Inorganic Ion Exchangers

II. Sorption Rate and Dehydration Studies on Zirconium Phosphate and Tungstate Gels

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The sorption rates of metal ions on zirconium phosphate gels depend on the composition of the gels, characterized by the ratio phosphate/zirconium, $(P/Zr)_s$, and the water content. If these quantities are chosen high enough, most ions can be sorbed at a quite satisfactory rate. The values wanted in order to achieve this vary considerably, however, between different ions, being much lower *e.g.* for Cs^+ and Sr^{2+} than for UO_2^{2+}.

For a gel of a ratio $(P/Zr)_s$ close to the upper limit of 2, a dehydration below approximately $1\frac{1}{2}$ mole of water per zirconium atom brings about a rapid decrease in the sorption of Sr^{2+} at equilibrium, indicating a rather sudden break-down of the ion exchange properties of the gel as the water content falls below the mentioned value. An ignited gel, *i.e.* the water free pyrophosphate, sorbs less than one tenth of the Sr^{2+} sorbed by a gel containing an appropriate amount of water.

Determinations of the water still held at equilibrium by the same gel of $(P/Zr)_s \approx 2$, as the temperature is increased, show that one mole of water per zirconium atom is held much more firmly than the rest. This final mole of water certainly stems from the phosphate groups, which thus contribute with half a mole of water each. They must therefore be monohydrogen groups, which circumstance is also compatible with the behaviour of the gel upon neutralization,[1] and also with the layer structure proposed lately for zirconium phosphates.[14]

For zirconium tungstate gels, the sorption properties depend crucially on the value of pH prevailing at their precipitation, as has been found in experiments with UO_2^{2+}. This is not unexpected, considering the different composition of the polytungstate ions dominating in solutions of various pH.

In the first part of this investigation[1] various basic salts of zirconium and titanium, noted for their ion exchange properties, were investigated with respect to their resistance to strong acids and degree of hydrolysis under various conditions. Also the resistance to attrition of grains of a size suitable

for column operation was observed. It turned out that, on the whole, zirconium phosphate was the material of greatest promise, and it was therefore primarily selected for further study. As is well known, the composition of the zirconium phosphate gel is very sensitive to the conditions prevailing at its preparation. It has been shown, however, that gels of a fairly reproducible ratio phosphate to zirconium, $(P/Zr)_s$, can nevertheless be prepared if certain precautions are taken. For some gels of various ratios $(P/Zr)_s$, the amounts of hydrogen and phosphate ions released have also been determined as functions of pH of the outer solution. In this way a good picture of the acidity and hydrolysis of gels of different compositions has been obtained.

This paper mainly deals with another property of great importance for the employment of the gels as ion exchangers, *viz.* the sorption rate. It turns out that this quantity depends both on the composition of the gel and on the nature of the ion to be sorbed. For some representative ions, the rate has therefore been determined as a function of the ratio $(P/Zr)_s$. Most of these measurements have been performed at 20°C, but a few also at 100°C, to yield some information about the increase of the sorption rate with the temperature. These experiments also show how the affinities of the gels for various ions vary with the temperature. For the ions UO_2^{2+} and Sr^{2+} the variation of the sorption rate with the water content of the gels has also been investigated. It was then found that while a moderate dehydration only seems to affect the sorption rate, and moreover to a very different extent for UO_2^{2+} and Sr^{2+}, a very strong dehydration always causes a virtual destruction of the ion exchange properties of the gels.

The great influence thus exerted by the water present in the gels compelled us to further investigate what happens on dehydration. This has been done in two ways. First the sorption of Sr^{2+} at equilibrium was determined for a gel of a certain ratio $(P/Zr)_s$ at several different values of the water content. These experiments were arranged in such a manner that the load of Sr^{2+} per functional group could be found for each state of the gel, at a specified value of pH in the outer solution. In this way, the sorption ability of the gel can be measured as a function of its water content under otherwise identical conditions.

The process of dehydration was also investigated by determining the amount of water still held by a gel after heating to constant weight at various temperatures. Hence it was possible to calculate the number of water molecules present per zirconium atom at each temperature and thus obtain information about the strength of bonding for various portions of the water.

Besides the zirconium phosphate studies, a few experiments have also been made with some zirconium tungstate gels prepared and treated in different ways.

