

## INTERPOLYELECTROLYTE COMPLEXES FOR CONTAMINATED SOIL IMMOBILIZATION AND REMEDIATION

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### ABSTRACT

Contamination of soils by radionuclides resulted from nuclear industry activities is still an important environmental concern. A joint VNIINM and MSU concept of in situ chemical immobilization and remediation of contaminated soils involves:

1. suppression of water and wind erosion by using earlier developed polymeric aggregators based on interpolyelectrolyte complexes (IPEC);
2. soil decontamination by separation methods;
3. site remediation through application of IPECs and perennial seeds.

IPECs are synthesized directly on topsoil from natural and synthetic active group-containing high-molecular compounds. The resulting crust 3-5 mm thick incorporates large soil-polymer aggregates and highly toxic finely divided matters. Laboratory and field tests (those within the Chernobyl site among them) have demonstrated protective polymeric properties, the effect of IPECs on water and wind erosion for various types of soils and dusty industrial waste (fly-ash, dust etc).

The decontamination technique developed is based on gravity separation of the most contaminated soil fraction in an aqueous medium. As a result, the amount of solid waste to be disposed of is as low as 10-15% of the initial contaminated soil.

Laboratory and field tests evidence of the better vegetation for soils treated with IPECs. On the strength of the data obtained, a new remediation technique has been proposed.

### METHODOLOGY

Areas contaminated with radioactive and toxic matters present environmental concern for a number of countries. Nuclear fuel cycle activities, NPP commissioning and decommissioning are potential sources of local accidents and releases. Literature [1,2] and our data demonstrate that the radioactivity bulk (approx. 95%) is localized within topsoil. So the problem of

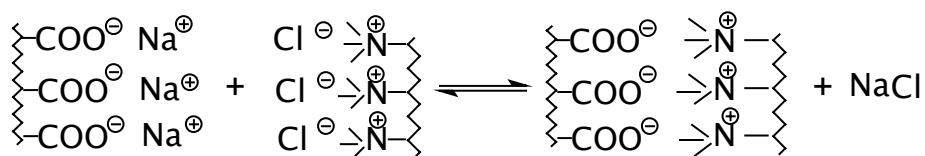
localization of contaminated topsoil and prevention of radioactivity spread with wind and water streams is very actually for many sites.

Thus and so a complex procedure and relevant equipment to prevent the spread of toxic and radioactive matters by wind and water erosion of soils have been developed. In cooperation with MSU, VNIINM has developed, tested and applied in the wide scale a soil immobilization technique and appropriate agents. The technique is to produce a protective soil-polymer crust by polymeric agents based on interpolyelectrolyte complexes (IPECs).

It is followed by decontamination capable of treating large areas of soil by gravity separation of fine fractions containing the bulk of radioactivity. Finally, the decontaminated soil is remediate through joint application of IPECs and perennial seeds.

### Polymers for soil stabilization

IPECs are products of the reaction between oppositely charged polyanion (PA) and polycation (PC). Interpolyelectrolyte reaction proceeds by the following mechanism:



The polycation interacts with negative silanol groups located on the silica surface. The negative charge results from replacing  $\text{Al}^{3+}$  cations in montmorillonite by cations of lower charge. Partial dissociation of silanol Si-OH groups produces a negative charge on the irregularities of the kaolinite surface. IPECs are amphiphilic macromolecular compounds, i.e., contain both hydrophobic and hydrophilic sites. Sites formed by coupling polyionic counterparts are sufficiently hydrophobic because of mutual screening by polyions of their charges. Because of the reversibility of the IPEC formation, hydrophobic and hydrophilic sites are able to spontaneously exchange their location within IPECs. Thus, IPECs can be considered as intelligent (smart) materials due to their ability to adapt themselves to complex structure of disperse systems via rapid exchange processes and to realise the optimal set of bonds with different colloidal particles and surfaces.

