Surface characterization of zirconium and thorium phosphate compounds

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As part of a study involving sorption experiments with actinide ions sorbed onto phosphate compounds and to understand the sorption mechanisms, we have first synthesized the following three solids: ZrP_2O_7 (zirconium diphosphate), $Zr_2O(PO_4)_2$ (zirconium oxophosphate) and $Th_4(PO_4)_4P_2O_7$ (thorium phosphate diphosphate). These compounds have been characterized using X-ray powder diffraction, IR spectroscopy and EPMA. The specific surface areas, measured by the N_2-BET method, are 5.5 ± 0.1, 0.9 ± 0.2 and 1.2 ± 0.2 $m^2\ g^{-1}$, respectively. The average grain size of the powdered samples is around 10 μm. The pH_{IEP} (pH corresponding to the isoelectric point) determined by electrokinetic measurements is 3.6 for ZrP_2O_7, 4.0 for $Zr_2O(PO_4)_2$ and 6.8 for $Th_4(PO_4)_4P_2O_7$. By simulation of the titration curves obtained for the three solids, we have determined, using the FITEQL code (constant capacitance model), the surface acidity constants using a sorption site number close to 7 sites nm^{-2} for the zirconium diphosphate, 7.5 sites nm^{-2} for the zirconium oxophosphate and 4 sites nm^{-2} for the thorium phosphate diphosphate.

Caractérisation des propriétés acido-basiques de surface de composés phosphatés à base de zirconium et de thorium. Dans le cadre d'une étude des mécanismes d'adsorption d'ions actinides sur des surfaces minérales phosphatées, nous avons réalisé la synthèse des trois composés suivants: ZrP_2O_7 (diphosphate de zirconium), $Zr_2O(PO_4)_2$ (oxophosphate de zirconium) et $Th_4(PO_4)_4P_2O_7$ (phosphate diphosphate de thorium). Les solides obtenus ont été caractérisés par diffraction des rayons X, spectroscopie infrarouge et microanalyse par sonde électronique (EPMA). La surface spécifique, déterminée par la méthode BET d'adsorption d'azote, est de 5,5 ± 0,1, 0,9 ± 0,2 et 1,2 ± 0,2 $m^2\ g^{-1}$, respectivement. La taille moyenne des échantillons pulvérulents est voisine de 10 μm. La valeur du pH_{PIE} (pH du point isoélectrique), déterminée par mesures électrocinétiques, est de 3,6 pour ZrP_2O_7, 4,0 pour $Zr_2O(PO_4)_2$ et 6,8 pour $Th_4(PO_4)_4P_2O_7$. La simulation des courbes de titrage de suspensions de chacun des solides a été réalisée à l'aide du code FITEQL (modèle à capacité constante), ce qui a permis de déterminer les constantes d'acidité de surface en utilisant des densités de sites de surface voisines de 7 sites nm^{-2} pour le diphosphate de zirconium, 7,5 sites nm^{-2} pour l'oxophosphate de zirconium et 4 sites nm^{-2} pour le phospate diphosphate de thorium.

Among the potential materials under investigation, phosphate compounds are expected to play an important role in the safety of underground radwaste repositories because they could be used for the engineered barrier. Sorption reactions at the mineral–water interface is one of the types of reactions by which radioactive contaminants such as U, Np, Pu, Am and Cm may be immobilized in the subsurface.[1–3] Therefore, a detailed knowledge of the sorption mechanisms is needed. They do not depend only on the chemical properties of the metal ion potentially sorbed (*e.g.*, hydrolysis), but also on the surface properties of the sorbent. Most of the studies done on phosphate compounds have been carried out on apatite[4–6] or on ion exchangers.[7,8] But the sorption mechanisms for such materials are rather difficult to understand because surface complexation and ion substitution can occur simultaneously. For this reason, it appears very interesting to investigate the sorption process onto phosphate solids, which do not present any possibility of such ion exchange.

