

## Inorganic Ion Exchangers

### V. The Influence of the Water Content on the Sorption of Zirconium Phosphate Gels of Different Crystallinity

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The sorption of  $\text{Cs}^+$ ,  $\text{UO}_2^{2+}$ , and  $\text{Ce}^{3+}$  on zirconium phosphate gels of different crystallinity has been investigated as a function of the water content of the gels. The sorption of  $\text{Cs}^+$  shows a high maximum at about 1 mole  $\text{H}_2\text{O}$ /mole Zr, *i.e.* just when the most firmly bonded water (outside the hydrogen phosphate groups) is removed. The sorption of  $\text{UO}_2^{2+}$  and  $\text{Ce}^{3+}$  increases little, or not at all, in this region. A dehydrated gel takes up water only slowly, and to a small extent. By dehydration, a lasting change of the selectivity can therefore be achieved which can be utilized for practical separation purposes.

In a previous investigation<sup>1</sup> it has been shown that zirconium phosphate (ZrP) preparations of different crystallinity possess very different sorption properties, even if they contain the same number of functional groups per gram water-free material, *i.e.* have the same ratio P/Zr (in the investigated cases  $\approx 2$ ). As the crystallinity very much depends upon even small variations in the mode of preparing the gels (*e.g.* the time and temperature used for precipitating, ageing, and washing), the notorious difficulties<sup>2-4</sup> to obtain products of a well reproducible sorption behaviour can readily be understood. The only easily reproducible form of ZrP is in fact the crystalline one.<sup>4</sup> From a practical point of view, however, the sorption properties of this state are, unfortunately, much inferior to those of suitably prepared gels.<sup>1</sup> It is therefore necessary to employ gels, and to prepare them so that they can be reliably reproduced. The crystallinity of the gels employed should also be determined, in order that a firm connexion may be established between this property, which largely determines the sorption characteristics, and the mode of preparation.

It has further been found<sup>3</sup> that the sorption behaviour of a gel of a given ratio P/Zr also very much depends upon its water content, once this quantity

becomes lower than a few moles  $\text{H}_2\text{O}/\text{mole Zr}$ . Of course, a rapid decline of the sorption capacity should be expected as soon as the hydrogen phosphate groups start to convert into pyrophosphate, as the process destroys the ion exchanging sites. This conversion should not be prominent before the water content has decreased to about 1 mole  $\text{H}_2\text{O}/\text{mole Zr}$ , and it turns out that spectacular changes of the sorption properties occur long before that, and furthermore in a manner which also very much depends upon the crystallinity.

The main purpose of this investigation has been to determine how the sorption of various important cations is influenced when the water content of ZrP gels of different crystallinity is varied. The gels have mostly had a molar ratio  $\text{P}/\text{Zr} \approx 2$ , for comparison a gel with  $\text{P}/\text{Zr} \approx 1.2$  has also been investigated. All experiments have been performed at  $20.0^\circ\text{C}$ .

### EXPERIMENTAL

*Preparation of the gels.* Three new gels have been prepared according to different methods, expected to result in products of widely different crystallinity, but with the same ratio  $\text{P}/\text{Zr} \approx 2$ . The first gel, 3.0-VII, was prepared in the way described before.<sup>2</sup> The gel was left in contact with the mother liquor until no more phosphate was taken up. Equilibrium was attained after five days; during this time the ratio  $\text{P}/\text{Zr}$  of the gel increased markedly ( $(\text{P}/\text{Zr})_i$  initial and final, respectively, of Table 1), as has also been noticed before.<sup>2</sup> The second gel, 3.0-VIII, was precipitated in the same manner, but the following treatment should yield a product as amorphous as possible. The gel was therefore centrifuged and thoroughly washed free from acid already 2 h after precipitation. Contrary to that, the third gel, 3.0-IX, was treated so that a fairly crystalline product should result. It was precipitated at  $70^\circ\text{C}$ , and then left in the mother liquor at this temperature for three days; afterwards it was worked up<sup>2</sup> like 3.0-VII.