EXPERIMENTAL

For the sorption experiments at 20°C, a volume v of a solution, containing the ion to be investigated in a concentration C_M, was shaken in a thermostat with a certain amount, m, of the gel, either for a specified time or until equilibrium had been reached. After centrifugation, the concentration C_{MS} remaining in the solution was determined. In the experiments at 100°C, the solution and the gel were mixed by mechanical stirring in a flask, placed on a boiling water bath. From time to time samples were withdrawn for analysis. With this procedure, the ratio v/m was altered during the series which should

be corrected for. As the samples were small in comparison with the solution volume v, and, moreover, sorption equilibrium was reached very soon at this temperature, this correction was always very small and in most cases quite negligible.

In the case of UO_2^{2+} and U^{4+}, the determination of C_{MS} was performed spectrophotometrically. For UO_2^{2+}, the thiocyanate methode was used, as described in Ref.[2], while U^{4+} was measured directly by its high absorption peak at 6450 Å. Provided the solutions are kept so acid that U(IV) exists only as the unhydrolysed species U^{4+}, the absorption of this peak obeys Beer's law with a molar extinction coefficient $= 58$ cm^{-1} M^{-1} (cf. Ref.[3]). Here an acidity of 2 M has been chosen which is certainly sufficient to suppress the hydrolysis completely[4] at the present concentrations of U(IV). The analysis of Sr^{2+} was done by EDTA titration[5] for concentration > 1 mM, while lower concentrations were determined radiometrically by means of the pure β-emitter ^{89}Sr ($t_{\frac{1}{2}} = 51$ d). For Ce^{3+} and Cs$^+$, all analyses were performed radiometrically, by the active isotopes ^{144}Ce ($t_{\frac{1}{2}} = 285$ d) and ^{134}Cs ($t_{\frac{1}{2}} = 2.19$ y), respectively. As to the former one, the combined β-emission of the mother nuclide and its shortlived daughter ^{144}Pr ($t_{\frac{1}{2}} = 7.5$ m) is much more intense than the γ-emission of the same pair. Also for ^{144}Ce β-counting is thus preferred, especially as the high energy of the β-particles permits the use of wet samples for counting, as in the case of ^{89}Sr. For ^{134}Cs, on the other hand, γ-counting is preferred. All radiometric determinations were done by scintillation counting, using anthracene for β- and thallium activited sodium iodide for γ-detection.

THE SORPTION RATE AS A FUNCTION OF THE PHOSPHATE CONTENT OF THE GELS, FOR IONS OF VARIOUS TYPES

Preliminary tests, further confirmed by the studies reported below, have shown that the gels have to contain a fair amount of water in order to sorb most ions at a desirable rate. For the following investigation of the influence
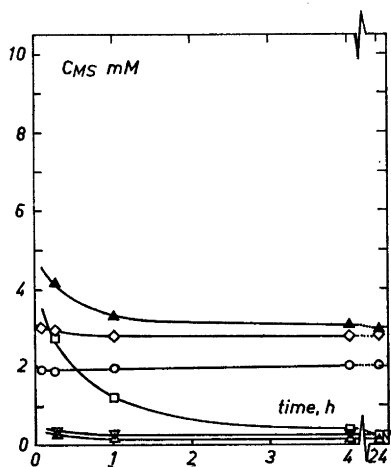

Fig. 1. Sorption rates of ions of various types on a zirconium phosphate gel of $(P/Zr)_s = 1.95$ and a water content of 50 %, at 20°C. $C_M = 10$ mM, $v/m = 10$ ml/g.

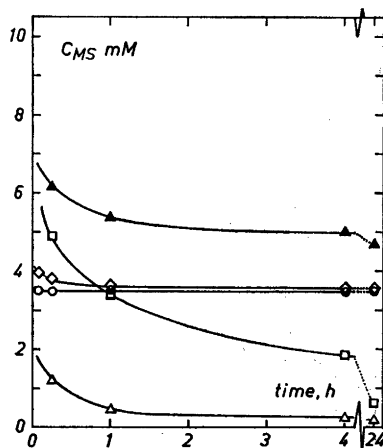| Ion:	U^{4+}	UO_2^{2+}	Ce^{3+}	Sr^{2+}	Cs$^+$
C_H, mM:	4000	300	10	10	0	300
Sign:	□	▲	△	▽	○	◇