The solid compounds chosen for this purpose were zirconium diphosphate (ZrP_2O_7), zirconium oxophosphate [$Zr_2O(PO_4)_2$] and thorium phosphate diphosphate [$Th_4(PO_4)_4P_2O_7$]. They have been chosen because of their low solubility[9] and therefore can be considered as possible candidates for long-term storage.[10,11] The two zirconium phosphate compounds allow us to study separately the effect of each of the two phosphate groups present in the thorium phosphate diphosphate. Sorption of Eu^{III}, U^{VI} and Cm^{III} ions onto these three matrices has been investigated and will be reported in coming papers.

We present in this paper the main structural characteristics of these phosphates such as crystallinity, morphology (size and shape of the grains) and their surface properties such as specific surface area, sorption site density and acid-base properties. Moreover, as the pH-dependent surface charge is needed to predict the ion sorption onto surfaces, we have determined the pH corresponding to the point of zero charge (pH_{pzc}) and the one corresponding to the isoelectric point (pH_{IEP}) of the three compounds under study. The pH_{IEP} is determined from electrokinetic measurements while pH_{pzc} is obtained from potentiometric titrations. The pH_{pzc} and pH_{IEP} are equal for a solid suspension in a given salt solution if there is no specific adsorption of the supporting electrolyte. These values will be useful to determine the surface acidity constants of the three solid compounds using the FITEQL code (version 3.2).[12]

Synthesis and Structural Characterization of the Phosphate Compounds

Since the surface properties of a solid are conditioned by its structure, we have first characterized the three synthesized

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phosphate compounds using X-ray powder diffraction, infrared spectroscopy and electron probe microanalysis (EPMA) to verify the crystallinity and the purity of the obtained products. Moreover, we have performed BET measurements to determine the specific surface area and we have also measured the size and the shape of the grains. As the structural characterization is not the subject of this paper, we will only give a brief outline of the main results.

Compound synthesis

The synthesis of the phosphate compounds is widely described in the literature.[13–15] Zirconium phosphate matrices were synthesized in aqueous medium from zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, Fluka–Aldrich) and ammonium phosphate ($NH_4H_2PO_4$, Fluka–Aldrich) solutions. The mole ratio ($r = PO_4/Zr$) was fixed to 1 : 1 and 2 : 1 for the zirconium oxophosphate [$Zr_2O(PO_4)_2$] and the zirconium diphosphate (ZrP_2O_7) compounds, respectively. The thorium phosphate diphosphate matrix [$Th_4(PO_4)_4P_2O_7$] was synthesized using the same route as for the zirconium phosphates but we have used the thorium nitrate salt [$Th(NO_3)_4 \cdot 4H_2O$, Rhône-Poulenc] to prepare the cation solution. The mole ratio ($r = PO_4/Th$) was equal to 3 : 2 for this synthesis. These solutions were mixed and the precipitate formed was dried at 120 °C and then heated at 400 °C to expel volatile substances. After heating under air atmosphere at 1250, 1280 and 950 °C for $Th_4(PO_4)_4P_2O_7$, $Zr_2O(PO_4)_2$ and ZrP_2O_7, respectively, well crystallized phases were obtained. The powdered samples were then washed with distilled water and ground to obtain a homogeneous grain size.

Thorium phosphate diphosphate[16] and zirconium oxophosphate (JCPDS file No 36-352) are both orthorhombic while zirconium diphosphate is cubic (JCPDS file No 24-1490) .

Physico-chemical characterization

Crystalline phases were identified by X-ray powder diffraction patterns recorded on a Philips PW 1050/70 apparatus using Cu Kα rays and a Ni filter. The powder diffraction patterns (not presented here) confirmed that all samples were very well crystallized and that no secondary phases were observed.

Infrared spectra were recorded by means of a Hitachi I-2001 spectrophotometer. This technique is particularly useful in order to determine if P—O—P bridges are present or not in the structure.[17] Thus, we have confirmed that there is no zirconium diphosphate minor phase formed during the synthesis of zirconium oxophosphate because of the absence of a vibrational band arising from P—O—P in the IR spectra. For thorium phosphate diphosphate, we have obtained a spectrum that presents vibrations corresponding to both P—O—P bridges and PO_4 groups, as already reported in the literature.[10] The zirconium diphosphate IR spectrum does not present any absorption band corresponding to PO_4 groups, which indicates that there is probably no secondary phase formed during the synthesis.