In Russia, a new IPEC generation was developed [3-11]. Such polymeric agents as MM-1, MT-1, MN-1, MJ-1 were studied and tested in laboratory and field conditions. An aqueous 1-2% MM-1 solution prepared industrially or in situ can be applied on topsoil ( $1,0 \text{ l/m}^2$ ) with any standard spraying equipment available (hand-held hoses, irrigating machine, hydroseeders, helicopters). The resulting soil-polymer crust 3-5 mm thick contains water resistant aggregates adhered to each other by the polymer. Polymers content in the crust not more 2.0 %wt. Of importance is that no solid impenetrable film is produced (Fig1).

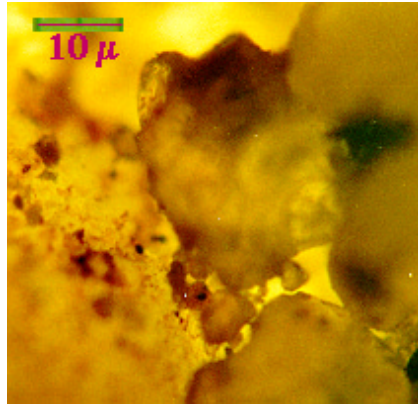


Fig 1. View of the soil-polymer crust

Soil particles stick together only at their juncture. This provides the soil filtration and the aeration of the lowermost layers. The protective crust which is water insoluble but water- and air-penetrable promotes vegetation.

During 1986-1993 IPECs were studied on a laboratory scale and used successfully within the 30-km Chernobyl zone. They were found to be efficient for suppressing water and wind erosion of soils. Of essential importance is their environmental safety and ability to promote vegetation. In addition to soil stabilization, IPECs yield better water resistance.

#### **Study the aggregation of soils exposed to IPEC.**

The performance of an aggregating agent is primarily characterized by its positive effect on such properties of topsoil to be protected as erosion resistance, water permeability, roughness. A criterion for the erosion resistance is the bottom water stream speed ( $V_{\Delta p}$ ), which can be experimentally measured in the field or laboratory conditions.

This approach was used for the long-term field tests of cultivated podzol sandy loam treated with the IPECs developed. To this end, the target area of 4 m<sup>2</sup> was covered three times with one of the IPECs in the amount of 1, 2 and 4 l/m<sup>2</sup>. Roundup was also used as a weed-killer three times per season (a day before IPEC-treating; July 21; September 10). To examine its physical properties, the soil was sampled once a month over a period from May to September.

These IPECs are found to contribute to the dry soil aggregation: the weighted mean diameter (D) of individual aggregates increases by a factor of 1.4-1.8. What is still better, the water resistance (d) of air-dry soil increases tenfold in the early stages of the treatment and by 3.5 times 120 days later. It should be noted that IPEC-treated specimens show a more limited amount (by 2 times early in the stage and by 1.7 times at the end) of very small water-resistant aggregates best suited to migration. As a rule, small particulates contain the bulk of radioactivity after soil contamination. The  $V_{\Delta p}$  value shows a three-fold increase early in the treatment by IPEC and a two-fold increase at the end.

