Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Misaelides, P. , Gallios, G. , Sarri, S. , Zamboulis, D. , Pavlidou, E. , Kantiranis, N. , Anousis, I. , Zhuravlev, I. and Strelko, V. V.(2006) 'Separation of Uranium from Aqueous Solutions Using Al^{3}- and Fe^{3}-modified Titanium- and Zirconium Phosphates', Separation Science and Technology, 41: 1, 97 — 110
To link to this Article: DOI: 10.1080/01496390500459429
URL: http://dx.doi.org/10.1080/01496390500459429

Separation Science and Technology, 41: 97–110, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500459429

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Abstract: The ability of four amorphous Al^{3+}- and Fe^{3+}-doped titanium and zirconium sorbents to separate U(VI) from acidic aqueous solutions ($pH_{init} = 3$, ionic strength 0.1 M established by $NaNO_3$) was investigated using a batch technique and instrumental neutron activation analysis. All investigated sorbents were found to be chemically stable and remove considerable amounts of uranium from acidic aqueous solutions ($pH_{init} = 3$). The scanning electron microscopic and powder-X-ray diffraction examination of the grains of the two investigated titanium phosphates after contacting the uranium solutions revealed the formation of sodium autunite ($Na_2(UO_2)_2(PO_4)_2 \cdot 6\text{-}8H_2O$) accompanied, in the case of the Fe^{3+}-doped

Received 15 June 2005, Accepted 19 October 2005

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titanium phosphate, by iron uranyl phosphate hydroxide hydrate ($Fe(UO_2)_2(PO_4)_2 (OH) \cdot 7H_2O$). No crystal formation was observed in the cases of uranium sorbed by zirconium phosphates indicating the different sorption mechanism involved.

Keywords: Uranium, separation, titanium, phosphates, zirconium, phosphates, sodium autunite

INTRODUCTION

The presence of uranium in the biosphere is not only due to natural sources but also to various human activities (e.g. mining, nuclear power production, military activities etc.) (1–6). Huge amounts of uranium ores are mined and treated every year in order to obtain its isotope ^{235}U which is the mostly used fissile material for the nuclear power production (7). U(VI) is highly soluble in water and can easily be transferred in the biosphere through aquatic pathways (8). Therefore, the protection of the environment and of the groundwater from the uranium contamination is a subject of continuously increasing interest.

Various natural and synthetic inorganic sorbents were investigated for the removal of uranium from aqueous solutions (e.g. zeolites, clay minerals, oxides, phosphates) (1, 8–15). Uranium shows enhanced toxicity and radiotoxicity for the living organisms possessing long-lived radioactive isotopes and radiation emitting decay products (2).

The beginning of the systematic investigation of the sorption properties and crystal chemistry of phosphates is directly connected with the efforts to separate uranium and plutonium from fission products (16). Numerous crystalline and amorphous titanium and zirconium phosphates have been synthesized and studied as selective sorbents for thorium, uranium, transuranium elements, rare earths, radiocesium, and also heavy metal cations from different solutions (13, 17–29). The crystalline materials showed the disadvantage of the small grain size restricting their application in columns. On the other hand, the literature data indicated that the actual exchange capacities of amorphous titanium and zirconium phosphates did not exceed half of the theoretical capacity calculated for the corresponding crystalline ion exchangers (23, 24). This is most likely connected to the cross-linking and random interlacing of closely packed metal-oxides chains keeping fixed phosphate groups. For this reason an attempt was made to increase the ion-exchange capacity by increasing the porosity of these materials (28). This could be achieved by introducing trivalent cations (e.g. Al^{3+}, Fe^{3+}) in the initial reagents used in the synthesis of the phosphates. It was assumed, that the trivalent metal cations could play a template-cations role linking part of phosphate groups during synthesis.

This paper reports the results of the investigation of the uranium separation from acidic aqueous solutions (pH_{init} 3) by the above mentioned Al^{3+}- and Fe^{3+}-modified titanium and zirconium phosphates.