EPMA experiments were performed on a Cameca SX 50 apparatus using an acceleration voltage of 15 kV and a 10 nA current beam. The diameter of the analytical spot was about 1 μm. The weight percentages obtained for zirconium, thorium, phosphorus and oxygen for the three phosphate compounds are in very good agreement with those expected. Furthermore, no evidence for polyphase systems has been detected.

The morphology of the grains is also very important when a surface interacts with ions. Thus, we have determined the grain size distribution using a Coulter LS 230 apparatus. The results indicate that the average particle size is around 10 μm for all of the compounds under consideration. Moreover, scanning electron microscopy experiments have shown a spherical shape of the grains for all samples.

Table 1 Average grain size, specific surface areas and surface site density for the three phosphates

Compound	Average grain size/ μm	Specific surface area/m^2 g^{-1}	Surface site density/ sites nm^{-2}
$Th_4(PO_4)_4P_2O_7$	10	1.2 ± 0.2	2–3
$Zr_2O(PO_4)_2$	10	0.9 ± 0.2	≈3
ZrP_2O_7	10	5.5 ± 0.1	≈6

We have determined the specific surface area for the three phosphates from N_2 adsorption isotherms using the BET method. The measured specific surface areas are very small except for ZrP_2O_7. These results are not surprising if we consider the high synthesis temperatures used for $Th_4(PO_4)_4P_2O_7$ and $Zr_2O(PO_4)_2$ and the much lower temperature needed for ZrP_2O_7.

The results concerning the specific surface area and the grain size are summarized in Table 1.

Surface Characterization

Study of the electrokinetic phenomena brings to the fore the fact that the surface of a solid (oxide or silicate) immersed in an aqueous solution develops an electrical charge.[18,19] The origin of this charge is attributed to the amphoteric dissociation of surface MOH groups created by hydration of the solid surface after immersion. This mechanism usually explains the pH dependence of the surface charge and the existence of a pH resulting in zero charge. Knowledge of this parameter is of practical interest because the nature and the quantity of the sorbed species, as well, depend on the surface charge state (by means of electrostatic interactions). The pH corresponding to the point of zero charge can be determined from potentiometric measurements while the pH at the isoelectric point can be obtained by performing electrophoretic experiments. Both are identical if the supporting electrolyte does not adsorb specifically onto the surface. Some authors have shown that hydroxyapatite and silicates immersed in aqueous solutions have the same surface behaviour as oxides (dissociation of the amphoteric surface sites).[19,20] Thus, we can expect that the three phosphate compounds under consideration will present similar properties and we have performed electrophoretic measurements in order to verify this assumption. Moreover, these results will allow us to model the pH dependence of the surface charge for the phosphate compounds under study, which is the first step to interpret ion sorption isotherms.

Electrophoretic measurements

The electrophoretic measurements were performed on suspensions containing the phosphate compounds using a Coulter DELSA 440 apparatus. Potassium nitrate salt was chosen in order to fix the ionic strength because it is usually admitted that K^+ and NO_3^- ions do not adsorb specifically.[21] KOH and HNO_3 solutions were used to adjust the pH value of the suspensions. All the solutions were prepared using deionized water.

The suspensions for both ZrP_2O_7 and $Zr_2O(PO_4)_2$ were prepared under the same conditions: about 2 g of the solid are immersed in 50 mL of the background salt solution and the resulting mixture is shaken for two days in a Turbula at 50 rpm. The aqueous suspension is then centrifuged at 3500 rpm for 30 min and part of the supernatant is taken off and adjusted to the desired pH with small volumes of acidic or basic solutions.

For $Th_4(PO_4)_4P_2O_7$, the suspensions were obtained using the same procedure as described above except for the centrifugation step, which was 3500 rpm for 10 min.

The results so obtained show a positive zeta potential at low pH values while it is negative for high pH values. This clearly indicates a change in the particle charge and consequently an amphoteric behaviour of the surface for the three compounds under study. Thus, the surface mechanism usually used for oxides will be used for the three phosphates under consideration.

