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MAGNETIC SORBENT FOR SOIL REMEDIATION—A WASTE FOR WASTE TREATMENT

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ABSTRACT

The possibility of decontaminating arable soil, forest soil, and gley soil, artificially contaminated by solutions of cesium-137, strontium-85, and europium-152, by contact in common suspension with magnetic residues of leached nickel ores (SOR) from the former Sered hydrometallurgical plant and its magnetic separation was demonstrated. More than 60–98% of cesium and strontium took part in the exchange between the soil and the magnetic sorbent and could be efficiently removed at sorbent mass to soil mass ratio as large as 5. Freundlich sorption isotherms were used for the evaluation of the driving forces of the transfer process. Actual soil remediation depends on the possibility of

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recycling used SOR: the speciation of sorbate indicates that the retention of strontium takes place in an exchangeable form but that of cesium and europium manifests through a more strong binding to the oxide component of SOR.

Key Words: Sorbent; Magnetic separation; Soil decontamination and remediation; Radiocesium; Radioactive contamination

INTRODUCTION

Separation of contaminants from suspensions and microheterogeneous (colloidal) systems is always connected with certain operational difficulties, such as interfacial mass transfer mechanism and phase separation. When other solid particles are present in the waste, the separation of the solid sorbent becomes difficult. This can be overcome by applying magnetic particles for adsorption followed by their selective separation in an external magnetic field.

At the former Sered (Slovakia) hydrometallurgical plant, there is a pile of six million tons of residues of leached iron–nickel laterite ores which itself presents a local environmental problem because of the resulting spread of the so-called black dusts, and the chromium contamination of underground waters. However, the waste is easily suspended and can be used in the sorbent-in-pulp separations for the removal of radionuclides and toxic elements from suspensions of contaminated material.[1–3]

In addition, soil decontamination without destroying the biological value of the soil is a specific problem.[4] For the soil remediation process these five basic steps should be considered: (i) suspension of soil in a suitable aqueous phase, (ii) contact of suspension with magnetic sorbent, (iii) magnetic separation of sorbent from the soil suspension, (iv) recovery of soil from suspending aqueous phase, and (v) recycling of used magnetic sorbent.

EXPERIMENTAL

Magnetic Sorbent

The raw material arose from alkaline high-pressure leaching of iron–nickel laterite ores: the Sered hydrometallurgical plant ores' residues (SOR) are finely powdered, the fraction below 20 μm represents about 70% of the material, and 16% is less than 2 μm. The chemical composition of SOR is given in Table 1.

The principal components of SOR consist of synthetic magnetite which was formed by the annealing of goethite or hematite of the original ore, and

Table 1. Chemical Composition of the Sered Hydrometallurgical Plant Ores Residues

Fe (various forms)	49–52 (wt%)
Fe_2O_3	42–43 (wt%)
FeO	27–28 (wt%)
Fe_{met}	0.25–0.35 (wt%)
SiO_2	8–10 (wt%)
Al_2O_3	4–6 (wt%)
CaO	3–4.5 (wt%)
MgO	2–3 (wt%)
Cr_2O_3	3.4–3.8 (wt%)
P_2O_5	0.06–0.18 (wt%)
H_2O	15–18 (wt%)
MnO, K_2O, SO_3, Ni, Cu, V, TiO_2, Na_2O	Trace levels

the silicate phase of dried silicate aggregates, both phases having a favorable microporous structure.

In preliminary experiments, the sorption properties of SOR were enhanced by creating a film of insoluble ferrocyanates, which are strong sorption agents for cesium,[5,6] by mechano-chemical activation in wet mills.[7]

In the present experiments, the magnetic sorbent (50 g) was preconditioned through a 7-day contact with 50 mL of 0.1 M sodium acetate–0.1 M acetic acid (1:1) buffer, washed by deionized water, and dried in air on a glass filter.

Radionuclides

Radiotracer cesium-137 and europium-152 were products of Polatom (Otwock-Świerk, Poland), strontium-85 was of Dupont de Nemours (BrusselZs). A single-channel scintillation detector NP-420 (Hungary) was used for gamma activity measurement.

Soils

Arable soil (marked MP1/1) and forest soil (MP3/1) from near surface, and also gley soil (MP3/3) from the 20–25 cm depth of the ground level were artificially contaminated by 24-hr contact with cesium-137, strontium-85, and europium-152 solutions at the isotopic carrier concentration of $10^{-4}\,M$. Montmorillonite K-10 (Aldrich) was used as a reference sorbent.

