Migration of strontium, cesium, europium and uranium from poly(methyl styrene)- and polystyrene-phosphate composites prepared using gamma radiation

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Abstract. Composites consisting of natural phosphate powder and two monomers (styrene or methyl styrene) have been prepared by means of gamma irradiation. The polymerization reaction was followed up using a thermogravimetric analyzer (TGA) to determine the conversion of the polymerization. Differential scanning calorimeter (DSC) was used to locate and determine the glass transition temperature (T_g) of the prepared samples. The distribution of ^{137}Cs, ^{152}Eu, ^{85}Sr and ^{238}U in a solid-aqueous system, composites of phosphate-poly(methyl styrene) and of phosphate-polystyrene in contact with groundwater, was investigated using γ-spectrometry and fluorometry. The effects of contact time, pH, and the concentration of concurrent element (Ca) were studied. The results were compared with earlier results with phosphate alone in the solid phase. The ability of the produced composites to keep the studied radioisotopes in the solid phase is much higher than in the mineral phosphate. This improvement is more remarkable for strontium and cesium than for europium and uranium, due to their high element ratio in the solid phase in phosphate experiments.

Key words: poly(methyl styrene) • polystyrene • composites • distribution • radionuclide • europium • strontium • cesium • uranium

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Introduction

The deposition of nuclear waste is one of the important issues of nuclear energy and its applications in many fields such as medicine and industry. Many research works in this topic include subjects such as chemical, physical, mechanical and geological safety studies. These studies can be divided in tow parts, the storage container itself and the surrounding environment (sediment and geological position). Aim of all these works is to find materials with high ability to keep radionuclides in normal and abnormal conditions [9, 11, 13, 15].

The fact that some phosphate is rich of uranium (about 100–120 ppm) with connection with its complexation properties has led to propose the phosphate area in Syria as potential site for radioactive waste deposition [3]. In a recent work [12] the distribution of uranium, thorium, americium, europium, radium, strontium and cesium in a solid-aqueous system, mineral phosphate in contact with groundwater, was investigated. Adsorption ratios of lanthanides and actinides were found to be more than 98%. The strontium ratio in the aqueous phase varies from 50 to 85%, and that of cesium from 20 to 50%, depending on experimental conditions. The mechanism of transport of elements between the phases

differs depending on element and conditions. The main mechanisms are cation-anion exchange, chemical and physical adsorption, precipitation, self-diffusion in the solid phase, and building of insoluble complexes.

In another work, poly(methyl acrylate)-phosphate composites had been prepared using gamma radiation [7]. The investigated radionuclides (strontium, cesium, europium, uranium) were injected in the mineral phosphate before the radiation-induced polymerization occurred. The presence of poly(methyl acrylate) surrounding the phosphate particulates in the composites leads to a shielding of the phosphate particles, and consequently to a higher element ratio incorporated in the solid phase compared with mineral phosphate.

Polymer composites have been used increasingly in building constructions, in the automotive industry and in aerospace technology. Polymeric materials are able to compete with conventional materials in most industrial fields [4–6]. Probably the use of polymer-phosphate composites in the storage of nuclear waste has the disadvantage of possible polymer degradation by high doses. Nevertheless, polymer composites can find applications in the solidification and/or treatment of low radioactive waste and short-lived isotopes.

The present study reports the preparation of mineral phosphate-polystyrene and poly(methyl styrene)-phosphate composites using gamma radiation, the characterization of the composites, and its ability to retain cesium and strontium in the solid phase, by keeping retention ratios of other elements in the same phase (e.g. lanthanides and actinides) as high as possible.

The use of styrene and methyl styrene has two advantages in comparison with methyl acrylate: the nucleophile properties of the styrene ring can lead to building of stable complexes with positive metal ions, which can increase the ratio of element ions trapped in the solid phase. Also the dose, at which possible polymer degradation occurs, is higher than that for poly(methyl acrylate), which means a long term stability by high-radioactive wastes.