We present in Fig. 1 the zeta potential variation *vs.* pH for the three phosphates. The obtained pH_{IEP} values are about 3.6 for ZrP_2O_7, 4.0 for $Zr_2O(PO_4)_2$ and 6.8 for $Th_4(PO_4)_4P_2O_7$. Despite the fact that the thorium phosphate diphosphate compound has the same structure as zirconium oxophosphate, the obtained pH_{IEP} values for both solids are quite different. On the other hand, the values obtained for the two zirconium compounds are roughly similar. This difference could indicate that the nature of the matrix cation is more influential than the structure of the solid, as has already been reported in the literature.[22–25]

Potentiometric titrations

We have performed potentiometric titrations of an aqueous suspension of each of the compounds in KNO_3 solutions at 25 °C, under an argon controlled atmosphere, using a combined Ag/AgCl electrode and a Radiometer Analytical SA titration system. During the experiment, the suspension is continuously stirred to prevent settling. About 3 g of dried powder sample are suspended in 150 mL of the supporting electrolyte solution. The suspension obtained is acidified with HNO_3 ($c = 0.1$ M and $V = 3$ mL for ZrP_2O_7 and 0.3 mL for the others) and shaken for at least 15 h. As titrants, 0.1 M and 0.01 M solutions of KOH were used. All the solutions were prepared using deionized water. The titration was carried out on the aged suspension by adding incremental volumes of base, for times in accordance with pH equilibration.

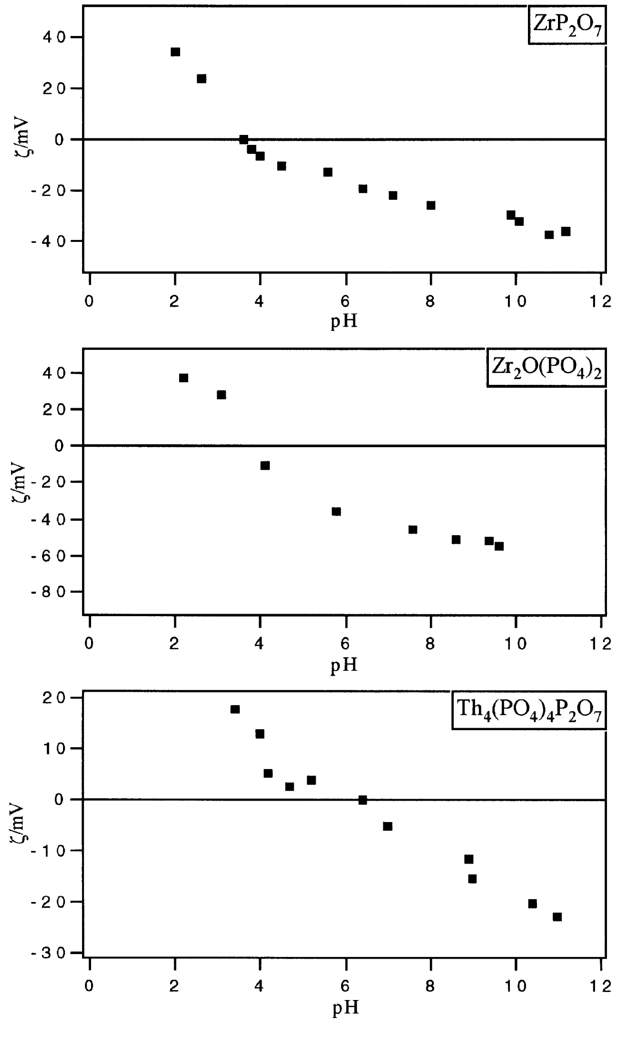

Fig. 1 Zeta potential variation *vs.* pH for ZrP_2O_7, $Zr_2O(PO_4)_2$ and $Th_4(PO_4)_4P_2O_7$ (medium: 0.05 M KNO_3)

First of all, we have determined the time required to reach equilibrium between the dried powdered solid and the aqueous medium (hydration time). For this purpose, we have performed titration experiments of different suspensions containing the same powdered sample mass (about 3 g) immersed in 150 mL of 0.5 M KNO_3 solution after several hydration times (1, 5, 10, 15 h, ...). Equilibration is considered to be reached when the obtained titration curve for a time t is the same as the one obtained at time $t - 5$ h. The hydration times determined for the three phosphates are close to each other and around 10 h. For all potentiometric experiments this time was fixed equal to 15 h.

