

Geocoprotective Technologies from Heavy Metal Ions Pollution for Transport Construction in Permafrost Regions



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Abstract Every year, 15–17 million tons mineral wastes are generated in Russia including permafrost regions. A large amount of these wastes contain minerals such as silicates and sulfates. Different industries leading to geosystem pollution by heavy metals, including lead, cadmium, copper, zinc, manganese, and iron compounds. Such pollution must be prevented. The purpose of the work was to study geocoprotective properties of mineral wastes of silicate and sulfate nature and how they can be used to create geocoprotective technologies against heavy metal ions pollution in permafrost regions. The silicate and sulfate mineral wastes were selected as objects of study in the form of phosphogypsum, foamed gypsum, calcium sulfate anhydrous, hemihydrate gypsum and calcium sulfate dihydrate, asbestos- and chlorite-containing crushed stone, and talc. A potentiometric method for determination of concentrations in solutions was used to define the absorptive capacity of mineral wastes against heavy metal ions. The detected absorptive capacities of aforementioned mineral wastes for such heavy metals as cadmium, copper, lead, and barium are presented in the article. The dependences of the absorptive capacity of the mineral waste on the initial concentration of heavy metal ions, on the interaction time with the solution and on the fraction size are also given in the article. The experimental results showed that the selected mineral wastes can be used in technological solutions for soil cleanup and surface runoff purification from heavy metal ions.

Keywords Geosystem pollution · Mineral wastes · Geocoprotective technologies · Heavy metal ions

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1 Introduction

According to the European Association for the Demolition of Buildings, about 2.5 billion tons of construction waste is generated annually on the planet as a result of human activity. Construction wastes resulting from natural and man-made disasters not included in this amount. Every year, 15–17 million tons mineral wastes are generated in Russia including permafrost regions. A large amount of these wastes contain minerals such as silicates and sulfates [1–4]. There are now also underway for the construction and reconstruction activities in the transport sector in permafrost regions. Also currently works on construction and reconstruction of the transport sector in permafrost regions. The construction and operation of facilities located in permafrost regions lead to the pollution of lithosphere by heavy metals, including lead, cadmium, copper, zinc, manganese, and iron compounds.

Heavy metal ions of (HMI) are supertoxicants the XXI century [5, 6]. Therefore, the development of technological solutions for the lithosphere protection from their negative impact is an urgent task of geoecology [7–11]. The authors propose to develop technological solutions for soil and surface waters protection from HMI pollution using mineral wastes. These mineral wastes can absorb and neutralize pollutants due to the formation of low-solubility compounds. For the application of such technological solutions, it is necessary [12–16]:

- To research and evaluate the mineral waste ability to neutralize heavy metal ions;
- To develop technological solutions for soil and surface water protection in permafrost regions from heavy metal ions through the use of mineral wastes.

2 Materials and Methods

The silicate and sulfate mineral wastes were selected as objects of study in the form of phosphogypsum, foamed gypsum, calcium sulfate anhydrous, gypsum hemihydrate and dihydrate, asbestos- and chlorite-containing crushed stone, and talc [17, 18]. They were chosen because a large amount of waste with a similar composition is formed in various industries.

Capacity was calculated by the use of this formula:

$$a = ((C_i - C_r)V)/m \quad (1)$$

where

- a absorptive capacity, mg g^{-1} ;
- C_i initial concentration of heavy metal ions in model solution, mg l^{-1} ;
- C_r residual concentration of heavy metal ions in model solution, mg l^{-1} ;
- V solution volume, l;
- M mineral waste mass, g.

A potentiometric method for determination of concentration of heavy metal ions in solutions was used to define the absorptive capacity of mineral wastes. Determination of the concentration in the solution before and after interaction with the mineral wastes was performed on an electronic analyzer «Expert- 001» and ion-selective electrodes [Cd (II), Cu (II), Pb (II), Ba (II)].

3 Research Results

Table 1 demonstrates the results of experiments to determine the dependence of the static capacity of sulfate-containing mineral wastes on the initial concentration of the solution for phosphogypsum as an example.