Materials and methods

The phosphate samples were collected from the Khnefies area. The Syrian phosphate has been analyzed in many works and its main content is calcium phosphate (mineral composition: P_2O_5: 29%, CaO: 50%, MgO: 1.2%, Al_2O_3: 0.13%, Fe_2O_3: 0.2%, SiO_2: 3.1%; elemental composition: Sr: 1570 ppm, Ba: 522 ppm, V: 125 ppm, Ni: 23 ppm, Co: 8.4 ppm, Cr: 105 ppm, Zn: 123 ppm, Cu: 16 ppm, Sc: 3 ppm, U: 100 ppm) [1, 2, 10, 17]. The phosphate mineral was milled and sieved. Samples with a diameter of 0.212–0.4 mm were used in all experiments.

The water sample was taken from the Loiuze borehole from the phosphate area. The anion concentrations were determined using high-performance liquid chromatography (HPLC) technique (F^-: 15 ± 0.007, Cl^-: 159.3 ± 0.4, Br^-: 0.56 ± 0.01, NO_3^-: 0.76 ± 0.44, PO_4^{-3}: < 0.25, SO_4^{-2}: 149 ± 1 all in mg/l) [7], and the elemental composition using instrumental neutron activation analysis (Al: 162 ± 4, As: 1.5 ± 0.5, Ba: 154 ± 5, Br: 30 ± 0.1, Ca: 73377 ± 4131, Ce: 1.1 ±

0.06, Cr: 0.188 ± 0.048, Fe: 7 ± 2, Mg: 18505 ± 503, Na: 88710 ± 310, Rb: 1 ± 0.07, Nb: 3.3 ± 0.02, Se: 4.5 ± 0.04, Sr: 1279 ± 9, Th: 0.01 ± 0.001, U: 3.7 ± 0.3, Zn: 24.1 ± 0.5 all in μg/l) [7]. The main characteristics of the aqueous phase were also measured (pH: 8.054, conductivity: 0.00127 S·m^{-1}, EH: – 0.514, density: 1.0046, total dissolved solids (TDS): 613 mg/l) [7].

From these analyses, it is to notify that the pH is near neutral, the redox conditions are normal and the concentration of complexing anions (e.g. phosphate) is very low [7, 12]. The concentration of calcium and sodium is very high, which can have a large effect on the element distribution, because these elements play the role of concurrent elements in the behavior of cesium and strontium.

A certain volume (about 10 μL) of the radionuclides ^{137}Cs, ^{152}Eu, ^{238}U, and ^{85}Sr was added to 0.5 g of phosphate. Then, 0.5 mL (≈ 0.7 g) of styrene or methyl styrene were added. The monomer/powder/mixtures were filled up in polyethylene tubes (inner diameter ca. 2.3 cm, length ca. 3 cm) and then subjected to a ^{60}Co γ-irradiation facility (Russian type: ROBO; nominal activity 666.10^{13} Bq). The irradiation was carried out at room temperature and a dose rate of 10 kGy/h to different doses.

The prepared composite samples (≈ 1 g), which have the described shape of used polyethylene tubes, were brought then into contact with the groundwater (5 ml) under ambient conditions. After a certain time, the phases were separated. The element ratios of Eu, Sr, and Cs were determined using γ-spectrometry (HPGe-Detector, 60% Eff., full width at half maximum (FWHM) = 0.998 at 122 keV and 1.88 at 1332 keV, Canberra 35 plus). The uncertainties of all γ-measurements were estimated as about 5%. For the determination of the element ratio of uranium G-M-Fluorometer was used (Advanced Technical Services GmbH, Switzerland). Uranium was determined in the used solution before the addition to the phosphate and in the water phase after phase separation. ^{137}Cs was taken from an IAEA-standard-solution. ^{152}Eu and ^{85}Sr were produced by irradiation of their nitrates with a neutron flux of 10^{11} cm^{-2}·s^{-1}. Uranium nitrate was obtained from Merck.