EXPERIMENTAL

Materials and Characterization

The investigated phosphates were prepared at the Institute for Sorption and Endoecology Problems of the National Academy of Science of Ukraine (Kiev, Ukraine) using a previously described sol-gel technique (24). For the synthesis 2M solution of $TiCl_4$ or $ZrOCl_2$, 5M solution of H_3PO_4 and 2M solution of $FeCl_3$ or $AlCl_3$ were efficiently mixed in a mixer. The molar ratio of tetravalent metal to phosphorous was 1:1.5. The reaction mixture obtained was dispersed into a vertical column filled with aliphatic hydrocarbons (e.g., C_9H_{20}-$C_{11}H_{24}$), where the formation of spherical granules took place. After separation from the organic solvent the gel granules were thoroughly washed with water and then air-dried at ambient temperature. The gel obtained was mechanically strong, glass-like, spherical beads with diameters in the range of 0.2–2 mm. The four Al^{3+} and Fe^{3+}- doped titanium and zirconium phosphates sorbents in H-form (abbreviation: TiAlP, TiFeP, ZrAlP and ZrFeP) used for the experimental work were characterized by chemical analysis, powder X-ray diffraction (powder-XRD using a Philips PW1820 diffractometer utilizing CuKα-radiation), scanning electron microscopy (SEM/EDS using a JEOL 840A SEM equipped with an OXFORD ISIS 300 EDS analyzer) as well as thermal stability, acidity, water content, porosity and surface area measurements (see also ref. (29)).

Uranium Sorption Experiments

The sorption of uranium from aqueous solutions by the abovementioned titanium and zirconium phosphates was investigated using a batch-type technique. For this purpose 50 mg of the sorbents were shaken for 48 hours in a rotary shaker with 10 mL of the uranium solutions in polycarbonate centrifuge tubes at room temperature. In preliminary experiments it was found that this duration of the treatment was sufficient for the establishment of the equilibrium. The required uranium solutions (concentration range; 10 to 500 mg/L) were prepared by dissolution of analytical grade $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water. The initial pH of the solutions was adjusted to 3. All experiments were performed under constant ionic strength established by 0.1 M $NaNO_3$. After the end of the sorption experiments the solid phase was separated, washed several times using distilled water and air-dried. The pH of the solutions was also measured after the end of the treatment.

The uranium content of the separated solid phases was determined by instrumental neutron activation analysis (INAA) combined with high resolution γ-ray spectroscopy. The research reactor of the NCSR Demokritos/Athens was used for irradiation of the samples (Fluency (Φ): 5×10^{14} $cm^{-2}\ s^{-1}$) and a standard γ-ray spectroscopy set-up with HPGe-detector for the measurements. For the determination of the uranium concentration the 106 and 278 keV γ-radiation of ^{239}Np ($T_{1/2} = 2.355$ days) was used ($^{238}U(n,\gamma)^{239}U \rightarrow {}^{239}Np$, $(T_{1/2})_{U\text{-}239} = 23.5$ min). As reference materials for the uranium determination the IAEA Soil-7 (U-concentration: 2.6 μg/g) and G1 of the USGS (U-concentration 3.4 μg/g) were utilized.

The sorbents were examined before and after the treatment with the uranium solutions by means of SEM/EDS and powder-XRD.

RESULTS AND DISCUSSION

The average atomic ratio of zirconium to phosphorous in the investigated sorbents, determined by SEM/EDS analyses, was found to be 0.55 and 0.56 for ZrFeP and ZrAlP respectively. The measured iron concentration of ZrFeP was 0.33 at.% (0.75 w.%). No aluminum was found in the investigated ZrAlP samples, most probably due to the thorough washing of the sorbent after the synthesis.

The average titanium to phosphorous atomic ratio of the TiFeP and TiAlP sorbents was 0.69 and 0.89 respectively. The iron concentration in the TiFeP was 1.1 at.% (3.58 w.%), whereas the aluminum concentration in the TiAlP 0.22 at.% (0.28 w.%).

Calcium was also found in all investigated samples (ZrAlP: 0.33 at.%, ZrFeP: 0.31 at.%, TiAlP: 0.29 at.%, TiFeP: 0.16 at.%) most probably due to its binding with phosphate groups during the washing of the sorbent during the preparation procedure.

