Polyhydrated Phases in the Exchange of H^+ and K^+ in α-Titanium Phosphate

J. R. García, Marta Suárez, Ricardo Llavona, and Julio Rodríguez *
Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, C/Calvo Sotelo s/n., Oviedo, Spain

The exchange of H^+ by K^+ in α-titanium phosphate, $Ti(HPO_4)_2{\cdot}H_2O$, was studied. The exchange isotherm and the hydrolysis and titration curves were obtained, and the evolution of the material was followed by *X*-ray diffraction. The existence of partially substituted phases was not detected. Phases saturated in potassium and highly hydrated, $Ti(KPO_4)_2{\cdot}3H_2O$ (interlayer distance 10.4 Å) and $Ti(KPO_4)_2{\cdot}2H_2O$ (9.6 Å), were obtained. The experimental results are explained by taking account of the structures of the materials.

Many products, natural as well as synthetic, exist which show ion-exchange properties. The first systematic studies in this field were carried out [1,2] on minerals of natural origin. Several natural ion exchangers are crystalline aluminosilicates with cation-exchange properties.[3]

The interpretation of the ion-exchange properties of clay minerals is difficult owing to their complexity. The study of simpler systems, with similar characteristics, can help us to understand the substitution mechanism. The α-zirconium bis(monohydrogenorthophosphate) monohydrate,[4] conventionally denoted as α-ZrP, shows resemblances with clay minerals [5] especially with those of the montmorillonite type.[6] Its lamellar structure with interconnected zeolitic cavities allows its ion-exchange properties to be explained. The crystals are monoclinic with space group $P2_1/n$. The size of the entranceways into the cavities is 2.61 Å and the interlayer distance is 7.55 Å.[7-9] The unit-cell dimensions are $a = 9.076$, $b = 5.298$, $c = 16.22$ Å, and $\beta = 111.5°$.[7,10] α-Titanium bis(monohydrogenorthophosphate) monohydrate,[11] α-TiP, is isomorphic with α-ZrP.[12,13] The unit-cell dimensions are $a = 8.631$, $b = 5.002$, $c = 16.176$ Å, and $\beta = 110.20°$.[10,13] As a consequence of the substitution of Zr by a smaller quadrivalent metal such as titanium, the tunnels connecting the cavities become narrower and ion exchange of large cations has a greater activation energy. Thus, in acidic media, α-ZrP retains Li^+, Na^+, and K^+,[10,12] while α-TiP only retains Li^+ and Na^+.[10,14] In the study of these ion-exchange processes, the detection of crystalline phases having a high interlayer distance is very important because they allow, by a catalytic phenomenon,[10] the retention of cations which because of their large size cannot enter the cavities of α-TiP.[10,15]

This paper reports the ion exchange of H^+ and K^+ in α-titanium phosphate at 5 °C, and the existence of fully exchanged phases having high degrees of hydration. For the sake of brevity, the various ionic forms are simply indicated by their counter ions (under a bar), and water content, while their interlayer distances are reported in parentheses. Thus, for example, $Ti(KPO_4)_2{\cdot}H_2O$ and $TiHK(PO_4)_2{\cdot}H_2O$ will be written as $\overline{KK}{\cdot}H_2O$ (8.9 Å) and $\overline{HK}{\cdot}H_2O$ (8.3 Å).[16]

Experimental

Reagents.—All chemicals used were of reagent grade. The KOH solutions were standardized with HCl, which was previously standardized against Na_2CO_3. The α-TiP was obtained by the method of Alberti *et al.*,[11] using 10 mol dm^{-3} H_3PO_4 and reflux times of 50 h. The titanium phosphate gel used in the reflux was prepared by precipitation from a hydrochloric acid solution of $TiCl_4$ with dilute H_3PO_4. The crystalline solid (α-TiP) was washed with deionized water until free from chloride (test with $AgNO_3$), dried at 60 °C, and ground to a particle size of less than 30 μm. It was then characterized by chemical analysis, thermal analysis (d.t.a. and t.g.a.), i.r. spectroscopy, and *X*-ray diffraction.