The element ratios in the solid phase were calculated according to the following equation:

$$D_s = (A_s/(A_w + A_s))*100 = C_s/C_0*100$$

where D_s is the element ratio in the solid phase; A_w is the activity of the liquid phase after phase separation; A_s is the activity of the solid phase after phase separation; C_s is the element concentration in the solid phase after phase separation, and C_0 is the initial element concentration.

The pH value was changed using LiOH and $HClO_4$ solutions, only in the pH-dependent experiments. Calcium concentrations were changed using its nitrates only in the experiments of concurrent elements.

A thermogravimetric analyzer (Mettler, TG50), and a differential scanning calorimeter (Setaram, DSC131) have been used to determine some physicochemical properties of the prepared samples, and were described previously [7].
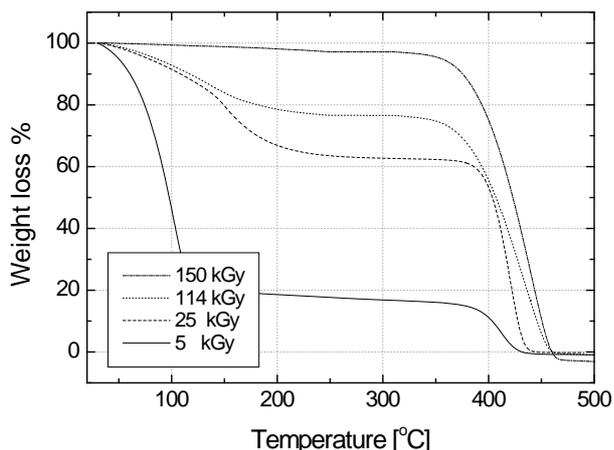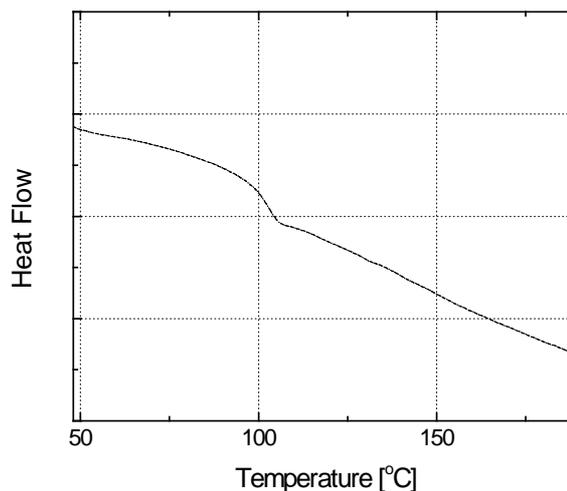
Fig. 1. TGA thermograms of polystyrene irradiated at different doses.

Results and discussion

Thermogravimetry

The conversion of the polymerization has been determined from thermogravimetrical spectra of the samples. Figure 1 represents the typical TGA thermograms of styrene conversion into polystyrene as an example with respect to irradiation dose. The first step in the thermogram corresponds to the evaporation of the unpolymerized monomer, and the second step is assigned to the decomposition of the formed polystyrene. It can be seen that the amount of monomer decreases, and the amount of formed polymer increases with increasing irradiation dose, what is due to the higher radical concentration induced by increased applied dose. Similar behavior had

Fig. 2. DSC thermogram of polystyrene prepared using an irradiation dose of 150 kGy.

been observed for the conversion of methyl styrene into poly(methyl styrene).

Glass transition temperature

Figure 2 represents a DSC thermogram of polystyrene prepared at an irradiation dose of 150 kGy. A glass transition region can be observed around 102°C.

