

INTERPOLYELECROLYTE COMPLEXES AS A BARRIER TO RADIONUCLIDE MIGRATION WITHIN SOIL

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ABSTRACT

Natural phenomena can cause migration of radioactive fallout captured by topsoil. It is of crucial importance to lower the pace of this migration. The development of an immobilization technique will provide the time it takes for contaminated soil to be remedied sooner or later.

One of the ways is to create barriers based on water-insoluble high molecular compounds (HMC) in the soil bulk. Similar compounds based on interpolyelectrolyte complexes (IPEC) have been developed by VNIINM and MSU to immobilize radioactivity captured by Chernobyl accident-contaminated soils (1986-1993).

The IPEC treatment produces a soil-polymer protective coat 3-6 mm thick which tightly attach fine grains to each other by aggregation of small particles and by coagulation of soil colloids. This essentially decreases the wind and water erosion of small particles containing the radioactivity bulk. Besides, IPEC having free functional groups has been found to be able to form strong complexes with water soluble radionuclides species.

Thus, IPEC is a multi-functional product capable of immobilizing radioactive matters within topsoil by lowering both the water and wind erosion of small soil particles (macro transfer) and vertical migration into soil (micro transfer).

Among a variety of factors (filtration, heat transfer, diffusion of free and adsorbed ions, transport through colloids, capillaries and root systems, farming) the major one under routine environmental conditions is diffusion convection [1,2].

A qualitative migration mechanism study shows that the diffusion is primarily caused by adsorbed ions, solution within soil pores being a conductive medium [2].

The treatment with IPEC containing hydroxyl, carboxyl and amino groups [3,4] can decrease the radionuclides mobility to a great extent.

The ^{235}U and ^{90}Sr complexing with polyelectrolytes HYPAN and VPK-402 as well as the ^{137}Cs diffusion rate in quartz sand with and without IPEC present have been investigated.

METAL IONS - POLYELECTROLYTE COMPLEXING

A homogeneous water soluble triple system comprising - polycation (N,N-polymethyl-N,N-diallylammoniumchloride, VPK-402) - polyanion (hydrolyzed polyacrylonitrile, HYPAN) - low molecular electrolyte (basic salts or ammonites) is widely used as a polymeric binder for dispersed media. The starting components are high molecular polymers of high molecular mass ($M = 10^4 - 10^6$), which makes possible to study complexing with metal ions by ultrafiltration. A variety of membranes: a propylenic UPP, a polysulfonamidic UPM-P-450 and an acetatcelulosic AC-300 of smaller pore diameter were used for comparative research. A starting solution (a mixture of IPEC components, water and radionuclides) was poured into a UF unit and filtered through a membrane [5].

To have comparable results, the starting solution - permeate - concentrate volume ratio was kept constant throughout the study. The ratio is described in terms of the volume reduction factor, K_v , given by:

$$K_v = \frac{V_s}{V_p} \quad , \quad (1)$$

where V_s is the starting volume, l; V_p is the permeate volume, l.

The permeate is sampled and analyzed at $K=2$. Comparing the concentration of a component in a starting solution and in its permeate the membrane selectivity i.e. its ability to hold this component can be evaluated. The permeability of a membrane is calculated in terms of the permeate amount passed through it per unit time.

$$G = \frac{V_p}{ST} \quad (2)$$

where G is the membrane permeability, l/ m² h ; V_p is the permeate volume, l; S is the membrane operating surface, m² ; t is the time, h ;

$$Y = \frac{C_s - C_p}{C_s} * 100 \quad (3)$$

where Y is the membrane selectivity, % ; C_s and C_p are the concentration of a component to be analyzed in a starting solution and in its permeate.

HYPAN - RADIONUCLIDE INTERACTION

A water-soluble polyanion - hydrolyzed polyacrylonitrile (HYPAN) - was used as a complexing agent. The U-235 content was determined with a gamma-spectrometer equipped with a scintillation detector. The selectivity and permeability of membranes are given in Table 1.