Analytical Procedures.—The analysis for phosphorus and titanium in the solids was carried out gravimetrically.[17] The pH measurements were made with a Crison model 501 pH-meter, equipped with glass and saturated calomel electrodes. The released phosphate groups were measured spectrophotometrically,[18] using a Perkin-Elmer model 200. The potassium ions in solution were determined by atomic absorption spectroscopy, using a Perkin-Elmer model 372. The diffractometer used was a Philips model PV 1050/23 ($\lambda = 1.5418$ Å).

Ion-exchange Studies.—The exchanger was equilibrated with 0.1 mol dm^{-3} (KCl + KOH) solution at 5.0 ± 0.1 °C, following a variation of the procedure described by Clearfield *et al.*[19] The hydroxide was slowly added in 1 cm^3 portions (every addition being followed by a 60-min wait), until the amounts of KOH given in the Results section had been added. After the total addition of KOH, the equilibration time was 48 h. The solid was present in the solution in a ratio of *ca.* 1 g per 500 cm^3.

Results

Data reported here were obtained at 5 °C because in the study of H^+/K^+ exchange similar titration curves are observed at 5, 25, and 40 °C. The amount of phosphate released by the exchanger indicates that the hydrolysis increases with increasing temperature and the extent of the exchange (referred to 1 g of non-hydrolyzed α-TiP) shows a greater increase at 5 °C according to the amount of KOH added.

During the exchange process the structural interlayer distances expand or contract thereby enabling the process to be followed qualitatively by *X*-ray diffraction. *X*-Ray patterns of the exchanged solids at the three temperatures show reflections in the region of the interlayer distance at the same 2θ values, but the variation of this spacing and its correlation with the degree of exchange is more clearly observed at 5 °C. The more highly hydrated phases are more stable to dehydration at lower temperatures. Exchange isotherms and titration and hydrolysis curves, as a function of the KOH added, are plotted in Figure 1.

The *X*-ray patterns of some of the most significant samples stabilized to a relative humidity of 100% are shown in Figure 2. The reflection at 10.4 Å corresponds to the interlayer distance of a new crystalline phase, and its intensity increases as the substitution progresses. During the entire titration, there is

