

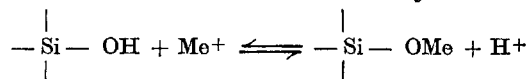
The Ion Exchange Properties of Silica Gel

I. The Sorption of Na^+ , Ca^{2+} , Ba^{2+} , UO_2^{2+} , Gd^{3+} , Zr(IV) + Nb , U(IV) and Pu(IV)

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In the present work the metal ion sorption on silica gel has been investigated. The silica gel acts in this respect as an ion exchanger of the weakly acid type and in the case of a monovalent cation the exchange reaction can be written schematically in the following way



For this equilibrium the law of mass action seems to be valid. Moreover an amount of hydrogen ions equivalent to the amount of metal ions sorbed are set free at the sorption on silica gel which has been saturated with hydrogen ions. The amount of metal ion sorbed depends strongly on the pH of the solution. At the sorption of strongly hydrolysed (presumably high molecular) ions the equilibrium is reached slowly, while the sorption of non-hydrolysed (low molecular) ions is quite rapid, the equilibrium usually being reached within five minutes.

Numerous silicon compounds with good sorption properties have long been known. Such compounds are the zeolites, of natural as well as synthetic origin, which are extensively used for the sorption of metal ions from water solutions. Silica gel has also been used previously as a sorbent, particularly for organic compounds and gases.

This investigation was performed in order to investigate more closely the ability of the silica gel to sorb metal ions from water solutions. The aim was especially to find out how this sorption depends on the previous treatment and grain size of the gel as well as on the hydrogen ion concentration of the solution. The sorption to and the affinity for the gel of different metal ions were also studied. Since all the results obtained can be interpreted on the basis of an ion exchange between gel and solution, a short account will first be given of these properties of the gel which makes such an exchange possible.

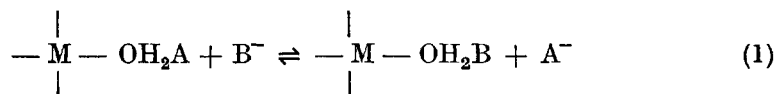
An ion exchanger consists primarily of an insoluble network containing charged groups. To these groups counter ions are bound in order to preserve the electroneutrality. As these ions do not belong to the structure, they are easily exchangeable. Cation or anion exchangers are obtained depending upon whether the network has a negative or positive charge, respectively. In the organic ion exchangers the network is produced by polymerization of suitable compounds, *e.g.* divinylbenzene and styrene, where the divinylbenzene forms crosslinkages between the chains of polymerized styrene. The charged groups are obtained by substitution in the carbon chain of acid or basic groups.

Hydroxides and hydrous oxides often have a structure where a network is formed by oxygen bridges between the metal atoms. These compounds show ion exchange properties which have recently been extensively investigated by Kraus *et al.*¹. Depending upon the pH, they act as anion exchangers (at sufficiently low pH) or as cation exchangers (at higher pH).

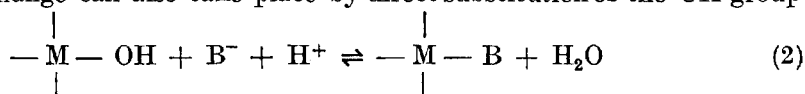
The anion exchange can take place in two different ways. In acid solution,

the basic group $\begin{array}{c} | \\ -M-OH \\ | \end{array}$ takes up hydrogen ions and $\begin{array}{c} | \\ -M-OH_2^+ \\ | \end{array}$ is

formed. At the same time an equivalent amount of anions are bound as counter ions. For the sake of simplicity, these anions could be assumed to be the monovalent A^- but the reasoning applies as well to the general case A^n . Then the exchange with another anion, B^- , proceeds according to

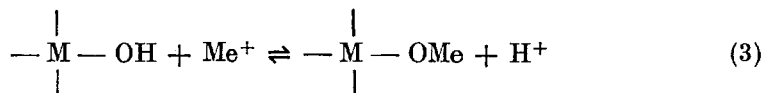


The ion exchange can also take place by direct substitution of the OH-group with B^-



In the latter case a bond is formed between B and M.

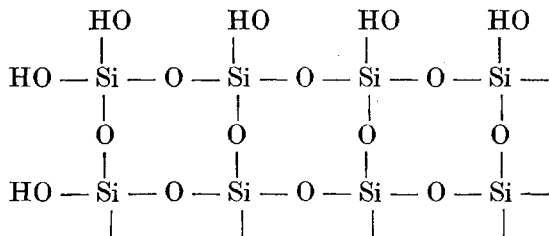
At higher pH, where cation exchange takes place, the reaction could for the simple case of a monovalent cation be written according to



The position of these exchange equilibria depends, of course, on the basicity of the group $\begin{array}{c} | \\ -M-O^- \\ | \end{array}$. The stronger the ability of this group to bind H^+ ,

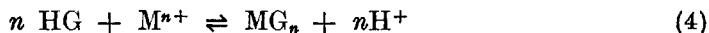
the higher the pH at which the transition from anion to cation exchange takes place. As the hydroxide is not strictly monofunctional, but contains groups of different basicity, it exhibits in a transition region both anion and cation exchange properties.

The structure of silica gel seems to be analogous to the structure of the hydroxides described above. It consists of a network of joined SiO_4 -tetrahedrons, where however the oxygen atoms are only partially required to make up the Si-O-Si bridges ^{2,3}. The rest of the oxygen atoms are free to bind ions from the solution out of which the gel is precipitated. Thus the silica gel consists of structural groups of the following type:



Here the central ion consists of Si^{4+} , which has a rather high electron affinity. This implies that the electron density around an oxygen atom bound to silicon is lower than around one bound to, say, a metal atom. Thus the free electron pairs on the oxygen atoms are comparatively inactive and therefore

the basicity relatively low. Hydrogen ions bound to a $-\text{Si}-\text{O}^-$ group can therefore be replaced rather easily by other positive ions. The basicity is in fact so low that even if one proton is bound with fair strength (the silica gel is a weak acid), a second proton will not be taken up. Hence cation exchange according to (3) is possible even at comparatively low pH, while anion exchange is not at all possible. So the silica gel will function solely as a weakly acid ion exchanger, for which the exchange reaction can be written schematically as



In this formula G stands for the unreactive gel framework with its attached functional groups.