It is known from the corresponding literature, that amorphous zirconium and titanium phosphates possess a complex composition containing various phosphate functional groups, such as H_3PO_4 (occluded phosphoric acid not chemically bonded to the matrix but linked by weak electrostatic forces), H_2PO_4, HPO_4^{2-}, PO_4^{3-}. These functional groups have many energy levels differing very little from each other. The presence of the different phosphate groups was verified by potentiometric titrations using NaCl/NaOH, KCl/KOH and HCl/NaOH (28). In addition these measurements gave information about the presence of OH-groups also previously observed (25) and about the chemical stability of the sorbents. The formation of metal-substituted forms of the sorbents by uptake of metal-cations from the solution was accompanied by phosphorous release from their matrix. The increase of OH- groups in metal-substituted forms was also found to be equivalent to the quantity of phosphate groups released (e.g. $\equiv Zr\text{-}O\text{-}P(O)(OH)_2 + 2NaOH \rightarrow \equiv Zr\text{-}OH + Na_2HPO_4 + H_2O$).

The absence of distinct diffraction peaks in the powder-XRD patterns indicated that all materials were amorphous.

The pore volume (V_s) of both Zr-phosphate sorbents was found to be 0.26 cm^3/g whereas the corresponding values for the Al- and Fe-doped Ti-phosphates were 0.31 and 0.32 cm^3/g respectively. The measured specific surface area (S_{BET}) of the Al- and Fe-doped Zr-phosphates (371.9 and 402.7 m^2/g) was found to be considerably higher than the corresponding Ti-phosphates (139.2 and 129.4 m^2/g). The water content of the sorbents was between 30 and 35% also depending on the storage conditions.

The ZrFeP and ZrAlP sorbents showed a sharp pore-size distribution around a maximum of ca. 25 Å. The TiFeP sorbent showed a rather wide pore size distribution with maximum at ca. 140 Å, whereas the TiAlP two maxima at ca. 80 and 150 Å. The pore size distribution data were obtained from nitrogen sorption–desorption data measured with a Micrometrics Gemini-2 porosimeter. The outgas temperature during these measurements was 160°C (28).

The uptake of uranium (in mg U/g sorbent) by the Al- and Fe-doped zirconium and titanium phosphates is given in Fig. 1. The uranyl-cations ($(UO_2)^{2+}$) are the dominant species in uranium solutions of pH 3, where a less than 10% fraction of $(UO_2)NO_3^+$ is also present.

The uranium sorption on the Fe-doped titanium phosphate can be reproduced by the Freundlich adsorption equation

$$\frac{x}{m} = K_{eq} \cdot C_{eq}^n$$

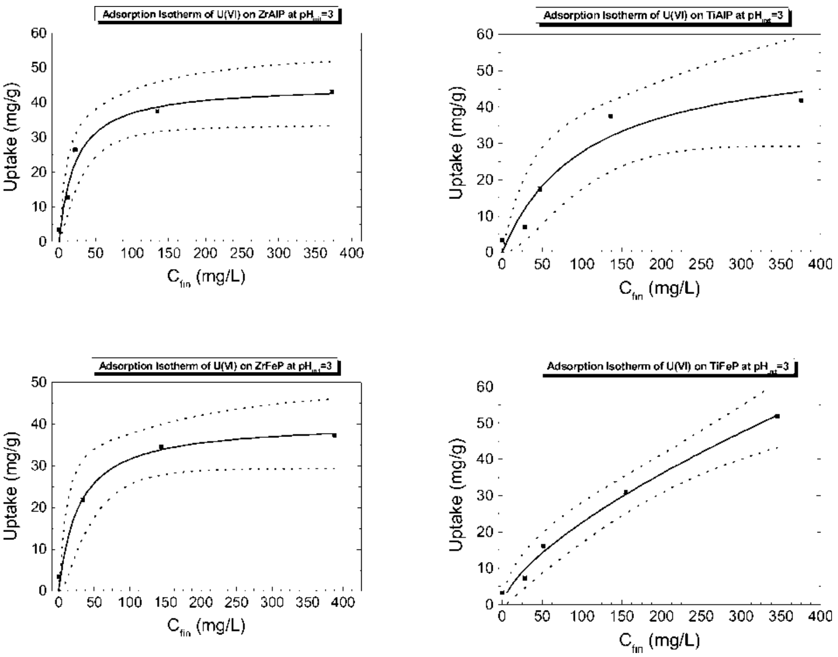

Figure 1. The uptake of uranium from aqueous solutions of initial pH 3 in the presence of 0.1 M $NaNO_3$ (C_{fin}: equilibrium concentration).

where C_{eq} is the equilibrium concentration of the cation under investigation in the solution. K_{eq} and n are constants. The n characterizes the heterogeneity of the surface of the sorbent.