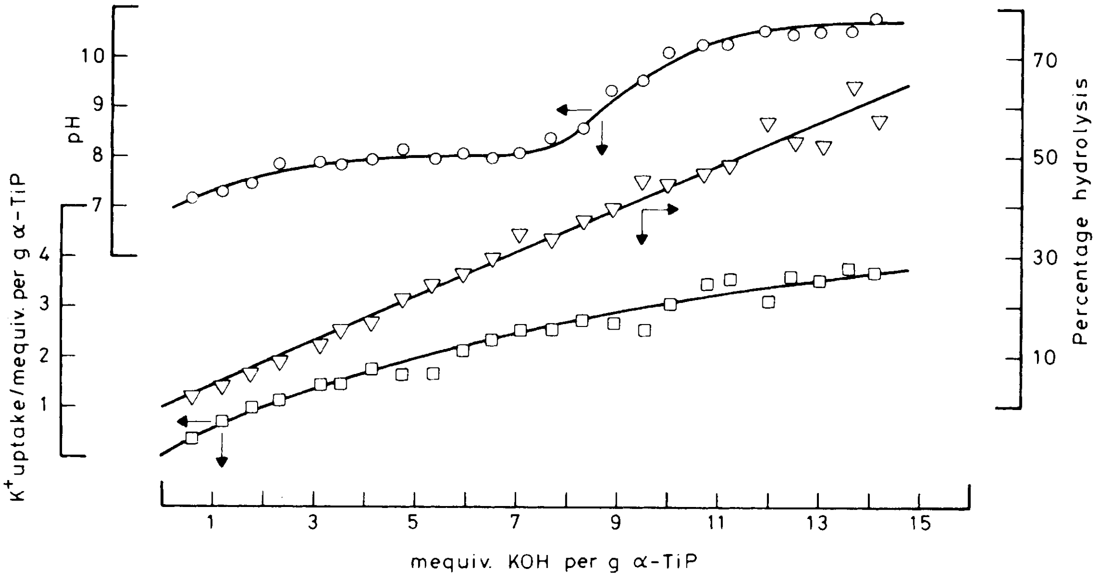

Figure 1. Exchange isotherm (□) and titration (○) and hydrolysis (▽) curves

another reflection at 8.9 Å with low intensity. The crystallinity of the material decreases continuously. A detailed study of the region of the interlayer distance (Figure 3) allows the evaluation of a relative intensity (by cutting out the peak areas and weighing them) of the reflection at $d = 10.4$ Å, compared to that of the $\overline{HH}\cdot H_2O$ (7.6 Å) phase (Figure 4).

The dehydration behaviour of the phase with $d = 10.4$ Å is easier to study on samples without α-TiP impurity. This is the case of the solid obtained by addition of 15.0 mequiv. KOH per g α-TiP, since the *X*-ray diffraction pattern, at a relative humidity of 100%, shows only two peaks at 8.9 and 10.4 Å [Figure 5(*a*)]. When the material is left in air for 3 h a new peak at 9.6 Å is detected [Figure 5(*b*)], and the reflection at 10.4 Å disappears. The *X*-ray pattern is not altered for 24 h [Figure 5(*c*)]. Nevertheless, if it is placed in a desiccator over P_2O_5 for 24 h only one diffraction line at 8.9 Å is found [Figure 5(*d*)].

X-Ray patterns obtained from the exchanged solids at 95 and 310 °C show reflections at 7.6 and 7.4 Å respectively, in the region of the interlayer distance. At 310 °C two low-intensity diffractions occur at 7.4 and 8.9 Å for the solids of maximum conversion.

Discussion

The titration curve shows an initial zone with an almost constant pH (Figure 1), in good agreement with earlier results.[11,20,21] The substitution is accompanied by a high degree of hydrolysis as a consequence of the slow diffusion of K^+ ($r_i = 1.33$ Å) through the tunnels which connect the zeolitic cavities of α-TiP (2.61 Å) (diffusion is impossible if the α-TiP structure is not deformable). This implies that the solid is in contact, for a certain time, with solutions having a higher pH than the equilibrium one, causing its partial decomposition.[14]

When α-TiP is hydrolyzed the phosphates released pass into solution, while solid $TiO_2\cdot nH_2O$ is formed. The hydrolysis processes, depending upon the pH, are as in equations (1)—(3).

The exchange isotherm (Figure 1) offers information about the capacity of the system to retain potassium ions. The titanium oxide can act as a cation exchanger at pH > 6. Thus,

$$Ti(HPO_4)_2\cdot H_2O + 6\,OH^- + (n-5)\,H_2O \longrightarrow TiO_2\cdot nH_2O + 2\,PO_4^{3-} \quad (1)$$

$$Ti(HPO_4)_2\cdot H_2O + 4\,OH^- + (n-3)\,H_2O \longrightarrow TiO_2\cdot nH_2O + 2\,HPO_4^{2-} \quad (2)$$

$$Ti(HPO_4)_2\cdot H_2O + 2\,OH^- + (n-1)\,H_2O \longrightarrow TiO_2\cdot nH_2O + 2\,H_2PO_4^{-} \quad (3)$$

since the equilibrium pH is high, not all replaced potassium ions are in the remaining α-titanium phosphate.

In the exchange of H^+ by K^+ on α-TiP, Alberti *et al.*[21] reported the existence of half-exchanged and fully exchanged monohydrated phases: $\overline{HK}\cdot H_2O$ (8.3 Å) and $\overline{KK}\cdot H_2O$ (8.9 Å). We suggest that the diffraction line at $d = 10.4$ Å corresponds to 50 or 100% exchanged phases, but with higher hydration than those described previously.