The position of this equilibrium depends not only on the basicity of the gel framework but also on its affinity for the metal ion in question. It is reasonable to suppose that those metal ions which have a strong tendency to form complexes with oxygen containing anions can also compete successfully with H^+ in quite acid solutions. This expectation has received full experimental confirmation for such metal ions, *i.e.*, those combining a high charge with a small ionic radius.

EXPERIMENTAL

Chemicals. All chemicals were, if not otherwise stated, of analytical grade and used without further purification.

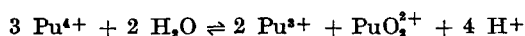
Two different makes of silica gel were used, *viz.* Kebo and Merck 'silica gel for chromatographic use'. The Kebo gel was used in two grain sizes, *viz.* 50-100 mesh and 100-200 mesh. The Merck product had a grain size finer than 300 mesh. Considerable quantities of hydrogen ions were sorbed by all the gels when treated with neutral or acid solutions.

Silica gel, saturated with hydrogen ions, was prepared by repeated washing of these gels with 5 M HNO₃ and/or 5 M HCl at 80–90°C. The gel was then freed from mechanically bound acid by washing with distilled water and dried for 20 h at 100°C. The product sorbed neither hydrogen ions nor water.

Uranyl perchlorate solution was prepared and analysed as described in Ref.⁴

Uranium (IV) perchlorate solution was prepared by electrolytic reduction of uranyl perchlorate solution and analysed according to Ref.⁵

Plutonium (A.B. Atomenergi, Stockholm), was obtained as the isotope ²³⁹Pu (*T*_{1/2} = 24 360 years), isolated from neutron irradiated uranium. It was supplied as a nitrate solution of Pu(IV), with *C*_{HNO₃} = 0.1 M and containing about 1 mg Pu/ml (*C*_{Pu} ≈ 4 mM). In this solution, however, there exist also appreciable amounts of Pu(III) and Pu(VI). These ions have been formed by the disproportionation of Pu(IV) which can be written as follows, if the nitrate complexes existing in the solution are temporarily neglected



If the acidity is increased, the equilibrium is evidently forced strongly to the left, H⁺ being present in the fourth power in the equilibrium expression. If nitric acid is used to increase the acidity, a stabilization of Pu(IV) of equal importance will however result from the addition of nitrate ions, as these form complexes preferably with Pu(IV). Thus the equilibrium constant for the plutonium(IV) disproportionation in 1 M perchloric acid⁶ is 0.0089 as compared with 4×10^{-7} in 1 M nitric acid⁷.

The value of the equilibrium constant also increases rapidly with raising temperature⁸. This is also the case with the tendency of nitric acid to oxidize Pu(IV) to Pu(VI)^{9,7 p. 270}. It is therefore impossible to convert the plutonium completely into Pu(IV) by heating with only moderately concentrated acid. On the other hand, evaporation with strong nitric acid works as a rule (cf. Ref.⁹). In those cases where this treatment failed, reduction with hydrogen peroxide has been performed as follows (cf. Ref.¹²).

To 5 ml 4 M HNO₃, 0.3 ml of the initial plutonium solution and some drops of 10 % H₂O₂ were added. Then this solution was evaporated nearly to dryness and a new addition of 4 M HNO₃ and 10 % H₂O₂ was made. After 20 h the evaporation was repeated. Then conc. HNO₃ was added and evaporated nearly to dryness. This operation was repeated twice, the solution having a final volume of 0.1 ml of conc. HNO₃. When the evaporation vessel had cooled down to room temperature the content was transferred to a receptacle with 10 ml 1 M HNO₃. In this way a stock solution with *C*_{Pu(IV)} = 1.2×10^{-4} and *C*_{HNO₃} ≈ 1 M was obtained, in which Pu(IV) is stable at room temperature.

The amount of plutonium(IV) was determined by investigation of the distribution of the plutonium between 1 M HNO₃ and 0.3 M thenoyltrifluoroacetone in benzene (only plutonium(IV) is extracted into the benzene phase at this acidity)^{10,11}. The stock solution contained less than 1 % of the plutonium as Pu(III) + Pu(VI).

All the work with plutonium was carried out either in a glove box or in well-ventilated fumehoods.

Radioactive *zirconium(IV)* solution was prepared by dissolving a known amount of neutron irradiated ZrO(NO₃)₂ · 2H₂O in perchloric acid. The zirconium(IV) concentration of the stock solution was 91.7 mM and its acidity 4 M. By the irradiation (15 g was irradiated for 11 days at a flux of 10^{12} neutrons · cm⁻² · sec⁻¹) the isotopes ⁹⁰Zr (*T*_{1/2} = 9.5×10^6 years) and ⁹⁵Zr (*T*_{1/2} = 65 days) are preferentially produced. Besides these zirconium isotopes, the preparation also contains two other active nuclides, viz. ⁹⁶Nb (*T*_{1/2} = 35 days) and to some extent also ¹⁸¹Hf (*T*_{1/2} = 46 days). ⁹⁶Nb is an inevitable constituent, as it is the result of the disintegration of ⁹⁵Zr. Hafnium occurs as a slight impurity in the zirconyl nitrate, but as it has a large thermal neutron cross section relative to zirconium, the formation of the active ¹⁸¹Hf is fairly considerable.

Radioactive *gadolinium(III)* solution was prepared by dissolving neutron irradiated Gd₂O₃ in perchloric acid. The excess of acid was evaporated and the residue dissolved in water. A solution with *C*_{Gd} = 9.19 mM and pH ≈ 3.5 was obtained. The irradiated oxide had been allowed to cool for 3 months and the activity was thus due mainly to ¹⁵³Gd (*T*_{1/2} = 236 days).

