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Historical perspective

Polymeric stabilizers for protection of soil and ground against wind and water erosion

A.B. Zezin *, S.V. Mikheikin, V.B. Rogacheva, M.F. Zansokhova, A.V. Sybachin, A.A. Yaroslavov *

Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russian Federation

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ABSTRACT

The article is devoted to the design, development and application of a new generation of binders for various dispersed systems, including soil, ground, sand, waste rock and others. The binders are formed by interaction of oppositely charged polyelectrolytes, both chemically stable and (bio)degradable. The fundamental aspects of interpolyelectrolyte reactions are discussed; the IPC structure and properties of the resulting interpolyelectrolyte complexes (IPCs) allow considering them as unique and universal binders. Numerous results of laboratory experiments and field trials of the IPC formulations are presented. In particular, large-scale tests have been done in the Chernobyl accident zone where the IPC binders were shown to be effective means to suppress water and wind erosion thereby preventing a spread of radioactive particles (radionuclides) from contaminated sites. Ecologically friendly IPC compositions are described, including those based on commercially available polymers; prospects for improving their efficiency and extending the range of their possible use are discussed.

Contents

1. Introduction

A destiny of present and future generations mostly depends on how they manage soil and its resources. The main problem of the world's land is the degradation of agricultural soils [1–3]. There are several reasons for that, the primary being the natural processes of water and wind erosion [1,4,5]. In addition to the natural factors, soil erosion develops due to imprudent human activities: breach of agro-technical requirements, excessive (uncontrolled) grazing, felling of protective forests and use of fertile soil for industrial developments. According to a rough estimation, approximately 10 billion hectares are being lost every year due to erosion giving rise to anthropogenic deserts [6,7]. In many countries, the work on developing methods for stabilizing soil and ground that could prevent or at least reduce an erosion-mediated damage is currently in progress [1,7,8].

By erosion, soil loses small particles and alters its chemical composition [1,9]. The key components: humus, nitrogen, phosphorus, potassium, etc., are removed from eroded soils. This leads to a decrease in bioproductivity of soils and reduction of crop yield [1,10,11]. A long-term aspect of erosion is not only this year's harvesting losses but the destruction of soil and waste of its important bioactive components in which restoration will require decades if not centuries.

2. Conventional anti-erosion methods: an overview

Anti-erosion methods could be divided into five groups. We will discuss all five.

* Corresponding authors.
E-mail addresses: zezin@genebee.msu.ru (A.B. Zezin), yaroslav@genebee.msu.ru (A.A. Yaroslavov).

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Biological methods: Countries suffering from erosion use a wide range of biological methods for soil protection: protective afforestation, creation of wind barriers and water regulating forest shelter-belts, conservation of green plantations around ponds and reservoirs and reforestation [12]. These methods are cheap and ecologically safe; however, the formation of forest belts and especially the extended forest areas requires rather long time.

Methods of rational agriculture with less compaction of soil by agricultural machinery: direct sowing (*no tillage*) in untilled soil; extensive mulching sowing (*low disturbance*) with a single tillage to a depth of 10 cm and less and intensive mulching sowing (*high disturbance*) with a tillage to a depth from 10 up to 30 cm [13,14]. Advanced agricultural technologies did not become widespread up to now because of the traditional farmer's conservatism or due to climatic characteristics of the region. In addition, shallow plowing often does not prevent the germination of weeds.

Mechanical methods: covering soil with straw mats, wire nettings, polymer meshes and films [15,16]. Sometimes, local materials such as clay, pebbles, etc., are applied for this purpose. However, simple mechanical constructs are not durable enough (mats and polymer meshes) and are unstable in acidic soils (metal meshes). Polymer films do not provide air- and moisture-exchange and suppress sprouting.

Engineering methods: up-to-date artificial irrigation with the use of energy efficient technologies (not always applicable, especially in regions difficult to access); aerial sowing for revegetation (ineffective); land leveling including water detention with banks (embankments) and ditches (requires sizable earth-moving work and occupies a large area); arrangement of dykes in gullies (often leads to waterlogging and silting) [17].

Chemical methods: use various substances for soil stabilization—viscous components of oil processing [18], plastic mulch (powder, shaving) [19], silicates [20] and polymers, including polyelectrolytes and polymer latexes [21–23], polycomplexes [24]. The use of viscous petroleum products has injurious effect on the environment, soil and groundwater. Polymer mulch forms unstable coatings. In addition, the mulch is usually non-biodegradable. Silicate compositions can favor acidification of soil and reduction of its biological productivity. Water-soluble polymeric binders are quickly removed from soil with rainwater that leads to the loss of the stabilizing effect even at mild precipitation. Hydrophobic binders cannot be uniformly distributed in soil and shortly concentrate on the soil surface and form a waterproof coating.

