# Adsorption of Orthophosphate on a Synthetic Silica-Alumina

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The characteristics and mechanism of the adsorption of orthophosphate on a commercial synthetic silica–alumina, Neobead D, were studied. The adsorption rate increased with decrease in pH and increase in the dose of silica–alumina below the concentration of 4 g dm$^{-3}$. The adsorption almost terminated in 24 h, but a very slow reaction was observed even after 3 d. The adsorption isotherm follows the Freundlich equation, the inflection in the log-log plot indicating difference in the adsorption mechanism between low and high phosphate concentrations. The adsorption capacity increased with decrease in pH, being the highest at an initial pH of 3.0. The silica–alumina exhibited buffer action, phosphate-free solutions of pH 4—10 showing pH of *ca.* 6 after 24 h. In coincidence with and in proportion to the adsorption, release of hydroxide, sulfate and silicate ions occurred in the reaction of initial pH of 4.7. The sum of the equivalents of the three anions released could well account for the moles of phosphate adsorbed. The adsorption thus proceeds mainly through the ion-exchange process between phosphate in solution and the anions on the solid, univalent phosphate ions taking part in the reaction.

Recently eutrophication of enclosed water areas has caused problems in fishery, agriculture and other industries, and development of effective methods for removal of nutrients has become necessary.

In order to remove phosphate from water, coagulation, chemical and biological methods have been utilized conventionally. Ion-exchange is also effective for removal of phosphate, but does not seem advantageous since ordinary organic anion-exchange resins remove not only phosphate ions but also other anions. Yee[1] proposed a selective ion-exchange process using a packed bed of acid-treated alumina, with which orthophosphate, pyrophosphate, triphosphate, and hexametaphosphate can be removed efficiently. Regeneration of the alumina consumed was conducted with small amounts of sodium hydroxide and nitric acid. Columnar studies[2—4] made on the activated alumina process have shown that it has advantages such as high selectivity for phosphate, simplicity in operation, easy regeneration and production of small amounts of solid waste.

The phosphate adsorption capacity of alumina is increased by addition of silica, which suppresses crystallization of alumina and increases its surface area, mechanical strength and heat resistance. Takimoto *et al.*[5] showed that silica–alumina containing 10% silica by weight exhibits the highest phosphate adsorption capacity.

In order to study the removal of phosphate from aqueous solution, we used a commercial synthetic silica–alumina. Useful information was obtained about the characteristics and mechanism of adsorption of phosphate.

## Experimental

*Synthetic Silica-Alumina.* Neobead D (Mizusawa Industrial Chemicals Ltd.) was pulverized to 105—250 μm in diameter. This is an X-ray amorphous hydrogel having the composition 79.4% $Al_2O_3$, 11.5% $SiO_2$, 1.1% $SO_4$, and 8.0% ignition loss, and a specific surface area of *ca.* 330 m$^2$ g$^{-1}$.

*Phosphate Solution.* Potassium dihydrogenphosphate, $KH_2PO_4$ (reagent grade) was dissolved in water, the pH being adjusted with hydrochloric acid or sodium hydroxide.

Orthophosphate was chosen as a model phosphate, since other forms of phosphates proved to be also adsorbed on alumina,[1] and readily converted into orthophosphate in natural water through chemical and biological reactions.

*Analysis.* JIS K 0102† was applied to the determination of phosphate, sulfate (the barium–chromate colorimetric method) and aluminum ions, and JIS K 0101†† to that of silicate (the molybdenum blue method). Sulfate and silicate were determined after removing phosphate as calcium phosphate in order to avoid its interference which became appreciable from a phosphate concentration of *ca.* 0.03 mmol dm$^{-3}$ in the sulfate determination and *ca.* 2 mmol dm$^{-3}$ in the silicate determination.

*Adsorption Rate.* 3—12 g of the silica–alumina was added to 3 dm$^3$ of 1.05-mmol dm$^{-3}$ phosphate solution, and stirred at 25 °C. An aliquot was taken at intervals and centrifuged, phosphate, sulfate, silicate, aluminum, and pH being determined for the supernatant.

*Adsorption Equilibrium.* Eighty cm$^3$ of 0—8.42-mmol dm$^{-3}$ phosphate solution was placed in a 100-cm$^3$ glass-stoppered Erlenmeyer flask, to which 0.2 g of the silica–alumina was added. This was shaken in a 25 °C water bath for 24 h and centrifuged, and then phosphate, sulfate, silicate, aluminum, and pH were determined for the supernatant.