0.1 M radioactive *sodium chloride* solution was prepared by neutralization of a known amount of neutron irradiated NaHCO₃. The CO₂ formed was carefully removed. By

neutron irradiation of NaHCO_3 , a product was obtained in which the activity comes mainly from ^{24}Na ($T_{1/2} = 15$ h).

Procedure. The metal ion sorption on the silica gel was established by shaking metal salt solutions of varying pH with a suitable amount of gel. The acidity was adjusted by additions of perchloric acid (for metal ions sorbed at low pH), acetate buffer (for Gd^{3+}), ammonia (for Ba^{2+} and Ca^{2+}) and sodium hydroxide (for Na^+). In principle, the solutions were then shaken until equilibrium was reached. As seen in Tables 3–5 below, this was achieved in quite a short time for ions of charge up to three, while four-valent ions needed several days. In the case of Zr, equilibrium was certainly not reached for $C_H \leq 400$ mM when the experiments were interrupted after three days, and possibly not even completely for values of $C_H \geq 800$ mM which are the ones used for the calculation of D_{Zr} in Fig. 6. The experiments were all performed at $20 \pm 0.1^\circ\text{C}$ except one especially mentioned below. The ratio between the volume of solution, v , and the amount of silica gel, m , was as a rule 10^{-2} l/g. The sorbed quantity of metal was obtained by determination of the metal ion concentration in the solution before and after the experiment. For this purpose different analytical methods were used.

The uranyl concentration was determined spectrophotometrically by Ahrlund's method¹³. Since the solutions contained perchlorate ions, $\text{Na}_4\text{Fe}(\text{CN})_6$ was used instead of $\text{K}_4\text{Fe}(\text{CN})_6$ for developing the "uranylhexacyanoferrat colloid". As a suitable wave length 4900 \AA was selected. The acidity and the concentration of cyanoferrate were 0.05 M and 0.2 M respectively. The colloid prepared in this manner has at $\lambda = 4900 \text{ \AA}$ a molar extinction coefficient which is only about half as large as that found when the potassium salt is used. Beer's law is however much better fulfilled when the sodium salt is used, especially at the lowest uranyl concentrations measured. In fact concentrations as low as 0.01 mM can be determined in this way with a fair accuracy ($\approx 2\%$).

Uranium (IV) was determined by cerimetric titration using ferroin (tris-*o*-phenanthroline iron(II) sulfate) as an indicator.

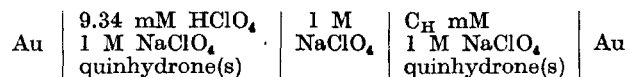
Plutonium was determined radiometrically. Its α -activity was measured with a gas-flow (90% A, 10% CH_4) proportional counter (Tracerlab SC-16 P). The samples were measured inside its ionization chamber in a well defined geometry (2 π). Absolute determinations of the concentration of the plutonium solutions were thus feasible. Owing to the short range of the α -particles, dry and very thin samples were prepared, so that the self-absorption of α -particles could be neglected. The α -samples were prepared by evaporation of 0.10 ml of solution to dryness on stainless steel or platinum dishes. The micro-pipette used for sampling was rinsed once with 1 M HNO_3 and the washing acid was evaporated on the same dish as the main portion of the sample.

Sodium, zirconium and gadolinium were also determined radiometrically. The γ -activities of the samples were measured with a scintillation counter (Tracerlab P 20) provided with a thallium activated sodium iodide crystal.

For each radiometrical measurement more than 10 000 counts were registered. Thus the error of counting was always $< 1\%$.

Calcium and barium were determined volumetrically with EDTA according to Schwarzenbach¹⁴.

The hydrogen ion concentrations of the UO_2^{2+} -solutions were determined by measuring the emf of cells of the type



In the rest of the experiments the hydrogen ion concentrations were measured by a glass electrode in connexion with a vacuum-tube potentiometer (Radiometer PHM 3h).

RESULTS

Uranyl sorption isotherms. The description of the sorption properties of the silica gel given here is based upon sorption isotherms obtained for UO_2^{2+} . These were determined at varying pH with three different gels. The results are given

Table 1. The sorption of UO_2^{2+} on silica gel saturated with hydrogen ions. $v/m = 10^{-2}$ l/g. Shaking time 24 h.

1 a. Kebo 50–100 mesh.

C_M mM	C_H mM	C_{MS} mM	$C_{MG} \times 10^3$ mmole/g	$[\text{H}^+]_S$ mM	$\frac{1}{2}([\text{H}^+]_S - C_H) \times 10^3$ mmole/g
0.20	1	0.073	1.27	1.11	0.55
0.50	1	0.264	2.36	1.30	1.5
0.70	1	0.419	2.81	1.45	2.3
1.00	1	0.655	3.45	1.50	2.5
1.50	1	1.09	4.10	1.65	3.3
2.00	1	1.51	4.86	1.77	3.9
3.00	1	3.12	—	2.15	5.8
4.00	1	3.36	6.40	2.15	5.8
0.20	2	0.111	0.89	2.10	0.5
0.50	2	0.340	1.60	2.51	2.6
1.00	2	0.764	2.36	2.54	2.7
1.50	2	1.20	3.0	2.46	2.3
2.00	2	1.64	3.6	2.71	3.6
3.00	2	2.59	4.1	2.67	3.4
4.00	2	3.52	4.8	3.15	5.8
6.00	2	5.38	6.2	2.99	5.0
0.20	5	0.162	0.38	5.01	
0.50	5	0.420	0.80	5.10	
1.00	5	0.869	1.31	5.21	
1.50	5	1.32	1.8	5.20	
2.00	5	1.80	2.0	5.42	
3.00	5	2.72	2.8	5.40	
4.00	5	3.68	3.2	5.44	
6.00	5	5.51	4.9	5.20	
0.20	10	0.186	0.14	10.05	
0.50	10	0.466	0.34	10.09	
1.00	10	0.93	0.7	10.28	
2.00	10	1.89	1.1	10.20	
3.00	10	2.84	1.6	10.50	
4.00	10	3.80	2.0	10.24	
6.00	10	5.80	2.0	10.45	

in Table 1 and Figs. 1 and 2. C_{MG} (mmoles UO_2^{2+} sorbed per gram silica gel) is plotted against C_{MS} (the concentration of UO_2^{2+} in the water solution expressed in mM) for various C_H (the initial concentration of hydrogen ions).