According to the data obtained, a concentration of 10^{-4} mol l⁻¹ has been chosen to determine the static capacity. The residual concentration under the chosen conditions was 2.195 mg l⁻¹ for phosphogypsum, 2.935 mg l⁻¹ for foamed gypsum, 4.783 mg l⁻¹ for calcium sulfate anhydrous, 1.195 mg l⁻¹ for gypsum hemihydrate, and 6.207 mg l⁻¹ for gypsum dihydrate. The purification rate was 52–91%.

Tables 2, 3, 4, 5 and 6 present the results of experiments to determine the dependence of the static capacity of sulfate-containing mineral wastes on the contact time with the solution.

Table 1 Dependence of the static capacity of phosphogypsum on the initial concentration of a solution containing cadmium ions

Mass (g)	Solution concentration Cd(NO ₃) ₂ (mol l ⁻¹)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
1	10 ⁻⁶	0.042	0.011	0.003
1	10 ⁻⁵	1.620	1.367	0.025
1	10 ⁻⁴	12.786	2.195	1.059
1	10 ⁻³	162.817	57.102	10.570
1	10 ⁻²	1537.309	663.379	87.393

Table 2 Dependence of the static capacity of phosphogypsum on the contact time with the Cd(NO₃)₂ solution

Contact time (h)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
0.25	12.786	2.195	1.059
2	12.786	2.170	1.062
6	12.786	2.573	1.021
24	12.786	2.322	1.046

Table 3 Dependence of the static capacity of foamed gypsum on the contact time with the $\text{Cd}(\text{NO}_3)_2$ solution

Contact time (h)	Initial concentration (mg l^{-1})	Residual concentration (mg l^{-1})	Capacity (mg g^{-1})
0.25	12.786	2.935	0.985
2	12.786	2.661	1.062
6	12.786	2.573	1.013
24	12.786	2.651	1.014

Table 4 Dependence of the static capacity of calcium sulfate anhydrous on the contact time with the $\text{Cd}(\text{NO}_3)_2$ solution

Contact time (h)	Initial concentration (mg l^{-1})	Residual concentration (mg l^{-1})	Capacity (mg g^{-1})
0.25	12.786	4.783	0.800
2	12.786	3.332	0.945
6	12.786	3.011	0.978
24	12.786	2.339	1.045

Table 5 Dependence of the static capacity of gypsum hemihydrate on the contact time with the $\text{Cd}(\text{NO}_3)_2$ solution

Contact time (h)	Initial concentration (mg l^{-1})	Residual concentration (mg l^{-1})	Capacity (mg g^{-1})
0.25	12.786	1.935	1.085
2	12.786	1.324	1.146
6	12.786	0.678	1.211
24	12.786	0.513	1.227

Table 6 Dependence of the static capacity of gypsum dihydrate on the contact time with the $\text{Cd}(\text{NO}_3)_2$ solution

Contact time (h)	Initial concentration (mg l^{-1})	Residual concentration (mg l^{-1})	Capacity (mg g^{-1})
0.25	12.786	6.207	0.658
2	12.786	4.850	0.794
6	12.786	4.423	0.836
24	12.786	4.137	0.865

Table 7 Static capacity of sulfate-containing construction and industrial mineral wastes

Mineral wastes	Static capacity (mg g ⁻¹)			
	Cd ²⁺	Cu ²⁺	Pb ²⁺	Ba ²⁺
Phosphogypsum	1.06	1.28	1.51	1.29
Foamed gypsum	0.99	1.21	0.85	1.33
Calcium sulfate anhydrous	0.80	1.09	1.17	1.30
Gypsum hemihydrate	1.26	1.34	1.52	1.31
Gypsum dihydrate	0.66	0.88	0.86	1.33

The data from Tables 2, 3, 4, 5 and 6 illustrate that for every contact time the difference in residual concentrations is 0.4 mg l⁻¹ for phosphogypsum and 0.36 mg l⁻¹ for foamed gypsum. Therefore, the increase of contact time more 15 min is impractical.

Additional studies have carried out for such heavy metal ions as copper, lead, and barium for selected conditions. Table 7 demonstrates the results.