Besides the newly prepared gels, the gels 3.0-III of  $\text{P}/\text{Zr} \approx 2$  and 1.4-II, of  $\text{P}/\text{Zr} \approx 1.2$ , both used earlier,<sup>2,3</sup> have been employed in this investigation.

*Stoichiometric composition.* The ratio  $\text{P}/\text{Zr}$  was determined for the gels both when still in contact with the solution,<sup>2</sup>  $(\text{P}/\text{Zr})_i$ , and when dried and ready for use,  $(\text{P}/\text{Zr})_s$ .

Table 1. Composition of the investigated gels.

Gel	$(\text{P}/\text{Zr})_i$		$(\text{P}/\text{Zr})_s$		P mmole/g gel <sup>d</sup>		$p^c$
	Initial	Final	A <sup>a</sup>	B <sup>b</sup>	A <sup>a</sup>	B <sup>b</sup>	
3.0-III	2.10	2.21	1.92	1.98	7.40	7.50	12.26
3.0-VII	1.98	2.07	2.01	—	7.56	—	9.97
3.0-VIII	1.97	— <sup>e</sup>	1.98	—	7.50	—	6.23
3.0-IX	1.82	— <sup>f</sup>	1.98	—	7.50	—	5.63
1.4-II	1.41	—	1.28	1.22	5.98	5.82	—

<sup>a</sup> X-Ray fluorescence and spectrographic determination of Zr and P, respectively.

<sup>b</sup> Gravimetric determination of Zr and P.

<sup>c</sup>  $p$  = mole  $\text{H}_2\text{O}/\text{mole Zr}$ , for gels used for the X-ray diffractograms of Fig. 1.

<sup>d</sup> Calculated for the gels in water-free state (cf. Ref. 2, Table 1).

<sup>e</sup> The gel was separated from the mother liquor before equilibrium was reached.

<sup>f</sup> No reliable value could be determined, on account of evaporation from the mother liquor during heat treatment.

The latter ratio was determined by X-ray fluorescence and optical emission spectrography analyses of Zr and P, respectively<sup>1</sup> (performed by Analytica AB, Sollentuna, Sweden). For 3.0-III and 1.4-II, previous gravimetric analyses were also available; they agree with the new analyses, Table 1.

For all the gels 3.0-III to 3.0-IX,  $(P/Zr)_s$  is very much the same and close to the value of 2.0 demanded by the formula  $Zr(HPO_4)_2 \cdot nH_2O$ .

The total water content of the gels has been determined as the loss of weight on ignition to pyrophosphate.

X-Ray diffractograms have been taken for all the 3.0-gels, by means of a Philips diffractometer (at Svenska Silikatforskningsinstitutet, Göteborg).

Curves of *dehydration*, *neutralization*, and *hydrolysis* (*i.e.* phosphate release from the gel as a function of pH) have been obtained as described previously.<sup>2,3</sup> Also the technique of the *sorption experiments* was the same as before.<sup>3</sup> For these, a grain size of 60–100 mesh was used.

### CRYSTALLINITY OF THE GELS

In Fig. 1, X-ray diffractograms are given for 3.0-gels of various water-content and crystallinity. The first four diffractograms refer to gels of a high water-content, ranging from almost 6 (for 3.0-IX) to over 12 moles  $H_2O$ /mole Zr (for 3.0-III; *cf.* Table 1). As will be proved below (p. 202), variations of the water content within this range do not change the affinity of the gels for various cations tested. It can then safely be assumed that their structures are not changed either. For comparison, the diffractograms of two partly dehydrated gels and of the crystalline compound have also been entered in Fig. 1 (the latter from Fig. 6 of Ref. 1). Crystalline ZrP has been obtained by refluxing a gel for 24 h in 12 M phosphoric acid; its composition conforms to the formula  $Zr(HPO_4)_2 \cdot H_2O$ .