In the experiments reported in Fig. 1, where silica gels washed only with water have been used the most different behaviour is found for the different gels though the initial concentrations of hydrogen ions were the same. At a given C_H Kebo 50—100 mesh sorbs only about half as much as Kebo 100—200 mesh. The Merck gel, not presented in the figure, sorbs 100 % in the whole range of concentration investigated. It is also evident however, that C_{MG} in-

I b. Kebo 100–200 mesh.

C_M mM	C_H mM	C_{MS} mM	$C_{MG} \times 10^3$ mmole/g	$[H^+]_s$ mM	$\frac{1}{2}([H^+]_s - C_H) \times 10^3$ mmole/g
0.20	1	0.130	0.70	1.12	0.6
0.50	1	0.265	2.35	1.25	1.3
0.70	1	0.419	2.81	1.31	1.6
1.00	1	0.664	3.36	1.46	2.3
1.50	1	1.09	4.1	1.58	2.9
2.00	1	1.54	4.6	1.70	3.5
3.00	1	2.43	5.7	1.85	4.3
4.00	1	3.35	6.5	2.05	5.3
0.20	2	0.113	0.87	2.02	0.1
0.50	2	0.336	1.64	2.09	0.5
1.00	2	0.763	2.37	2.24	1.2
1.50	2	1.22	2.8	2.43	2.2
2.00	2	1.66	3.4	2.48	2.4
3.00	2	2.56	4.4	2.71	3.6
4.00	2	3.49	5.1	2.71	3.6
6.00	2	5.35	6.5	2.92	4.6
0.20	5	0.163	0.37	4.94	
0.50	5	0.422	0.78	—	
1.00	5	0.867	1.33	5.17	
1.50	5	1.33	1.7	4.03	
2.00	5	1.81	1.9	5.31	
4.00	5	3.66	3.4	5.31	
6.00	5	5.56	4.4	5.05	
0.20	10	0.187	0.13	9.89	
0.50	10	0.465	0.35	10.05	
1.00	10	0.930	0.70	9.85	
1.50	10	1.40	1.0	10.05	
2.00	10	1.89	1.1	10.17	
3.00	10	2.83	1.7	10.01	
4.00	10	3.78	2.2	10.29	
6.00	10	5.71	2.9	10.34	

creases when the hydrogen ion concentration decreases at constant C_{MS} , as could be expected (*cf.* p. 1060).

When the experiments were repeated, using silica gel saturated with hydrogen ions, the results given in Fig. 2 were obtained. At a given pH, the different gels obviously given the same sorption isotherms, within experimental error.

In the series performed with water-washed gels, $[H^+]_s$, the hydrogen ion concentration after the sorption, has dropped considerably below the original hydrogen ion concentration C_H . If the initial concentration of UO_2^{2+} is 0.20 mM and $C_H = 1$ mM, $[H^+]_s$ is 0.61 mM for the Kebo 50–100 mesh, 0.30 mM for

1 c. Merck.

C_M mM	C_H mM	C_{MS} mM	$C_{MG} \times 10^3$ mmole/g	$[H^+]_s$ mM	$\frac{1}{2}([H^+]_s - C_H) \times 10^3$ mmole/g
0.20	1	0.138	0.62	1.04	0.2
0.50	1	0.275	2.25	1.09	0.5
0.70	1	0.428	2.72	1.19	1.0
1.00	1	0.692	3.08	1.27	1.4
1.50	1	1.10	4.0	1.40	2.0
2.00	1	1.54	4.6	1.51	2.6
3.00	1	2.43	5.7	1.69	3.5
4.00	1	3.41	5.9	1.88	4.4
0.20	2	0.127	0.73	1.88	
0.50	2	0.358	1.42	2.04	0.2
1.00	2	0.779	2.21	2.18	0.9
1.50	2	1.23	2.79	2.29	1.5
2.00	2	1.67	3.30	2.36	1.8
3.00	2	2.55	4.5	2.48	2.4
4.00	2	3.49	5.1	2.60	3.0
6.00	2	5.39	6.1	2.81	4.1
0.20	5	0.170	0.30	4.71	
0.50	5	0.435	0.65	4.83	
1.00	5	0.890	1.10	4.92	
1.50	5	1.36	1.40	5.02	
2.00	5	1.83	1.7	4.96	
3.00	5	2.77	2.3	4.83	
4.00	5	3.70	3.0	5.18	
6.00	5	5.54	4.6	5.00	
0.20	10	0.190	0.10	9.89	
0.50	10	0.474	0.26	10.09	
1.00	10	0.950	0.50	9.96	
1.50	10	1.43	0.7	9.96	
2.00	10	1.91	0.9	10.04	
3.00	10	2.84	1.6	10.16	
4.00	10	3.80	2.0	10.16	
6.00	10	5.72	2.8	10.26	

the Kebo 100—200 mesh and 0.002 mM for the Merck. The decrease in hydrogen ion concentration in the outer solution causes in its turn an increased sorption of UO_2^{2+} .

In the second series on the other hand, $[H^+]_s$ is even somewhat greater than C_H , Table 1. This behaviour is expected, as hydrogen ions must be released from a gel already saturated with these ions, when other cations are sorbed. $[H^+]_s - C_H$ ought to be equivalent to C_{MG} . Bearing in mind the great error inherent in the calculation of $[H^+]_s - C_H$, due to the fact that $[H^+]_s \approx C_H$, it might be considered that this equivalence has been proved, Table 1. A more careful investigation of this point is described later.

