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Alvaro Rocha
Ekaterina Isaeva *Editors*

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Innovative Techniques of Ground Infiltration Characteristics Reduction with Chemical and Biotechnological Precipitation of Calcium Salts

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Abstract. Reduction of the infiltration characteristics of rocks and grounds is an important task in mining, constructing, and economic development of territories, as well as in ecological problems solving. Within the framework of the research, the possibility of reduction of the filtration characteristics of the ground by precipitation of calcium salts in ground pore space was studied. Two chemical and one biotechnological techniques were used. The field test of the techniques was conducted in experimental plots consisted of fine- and medium-grained sand. It was found that the maximum reduction of the filtration rate was recorded at the level of 79–81% compared to the initial characteristics, when these innovative techniques were implemented. Mineralogical studies, including SEM and XRD analyses, indicated the appearance of secondary mineral formation ($CaSO_4$ and $CaCO_3$) after ground treatment, which led to a reduction in its filtration characteristics. A potential application area of the proposed innovative techniques could be mining, constructing, and implementing of environmental protection measures.

Keywords: Infiltration rate reduction · Calcium salts precipitation · Soil properties

1 Introduction

The use of permeable geochemical barriers is a promising method to protect water resources and soils from pollution. According to A.I. Perelman, a permeable geochemical barrier represents a zone where an intensity of chemical elements migration is reduced sharply, causing accumulation of elements [1]. Different kinds of geochemical barriers form chemistry of soil horizons, sediments, and ore deposits. Artificial geochemical barriers are constructed to minimize negative impact of industry on the environment. Different materials are utilized in their construction depending of the goals [2]. The construction of anti-filtration screens, as well as the reduction of filtration rate of solutions through a barrier, and simultaneous precipitation or sorption of pollutants is one of promising applications of artificial geochemical barriers.

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Three techniques were applied to construct permeable geochemical barriers based on the precipitation of water-insoluble calcium salts in ground pore space – two chemical techniques, and a biotechnological one. The first chemical technique used 2 solutions, one of which was saturated with sodium sulfate, and the second solution was the eutonic of four component KCl-NaCl-$CaCl_2$-H_2O system. Mixing of these solutions provided precipitation of insoluble calcium sulfate particles:

$$CaCl_2 + Na_2SO_4 = CaSO_4 \downarrow + 2NaCl \ [3]$$

The second chemical technique used oversaturated solution of calcium sulfate admixture with carboxymethylcellulose (CMC) inhibited crystallization of calcium sulfate [4, 5]. An addition of the solution to a ground induced hydrolysis of CMC and precipitation of calcium sulfate particles as a result.

The biotechnological technique was based on metabolic processes of a ground microflora. An addition of nutrient solution, contained urea, activated ureolytic bacteria which hydrolysed urea, and a precipitation of calcium carbonate particles occurred in presence of calcium ions:

$$NH_2CONH_2 + H_2O = 2NH_3 + CO_2,$$
$$Ca^{2+} + HCO_3^- + OH^- = CaCO_3 \downarrow + H_2O \ [6, 7].$$

2 Materials and Methods

The field test of the techniques was conducted on the territory of the Institute's testing area situated in Perm township on the right coast of Kama-river, where alluvial quaternary deposits, consisted of fine- and medium-grained sand, lied under a thin layer of a soil. The climate of the study area is temperate continental, the average monthly humidity ranges from 60% in May to 84% in November, the average annual humidity is 75%. The annual precipitation rate is 639 mm, most of which falls in the form of rain. The height of the snow cover can reach 111 cm in winter.

Seven plots, 1.0 × 1.0 m in dimensions, were prepared as follows: the upper soil layer was removed completely, and surface of the plots was leveled.

Two plots were used to test the first chemical technique – the precipitation of calcium sulfate after the mixing of eutonic four-component solution and saturated sodium sulfate one. One plot was an experimental one, another one was a control plot.