Fig. 2. Sorption rates on a gel of $(P/Zr)_s = 1.73$, other conditions being the same as for the gel of $(P/Zr)_s = 1.95$ (Fig. 1).
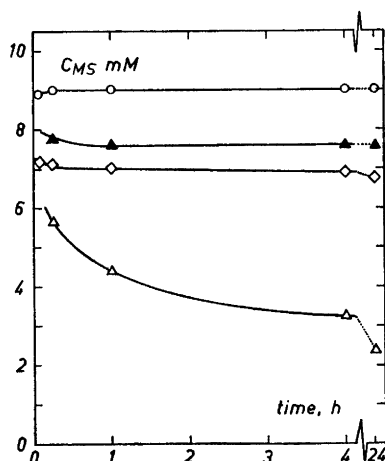
Fig. 3. Sorption rates on a gel of $(P/Zr)_s =$ 1.22, other conditions being the same as for the gel of $(P/Zr)_s = 1.95$ (Fig. 1).

of the phosphate content, expressed by the ratio $(P/Zr)_s$, on the sorption rate, the water content of all gels tried has therefore been kept at a high value, *viz.* 50 %. The amount was determined as the loss of weight on ignition. The ions to be sorbed were chosen so that all types likely to occur in actual separations should be represented (*cf.* Ref.[1]). The original concentration C_M has for all ions been 10 mM, and the ratio $v/m = 10$ ml/g. The experiments have been performed at the acidities specified in connexion with Fig. 1, chosen so that a suitably high sorption occurs. Nitrate solutions of all ions have been used except in the case of U^{4+}, selected especially as a model for Pu^{4+}, where perchlorate solutions have to be used in order to avoid oxidation.

At 20°C, gels with $(P/Zr)_s = 1.95$, 1.73, and 1.22 have been tried. The results are reported in Figs. 1—3. For Sr^{2+}, equilibrium is reached almost instantaneously over the whole range of $(P/Zr)_s$. Also Cs^+ is sorbed quite rapidly by all the gels, though the final adjustment to equilibrium on the gel of the lowest ratio $(P/Zr)_s = 1.22$ takes a few hours, Fig. 3. For UO_2^{2+} the sorption is considerably slower, and even for the gel richest in phosphate some hours are wanted for the attainment of equilibrium. The four-valent U^{4+}, finally, hardly reaches equilibrium completely within the allotted time of 24 h.

Provided that the gels are working in a similar manner at 100°C as they do at 20°C, the sorption rates ought to increase with the temperature. This really also occurs, as is evident from a comparison of the UO_2^{2+}-curves of Figs. 4 and 5. These figures give the results for the gels of $(P/Zr)_s = 1.95$ and 1.73, respectively. For Sr^{2+} and Cs^+, which are sorbed rapidly even at 20°C, such a comparison is of course futile. The results also show, however, that a rise of temperature markedly decreases the sorption of Sr^{2+} and even more of Cs^+, in agreement with the findings of Baetslé.[6] Contrary to that, the sorption of UO_2^{2+} is only slightly influenced, decreasing a little with the temperature when $(P/Zr)_s = 1.95$, but increasing a little when $(P/Zr)_s = 1.73$.
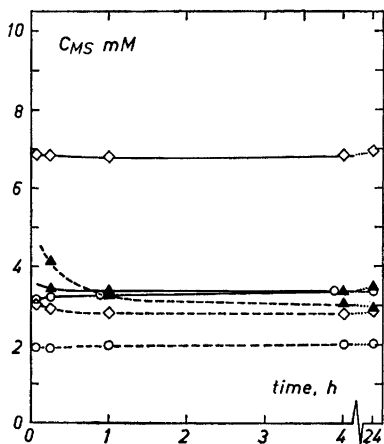
Fig. 4. Sorption rates on a gel of $(P/Zr)_s =$ 1.95 at 100°C, other conditions being the same as stated in Fig. 1 (fulldrawn lines). The corresponding results for 20°C (from Fig. 1) have been introduced for comparison (dashed lines).