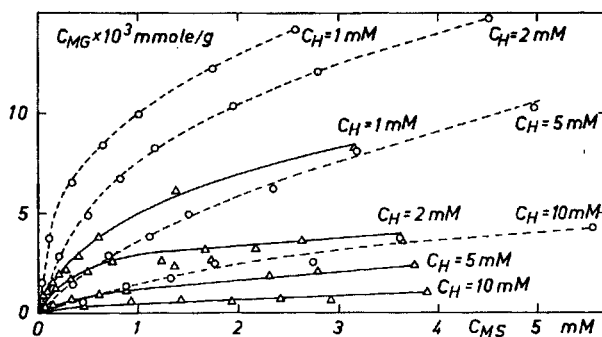


Fig. 1. The sorption of UO_2^{2+} on silica gel washed only with water, $v/m = 10^{-2}$ l/g. Kebo 50–100 mesh Δ , Kebo 100–200 mesh \circ .

From the experiments above, it seems reasonable to assume, that the difference between the water-washed gels is due to different counter ions having been sorbed in varying amounts during the preparation of the gel. Hence the more or less pronounced uptake of hydrogen ions from the solution and the lack of reproducibility between different preparations. In order to achieve reproducible conditions only gels saturated with hydrogen ions were used in the subsequent experimental work. These do not alter the pH of the solutions by any irrelevant process.

Alkalimetric titration of H^+ -saturated gel. The weakly acid properties of the silica gel are also apparent from an alkalimetric titration of the H^+ -saturated gel. The titration was performed by shaking 5 g gel at 20°C with 50 ml sodium hydroxide solution of varying concentration, containing neutral salt to a constant initial concentration of $\text{Na}^+ = 100$ mM. The solution and the gel were separated and the pH was determined with a glass electrode or if a substantial part of the base was left by titration. In this case the pH was computed from the relation $\text{pH} = 14 - \text{p}[\text{OH}^-]$. Experiments were performed with Kebo

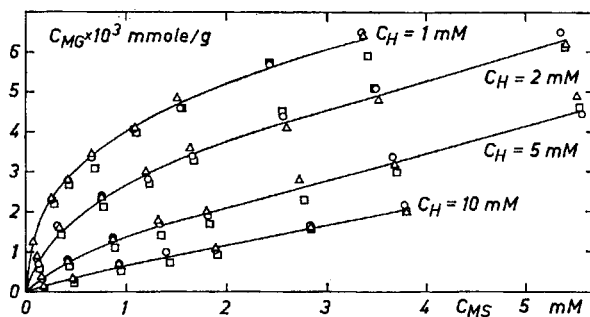


Fig. 2. The sorption of UO_2^{2+} on silica gel washed with acid, $v/m = 10^{-2}$ l/g. Kebo 50–100 mesh Δ , Kebo 100–200 mesh \circ , Merck \square .

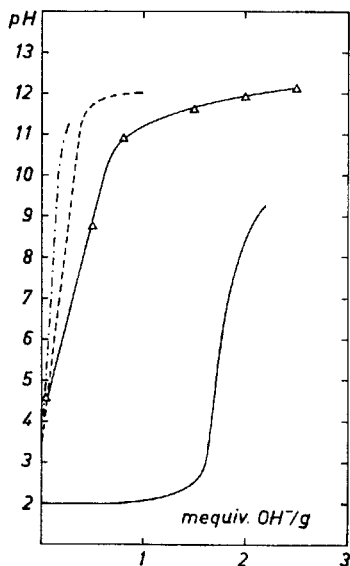


Fig. 3. pH of the outer solution as a function of the total amount of sodium hydroxide added to the solution per g dried ion exchanger. Silica gel Δ and — , sulfonated resin --- , phenolic resin -.-.- , glauconite -.-.- .

50—100 mesh and Kebo 100—200 mesh, both of which gave the same results. Mean values of these are plotted in Fig. 3. Here the titration curves are also drawn for two organic ion exchangers (phenol resin and sulfonated resin) as well as for the ion exchanging mineral glauconite (in greensand)¹⁵. The titration curve of the silica gel is similar to those of the weakly acid ion exchangers.

Verification of the equivalence between the amount of metal ions sorbed and the amount of hydrogen ions set free. In order to prove more strictly that the silica gel acts as an ion exchanger, a closer investigation than the one previously mentioned has been performed of the relation between the metal ions sorbed and the hydrogen ions set free.

By choosing an ion, e.g. Na^+ , that is not hydrolysed, it is possible to work with alkaline solutions, thereby obtaining a high sorption. Consequently amounts of H^+ large enough to be accurately determined are set free. This could not be realized for the sorption of UO_2^{2+} .

As in the titration just described the gel was shaken with solution of varying $[\text{OH}^-]$, containing a constant initial concentration of $\text{Na}^+ = 100 \text{ mM}$. In this case the neutral salt was however NaCl , labelled with ^{24}Na . By the determination of the sorbed Na^+ it is necessary to correct for the error caused by the decay of ^{24}Na . This was done by measuring several times during a series the activity of an identical solution with no silica gel added. The amount of H^+ set free was determined by acidimetric titration of the alkali left after the shaking. The results from two series are given in Table 2. In one of the series where as much as 5 g gel was used, it was necessary to correct for the amount of H^+ adhering to the gel on account of incomplete preparatory washing of the gel sample used in these experiments. The correction, which amounted to 0.011 mequiv./g of silica gel, was determined in a special experiment, where silica gel was shaken only with water.

Table 2. The equivalence between the amount of Na⁺ sorbed and the amount of H⁺ set free. $v = 50$ ml, $m = 0.5$ g and 5 g. Experiments performed with 5 g silica gel are indicated by *. In these cases the amount of H⁺ set free is corrected by the amount of acid liberated when the gel is washed only with water (0.011 mequiv./g).