Tables 8, 9 and 10 present the results of experiments to determine the dependence of the static capacity of magnesium silicate-containing mineral waste on the initial concentration of the solution.

Table 8 Dependence of the static capacity of chlorite-containing crushed stone on the initial concentration of the cadmium ions solution

Mass (g)	Solution concentration Cd(NO ₃) ₂ (mol l ⁻¹)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
1	10 ⁻⁶	0.042	0.000	0.004
1	10 ⁻⁵	1.620	0.097	0.152
1	10 ⁻⁴	12.786	1.335	1.145
1	10 ⁻³	162.817	142.396	2.042
1	10 ⁻²	1537.309	1431.389	10.592

Table 9 Dependence of the static capacity of asbestos-containing crushed stone on the initial concentration of the cadmium ions solution

Mass (g)	Cd(NO ₃) ₂ solution concentration (mol l ⁻¹)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
1	10 ⁻⁶	0.042	0.000	0.004
1	10 ⁻⁵	1.620	0.072	0.155
1	10 ⁻⁴	12.786	1.488	1.130
1	10 ⁻³	162.817	142.066	2.075
1	10 ⁻²	1537.309	1408.498	12.931

Table 10 Dependence of the static capacity of talc on the initial concentration of the cadmium ions solution

Mass (g)	Cd(NO ₃) ₂ solution concentration (mol l ⁻¹)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
1	10 ⁻⁶	0.042	0.000	0.004
1	10 ⁻⁵	1.620	0.043	0.158
1	10 ⁻⁴	12.786	0.528	1.226
1	10 ⁻³	162.817	137.848	2.497
1	10 ⁻²	1537.309	1424.811	11.250

Table 11 Dependence of the static capacity of chlorite-containing crushed stone on the contact time with the Cd(NO₃)₂ solution

Contact time (h)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
0.25	12.786	1.335	1.145
2	12.786	0.499	1.229
6	12.786	0.196	1.259
24	12.786	0.008	1.278

According to the received data a concentration of 10⁻⁴ mol l⁻¹ was chosen to determine the static capacity. At the same time, the residual concentration for selected conditions was 1.335 mg l⁻¹ for chlorite-containing crushed stone, 1.488 mg l⁻¹ for asbestos-containing crushed stone, and 0.528 mg l⁻¹ for talc. The purification rate was 88–96%.

Tables 11, 12 and 13 demonstrate the results of experiments to determine the dependence of the static capacity of magnesium silicate-containing mineral wastes on the contact time with the solution.

The results showed that the increase of contact time increases of the purification rate. This means that the tested materials have «reserve» of the absorptive capacity.

Table 12 Dependence of the static capacity of asbestos-containing crushed stone on the contact time with the Cd(NO₃)₂ solution

Contact time (h)	Initial concentration (mg l ⁻¹)	Residual concentration (mg l ⁻¹)	Capacity (mg g ⁻¹)
0.25	12.786	1.488	1.130
2	12.786	0.253	1.253
6	12.786	0.080	1.271
24	12.786	0.000	1.279

Table 13 Dependence of the static capacity of talc on the contact time with the $\text{Cd}(\text{NO}_3)_2$ solution

Contact time (h)	Initial concentration (mg l^{-1})	Residual concentration (mg l^{-1})	Capacity (mg g^{-1})
0.25	12.786	0.528	1.226
2	12.786	0.406	1.238
6	12.786	0.672	1.211
24	12.786	0.568	1.222

Table 14 Static capacity of mineral wastes

Mineral wastes	Static capacity (mg g^{-1})			
	Cd^{2+}	Cu^{2+}	Pb^{2+}	Ba^{2+}
Asbestos-containing crushed stone	1.13	1.30	1.46	0.47
Chlorite-containing crushed stone	1.15	1.11	1.26	0.47
Talc	1.23	1.33	1.51	0.50

However, taking into account received data from other mineral wastes the contact time for chlorite-containing and asbestos-containing crushed stone was taken 0.25 h.

The data from Table 13 shows that for every contact time the difference in the residual concentrations is 0.27 mg l^{-1} . Therefore, it is not necessary to increase the contact time more than 15 min. Additional studies were carried out for such heavy metal ions as copper, lead, and barium in the same conditions. Table 14 presents the analysis results.