In Fig. 1, the preparations are ordered after increasing crystallinity. As expected, 3.0-VIII is the most amorphous gel, with only one weakly separated peak. Next comes 3.0-III, and the difference between this gel and the markedly more crystalline 3.0-VII is remarkably large, in view of the fairly similar modes of preparation. Most crystalline among the gels is, as expected, 3.0-IX which shows a fourth, rather welldeveloped peak; otherwise the difference between this gel and 3.0-VII is not very spectacular. In comparison with the crystalline ZrP, however, all gels must be considered as fairly amorphous.

Nevertheless, all the principal reflexions of the crystalline phase are still present in the most crystalline gel, and in almost the same positions. As the gels become more amorphous, the reflexions broaden and disappear, but on the whole they still keep their positions. The so called gels can thus be considered as a chaos of very small fragments of the crystalline phase. In this extremely disordered structure, no fixed stoichiometric ratio  $H_2O/Zr$  is preferred, as is evident from the dehydration curves presented below. No definite hydrates, like  $Zr(HPO_4)_2 \cdot H_2O$  for the crystalline phase, can therefore be formulated for the gels.

The reflexion to the extreme left, Fig. 1, does move perceptibly towards lower angles with decreasing crystallinity, as has also been repeatedly observed before.<sup>1,4</sup> The significance of this displacement will be discussed below.

Clearfield<sup>5</sup> has performed an extensive X-ray diffraction study of crystalline ZrP. He finds a hexagonal unit-cell with  $a = b = 10.5 \text{ \AA}$  and  $c = 45.6 \text{ \AA}$ .

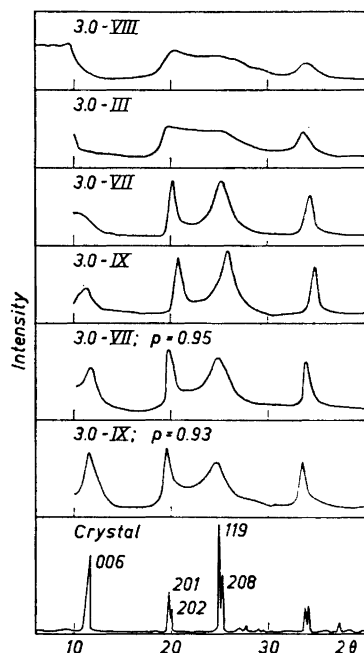


Fig. 1. X-Ray diffractograms of gels prepared in different ways, and of crystalline  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ .

The zirconium atoms occupy the positions  $000$ ;  $1/3 \ 2/3 \ 2/3$ ;  $2/3 \ 1/3 \ 1/3$  in a rhombohedral centered pseudo-cell of half the cell dimensions. They are thus ordered in layers, with an intraplanar zirconium-zirconium distance of  $a/2 = 5.25 \text{ \AA}$ , while the distance between the zirconium layers is  $c/6 = 7.6 \text{ \AA}$ . Within the layers, the zirconium atoms are presumably connected by phosphate bridges. How the layers are held together is not yet clearly understood. One may assume, however, that the exchangeable hydrogen ions are to be found in the interlayer space.

Using Clearfields<sup>5</sup> cell-dimensions, Albertsson<sup>1</sup> has indexed the strong reflexions as indicated on the diffractogram of the crystalline ZrP in Fig. 1. Thus, of the most prominent peaks, 006 refers to reflexions from the planes of zirconium atoms, with  $d =$  the interlayer distance,  $7.6 \text{ \AA}$ . The peak 119 originates from planes at an angle of  $\approx 34^\circ$  to the plane mentioned, and 201 from planes almost perpendicular to it, the angle being  $\approx 83.5^\circ$ . The planes causing the main reflexions are thus of very different orientation. For a layered structure like the one proposed here, cleavage should occur much easier along than across the layers. Thus, on disruption, the mean extension of the crystallites should be smaller in the  $c$ - than in the  $a$ - or  $b$ -directions; the crystallites should be flakelike.

At least a rough estimate of the mean crystallite size can be obtained by the Scherrer formula:<sup>1</sup>

$$D_{hkl} = 0.9\lambda/\beta_{hkl} \cos \theta$$

$D_{hkl}$ , the mean extension perpendicular to the plane  $hkl$ , is thus obtained from the broadening  $\beta_{hkl}$  of the peak  $hkl$ . The broadening of the peaks 006 and 201 will thus yield the mean extension of the crystallites across and, practically, along the layers, respectively, while 119 will give some intermediate measure.