The surface site density can be directly determined from the potentiometric titration curve of the suspension. If we plot the mole number of OH^- ions added to the suspension *vs.* the mole number of these aqueous ions (related to the pH measurement), the final part of the obtained curve is linear. In this range, reaction no longer occurs and the total quantity of hydroxide ions introduced is entirely found in the solution. The solid surface has totally reacted and the amphoteric sites are no longer protonated. The obtained titration curve for the background salt alone (without solid) presents a linear part as well. After extrapolation of this linear part to a zero OH^- concentration for both suspension and background salt we can determine the uptake of OH^- by the solid phase by subtracting these two values.[26] Thus, knowing the specific surface area and the quantity of powdered solid in the suspension we can calculate the surface site density. As an example, we present in Fig. 2, the result obtained for the thorium phosphate diphosphate compound. The extrapolation of the linear part for both suspension and background salt alone leads to 7.5×10^{-5} and 4.9×10^{-5} moles, respectively. Thus, 2.6×10^{-5} moles of hydroxide ions have been consumed by the solid surface. Considering that, at the initial pH value of the titration experiment, the amphoteric sites were fully protonated, the number of surface sites is 1.3×10^{-5} moles, which leads to a surface site density equal to 2.2 sites per nm^2. The values obtained for the three compounds are reported in Table 1. However, although this procedure allows one to obtain the titration curve with only a single experiment in contrast to the one consisting of performing separately acidic and basic titrations,[27] it is necessary to assume that the

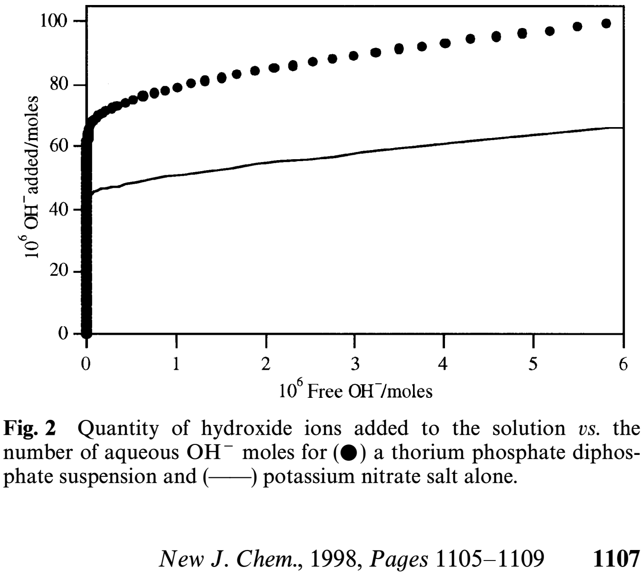

Fig. 2 Quantity of hydroxide ions added to the solution *vs.* the number of aqueous OH^- moles for (●) a thorium phosphate diphosphate suspension and (——) potassium nitrate salt alone.

surface sites are fully protonated after the initial addition of HNO_3 to the solution. In fact, this condition can only be verified if the first acidity constant of the amphoteric sites is rather high compared to the initial pH value of the titration experiment. In the case of the simplest compound under investigation (ZrP_2O_7), the obtained pH_{IEP} value is 3.6. The initial pH value of the titration experiment was around 3, and thus, the fully protonated sites assumption is probably not justified and the surface site density value determined from the potentiometric titration leads to a lower value than the real one.

Therefore, although our results are in good agreement with the ones reported by several authors.[28,29] who proposed surface site densities ranging from 1 to 20 sites per nm^2, the values presented in Table 1 will be considered only as an initial guess for modelling the titration curves, and not as accurate experimental values.