## Results and Discussion

*Adsorption Rate.* Since adsorption of phosphate on silica–alumina is a solid-liquid reaction, the adsorption rate is strongly dependent on the total surface area of the solid, or solid concentration. Figure 1 shows decrease of phosphate concentration in solution at an initial pH of 5.0 with addition of 1.0—4.0 g dm$^{-3}$ of the silica–alumina. The adsorption rate was extremely great immediately after the addition of the silica–alumina. The reaction seemed to almost terminate in 24 h, but the phosphate concentration decreased very slowly even after 3 d. Such a slow reaction was observed in the reaction between phosphate ions and alumina or kaolinite by Chen *et al.*[6] who postulated that it follows the first-order reaction rate law and

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† Japanese Industrial Standard, "Testing Methods for Industrial Waste Water."

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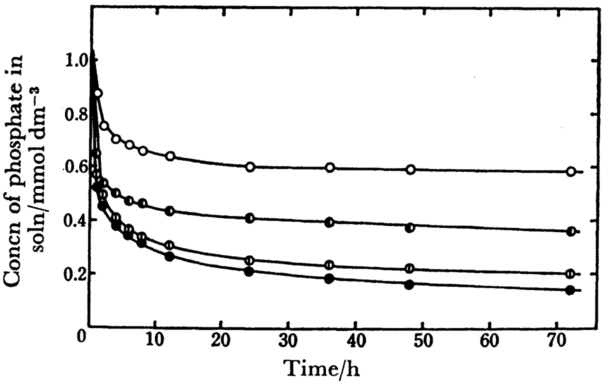

Fig. 1. Relation between adsorption rate and concentration of the silica–alumina.
Initial phosphate concentration: 1.05 mmol dm$^{-3}$, initial pH: 5.0, temperature: 25 °C, concentration of the silica-alumina (g dm$^{-3}$); ○: 1.0, ◐: 2.0, ⦶: 3.0, ●: 4.0.

continues as long as for 60 d. The initial adsorption rate increased with increase in solid concentration, but this tendency became unappreciable with addition of a large amount of solid, indicating that diffusional effects become significant.

Effects of initial pH on the adsorption rate are shown in Figs. 2 and 3. The adsorption rate decreased considerably with increase in the initial pH value from 5.0 to 8.5. The pH variation and release of sulfate, silicate and aluminum ions were determined with the progress of phosphate adsorption. The release of sulfate rapidly reached a plateau possibly due to depletion of sulfate group on the solid. The release of the other ions was almost in line with the adsorption of phosphate. The pH variation in the alkaline solution seems independent of phosphate adsorption.

*Adsorption Isotherm.* Though phosphate concentration decreased very slowly even after 3 d, the adsorption rate was much higher at the initial stage, the greater part of the reaction having proceeded in several hours.

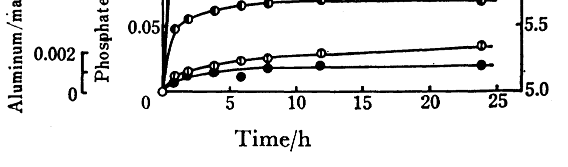

Fig. 2. Release of sulfate, silicate, and aluminum ions and pH variation concomitant with the adsorption of phosphate at an initial pH of 5.0.
▲: Amount of phosphate adsorbed (mmol g$^{-1}$), ◐: amount of sulfate released (mmol g$^{-1}$), ⦶: amount of silicate released (mmol g$^{-1}$), ●: amount of aluminum released (matom g$^{-1}$, on the enlarged scale on the left), ○: pH (on the right scale).