It is immediately obvious from Fig. 1 that 006 becomes broader and also disappears sooner than the other peaks. The crystals are thus preferentially disrupted parallel to the  $ab$ -plane, as demanded by the structure proposed. Also the displacement of the 006 reflexion towards lower angles fits well into the picture, as indicating an increase of the interlayer distance on disruption of the crystals.

As to the water-rich gels, only 3.0-IX has the peak 006 sufficiently marked to allow a calculation of  $D_{006}$ , while  $D_{201}$  and  $D_{119}$  can be calculated also for 3.0-VII. Unfortunately the reflexions 202 and 208 are very close to 201 and 119, respectively; as the peaks broaden, the neighbours melt together. This means an extra broadening for the original peaks causing the values of  $D_{201}$  and  $D_{119}$  to come out too low.

In Table 2, values of  $D_{hkl}$  found from Fig. 1 have been entered both for gels of high water-content and for gels dehydrated so far that no water remains

Table 2. The mean dimensions of crystallites in various gels. The water-content is denoted by  $p$  (cf. Table 1).

Gel	$p$	$D_{006}$	$D_{201}$	$D_{119}$
3.0-VII	9.97	—	88	50
	0.95	50	88	33
3.0-IX	5.63	60	105	47
	0.93	75	88	38

except that present as hydrogen phosphate groups. The dehydration causes no extensive disruption of the gels. The peak 119 certainly becomes broader but, on the other hand, the peak 006 rather becomes sharper for both gels. The main features of the structure is still there, however, as is also found <sup>4,1</sup> by the dehydration of crystalline  $Zr(HPO_4)_2 \cdot H_2O$  to  $Zr(HPO_4)_2$ .

#### DEHYDRATION CURVES

A dehydration curve, stating the water content at equilibrium as a function of the drying temperature, yields information about the strength of bonding of various parts of the water taken up by a gel. The crystalline compound loses just 1 mole  $H_2O$ /mole Zr around 100°C, and another mole between 400 and 500°C. The first mole is most probably situated between the layers, taking part in the bond between them, the second one evidently stems from

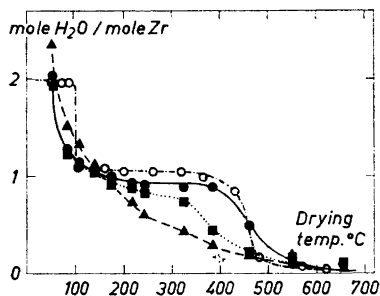


Fig. 2. Dehydration curves for the gels 3.0-VIII ( $\blacktriangle$  ---), 3.0-VII ( $\blacksquare$  .....), and 3.0-IX ( $\bullet$  —); also for crystalline ZrP ( $\circ$  ———).

the hydrogen phosphate groups.<sup>1,4</sup> In gels, the water cannot be expected to be as orderly arranged; especially of the part not tied up as hydrogen phosphate groups, various portions must be held very differently. The steps characteristic for the crystals will therefore more or less disappear for the gels.<sup>3,4</sup> It should be expected however, that the more crystalline the gels, the better developed their steps. Moreover, the high temperature step should turn up first, as originating from the hydrogen phosphate groups which are certainly fairly well-ordered *within* the layers long before any strict *inter-layer* order has been imposed.

In Fig. 2, the dehydration curves are shown for the gels 3.0-VII, VIII, and IX, and also<sup>1</sup> for the crystalline  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ . As expected, the high temperature step develops nicely with increasing crystallinity. Even the most crystalline among the gels, however, is not sufficiently well ordered to develop even a trace of the first step around 100°C; the interlayer water is evidently in the right place only in case of a rather perfect structure. The most amorphous gel does hardly show even the second step. Here the crystallites are obviously so small that even the hydrogen phosphate groups are no more in ordered surroundings.