3. Soil erosion: current challenges

The erosion problems become particularly acute when the soils, exposed to erosion, are heavily polluted. For the first time, humanity was faced with this challenge on a global scale in the end of the last century. After the Chernobyl nuclear power plant accident (1986), a huge amount of radionuclides was found on the soil surface around the plant and far beyond [25,26]. In addition to this "primary" contamination of soil, the radionuclides transferred from contaminated sites on the adjacent territory owing to wind and water erosion of soil ("secondary" contamination) [26,27].

In order to prevent the erosion-mediated transfer of contaminated soils, the authors of the present article have designed and developed novel original binders for dispersed systems, first of all, for soils and fine grounds. We focused on the study of a broad class of amphiphilic binders based on interpolyelectrolyte complexes (IPCs). This choice was determined by the following reasons: the availability and wide variety of polymers for IPC fabrication, among which both polymers highly resistant to external influence and biodegradable polymers can be found, as well as ecological and biocompatibility of IPCs. In this review, we discuss the results of laboratory studies and large-scale testing that have been carried out for many years in different sites (areas), including the 30-km zone around the Chernobyl accident. These results are of particular interest in connection with the accident at the nuclear power plant in Fukushima in 2011 [28,29], whose scale and consequence were comparable with Chernobyl [30–35].

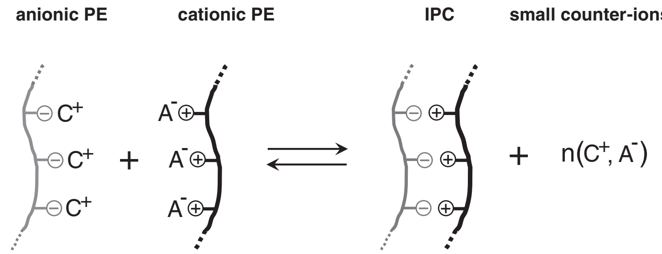

Fig. 1. IPC formation (schematic presentation).

4. Interpolyelectrolyte complexes: a new generation of binders

IPCs are formed upon interaction (coupling) of oppositely charged polyelectrolytes (PEs) as shown in Fig. 1; polyion chains electrostatically bind to each other and small counter-ions are released in aqueous medium. Depending on the polyanion-to-polycation ratio, IPC can be either insoluble but limitedly swellable, or soluble in water solution [24, 36–39].

This reaction is reversible; it proceeds from left to right in aqueous media with total concentration of polyions less than 10 wt.% and rather low concentrations of simple salts, typically below 0.5 M [24,36]. In the early works, it has been found that the reaction is nearly athermal and a driving force of the process is an entropy gain due to a release of small A^- and C^+ counter-ions originally localized in the vicinity of both polyions. The resulting IPC, if it includes equimolar amounts of oppositely charged polyions (stoichiometric IPC), precipitates as a highly concentrated (≈50 wt.%) dispersed phase. The reverse process, IPC dissociation, proceeds from right to left at higher salt concentration (>0.5 M), followed by the dissolution of IPC and the formation of a homogeneous solution with co-existing individual PEs [24,36]. This reversible interpolyelectrolyte reaction is the basis for fabrication and practical application of IPC binders.

The structure of IPC species shown in Fig. 2 is usually regarded as an alternating sequence of hydrophobic blocks composed of mutually neutralized PE units and loops and tails consisting of separated hydrophilic PE units [36,37,40]. This model has been confirmed by numerous works on the properties of IPC in aqueous solutions [36,40,41], and we will follow this model in our review.

The cooperative character of the multisite electrostatic complexation ensures the very high stability of IPCs with respect to splitting up polyelectrolyte counterparts. The degree of conversion θ for IPC formation, defined as the ratio of an equilibrium number of interpolyion salt bonds (ion pairs) to their maximum number, changes from 0 up to 1 with only minor alterations of an external parameter, e.g., pH or salt concentration [41]. In other words, the formation/dissociation of IPC develops in accordance with the "all or nothing" principle.

As follows from the above, IPCs relate to amphiphilic block-copolymers composed of hydrophilic and hydrophobic fragments. It is

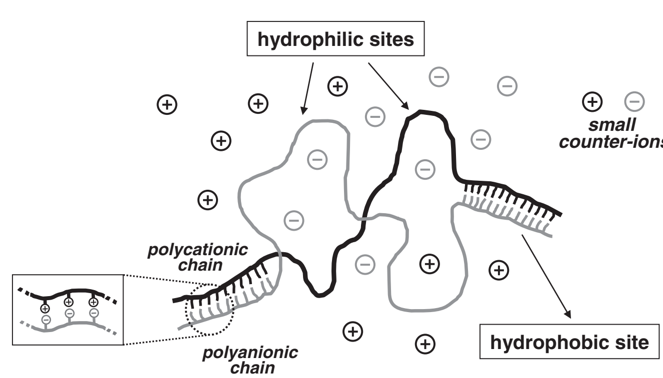

Fig. 2. IPC structure (schematic presentation).