OH ⁻ added mequiv./g	OH ⁻ at equilibrium mequiv./g	H ⁺ set free mequiv./g	Na ⁺ sorbed mequiv./g
0.025	0.000	0.014 *	0.019
0.050	0.000	0.039 *	0.043
0.075	0.000	0.064 *	0.064
0.100	0.000	0.089 *	0.090
0.125	0.000	0.114 *	0.115
0.150	0.000	0.139 *	0.140
0.200	0.000	0.189 *	0.188
0.250	0.020	0.230	0.224
0.500	0.050	0.450	0.435
0.750	0.130	0.620	0.597
1.00	0.25	0.75	0.72
1.25	0.41	0.84	0.81
1.50	0.60	0.90	0.88
2.00	1.02	0.98	0.94
3.00	1.65	1.35	1.28
3.50	2.16	1.34	1.27
4.00	2.66	1.33	1.35
5.00	3.77	1.23	1.24

The complete agreement between the amount of sorbed Na⁺ and the amount of H⁺ set free, fully confirms that the sorption is an ion exchange, as had already appeared probable from the UO₂²⁺-measurements. This equivalence has also been proved by other workers¹⁶.

The possibility of applying the law of mass action to the exchange reaction (4), was tried on the UO₂²⁺-H⁺ measurements previously mentioned. In this case the reaction could be written as follows



Thus from the law of mass action

$$K = \frac{[\text{H}^+]^2 [\text{UO}_2\text{G}_2]}{[\text{HG}]^2 [\text{UO}_2^{2+}]} \cdot \frac{\gamma_{\text{H}^+}^2 \cdot \gamma_{\text{UO}_2\text{G}_2}}{\gamma_{\text{HG}}^2 \cdot \gamma_{\text{UO}_2^{2+}}} \quad (6)$$

The distribution coefficient D for uranium is defined as the ratio between the concentration of uranium in gel and solution, *viz.* $D = C_{\text{MG}}/C_{\text{MS}}$ C_{MG} is expressed in mmole/g of silica gel and C_{MS} in mmole/litre. Thus the dimension of D is $\text{l} \cdot \text{g}^{-1}$. As UO₂²⁺, under the present conditions, neither forms complexes nor is hydrolysed, the distribution coefficient becomes $= [\text{UO}_2\text{G}_2]/[\text{UO}_2^{2+}]$.

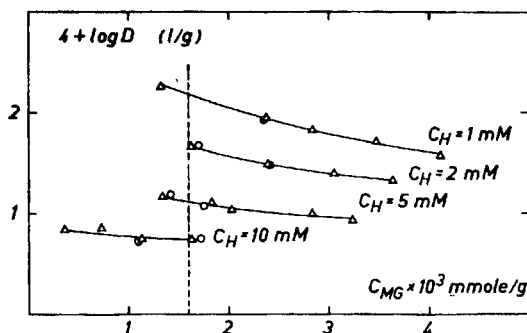


Fig. 4. $\log D$ as a function of C_{MG} for the sorption of UO_2^{2+} on H^+ — saturated silica gel, $v/m = 10^{-2}$ l/g. Kebo 50–100 mesh Δ , Kebo 100–200 mesh \circ .

In Fig. 4, $\log D$ is plotted as a function of C_{MG} with C_H as a parameter. The curves are intersected at $C_{MG} = 1.6 \times 10^{-3}$ mmole/g. Thus $\log D$ is obtained at a constant and low load. Under these conditions the activity coefficients $\gamma_{UO_2^{2+}}$ and γ_{HG} as well as $[HG]$ can be considered as fixed.

By taking the logarithms of eqn (6) we obtain

$$\log D = -2 \cdot \log[H^+] \cdot \frac{\gamma_{H^+}}{\sqrt{\gamma_{UO_2^{2+}}}} + \log K \cdot [HG]^2 \frac{\gamma_{HG}^2}{\gamma_{UO_2^{2+}}} \quad (7)$$

The last term is a constant and the activity coefficients γ_{H^+} and $\gamma_{UO_2^{2+}}$ could be computed from the equations of Debye-Hückel. $[H^+]_s$ is obtained by interpolation of the measured $[H^+]_s$ for the points situated on each side of the intersection. If the assumptions made are true, $\log D$ plotted as a function of $\log [H^+] \frac{\gamma_{H^+}}{\sqrt{\gamma_{UO_2^{2+}}}}$ should give a straight line of slope -2 .

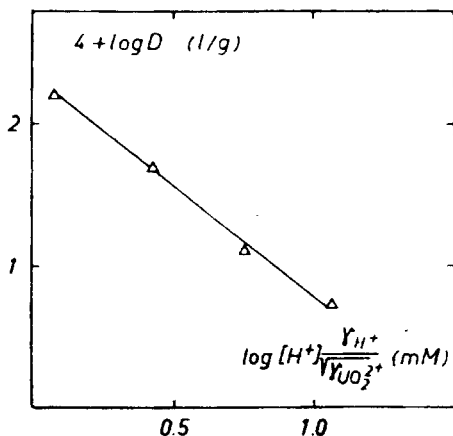


Fig. 5. $\log D$ as a function of $\log [H^+] \frac{\gamma_{H^+}}{\sqrt{\gamma_{UO_2^{2+}}}}$ at constant load $C_{MG} = 1.6 \times 10^{-3}$ mmole/g.

From Fig. 5 it is evident that a straight line is obtained, but its slope is only $-(1.6 \pm 0.1)$. This discrepancy can partly be accounted for by the ion invasion into the gel which takes place according to the Donnan equilibrium. The concentration of free hydrogen ions thus established within the gel will strongly influence γ_{HG} which therefore might vary considerably in spite of the load being constant.