The main part of the pyrophosphate formation evidently occurs at lower temperature, the lower the crystallinity. Some of the crystallites will be sizable even in a very amorphous gel, however, and so it happens that the pyrophosphate formation for 3.0-VIII is complete only at about the same temperature as for the more crystalline preparations.

#### NEUTRALIZATION AND HYDROLYSIS

The neutralization and hydrolysis curves of crystalline ZrP differ essentially from those of a typical gel. In a  $\text{Na}^+$ -medium, no extensive hydrolysis of the crystals occurs before  $\text{pH} \simeq 12$  and the neutralization curve has two distinct steps.<sup>1</sup> For the gel 3.0-II, of very much the same crystallinity as 3.0-III, hydrolysis becomes prominent already at  $\text{pH} \simeq 8$  and the neutralization curve shows a general slope, without any distinct steps.<sup>2</sup> In order to investigate how these features develop with increasing crystallinity, the neutralization and hydrolysis curves have been determined for the most crystalline gel, 3.0-IX, in a state containing 27.8 % water (= 5.63 mole/mole Zr). To allow a

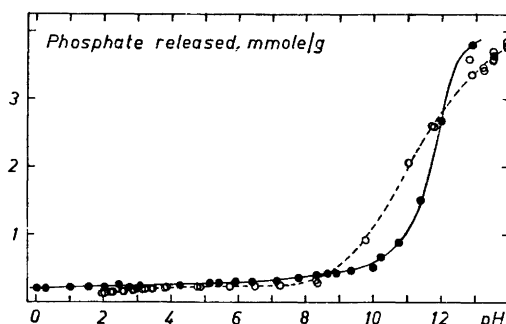


Fig. 3. Phosphate released to the solution as a function of pH at equilibrium for the gels 3.0-IX (● —) and 3.0-II (○ - - -).<sup>2</sup> The curves have been obtained with a ratio  $v:m = 100$  ml/g gel; they refer to gels containing 50 % water. The ionic medium is varying along the curves.<sup>2</sup>

direct comparison with the curves of 3.0-II, the data have then been recalculated to a water content of 50 % (= 14.63 mole/mole Zr). The more crystalline gel does show a considerably higher resistance to hydrolysis, Fig. 3. As a consequence, an embryonal step can also be discerned in the neutralization curve, Fig. 4.

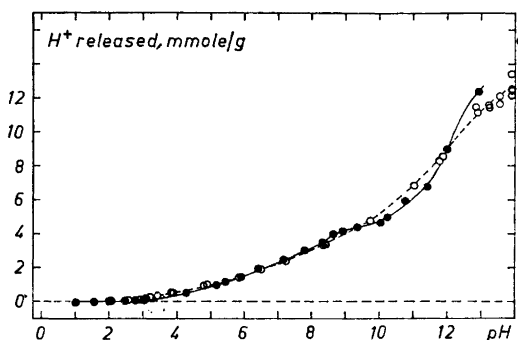


Fig. 4. Neutralization curves for the gels 3.0-IX and 3.0-II, obtained under the conditions stated for Fig. 3.

#### THE SORPTION AS A FUNCTION OF THE WATER CONTENT

The sorption of  $\text{Cs}^+$ ,  $\text{UO}_2^{2+}$  and, for two of the gels,  $\text{Ce}^{3+}$  from 100 mM nitric acid has been studied under conditions stated in the legend of Fig. 5. The results are collected in Figs. 5—9. The distribution coefficients  $\varphi = C_{\text{MG}}/C_{\text{MS}}$  have throughout been calculated with the load  $C_{\text{MG}}$  counted per gram water-free gel, *i.e.* for a certain number of functional groups, independent of the water-content. This number is moreover about the same for all 3.0-gels, *viz.*  $\approx 7.5$  moles/g water-free gel, Table 1. For the gel 1.4-II, it is of course substantially lower.