The sorption on the rest of the investigated phosphates can be well reproduced by the Langmuir equation

$$\frac{x}{m} = \frac{Q_{\max} K C_{eq}}{1 + K C_{eq}}$$

where $Q_{\max}$ is the maximum sorption capactity of the sorbent in mg/g and K a constant.

The curves fitting the experimental data, along the 95% confidence region (dotted lines), are given in Fig. 1 and the corresponding maximum capacity values ($Q_{\max}$) in Table 1. In the case of TiFeP the values for the constants K_{eq} and n obtained by fitting the Freundlich equation are respectively 1.003 and 0.67. The last one indicates that two uranyl-ions are occupying three sites available for adsorption.

The variation of the equilibrium pH of the solutions as a function of the initial uranium concentration of the solutions is given in Fig. 2. It is clear that for initial uranium concentrations 0–100 mg/L there is an almost linear decrease of the pH with increasing uranium concentrations, while further increase does not affect the pH which is stabilized. The final pH of the solutions is slightly different for the 4 sorbents. The form of these curves justifies the previously mentioned finding, that during the sorption acidic phosphorous-containing groups are liberated by the sorbents and $(OH)^-$ removed from the solution simultaneously with metal cations.

Scanning electron microscopic examinations of the sorbents before and after the treatment with the uranium solutions indicated the presence of well-formed crystallites on both titanium phosphate sorbents. Characteristic microphotographs of the two materials are respectively given in Fig. 3. The density of appearance on the Fe-doped titanium phosphate was considerably higher than on the Al-doped sorbent. No crystal formation was observed in the cases of uranium removal by ZrAlP and ZrFeP indicating the different sorption behavior of the zirconium phosphates (s. Fig. 4).

Table 1. The maximum uptake values ($Q_{\max}$ in mg/g) calculated by the fitting of the experimental data by the Langmuir equation. R is the correlation coefficient of the fit

Sorbent	$Q_{\max}$ (mg/g)	R^2
ZrFeP	40.4	0.985
ZrAlP	45.1	0.964
TiAlP	56.6	0.939

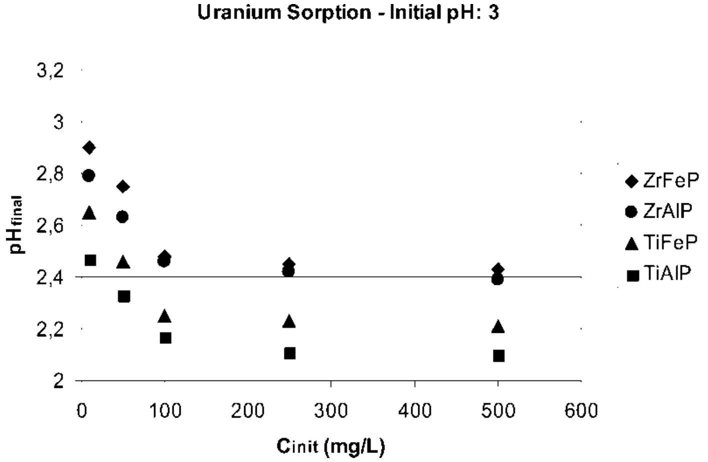

Figure 2. Variation of the equilibrium (final) pH of the solutions after contacting the sorbents for 24 hours as a function of the initial uranium concentration. The initial pH of the solutions was adjusted to 3 by HNO_3.

The P- and U- mappings (s. Fig. 5) showed that uranium is mainly distributed on the formed crystals, whereas phosphorous is almost equally distributed.

The powder-XRD examination of the samples indicated, that the well-formed crystallites observed in the SEM examination on the titanium phosphates have a tetragonal structure most probably belong to a mineral phase of the autunite ($Ca(UO_2)_2(PO_4)_2 \cdot (10-12)\ H_2O$) group (6). The presence of sodium on the crystals could be considered as an indication of the presence of sodium uranyl phosphate hydrate (sodium autunite, $Na_2(UO_2)_2(PO_4)_2 \cdot 6-8H_2O$) (6, 29). Sodium originates from the sodium nitrate used as background electrolyte. On the other hand, the presence of iron leads in the case of the crystallites formed on TiFeP could indicate the formation of iron uranyl phosphate hydroxide hydrate ($Fe(UO_2)_2(PO_4)_2(OH) \cdot 7H_2O$ (6, 30). The XRD characteristic peaks attributed to the formed sodium meta-autunite ($Na(UO_2)(PO_4) \cdot 8H_2O$) and iron uranyl phosphate hydroxide hydrate ($Fe(UO_2)_2(PO_4)_2OH \cdot 7H_2O$) were confirmed by the 29-1283/29-1284 and 37-0245 cards of the International Center for Diffraction Data respectively (s. Fig. 6).