Thus, in summing up, the following points are valid for the metal ion sorption on the silica gel:

I. For gel not saturated with hydrogen ions the sorption depends on the manner in which the gel is prepared.

II. If the gel is saturated with hydrogen ions the same sorption isotherms are obtained even with different gel makes.

III. The H^+ -saturated gel gives a titration curve similar to those found for weakly acid ion exchangers.

IV. At the sorption of metal ions on a H^+ -saturated gel, the amount of hydrogen ions set free is equivalent to the amount of metal ions sorbed.

V. The law of mass action is approximately valid for the exchange reaction.

The affinity of different metal ions to the gel. As previously stated, the sorption of metal ions depends strongly on the pH of the solution. This is true for all of the investigated ions, viz. Na^+ , Ca^{2+} , Ba^{2+} , UO_2^{2+} , Gd^{3+} , $\text{Zr(IV)} + \text{Nb}$, U(IV) and Pu(IV) , as is evident from Fig. 6 where $\log D$ for the different metal ions is plotted as a function of pH. It is also clear that the $\log D$ -curves are displaced to more acid solutions with increasing ratio between the charge and the size of the metal ion. This means that the affinity for the gel follows the

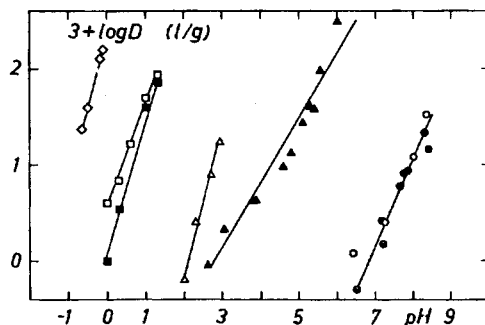


Fig. 6. $\log D$ for some metal ions as a function of pH. Kebo 50–100 mesh, $v/m = 10^{-2}$ l/g.

Element (state)	Zr + Nb	U(IV)	Pu(IV)	U(VI)	Gd	Ca	Ba	Na
Sign	◇	□	■	△	▲	○	◐	●
C_M mM	1.1	2.0	10^{-2}	1.0	0.092	25	25	30

same order which has also been found for the sorption on organic cation exchangers. The position of the UO_2^{2+} -curve about six pH units to the left of the curves of the other ions with charge + 2 is noteworthy. But even though the uranyl ion formally has a charge of only + 2, it often behaves as if its charge is considerably higher¹⁷, e.g. on hydrolysis and complex formation.

Obviously the sorption is important only when the pH has passed a definite value. To the left of the log D -curve very little of the metal ion is sorbed, whereas to the right complete sorption occurs. Therefore ions with curves sufficiently apart could, by a suitable choice of pH, be separated from each other.

For practical separations, the sorption capacity, C_{MG} , is of great interest. According to Table 2 the total capacity at saturation is 1.2—1.4 mequiv/g gel. If the total capacity is required the pH must be relatively high at least for ions with a low charge. The sorption capacities for some ions as a function of pH are reported in part II of this work.

The sorption rate is both of theoretical and practical interest. In this respect the different ions can be placed in two groups. Ions like Na^+ , Ca^{2+} , Gd^{3+} and UO_2^{2+} are sorbed very fast (in general more than 95 % of the final amount is sorbed within 5 min), whereas ions formed by Zr(IV) + Nb, U(IV) and Pu(IV) are taken up more slowly, see Tables 3, 4 and 5 as well as Fig. 7. The latter group contains those ions which are strongly hydrolysed even in rather acid solution. Moreover large and polynuclear species are formed on the hydrolysis of these ions¹⁸⁻²⁰.

In order to investigate whether the low reaction rate in the second group is caused by a slow hydrolysis or by a slow sorption, the following experiment was performed.

From the stock solution of Pu(IV), solutions with $C_{\text{Pu}} \approx 2 \times 10^{-6}\text{M}$ and C_{HNO_3} varying between 0.02 and 1 M were prepared. Within the range of $[\text{H}^+]$ where the hydrolysis is considerable, viz. at $[\text{H}^+] \leq 0.5\text{M}$, the sorption rate of both freshly prepared and aged solutions was investigated by analysis of samples taken at different times. When this technique is used the original relations between v and m is admittedly somewhat changed during the experi-

Table 3. The sorption rate of UO_2^{2+} , Gd^{3+} , Ca^{2+} and Na^+ . Kebo 50—100 mesh, $v/m = 10^{-2}$ l/g. The initial concentrations and acidities were: $C_{\text{U}} = 0.20\text{ mM}$ at $C_{\text{H}} = 2\text{ mM}$, $C_{\text{Ca}} = 0.092\text{ mM}$ at $\text{pH} = 5.0$, $C_{\text{Ca}} = 25.3\text{ mM}$ at $C_{\text{NH}_4} = 140\text{ mM}$, $C_{\text{Na}} = 100\text{ mM}$ at $C_{\text{OH}} = 50\text{ mM}$.

Time min	% sorbed			
	UO_2^{2+}	Gd^{3+}	Ca^{2+}	Na^+
5	37.5	68.0	94.7	48.0
15	39.5	67.7	95.4	48.0
30	41.0	—	95.0	48.0
60	39.5	67.8	95.4	48.0
90	40.0	—	95.4	—
120	40.0	67.7	95.4	—
1 200	40.5	68.0	95.5	46.6

Table 4. The sorption rate of Pu(IV) at different concentrations of nitric acid. Kebo 50–100 mesh, $v/m = 10^{-2}$ l/g. $C_{Pu} = 1.7 \times 10^{-3}$ mM.

C_H mM	Aged 8 days				Freshly prepared				
	20	50	100	500	20	50	100	500	946
Time, h	% sorbed								
1/2	32	43	55	24	74	66	66	23	11
3	44	47	57	26	77	68	67	25	9
7.5	53	56	62	28	80	71	71	28	10
24	70	77	78	27	85	80	80	28	—
48	84	87	79	25	88	86	84	26	—
96	88	88	80	31	92	90	84	30	11
150	89	89	82	27	94	89	84	27	—

ment. In the actual case the change was however slight ($\approx 5\%$) and could not possibly influence the results very much. The results are given in Table 4.

