J Radioanal Nucl Chem (2009) 282:787–791
DOI 10.1007/s10967-009-0170-z

Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions

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Received: 19 June 2009 / Published online: 10 July 2009

Abstract A sorption ability of titanium silicates (TiSi) and iron oxides towards Cs, Sr, Pu and Am was tested using the laboratory batch method. The obtained results are expressed as distribution coefficients (K_d). TiSi synthesised using $TiOSO_4$ revealed better sorption ability towards all studied radionuclides in comparison with TiSi produced on the basis of $TiCl_4$. The K_d values ranged from 3.9×10^2 to 1.6×10^5 mL g^{-1} for Sr, from 6 to 4.1×10^4 mL g^{-1} for Cs, from 2.2×10^2 to 2.6×10^5 mL g^{-1} for Pu and from 50 to 1.6×10^4 mL g^{-1} for Am. The highest Pu K_d values (9×10^3–6.2×10^4 mL g^{-1}) and better kinetics were found for iron oxides.

Keywords Titanium silicates · Iron oxides · Cs · Sr · Pu · Am · Distribution coefficients

Introduction

Anthropogenic radionuclides such as ^{137}Cs, ^{90}Sr, ^{239,240}Pu and ^{241}Am which originated as global fallout, as discharges from nuclear industry, as well as releases into the environment after various accidents, have recently been studied at ultra-low level concentrations [1–3]. From these studies it is evident that one of the important needs nowadays is development of effective and low-cost water treatment methods, capable of reducing discharges to low-levels for the purpose of protection of the environment from anthropogenic radionuclides and their harmful ecological effects.

The most commonly applied treatment technologies involve precipitation, ion exchange, evaporation and solvent extraction. Recently growing concern about contamination of the environment by radioactive and non-radioactive pollutants resulted in intensive studies related to the development of new technologies for separation of radionuclides from liquid waste. These new technologies should be based on highly selective materials, which are hard to decompose over a wide range of pH, which remain stable at high temperatures, and which are resistant to ionizing radiation. These materials have to be able to operate in the presence of a great excess of competitive ions, organic solvents and oxidants [4–6]. Crystalline TiSi showed high selectivity towards low concentrations of Cs^+ and Sr^{2+} ions in high ionic strength solutions, typical for high level waste cooling ponds, and it also showed a capability of operating under chemically harsh conditions [7].

Complicated technologies, high capital and regeneration costs stimulated studies to develop low-cost and efficient technologies based on naturally occurring minerals such as zeolites and clay minerals [8, 9]. Another option could be an application of amorphous porous mixed oxides—a rapidly developing class of materials prepared by sol-gel procedures, the main benefit of which are very simple procedures conducted under mild reaction conditions in the ambient atmosphere [10].

In addition, ferrites and a variety of iron-containing minerals such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite have also been widely used as inorganic ion exchangers for

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the treatment of liquid wastes containing radioactive and hazardous metals. These materials have certain advantages, and they are also a promising class of materials for radioactive waste treatment. Ferrites possess the property of spontaneous magnetization, they are low-cost crystalline materials soluble only in a strong acid and they can be used for efficient separation by magnetic methods [11, 12].

The aim of this study was to prepare amorphous TiSi by sol-gel procedures under mild conditions using cheap a local technical titanyl sulfate, and organic complexions as stock materials. Further, to carry out a comparative assessment of possible application of these low-cost synthetic inorganic sorbents with conventional and natural sorptive materials in liquid waste treatment technologies to remove long-lived radionuclides such as Cs, Sr, Pu and Am.

