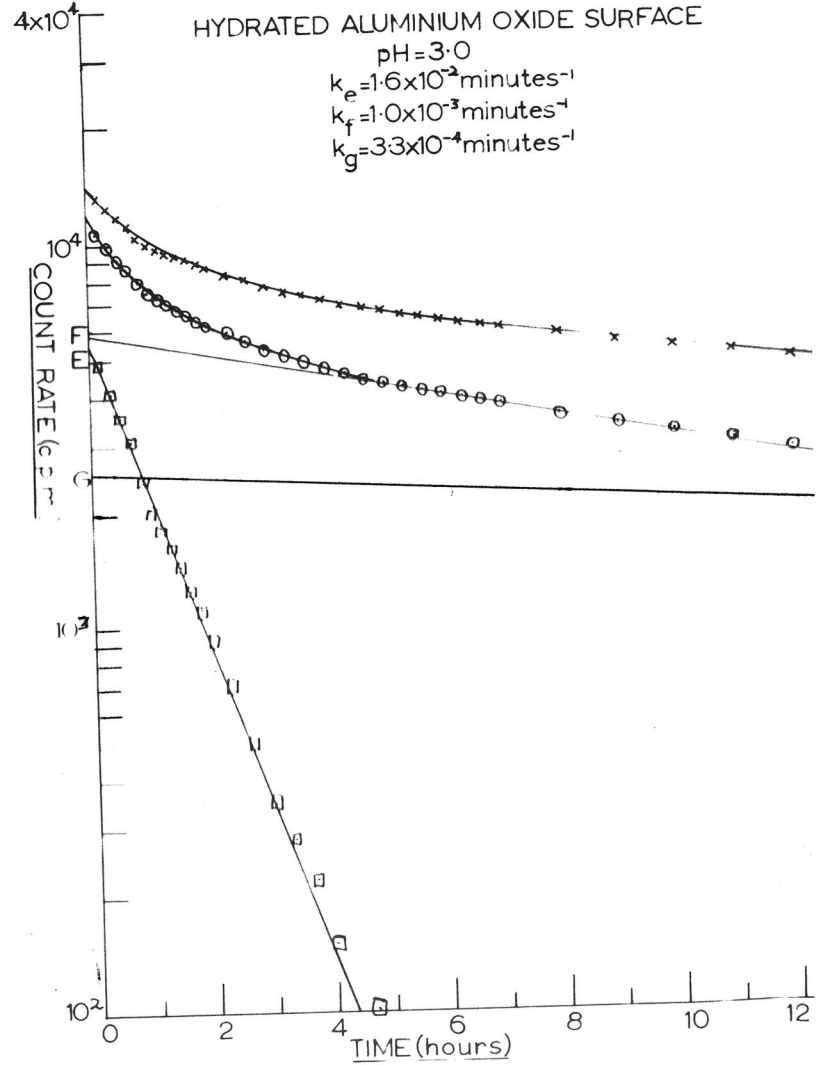


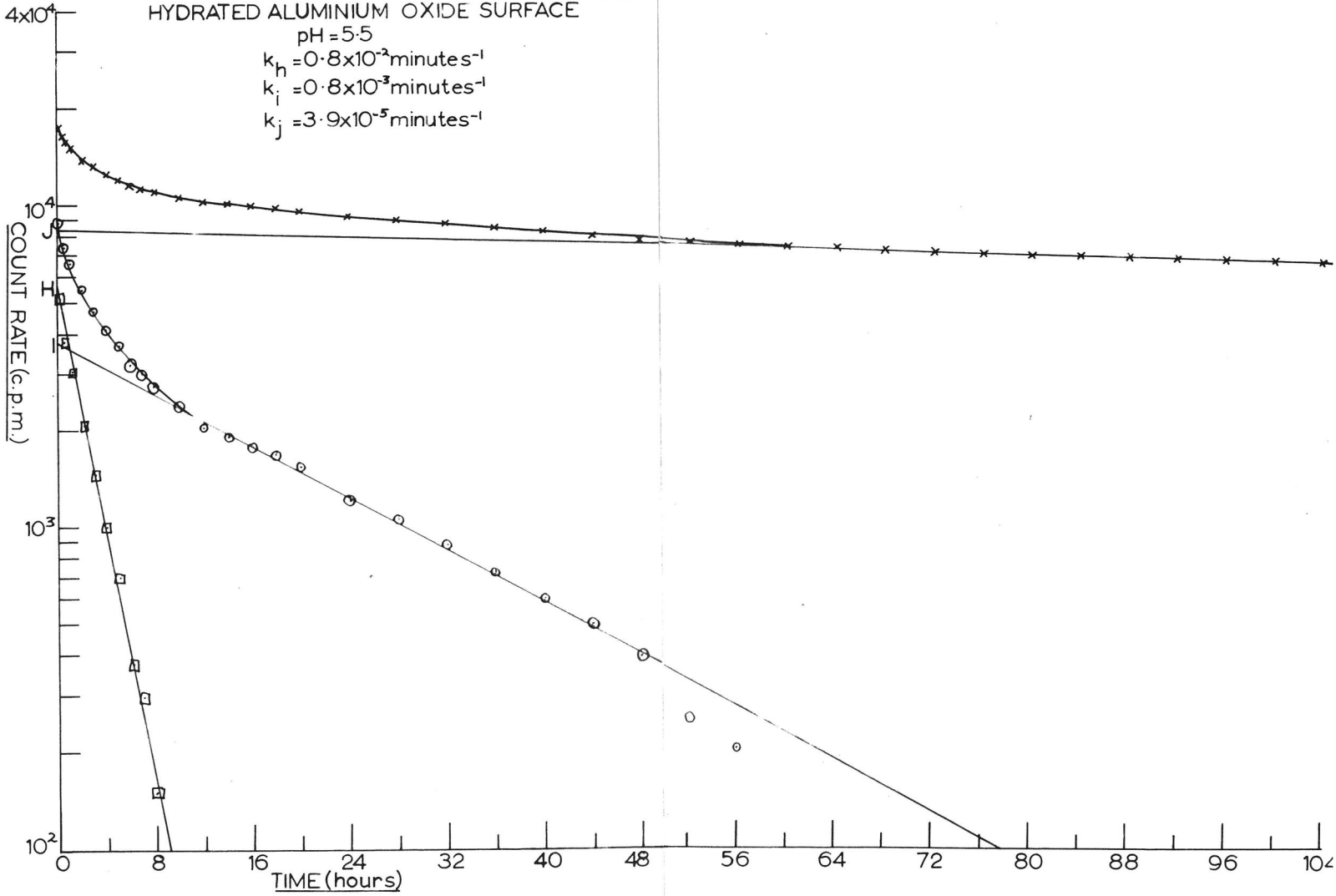

AMMONIUM ION SATURATED MICA
pH = 5·5
$k_a = 1.9 \times 10^{-2}$ minutes^{-1}
$k_b = 2.3 \times 10^{-3}$ minutes^{-1}
$k_c = 4.5 \times 10^{-5}$ minutes^{-1}
4x10³
10³
10²
10
COUNT RATE (c.p.m.)
A
B
C
0
8
16
24
32
40
48
TIME (hours)