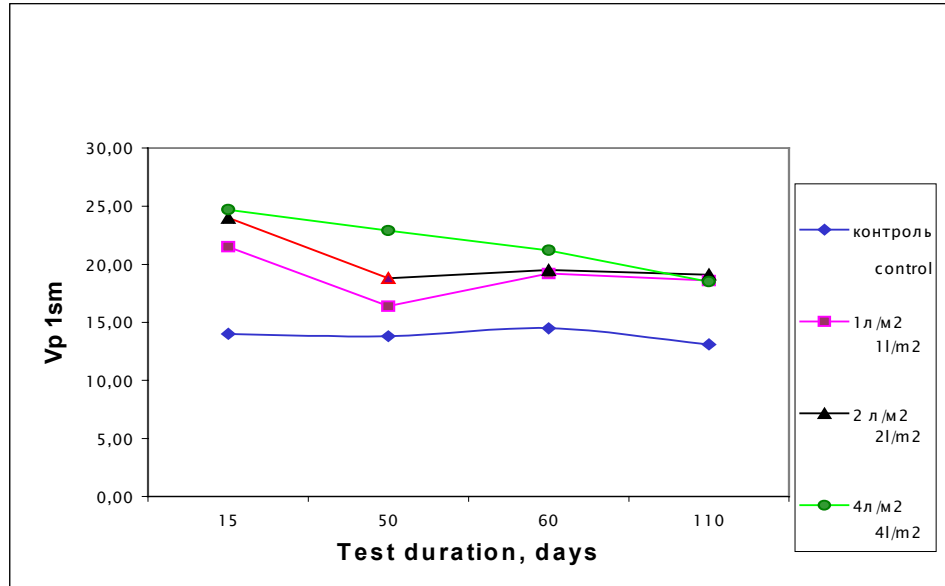


Fig. 2 Dynamics of the water resistance of protective coats

The treatment by 4 l/m<sup>2</sup> IPEC shows the best erosion resistance. The highest efficiency expressed in terms of an increase in erosion resistance per unit consumption of IPEC is observed over the range from 1.5 to 2.5 l/m<sup>2</sup>.

Even though the polymer penetrates not deeply, the treated soil shows a significant increase in water permeability due to its aggregation by the polymer. The approach used makes it possible to form a correct estimation of good protective properties of these IPECs and to specify their best doses for a particular soil.

#### Study the IPEC and coat resistance.

Specimen soil was placed in a rectangular container, rolled smooth and slightly compressed. The density of all specimens of 1.50 g/cm<sup>3</sup> was constant. Untreated dry soil, water- and KNO<sub>3</sub> – treated specimens were used for comparison purpose. The rolled and compressed specimen was exposed to an air stream over a velocity range from 10.0 to 90.0 m/s in a wind tunnel.

The velocity which initiates an extensive motion of particles was chosen as a criterion of the stability of a protective crust. The resulting limiting velocity can be a measure of the relationship between the crust mechanical strength and the polymeric product concentration (Table 1).

Table 1  
*Effects of various polymeric amounts*

<i>Agent</i>	<i>IPEC,</i> <i>wt%</i>	<i>U<sub>k</sub>,</i> <i>m/s</i>	<i>(q<sub>cp</sub>,<math>\square</math>y),</i> <i>kg/m<sup>2</sup>s</i>	<i>K (concerning the agent)</i>		
				Without agent	Water	KNO <sub>3</sub>
Without agent	0	6,9	329,902	1	0,000001	0,000004
Water	0	7,8	3,9*10 <sup>-4</sup>	8,4*10 <sup>5</sup>	1,00	3,1
<b>KNO<sub>3</sub></b>	0	7,9	1,2*10 <sup>-3</sup>	2,7*10 <sup>5</sup>	0,33	1,0
<b>IPEC</b>	0,02	8,7	7,9*10 <sup>-4</sup>	4,1*10 <sup>5</sup>	0,50	1,5
<b>IPEC</b>	0,064	7,5	1,3*10 <sup>-3</sup>	2,4*10 <sup>5</sup>	0,29	0,9
<b>IPEC</b>	0,2	8,4	5,3*10 <sup>-4</sup>	6,2*10 <sup>5</sup>	0,74	2,3
<b>IPEC</b>	0,64	21	3,6*10 <sup>-4</sup>	9,1*10 <sup>5</sup>	1,09	3,3
<b>IPEC</b>	2	33	4,4*10 <sup>-5</sup>	7,5*10 <sup>6</sup>	8,96	27,5