Speciation

Speciation of sorbed radionuclides was performed either by sequential leaching according to the Tessier scheme,[8] or by the scheme of the European Community Bureau of Reference—BCR.[9] The sequential leaching speciation schemes are given in Table 2.

Phase Contact and Separation

Sorbents (0.1–0.5 g) were contacted with radioactive-spiked or leaching solutions in 7 mL polypropylene tubes in a thermostated head-over-head shaker for 2 hr, unless a different contact time is indicated. Aqueous and sorbent phases were separated by centrifugation at 3000 rpm. If necessary, in double suspensions of soil and magnetic sorbent, the latter was removed from the suspension by a permanent magnetic field.

Sorption Isotherms

Isotherms were established at the sorption of radionuclides from KCl solutions of 0.001 M with initial carrier concentrations of 10^{-6}–5×10^{-2} mol dm^{-3}. The equilibrium concentration, c, of sorbate in solution was calculated from the initial concentration, c_0, of sorbate in solution, and initial and equilibrium specific (volume) activity of solution a_0 and a, respectively,

$$c = ac_0/a_0 \tag{1}$$

Sorbed amount Γ was obtained from mass balance of sorbate as

$$\Gamma = (c_0 - c)V/m = c_0(1 - a/a_0)V/m \tag{2}$$

where V is the volume of the solution and m is the mass of sorbent. Then, the distribution ratio was found as

$$K_\mathrm{d} = \Gamma/c \tag{3}$$

Sorption fraction in percentage is

$$R = \frac{a_0 - a}{a_0}100 = \left(1 - \frac{a}{a_0}\right)100 \tag{4}$$

Table 2. The Sequential Leaching Speciation Schemes Applied for 0.1 g Samples of Solid (Ac = Acetyl)

Tessier Scheme		BCR Scheme	
Fraction	Leaching Solution	Fraction	Leaching Solution
(1)	4 mL 1 *M* $MgCl_2$ at room temperature, contact 10 min	(1)	4 mL 0.11 *M* HAc at room temperature, contact 16 hr
(2)	4 mL 1 *M* (Na,H)Ac pH 4, contact 5 hr	(2)	4 mL 0.1 *M* $NH_2OH \cdot HCl$ (pH 2) at room temperature, 16 hr
(3)	4 mL 0.04 *M* $NH_2OH \cdot HCl$ in 25% HAc at 96°C, 6 hr	(3)	1 mL 30% H_2O_2 pH 2 (HNO_3) at 85°C for 5 hr, and after centrifugation 5 mL 3.2 *M* NH_4OAc in 20% HNO_3 added to solid phase and left overnight
(4)	1 mL 30% H_2O_2, pH 2 (HNO_3) at 85°C for 5 hr, after centrifugation 5 mL 3.2 *M* NH_4OAc in 20% HNO_3 added and left overnight	(4)	Nonleachable residue
(5)	4 mL HF + $HClO_4$ (5:1), 1 hr		
(6)	Nonleachable residue		

Sorption Kinetics

Sorption dynamics was followed by sampling of the aqueous phase during its continuous contact with sorbent in intervals 0, 0.25, 0.5, 1, 1.5, 2, 4, 6, 8, 24, 48, and 72 hr. Considering x_s to be the fraction $(0 < x < 1)$ of the sorbent connected with the slow kinetics of radionuclide adsorption, sorption kinetics data were modeled by pseudo-first-order kinetics on two different sorption sites,

$$R = R_\infty[x_s(1 - e^{-k_s t}) + (1 - x_s)(1 - e^{-k_r t})] \tag{5}$$

where R is the percentage of sorption (R_∞ is its value at true equilibrium) and k_s and k_r are the rate constants of fast and slow sorption, respectively.

Because of sampling, the volume of aqueous phase decreases after each withdrawal of the ith aliquot of aqueous phase of volume v and activity A_i. Therefore, the sorption fraction after the ith sampling, R_i, was evaluated from the total activity balance as follows:

$$R_i = \left[1 - \frac{1}{a_0 V_0}\left(A_i[V_0/v - (i-1)] + \sum_{i=1}^{i-1} A_i\right)\right]100 \tag{6}$$

All calculations and graphics were performed using SigmaPlot® 4.0 software (SPSS, Chicago, IL).

RESULTS AND DISCUSSION

Because of the presence of nickel, cobalt, and vanadium in SOR, the sorption properties towards cesium can be substantially enhanced[1,3] by wet grinding of SOR paste with 3–15% solutions of ferrocyanide. The cesium sorption increase was higher than it should correspond to the decrease in mean size of SOR particles, and best results were obtained by attrition milling (Table 3).