Experimental

Synthesis of titanium silicates and iron oxides

The co-precipitation and the sol-gel method followed by the hydrothermal treatment was used for the synthesis of TiSi from alkaline solution Me_2O–TiO_2–SiO_2. The synthesis of TiSi by the precipitation method was conducted under mild conditions. TiSi's were synthesised using cheap raw materials available in the Ukraine—alkali silicate (Na_2SiO_3), potassium/sodium methylsilicates $CH_3Si(OH)_2ONa/K$, titanium tetrachloride ($TiCl_4$) and titanyl sulphate ($TiOSO_4$) [13, 14]. The following prepared ion exchangers were used in sorption experiments: TiSi 17(SO_4), TiSi 20(Cl), TiSi 30(SO_4), TiSi 32(SO_4), TiSi 55(Cl), TiSi 57+58(Cl), TiSi 59(Cl).

The sol-gel method of the TiSi synthesis developed at the Institute for Sorption and Problems of Endoecology of the National Academy of Sciences of Ukraine is based on the use of local technical titanyl sulfate and organic complexions as stock-materials for the synthesis [13]. Ion exchangers TiSi 82-1, TiSi 84-3, TiSi 40, TiSi 86-1, TiSi 84-4, TiSi 82'-1, TiSi 86-4, TiSi 82-3 were tested for their sorption characteristics towards Cs, Sr, Pu and Am.

Iron oxide synthesis was performed using methods described in publications with some modifications. Synthesis details are given in the previously published paper [15].

Physical and chemical analysis of prepared samples

The BET surface area and pore volume of studied sorbents were determined using the nitrogen adsorption/desorption method at a liquid nitrogen temperature by means of a surface area analyzer NOVA 2200. The pore size distribution was determined according to the BJH method using the desorption branch of the isotherms. The X-ray diffraction studies of the prepared Ti–Si sorbents were conducted with an automated diffractometer (DRON -4-07) using Ni-filtered Cu $K\alpha$ radiation. Synthesised iron oxides were characterised by using Mössbauer spectroscopy [15].

Synthesised sorbents, both titanium silicates and iron oxides, as well as natural clay minerals with 14% of montmorillonite were used in sorption experiments. The laboratory batch method was applied to determine the distribution coefficient values of Cs, Sr, Pu and Am radionuclides (background electrolyte—0.1 mol L^{-1} Na^+) at the 1:100 and 1:1,000 g mL^{-1} liquid : solid.

The total concentrations of caesium in solutions were 2.30×10^{-10} mol L^{-1} and 6.80×10^{-5} mol L^{-1} (the solutions were labelled by ^{134}Cs). A mixture of Pu(IV) isotopes ($^{238,239,\ 240,\ 241}$Pu prepared from highly contaminated Chernobyl soil) [16] was used in sorption experiments. Starting concentrations of Pu(IV) and ^{241}Am were 1.10×10^{-9} and 3.20×10^{-11} mol L^{-1}, respectively.

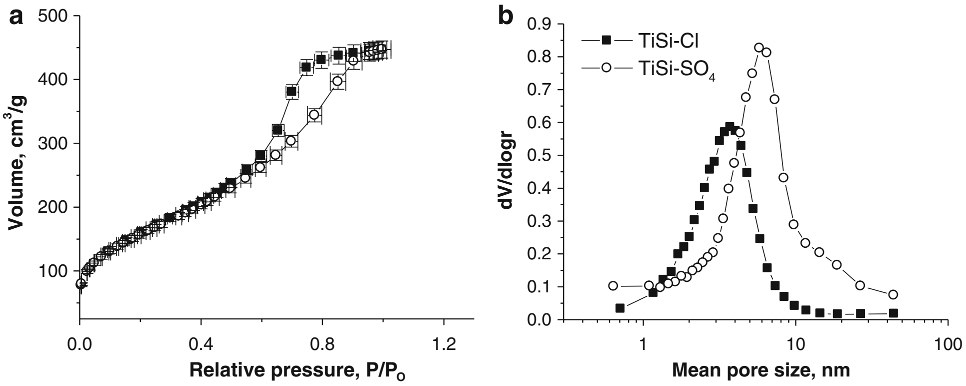
pH was measured before and after sorption experiments under continuous Ar flow using WTW pH-electrode SenTix 41, calibrated with standard buffers DIN 19266 (pH values 4.006, 6.865, 9.180) and a WTW inoLab Multi Level 1 m. The solids were separated from the liquid-phase by centrifugation for 20 min at 10,000–20,000 G. ^{134}Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV @ 1.33 MeV, and efficiency 42%). Plutonium and americium in the solution and the solid-phase were determined after radiochemical separation using UTEVA and TRU (Eichrom Industries) resins, and their activities were measured by alpha spectrometry. ^{242}Pu and ^{243}Am were used as tracers in the separation procedures. Precision of radionuclide measurements by gamma–alphas spectrometry was for Cs $\leq$ 2%, Pu $\leq$ 5%, Am $\leq$ 7%. Sr concentrations in the liquid-phase were measured with a Perkin Elmer Zeeman/3030 AAS-GF. Details of this experiment and the characterization of sorbents are described in previous publications [17, 18].