ALUMINIUM SATURATED MICA
(Dried over silica gel)
pH = 5·5
$k_b = 1{\cdot}7 \times 10^{-3}$ minutes^{-1}
$k_c = 5{\cdot}8 \times 10^{-5}$ minutes^{-1}
COUNT RATE (c.p.m.)
10^4
10^3
10^2
40
C
B
0
16
32
48
64
80
96
TIME (hours)


ALUMINIUM SATURATED MICA
(dried over silica gel)
pH = 5·5
$k_a = 1{\cdot}9 \times 10^{-2}$ minutes^{-1}
$k_b = 1{\cdot}7 \times 10^{-3}$ minutes^{-1}
$k_c = 5{\cdot}8 \times 10^{-5}$ minutes^{-1}
COUNT RATE (c.p.m.)
10^4
10^3
10^2
40
A
C
B
0
2
4
6
8
10
12
TIME (hours)


HYDRATED ALUMINIUM OXIDE SURFACE
pH = 3·0
k_f = 1·0x10⁻³ minutes⁻¹
k_g = 3·3x10⁻⁴ minutes⁻¹
4x10⁴
10⁴
10³
10²
COUNT RATE (c.p.m.)
F
G
0
16
32
48
64
80
96
TIME (hours)

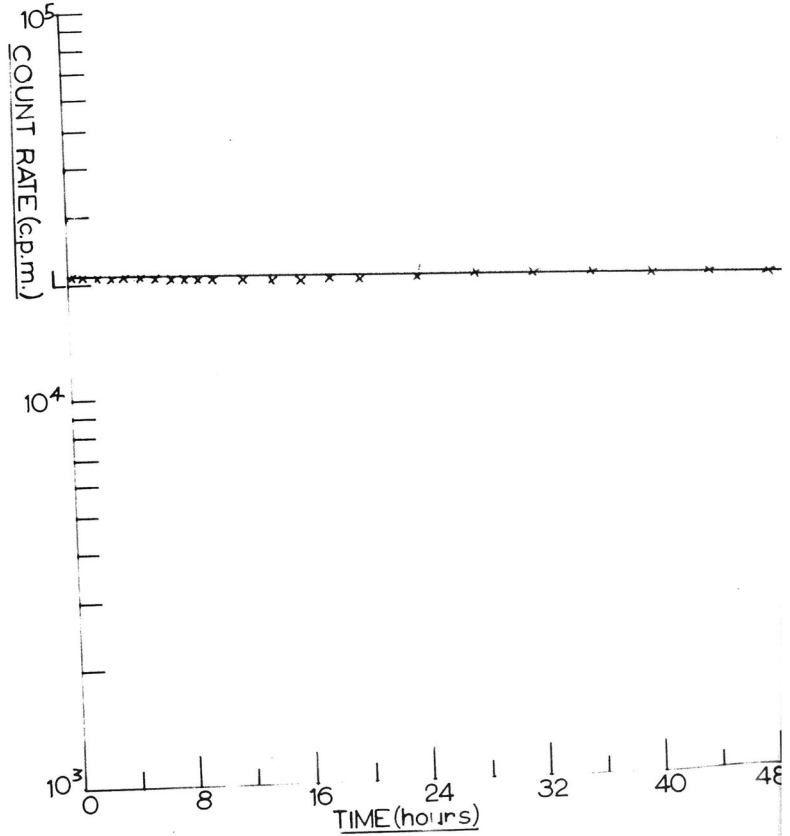

HYDRATED ALUMINIUM OXIDE SURFACE
pH = 3·0
k_e = 1·6x10^{-2} minutes^{-1}
k_f = 1·0x10^{-3} minutes^{-1}
k_g = 3·3x10^{-4} minutes^{-1}
4x10^4
10^4
COUNT RATE (c.p.m.)
F
E
G
10^3
10^2
0
2
4
6
8
10
12
TIME (hours)

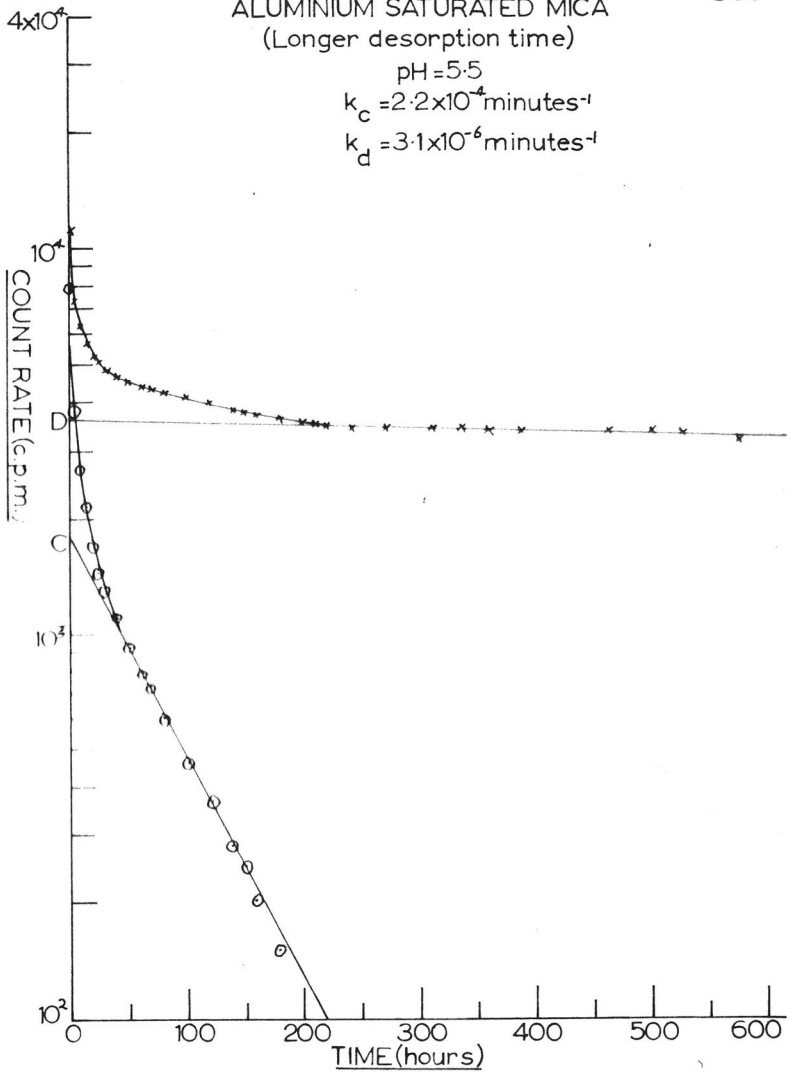

HYDRATED ALUMINIUM OXIDE SURFACE
pH = 5·5
k_h = 0·8x10^{-2} minutes^{-1}
k_i = 0·8x10^{-3} minutes^{-1}
k_j = 3·9x10^{-5} minutes^{-1}
4x10^4
10^4
10^3
10^2
COUNT RATE (c.p.m.)
J
H
I
0
8
16
24
32
40
48
56
64
72
80
88
96
104
TIME (hours)