Table 3. Activation of SOR by Wet Grinding with Ferrocyanide Solutions

No.	Material (SOR) Activation	Distribution Ratio of Cesium in 0.001 *M* KCl (mL/g)
1	None	50 ± 4
2	5% $K_4Fe(CN)_6 \cdot 3H_2O$, vibrating mill/2 min	681 ± 44
3	5% $K_4Fe(CN)_6 \cdot 3H_2O$, ball mill/15 min	77 ± 6
4	5% $K_4Fe(CN)_6 \cdot 3H_2O$, attrition mill/15 min	814 ± 54

Investigation of specific leaching of the radionuclides after sorption on magnetic sorbents indicates a striking difference in the behavior of the radionuclides. While the major fraction of strontium is in an exchangeable form, both cesium and europium are predominantly bound by the metal (iron, manganese, etc.) oxide component of SOR (Tables 4 and 5).

Kinetics of the sorption on SOR has a complex character and their assessment is given later. Pseudo-equilibrium was achieved after 2 hr of contact (Fig. 1), which was taken as a standard time, from the view of practically available contact time at technological conditions, for obtaining relevant sorption distribution data.

The individual sorption isotherms of Cs, Sr, and Eu on the sorbents investigated were fitted to a Freundlich type isotherm (Figs. 2–4):

$$\Gamma_i = k_i c_i^{b_i} \tag{7}$$

The results fitting parameters are given in Table 6.

In two-solid suspensions, each contact stage of soil (phase I) and magnetic sorbent (phase II) leads to pollutant distribution between the intermediate aqueous phase and the two sorbents, which is characterized by a pair of sorption isotherms with common equilibrium concentration of sorbate in the aqueous phase. When both particular isotherms are of Freundlich type—Eq. (7)—i.e., mutual equilibrium is considered:

$$\Gamma_{\text{soil}} = k_1 c^{b_1} \quad | \quad c \quad | \quad \Gamma_{\text{SOR}} = k_2 c^{b_2}$$

their ratio which expresses maximal capability of transfer also follows the function

$$Q_{\text{c}} = \frac{k_2 c^{b_2}}{k_1 c^{b_1}} = k c^{b} \tag{8}$$

$(k = k_2/k_1, b = b_2 - b_1)$ dependence in terms of the equilibrium concentration c in the aqueous phase.

Table 4. Sequential Leaching Speciation of the Radionuclides Sorbed on Magnetic Sorbent by Tessier Scheme

Fraction	Cs	Eu
(1) Exchangeable	22.8 ± 1.2	3.1 ± 0.01
(2) Carbonates	30.2 ± 2.2	10.7 ± 2.7
(3) Oxides	29.1 ± 0.9	78.7 ± 0.8
(4) Organic and sulfidic	15.2 ± 1.6	4.9 ± 0.2
(5) Silicates	2.2 ± 0.3	0.04 ± 0.02
(6) Nonleachable residue	0.83 ± 0.12	0.1

Table 5. Sequential Leaching Speciation of the Radionuclides Sorbed on Magnetic Sorbent by BCR Scheme

	Leached Fraction (%)		
Fraction	Cs	Sr	Eu
(1) Exchangeable	14.0 ± 4.0	90.2 ± 3.7	18.2 ± 1.3
(2) Oxides	78 ± 9.1	9.1 ± 0.1	71.1 ± 1.0
(3) Organic and sulfidic	5.5 ± 0.2	0.62 ± 0.05	7.5 ± 0.5
(4) Nonleachable residue	0.41 ± 0.02	0.13 ± 0.02	0.80 ± 0.04

The relative sorption ability Q is the main parameter of driving force that controls the transfer from soil to sorbent. At varying composition of the aqueous phase, the distribution coefficients K_d will change in the same direction, and when $b = b_1 - b_2 \approx 0$ ($b = 0$ corresponds to the ideal linear sorption isotherms) Q remains more or less constant. If $b < 0$ then the derivative of Q with respect to c, i.e.,

$$\frac{\mathrm{d}Q}{\mathrm{d}c} = bkc^{b-1} \tag{9}$$

becomes negative (i.e., Q increases with decreasing equilibrium concentration in the solution), and a weak desorption agent can be applied in the suspending

