IPEC Gels for Remediating Soils Contaminated as Result of Nuclear and Industrial Activities

S.V. Mikheykin, E.Yu. Anciferova, V.P. Simonov
Moscow Scientific and Industrial Association “Radon” (Mos SIA Radon)
Moscow
Russia

A.B.Zezin, V.B.Rogacheva, T.N.Bolusheva
Moscow State University (MSU)
Moscow
Russia

ABSTRACT

Under International Scientific and Technological Center (ISTC, Moscow) Project #1567 the Moscow research team in collaboration with Los Alamos National Laboratory developed and tested new kind of interpolyelectrolyte complexes with microgel (#IPECs) for soil surface stabilization, prevention of radioactive contamination distribution with wind and water streams and for site remediation using mixtures of new water-soluble polymers with seeding grasses.

Evidently, the most important factor responsible for the effectiveness of a polymeric aggregator is the ratio of the size of polycomplex particles to that of dispersion particles being aggregated. The particle size of IPEC produced of a pair of linear oppositely charged polyelectrolytes is usually fractions of a micron. Such a particle can fix only small aggregates (~ 10 µm and less). One of the ways of improving polycomplex aggregators is to use loose cross-linked polyelectrolytic gels as an IPEC component. When generating/dispersing these polyelectrolytic gels, particles of specified sizes can be produced. These polyelectrolytic micro-gels introduced into soil save moisture, what is important for arid sites.

Wind erosion was studied as a function of soil physical-chemical properties and the air stream velocity. A laboratory wind tunnel instrumented to follow the process on a real-time basis was used for our study. Polymer-treated samples show a high wind erosion resistance in the wind velocity range up to 40 m/s.

The micro-gel dispersion MGD-2 was injected in combination with MLA-1 in the experiments with water flow – water erosion resistance. With an increase in the water-polymer solution application rate from 2.0 to 4.0 l/m2 the soil resistance to eroding water streams with velocity of 55 cm/s (2.0 l/m2) and at 70.0 cm/s with 4.0 l/m2. Based on the classification of soils by erosion resistance, soils eroded with a water stream 1 cm high at a velocity of 50 cm/s are considered to be highly erosion-resistant.

It showed that new kinds of IPECs based with micro-gels are very useful as soil stabilizers and applicable as activating agent of grass vegetation in the remediation activities. It may

successfully apply also in the post-accidental activities in the case of spray radioactive materials onto topsoils.

SYNTHESIZE A NEW AGGREGATOR FOR DISPERSED SYSTEMS.

Within the framework of the project #1567, interpolyelectrolyte reactions between loosely cross-linked gels and oppositely charged linear polyelectrolytes were studied. Polyacrylic acid (#PAA) and poly-N,N-diallyl-N,N- dimethylammonium chloride (#PDADMAC) were selected.
These polyelectrolytic gels are of high swelling capacity (~1000) in pure water but this swelling capacity decreases greatly in the presence of screening low molecular weight electrolytes.

These polyelectrolytic gels were found to be capable of sorbing linear oppositely charged polyelectrolytes from aqueous solutions, with a maximum of sorbed polyelectrolytes corresponded to the stoichiometric ratio of oppositely charged linear polyions to ***cross-linkage***. Because the sorption requires for at least partial charge of the both components, the interpolyelectrolytic reaction (IPR) (schematically shown below) producing an electrically neutral ***(#IPEC***) within the gel body is expected to be the moving force of this activated sorption.

The kinetics of sorption of linear polyions by oppositely charged polyelectrolytic gels was studied using minor (1-3 g) samples of #PANa and #PDADMAC. The conversion of a starting highly swollen polyelectrolytic gel into the product of the sorption finished (#IPEC) is schematically shown below.