Contact time

Figure 3 shows the element ratios in the aqueous phase as a function of the contact time of the phases. The time
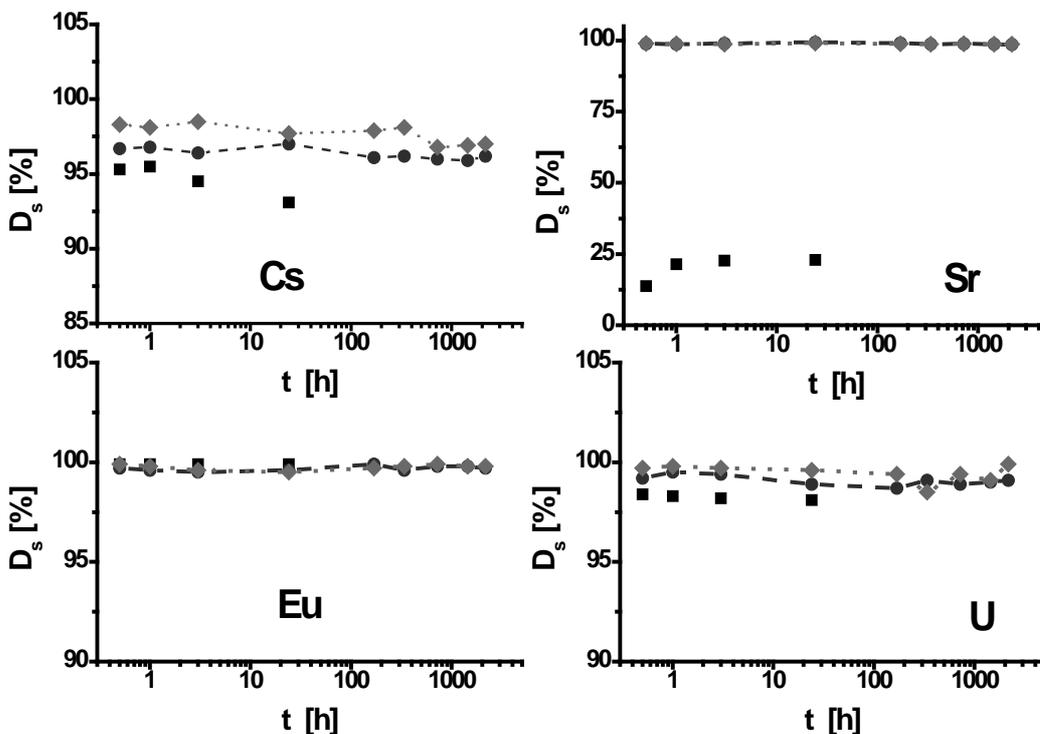
Fig. 3. Fraction of Cs, Eu, Sr and U in the solid phase as a function of contact time (■ – mineral phosphate [12]; ● – phosphate-polystyrene composite; ♦ – phosphate-poly(methyl styrene) composite), weight of solid phase 1 g, volume of aqueous phase 5 ml, pH = 8.
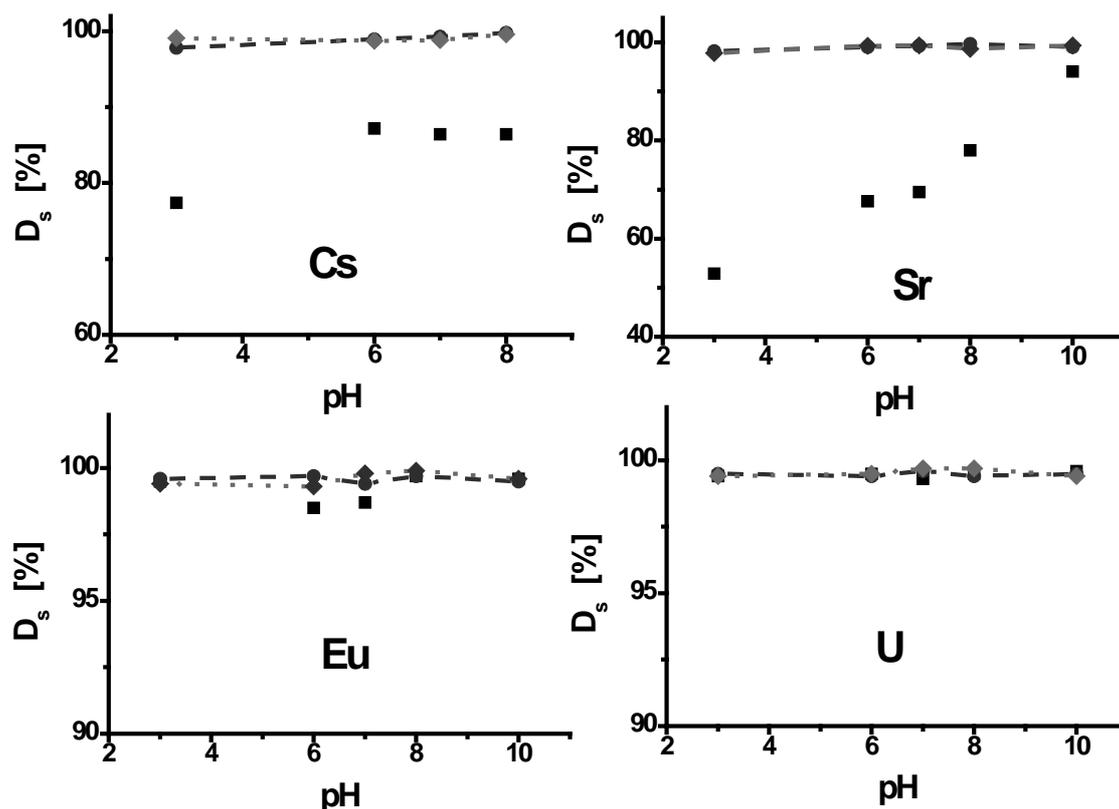
Fig. 4. Fraction of Cs, Eu, Sr, and U in the solid phase in equilibrium with a solution with different initial pHs (■ – mineral phosphate [12]; ● – phosphate-polystyrene composite; ♦ – phosphate-poly(methyl styrene) composite), $t = 24$ h, weight of solid phase 1 g, volume of aqueous phase 5 ml.

