INTERPOLYELECTROLYTE COMPLEXES FOR STABILIZING AND REDUCING MIGRATION OF CONTAMINATION IN ERODIBLE SOIL HORIZONS

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ABSTRACT

Nowadays the world community attention focuses on soil contamination by nuclides from global fallout after nuclear weapons tests and nuclear fuel cycle accidents, or by man-made activities-induced heavy metals and other pollutants migrating in the environment.

Results of an investigation into a protective polymeric layer applied on topsoil are reported (since the Chernobyl accident liquidation). The assessment has been made of the effect of interpolyelectrolyte complexes (IPEC) on physical-chemical properties of soils; process procedures; the effect of climatic factors on the soil-polymer complex; the effect of amount and components of IPECs on the microbial community and on germination of grasses of various botanical groups.

In the final analysis it may be stated that IPEC is an effective structure-former capable of stabilizing to advantage radionuclide-contaminated erodible topsoils.

Combination of IPECs and mixed grass crop provides a high effective, peculiar technology for soil remediation. This technology was tested successfully in field experiment performed over the last two years.

EFFECT OF EROSION ON THE RADIONUCLIDE REDISTRIBUTION IN AGRICULTURAL LANDS

As a result of the Chernobyl accident, about 5 700 km$^2$ of Russian territories are contaminated with $^{137}$Cs, $^{90}$Sr and TUE (~ 1 Ci/km$^2$). Some 95% of contaminants gather on topsoil 5-8 cm thick [1, 2, 3].

Around 25 million persons living and working in the place are exposed to radioactivity. Due to water and wind erosion, contaminated soil is a permanent source of radionuclides penetrating to the biosphere and food chains and contaminating adjacent regions.
Based on the $^{137}$Cs migration predictions, erosion is the major process responsible for release of the radionuclide from soil.

The cesium release with erosion products is more than by an order of magnitude higher than that with cropping [4] while its annual penetration deep into soil horizons through filtration and diffusion accounts for hundredths of a percent of radionuclides available [5].

Numerous studies of accidental radioactive releases report the accumulation of the radioactive bulk (~90%) in the finest fraction (<50 µm) [6,7,8] most liable to migration. These fractions rapidly reach geochemical barriers and are trapped by them [9], with a subsequent increase in the specific radioactivity by 1.5-6.0 times [10,11,12]. Besides, a considerable portion of finely divided particles rich in radionuclides can be further spread by water streams.

Thus, one of the most important objectives of the environmental protection is to develop erosion suppression methods.

In view of ever increasing risk of great anthropogenic accidents (Chernobyl, 1986; Tokai Mura, 1999) and the similarity of pollutants (heavy metals, organics, radionuclides) in behavior the task is of prime importance not only for the Russian Federation.

**SOIL PROTECTION TECHNOLOGY AND EFFECTIVENESS**

The use of polymeric structure-formers is a current method for improving and stabilizing the surface structure of contaminated soils, sands, spent peatland, sand pits, tailing dumps, etc. [13]. Such polymers stick fine particles (≤50 µm) containing the radioactivity bulk (~90%) together to form larger aggregates less liable to erosion.

*Polymeric formulations to be used for the purpose must be capable of:*  
- producing a rapidly solidified stable crust durable for a quite long vegetation period without interfering with vegetable germination;  
- exerting no adverse effect on the environment;  
- susceptible to mechanization to be easy in preparation and application as much as possible;

Interpolyelectrolyte complexes (IPEC)-based formulations having been developed by joint efforts of VNIINM and the MSU low molecular chair for the last 14 years satisfy all these requirements [6, 7, 8, 14, 15, 16]. IPEC applied on contaminated soils is expected to promote the vegetation germination inhibiting the water and wind erosion.

The preparation and application of IPEC follow a very simple procedure. Technological options exist. A process solution can be prepared at a factory or in the field. Polycation (PC), polyanion (PA) and a low molecular electrolyte solubilized are
mixed to yield a polymer concentration of 2.0 – 4.0 wt.%. The resulting process solution is applied on the soil surface on a 1.0 - 1.5 l/m\(^2\) basis.