A most remarkable feature common to all investigated gels is that the sorption of  $\text{Cs}^+$  has a very marked maximum at about 1 mole  $\text{H}_2\text{O}/\text{mole Zr}$ , *i.e.* around the composition  $\text{Zr}(\text{HPO}_4)_2$ . For higher concentrations of water, the sorption soon becomes constant, for lower it decreases steeply as the formation of pyrophosphate starts. The sorption peak is sharper the more crystalline the gel, and it is more marked for the 3.0-gels than for 1.4-II. As the latter

Table 3. Symbols used in Figs. 5–9.

Time → h	4	40	110	165	350
$\text{Cs}^+$	□	◇	○ <sup>a</sup>	○ <sup>b</sup>	▽
$\text{UO}_2^{2+}$	■	◆		●	
$\text{Ce}^{3+}$	▾				

<sup>a</sup> In Fig. 6. <sup>b</sup> In Figs. 5, 7–9.

gel is less acidic,<sup>2</sup> also the height of its maximum is much lower. Among the 3.0-gels, the height is very much the same, decreasing only a little for the most crystalline gels.

On the other hand,  $\text{UO}_2^{2+}$  and  $\text{Ce}^{3+}$  show no maxima at all for 3.0-VIII and 3.0-III, and only very low ones for 3.0-VII. In the case of 3.0-IX, and also 1.4-II, the peaks of  $\text{UO}_2^{2+}$  are sizable, though considerably smaller than for

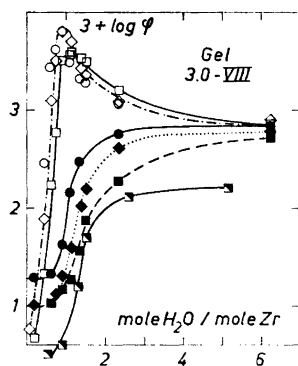


Fig. 5. Sorption of  $\text{Cs}^+$ ,  $\text{UO}_2^{2+}$ , and  $\text{Ce}^{3+}$  on the gel 3.0-VIII, as a function of its water content and the time of contact. Initial concentration of the various ions  $C_M = 1$  mM, in 100 mM nitric acid;  $v/m = 73$  ml/g water-free gel. Symbols, see Table 3.

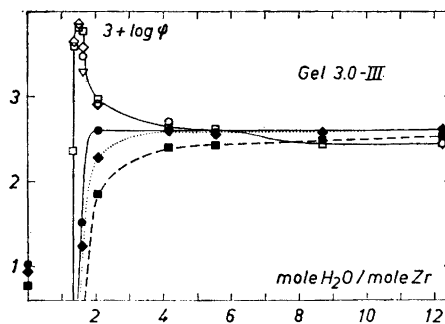


Fig. 6. Sorption of  $\text{Cs}^+$  and  $\text{UO}_2^{2+}$  on the gel 3.0-III. Conditions, see Fig. 5; symbols, see Table 3.



$\text{Cs}^+$ . It is known previously<sup>3</sup> that on dehydration of 3.0-III, no maximum occurs for  $\text{Sr}^{2+}$ .

For all gels except 1.4-II, the sorption of  $\text{Cs}^+$  reaches equilibrium quite rapidly, provided formation of pyrophosphate has not begun (*i.e.* the water content must not be  $< 1$  mole  $\text{H}_2\text{O}/\text{mole Zr}$ ). On the contrary, the sorption of  $\text{UO}_2^{2+}$  proceeds rather slowly on all amorphous gels, even if the water content is appreciably higher than 1 mole/mole Zr, Figs. 5 and 6. As the crystallinity and/or the water content increases, however, also the sorption of  $\text{UO}_2^{2+}$  becomes fast, except on 1.4-II, Fig. 9.