Two plots were used to test the second chemical technique – the precipitation of calcium sulfate from the oversaturated solution after destruction of the precipitation inhibitor, CMC. One plot was an experimental one, another one was a control plot.

Three plots were used to test the biotechnological technique – the precipitation of calcium carbonate after an activation of ground ureolytic microorganisms. Two plots were experimental ones, 1 plot was a control one.

Chemical content of the treatment solutions, and methods of plots treatment were described earlier [8]. The duration of field experiments was 60 days. At the end of the experiments filtration traits of the plots' ground were studied with the field infiltrometer ("Eijkelkamp Soil & Water", The Netherland) (Fig. 1). Samples of the plots' ground were analysed with XRD (diffractometer D2 Phaser, "Brueker", Germany) and scanning electron microscopy (microscope JSM-6390LV, "JEOL", Japan).

3 Results of the Field Test of the Techniques

The main purpose of the research was to evaluate the efficiency of techniques to reduce the filtration characteristics of grounds by means of the precipitation of calcium salts in the field conditions.

All 3 techniques of ground treatment led to a reduction of water filtration rate and a precipitation of calcium sulfate (up to 3.7%) or carbonate (up to 3.1%) particles in ground pore space. Calcium carbonate formed particles and thin films, covered ground grains and cemented them together. Particles of calcium sulfate tended to form aggregates and coatings on ground grains (Fig. 2). Neither calcium sulfate nor calcium carbonate particles were detected in control plots' ground.

Fig. 1. General view on the plots of chemical treatment

Field infiltrometer settled on the plots are seen in the right part of the figure.

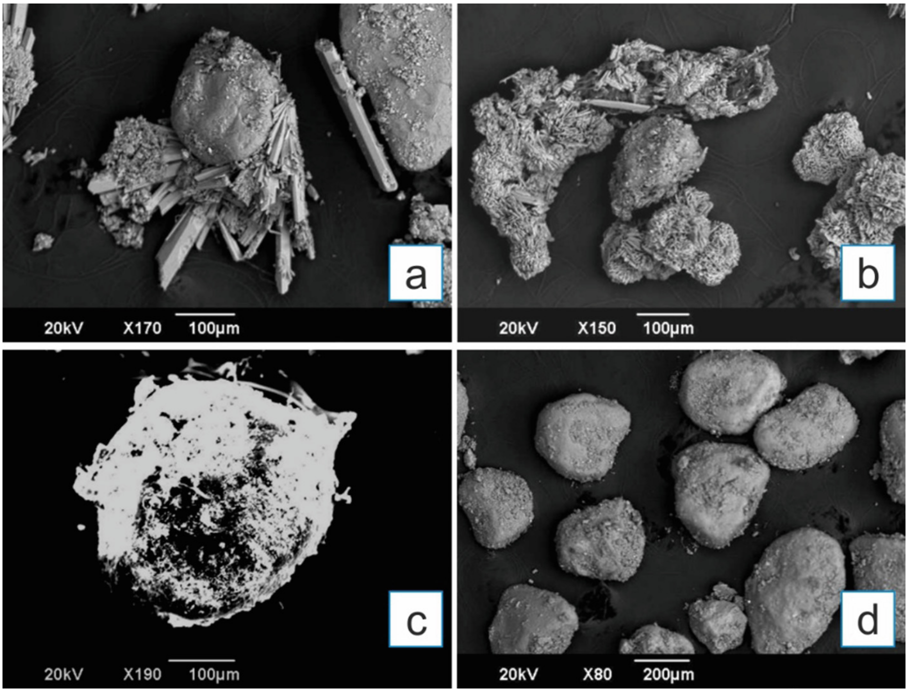

Fig. 2. Scanning electron microscopy images of the grounds

a, b – aggregates of calcium sulfate on ground grains after chemical treatment according to techniques 1 and 2, correspondingly; c – films of calcium carbonate on ground grain after biotechnological treatment; d – grains of control plot's ground.