IPEC is synthesized in-situ upon leaching the low molecular electrolyte from the system by rainfall. A water-insoluble air-penetrable erosion-preventive stable crust 1.0-5.0 mm thick containing 0.5-2.5 wt. % of polymer develops. Of importance is that the crust is not overall, dispersed particles being stuck together only at points of their contact. Therefore the crust is filtrated and aerated with no interference with vegetation growth. A year later the cohesion of the IPEC-treated soil is much more superior to that of untreated one.

After the Chernobyl accident VNIINM in cooperation with MSU developed a series of new polymeric formulations (MM-1, MT-1, MN-1) for stabilizing the topsoil finely divided toxic matters, radioactive ones among them [15]. Field tests evidence that these formulations are highly effective and resistant to rainfall for prolonged periods (over 13 months) [16,14].

Experience in eliminating the Chernobyl accident consequences showed that a polymeric crust was necessary but still inadequate for long-term conservation of contaminated soils. Combined application of the polymeric formulations and perennial seeds is best suited for the purpose. In this case the soil is first protected by the vegetation-improving polymeric crust during a year and then by the vegetable layer germinated.

Apart from the Chernobyl site, these formulations have been used for the disastrous Aral Sea to show that the transfer of sands of high salinity aroused from the sea-dried bottom can be successfully suppressed.

The report describes the results of research into the erosion resistance of IPEC-based polymers.

**FIELD EXPERIMENTATION**

The erosion-preventive stability of soils is defined as the soil capacity to resist the impact of water streams [17,18].

Quantitatively, the erosion resistance is estimated in terms of the minimum erosional rate of water streams at which soil particles are uninterruptedly separated and carried away.

In 1998-99 laboratory and field experiments were performed to study the effect of IPEC doses and components on agrophysical and erosion-preventive properties of soils, vegetation germination and microbial community [19,20].

Sudogod region’s (Vladimirskaya oblast) soddy podzolic soils similar in their properties to Chernobyl-contaminated Bryansk soils were selected for experimentation.
Experiment 1. (1998)

An experimental field was ploughed and sown to clover. The field was divided into 1.5x1.55 m plots. Each plot except a check one was treated with 1.0, 2.0 or 4.0 l/m² IPEC and low molecular electrolytes. The fallow plots were treated with a weed killer (Roundup) to protect against weeds. All the treatments were carried out three times per growing season.

The clover and weed biomass was evaluated three months later for all experimental options. The soil was sampled once a month from May to September for studying its physical properties. In 1999 the effect of IPEC on the clover germination was investigated.

Experiment 2. (1999)

Experimental plots were sown to a mixture of ryegrass (50%), meadow grass (25%) and fescue (25%). The experimental procedure was similar to that described above. Sampling was performed once a month from June to September. In addition, the effectiveness of various technologies of application of IPEC and IPEC components (separately or in combination) was studied.

Effect Of IPEC On The Soil Structure

Effect Of IPEC On The Microaggregation

The IPEC application improves the soil microaggregation, i.e. increases the diameter of microaggregates incorporated into soil aggregates. In the 110th experimental day after treatment with 2,0 l/m² IPEC the weighed mean diameter of microaggregates ($d_{ma}$) in the fallow layer 0-2.0 cm deep increased by 1.2-2.0 times (from 0.25 mm to 0.35 mm) against check.

Effect Of IPEC Dose On The Macroaggregation

Field experiment 1 evidenced a positive effect of IPEC on the structure of an air-dry soil. The lumpiness (the weighed mean diameter, $D$, of air dry lumps) increased against check by 1.4-1.8 times (from 8.0 to 14.0 mm). At the close of the experiment the lumpiness decreased in all plots (down to 4.0 mm for IPEC-treated plots and to 2.0 mm for check plots) due to destruction by rainfall.

Field experiment 2 showed no decrease in the lumpiness irrespective of IPEC doses. This resulted from an extraordinary low amount of rain falling in 1999. This experiment confirmed a double increase in $D$ (from 2.0 to 4.0 mm) with increasing IPEC doses both for fallow and sown plots.
Effect Of IPEC On The Water Resistance

The water resistance ($d_{wr}$) when the air-dry aggregate diameter remained unaffected by weakly agitated water (the Savinkov method [17, 18]) was experimentally found to increase substantially with higher IPEC doses.