Table 1
The selectivity and permeability of various membranes relative to ^{235}U
 $^{235}\text{U} : \text{HYPAN} = 1 : 10$

<i>Membrane type</i>	<i>C_s, mg/l</i>	<i>C_p, mg/l</i>	<i>Y, %</i>	<i>G, l/m² h</i>
UPP	24,92	0,43	98,1	63,0
UPM-P-450	25,12	1,21	95,7	110,2
AC -300	24,95	1,07	95,2	80,7

With HYPAN as a complexing agent, the U-235 selectivity is high for all membranes (95-98%), a polypropylenic membrane having the highest selectivity, Ac-300 the lowest one. The permeability is the worst for UPP (63.0 l/m² h) and the best for UPM-P-450 (110.2 l/m² h).

Table 2
The selectivity and permeability of various UF membranes
relative to Sr-90,
 $^{90}\text{Sr} - 4,17.10^{-7} \text{ Ci/l}$ **HYPAN 10 mg/l**

<i>Membrane type</i>	<i>C_s, Ci/l</i>	<i>C_p, Ci/l</i>	<i>Y, %</i>	<i>G, l/m² h</i>
UPP	$4,17.10^{-7}$	$5,29.10^{-9}$	98,7	44,1
UPM -p-450	$4,17.10^{-7}$	$1,08.10^{-9}$	97,4	229,3
Ac-300	$4,17.10^{-7}$	$5,52.10^{-9}$	98,2	88,2

The ^{90}Sr selectivity is found to be high for all membranes (98-99%) and somewhat higher for UPP. The permeability behavior is similar to that for ^{235}U . UPM-P-450 has the highest permeability and UPP the lowest.

VPK-402 - RADIONUCLIDE INTERACTION

A component of IPEC - N,N - dimethyl-N,N-diallylammonium chloride (VPK-402) - having a molecular mass of $3 \cdot 10^5$ was used as a complexing agent at the second stage of our research following the same procedure. The following working mixtures were used:

1. ^{235}U - - 25 mg/l; VPK-402 - 250 mg/l;
2. ^{90}Sr - - $3.81 \cdot 10^{-7}$ Ci/l; VPK-402 - 10 mg/l;

Table 3
The membrane selectivity when filtering solutions
containing VPK-402 and ^{235}U
 $^{238}\text{U} : \text{VPK-402} = 1 : 10$

<i>Membrane type</i>	<i>C_s, mg/l</i>	<i>C_p, mg/l</i>	<i>Y, %</i>	<i>G, l/m² h</i>
UPP	24,95	6,34	74,6	74,4
UPM -p-450	24,06	10,91	54,7	150,9
Ac-300	24,99	12,69	49,2	91,0

With VPK-402 as a complexing agent, the ^{235}U selectivity was 24-46% less than with HYPAH., UPP is of the highest selectivity (74.6%) while AC-300 is of the lowest one. The resulting data suggest the formation of strong complexes in the polyanionic polyelectrolyte - uranium system, the interaction being much less with VPK-402.

Table 4
The membrane selectivity when filtering solutions,
containing ^{90}Sr and VPK-402
 $\text{Sr}^{90} - 3,81 \cdot 10^{-7}$ Ci/l; VPK-402 - 10 mg/l

<i>Membrane type</i>	<i>C_s, Ci/l</i>	<i>C_p, Ci/l</i>	<i>Y, %</i>	<i>G, l/m² h</i>
UPP	$3,81 \cdot 10^{-7}$	$4,94 \cdot 10^{-9}$	98,7	60,3
UPM -p-450	$3,81 \cdot 10^{-7}$	$3,94 \cdot 10^{-9}$	98,9	208,5
Ac-300	$3,81 \cdot 10^{-7}$	$8,38 \cdot 10^{-9}$	97,8	74,0

It is evident from the table that the selectivity of ^{90}Sr is high (97-99%) for all membranes, especially for UPM-P-450. The data obtained indicate that ^{90}Sr can produce complexes of around the same dimension with both polyelectrolytes under study.