Ground properties of control plots and plots undergone chemical and biotechnological treatments presented in Table 1. The treatment of the ground according to the first chemical technique led to formation of fractures on the plot surface. Such fractures were not observed on the surface of the plot treated according to the second chemical technique (Fig. 3). We suppose, these fractures were the results of calcium sulfate crystallization within the upper layer of the ground preferentially. This supposition could also explain the results of filtration rate reduction in that plot (7.20 m day^{-1}), which was worse compared to the result of the treatment according to the second chemical technique (2.11 m day^{-1}). The treatment of the ground with the biotechnological technique reduced water filtration rate of the ground to 1.04–3.50 m day^{-1} compared with 5,76 m day^{-1} in control plot [8]. The difference in the reduction of the filtration rate in the chemical (minimum 2.11 m day^{-1}) and biotechnological techniques occurred probably due to a slight difference in the initial filtration characteristics of the ground, which was also confirmed by field measurements of the filtration rate at the control plots. At the plots where the chemical techniques were implemented, the initial filtration rate in the control plots varied from 8.89 to 10.45 m day^{-1}.

Table 1. The field plot's ground characteristics

Sample number	Density, g cm^{-3}	Porosity coefficient	Natural moisture	Particle size distribution, %				Treatment
				2,0–0,5 mm	0,5–0,25 mm	0,25–0,1 mm	0,1–0,05 mm	
1	1.63	0.737	0.069	2.38	62.38	32.48	2.76	Control plot
2	1.68	0.692	0.079	2.82	49.23	38.03	9.92	Control plot
3	1.72	0.682	0.094	2.40	50.61	36.77	10.22	Biotechnological technique
4	1.65	0.808	0.129	2.08	59.94	29.10	8.88	Chemical technique 1
5	1.62	0.796	0.103	2.21	56.12	26.97	14.71	Chemical technique 2

So, biotechnological precipitation of calcium carbonate in the ground could be as effective as chemical precipitation of calcium sulfate to reduce filtration traits of the ground.

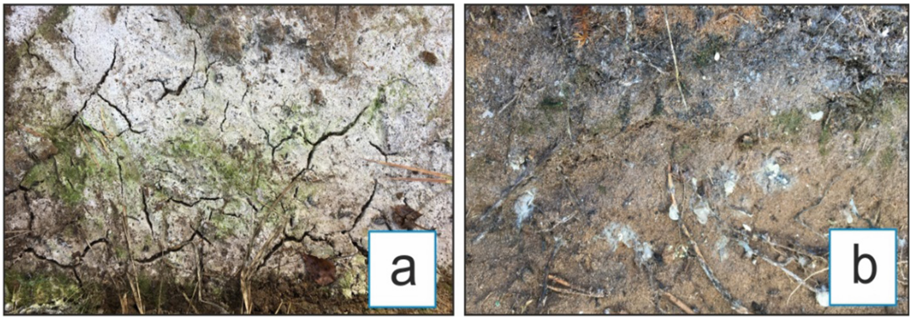

Fig. 3. Views of surface of plots after chemical treatment according to techniques 1 (a) and 2 (b)

Numerous fractures are developed on plot surface after the treatment according to technique 1.

4 Conclusions

The possibility of changing the filtration characteristics of sandy ground during chemical or biotechnological precipitation of calcium salts has been experimentally confirmed.

It was found that the maximum reduction in the filtration rate was recorded at the level of 79–81% compared to the initial characteristics, when the tested techniques were implemented. The difference in the reduction of the filtration rate after the using of biotechnological and chemical techniques was also revealed. This difference was probably due to the unevenness of the initial filtration characteristics of the ground. However, the results obtained indicated the potential efficiency of the techniques in mining, constructing, and implementing of environmental protection measures.

Mineralogical studies, including scanning electron microscopy and diffractometric analysis, indicated the appearance of secondary minerals with characteristic morphological features (gypsum and calcite) after the ground treatment, due to which a reduction of ground filtration characteristics was observed. The practical implementation of the chemical and biotechnological techniques were patented.

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