The reflection at 7.6 Å detected in the *X*-ray patterns of exchanged solids heated at 95 °C is characteristic of α-TiP and its intensity decreases as the amount of KOH added increases. In the heat treatment at 310 °C, α-TiP loses its water of crystallization, the spacing between layers varying from 7.6 to 7.4 Å.

The phases $\overline{HK}\cdot H_2O$ (8.3 Å) and $\overline{KK}\cdot H_2O$ (8.9 Å) may lose their molecule of water yielding the $\overline{HK}$ (7.6 Å) and $\overline{KK}$ (8.9 Å) phases, respectively. The hydration of the phase reported in this paper ($d = 10.4$ Å) is totally or partially lost in the heat treatment, giving rise to a phase with very low crystallinity due to the sudden dehydration. This explains the reflection of low intensity at 8.9 Å detected in *X*-ray patterns of solids with highest conversions (310 °C), and suggests the existence of totally exchanged phases. In air (slow dehydration), this phase loses part of its crystallization water, and is transformed into a less hydrated phase ($d = 9.6$ Å). Both phases ($d = 10.4$ and 9.6 Å), stored over P_2O_5, show a characteristic interlayer distance of 8.9 Å, corresponding to the $\overline{KK}\cdot H_2O$ phase (or $\overline{KK}$ phase). Thus, the phases which yield lines of highest interlayer spacing have a composition $\overline{KK}\cdot zH_2O$, where $z > 1$.

Due to the low stability of the phase having $d = 10.4$ Å, the impossibility of obtaining it pure (without the hydrolysis product), and the possible existence of non-crystalline forms

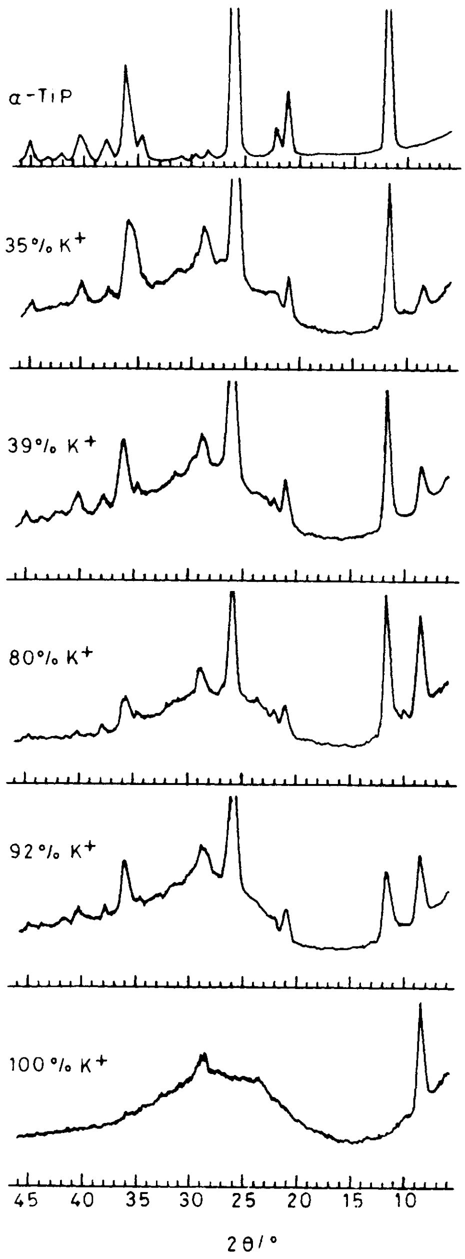

Figure 2. *X*-Ray patterns of the exchanged solids stabilized at a relative humidity of 100%

upon partial exchange, it is not possible, by direct methods, to determine its water content and to obtain phase distribution curves.