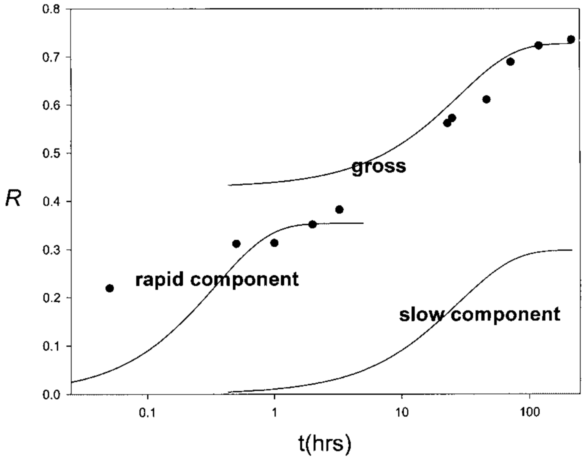

Figure 1. Kinetics of sorption of cesium on SOR: the gross, rapid, and slow sorption fractions as a function of contact time t.

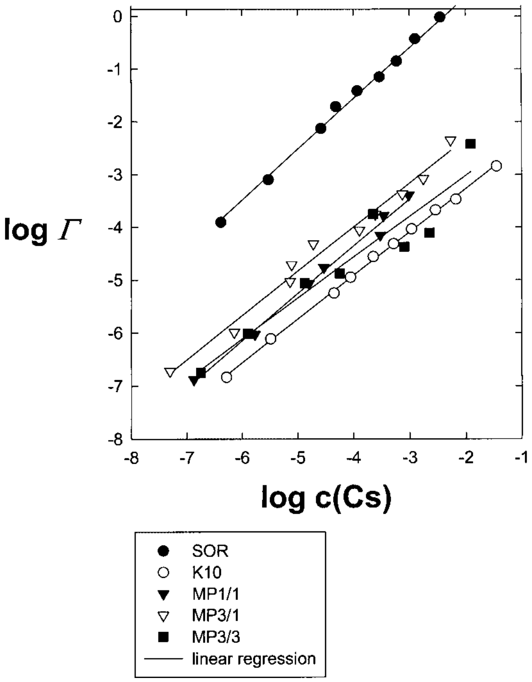

Figure 2. Freundlich sorption isotherm of cesium—Eq. (1)—in bilogarithmic coordinates Γ vs. equilibrium concentration of cesium c(Cs). For isotherm parameters see Table 6.

aqueous phase. This, in principle, enables the application of very mild desorption agents, minimally destroying soil structure and its biological value, in suspending aqueous solutions for soil decontamination. Unfortunately, with respect to one of the most critical radioactive contaminants, radiocesium, $\mathrm{d}Q/\mathrm{d}c > 0$ for all the soils under investigation (Table 7), and Q reaches only a value of 2 at the equilibrium concentration of cesium (or isomorphous ammonium ion) about $c = 0.003\,\mathrm{mol\,dm^{-3}}$ (Fig. 5). It should be emphasized in this respect that the sorption isotherms were estimated in $0.001\,M$ KCl solutions, i.e., at the concentration of potassium which can be expected in real soil suspensions.

However, the mass transfer resistance in the aqueous phase is higher at larger distribution coefficients. In reality, the dynamics of sorption of the radionuclides proceeds as a comparatively rapid sorption completed within a few hours and the slow process approaching equilibrium only after several days of contact (Table 8).

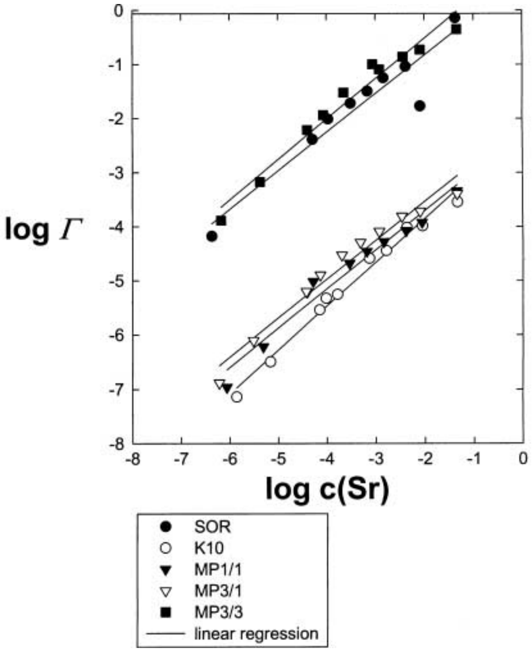

Figure 3. Freundlich sorption isotherm of strontium—Eq. (1)—in bilogarithmic coordinates Γ vs. equilibrium concentration of cesium c(Sr). For isotherm parameters see Table 6.