required to reach the equilibrium by cesium, uranium and europium is less than one hour. Strontium needs about 24 h to reach its equilibrium. As mentioned before the squares represent the adsorption on mineral phosphate from an earlier work [12]. Adsorption and migration by mineral phosphate, in the absence of the polymer, give the same element ratio in equilibrium, which is not the case by the composite. All other experiments were done after the equilibrium time, which make comparison of the results (phosphate vs. composite) reasonable. Actually, this comparison is only a comparison of results. The mechanisms of both processes are different, due to the different specific areas of phosphate powder and uncrushed composite and due to the difference in hydrophilic/hydrophobic behavior of composite and phosphate.

We can observe an effect of coverage of the phosphate with the polymer, which prevents the migration from the solid to the aqueous phase. This effect is large by strontium in comparison with cesium, europium and uranium, due to their high element ratio in the solid phase in the phosphate experiments.

Effect of pH

Usually, the effect of pH in such a system could be a result of three possible changes: a) changes in the solid phase such as protonation or deprotonation of functional groups, solubility and formation of mono- or polynuclear hydroxo- or phosphate complexes, b) changes in the aqueous phase such as changes of species and charges

of dissolved cations and anions, c) changes resulted from the changes in the solid and aqueous phases such as a change of potential between the solid and the aqueous phase and electrostatic attraction or repulsion between charged hydrous and elemental species [8, 14, 16].

In our case, the phosphate containing the radioisotopes is surrounded by the polymer. As a result, the element ratios of cesium and europium do not show big variations as a function of pH (Fig. 4). The effect of pH is very low and can be neglected by the use of the composite, which gives an additional advantage in comparison with mineral phosphate.

Effect of concurrent elements

Calcium has the highest element concentration in the groundwater samples. The concentration of sodium is also very high. For this reason, calcium was chosen to study the effect of concurrent elements on the distribution of the elements in the phases.

Figure 5 shows the effect of calcium concentration on the distribution of cesium and strontium, europium and uranium, respectively. The effect of calcium concentration is very strong in the case of mineral phosphate, especially on the distribution of strontium.