It is evident, from a comparison between fresh and aged solutions, that both require about the same time to be equilibrated with the gel. A pronounced difference appears, however, in the beginning of the sorption. From the aged solutions with $C_{HNO_3} = 0.02, 0.05$ and 0.1 M, about half the final amount is sorbed in 30 min, whereas the freshly prepared solutions have sorbed as much as 80% of this amount in this time. A probable explanation of this behaviour is that Pu^{4+} and other low molecular species are preferentially sorbed by the gel. In freshly prepared solutions the polynuclear hydrolysis is not yet finished and therefore the concentration of low molecular easily sorbable species is much higher than in aged ones. Thus the slow sorption of the aged solutions is presumably due to the slow breaking up of the polymerized species dominating there. No difference could be detected at $C_{HNO_3} = 0.5$ M. In this case, as well as for $C_{HNO_3} > 0.5$ M, the equilibrium is also quickly attained. At this acidity Pu(IV) is in fact mainly present ($> 95\%$) as Pu^{4+} and monomer nitrate complexes^{21,22} and the sorption is therefore of the same nature as for Na^+ , Ca^{2+} , Gd^{3+} and UO_2^{2+} .

Similar behaviour was found for Zr(IV) + Nb, where only aged solutions were investigated, Table 5. Although the γ -activity used for the analysis

Table 5. The sorption rate of Zr(IV) + Nb at different concentrations of nitric acid. Aged solutions. Kebo 50–100 mesh, $v/m = 10^{-2}$ l/g. $C_{Zr} = 1.1$ mM.

C_H mM	50	100	200	400	800	1 500	3 000	4 500
Time, h	% sorbed							
0.5	23.2	23.7	31.0	31.2	44.4	49.4	52.3	48.4
3	33.2	29.6	39.2	44.3	60.5	63.9	59.1	58.6
18	56.5	59.0	60.5	65.2	74.7	81.1	72.5	63.5
43	68.0	69.3	70.2	79.4	86.2	87.3	75.1	66.4
74	91.5	86.1	81.0	81.1	94.1	92.8	79.9	70.1

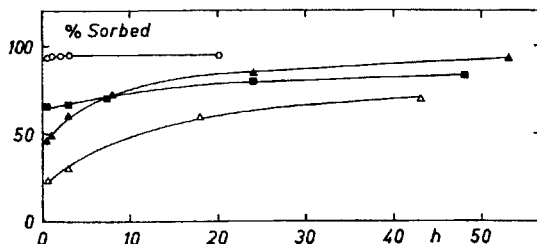


Fig. 7. The sorption rate of Zr + Nb, U(IV), Pu(IV) and Ca. Kebo 50-100 mesh, $v/m = 10^{-2}$ l/g.

Element (state)	Zr + Nb	U(IV)	Pu(IV)	Ca
Sign	\triangle	\blacktriangle	\blacksquare	\circ
C_M mM	1.1	4.2	1.7×10^{-3}	25.3
pH	1	1	1	10.9

of the solutions partly comes from ^{181}Hf , the results obtained should nevertheless represent the sorption properties of Zr(IV) + Nb, as ^{181}Hf occurs only in tracer concentrations and has such a great chemical resemblance to Zr. This is moreover conclusively proved by the fact that the γ -spectrum of the solution indicates the same ratio Hf to Zr + Nb before and after the sorption. As seen from Table 5, the sorption after 74 h for $0.8 \text{ M} \leq C_{\text{HNO}_3} \leq 4.5 \text{ M}$ is increasing with decreasing hydrogen ion concentration as is normally the case. The decrease found for $C_{\text{HNO}_3} < 0.8 \text{ M}$ must be due to the fact that equilibrium had not yet been established for these low acidities, in spite of the long shaking time. As is also seen from Table 5, the time necessary for the sorption to reach half the final value decreases with increasing C_{HNO_3} . This is also true for aged

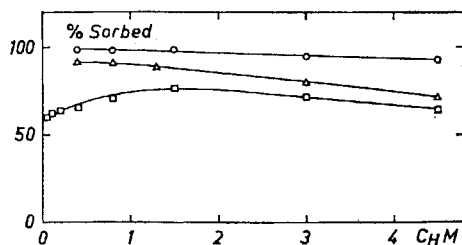


Fig. 8. The sorption rate of Zr + Nb on Kebo 50-100 mesh in hydrochloric (O), perchloric (Δ) and nitric (\square) acid. Shaking time 21 h, $v/m = 10^{-2}$ l/g, $C_{\text{Zr}} = 1.1$ mM.

Table 6. The sorption rate of Pu(IV) at 49°C and different concentrations of nitric acid. Freshly prepared solutions. Kebo 50–100 mesh, $v/m = 10^{-3}$ l/g. $C_{\text{Pu}} = 2.2 \times 10^{-3}$ mM.

C_{H} mM	20	50	100	500
Time, h	% sorbed			
1/4	74	66	34	29
1/2	75	50	34	34
1	77	38	38	36
4	81	70	67	41
7	84	84	76	43
24	95	91	88	41
72	96	92	88	41

Pu(IV)-solutions (Table 4). A comparison was also performed of the sorption of Zr(IV) + Nb from nitric, hydrochloric and perchloric acid, Fig. 8. The shaking time was fixed at 21 h. In the figure one notices particularly, that the curves separate widely at small C_{H} . In perchloric and hydrochloric acid equilibrium is evidently attained faster than in nitric acid, which is rather remarkable.

In order to investigate the influence of the temperature on the sorption rate, a series with Pu(IV) at 49°C was also performed, Table 6. No significant differences in the rate, compared with the series obtained at 20°C, could be observed. The equilibrium sorption, however, was somewhat higher.

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