Early in the experiment $d_{wr}$ (4.5 mm) for IPEC-treated soil was 5.0-10.0 times that for check (0.45 mm) while 120 days later the $d_{wr}$ values differ by 3.5 times (1.2 mm and 0.35 mm, respectively). As to the fallow plots (without plant cover), experiment 1 showed a marked decrease (by 2.0 times at the start and 1.7 times at the end) in the content of fine water resistant aggregates ($<0.63$ mm) in IPEC-treated soils.

Environmental Influences On The IPEC-Treated Soil Water Resistance During Cold Seasons

One of the basic factors influencing the water resistance ($d_{wr}$) is repeated frosting and defrosting of soil horizons.

The experiments performed (1998-99) showed an evident tendency for a decrease in water resistance after repeated (seasonal) frosting-defrosting cycles for all experimental options. With 4.0 l/m² polymer, the $d_{wr}$ value drops from 2.8 to 1.5 mm.

Effect Of IPEC On The Erosion Resistance Dynamics

As it follows from experiment 1, IPEC-induced structural properties (lumpiness, water resistance) have a pronounced effect on the erosion resistance, $V_7$. Compared to untreated soils, the IPEC-treated fallow soil showed an increase in $V_7$ by three times at the start and by 2 times at the end of the experiment (from 7.0 cm/s to 12.0-25.0 cm/s as a function of the IPEC dose). With 4.0 l/m² IPEC applied, the erosion resistant was found to increase most.

The IPEC treatment changed the erosion resistance of the soil unprotected by the vegetation layer from very low (checks at the experiment start) to medium values [18].
IPEC doses under 2.0 l/m² were shown (1999) to have little effect on the erosion resistance (due to a small amount of rainfall). Two months after perennial grass was sown the erosion resistance depended on the roots germinated rather than on the water resistance. The germination increased the erosion resistance by 1.1-1.2 times.

At the end of the experiment all experimental plots, including the check one, had a very high $V_\Delta$ but with 2.0 l/m² the progress was faster (from 12.0 to 78.0 cm/s within 110 days).

**Effect Of IPEC On The Microbial Community**

The soil state can be characterized by the intensity of soil respiration, i.e. the release of the microbial community/CO₂ activity products [21, 22, 23]. Besides, the respiration intensity is an implicit indication of decomposition of IPEC and its components. Comparative analysis shows that only polyanion promotes the CO₂ release throughout the experiment. This is most evident at a period when the microbial biomass is maximum (Fig.2). It is statistically reliable that at the same period polycation and electrolyte lower the respiration intensity. An electrolyte-induced high osmotic pressure affecting adversely the soil community as well as a labile chlorine of polycation can be responsible for this.

The behavior of IPEC and its components applied separately or in combination displays a generality. However as followed from the statistical reliability, starting from the 25th experimental day the CO₂ release was inhibited by IPEC applied. Electrolyte-containing IPEC had the most significant inhibiting effect.
Fig. 2. Effect of IPEC components on the dynamics of potential soil respiration

**EXPERIMENT ON INTENSIVE FURROW ERODING**

The effect of IPEC on the soil erosion was tested using furrows made on 2.0° – 3.5° slopes of Sudogod soils. The furrows were eroded by a controlled water amount supplied with a motor-driven pump (Fig. 3).

The procedure allowed for estimating the limiting water load on the soil for various IPEC doses. The results are given in Table I.
The active experiment has shown, that at a IPEC application 2.0 l/m² – $V_{\Delta}$ grows in 1.5, and at IPEC application 4.0 l/m² - in 2 times. The erosion resistance thus from gradation «very low» (on the control) becomes «high» (on classification M.,S.Kuznetsov [17,18]).

The study of erosion resistance soils treated with IPEC has allowed to estimate limiting loadings of water flows on ground at use of various doze. Thus the entering IPEC has resulted in decrease turbidity of a drain at speeds smaller, than washing away in 6 time, and at speeds large washing away - in 7,0 times, that in a reality conducts to reduction of specific activity of products of erosion.