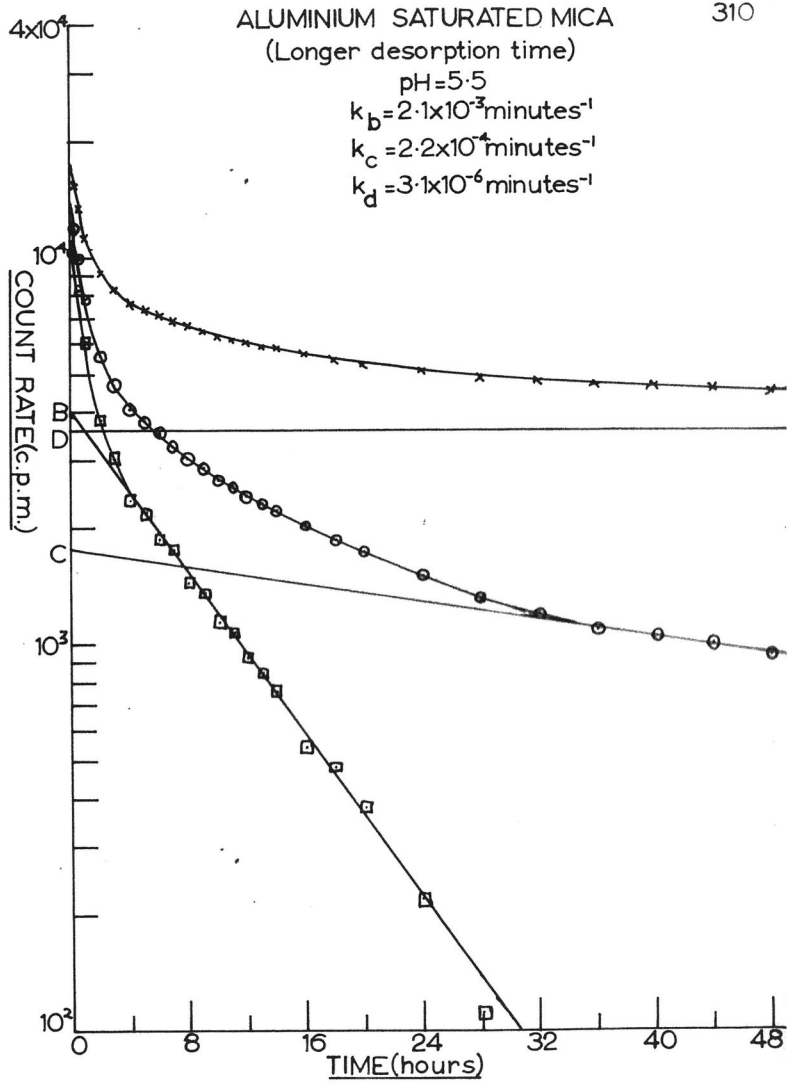
HYDRATED ALUMINIUM OXIDE SURFACE

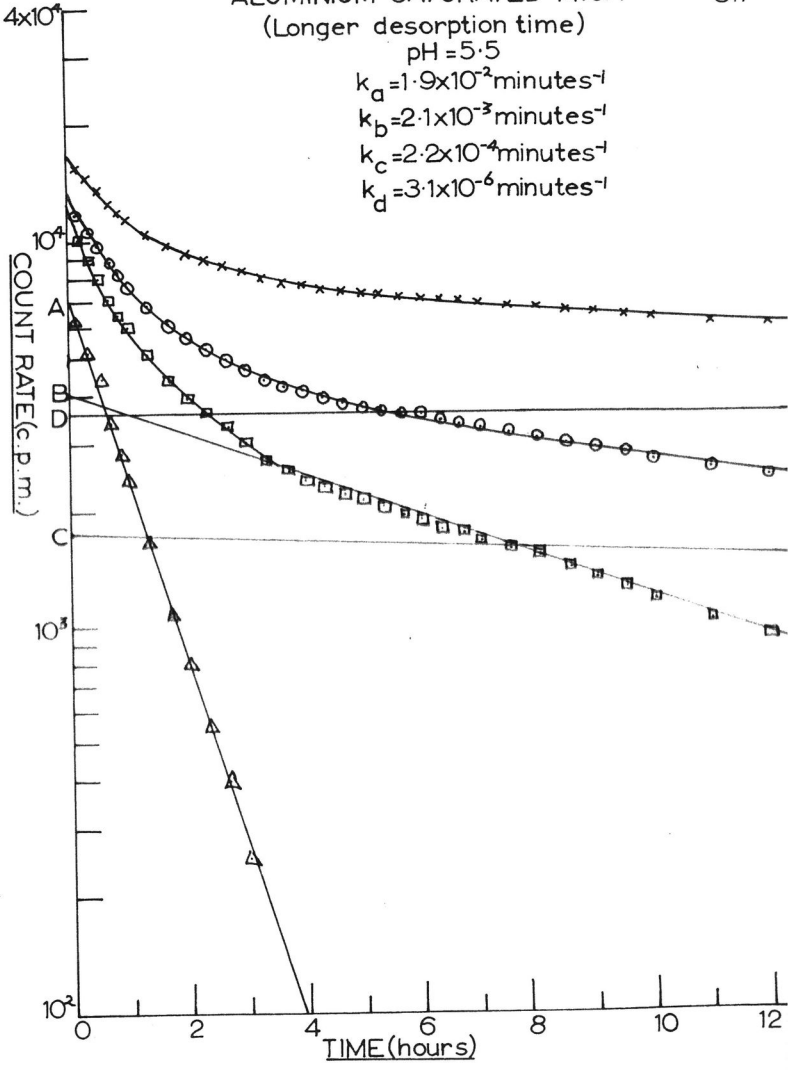
pH = 9·0

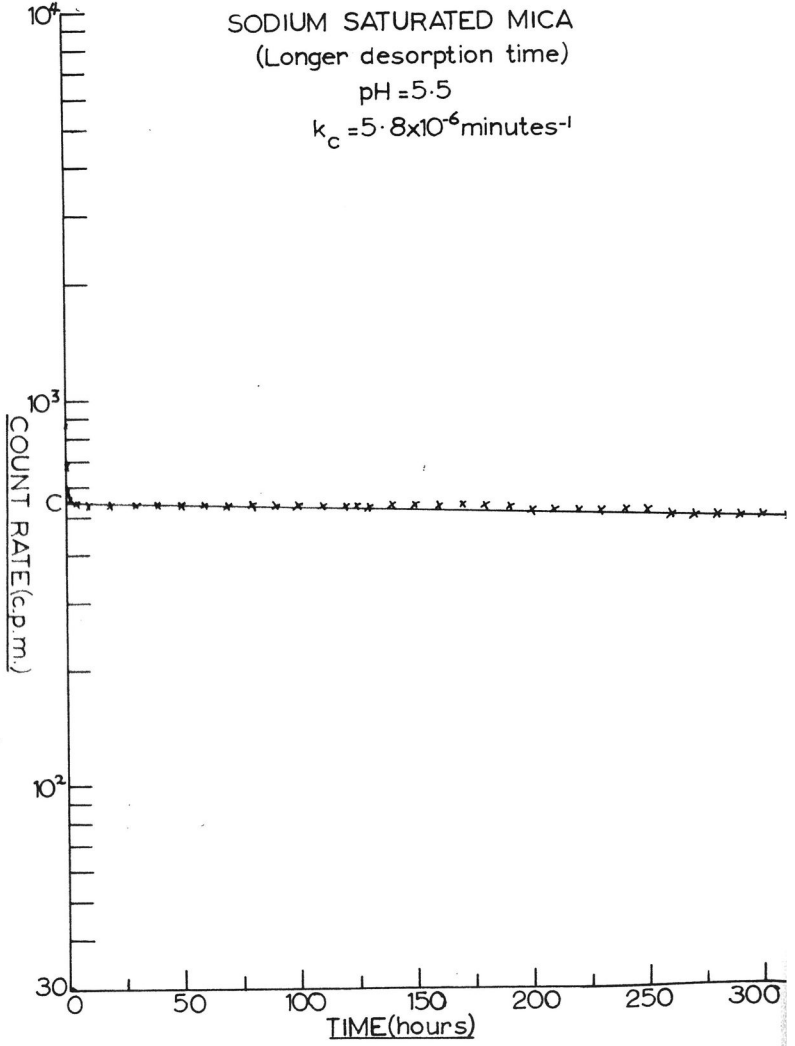
$k_1 = 3{\cdot}3 \times 10^{-5}$ minutes^{-1}




ALUMINIUM SATURATED MICA
(Longer desorption time)
pH = 5·5
$k_c = 2{\cdot}2 \times 10^{-4}$ minutes^{-1}
$k_d = 3{\cdot}1 \times 10^{-6}$ minutes^{-1}
4x10⁴
10⁴
10³
10²
D
C
COUNT RATE (c.p.m.)
0
100
200
300
400
500
600
TIME (hours)


ALUMINIUM SATURATED MICA
(Longer desorption time)
pH=5·5
k_b=2·1x10^{-3}minutes^{-1}
k_c=2·2x10^{-4}minutes^{-1}
k_d=3·1x10^{-6}minutes^{-1}
4x10^4
10^4
10^3
10^2
B
D
C
COUNT RATE(c.p.m.)
0
8
16
24
32
40
48
TIME(hours)


ALUMINIUM SATURATED MICA
(Longer desorption time)
pH = 5·5
k_a = 1·9x10^{-2} minutes^{-1}
k_b = 2·1x10^{-3} minutes^{-1}
k_c = 2·2x10^{-4} minutes^{-1}
k_d = 3·1x10^{-6} minutes^{-1}
4x10^4
10^4
10^3
10^2
A
B
D
C
COUNT RATE (c.p.m.)
0
2
4
6
8
10
12
TIME (hours)


SODIUM SATURATED MICA
(Longer desorption time)
pH = 5·5
$k_c = 5 \cdot 8 \times 10^{-6}$ minutes^{-1}
10^4
10^3
C
10^2
30
COUNT RATE(c.p.m.)
0
50
100
150
200
250
300
TIME(hours)

CHAPTER 8.

DISCUSSION OF RESULTS

In this thesis a study has been made of the adsorption of radioactive phosphate onto various surfaces under the influence of a number of factors. The majority of the work carried out has been on adsorption onto aluminium saturated and sodium saturated mica surfaces. The results obtained indicated that there were three different radioactive phosphate-aluminium saturated mica surface complexes and only one radioactive phosphate-sodium saturated mica surface complex, this last complex having the same rate constant for desorption as the least readily desorbed complex on the aluminium saturated mica surface. These complexes all appeared to exist in significant relative amounts over a wide range of pH values (3.0 - 9.0).

Some experiments that were performed at the end of this thesis indicated that, at least at one pH value (5.5) the least readily desorbed radioactive phosphate complex, present with both aluminium saturated and sodium saturated mica surfaces, may be composed of a mixture of two complexes one of which has an extremely low rate constant for desorption (see chapter 6.7 p 217). The detection of the existence of this very slowly desorbed complex had no effect on the analysed rate constants for the two most readily desorbed complexes.

The mica surface used in radioactive phosphate

adsorption was the 001 face of muscovite mica. As described in the introduction (p. 9) almost all other possible adsorption sites on the mica particle surfaces were excluded from the experimental system by the use of paraffin wax. Thus the various desorption complexes detected must have been between radioactive phosphate and either the mica surface (001 face) itself or cations adsorbed onto this surface to neutralize the net negative charge thereon.