After one separation, the fraction of reversibly sorbed pollutant retained in soil can be derived as in other three-phase systems

$$R = \frac{R_0}{1 + R_0 Q r} \tag{10}$$

where r is the magnetic sorbent-to-soil mass ratio and R_0 is the fraction of pollutant bound by the soil in the absence of the magnetic sorbent ($r = 0$).

When the distribution coefficients of the pollutant on the soil and the magnetic sorbent are of the same order of magnitude, Q is close to 1, and decontamination is insufficient unless the ratio of magnetic sorbent and soil (r) is extremely high. In the last case, the effective decontamination can be achieved by repeated n contacts with a fresh (or recycled) sorbent. Then, the fraction of exchangeable pollutant retained by contaminated soil is

$$R_n = R^n \tag{11}$$

However, as a rule, the soil also contains a practically irreversibly absorbed (fixed, nonexchangeable) fraction of pollutant, R_{fix}, as it is a typical case for

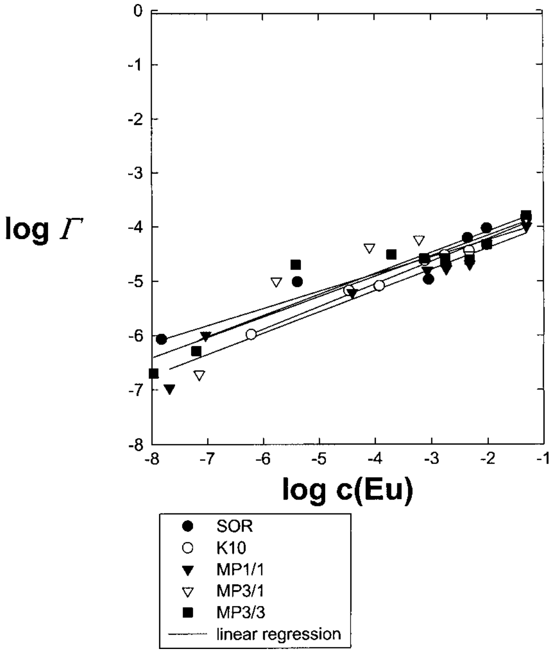

Figure 4. Freundlich sorption isotherm of europium—Eq. (1)—in bilogarithmic coordinates Γ vs. equilibrium concentration of cesium c(Eu). For isotherm parameters see Table 6.

cesium adsorption by clay minerals.[4] Now, the effective value (R_{ef}) of total reachable residual contamination after n contacts is:

$$(R_{\mathrm{ef}})_n = R_{\mathrm{fix}} + (1 - R_{\mathrm{fix}})R^n \tag{12}$$

i.e., it is adequately higher as compared with fully exchangeable pollutant.

The decontamination factor is found from the relation of initial and resulting specific activities of soil, a_0 and a, respectively. It can be defined as a ratio (DF_1) between the removed radionuclide and the removable (exchangeable) radionuclide but still retained by the soil

$$\mathrm{DF}_1 = \frac{1 - R}{R - R_{\mathrm{fix}}} \tag{13}$$

or else as a ratio between removed radionuclide and the total nonremoved radionuclide,

$$\mathrm{DF}_2 = \frac{1 - R}{R} \tag{14}$$

Table 6. Freundlich Isotherm Parameters of Radionuclides Sorption from 0.001 *M* KCl

	Cs		Sr		Eu	
Sorbent	k (mol^{1-n} dm^{3n} kg^{-1})	b	k (mol^{1-n} dm^{3n} kg^{-1})	b	k (mol^{1-n} dm^{3n} kg^{-1})	b
K-10	24.0 ± 0.4	0.82 ± 0.01	5.84 ± 0.03	0.81 ± 0.04	0.41 ± 0.07	0.42 ± 0.03
MP1/1	155.7 ± 0.2	0.90 ± 0.03	5.57 ± 0.17	0.73 ± 0.05	0.25 ± 0.20	0.39 ± 0.04
MP3/1	221.5 ± 0.4	0.84 ± 0.04	8.07 ± 0.18	0.72 ± 0.05	0.49 ± 0.35	0.39 ± 0.09
MP3/3	34.3 ± 0.5	0.77 ± 0.10	9.59 ± 0.19	0.75 ± 0.05	0.15 ± 0.24	0.38 ± 0.05
SOR[a]	181.3 ± 0.1	0.95 ± 0.02	3.98 ± 0.33	0.71 ± 0.09	0.20 ± 0.19	0.32 ± 0.05
SOR[b]	185.5 ± 0.1	0.96 ± 0.02	—	—	—	—
SOR[c]	190.0 ± 0.2	0.96 ± 0.03	—	—	—	—

[a] Sorption 2 hr.