The effect of phosphate concentration on the formation and precipitation of uranyl-phosphates from solution is shown in Figs 7 and 8 for pH 2.5 and 2.9 respectively. The data were calculated using the computer code Visual MINTEQ using the MINTEQA 4.0 thermodynamic database (31). It is observed that the total phosphate concentration affects greatly the solid form that will precipitate. At pH 2.5 with smaller phosphate concentrations (up to 75 mg/L) only uranyl phosphate ($(UO_2)_3(PO4)_2$) is formed. As the total phosphate concentration increases the formation of sodium autunite

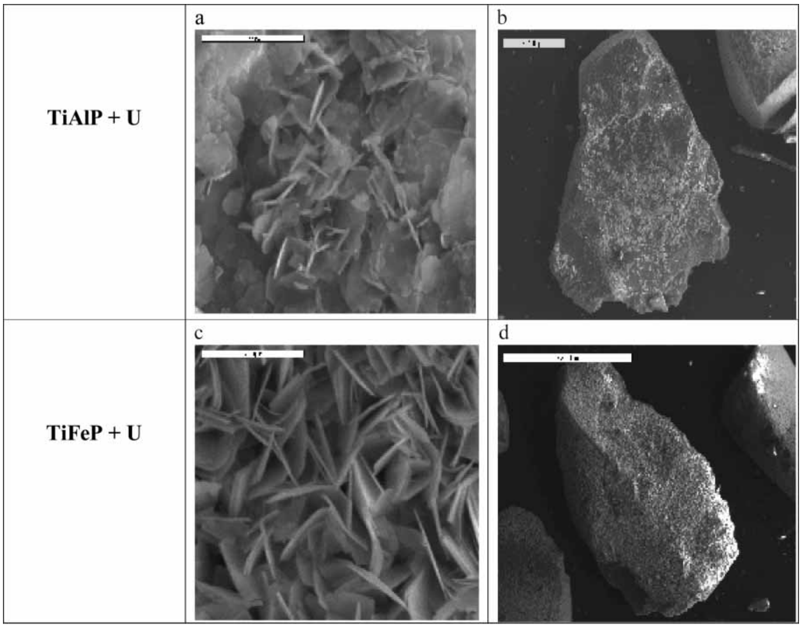

Figure 3. Microphotographs of the U-crystallites formed on Al- (a, b) and Fe- (c, d) doped titanium phosphates.

starts to compete with the uranyl phosphate. Equivalent amounts of uranyl phosphate and sodium autunite are formed at 92 mg/L of total phosphates. At phosphate concentrations higher than 110 mg/L only sodium autunite is formed. It should be noted that with increasing total phosphate concentration the dissolved fraction of the uranyl-cations steadily decreases.

At pH 2.9 a considerable shift of the curves can be observed (see Fig. 7). Uranyl phosphate is the only phase observed in solutions with total phosphate concentration up to 50 mg/L. As the total phosphate concentration increases the formation of sodium autunite is initiated. At total phosphate concentration of 64 mg/L equivalent amounts of uranyl phosphate and sodium autunite are formed. According to the calculations, sodium autunite is the only phase formed at total phosphates concentrations greater than 85 mg/L.

It should be mentioned that the only source of phosphates in these experiments was the sorbent and no additional phosphates were added to the solutions. Uranyl phosphate phases were also observed in the case of the interaction of uranium solutions with hydroxyapatite (15). Different uranium phosphates have been frequently investigated in the past because of their potential application as ceramic matrix for the immobilization of actinides containing radioactive wastes (e.g. 32–34).