The method of anion adsorption onto clay mineral surfaces has been discussed by numerous authors in the literature and a variety of mechanisms postulated. Mattson(1931) believed that adsorption involved the simple replacement of hydroxyl ions by anions of the added salt. However such a hypothesis fails to explain why the pH value of the adsorbing solution seldom rises on addition of the salt and in fact is usually lowered. Schofield and Samson (1954) believed that the edges of clays changed from being negatively charged to being positively charged by proton adsorption at low pH values. This however does not explain how cations and anions are removed from solution together. Also unaccounted for by this mechanism is the manner in which the number of anions retained increases with time. However previous work by one of these authors (Schofield,1940) had given rise to the suggestion that clay particles may have both positive and negative charges sufficiently far apart to be separately

balanced by cations and anions.

The suggestion by Ayres and Hagihara (1953) that the adsorption of ions onto clay mineral surfaces must be molecular, based on the simultaneous disappearance of cations and anions from solution, seems most unlikely. Such a phenomenon would be most unexpected especially for such highly ionised salts as sodium chloride, potassium sulphate, etc. There is also no means to explain the change in the pH value of the solution that often accompanies adsorption.

Schell and Jordan (1959) as a result of their studies with pure clay minerals, postulated that anion adsorption by clays was partly due to substitution in the lattice for aluminium or silicon atoms. Such anions would be released only by prolonged electrolysis. They believed that the more readily exchangeable anions were adsorbed either on exchange sites or else as an extension to the lattice structure.

In the present work only a single clay surface was available for adsorption and thus it would be unlikely that there would be any lattice substitutions or extensions caused by adsorption of the phosphate ions. It is believed that some of the adsorption complexes formed were associated with the exchangeable cations present on the mica surfaces being studied.

The radioactive phosphate-cation saturated mica surface complex with the lowest rate constant (or longest half-life)

for desorption that was detected was found to be present whatever cation was used to saturate the mica surface. Because of this, as it would not be expected that monovalent cations such as sodium, potassium, etc., would form any complexes with radioactive posphate ions when their single positive charge was already being used to neutralize the net negative charge on the mica surface, it was believed that this complex involved the adsorption of radioactive phosphate onto the mica surface itself.