[b] Sorption 14 days.

[c] Desorption by 0.001 *M* NH_4Cl.

Table 7. Parameter d*Q*/d*c* of the Radionuclide Transfer from Soil to Magnetic Sorbent at the Contaminant Concentration in Aqueous Phase $10^{-6}\,M$

Soil	MP1/1	MP3/1	MP3/3
Cs	2.7×10^4	2.0×10^4	8.5×10^4
Sr	-1.1×10^4	-3.2×10^4	-2.4×10^4
Eu	-1.8×10^5	-8.1×10^4	-2.0×10^5

If the value of R_{fix} is obtained from separate experiments, e.g., by sequential leaching,[10] an equation which is linear towards the ratio r,

$$\frac{R_0 + R_{\text{fix}}(1 - R_0) - R_{\text{ef}}}{R_0(R_{\text{ef}} - R_{\text{fix}})} = Qr \tag{15}$$

can be used for a one-stage contact of soil suspension with magnetic sorbent ($n = 1$). The fit of Eq. (12) to experimental data, i.e., the linearity of the left side

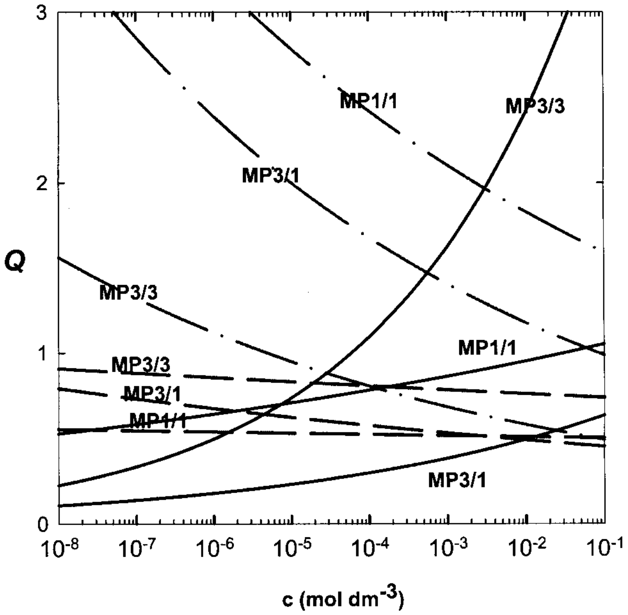

Figure 5. Maximal capability of transfer from soil to magnetic sorbent expressed as a function[8] of equilibrium concentration of various ions in aqueous phase: (—) Cs^+, (———) Sr^{2+}, (—·—·—) Eu^{3+}.

Table 8. Rate Constants of Rapid (k_r) and Slow (k_s) Sorption on the SOR—Eq. (5)

	k_r (hr^{-1})	k_s (hr^{-1})	x_s
Cs^+	23 ± 4	0.04 ± 0.90	0.064 ± 0.004
Sr^{2+}	1.4 ± 1.7	0.011 ± 0.001	0.904 ± 0.052
Eu^{3+}	2.7 ± 0.9	0.010 ± 0.006	0.560 ± 0.013

of Eq. (12) vs. r, heavily depends on the R_{fix} value applied, and reliability of the accepted R_{fix} becomes significant.

Because R_0 is usually close to 1 for the majority of considered radionuclides, the last equation can be reduced to a form which can be used for a nonlinear regression treatment to obtain both the Q and R_{fix} values at variable r:

$$\frac{1 - R_{ef}}{R_{ef} - R_{fix}} = Qr \tag{16}$$

When R_{fix} is neglected ($R_0 = 1$, $R_{fix} \ll R_{ef}$), a straight-line plot of R_{ef} vs. r is obtained

$$\frac{1 - R_{ef}}{R_{ef}} = Qr \tag{17}$$

where R_{ef} is obtained experimentally as a fraction of pollutant retained by the soil at a one-stage contact with the magnetic sorbent (Figs. 6 and 7). However, this fitting is sensitive towards estimation of the R_{fix} value and provides it only with a very large uncertainty (Table 7). Especially for cesium, zero values are improbable, and using the independent values of R_{fix} obtained from fraction leaching is much more reliable[10] (Table 9).