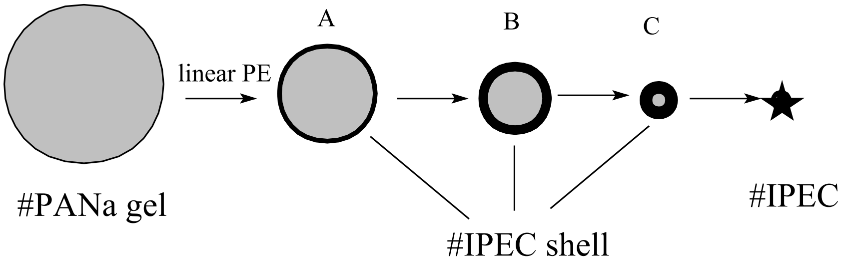

Fig 1. Scheme of # IPEC formation

As soon as a transparent gel sample is immersed into an aqueous oppositely charged linear polyelectrolyte solution it swells highly. The gel surface develops a very thin dull film that increases in thickness as time passes while the gel sample decreases in volume. In section, this intermediate product shows a macroscopic phase separation into an outer poorly swollen dull #IPEC shell and the internal core of the initial highly swollen gel. Elemental analysis of these phases evidences that the whole sorbed linear polyelectrolyte is contained only in the outer IPEC shell.

This evidences a thermodynamic stability of these macroscopic two-phase structures of the "core-shell" type. On the whole, the interaction between cross-linked polyelectrolyte and oppositely charged linear polyelectrolyte can be represented as a smooth conversion of the highly swollen gel phase to the dense new #IPEC phase.

Our findings clearly demonstrate that interaction between loosely cross-linked polyelectrolytic gels and oppositely charged polyelectrolytes produces gel structures of the core-shell type. The shell thickness can be varied over a wide range by changing either the polyelectrolyte amount in the reaction system or the gel aging time in the polyelectrolytic solution. Such polycomplex gels offer an evident benefit of being capable to provide tight adhesion between many large particles dispersed. Below is a schematic of probable interactions of oppositely charged linear polyelectrolytes (IPEC) and of polycomplex gel (#IPEC) with soil particles different in size.

Results suggest that, basically, partially hydrolized polyacrylamide micro-gel can be used for producing polycomplex formulations to be used as a soil aggregating agent. Such formulations can include either IPECs based on #PAA and linear polycation or mixtures of IPECs based on linear oppositely charged polyelectrolytes and polycomplex gels.

EFFECT OF #IPEC ON THE WIND EROSION OF CONTAMINATED SOILS

Wind erosion was studied as a function of soil physical-chemical properties and the air stream velocity. In practice, the limiting air stream velocity corresponding the onset of soil particle erosion and destruction of soil or a protective coating, if any, was identified for a specific soil sample. The extensive soil loss by an air stream is also an important parameter characterizing the erosion intensity. The dust content of the air stream can indicate the effectiveness of a polymeric formulation used for a specific soil. A laboratory wind tunnel instrumented to follow the process on a real-time basis was used for our study.

For experiments, use was made of the following materials: mortar sand, uranium mining tails, sandy loams sampled from VNIPTIOY fields (200 km far from Moscow).

Earlier developed IPEC-based formulations serving as the basis for new micro-gel-containing formulations were used as aggregators:

- IPEC-1;
- IPEC-2;
- MLA-1;
- MGD-1(micro-gel dispersion);
- MGD-2 (micro-gel dispersion).

In the experiment, the rate of the first wind erosion stage – deflation – was determined for a given sample as a first approximation. The deflation is characterized by the constant or increased material loss from the surface with time.

Polymer-treated samples show a high wind erosion resistance in the wind velocity range up to 40 m/s. However at higher velocities a high aerodynamic drag of the wind tunnel increases sharply its vibration.

As evidenced by more quiet curves, the updated wind tunnel increased the limiting air velocity (up to 70 m/s) and decreased sharply the air path vibration as well.

EFFECT OF IPEC ON THE WATER EROSION OF CONTAMINATED SOILS

The state of soil aggregation was evaluated in the following way. First, the weighted mean of the soil aggregate diameter was determined following Savvinov's method (dry sieving), and averaged samples weighing 50 g were prepared. The weighted mean of the diameter of soil aggregates sampled from Vladimirskaya oblast was measured to be 3.27 mm. The experimental results are given in Table I.