Experiments with the multivalent cation aluminium have shown the presence of two more radioactive phosphate-cation (aluminium) saturated mica surface complexes. These extra complexes were not detected when the mica surface under study had been completely saturated with monovalent cations such as sodium. It is thus believed that the two complexes are formed between the radioactive phosphate ions and the aluminium ions themselves. The rate constants for the desorption of radioactive phosphate from these complexes are both greater than the rate constant for desorption of the complex detected with all the cation saturated mica surfaces studied. Thus, assuming that the activation energies for the desorption of radioactive phosphate from all the different types of complex formed were comparable in magnitude, the radioactive phosphate would have been held less tightly in the complexes between it and the aluminium ions present than in the complex with the mica surface itself.

From the experiments that have been performed it appears that there are two different radioactive phosphate-aluminium ion complexes, where the aluminium is adsorbed onto a mica surface to neutralize the net negative charge thereon. These two complexes appear to exist in significant proportions over a range of pH values at least from pH 3.0 to pH 9.0. At a pH value of 3.0 almost all (91%) the phosphate will be present as $H_2PO_4^-$ ions, and at a pH value of 9.0 the phosphate present will be almost exclusively (99.5%) HPO_4^{2-} ions. At intermediate pH values varying proportions of these two ions will coexist (see Table 2 p. 85 a).

The actual nature, at various pH values, of the aluminium ion when it is adsorbed onto a mica surface is unknown. At low pH values (about 4 or less) aluminium exists in solution as Al^{3+} ions, while at high pH values (greater than about 9) the aluminium species present is either $Al(OH)_3$ or $Al(OH)_4^-$. Aluminium ions adsorbed onto a mica surface will have one of their three positive charges used to neutralize the net negative charge present on the mica surface. It is assumed because of steric difficulties (see p. 115) that each aluminium atom can neutralize only one negative charge on the mica surface. It might thus be expected that at low pH values some at least of the aluminium ions adsorbed onto the mica surface would be effectively (with regard to the surrounding solution)doubly charged as shown on page 122.

As the pH value of the solution in contact with the mica surface was raised the possibility of one or more of the remaining two positive charges on the adsorbed aluminium ions being neutralized by hydroxyl groups would arise. Owing to the solubility of the aluminium salts used it is not thought that the anions of these salts(e.g. the nitrate ion) would readily form complexes with aluminium ions that were adsorbed onto a mica surface. The nature of an aluminium saturated mica surface with one or two hydroxyl groups per aluminium ion is shown on p.122 and p.123.

If the above hypotheses of the nature of an aluminium saturated mica surface at various (but unknown) pH values are correct an explanation can be advanced for the presence of two different radioactive phosphate-aluminium saturated mica surface complexes, associated with the aluminium ions themselves, at a pH value of 3.0. It is known that almost all the radioactive phosphate will be present as $H_2PO_4^-$ ions, and it is assumed that there is a significant amount of the two different types of adsorbed aluminium ions, those with two free positive charges and those with one free charge and one hydroxyl group. These two different types of aluminium ion are shown together on a mica surface in figure 15 :

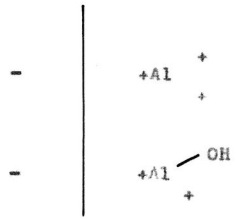
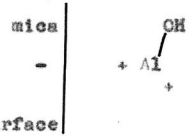


Figure 15 .

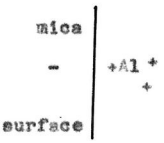
It would be expected that a complex between $H_2PO_4^-$ ions and the uppermost group shown in Figure 15 , where the aluminium ion has two free positive charges, would be less readily dissociated than a complex between the $H_2PO_4^-$ ions and the lower aluminium ion grouping shown in Figure 15 . Thus the desorption of radioactive phosphate from an aluminium saturated mica surface at this pH value (3.0) would be expected to yield two different desorption rates for radioactive phosphate ions actually complexed with the aluminium ions.

The two different radioactive phosphate-aluminium ion complexes that were actually detected at a pH value of 3.0 had rate constants for desorption of 2×10^{-2} minutes^{-1} and 2×10^{-3} minutes^{-1}. It is believed that the rate constant of 2×10^{-2} minutes^{-1} arises from the desorption of a complex

between $H_2PO_4^-$ ions and



aluminium groups. Similarly desorption of the complex between $H_2PO_4^-$ ions and



aluminium groups gives rise to the desorption rate constant of 2×10^{-3} minutes^{-1}.

At a pH value of 5.5 the radioactive phosphate would still be present predominantly as $H_2PO_4^-$ ions (94 %) but there would be an appreciable percentage of HPO_4^{2-} ions (6 %) present also. Experimental results at this pH value revealed the presence of two radioactive phosphate-aluminium ion complexes with the same rate constants, and in approximately the same relative amounts as the two complexes detected at a pH value of 3.0. It would be expected that at a pH value of 5.5 there would be less of the type of adsorbed aluminium ions with two free positive charges (i.e. the upper aluminium ion in Figre 15) than at lower pH values such as pH 3.0.

If, however, there was still some of this species of aluminium ion present there could be four possible radioactive phosphate-aluminium ion complexes present as shown in Figure 16 :

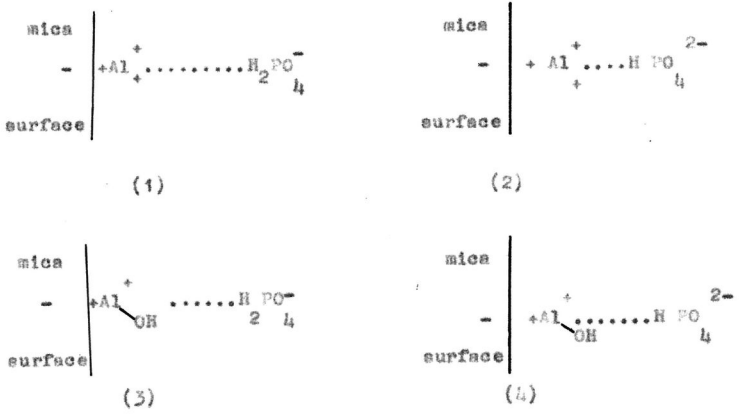
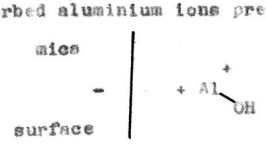


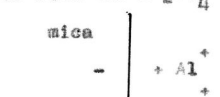
Figure 16.

The complex depicted in Figure 16 as (3) is the same complex that the rate constant of 2 x 10^{-2} $minutes^{-1}$ was attributed to at a pH value of 3.0. While it is known that the relative amount of phosphate present as $H_2PO_4^-$ ions is less at a pH value of 5.5 than at a pH value of 3.0 it would also be expected that the relative amount of the adsorbed aluminium ions present as :



would be greater at this higher pH value. The overall result of the change in these two species could lead to the same proportion of the total amount of radioactive phosphate adsorbed at the two pH values in question (5.5 and 3.0) being present in this type of complex (i.e. Figure 16 (3)). This was actually observed, between 40 and 45 per cent of the total adsorbed radioactive phosphate desorbing with a rate constant of 2×10^{-2} minutes^{-1} at pH values of both 3.0 and 5.5.