Fig. 5. Sorption rates on a gel of $(P/Zr)_s =$ 1.73 at 100°C, other conditions being the same as stated in Fig. 1 (fulldrawn lines). The corresponding results for 20°C (from Fig. 2) have been introduced for comparison (dashed lines).
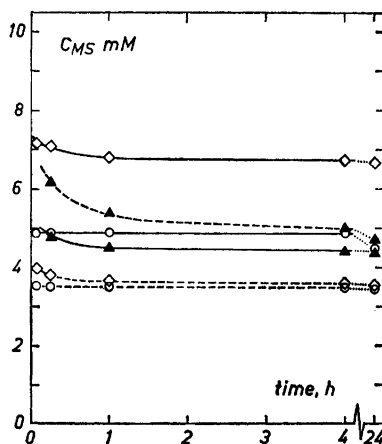
The gels thus seem to behave quite normally also at 100°C. There is every reason to believe that they can be used at even considerably higher temperatures, though their hydrolysis may be more troublesome under such conditions.

THE SORPTION RATES AS A FUNCTION OF THE WATER CONTENT OF THE GELS

Preliminary tests showed that while the sorption rate of UO_2^{2+} is very sensitive to variations of the water content of the gel, this does not seem to apply to the sorption rate of Sr^{2+}. A systematic investigation of the behaviour of these two ions should therefore yield a good picture of the influence of the water content on the sorption rate of ions acting quite differently in this respect.

As before, sorption took place from nitrate solutions of an original concentration $C_M = 10$ mM, and the ratio v/m was kept $= 10$ ml/g. The solutions of UO_2^{2+} originally also contained 10 mM nitric acid, while no extra acid was added to the Sr^{2+} solutions. Gels of the desired content of water were prepared by drying, or even igniting, the original gel containing 50 % water.

For UO_2^{2+}, the results found for gels of $(P/Zr)_s = 1.95, 1.89, 1.58,$ and $1.22,$ with a water content varying between 0 and 50 %, are reported in Figs. 6 and 7. The sorption rate soon decreases considerably, as the water content is lowered, and in a higher degree, the lower the ratio $(P/Zr)_s$. On the other hand there is no certain indication that the sorption at equilibrium decreases, except for ignited gels, containing no water, which undoubtedly sorb very little. Already at a water content of 10 %, the amount finally sorbed is evidently of
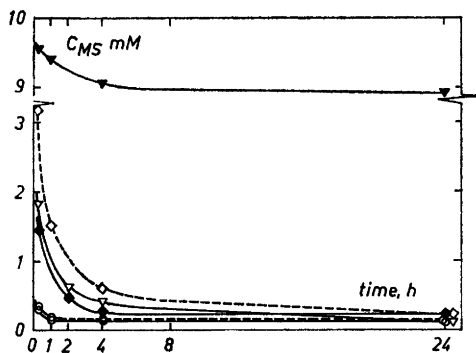
Fig. 6. Sorption rates of UO_2^{2+} on zirconium phosphate gels of varying water content at 20°C. Fulldrawn lines refer to $(P/Zr)_s = 1.95$, dashed lines to $(P/Zr)_s = 1.89$. $C_M = 10$ mM, $C_H = 10$ mM, $v/m = 10$ ml/g.

Water, %:	50	40	30	20	10	0
Sign:	O	●	◇	◆	▽	▼

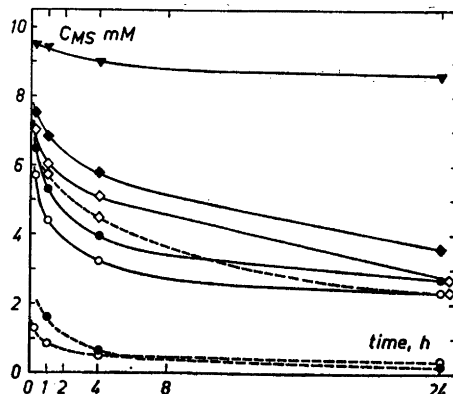*Fig. 7.* Sorption rates of UO_2^{2+} on gels of varying water content. Dashed lines refer to $(P/Zr)_s = 1.58$, fulldrawn lines to $(P/Zr)_s = 1.22$. Other conditions are the same as stated in Fig. 6.

the same order of magnitude as for gels of a high water content, though the equilibrium is reached only slowly.

In the case of Sr^{2+}, only the gels of the highest and lowest ratio $(P/Zr)_s$, *viz.* 1.22 and 1.95, have been investigated. The results are reported in Fig. 8. They differ strikingly in several respects from those found for UO_2^{2+}. Thus the sorption rate is on the whole much faster, and for $(P/Zr)_s = 1.95$ equilibrium is attained almost instantaneously also when the water content is as low as 20 %. Even for a gel of $(P/Zr)_s = 1.22$ with such a low water content, equilibrium has been reached within an hour, while for UO_2^{2+} this process takes several days. For ignited gels, however, even the sorption of Sr^{2+} is slow and low.