The humus content of soil exhibits significant influence on europium adsorption.[11] This means that for lanthanides and actinides, probably more efficient magnetic separation would be based on the polymer covered magnetite sorbent MAG*SEP,[12] but the decontamination from cesium is of particular interest for soils contaminated after the Chernobyl accident.[13–15] In addition, from Tables 3, 4, and 10, it can be concluded that 60–70% of cesium and above 98% of strontium can take part in the exchange between soil and SOR and the decontamination process can be efficiently performed.

Recycling of the used SOR is an open question, and this cycle should be thoroughly investigated if the overall feasibility of the sorption stage of the process is considered in future applications: at low Q values, huge amounts of fresh SOR should be required to reach effective soil decontamination. A combination with pyrometallurgical (plasma melting) of the resulting material comes into consideration as well.[16]

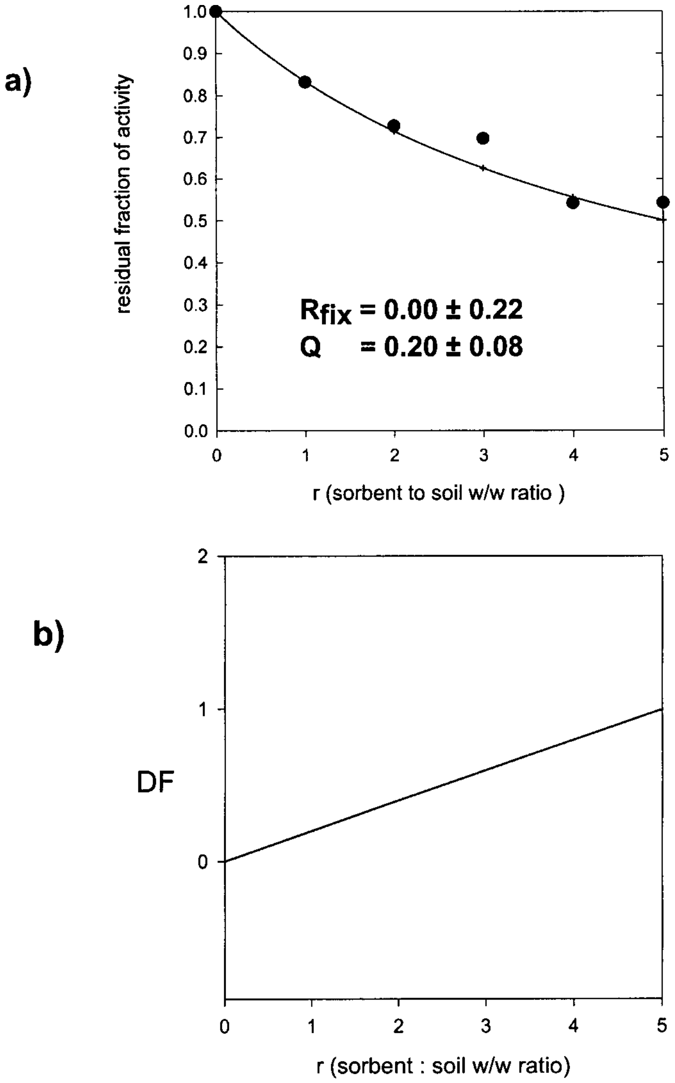

Figure 6. (a) Residual fraction of activity *R* of cesium in MP1/1 soil as a function of SOR to soil mass ratio. (b) Decontamination factors DF_1 and DF_2 (identical fit for exchangeable and total cesium).