Surface acidity constants

We have determined the surface acidity constants for the three phosphate compounds using the FITEQL 3.2 code.[12] Several surface complexation models are able to simulate the experimentally observed acid-base titration properties[28–30] but the three most important ones are the double layer model (DLM), the constant capacitance model (CCM) and the triple layer model (TLM). The DLM, which is the simplest one, is usually limited to low ionic strength conditions. In contrast to this model, application of the CCM is restricted to constant ionic strength conditions and is also usually limited to high ionic strengths (higher than 0.1 M). The TLM may be expected to model titration data successfully over a wide range of ionic strengths and it allows to take into account surface reactions between the background electrolyte ions and the surface sites. Considering our experimental conditions (ionic strength = 0.5 M) we can use both CCM and TLM, but the latter model is the more complex with seven adjustable parameters and the first one has been preferred for simplicity (only four adjustable parameters). These parameters in the CCM are the protonation constant K_1, the acidity constant K_2, the total number of surface sites N_t and the inner-layer capacitance term C. The two constants correspond to the following equilibria:

$$MOH + H^+ \xrightleftharpoons{K_1} MOH_2{}^+$$

$$MOH \xrightleftharpoons{K_2} MO^- + H^+$$

For fluoroapatite some authors[20] propose $\equiv Ca{-}OH_2{}^+$ and $\equiv P{-}O^-$ as the dominant surface groups. But, in a previous paper,[31] we have shown that the cations sorbed onto the phosphate compounds under study are only bound to the oxygens of the surface phosphate groups. Moreover, we have shown that for the zirconium diphosphate compound there is only one sorption site while there are two different types of sorption sites for both the thorium phosphate diphosphate and zirconium oxophosphate compounds. For ZrP_2O_7, the single type of surface site corresponds to the surface oxygens of the diphosphate groups. For the two others, the surface sites were assigned to the surface oxygens of both phosphate and diphosphate groups for $Th_4(PO_4)_4P_2O_7$ (according to the structure of this compound) and to the oxygens of both oxo and phosphate groups in the case of the zirconium oxophosphate. Thus, we have considered phosphate and oxo groups for modelling the titration curves obtained for $Zr_2O(PO_4)_2$ and phosphate and diphosphate groups for $Th_4(PO_4)_4P_2O_7$.

For the determination of the surface acidity constants, we proceeded as follows. The total number of surface sites has been approximately determined from potentiometric measurements and these values were used as initial guess. The values determined previously from electrophoretic measurements allow us to reduce the number of degrees of freedom by one, according to the fact that the two intrinsic acidity constants are linked by this simple relationship to the point of zero charge:

$$[\log(K_1) - \log(K_2)]/2 = pH_{pzc}$$

As phosphate compounds were not extensively studied, there is no reported value for the inner-layer capacitance for such solids. Nevertheless, for oxides the values used in most of the studies range from 1.0 to 1.5 F m^{-2} and some authors[29] propose to adopt a value of 1.0 F m^{-2} for CCM simulation, unless some other value gives substantially better results. Therefore, we have first tried to simulate our titration curves using the above cited values. But, no good fit has been obtained under such conditions and we have been compelled to use higher values. For all the phosphate compounds considered here, the capacitance value needed to fit quite well the titration curves is higher than 2 F m^{-2}. Although it was possible to fit the thorium phosphate compound using a value around 2.5 F m^{-2}, we chose to use the same capacitance value for the different phosphate compounds under study, $C = 3.08$ F m^{-2}, which gives quite good fits for the three matrices. This value seems to be rather high compared to the one usually used for oxides but it could be explained considering that phosphate compounds are very insulating materials and thus the capacitance value should be rather high in comparison with the ones used for oxide materials.

In a first step, we have considered the simplest compound (ZrP_2O_7), which presents only one single type of surface site. The surface acidity constants so determined for the diphosphate groups were used in a second step as initial guess for modelling the titration curve obtained for $Th_4(PO_4)_4P_2O_7$. We have pointed out from the electrophoretic measurements that the nature of the cation matrix is very influential. Consequently, the acidity constant values are expected to be slightly different for the diphosphate groups belonging to thorium phosphate diphosphate and to zirconium diphosphate. Moreover, the crystalline structure of these two compounds is different (orthorhombic and cubic). The best fit was obtained considering that the diphosphate groups are less acidic in the case of $Th_4(PO_4)_4P_2O_7$ than in the case of ZrP_2O_7.