Table 5
Interaction of Sr with IPEC and its components

<i>IPE</i>	<i>Sr :IPE</i>	<i>C_s, Ci/l</i>	<i>C_p, Ci/l</i>	<i>Y, %</i>	<i>G, l/m² h</i>
VPK402	1:1	10	8,83	182	11,7
	1:5		8,96	91	10,4
	1:10		9,77	68	2,3
	1:20		10,5	39	0
NaCMC	1:1	10,0	9,5	61	7,3
	1:5		8,67	30	15,4
	1:10		8,63	21	15,8
	1:20		9,25	17	9,7
VPK402 +NaCMC	1:1	10	9,92	91	0,8
	1:5		9,75	39	2,5
	1:10		8,94	27	10,6
	1:20		9,46	18	5,4
HYPAN	1:1	10,25	7,88	138	23,1
	1:5		7,97	34	22,3
	1:10		7,69	20	25,6
	1:20		8,7	12	15,3
MM-1 (HYPAN+ VPK-402)	1:1	10,25	4,58	91	55,2
	1:5		4,74	39	54,5
	1:10		4,85	27	53,9
	1:20		4,84	15	53,4

Interaction of IPEC (Na-CMC) with U-235,238 and Co-60

The ability of modified natural polyanion Na-CMC to form stable compounds with U-235,238 (specific activity $1.084 \cdot 10^{-7}$ Ci/l) and Co-60 (specific activity $1.1 \cdot 10^{-8}$ Ci/l)

was investigated at a pressure of 0.2 MPa and a pH of 7.0. The resulting decontamination factors as a function of the Na-CMC content are listed in Tables 6 and 7.

Table 6
*Dependence of the decontamination factor of Co-60
on the Na-CMC content*

C_{CMC} , mg/l	C_{Co} in permeate, Ci/l	DF
10	$7,8 \cdot 10^{-8}$	1,4
50	$6,4 \cdot 10^{-8}$	1,7
100	$4,4 \cdot 10^{-8}$	2,5
175	$3,5 \cdot 10^{-8}$	3,1
250	$2,3 \cdot 10^{-8}$	4,7

Table 7

*Dependence of the decontamination factor of
U on the Na-CMC content*

C_{CMC} , mg/l	C_U in permeate Ci/l	DF
10	$8,8 \cdot 10^{-9}$	1,4
50	$4,4 \cdot 10^{-9}$	2,7
100	$6,4 \cdot 10^{-10}$	16,2
175	$1,5 \cdot 10^{-10}$	69
250	$9,5 \cdot 10^{-11}$	114

CONCLUSION

The ultrafiltration study of the interaction between IPEC or its component and multi-charge ions (^{235}U , ^{90}Sr) evidences a high membrane selectivity. HYPAN is the most effective complexing agent. The MM-1 selectivity is 55%.

ACKNOWLEDGMENTS

We are thankful to the Moscow State University team under the supervision of Professor A.B.Zezin for their help in synthesizing IPECs.

The study is now financially supported by the ISTC, Moscow (Project # 589-97).

REFERENCES

1. Yu.Polyakov Radioecology and Soil Decontamination.M,1970
2. V.Prokhorov Contaminant Migration in Soils. Physical- Chemical Mechanism and Modeling.M, Energoizdat,1981
3. S.Mikheikin, L.Pronina ,A. Smirnov, A.. Zezin, G. Glazunov, A.Fless “Polymeric Agents as Toxic Dust and Erosion Suppressants” Proc. of Int. Conf. “Dust Aerosols, Loess Soils and Global Change”, Waschington State Univercity, Seattle, 1998
4. V.Kabanov et al. Aggregating and Gelling in IPEC solutions Macromol Chem Symp. 39, 155-159, 1990
5. M.Bryk, E.Tsapyuk Ultrafiltration, Kiev, Naukova dumka, 1998