The efficiency of 0.064% IPEC solution in amount of 2 .0 l/m<sup>2</sup> is no different from that of water or KNO<sub>3</sub> solution taken in the same amount. An increase in the polymeric concentration cause the limiting velocity and hence the mechanical strength to increase smoothly. Although the limiting velocity is representative of the crust mechanical strength it cannot provide the quantitative characteristic of soil loss. It makes sense to assess the polymeric product efficiency in terms of the ratio of polymer-treated soil loss to untreated soil loss. Table 1 shows the effects of various polymeric amounts in comparison to untreated soil, water- and KNO<sub>3</sub>-treated soil. The results evidence a high efficiency of the water-produced protective crust ( $K = 8.4 * 10^5$ ). It is better than that from applying IPEC at a concentration below 0.2%. From the other hand, at 2.0% IPEC outperforms water ( $K = 8.96$ ) by 9 times and produces a crust with adequate wind resistance at a velocity as high as 40 m/s. Besides, contrary to water the polymeric protective cover offers a long-term protection.

The generation of aerosols 0.3-10 mkm in size was studied in the wind tunnel in a velocity range between 7.5 – 25.0 m/s [14]. It is clearly shows essentially no aerosols over an intact protective cover and a sharp increase in their amount when the protective cover is demolished.

**Study migration of soluble radionuclides in imitated media with and without IPEC**

To assess the IPEC efficiency in immobilizing heavy metal ions within soils, the lead absorption by soddy podzolic sandy loams containing IPECs and waste water sediments was studied in the field conditions. IPECs were found to have a positive effect on the lead immobilization. The untreated soil (control) showed a maximum absorption ( $Q_{max}$ ) of 0.009 mm/g while that treated with IPEC showed a three times higher absorption (0.015 mm/g). When there was a great amounts of heavy metals present in soils, the  $Q_{max}$  value was somewhat less (0.011 mm/g) since the polymeric bulk was expended for binding metals and producing polycomplexes. Thus, IPEC-treated soil can immobilize contaminants.

The soil immobilization with IPECs is followed by soil decontamination.

### **Soil decontamination technology**

As soil acts as a radionuclide collector it can be decontaminated with the dressing type method. The method is to recover radionuclides from contaminated finely divided soil fractions of various densities. In such a manner as high as 95% of radionuclides can be recovered and concentrated to a small volume (10-15% of the initial one). The method is based on soil hydraulic classifying to separate finely divided organic and mineral fractions in an aqueous medium.

Contaminated topsoil 5-10mm thick is removed off to reprocessing locations. Screen sized and disintegrated soil is delivered as a pulp to a separator. Mineral fractions are classified by size. Finely divided mineral and organic fractions containing the bulk of radioactivity (95%) represent solid radwaste to be transported to off site locations for concentrating and final disposal.

The radionuclide removal efficiency depends heavily on the soil type, the organic content, structure and properties and on the contamination type. Our experience shows that the most important factors in this respect are:

- chemical and mineralogical soil composition;
- physical and mechanical soil composition;
- level, type and distribution of radionuclides throughout soil fractions.

The experimental data confirm that the soil (from Chernobyl accident plume) consists of three principal components different in composition and radioactivity distribution [12,13]:

1. The **mineral bulk** (contains as much as 20% of the total radioactivity).
2. The **sludge portion** (30-40% of radioactivity)
3. The **organic-mineral portion** (30-40% of radioactivity)

The decontamination efficiency depends on the content of fine particles and the level to which they can be separated from the soil bulk. Gravity separation shows much promise in classifying mineral particles into sizes and densities. If necessary, other procedures (floatation, washing, etc.) can be used as supplementary ones. The dressing procedure has also been successfully tested on a large scale at Novosybkovo (Bryansk region ) and Khalch (Gomel region, Belorussia).

The decontamination procedure is based on classifying soils hydraulically and separating fine-grained particles in an aqueous medium, the water circulated around a closed path and solid waste compacted. The personnel is protected against radioactive dust and aerosols by a special system of dust collectors and discharges. Besides, the aqueous medium gives no way of generating dust.

A thin contaminated layer 5 -10 cm thick is removed with a special device to be coarsely screened and further disintegrated into small particles. The pulp is separated. The mineral portion is also classified into sizes. The fine-grained portion is concentrated, compacted and discharged while the remainder is returned to a field.