We have applied the same rules in order to determine the two constants for the zirconium oxophosphate compound. The obtained values corresponding to the PO_4 groups of the thorium phosphate have been used as initial guesses and then these values have been slightly adjusted. The phosphate groups of the zirconium oxophosphate compound have been found to present a more acidic character than the ones of the thorium phosphate.

The intrinsic acidity constants determined for the three phosphate compounds are reported in Table 2. We can note that for the thorium phosphate compound, the surface amphoteric sites are less acidic than for the zirconium compounds. For example, if we consider the phosphate groups for both $Th_4(PO_4)_4P_2O_7$ and $Zr_2O(PO_4)_2$, which present the same crystalline structure, the obtained constants values are about 2 orders of magnitude lower in the case of the zirconium compound.

Table 2 Surface acidity constants determined using the CCM with a capacitance of 3.08 F m^{-2}

Compound	Site density/ sites nm^{-2}	$\log(K_1)$	$\log(K_2)$	Groups
$Th_4(PO_4)_4P_2O_7$	4	6.5	−7.8	PO_4
			−6.3	P_2O_7
$Zr_2O(PO_4)_2$	7.5	4.4	−5.3	PO_4
		3.3	−3.9	oxo
ZrP_2O_7	7	3.2	−4.2	P_2O_7

The obtained site densities for the three phosphates under investigation are quite close to the experimental ones determined from the potentiometric titrations. The obtained concentration ratios for the two types of sites of the thorium phosphate diphosphate and the zirconium oxophosphate compounds are, respectively, $PO_4/P_2O_7 \approx 3.2$ and $PO_4/oxo \approx 1.2$. According to the formula of these two materials, $Th_4(PO_4)_4P_2O_7$ and $Zr_2O(PO_4)_2$, the concentration ratios are in rather good agreement with the ones expected, 4 and 2, respectively. Nevertheless, we can only consider the trend of these ratios because the compounds under study are nanocrystallines and thus all crystallographic orientations are possible.

Conclusions

The aim of the present work was to determine the surface acidity constants for different phosphate compounds using surface complexation modelling. We have chosen the constant capacitance model because of its ability to simulate titration curves for high ionic strength conditions and the use of a reasonable number of adjustable parameters (4).

We have performed electrophoretic measurements using a non-specific adsorbable electrolyte as background salt in order to determine the point of zero charge for each compound. Using the fact that the two surface acidity constants are related to the point of zero charge, we have reduced the degrees of freedom by one in the calculation. Moreover, the surface site density determined from potentiometric titrations have been used as the initial guess in the simulation.

The thorium phosphate compound under consideration presents two types of phosphate groups and thus, the determination of its surface properties appears to be rather complex. In order to study separately the effect of each of these phosphate groups, we have also studied both zirconium diphosphate and zirconium oxophosphate compounds and we have correlated the results obtained for the three matrices.

First, the titration curve for the zirconium diphosphate compound was simulated. The obtained acidity constants were used as initial guesses for the surface acidity constants of the diphosphate groups belonging to the thorium compound. In the same way, we have used the value obtained for the PO_4 groups of the thorium phosphate diphosphate as an initial guess for the PO_4 groups of the zirconium oxophosphate. The final simulations fit the experimental data rather well. However, the inner-layer capacitance used in these calculations (around 3 F m^{-2}) seems rather high compared to the ones usually used for oxide compounds (around 1 F m^{-2}). This result could be due to the very insulating character of the materials under consideration.

This work is the first step of an extensive study of the sorption mechanism of uranium(VI) and europium(III) on phosphate surfaces. Using the surface acidity constants determined in this work and the results of a structural study published elsewhere,[31] it will be possible to simulate accurately with the same model the experimental sorption isotherms for these two ions and then to calculate the corresponding surface complexation constants.

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