Two mechanisms might be considered in order to explain the formation of the uranyl phosphate phases on the sorbent surface: the attraction of

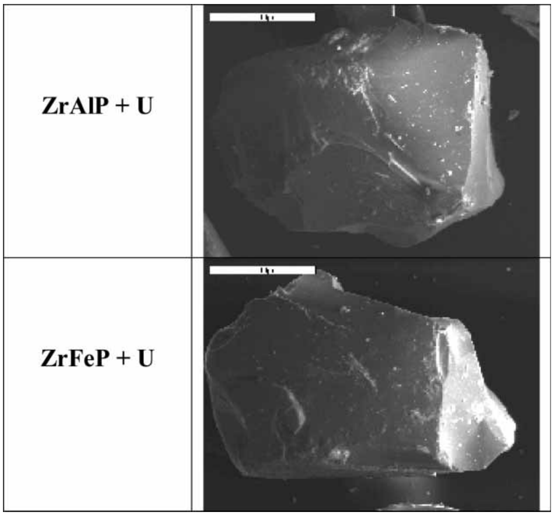

Figure 4. Microphotographs of ZrAlP and ZrFeP after the interaction with the uranium solutions.

uranyl-cations and subsequent formation of insoluble precipitate which remains attached to the surface of the solid and/or the liberation of surface phosphate groups which migrate to the solid/solution interface and interact with the uranyl-cations held on the surface by attractive forces. Although we believe that the former mechanism could eventually better explain the good attachment of the precipitate to the sorbent surface, further studies are required in order to elucidate the prevailing mechanism. Drot et al. also found, studying the sorption of U(VI) onto ZrP_2O_7 by X-ray absorption spectroscopy, that the uranyl ions are directly bound to the sorbent with two oxygen atoms belonging to the surface diphosphate groups (35).

Concluding one could mention that all investigated sorbents are rather effective in separating uranium from acidic solutions (pH 3, ionic strength 0.1 established by $NaNO_3$). The uranium sorption capacities of the sorbents are considerably lower than those observed by Zhuravlev (36), who studied

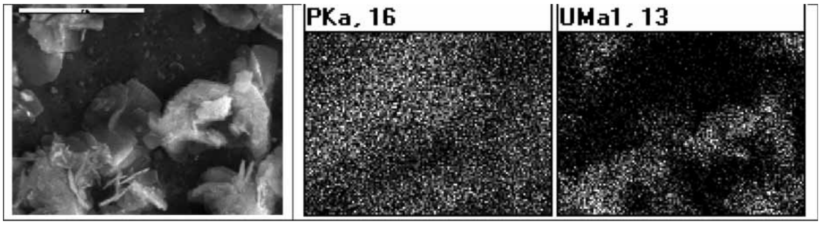

Figure 5. P- and U-mappings on TiAlP interacted with uranium solutions.

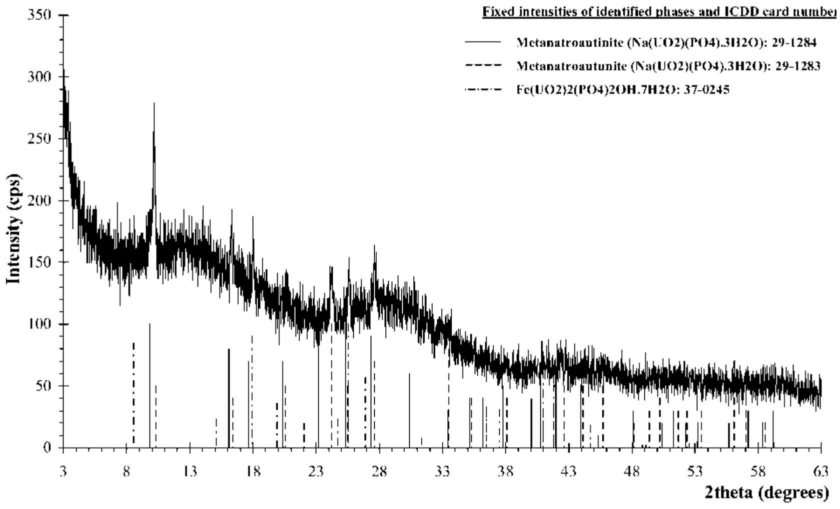

Figure 6. Powder XRD-pattern of TiFeP interacted with U-solution in the presence of 0.1 M $NaNO_3$.

the uranium sorption from acetate solutions at pH 5.2. In these cases uranium sorption capacities of up to 1.7 meq $(UO_2)^{2+}/g$ (equivalent to 229.5 mg/g) were observed. However, it is well known that the pH and the presence of competing cations play an important role in sorption procedures. On the other hand, the investigated materials show higher sorption capacity than