Table I. Weighted Mean of the diameter of soil aggregates as a function of the IPEC composition in the process of frosting – defrosting (wet sieving)

Polymer	**Weighted mean of the diameter, mm**					
	0 cycle	**1 cycle**	**2 cycle**	**3 cycle**	**4 cycle**	**5 cycle**
No polymer	0.381	0.311	0.283	0.281	0.284	0.279
2.0 l/m^2 MLA-1, (split introduction)	0.410	0.364	0.332	0.335	0.333	0.337
2.0 l/m^2 MLA-1, (simultaneous introduction)	0.429	0.388	0.384	0.382	0.364	0.356
2.0 l/m^2 MLA-1 + gel (simultaneous introduction)	0.531	0.404	0.389	0.391	0.368	0.360
2.0 l/m^2 MLA-1 + gel (split introduction)	0.546	0.421	0.401	0.398	0.377	0.372
4.0 l/m^2 MLA-1 + 1%gel (split introduction)	0.551	0.424	0.399	0.398	0.385	0.383

IPEC components introduced result in an increase in the weighted mean of the diameter of soil aggregates both with their split and simultaneous introduction, as shown in Table 1. The introduction of IPEC + gel shows the best results.

Soil erosion resistance using a hydrodynamic facility

A set of experiments was conducted on a laboratory scale using an hydrodynamic facility to study the erosion resistance of polymer-treated soils.

The effect of polymeric formulations on the erosion resistance was tested as a function of the water stream velocity, a soil treatment procedure, the composition and concentration of polymeric formulations like MM-1, MLA1, MGD.

Mixing the MLA1 - treated soil to a depth of 1.0 cm followed by leveling was found to result in a more durable protective layer. The soil treated with 4.0 l/m^2 MLA-1was markedly denuded at 23.0 cm/s while that treated, mixed to 1.0 cm and leveled was denuded at a velocity of 55 cm/s.

The soil washout was pronounced at a water stream of 23.0 cm/s. for a MLA-1-treated soil and at 35.0 cm/s with MGD added. After injection of the polymeric formulations the soil surface was not mechanically disturbed (no loosening and leveling). A higher erosion resistance with MGD used is attributed to the fact that the dispersion micro-particles extend the area of contact between soil aggregates of medium size to form larger water resistant clusters.

The data shows that the use of 2.0 wt. % #PAA-PDADMAC as a completely prepared polycomplex microgel after dilution in water and holding in time increases greatly the performance of the soil stabilizer. It provides a further support for a high aggregating ability of the IPECs under study which produce larger water-proof aggregates.

Thus, the selection of IPEC (MM-1 or MLA-1) and its amount to be consumed should be dictated for each specific application by economic expediency and designated purpose. Based on the investigation performed, water-soluble polymers and MGD used in combination offer promise for increasing the erosion resistance of soils.

Effect of IPEC on the washout of soil (field experiment)

To measure the soil washout when employing these new polymeric aggregators, trenches to be exposed to artificial water streams were specially made on experimental plots of VNIPTIOU (200 km East of Moscow).

In testing such IPEC as MM-1 and microgel dispersion MGD- 2, prior to their injection the latter was pre-diluted with water by 10 times and allowed to stay for no less than 12 hours. A 2.0% MM-1 solution was prepared under field conditions.

The trenches were made on the southwest slope (3.5^{o}) 1 m apart in the form of isosceles triangles (25 cm in base, 25 cm deep) by a cultivator "Mantis". The trench length to be irrigated was 5.8 m. The IPECs tested were injected by a backpack sprayer or a watering can.
The experimental options were as follows:

1. No IPEC (control);
2. 4.0 l/m^2 MM1 – over the surface;
3. 4.0 l/m^2 MM1 + MGD 2 (φ=1%) (in succession);
4. 4.0 l/m^2 MM1 + MGD 2 (φ=2%) (in succession);
5. MGD 2 (φ=1%) to the 5-10 cm depth + soil mixing; then 4.0 l/m^2 MM1 + MGD 2 (φ=1%) (in succession);
6. MGD 2 (φ=1%) to the 5-10 cm depth + soil mixing; then 4.0 l/m^2 MM1 + MGD 2 (φ=2%) (in succession);

Water streams were supplied with a motor-driven pump from a well-drained pond. The runoff consumption was measured by measuring sleeves of 0.5, 1.0 and 1.5 l. After each measurement of the runoff consumption the width and depth of a stream were recorded. The run-off turbidity was measured after filtration of a fixed runoff volume through a pre-weighed filter (a white ribbon).