Once dehydrated, the gels take up water again only slowly and to a small extent. The rehydration is most marked for the most amorphous gel, 3.0-VIII. Here the curve obtained for  $\text{Cs}^+$  after a long contact time between gel and solution (shaking for several days) is seemingly displaced to the left of the curve obtained after only 4 h, Fig. 5. Evidently, as water is slowly taken up, the real water content will, after prolonged shaking, be perceptibly higher than the figure determined for the various samples before shaking. The displacement is not very large, however, and it disappears above 4 or 5 moles  $\text{H}_2\text{O}/\text{mole Zr}$ . For 3.0-III, the effect is even slighter, and discernible only if the water content is less than 2 moles  $\text{H}_2\text{O}/\text{mole Zr}$ , Fig. 6. For more crystalline gels, no rehydration can be observed, except possibly for gels dehydrated so far that pyrophosphate formation has started, Figs. 7 and 8. In such cases it

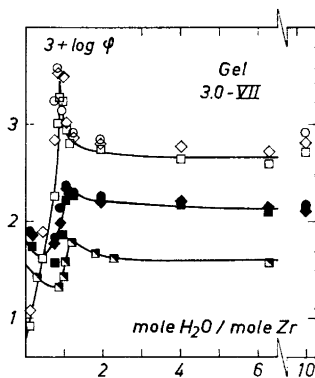


Fig. 7. Sorption of  $\text{Cs}^+$ ,  $\text{UO}_2^{2+}$ , and  $\text{Ce}^{3+}$  on the gel 3.0-VII. Conditions, see Fig. 5; symbols, see Table 3.

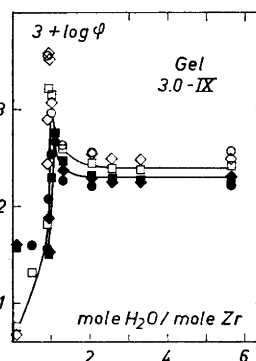


Fig. 8. Sorption of  $\text{Cs}^+$  and  $\text{UO}_2^{2+}$  on the gel 3.0-IX. Conditions, see Fig. 5; symbols, see Table 3.

is not possible to decide, however, whether the increase with time of, *e.g.*, the  $\text{Cs}^+$  sorption depends upon a slow uptake of  $\text{Cs}^+$ , or upon a slow rehydration of the gel. For the amorphous gels 3.0-VIII and 3.0-III, on the other hand, where all values of  $\phi$  to the left of the maximum increase with time, while all to the right decrease, the rehydration is obviously responsible.

## DISCUSSION AND CONCLUSIONS

Evidently, the gels on dehydration change their structure so that their affinity to certain ions, such as  $\text{Cs}^+$ , increases enormously, while other ions, such as  $\text{UO}_2^{2+}$  and  $\text{Ce}^{3+}$ , are sorbed to about the same extent as before. These changes take place *before* conversion of the gels into pyrophosphate begins, the steep fall of the  $\text{Cs}^+$  curves to the left of the maximum, obviously coincid-

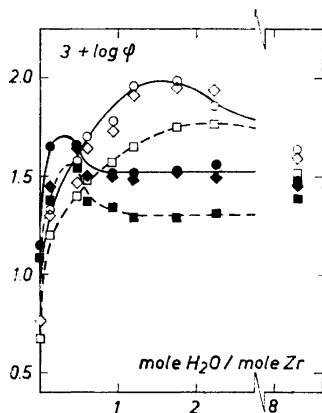


Fig. 9. Sorption of  $\text{Cs}^+$  and  $\text{UO}_2^{2+}$  on the gel 1.4-II. Conditions, see Fig. 5; symbols, see Table 3.

ing with the beginning of the condensation reaction. This is borne out already by the position of the maxima at around 1 mole  $\text{H}_2\text{O}/\text{mole Zr}$  for all 3.0-gels (or even somewhat higher for 3.0-III). Moreover the temperatures wanted for dehydration of the gels to maximum affinity are about  $130^\circ\text{C}$  for 3.0-VIII, and  $190^\circ\text{C}$  for the more crystalline 3.0-VII and 3.0-IX, as can be gathered from a comparison of Fig. 2 with Figs. 5, 7, and 8. At the latter temperature, the formation of pyrophosphate just starts, according to the analyses of Alberti *et al.*<sup>6,7</sup>

On crystalline  $\text{ZrP}$ ,  $\text{Cs}^+$  is sorbed only with difficulty, and as the load becomes heavy, the structure is broken up.<sup>1,4</sup> In the crystals, the interlayer space is too small for the unhindered diffusion of  $\text{Cs}^+$ . In the gels, the distance between the layer is not so strictly fixed and, as is evident from the displacement of the 006 reflexion, the mean distance is also longer than in the crystals, making the observed increase of the  $\text{Cs}^+$  sorption possible. Nevertheless the interlayer space may still be less than optimal. If so, a dehydration will be able to increase the sorption further, by removing water firmly held in the interlayer space and thereby loosening the structure still more.