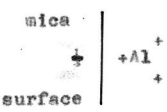
The other adsorbed radioactive phosphate-aluminium ion complex that is believed to exist at a pH value of 3.0 is the same as that shown in Figure 16 as (1). As was discussed above it would be expected that this complex would also be present at a pH value of 5.5. However as the relative concentrations of both the $H_2PO_4^-$ ions and the



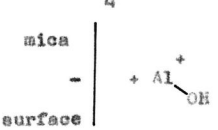
groups would be less at a pH value of 5.5 than at a pH value of 3.0 it would be expected that the amount (relative to the total amount of adsorbed radioactive phosphate) of a complex such as that shown in Figure 16 as (1) would be noticeably less at the higher pH value. This was not found experimentally, the relative amounts of the complexes with rate constant 2×10^{-3} minutes^{-1} being the same (approximately 20%) at both pH values. (As has already

been discussed it was believed that the complex in question (i.e. Figure 16 (1)) is associated with this rate constant for desorption of the radioactive phosphate at least at a pH value of 3.0).

The complex shown in Figure 16 as (1) involves the bonding in some manner of an effectively doubly charged species:



with a singly charged species ($H_2PO_4^-$). It might be expected that the complex shown in Figure 16 as (4), which also involves the formation of a linkage between a doubly charged species (HPO_4^{2-}) and an effectively singly charged species:



would also have a similar rate constant for desorption of the radioactive phosphate ions as would the complex (1) in Figure16 . If these two complexes did have the same (or very similar) rate constants for desorption of radioactive phosphate ions the experimental results would only indicate the existence of one type of complex, the amount of which would be equal to the sum of the actual amounts of the two complexes. Thus the total amount of radioactive phosphate with a rate constant for desorption of 2×10^{-3} minutes $^{-1}$ that was

detectable at a pH value of 5.5 could still be the same proportion of the total amount of radioactive phosphate adsorbed at this pH value as the proportion of adsorbed radioactive phosphate with this same rate constant for desorption detected at a pH value of 3.0. Such an explanation as this could account for the similarity of the experimental results obtained at the two pH values of 3.0 and 5.5.

If Figure 16 represents a true picture of the complexes formed between radioactive phosphate ions and the adsorbed aluminium ions on the mica surface at a pH value of 5.5 it is still necessary to account for the existence of the complex (2) shown in this figure. As only a small proportion of the radioactive phosphate present will exist as $H PO_4^{2-}$ ions and it is also expected that the aluminium ions will exist mostly as the effectively singly charged ion present in complexes (3) and (4), the relative amount of complex (2) will be small. This complex is formed by a bond of some type between two double-charged species and thus it would be less readily dissociated than any of the other three complexes shown in Figure 16 . Thus the rate constant for the desorption of radioactive phosphate ions from such a complex would be expected to be lower than either of the other two rate constants discussed above.

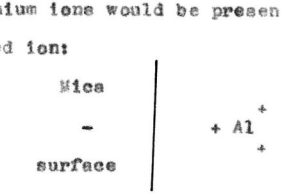
As has been mentioned previously (p.217) some experiments

conducted at a pH value of 5.5 in which desorption was carried out for a much longer period of time than usual revealed the existence of four different, simultaneously occurring desorption rates. The two fastest of these desorption rates were the same as had been detected in other experiments at this and other pH values, namely 2×10^{-2} minutes^{-1} and 2×10^{-3} minutes^{-1}. The slowest rate constant that had been observed in other experiments, 5×10^{-5} minutes^{-1} was not observed in these experiments. Instead two desorption rates with rate constants 2×10^{-4} minutes^{-1} and 5×10^{-6} minutes^{-1} were detected. The slow rate constant of 5×10^{-5} minutes^{-1} has been attributed to a complex between the radioactive phosphate ions and the mica surface itself (see p. 316). Consequently in these experiments at a pH value of 5.5 involving very long desorption times it was believed that the complex between the radioactive phosphate ions and the mica surface itself was represented by the desorption rate constant of 5×10^{-6} minutes^{-1}.

The only rate constant for desorption of the radioactive phosphate ions that has not been accounted for is 2×10^{-4} minutes^{-1}. The amount of the complex associated with this desorption rate was less (only about 10% of the total adsorbed radioactive phosphate) than the other two complexes of radioactive phosphate ions with the adsorbed aluminium ions on the mica surface. From the above considerations, it appeared

that the rate constant for the desorption of radioactive phosphate ions of 2×10^{-4} minutes $^{-1}$ was associated with the complex shown in Figure 16 on p. 321 as (2). It was thus possible to account for the existence of all four of the postulated radioactive phosphate -aluminium ion complexes at a pH value of 5.5.

Experiments performed at a pH value of 9.0 revealed the presence of three desorption rates including those of two radioactive phosphate-aluminium ion complexes with the same rate constants for desorption of 2×10^{-2} minutes $^{-1}$ and 2×10^{-3} minutes $^{-1}$ as has been detected at other pH values. At a pH value of 9.0 all the radioactive phosphate would be present as $H PO_4^{2-}$ ions (see Table 2 p.85a). It seemed very unlikely that at such a high pH value any of the adsorbed aluminium ions would be present as the effectively doubly charged ion:



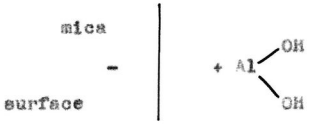
It might be expected that some of the aluminium ions would be present as the effectively singly charged species with one hydroxyl group, while the remainder would exist as the effectively uncharged ion with two attached hydroxyl groups. These two possibilities are shown in Figure 17 :

Figure 17

It would also be expected that at such a high pH value there would be more of the effectively uncharged aluminium ions than of the effectively singly charged ions.

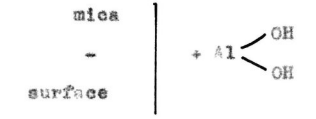
If the two species of aluminium ions shown in the above figure are the only forms of the aluminium ion which exist attached to a mica surface at a pH value of 9.0 then it might be possible for HPO_4^{2-} ions to form a complex with each species. This would give rise to two rates of desorption of HPO_4^{2-} from the mica surface which would be expected to be considerably different. The complex between the radioactive phosphate ions and the effectively singly charged species of aluminium ion shown in Figure 17 is the same as the complex shown in Figure 16 as (4) and believed to exist to a small extent at a pH value of 5.5. Thus from a comparison of the rate constants for the desorption of radioactive phosphate that were detected at pH values of 5.5 and 9.0, it would seem that at a pH value of 9.0 the rate constant for desorption of 2×10^{-3} minutes^{-1} that has been detected

is attributable to a complex between the $H PO_4^{2-}$ ions and the effectively singly charged aluminium ion shown at the top of Figure 17 . The other radioactive phosphate-aluminium ion complex that would be formed at a pH value of 9.0 would be between $H PO_4^{2-}$ ions and:



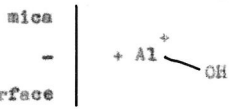
groups. This complex would be more readily dissociated than the similar complex involving effectively singly charged aluminium ions described above. Thus it would have a higher rate constant for desorption.