Based on these experiments, joint application of water-soluble polymers and micro-gel dispersions offers a great promise.

The eroding water velocity was 12.0 cm/s for the control, 20.0 cm/s for 2.0 l/m^2 MM-1 application and 35 cm/s for 4.0 l/m^2 MM-1 application, i.e. almost 3 times as high, with a maximum eroding water velocity of 47.0 cm/s observed for 2.0 l/m^2 MM-1 + 2.0% MGD-1. With MGD-2, the soil was not denuded by a hydraulic pump (not less 50 cm/s) used during the period under study. This suggests that a combination of 2.0 l/m^2 MM-1 and 2.0 % MGD-2 is an optimum polymeric composition for water erosion resistance.

Radionuclide sorption in a dispersed medium

A soil sample was placed into a flask and exposed to various simulated solutions until the equilibrium state was reached, as evidenced by the results of regular sampling. From the equilibrium concentration of the radionuclide, the Cs-137 distribution coefficient in the soil-simulated solution system was determined. The data evidences a slight sorption of Cs-137 (K_d = 1996) in pure water. Any electrolyte impurities leads to a decrease in Kd. Equal proportions of different electrolytes variously affect the sorption depending on the cation nature. The electrolytes can be arranged in order of decreasing sorption as follows: KNO_3 (with 5.0 % KNO_3, Kd=4.90) – $Ca(NO_3)_2$ – $NaNO_3$.

The mechanism of this phenomenon is well-known Univalent cations Cs^+ and K^+ are quite close in chemistry but the K^+ sorption is preferential because its concentration is by a few orders of magnitude greater than that of Cs^+. Cations Na^+ and Ca^{2+} show much less pronounced effect. Most likely the reason is a lower chemical affinity between these cations and Cs^+ due to an increase in the ionic radius of the former.

For IPEC-3 the distribution coefficient (K_d =6.14) depends primarily on the presence of 5.0% KNO_3. The use of $NaNO_3$ instead of KNO_3 can be positive due to a resulting less mobility of Cs-137. Such an approach to selection of polymeric compositions, capable of lowering the Cs-137 mobility among other properties, has considerable promise.

Besides, data shows that the sorbability of Sr-90 at the soil particle surface is much lower than that of Cs-137, suggesting a faster vertical migration of the former to the soil's interior as compared to the Cs-137 migration.

Study the effect of IPEC on environmental items

To study the effect of IPECs on the environment, field (Fig. 2) and greenhouse experiments were performed in 2002 jointly with VNIPTIOU (the All-Russia Research Institute for Fertilizers and Turf, Vladimir region, Vyatkino village).

Fig.2. View of the experimental plots

According to VNIPTIOU information, the experimental soil has been in agricultural use for about 300 years. By the moment of our experiments, the soil cultivation can be classified as poor.

In the greenhouse experiment use was made of plastic tanks holding 9 kg of soil sampled from the arable layer of the control option of the field experiment. The soil was pre-screened to a size grade of 10 mm and thoroughly homogenized. To contaminate the soil with heavy metals, air-dry TPR on a 275-ton/ha basis (1.0 kg TPR per tank at a soil/TPR ratio of 8:1) was added along with the soil to several tanks.