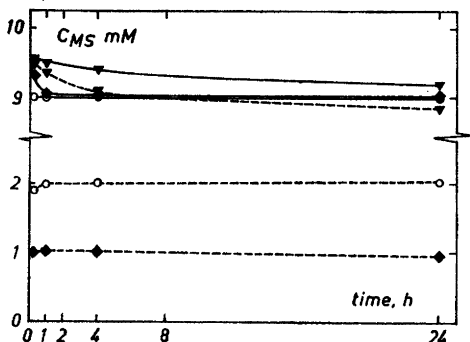*Fig. 8.* Sorption rates of Sr^{2+} on gels of varying water content. Dashed lines refer to $(P/Zr)_s = 1.95$, fulldrawn lines to $(P/Zr)_s = 1.22$. Other conditions are the same as stated in Fig. 6.

In order to secure, at room temperature, the attainment of equilibrium within a day for gels of all tried ratios $(P/Zr)_s$, it is thus necessary to operate with a rather high water content, 40 to 50 %. This has also been duly observed, not only for the measurements described above in this paper but also for those referring to the acidity and hydrolysis of various gels, reported in the first paper of this series.[1]

For several ions of great importance for the reprocessing of nuclear fuels, zirconium phosphate thus provides a fast sorbent, especially if the ratio $(P/Zr)_s$ and the water content of the gel are kept high. The sorption occurs in those cases fast enough to make possible column operations without any leakage, as has also been found in a few experiments of this kind.[7-9] For ions as U^{4+}, on the other hand, such operations are certainly not feasible which circumstance resembles the behaviour of Zr(IV) on silica gel.[10] In the case of zirconium phosphate, it is, moreover, to be suspected that slow irreversible processes take place in addition to the slow sorption, as has already been pointed out.[1] From the abnormal course of the distribution coefficient as a function of pH, to be reported in the next paper of this series, it is in fact possible to infer with certainty that such additional reactions occur.

THE SORPTION AT EQUILIBRIUM AS A FUNCTION OF THE
WATER CONTENT OF THE GEL

In order to investigate more closely when a dehydration of a zirconium phosphate gel starts to interfere not only with the rate of sorption of a certain ion, but also with the amount sorbed at equilibrium, Sr^{2+} was sorbed on gels of $(P/Zr)_s = 1.98$, containing various amounts of water, until equilibrium had been reached certainly in all cases. The sample weights of the various gels were chosen so that they would give the same residue on ignition, *viz.* 0.1370 g. In this way all samples were made to contain the same number of phosphate groups. As far as the condition of these groups is independent of the water con-

Table 1. The load per g water-free gel, C_{MG}, (proportional to the load per zirconium or phosphate group) as a function of the water content. The ratio $(P/Zr)_s = 1.98$, $C_M = 1$ mM and $v/m = 73.0$ ml/g water-free gel.

Water %	$\dfrac{\text{mole water}}{\text{mole Zr}}$	$10^3 \times C_{MG}$ mmole/g	pH	$10^3 \times C_{MG}$ pH = 2.00
45.2	12.06	59.8	1.90	62.6
42.7	10.92	59.9	1.90	62.7
35.5	8.05	59.7	1.89	62.7
26.6	5.30	59.4	1.88	62.6
24.4	4.72	59.1	1.88	62.4
19.1	3.46	58.4	1.88	61.9
14.2	2.42	56.9	1.87	60.9
12.5	2.10	56.6	1.87	60.8
10.3	1.68	55.8	1.85	60.7
8.9	1.43	55.0	1.85	59.3
7.6	1.21	44.2	1.92	47.9
0	0	5.2	1.97	5.6

tent, the same distribution should be observed for all samples, provided the pH value of the equilibrium solutions is kept constant. To facilitate this, the original nitrate solution of Sr^{2+} contained 10 mM nitric acid, while C_M was kept as low as 1 mM. Furthermore, the ratio v/m was chosen rather high (= 73.0 ml/g, calculated on the weight of water-free gel, which is equivalent to 36.5 ml/g gel of the water content of 50 % usually employed). Due to the fact that gels of a lower water content are slightly more hydrolysed in acid solutions, exactly the same value of pH does not result however, even if the sorption of Sr^{2+} takes places in the same way. This variation of pH will in its turn change the amount of Sr^{2+} sorbed a little. To account for this, all values observed have been corrected to one and the same value of pH = 2.00, by means of those $\log \varphi$(pH) curves for various C_{MS} which will be presented in the next paper of this series. For the gels of very low water content, the equilibrium value of pH will also be influenced by that rapid decline of the sorption of Sr^{2+} which has already been anticipated.