The resulting decontamination factor ranges from 4.5 to 2.0 as a function of the extent to which the sludge and organic-mineral particles are removed. The cleaned soil radioactivity can be as low as 1.3 - 1.6 Bk/g.

### Decontamination efficiency

Portions separated	Decontamination factor ( $K_d = A_H / A_K$ )
Sludge ( <0.06 mm )	2.0
Sludge + organics	4.5

$A$  - the Cs-137 content prior to decontamination

$A$  - the Cs-137 content after decontamination

### Study the IPEC effect on grass vegetation.

Since 1998 comprehensive studies on the effect of IPECs on the soil erosion resistance and vegetation have been in progress on experimental fields (Vlamimir, Vyatkinno site). Finely divided soddy podzolic gley soils were used for experiments. The plots of 4.0 m<sup>2</sup> were plowed to a depth of 20 cm, borrowed, planted with red clover seeds and sprayed with an IPEC solution (1.0, 2.0 or 4.0 l/m<sup>2</sup>). Some plots were treated with 5% KNO<sub>3</sub> (without IPEC) for control purposes. Growing MJ-1 doses increased the biomass of the clover and weeds from 77.5 centner/ha for the control plots to 245.7 centner/ha for the maximum MJ-1 dose (4.0 l/m<sup>2</sup>). It should be noted that this is caused by positive effects of MJ-1 on aqueous and physical soil properties rather than by fertilizing with KNO<sub>3</sub>. Also, tests with hen's millet demonstrated that excess MJ-1 (above 1.0-2.0 l/m<sup>2</sup>) could affect adversely and decrease the biomass. It suggests the need for thorough choice of IPEC concentrations and uniform spraying.

In 1999 the effect of IPECs components on the vegetation of perennials (mixed meadow grass and fescue used for lawns) was studied. Perennial seeds in an amount of 16 kg/ha were planted. The results shows that treatment with 1.0 l/m<sup>2</sup> of mixed KNO<sub>3</sub> and CaCl<sub>2</sub> ( 3.5 wt.% in aggregate) depress the vegetation and with 2.0 l/m<sup>2</sup> of the mixture sprayed the negative effect is intensified. Application of polycation and polyanion (0.25 l/m<sup>2</sup> each) singly or in combination with no salts present yields the best results, i.e. a harvest of 157% in respect to the control. It follows from the tests that PA and PC composing IPECs, provided there is no salt mixtures present, are favorable for vegetation. It is good practice to apply IPEC components successively, planting seeds along with the second component. In this case there is no need for adding electrolytic salts.

On the strength of these experiments the following preliminary conclusions can be made:

1. Treatment with a 1.0% PA solution produces the maximum release of CO<sub>2</sub> as compared to all other options. This suggests the contribution of this product to the progress of soil microorganisms, presumably microscopic mushrooms, first of all, for the metabolism of which this intensive CO<sub>2</sub> yield per time unit is typical.
2. 1.0% polycation and 3.5% KNO<sub>3</sub> (applied separately) inhibit microbiologic processes, the PC having the most essential inhibiting impact. The latter case can be attributed to a considerable chlorine ion content of PC. The inhibiting impact of 3.5% KNO<sub>3</sub> can occur through a high osmotic pressure within the soil solution due to a high rate of application of the violent electrolyte.

3. Treatment with such IPEC mixture has a weak inhibiting effect. The addition of 3.5% KNO<sub>3</sub> adversely affects the soil respiration. But it should be pointed that the inhibiting impact of the mixture is somewhat lower than that of PC, suggestion the PA decomposition with a consequent higher CO<sub>2</sub> release.

## CONCLUSIONS

1. Interpolyelectrolyte complexes - based agents and a procedure have been developed for preventing contaminated soil erosion.
2. The performance of the polymeric agents has been specified, tested and compared with polymeric alternatives.
3. The polymeric agents developed are recommended for wide application in the event of industrial or ecological emergency. It is very good choice is polymer-seeding grass joint application for site remediation.
4. A soil decontamination procedure has been developed, researched and tested on Chernobyl-contaminated soils.