As this complex is between a doubly charged species and an effectively uncharged species it would be possible for it to have a simil r rate constant for desorption to that of a complex between two singly charged species. Thus the rate constant for desorption for this complex between the $H PO_4^{2-}$ ions and the

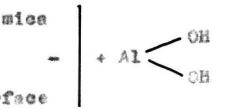


group could possibly be similar to the observed rate constant for desorption of 2×10^{-2} minutes $^{-1}$ for the complex formed

at lower pH values between $H_2PO_4^-$ ions and



groups. As the other rate constant for desorption associated with radioactive phosphate-aluminium ion complexes at a pH value of 9.0 was also 2 x 10^{-2} minutes^{-1} it was believed that this rate constant was indeed associated with the HPO_4^{2-} :



complex at a pH value of 9.0. If the above assumptions are correct it is thus possible to account for the existence of the two rate constants for desorption of 2 x 10^{-2} minutes^{-1} and 2 x 10^{-3} minutes^{-1} at a pH value of 9.0, as well as at lower pH values.

In the above treatment it has been assumed that the energy of activation for the desorption of the various forms of radioactive phosphate from the aluminium ions adsorbed onto a mica surface was comparable for all the different radioactive phosphate-adsorbed aluminium ion complexes discussed. The validity of this assumption could well be investigated by performing desorption experiments over a range of temperatures, a series which could be undertaken in the future.

As was mentioned previously (p. 316) one desorption

complex was found to be present in all experiments regardless of the saturating cation used or the pH value at which the experiment was carried out. Because of this it was believed that this complex was formed between the radioactive phosphate ions and the mica surface itself.

The mica lattice consists of two tetrahedral silicate layers with an octahedral aluminium layer sandwiched between them. Some of the silicate ions are replaced by aluminium ions thus creating a negative charge. This negative charge could be satisfied by the oxygen atom on the mica surface acquiring a hydrogen atom from the environment of the mica surface and thus becoming in effect a hydroxyl group as shown in Figure 18 :

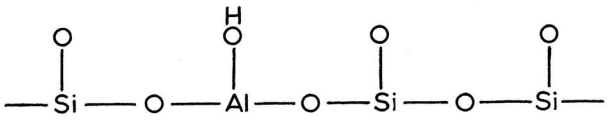


Figure 18

It if were possible for this hydroxyl group to dissociate it could be replaced by a negatively charged phosphate group. If phosphate groups were adsorbed in this manner they might be expected to be held more tightly than phosphate groups that were associated with the exchangeable cations, such as aluminium, that were present on the mica surface. Thus, if the activation energies for desorption of phosphate from both

types of adsorption site (exchangeable cations and tetrahedally bound aluminium in the mica surface) were comparable, it would be expected that the complex between the radioactive phosphate and the aluminium atoms that were part of the mica surface itself would dissociate less readily than the other complexes, thus leading to a lower rate constant for desorption. The only rate constant for desorption that was present with both aluminium saturated and sodium saturated mica surfaces was the lowest rate constant observed in experiments with aluminium saturated mica surfaces. This complex has therefore a rate constant (relative to the other rate constants observed) that would be expected if it were actually a radioactive phosphate-mica surface complex.

The rate constant for desorption of radioactive phosphate from the complex involving the mica surface had the same value (5×10^{-5} minutes^{-1}) over a range of pH values from 3.0 to 9.0. Over this range of pH values the actual phosphate species changes from $H_2PO_4^-$ ions to HPO_4^{2-} ions. As there is no change in the rate constant for desorption with change in pH value it would appear that the strength of the radioactive phosphate-mica surface complex did not alter markedly over this pH range. A possible explanation for this is that it is only possible for one of the negative charges on the phosphate ions to be associated with the tetrahedral aluminium atom in the mica surface.

Thus if the phosphate ion had a second negative charge (as in the HPO_4^{2-} ion) this second charge would take no part in the radioactive phosphate -mica surface complex. This would explain the observed result, namely, that there was no appreciable change in the strength of the radioactive phosphate-mica surface bond whether the phosphate ions present were $H_2PO_4^-$, HPO_4^{2-} or a mixture of both.

Some experiments have been carried out in which the total amounts of radioactive phosphate adsorbed by sodium saturated mica surfaces, and by aluminium saturated mica surfaces, at the same pH value, has been determined (see Chapter 6.21 p. 128). The total amount of radioactive phosphate adsorbed by an aluminium saturated mica surface has been shown to be approximately ten times as great as the amount adsorbed by the same mica surface when completely saturated with sodium ions at pH values of 3.0 and 5.5 (the only pH values at which this comparison has been made.) All the radioactive phosphate adsorbed by the sodium saturated mica surface was present as a single complex with a rate constant for desorption of 5×10^{-5} minutes^{-1}. The amount of radioactive phosphate adsorbed by the aluminium saturated mica surface and having the same rate constant for desorption of 5×10^{-5} minutes^{-1} was about 30% of the total amount of adsorbed radioactive phosphate. Thus the amount of this complex present on the aluminium saturated mica surface was about three times as great as the amount present on the sodium saturated mica surface.

The reason for this increase in the adsorption of radioactive phosphate by the mica surface itself when saturated with aluminium ions may be related to the effect of the multivalent aluminium ions on the Gouy electrical double layer. As has already been mentioned in the introduction (p. 18) the larger ionic charges of multivalent cations have the effect of concentrating the liquid charge closer to the surface of the mica particles. Thus there is less screening effect for anions at a distance from the mica surface and consequently greater opportunity for phosphate adsorption. Because of this it might be expected that, in the same time interval, there would be greater radioactive phosphate adsorption onto a mica surface itself when it was saturated with aluminium ions than when it was saturated with sodium ions. This is what has actually been observed in the comparison experiments performed on mica surfaces saturated with sodium and aluminium ions.

A study has been made in this thesis on the effect of varying the time for which radioactive phosphate was adsorbed onto an aluminium saturated mica surface on the amount of adsorption (chapter 6.4 p. 197). It has been found that, for adsorption times of up to at least one hour, the number and relative amounts of the desorption complexes formed remained constant. The only change with increase in adsorption time was an increase in the total amount of radioactive phosphate adsorption. As a result of this

it appeared that the adsorption of radioactive phosphate by the various types of available site on aluminium saturated mica surfaces could occur with equal facility and that there was no tendency for preferential adsorption onto any particular type of adsorption site.

With sufficiently long periods of adsorption time it might be expected that there would be a greater percentage of the complexes with lower rate constants for desorption detected. When the radioactive phosphate solution was in contact with the mica surface phosphate ions would be continuously adsorbing and desorbing. Because desorption would occur more readily from those types of adsorption site having the higher rate constants for desorption of phosphate the effective rate of increase of adsorbed phosphate on the least readily desorbing sites would be greater than that on the more readily desorbing sites as these latter sites would more rapidly approach their equilibrium concentration of radioactive phosphate.

Up to an adsorption time of about one hour there appeared to be no alteration in the proportion of the various radioactive phosphate-aluminium saturated mica surface complexes formed. A possible reason for this would be that all the complexes were formed very readily, providing a phosphate ion approached sufficiently close to the adsorption site on the mica surface. Thus, the only factor controlling the adsorption would be the

amount of the radioactive phosphate in the adsorbing solution.