When in α-titanium phosphate the hydrogen ion is replaced by another cation, the arrangement of the layers remains unaltered, but the distance between them usually varies.[22] The value of the interlayer distance of a fixed crystalline phase increases with the counter-ion diameter and the hydration degree.[16,23,24] In a study of the ion-exchange phases of α-ZrP, in order to find out the effect of the water content, Kullberg and Clearfield[25] proposed the elimination of the cation contribution by the use of a corrected interlayer distance in the form (4) where φ_M and $\varphi_{M'}$ are the diameters of the ex-

$$d_{corr} = d - \frac{\varphi_M + \varphi_{M'}}{2} \quad (4)$$

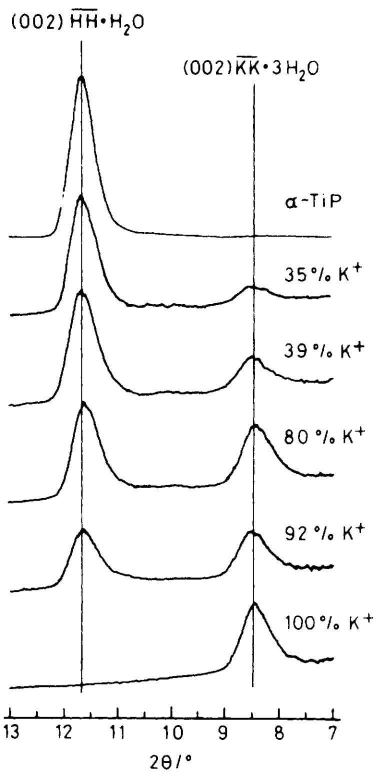

Figure 3. Detailed study by *X*-ray diffraction of the diffraction lines corresponding to the interlayer distance of exchanged solids stabilized at a relative humidity of 100%

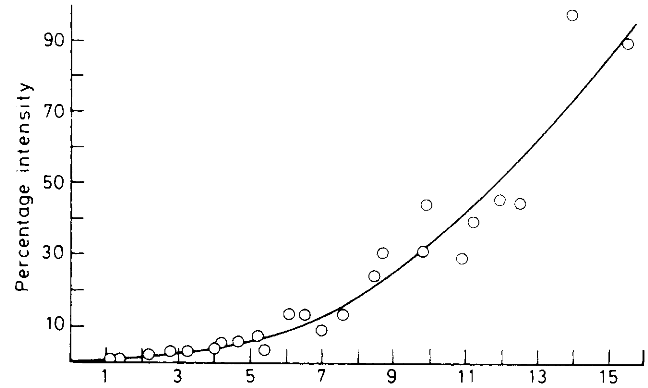

Figure 4. Relative intensity of the reflection having d = 10.4 Å to that at d = 7.6 Å

changed ions. Plotting this function against the water content of the phase a straight line was obtained. We carried out a similar treatment with ion-exchange phases arising from α-TiP (Figure 6). The values of the interlayer distances were taken from our exchange experiments[26] and from the literature.[21,27] For ionic radii the values 0.35 (H^+), 0.66 (Li^+), 0.97 (Na^+), and 1.33 Å (K^+) were taken.

In Figure 6 a similar trend to that found with α-ZrP is observed. This plot can be of great utility in predicting the water content of a phase of low stability when the exchange molar fraction and the interlayer distance are known. In the $\overline{KK}\cdot zH_2O$ phases with corrected interlayer distances of 7.7

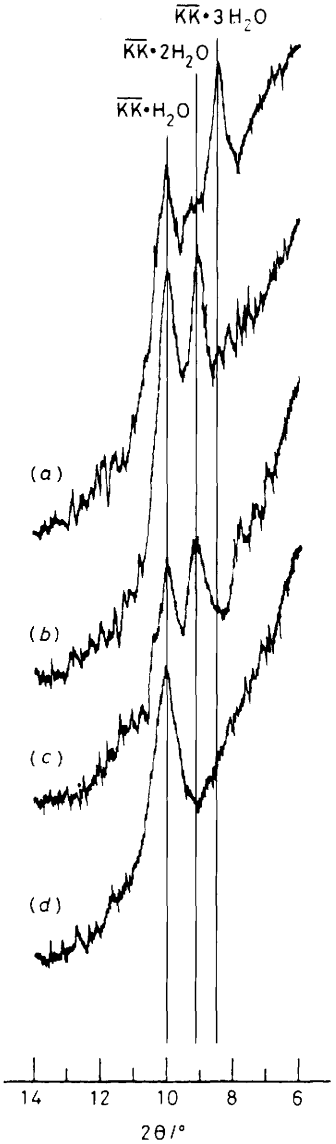

Figure 5. Evolution of the interlayer distance of the exchanged solids: (*a*) relative humidity of 100%; (*b*) 3 h in air; (*c*) 27 h in air; (*d*) 24 h over P_2O_5