The authors suggest using of the construction and industrial mineral wastes as an additional drainage fills in areas polluted by heavy metal in permafrost regions. It will be geocoprotective screens for the highways construction and repair.

One of the most frequently used ways to reinforcement of ramps from subgrade deformation erosion is mechanized grass cultivation. It is possible to build the geocoprotective screen for this operation at the same time strengthening the ramps using mechanisms for grass cultivation. Experimental testing of some investigated mineral wastes in a model experiment was carried out on a test site in the zone of highway and railway. Tests showed the possibility of the use them to create geocoprotective screen in permafrost regions (Table 15).

The use of construction and industrial mineral waste as a drainage material directly in the drainage trays of highways is considered. Such a solution will help to prevent soil contamination by surface wastewater containing HMI during the construction of transport networks. Preventive protection of soil and groundwater during the surface runoff treatment can be achieved through the use of construction and industrial mineral waste as a filtering material [19–21]. The experimental operation of stormwater runoff purification from lead ions and oil products was carried out using a combined filter cartridge on the gas station territory. The upper part of the combined filter cartridge on one-third the height was filled by phosphogypsum. He was placed instead of a part of the non-woven fabric. The concentration of lead ions in the purified

Table 15 Results of soil cleanup through the use of mineral wastes

Materials	pH	Initial concentration of lead ions (mg l^{-1})	Residual concentration of lead ions (mg l^{-1})	Purification rate (%)
Sand clay	6.3	235.875	43.441	81.58
Sand clay + phosphogypsum	7.1	235.875	0.760	99.68
Sand clay + foamed gypsum	7.20	235.875	0.075	99.97
Sand clay + chlorite-containing crushed stone	7.2	235.875	0.012	99.99
Sand loam	5.2	235.875	155.674	34.00
Sand loam + phosphogypsum	6.9	235.875	0.413	99.82
Sand loam + foamed gypsum	7.2	235.875	0.438	99.81
Sand loam + chlorite-containing crushed stone	7.1	235.875	0.060	99.97
Bog peat	5.0	235.875	152.375	35.40
Bog peat + phosphogypsum	5.5	235.875	10.216	95.67
Bog peat + foamed gypsum	5.9	235.875	10.821	95.41
Bog peat + chlorite-containing crushed stone	6.4	235.875	0.584	99.75

surface runoff has decreased by ten times (from 0.1 to 0.01 mg l^{-1}) during the entire test period. The purification level has reached the admissible concentration limit.

4 Conclusions

1. The dependences of the absorption capacity of calcium sulfate and hydrosilicate systems on the initial concentration of the solution containing heavy metal ions on the contact time with the solution and on the fraction size were determined.
2. The absorption capacity of sulfate-containing calcium mineral wastes was determined. It corresponds to the values in the intervals: 0.66–1.26 mg g^{-1} for cadmium ions; 0.88–1.34 mg g^{-1} for copper ions; 0.85–1.52 mg g^{-1} for lead ions; 1.29–1.33 mg g^{-1} for barium ions.

3. The absorptive capacity of silicate-containing magnesium mineral wastes was determined, which corresponds to values: 1.26–1.52 mg g⁻¹ for lead ions and 0.47–0.88 mg g⁻¹ for barium ions.
4. Construction and industrial mineral wastes that are wastes of hazard class IV spontaneously interact with heavy metals ions of hazard classes I and II. They bind and neutralize them. In the resulting compounds with a low solubility are produced in the form of salts and hydroxides of heavy metals of hazard class IV.
5. Technological solutions were proposed to protect the lithosphere during transport construction using construction and industrial mineral waste. These solutions include steps:
 - The creation of geocoprotective screen for highways and railways construction for the preventive protection of roadside land from HMI;
 - Preventive protection of soils and groundwater by using of the surface runoff purification from the HMI in the drainage tray during the transport highway construction, and in the gas station during the highway reconstruction.
6. Aforecited technological solutions can be applied in permafrost regions under positive temperatures conditions.

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