The increasing of calcium concentration leads at its high concentrations to the exchange between calcium and strontium in the solid phase and to lowering of strontium concentration in the solid phase. The effect can be neglected by using the composite, due to blocking the exchange process by the covering polymer.
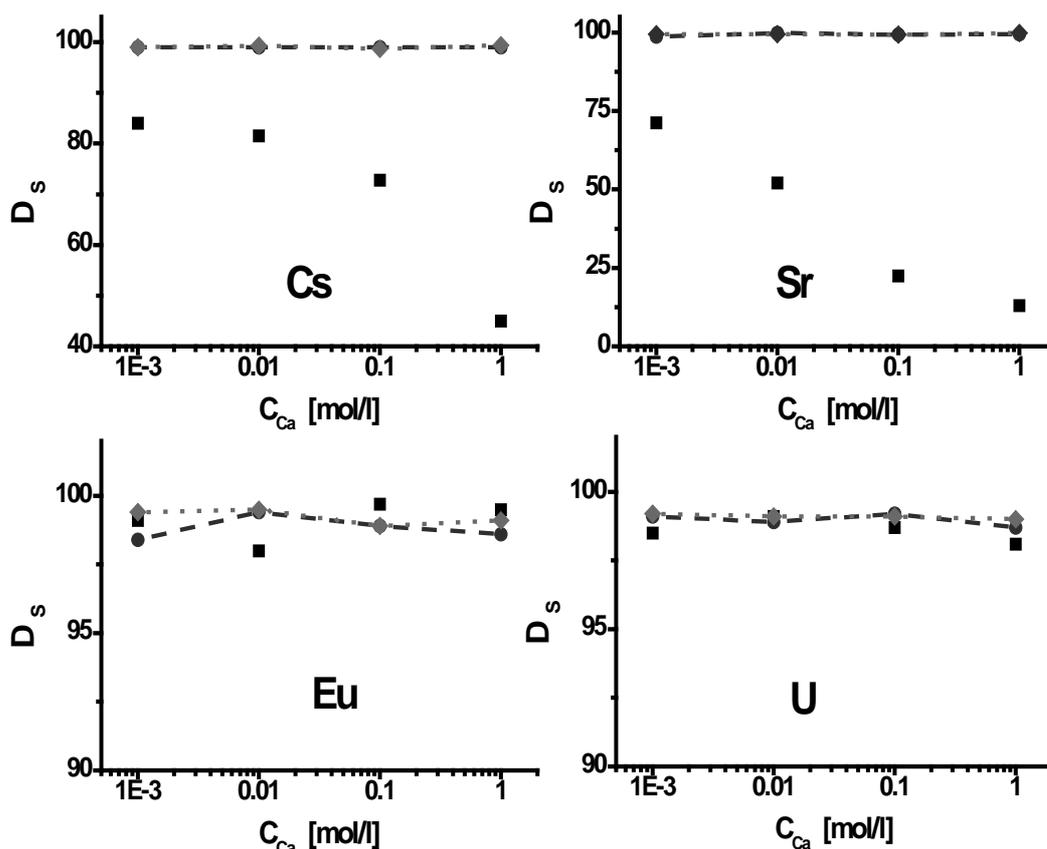
Fig. 5. Fraction of Cs, Eu, Sr, and U in the solid phase in equilibrium with a solution with different initial calcium concentrations (■ – mineral phosphate [12]; ● – phosphate-polystyrene composite; ♦ – phosphate-poly(methyl styrene) composite), $t = 24$ h, weight of solid phase 1 g, volume of aqueous phase 5 ml.

Conclusion

In this study, polystyrene-phosphate and poly(methyl styrene)-phosphate composites have been prepared using gamma radiation. The conversion of the polymerization reaction and the glass transition temperature were determined from TGA thermograms and DSC spectra, respectively. The presence of polymers surrounding the phosphate particulates leads to a shielding of the phosphate particles, and consequently to a higher element ratio incorporated in the solid phase compared with mineral phosphate. These results suggest that such polymer composite systems could be considered for using as storage containers for radioactive waste of the studied radionuclides by low radiation doses.

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