## REFERENCES

1. V.M.Prokhorov Contaminant Migration within Soils, Physical-Chemical Mechanisms and Modeling, Moscow. Energoizdat,1981
2. A. Zimon Decontamination, Moscow,1994
3. S.V.Mikheikin, L.A.Mamaev, K.A.Rybakov, A.N.Alekseev “The technology of long-term localisation of soils, contaminated with radioactive and high-toxic substances”. One decade after Chernobyl: Summing up the Consequences of the Accident. IAEA- TECDOC-964, vol 2, pp266-269, Vienna, IAEA, 1996.
4. S.V.Mikheikin, A.N.Alekseev, L.V.Pronina, A.Yu.Smirnov “Interpolyelectrolyte Complexes as Contaminated Topsoil Structureformers” Proceedings of the Int. Conf “Waste Management’98”, Tucson, AZ, 1998.
5. 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
6. SV.Mikheikin, A.N.Alekseev, LV.Pronina, A.Yu. Smirnov “Confinement Techniques for Contaminated Topsoil” Proc. of the 6 International FZK/TNO Conference on Contaminated Soil, Edinburgh, UK, 1998 Thomas Telford, London, 1998, v 2, pp1175-1176.
7. S.V.Mikheikin, A.N.Alekseev, L.A.Mamaev “ Confinement Techniques for Contaminated Topsoil” Proceedings of ICONE 5: 5<sup>th</sup> International Conference on Nuclear Engineering 1997, Nice, France ICONE5-2476
8. S.V. Mikheikin, A.N.Alekseev, E.A.Laguzin, P.G.Ogulnik, L.V.Pronina, A.Yu.Smirnov, T.N.Bolysheva, G.P.Glazunov, A.D.Fless “Modern Techniques For Contaminated Sites Remediation” Proceedings of the Int. Conf “Waste Management’99”, Tucson, AZ, 1999.
9. S.Mikheikin, L.Pronina, P.Ogulnik, A. Smirnov, A.. Zezin, T.Bolysheva G. Glazunov, A.Fless “Techniques For Contaminated Site Localization And Decontamination” Proc. of Int. Seminar on analysis, Methodology of Treatment and Remediation of Contaminated Soils, Paris-Villepinte, April 1999.
10. S.V. Mikheikin, V.D.Akhunov, P.G.Ogulnik, L.V.Pronina, A.Yu.Smirnov, A.B.Zezin, T.N.Bolysheva, G.P.Glazunov, A.D.Fless “Protection And Recultivation Of Soil,



Contaminated As A Result Of Nuclear Fuel Cycle Activity.” Proc. of The 4th. International Conference On Environmental Radioactivity In The Arctic Edinburgh, Scotland, 1999 p 232-234

11. S.V.Mikheikin, P.G.Ogulnik, L.V.Pronina, A.Yu.Smirnov, M.R.Petrov, B.Zezin  
“Interpolyelectrolyte Complexes as a Barrier to Radionuclide Migration” Proc. of The 7<sup>th</sup> International Conference Waste Management and Environmental remediation, Nagoya, Japan, 1999
12. L.A.Mamaev et al. Radionuclide-Polluted Soil Decontamination. All-Russia Conference “Radiological, medical and social-economic consequences of the Chernobyl accident”, Golitsino, 1995
13. L.A.Mamaev et al. Radionuclide Contaminated Soil Remediation. Russian Nuclear Society Conference, Moscow, 1991
14. E.Emets, G.Kolomeytsev, S.Mikheikin, P.Poluektov, A.Smirnov, V.Timonin.  
“Investigation of dust generation processes over radioactive contaminated soil under Wind action” J.Aersol Sci., Vol.29, Suppl.1, pp211-212, 1998