The behavior of gels after heat treatment has also been investigated by Alberti *et al.*<sup>6,7</sup> They notice that heating to  $260^\circ\text{C}$  for 1 h will increase the equilibrium sorption of  $\text{Cs}^+$ . This treatment results, however, in an extensive dehydration so that the gels in fact arrive at a composition to the left of the maximum of the  $\text{Cs}^+$  sorption curves (*cf.* Figs. 5–8). A rehydration must therefore take place before the sorption of  $\text{Cs}^+$  gets high. As pointed out above, this procedure is very slow, and the high equilibrium value for  $\text{Cs}^+$  will conse-

quently be reached only after about a week. For the gel treated still more severely, for 24 h at 260°C, the immediate sorption is, of course, quite low, a slow rise due to rehydration occurring only after one or two weeks.

The opinion of Alberti *et al.*<sup>6</sup> that dehydration does not change the sorption properties before formation of pyrophosphate occurs, can hardly be upheld in view of the present results.

Amphlett and Jones<sup>8</sup> have observed that a ZrP gel, when treated in an autoclave with a solution of nitrate, sorbs  $K^+$  much better at 300°C than at 160°C, or at room temperature. The high sorption persists even if the gel later on is cooled to room temperature before sampling. It thus seems as if  $K^+$  would behave similarly to  $Cs^+$  on dehydration of ZrP gels.

The distribution coefficients of  $Cs^+$  and  $UO_2^{2+}$  which have about the same value for most gels of high water content can thus be made to differ by a power of ten, or even considerably more, by suitable dehydration of the gels. This is most interesting from a practical point of view, especially as rehydration is so slow that the difference will persist for a long time even for gels in contact with aqueous solution. Provided the gels are not too amorphous, their mechanical properties are moreover good enough to permit their use in sorption columns. Thus some very important conditions are fulfilled as to the use of suitably dehydrated ZrP gels for the separation of small amounts of  $Cs^+$  from a large bulk of  $UO_2^{2+}$ , an operation which is very essential for the working of certain reprocessing methods for irradiated nuclear fuels. For the purpose in mind, only gels of  $P/Zr \simeq 2$  should be applied, as they possess the highest sorption capacity and, as important, sorb  $Cs^+$  much more quickly than gels of low  $P/Zr$ . The practical working out of the separation will be described in a following paper of this series.

This work has been performed under a contract with *AB Atomenergi (The Swedish Atomic Energy Company)*, Stockholm, whose generous support is gratefully acknowledged.

#### REFERENCES

1. Albertsson, J. *Acta Chem. Scand.* **20** (1966) 1689.
2. Ahrland, S., Albertsson, J., Johansson, L., Nihlgård, B. and Nilsson, L. *Acta Chem. Scand.* **18** (1964) 707.
3. Ahrland, S., Albertsson, J., Johansson, L., Nihlgård, B. and Nilsson, L. *Acta Chem. Scand.* **18** (1964) 1357.
4. Clearfield, A. and Stynes, J. A. *J. Inorg. Nucl. Chem.* **26** (1964) 117.
5. Clearfield, A. *Private communication.*
6. Alberti, G., Conte, A. and Torracca, E. *J. Inorg. Nucl. Chem.* **28** (1966) 225.
7. Alberti, G., Torracca, E. and Conte, A. *J. Inorg. Nucl. Chem.* **28** (1966) 607.
8. Amphlett, C. B. and Jones, P. J. *J. Inorg. Nucl. Chem.* **26** (1964) 1759.

Received September 29, 1966.