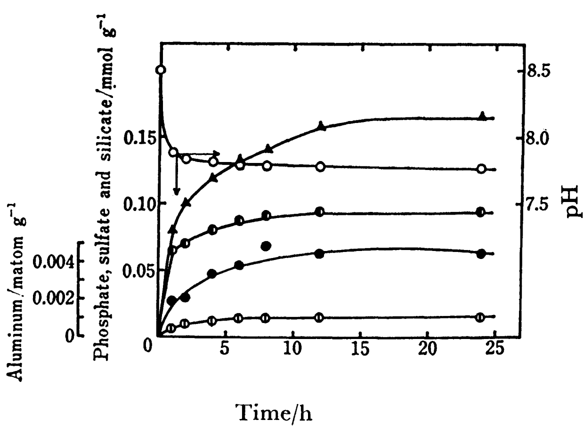

Fig. 3. Release of sulfate, silicate, and aluminum ions and pH variation concomitant with the adsorption of phosphate at an initial pH of 8.5.
▲: Amount of phosphate adsorbed (mmol g$^{-1}$), ◐: amount of sulfate released (mmol g$^{-1}$), ⦶: amount of silicate released (mmol g$^{-1}$), ●: amount of aluminum released (matom g$^{-1}$, on the enlarged scale on the left), ○: pH (on the right scale).

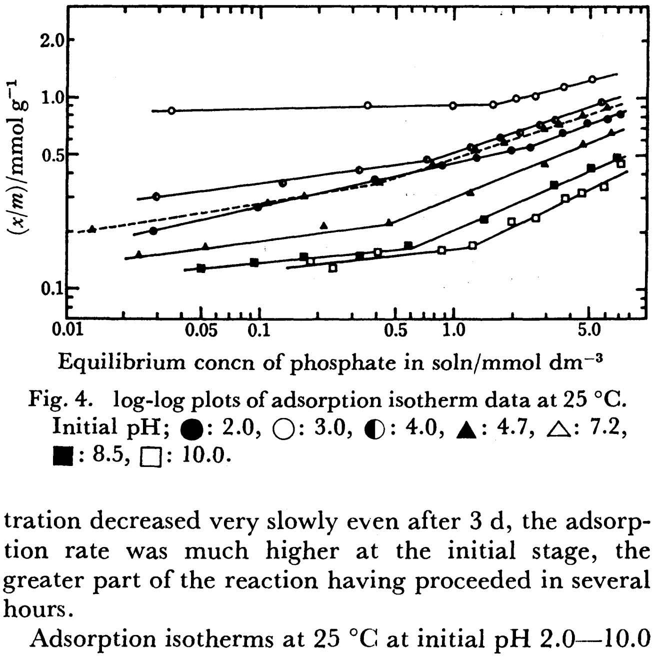

Fig. 4. log-log plots of adsorption isotherm data at 25 °C. Initial pH; ●: 2.0, ○: 3.0, ◐: 4.0, ▲: 4.7, △: 7.2, ■: 8.5, □: 10.0.

Adsorption isotherms at 25 °C at initial pH 2.0—10.0 are shown in Fig. 4. The amount of phosphate adsorbed is plotted against the equilibrium concentration of phosphate in solution in logarithmic scale. A linear relationship was obtained. There is an inflection at a phosphate concentration of 0.38—2.58 mmol dm$^{-3}$. The linear relationship indicates that the adsorption reaction is of Freundlich type:

$$\log x/m = 1/n \log c + k,$$

where

$x/m$ = quantity of phosphate adsorbed per unit mass of silica-alumina, mmol g$^{-1}$,
$c$ = equilibrium concentration of phosphate in solution, mmol g$^{-1}$, and
$k$ and $1/n$ = constants.

The inflection in the isotherms indicates the difference in the adsorption mechanism between low and high

Table 1. Isotherms of phosphate adsorption on silica–alumina

| Initial pH | Inflection point (mmol dm$^{-3}$) | Low concn | | High concn | |
|---|---|---|---|---|---|
| | | $1/n$ | $-k$ | $1/n$ | $-k$ |
| 2.0 | 2.58 | 0.217 | 0.350 | 0.387 | 0.420 |
| 3.0 | 1.75 | 0.050 | 0.033 | 0.264 | 0.085 |
| 4.0 | 0.70 | 0.152 | 0.310 | 0.307 | 0.286 |
| 4.7 | 0.38 | 0.154 | 0.400 | 0.349 | 0.318 |
| 7.2 | 0.50 | 0.102 | 0.620 | 0.417 | 0.525 |
| 8.5 | 0.59 | 0.092 | 0.776 | 0.417 | 0.701 |
| 10.0 | 1.31 | 0.130 | 0.783 | 0.509 | 0.828 |

Freundlich's adsorption equation:
$\log x/m = 1/n \log c + k$.

phosphate concentrations. The values of the slope ($1/n$), intercept ($k$) and inflection of each isotherm are given in Table 1. The higher values of $1/n$ at higher phosphate concentrations indicate greater increase in phosphate adsorption value with increase in phosphate concentration. On the other hand, the lower values of $1/n$ and the higher values of intercepts at lower concentrations indicate that relatively high phosphate adsorption still takes place at lower concentrations of phosphate.