Results and discussion

Identification and characterization

Typical adsorption isotherm of studied TiSi and distribution of effective pore radii for TiSi synthesised in the presence of chloride and sulphate ions are presented in Fig. 1. Nitrogen adsorption-desorption isotherms belong to type IV in the IUPAC classification. *S*-shaped character indicates the mesoporous structure of synthesised samples. The specific surface area estimated using the BET method varied from 120 to 726 m^2 g^{-1}, the total volume of pores from 0.20 to 0.90 cm^3 g^{-1}, depending on the synthesis

Fig. 1 Typical isotherm of adsorption/desorption N_2 for TiSi samples (**a**), and pore size distribution (*V*-pore volume, *r*-pore radius) of synthesised TiSi (**b**)



conditions, while volume of micropores ranged from 0.02 to 0.09 $m^3\ g^{-1}$, and the effective pores radii from 2.5 to 15.5 nm. It can be seen that the average pores radii in the presence of SO_4-ion increased from 5.7 to 7.8 nm. X-ray investigations of titanium silicates synthesised by different techniques (precipitation and sol-gel methods) showed their amorphous structure.

Preliminary studies were performed in order to determine the sorption ability of synthesised inorganic sorbents towards Sr, Cs, Pu and Am from natural groundwater, 0.1 mol L^{-1} $NaNO_3$ solutions, and fuel pond water. The highest K_d values were found for the system groundwater—TiSi ion exchangers. The data obtained indicated that Sr K_ds varied from 2.9×10^2 to 2.2×10^5 mL g^{-1} for inorganic sorbents and groundwater solutions. Cs K_d for the same sorbents and 0.1 mol L^{-1} $NaNO_3$ solutions varied from 30 to 4.1×10^4 mL g^{-1} whereas Pu K_d varied from 2×10^2 to 4.6×10^3 mL g^{-1}.

The obtained results indicate an effective use of TiSi sorbents during removal of cesium, strontium and plutonium from natural groundwater. It should be noted that a better sorption ability towards studied radionuclides was found for TiSi synthesised using titanilsulfate, whereas the method itself—precipitation or sol-gel—was not important.

Comparably high K_d values found for TiSi-17(SO_4) and TiSi-55(Cl) are promising for particular separations, and it is probably an indication that amorphous TiSi can act as exchangers towards a wide range of cations with dissimilar sizes and charge. On the other hand, the highest Pu K_d value found for sorbent TiSi-17(SO_4) in 0.1 mol L^{-1} $NaNO_3$ solution can be explained by an effect of the methyl groups introduced into the Ti silicate structure using the potassium methyl silicon and the hydrogen peroxide as complexion during the synthesis procedure. The presence of these groups provided formation of sorbent with a mesoporous structure, appropriate for sorption of large size ions.