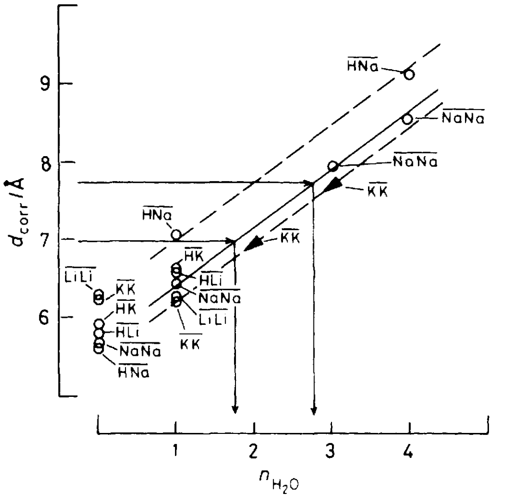

Figure 6. Corrected interlayer distance of the exchanged phases of α-TiP as a function of their water content

and 6.9 Å, such plots give ambiguous hydration degrees, because for the former 2—3 water molecules are predicted and 1—2 for the latter. Nevertheless, since $\overline{\mathrm{KK}}\cdot H_2O$ has a known interlayer distance of 8.9 Å (d_{corr} = 6.24 Å), a hydration degree of 1 for the phase having d_{corr} = 6.9 Å is not possible, leaving $\overline{\mathrm{KK}}\cdot 2H_2O$. For identical reasons, the diffraction line at 10.4 Å (d_{corr} = 7.7 Å) might originate from the $\overline{\mathrm{KK}}\cdot 3H_2O$ phase. The dispersion in the experimental points observed is perhaps due to the fact that the formula used to correct the cationic effect is too simple, since other factors (especially electrostatic interactions) might also influence the value of the interlayer distance.

In a laminar ion exchanger it might be expected that, when the zeolitic cavities are occupied by two identical cations, the disposable space will be distributed equally such that each ion will be placed near to the limit of the cavity, in order to avoid electrostatic repulsions. When only a single counter ion exists this is not the case because it will only have to contend with the H^+ associated with the layers and it will occupy a position near the centre of the cavity. Thus, in the former case, when a molecule of water enters the cavity it will be placed between the two counter ions in order to diminish the repulsions and the phase will be more stable to dehydration than the partially substituted phase in which the electrostatic repulsions are lower.[26] It was found experimentally that the $\overline{\mathrm{HNa}}\cdot 4H_2O$ phase is transformed at 21 °C into $\overline{\mathrm{HNa}}\cdot H_2O$ and at 80—100 °C is dehydrated to $\overline{\mathrm{HNa}}$, while $\overline{\mathrm{NaNa}}\cdot H_2O$ is stable at this temperature.[27]

This stability means that the characterization of these phases is simpler and more reliable. It can be observed (Figure 6) that the variation of d_{corr} for $\overline{\mathrm{HNa}}\cdot xH_2O$, $\overline{\mathrm{NaNa}}\cdot yH_2O$, and $\overline{\mathrm{KK}}\cdot zH_2O$ ($x,y,z \geqslant 1$) with the water content is linear with a slope of about 0.7 but different intercepts at the ordinate (for $n_{H_2O} = 0$). The approximate method used earlier is more rigorous when d_{corr} values of crystalline phases differentiated only by the degree of hydration are considered. The fact that the slopes of the straight lines are about 0.7 means that each molecule of water which enters the cavity increases the interlayer distance by 0.7 Å as against 0.95 Å for α-ZrP.[25]