The quantity of phosphate adsorbed per unit mass of the silica–alumina was very small in alkaline solutions. It increased with decrease in pH value, becoming the greatest (>1 mmol g$^{-1}$) at an initial pH of 3.0. However, it was very low at an initial pH of 2.0.

The effects of pH in this system seem to change with the species of phosphate in solution and the adsorption reaction. The pH of the solutions varied during the course of reaction, the initial pH values 3.0, 4.0, and 4.7, at which high adsorption values were attained, finally increasing up to 4.2—5.5, 6.3—7.0, and 6.3—7.0, respectively, depending on adsorption values. The dissociation constants of orthophosphoric acid[†††] indicate that the univalent phosphate species, $H_2PO_4^-$, predominates in this range of pH. It can thus be said that univalent phosphate ion is most easily adsorbed, while molecular phosphoric acid and ionic species of higher valence are adsorbed with difficulty or not at all. Acidic condition seems to favor the adsorption of phosphate, since the highest adsorption values were obtained at an initial pH of 3.0.

*Release of Hydroxide, Sulfate, Silicate, and Aluminum Ions.* Increase in pH and release of sulfate, silicate, and aluminum ions were observed coincidently with the adsorption of phosphate. This is discussed for the case of initial pH of 4.7, where $H_2PO_4^-$ is the predominant form of phosphate and high adsorption values were obtained, and for that of initial pH 8.5 for comparison.

At zero phosphate-adsorption where the silica–alumina was added to phosphate-free water, the initial pH values 4.0, 4.7, 7.2, 8.5, and 10.0 turned to 5.7, 5.8, 6.0, 6.2, and 6.2, respectively ater 24 h. Sacconi[7)] reported such surface buffer action for pure activated alumina in acid or salt solution and explained that it is due to displacement of $Al^{3+}$ ions with $H^+$ ions in the solution. However, we found no such evidence in our silica–alumina study. The phenomenon can be explained in terms of adsorption and desorption of hydroxide ions on and from the silica–alumina, *i.e.*, desorption of hydroxide ions in acidic solution causes increase in pH, adsorption in alkaline solution a decrease.

Table 2. Approximate value of hydroxide-ion release

| Phosphate concn µmol dm$^{-3}$ | | | pH | | Δeq/mol[a)] ratio | ΔOH[b)] |
|---|---|---|---|---|---|---|
| Init. ($A$) | Fin. ($B$) | $(A+B)/2$ | Init. | Fin. | ($C$) | µeq g$^{-1}$ |
| 0 | 0 | 0 | 4.73 | 5.80 | — | 0 |
| 526 | 14 | 270 | 4.72 | 6.70 | 0.41 | 44 |
| 790 | 113 | 452 | 4.79 | 6.94 | 0.54 | 98 |
| 948 | 170 | 559 | 4.76 | 7.00 | 0.58 | 130 |
| 1316 | 418 | 867 | 4.73 | 7.04 | 0.60 | 208 |
| 1974 | 776 | 1375 | 4.77 | 6.92 | 0.52 | 286 |
| 2632 | 1323 | 1979 | 4.79 | 6.83 | 0.46 | 364 |
| 3291 | 1812 | 2552 | 4.70 | 6.71 | 0.40 | 408 |
| 4607 | 2854 | 3731 | 4.73 | 6.54 | 0.30 | 448 |
| 5265 | 3412 | 4339 | 4.68 | 6.49 | 0.29 | 503 |
| 6581 | 4615 | 5598 | 4.78 | 6.41 | 0.23 | 515 |
| 8424 | 6143 | 7284 | 4.76 | 6.32 | 0.20 | 583 |

a) Increment of (OH equivalent: $PO_4$ mole) ratio corresponding to difference in pH, obtained on the titration curve. b) Equals $\frac{(A+B)}{2} \times C \times 0.08 \div 0.2$ (volume of sample solution=0.08 dm$^3$, and amount of the silica–alumina added=0.2 g).