The first sprouts of the plants under study appeared 3 days later. The Sudan grass proved to be the least sensitive to soil liquors (containing extra salts from IPEC introduced). The amount of this crop perished was 5-10% more than that in the control plot. But later, the Sudan grass grew more intensively and got superior in the living weight to that without IPEC or with CMC or VPK. Better mineral nutrition, specifically nitrogen nutrition, provided by IPEC and salts is responsible for that and especially useful for nitrogen-deficient soils (Fig. 3). Within seven days after introduction of the polymers chemical properties of the IPEC-treated soils were determined. IPEC had little effect on acidic-basic properties of the soil but changed the electrical conductivity of the liquor extracted from the soil by the standard procedure

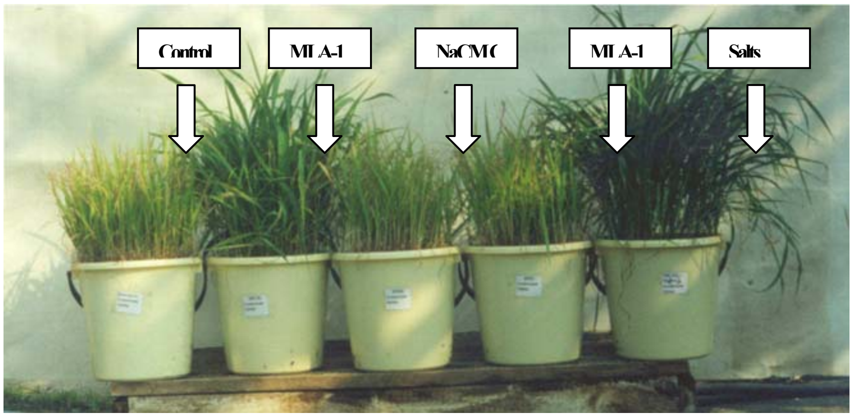

Fig.3. Effect of IPEC and IPEC components on the Sudan grass growth

Effect of IPEC and its components on the Cd mobility within soil

Greenhouse experiments were performed to test the effect of IPEC and its components on the Cd mobility and its ingress into Canadian mixed lawn grass used for soils having negative properties (a high content of water-soluble salts). The grass mixture involved fescue (*Festuca rubra rubra and Festuca ovina),* rye grass (*Lolium perenne*), meadow grass (*Poa protense*). Before experiment 30 PDK (Concentration limit) cadmium nitrate solution (PDK – 2 mg/kg soil) was introduced into soil.

Interaction between IPEC and soil constituents

In the framework of the project, the strength of a coating developed on the IPEC-treated soil surface was tested on a laboratory scale. The objective was to identify the optimal composition of individual constituents of IPEC and the minimum amount of IPEC capable of producing a sound coating that can prevent dust generation.

The strength of the coating developed due to treatment of topsoil with formulations based on MM1, MLA1 and micro-gel dispersions MGD-1 and MGD-2 was tested on a laboratory scale. The objective of the present task was to determine the optimum composition of these IPECs and to develop an adequate technique for their introduction.

A sandy soil with particles of 0.2-0.315 cm was used for experimentation. The samples dried at 50^{o} C developed a sound aggregated soil-polymer coating 0.3-0.5 cm thick.

The results of split and joint application of IPEC components suggest that:

- The coating strength is 1.2-1.5 times as high with split application of IPEC and MG (up to 30.0 N/cm^2) as with joint application (20.0 N/cm^2);
- The coating strength is 1.2-1.6 times as high with MGD2 treatment (10.0- 30.0 N/cm2) as with MGD1 treatment (6.0- 20.0 N/cm2);
- With higher φ (MGD/IPEC), the coating strength decreases (from 30.0 N/cmм2 at φ=0.01 to5.0 N/cm2 at φ=0.2);
- The coating strength at φ<0.01 is higher than that with treatment by IPECs based on MM-1 и MLA-1 alone (6.0-8.0 N/cm^2).

Formulations based on pure microgel are capable of healing large defects but incapable of penetrating via soil capillaries to the soil's interior. Micro-gel - based IPECs can closely connect large particles and a lot of fine divided particles, strengthening their contacts throughout the soil thickness. Thus, micro-gel without IPEC produces a very thin protective layer (1.0-2.0 mm) while only a layer 5-15 cm thick provides an adequate resistance to water streams.

The technique for introducing these formulations to the soil's interior was optimized on a laboratory scale. The optimization involved introduction of micro-gel dispersions, soil loosening and mixing to a given depth at a time. Then the surface was immobilized with IPEC solutions. The strength of the coating produced in such a way was much higher.

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