The results are reported in Table 1 and Fig. 9. If the water content is > 5 mole/mole Zr (*i.e.* >25 %), its variation has no influence upon the number of Sr^{2+} sorbed per mole phosphate present in the gel. As the water content becomes lower, a slight decrease of sorption is observed down to about $1\frac{1}{2}$ mole water/mole Zr, where the decrease rather suddenly turns quite drastic.
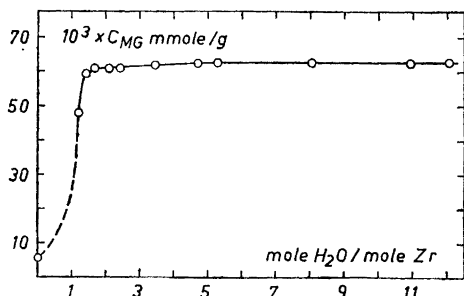

Fig. 9. Sorption of Sr^{2+} at equilibrium on gels of $(P/Zr)_s$ = 1.98, as a function of their water content. The sorption is referred to the amount of water-free gel, and to a value of pH = 2.00 in the equilibrium solution. C_M = 1.00 mM; v/m = 73.0 ml/g water-free gel.
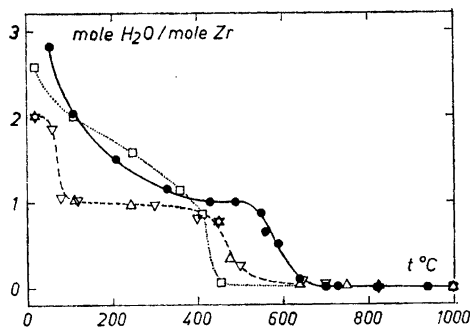
Fig. 10. The water still held by various zirconium phosphate preparations of $(P/Zr)_s$ ≈ 2, as a function of the temperature. The signs refer to: This work, gel 3.0-III (*cf.* Ref.[1]), ●—; Clearfield and Stynes[11], gel XIV, □·······; crystal XIII, △·······; crystal XXII, ▽······.

For an ignited gel, the sorption under otherwise identical conditions is less than 1/10 of that found for a sufficiently "wet" gel. The functional groups of the gel evidently cease to exchange, or even to exist, as the water content falls below around $1\frac{1}{2}$ mole/mole Zr.

Above this critical limit, the actual amount of water in the gel is not very essential, at least as far as the sorption of Sr^{2+} is concerned. If it is important, however, to keep down the weight of sorbent, the water content should be

chosen towards the lower end of the shelf of nearly constant C_{MG}, Fig. 9, as the sorption per g gel, water included, obviously increases as the water content decreases within this range. It should be remembered, however, that the sharp decline will presumably occur at different values of hydration for various ions, so that a dehydration may very likely change the order of selectivity found for gels of a high water content. In addition, the sorption rates will be influenced, as described above.

THE DEHYDRATION AS A FUNCTION OF THE TEMPERATURE

The last one or two moles of water connected with a zirconium atom are evidently of crucial importance for the ion exchange properties. It may then be presumed that this quantity is bound much more firmly within the zirconium phosphate network than is the rest of the water. This should be possible to prove by determining the amount of water still held by the gel at equilibrium as a function of the temperature. If our postulate is true, such a thermogravimetric curve ought to exhibit one or more shelves, or at least a somewhat wavy appearance.

For these experiments, the same gel of $(P/Zr)_s = 1.98$ has been used as for the determinations of the Sr^{2+} equilibria, and the result is found in Fig. 10. Evidently one mole of water per zirconium, or half a mole per phosphate group, is bound much more strongly than the rest of the water. In Fig. 10, the results of Clearfield and Stynes [11] have also been introduced for comparison. For two crystalline materials, they find coinciding curves with a very marked shelf for one mole of water, though at a lower temperature than we find for our gel. Another shelf shows up at two moles of water, which has no counterpart in our measurements. This difference is presumably due to the better order prevailing in the crystalline state, which seemingly allows one further mole of water to be incorporated as a rather firmly held structural unit. The gel prepared by Clearfield and Stynes does not exhibit a shelf along its dehydration curve, which nevertheless has several inflexions. This difference between the gels certainly reflects a difference of structure, caused by different modes of preparation.