In the phosphate solutions, the final pH increased with the adsorption of phosphate, indicating that hydroxide ions were released. Due to the buffer action

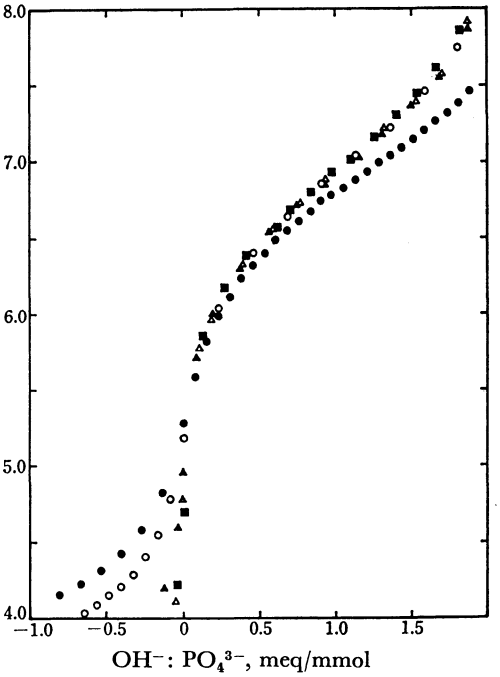

Fig. 5. Titration curves of dihydrogenphosphate solutions. (The positive and negative abscissae correspond to the titration with NaOH and HCl, respectively.) Phosphate concentration (mmol dm$^{-3}$); ●: 0.15, ○: 0.25, ▲: 1.00, △: 4.00, ■: 8.00.

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[†††] $pk_1=2.2$, $pk_2=7.2$, and $pk_3=12.3$.

of phosphate solution and decrease in phosphate concentration during the course of reaction, the amount of hydroxide ions released can not be calculated only from the initial and final pH values. If phosphate concentration remains constant during the course of reaction and pH increases, the amount of hydroxide ions released can be calculated using a titration curve of phosphate solution. The actual amount of hydroxide ions released should be between the value calculated from the initial phosphate concentration and that from the final concentration. We have calculated the approximate values of the hydroxide-ion release as follows (Table 2). The arithmetical mean value of the initial and final phosphate concentrations $((A+B)/2)$ was chosen to represent phosphate concentrations during the course of adsorption. This was multiplied by the increment of the ratio of hydroxide-ion equivalent and phosphate-ion mole $((C))$ corresponding to the difference between the initial and final pH values on the titration curves (Fig. 5). The curve was prepared by means of titration, adding sodium hydroxide or hydrochloric acid stepwisely to dihydrogenphosphate solutions of various concentrations. The shapes of the curves are almost the same in the pH range 5—8 and phosphate concentrations 0.25—8.0 mmol dm$^{-3}$.

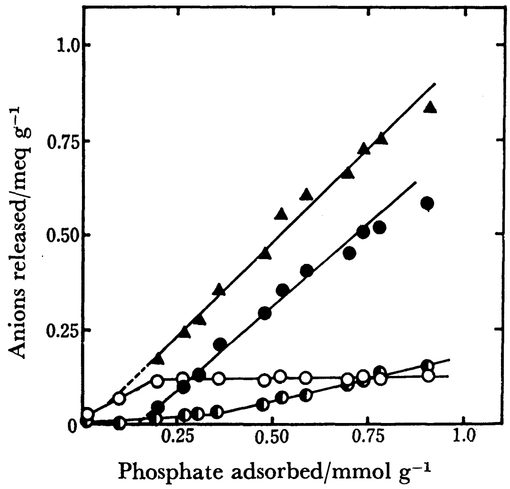

Fig. 6. Relation between adsorption of phosphate and release of hydroxide, sulfate and silicate ions at an initial pH of 4.7.
Amount of anions released (meq g$^{-1}$); ●: hydroxide ion (approximate value), ○: sulfate ion, ◐: silicate ion, ▲: sum of the equivalents of the three anions.