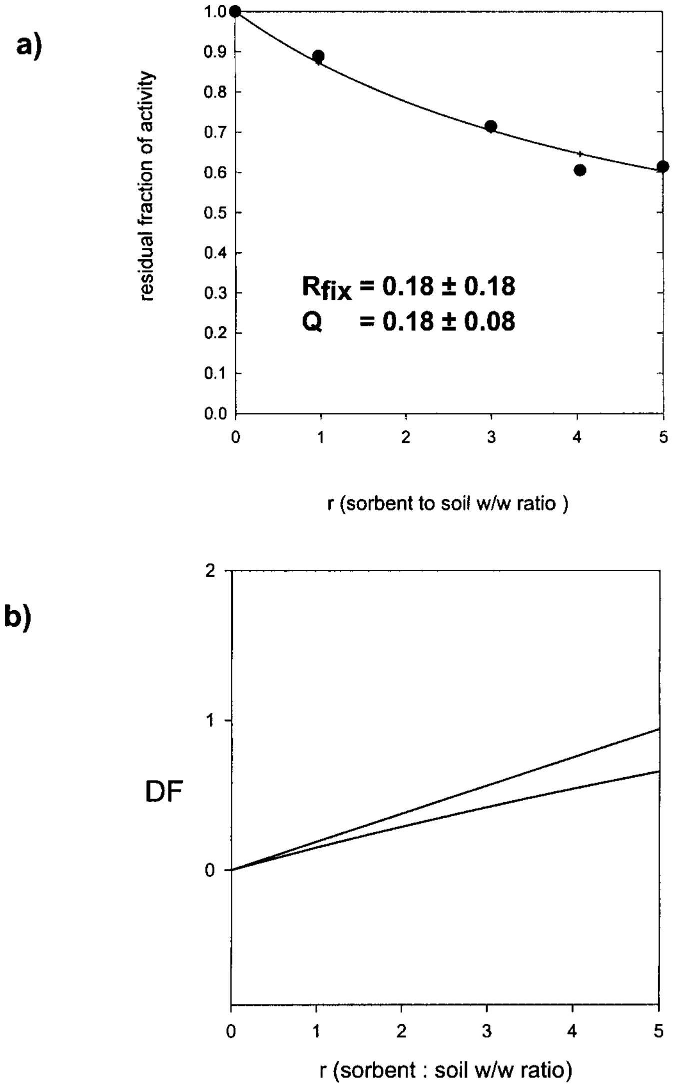

Figure 7. (a) Residual fraction of activity *R* of europium in MP3/3 soil as a function of SOR to soil mass ratio. (b) Decontamination factors DF_1 and DF_2 (upper line for easily exchangeable europium, lower line for total europium).

Table 9. Relative Distribution Factor Q, Nonexchangeable Fraction R_{fix}, and Efficient Decontamination Factors for the Soils Contacted for 2 hr at the SOR:Soil = 5:1 Ratio

	Q			R_{fix}			DF_1			DF_2		
Soil (Clay)	Cs	Sr	Eu	Cs	Sr	Eu	Cs	Sr	Eu	Cs	Sr	Eu
K-10	0.28	1.1	1.95	0 (?)	0.03	0.19	1.20	5.8	5.40	1.20	4.9	2.20
MP1/1	0.20	1.7	0.22	0 (?)	0.02	0 (?)	0.84	6.5	1.10	0.84	5.8	1.10
MP3/1	0.15	0.70	0.10	0 (?)	0.05	0.27	0.63	3.5	0.53	0.63	2.8	0.32
MP3/3	0.11	0.80	0.18	0 (?)	0.02	0.15	0.64	3.4	0.84	0.64	3.1	0.63

Table 10. The Fraction of Radionuclide Which Is Irreversibly Retained by Soils, as Obtained from Fitting of Eq. (13)

		R_{fix}		
Soil (Clay)	Humus Content (%)	Cs	Sr	Eu
Montmorillonite	0	0 ± 26	3 ± 2	20 ± 2
MP1/1	2.4	0 ± 22	2 ± 2	0 ± 28
MP3/1	8.3	0 ± 53	5 ± 8	2.7 ± 8.6
MP3/3	1.5	2 ± 38	2 ± 2	15 ± 10

CONCLUSIONS

The feasibility of soil or bottom sediment remediation by magnetic sorbents is demonstrated by laboratory experiments with the solids artificially contaminated by radiocesium, radiostrontium, and radioeuropium.

The sorption properties of leaching residues of the iron–nickel laterite ores from the Sered hydrometallurgical plant were investigated. Cesium and europium are bound by the oxide component of the magnetic sorbent, while strontium is absorbed by a slow ion-exchange mechanism.

At the mass ratio of magnetic sorbent to soil (the arable, forest, and gley soil) or clay 5:1 w/w in common suspension with soft desorption agents (0.001 *M* KCl), decontamination factors of 0.6–1.2 for cesium, 2.8–5.8 for strontium, and 0.3–2.2 for europium were observed. Though the decontamination factors are not high, the decontamination process proceeds at mild conditions and the biological value of soil can be preserved. Furthermore, the most mobile, and therefore most environmentally dangerous, exchangeable fraction of radionuclide is removed.

The leaching wastes from the Sered (Slovakia) hydrometallurgical plant represent a large stock of inexpensive, ready-to-use magnetic sorbent for the decontamination of soil or sediments in their common suspensions, followed by the magnetic separation and sorbent recycling.

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