The firmly held water which finally leaves the gel at 500—600°C does most certainly come from the phosphate groups and its hydrogen may thus be identified with the exchangeable hydrogen ions of the gel. This is also confirmed by the fact that half a mole of water, i.e. one hydrogen, comes out per phosphate group which is just equal to the number of exchangeable hydrogen ions present, as this quantity has been determined from the neutralization curves of the gels.[1] Moreover, it is by now proved that no hydrogens besides the exchangeable ones exist within the phosphate groups. These must therefore most certainly be monohydrogen groups. Consequently all formulas proposing dihydrogen groups within the gel structure [12,13] have to be ruled out. Lately, a layer structure has been proposed [11,14] for zirconium phosphate, where the zirconium atoms are joined by O-P-O bridges, as part of monohydrogen phosphate groups. As the phosphate is hydrolysed, these bridges are substituted

by -OH- bridges. This picture agrees well with the known properties of the gels, especially as regards their neutralization and dehydration behaviour, as has been described above.

SORPTION PROPERTIES OF ZIRCONIUM TUNGSTATES OF VARIOUS PREPARATION AND TREATMENT

For the two tungstate gels precipitated at widely different values of pH, as described in the previous paper of this series,[1] the sorption at equilibrium from a 10 mM nitrate solution of UO_2^{2+} has been determined, and also the time wanted for its attainment. To achieve a suitably high sorption of UO_2^{2+}, the solution contained in addition 10 mM nitric acid, and the ratio v/m was as before chosen $= 10$ ml/g. The results are reported in Fig. 11. The sorption is much lower for the gel precipitated at the low pH $= 1.95$ (denoted A) than for the one precipitated at the high pH $= 4.20$ (B). The sorption rate is, however, rather acceptable in both cases. But if the gel B is treated with strong acid of fairly high concentration (1 M nitric acid), it is converted into a form B′ which shows a lower and, most important, much slower sorption than B, Fig. 11. It thus seems, as if zirconium tungstate gels should neither be prepared, nor used at low values of pH. Their marked dissolution in strong acids[1] moreover leads to the same conclusion.
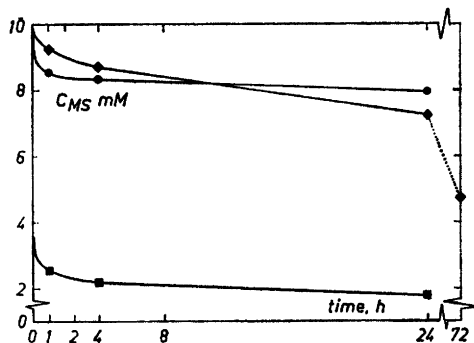

Fig. 11. Sorption of UO_2^{2+} on zirconium tungstate gels of different preparation and treatment. Water content $= 30$ %, $C_M = 10$ mM, $C_H = 10$ mM, $v/m = 10$ ml/g. Gel A ●; B ■; B′ ◆.

It should further be noted that the hydrogen ion concentration of the solution obtained after 24 h shaking is higher than that calculated on the basis of an ideal cation exchange in the case of A (found: 21.1 mM; calc. 14.2 mM), but lower in the case of B (found: 15.0 mM; calc. 26.5 mM). For B′, equivalence is found (found 15.7 mM; calc. 15.6 mM). A gel precipitated from a fairly acid solution (A) thus releases an extra amount of acid when shaken with a solution of pH ≈ 2, while a gel precipitated at a higher value of pH (B) instead takes up acid from such a solution. A gel treated with acid after its preparation, in the way described for B′, may arrive at a state where acid is neither taken up nor released when pH ≈ 2.

The strong influence of pH on the sorption properties of zirconium tungstate gels is not unexpected. In acid solutions, the tungstate exists as poly-

anions, the composition of which largely depends upon the prevailing value of pH (though equilibrium is as a rule not reached at once). Gels precipitated at different values of pH may therefore contain quite different functional groups and consequently have very dissimilar sorption qualities.

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