Data on the Pu sorption kinetics have indicated that a rather short time period is required to reach equilibrium (Figs. 2, 3). Equilibrium was reached after about 2 h of sorption. Kinetic data were fitted to the pseudo-first-order kinetic model: $q_t = q_e(1\text{-}e^{-k_{ad}t})$, where q_t and q_e are Pu concentrations (mol/g) at time t and equilibrium, respectively as well as k_{ad} (min^{-1}) is the pseudo-first-order rate constant. It can be seen from the obtained parameters that the iron oxide kinetic data fit well the pseudo-first-order equation, whereas the TiSi's data require additional

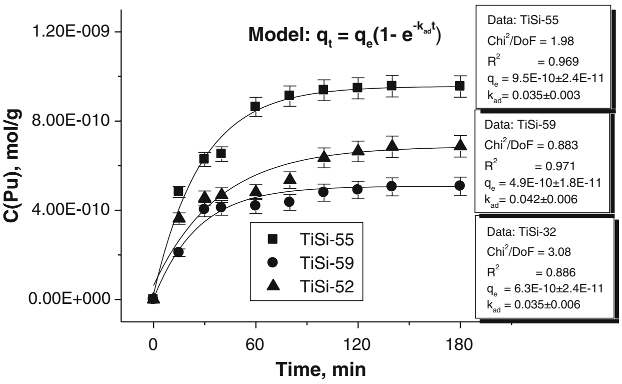


Fig. 2 Kinetics of Pu(IV) sorption to TiSi sorbents (0.1 mol L^{-1} $NaNO_3$ solution, pH 6.08–7.02 ±0.06, solid: liquid ratio 1: 1,000 g/mL)

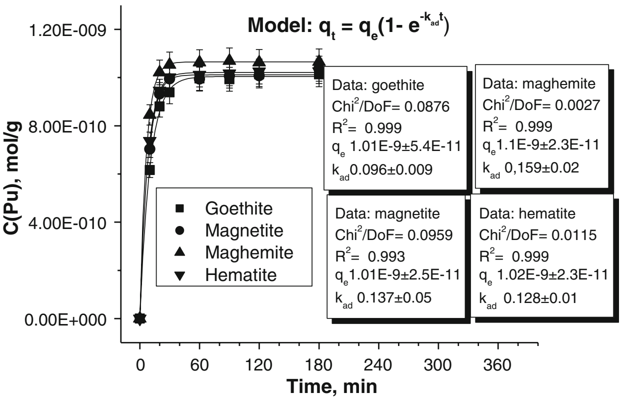


Fig. 3 Kinetics of Pu(IV) sorption to Fe oxides (0.1 mol L^{-1} $NaNO_3$ solution, pH 6.08–7.02 ±0.06, solid: liquid ratio 1: 1,000 g/mL)

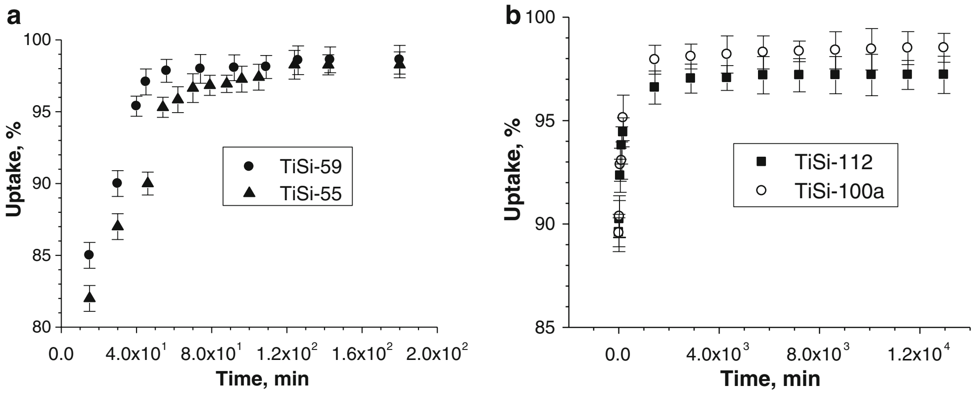


Fig. 4 Kinetics of Cs sorption to Ti–Si sorbents (0.1 mol L^{-1} $NaNO_3$ solution, pH 5.6–6.2 ±0.1, solid: liquid ratio 1: 1,000 g/mL)

analyses. Pu K_d equilibrium ranged from 2.5×10^3 to 4.1×10^3 mL g^{-1} for studied sorbents TiSi-17(SO_4), TiSi-32(SO_4), TiSi-55(Cl) and TiSi-59(Cl).