If the above explanation were correct it would still be expected that eventually the total number of adsorption sites with a phosphate ion complexed to them would be relatively greater for the sites with the lower rate constants for desorption, as these sites would have lost least of their adsorbed radioactive phosphate ions through simultaneously occurring desorption processes. It would thus appear that for adsorption times of at least one hour the desorption rate of the most readily desorbed radioactive phosphate-aluminium saturated mica surface complex was not sufficient to give a significant reduction in the relative amount of this complex formed by the end of the adsorption period.

In the course of this work some experiments have been carried out on the adsorption of radioactive phosphate onto the surface of aluminium (see chapter 6.6 p. 208). The surface of aluminium is always covered with an oxide coating. Under perfectly dry conditions this coating is very thin (about 10 Å at room temperature (Keller and Edwards, 1948 a)) but whenever the surface encounters moist conditions the formation of hydrous oxides occurs, the ultimate thickness of this hydrous oxide coating not being reached for many months or even years (Cabrera and Mamon, 1947; Steinheil, 1934). It has however been shown that the very thin oxide coating is still present,

with a thickness of about 10 Å, on the surface of the aluminium under the hydrous oxide layer in moist conditions (Keller and Edwards,1948 b).

In the present studies any adsorption of radioactive phosphate will have taken place onto the outermost hydrous oxide layer on the aluminium sheet studied. Although it is recognised that this outer layer contains appreciable water (Hunter and Fowle , 1956; Keller and Edwards,1948 c) the exact natures of the hydrous oxides formed are not known. Beletskii (1953) has postulated the existence of a complex mixture of hydrous oxides such as Al O_2H, $Al_2O_3 \cdot H_2O$, $Al(OH)_3$, $Al_2O_3 \cdot 3H_2O$ and it seems likely that the actual composition of this hydrous oxide layer will depend on the extent of hydration.

It would be expected that the nature of the aluminium-oxygen or aluminium-hydroxyl groups exposed at the surface of these hydrous oxide layers on aluminium would be dependent on the pH value of any solutions that the aluminium came into contact with. As the exact nature of the surface of aluminium is unknown it would be difficult to make an accurate prediction of the nature of the possible sites for adsorption of radioactive phosphate onto this surface.

The rate constants for the desorption of radioactive phosphate from aluminium surfaces show a certain amount of similarity to the rate constants obtained for the desorption of radioactive phosphate from aluminium saturated mica surfaces. Consequently some at least of the complexes formed with the

hydrous oxide coating on the aluminium surface may be the same as, or very similar to, those formed by the adsorption of radioactive phosphate onto an aluminium saturated mica surface. However more work would need to be done to establish precise values for the rate constants for desorption of radioactive phosphate from aluminium surfaces before any detailed comparison could be made.

During the course of this thesis some similar work was done by Rankin (1964) at Victoria University of Wellington on the adsorption of radioactive sulphate onto cation saturated mica surfaces. He used the techniques described here and developed by the present author. The results of desorption experiments that he perfommed using radioactive sulphate and aluminium saturated mica surfaces were similar to those obtained in the present thesis. Mathematical analysis of his results in an analogous manner to that described earlier in this thesis (chapter 5 p. 72) revealed the presence of a number of different radioactive sulphate-aluminium saturated mica surface complexes. Radioactive sulphate was found to desorb from these complexes at comparable rates to the desorptions of radioactive phosphate from aluminium saturated mica surfaces studied in this work.

As it is a soluble salt (solubility = 31.3 gm./100ml H_2O at 0^oC (Hodgman, 1962) aluminium sulphate would not have been precipitated onto the mica surfaces studied, especially at the

low concentrations used. Thus the similarity of the results obtained with the radioactive phosphate ion make it seem most unlikely that the complexes between this ion and an aluminium saturated mica surface could be of an entirely different nature to those obtained when sulphate was the adsorbed anion.

The desorption curves obtained in the studies with radioactive phosphate in this work were characteristic of adsorption and not precipitation phenomena. If the actual phenomenon observed was the dissolution of a precipitate it would be expected that the rate of loss of radioactive phosphate from the mica surface would be either uniform or tending to increase with increasing solubility of particles of decreasing size until the precipitate was all dissolved. This was not the case, the rate of loss of radioactive phosphate decreasing exponentially so that the actual rate of loss at any particular time was proportional to the amount remaining at that time. This is exactly the manner in which desorption of an adsorbed species would be expected to occur. It can thus be seen that the actual phenomenon studied in this thesis has been the adsorption of radioactive phosphate onto a cation saturated mica surface and its subsequent desorption, and not the formation and dissolution of a precipitate.

From the similarity of the results of the desorption experiments using hydrated aluminium oxide surfaces to those obtained when the desorption of radioactive phosphate from aluminium saturated mica surfaces was studied it is evident

that the phenomenon studied with the aluminium surfaces was also an adsorption and not a precipitation phenomenon.

SUMMARY

A technique has been developed whereby the adsorption of radioactive phosphate onto various surfaces can be studied and the rate of its subsequent desorption into suitable solutions measured continuously. The surfaces studied have been the 001 face of mica saturated with various cations and the surface of aluminium metal which is hydrated aluminium oxide.

A mathematical method of analysis has been evolved whereby the desorption of radioactive phosphate from the surfaces studied can be shown to be consistent with a model where there are a number of independent first order (or pseudo first order) desorption processes. These processes have widely differing rate constants and it is believed that these rate constants are characteristic of different radioactive phosphate-surface complexes.

The desorption of radioactive phosphate from aluminium saturated mica surfaces and sodium saturated mica surfaces has been studied over a range of pH values (3·0 - 9·0). It was found that radioactive phosphate formed one complex with the mica surface itself regardless of the saturating cation. When aluminium was the saturating cation used the radioactive phosphate was found to form two or more complexes with the adsorbed aluminium ions themselves. Similar complexes were not found when sodium was the saturating cation.

The relative amounts of radioactive phosphate adsorbed by aluminium saturated and by sodium saturated mica surfaces was determined at pH values of 3·0 and 5·5. Investigations were carried out on the effects on the number and relative and total amounts of radioactive phosphate-aluminium saturated mica surface complexes of the following: drying, temperature changes, time of adsorption and time of desorption of radioactive phosphate. The relative amounts of radioactive phosphate adsorbed by aluminium saturated mica surfaces at different pH values were also determined.

The desorption of radioactive phosphate from other cation saturated mica surfaces was studied briefly.

The desorption of radioactive phosphate from hydrated aluminium oxide surfaces was studied over a range of pH values (3.0 - 9.0).

The effects of a number of substances on the rates of desorption of radioactive phosphate from aluminium saturated mica surfaces and from hydrated aluminium oxide surfaces were investigated.

Studies were carried out on the amounts of adsorption of phosphate from radioactive phosphate solutions of increasing concentration (of both radioactive and non-radioactive phosphate) onto aluminium saturated mica surfaces at a pH value of 5.5. The rate of exchange of radioactive and non-radioactive phosphate adsorbed onto a mica surface was studied briefly.

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