Table I. Results of erosion resistance tests by watering experimental furrows

<table>
<thead>
<tr>
<th>Date</th>
<th>IPEC dose, l/m²</th>
<th>Vp, cm/s</th>
<th>Flow time, T, min.</th>
<th>Flow volume, W m³</th>
<th>General loss, Qg, kg</th>
<th>Suspended load, Qg/W, kg/m³</th>
<th>Average flow rate, l/s</th>
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</thead>
<tbody>
<tr>
<td>10.09.98</td>
<td>0</td>
<td>16,4</td>
<td>202</td>
<td>1,012</td>
<td>1,240</td>
<td>1,23</td>
<td>0,080</td>
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<tr>
<td></td>
<td>for $V_{\Delta}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>after $V_{\Delta}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.11.09</td>
<td>1</td>
<td>16,8</td>
<td>282</td>
<td>2,294</td>
<td>1,337</td>
<td>0,63</td>
<td>0,138</td>
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<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>after $V_{\Delta}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>10.09.98</td>
<td>2</td>
<td>21,1</td>
<td>174</td>
<td>1,152</td>
<td>0,246</td>
<td>0,21</td>
<td>0,110</td>
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<td>11.09.98</td>
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<tr>
<td></td>
<td>after $V_{\Delta}$</td>
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</tbody>
</table>

DEMONSTRATION OF THE IPEC TREATMENT EFFECTIVENESS WITH RADIONUCLIDE-CONTAMINATED SOILS OF BRYANSK

The effect of IPEC on the erosion resistance of radionuclide-contaminated Bryansk soils was carried out on a laboratory scale using an erosion pan with a closed water circuit (Fig.4). The erosion resistance was evaluated in terms of the soil amount removed from the sample surface and collected in a collector-settler. The soil collected was analyzed for specific and absolute activities.
The data listed in Table II show the IPEC effectiveness for radionuclide-contaminated soils. The IPEC treatment halves the specific activity of the soil lost. This can be explained by aggregation of small particles.
Table II. Effect of IPEC on the erosion resistance of contaminated soils. IPEC consumption – 4 l/m²

<table>
<thead>
<tr>
<th>Water stream rate, cm/s</th>
<th>Soil loss, g</th>
<th>Absolute activity, Bq</th>
<th>Specific activity, Bq/g</th>
<th>Coating efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>check</td>
<td>IPEC</td>
<td>check, Ac</td>
<td>IPEC</td>
</tr>
<tr>
<td>10</td>
<td>0,64</td>
<td>0,35</td>
<td>13,12</td>
<td>3,68</td>
</tr>
<tr>
<td>28</td>
<td>1,14</td>
<td>0,42</td>
<td>14,12</td>
<td>3,95</td>
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<tr>
<td>40</td>
<td>1,18</td>
<td>0,49</td>
<td>13,8</td>
<td>4,95</td>
</tr>
<tr>
<td>50</td>
<td>1,77</td>
<td>0,73</td>
<td>18,02</td>
<td>6,28</td>
</tr>
<tr>
<td>67</td>
<td>3,08</td>
<td>0,97</td>
<td>27,75</td>
<td>8,73</td>
</tr>
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<td>83</td>
<td>&gt; 50</td>
<td>1,22</td>
<td>-</td>
<td>9,88</td>
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<tr>
<td>120</td>
<td>-</td>
<td>1,48</td>
<td>-</td>
<td>12,58</td>
</tr>
<tr>
<td>145</td>
<td>-</td>
<td>&gt; 50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Experimental conditions:
- Time: 6 hours
- Water level in a pan: 1-2.0 cm
- Sample cross section area: 0.02 m²
- Sample weight: 900 g
- Initial specific activity: 2.92 Bq/h
ACKNOWLEDGEMENTS

The study is now financially supported by the International Science and Technology Center, Moscow (ISTC, Project # 589-97).

CONCLUSIONS

- IPEC is an effective erosion-preventing soil-stabilizer;
- the field experiments show no negative impact of IPEC on the soil vegetation and microbial community;
- IPEC is suitable for suppressing environmental spread of radionuclides and heavy metals aroused in soils from man-made accidents and ecological disasters

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