The calculated values together with the amounts of sulfate and silicate released‡ are plotted in Fig. 6 against the amounts of phosphate adsorbed. From an adsorption value of *ca.* 0.2 mmol g$^{-1}$, the release of hydroxide ions is in a linear relation with the adsorption of phosphate, indicating that phosphate ions in solution were exchanged with hydroxide group on the solid. However, at high adsorption values, it deviated downward from the linear relation, suggesting the existence of weakly and strongly bonded hydroxide groups on the silica–alumina, as reported by Takimoto *et al.*[5])

The silica–alumina originally contains *ca.* 0.2 meq g$^{-1}$ of sulfate derived from aluminum sulfate. When it was brought into contact with neutral phosphate-free solution, *ca.* 0.06 meq g$^{-1}$ of sulfate ions was released. In alkaline solution, sulfate release increased up to 0.2 meq g$^{-1}$, the total amount of sulfate contained in the silica–alumina. In acidic phosphate solutions, sulfate ions are released in proportion to the adsorption of phosphate, the release becoming constant as the sulfate on the solid is depleted. Thus the exchange process with sulfate ions is significant only at low phosphate adsorption values less than *ca.* 0.2 mmol g$^{-1}$. In alkaline phosphate solutions, on the other hand, a constant amount of sulfate ions, *ca.* 0.2 meq g$^{-1}$, was brought into solution irrespective of the phosphate adsorption, the sulfate ions undergoing exchange only with hydroxide ions.

The release of silicate ions was insignificant in alkaline phosphate solutions. In acidic phosphate solutions, it was very small in quantity at low adsorption values, but increased in proportion to the adsorption of phosphate above an adsorption value of *ca.* 0.2 mmol g$^{-1}$. In general, silicate tends to polymerize in aqueous solution, making determination by the molybdenum blue procedure impossible.[8]) However, silicate determination before and after the sodium-carbonate fusion on the same sample gave almost the same results, indicating that the silicate exists in the monomeric state. Silicate groups at the terminal of the structure of the silica–alumina seem to be easily exchangeable with phosphate ions in solution, and consequently released as univalent anions such as $H_3SiO_4^-$.

From the coincidence of the release of the three anions with the adsorption of phosphate and the proportionality between the amounts of phosphate adsorbed and the three anions released, it is certain that the adsorption reaction involves an ion-exchange process between phosphate ions in solution and the three anions on the solid.

In consideration of the contribution of the three anions to the adsorption reaction, we see that the sulfate group plays the greatest role in the ion-exchange reaction for adsorption values less than *ca.* 0.2 mmol g$^{-1}$, while the contribution of sulfate rapidly decreases with increase in adsorption value due to depletion of the effective sulfate group on the solid. The contribution of hydroxide and silicate ions to the exchange reaction increases at higher adsorption values.

For a better understanding of the process of phosphate adsorption on silica–alumina, we should consider the species of phosphate adsorbed on the solid. By X-ray study Cole and Jackson[9]) found that crystalline aluminum dihydroxide dihydrogenphosphate, $Al(OH)_2H_2PO_4$, is obtained by the reaction between aluminum oxide and potassium dihydrogenphosphate in acidic solution. It was suggested that phosphatized silica–alumina contains the $H_2PO_4$ group. However, we found no decisive evidence for the formation of crystalline material by means of X-ray diffraction.

We made stoichiometrical discussion on the basis of the release of the anions. The sums of the equivalents

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‡ Blank values for phosphate-free solution were subtracted from individual measured values for phosphate solutions.

of the three anions released are plotted against moles of phosphate adsorbed (Fig. 6). These plots give a straight line with a 1.0 slope almost passing through the origin, indicating that the sum values can account for the moles of phosphate adsorbed. It can be concluded that the adsorption of phosphate on the silica–alumina proceeds mainly through the ion-exchange reaction between phosphate ions in solution and hydroxide, sulfate and silicate ions on the solid, and that the phosphate ions adsorbed should be univalent, the latter conclusion being supported by the results obtained from a similar study with an ion-exchange resin, Amberlite IRA-410 in the $Cl^-$-form, in pH 4.0 solutions. The exchange ratio of phosphate and chloride ions was 1: 1, indicating that phosphate ions taking part in the exchange reaction are univalent.

The amount of the release of aluminum ions was small, *ca*. 1/5—1/10 that of silicate ions. Aluminum ions were determined also by the atomic absorption method, which gave almost identical results with those obtained by the colorimetric method, indicating that the values obtained represent the total amount of aluminum ions which may be present in solution in various species. It tended to increase with the adsorption of phosphate and was greater in alkaline solutions, but was at most less than 0.08% of the total aluminum of the silica–alumina. It seems that the solubility of alumina hydrogel increases with increase in the concentration of phosphate.

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