It should be noted that TiSis are porous materials with pore size distribution from 0.8 to 1.5 nm and their sorption ability towards studied radionuclides depends on their structural parameters. In addition, modification of methods used for preparation of TiSi gives opportunities to change their microstructure and porosity. Despite the fact that TiSi synthesised using the sol-gel methods showed a lower sorption ability towards studied radionuclides, they have great potential for tailoring of the chemical composition, the porosity and the surface properties, as well as for the synthesis of these materials in a granulated form, which is important for practical purposes of natural groundwater treatments.

Pu K_d values ranged from 4.8×10^3 to 1.6×10^4 mL g^{-1}, while Am K_d varied from 9×10^3 to 2.6×10^5 mL g^{-1} for Pu in the system iron minerals—natural groundwater. The obtained values were in a close range as determined for natural clay [17, 18]. An increase in the Pu K_d value by a factor of 6.8 was found for magnetite/hematite composite in comparison with the value for pure magnetite, and lower by a factor of 4 in comparison with the K_d value obtained for pure hematite. Nevertheless, synthesised magnetite/hematite composites possess magnetic properties and comparatively a high sorption ability towards Pu. Therefore, they can be used for separations.

Sorption kinetics is an important parameter of sorbents reflecting their efficiency and cost. Kinetics data for four sorbents are presented in Fig. 4. Better sorption parameters were found for sorbents TiSi-112 and TiSi-100a, when 90% of Cs was removed in the first 10 min. These better sorption parameters can be explained by their structure. Cs kinetics data of sample TiSi-55(Cl) indicated that there is a limitation on Cs ion diffusion into the mesoporous sorbent matrix. Studies of plutonium sorption kinetics indicated a faster plutonium sorption to iron oxides in comparison to TiSi.

Conclusions

The obtained results revealed that the highest sorption ability towards studied radionuclides showed titanium silicates synthesized using $TiOSO_4$ without reference to the chosen method (a co-precipitation or sol-gel). Magnetite and clay minerals showed better sorption ability towards americium. The highest Pu K_d values and better Pu sorption kinetics were found for synthetic iron oxides. An increase in the Pu K_d value by a factor of 6.8 found for magnetite/hematite composite in comparison with the pure magnetite suggests that this sorbent is efficient for plutonium removal and it is promising for its separation from contaminated solutions. Reported K_d values for uptakes of activated corrosion nuclides, fission products and transuranium elements (including ^{241}Am and ^{236}Pu) from 0.1 mol L^{-1} $NaNO_3$ for Am were 7.1×10^4 and 3.2×10^6 mL g^{-1} and for plutonium varied from 1.5×10^4 to 6.7×10^4 mL g^{-1} under similar conditions [19]. The published K_d values obtained using crystalline TiSi for Cs and Sr ranged from 8.9×10^5 to 9×10^5 mL g^{-1} and from 7.4×10^4 to 8.6×10^5 mL g^{-1}, respectively [20, 21]. Thus, TiSi tested in this study showed close sorbtion ability towards studied radionuclides, whereas they were synthesised under mild conditions using cheaper materials. It should be noted that modification of methods used for preparation of TiSi gives great opportunities to change their microstructure and porosity. Thus, despite the lower sorption ability of TiSi prepared by the sol-gel method, it has certain advantages in comparison with the fine powder TsSi. This is because of a huge potential for the tailoring of chemical composition, porosity and surface properties, as well as for the production in the granular form, which is especially important for practical purposes.

Acknowledgments This study was supported by the Ukrainian Ministry of Education, the Lithuanian Ministry of Education and the Lithuanian State Science and Studies Foundation project (grant No. 580 and No. V-35/2007, V-19/2009).

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