These results are a consequence of the fact that the forces between the layers of the salt forms are essentially due to the coulombic attraction between the negative fixed charges of adjacent planar macroanions and the counter ions placed among them. Thus, it is likely that these forces become stronger as the density of the fixed charges increases, in other words, as the product of the unit-cell parameters *a* and *b* decreases. Thus, the smaller *ab*, the more the α-layered exchangers tend to behave like materials having a rigid structure.[10]

The formation of fully exchanged phases upon exchange of H^+ by K^+ in α-TiP, without half-exchanged phases, can be attributed to the slow diffusion of potassium ions in the lattice of the exchanger. This allows entry of a second cation into a lattice already deformed by the entry of the first, instead of into a new α-TiP zeolitic cavity with the initial size. A similar effect, but less marked as a consequence of the larger size of the tunnels connecting the zeolitic cavities, is observed with K^+ and α-ZrP,[28,29] where high rates of hydroxide addition lead to the attainment of a large proportion of fully exchanged phases.

References

1 H. S. Thompson, *J. R. Agr. Soc. Engl.*, 1850, **11**, 68.
2 J. F. Way, *J. R. Agr. Soc. Engl.*, 1850, **11**, 313.
3 C. B. Amphlett, 'Inorganic Ion Exchangers,' Elsevier, Amsterdam, 1964.
4 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
5 D. Leigh and A. Dyer, *J. Inorg. Nucl. Chem.*, 1972, **34**, 369.
6 D. M. C. Macewan, 'The X-Ray Identification and Crystal Structure of Clay Minerals,' Mineralogical Society, 1961, ch. 4.
7 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
8 S. Ahrland and J. Albertsson, *Acta Chem. Scand.*, 1969, **23**, 1446.
9 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
10 'Inorganic Ion Exchange Materials,' ed. A. Clearfield, CRC Press, Boca Raton, 1982.
11 G. Alberti, P. Cardini-Galli, U. Costantino, and E. Torracca, *J. Inorg. Nucl. Chem.*, 1967, **29**, 571.
12 'Ion Exchange and Solvent Extraction,' vol 5, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973.
13 A. M. Landis, M.S. Thesis, Ohio University, Athens, 1970, p. 18.
14 M. Suárez, J. R. García, and J. Rodríguez, *J. Phys. Chem.*, 1984, **88**, 159.
15 G. Alberti, U. Costantino, and J. P. Gupta, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2109.
16 G. Alberti and U. Costantino, *J. Chromatogr.*, 1974, **102**, 5.
17 I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, 'Quantitative Chemical Analysis,' Nigar, Buenos Aires, 1972.
18 O. B. Michelsen, *Anal. Chem.*, 1957, **29**, 60.
19 A. Clearfield, A. Oskarsson, and C. Oskarsson, *Ion Exch. Membr.*, 1972, **1**, 91.
20 E. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3114.
21 G. Alberti, U. Costantino, and M. L. Luciani, *Gazz. Chim. Ital.*, 1980, **110**, 61.
22 G. Alberti, U. Costantino, S. Allulli, and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 113.
23 J. P. Gupta and D. V. Nowell, *Chem. Ind.* (*London*), 1977, **15**, 649.
24 G. Alberti, *Acc. Chem. Res.*, 1978, **11**, 163.
25 L. H. Kullberg and A. Clearfield, *J. Phys. Chem.*, 1981, **85**, 1585.
26 J. R. García, Thesis, Universidad de Oviedo, Spain, 1983.
27 N. G. Chernorukov, *Zh. Prikl. Khim.*, 1978, **51**, 431.
28 M. G. Bernasconi, M. Casciola, and U. Costantino, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1047.
29 J. Korney, L. Szirtes, and L. Zsinka, *Radiochem. Radioanal. Lett.*, 1979, **40**, 263.

Received 11*th July* 1983; *Paper* 3/1188