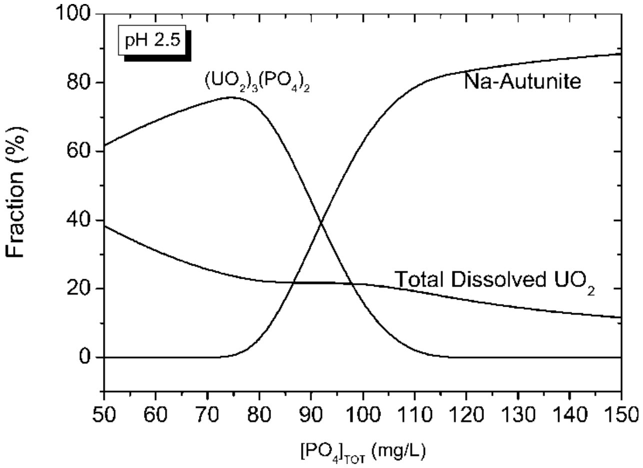

Figure 7. Effect of total phosphate concentration on uranium (VI) solubility and the fraction of solid phase formed. Total UO_2^{2+} concentration: 250 mg/L, $NaNO_3$ concentration: 0.1 M.

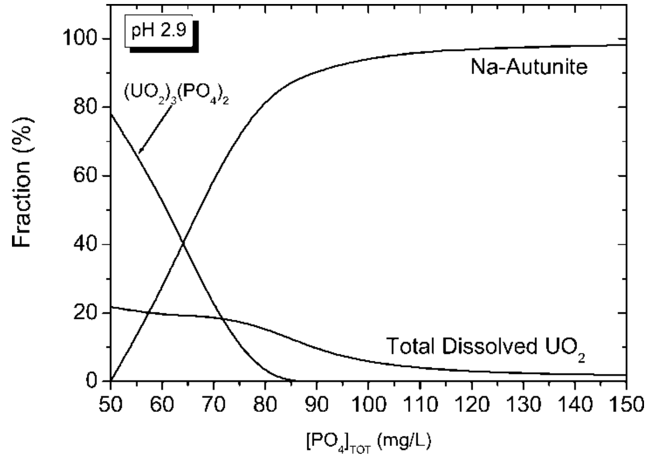

Figure 8. Effect of total phosphate concentration on uranium (VI) solubility and the fraction of solid phase formed. Total UO_2^{2+} concentration: 250 mg/L, $NaNO_3$ concentration: 0.1 M.

natural zeolites (37, 38) and the natural microporous manganese oxide todorokite (39) but lower than the clay minerals montmorillonite and vermiculite, which were found to exhibit maximal sorption capacity of 100 and 93 meq/100 g (40). Short time uranium(VI) sorption experiments performed with Union Carbide synthetic Na13X zeolite gave results similar to montmorillonite and vermiculite, where longer contact times with acidic uranium solutions led to gradual degradation of the sorbent (40). It should also be pointed out that in the case of titanium sorbents uranyl phosphates were formed on the sorbent surface; solids quite insoluble in acidic solutions.

CONCLUSIONS

All investigated amorphous Al^{3+}- and Fe^{3+}-doped titanium and zirconium phosphates show a considerable ability to separate uranium from acidic aqueous solutions ($pH_{init} = 3$, constant ionic strength established by 0.1 M $NaNO_3$). Their maximum sorption capacity values were found to be higher than those of the natural zeolites and the natural microporous manganese oxide todorokite but lower than the corresponding values of the clay minerals montmorillonite and vermiculite given in the literature.

The SEM/EDS and powder-XRD examination of the grains of the two investigated titanium phosphate sorbents after contacting the uranium solutions revealed the formation of sodium uranyl phosphate hydrate crystals (sodium autunite, $Na_2(UO_2)_2(PO_4)_2 \cdot 6{-}8H_2O$). The formation of the sodium uranyl phosphate can also be thermodynamically verified and justified (Visual MINTEQ calculations). In the case of TiFeP sorbent, the formation of iron uranyl phosphate hydrate crystals (iron uranyl phosphate hydroxide hydrate ($Fe(UO_2)_2(PO_4)_2(OH) \cdot 7H_2O$) along the sodium autunite ones was verified by powder-XRD. No crystal formation was observed in the cases of uranium separation by ZrAlP and ZrFeP indicating the different sorption behaviour of the studied zirconium phosphate sorbents.

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